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Ketene Chemistry and Applications to Polymer Systems

by

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A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

The Department of Chemistry

Carleton University

Ottawa, ON Canada

March 1998

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the Faculty of Graduate Studies and Research
acceptance of the thesis

Ketene Chemistry and Applications to Polymer Systems

submitted by

Laurence M.-F. Suzzarini, Ingénieur Chimiste

in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

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Abstract

Curing is a common process to increase the use temperature and solvent resistance of polymers. The use of ketene chemistry for curing purposes was tested using two ketene precursors: benzocyclobutenone and cyclobutenedione. The use of the ketene chemistry was rationalized based on the possible generation and reaction of ketene with alcohol without producing any by-product and the availability of a wide range of hydroxy containing polymers.

The synthesis of benzocyclobutenone (BCBO) by solution and gas phase chemistry was examined for its preparation in large quantities. Since the presence of a functional group is necessary to introduce BCBO into polymers, the direct functionalization of BCBO was investigated. The thermal and photochemical reactions of BCBO with alcohol have been studied in detail. The influence of the nature and the ratio of alcohol as well as the presence of acid was probed. In an attempt to lower the temperature of the thermal reaction, the effect of the substituent on the ring-opening temperature and the use of catalysts were examined.

Benzocyclobutenone was then used to end-cap diisocyanate prepolymers for the preparation of a one-component heat-curing polyurethane. Bis-BCBO derivatives were also synthesized and used as chain extenders for a polyester diol which produced poly(imide ester)-type elastomers. Benzocyclobutenone was also introduced in polystyrene as a pendant group. The modified BCBO-polystyrene was reacted with poly(ethylene glycol) methyl ether to form a grafted polymer.

This thesis also reports the design and synthesis of a new monomer, 3,4-di(4-fluorophenyl)cyclobut-3-ene-1,2-dione, for poly(aryl ether)s. This monomer allows the introduction of the cyclobutenedione unit, a latent bis-ketene group upon thermolysis or photolysis, into poly(aryl ether)s. Due to gel formation during polymerization, low molecular weight polymers were obtained from 4,4'-difluorophenylcyclobutenedione and various bisphenols. Higher molecular weight polysulfones were prepared by copolymerization with 4,4'-difluorophenylsulfone and 4,4'-(hexafluoroisopropylidene)diphenol. Thermal and photochemical grafting of the cyclobutenedione containing polysulfone was successfully demonstrated with 1-octanol.

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Table of Contents

Abstract.....	i
Acknowledgments.....	iii
Table of Contents.....	iv
List of Tables.....	ix
List of Schemes.....	x
List of Figures.....	xiv
Symbols and Abbreviations.....	xvi
 I. Polymer Curing and Ketene Chemistry	
I.1. Curing Chemistry.....	2
I.1.1. Curing System With Volatile By-Products.....	3
I.1.2. Curing System Without Volatile By-Products.....	4
I.1.2a. Carbon Based Systems.....	4
I.1.2b. Non-Carbon Based Systems.....	7
I.2. Ketenes.....	7
I.2.1. Preparation of Ketenes.....	8
I.2.2. Reactions of Ketenes.....	12
I.1.2a. Cycloadditions.....	12
I.1.2b. Nucleophilic Addition.....	15
I.1.2c. Electrophilic Addition.....	16
I.1.2d. Radical Reaction.....	17
I.3. Rationale and Objectives.....	17
I.3.1. Benzocyclobutenone.....	19
I.3.2. Cyclobutenedione.....	20
I.4. References.....	21

II. Benzocyclobutenone: Synthesis and Reactions

II.1. Synthesis of Benzocyclobutenone.....	28
II.1.1. Introduction.....	28
II.1.2. Synthesis of Benzocyclobutenone.....	30
II.1.2a. Solution Chemistry.....	32
II.1.2b. Gas Phase Chemistry.....	33
II.2. Reactions of Benzocyclobutenone.....	37
II.2.1. Self-coupling.....	39
II.2.1a. Dimerization of Benzocyclobutene.....	39
II.2.1b. Dimerization of Benzocyclobutenone.....	40
II.2.2. Reaction with Alcohols.....	41
II.2.2a. Thermal Reaction with Alcohols.....	41
II.2.2b. Photochemical Reaction with Alcohols.....	44
II.2.2c. Acid Catalysts.....	49
II.3. Conclusion.....	51
II.4. Experimental Section.....	52
II.5. References.....	58

III. Ring-opening Temperature of Benzocyclobutenones

III.1. Introduction.....	63
III.2. Functionalization of Benzocyclobutenone.....	63
III.2.1. Nitration.....	64
III.2.2. Aminobenzocyclobutenone and its Derivatives.....	66
III.2.2a. 5-Aminobenzocyclobutenone.....	66
III.2.2b. 5-Acetylamidobenzocyclobutenone.....	67
III.2.2c. 5-Succinylimidobenzocyclobutenone.....	68
III.2.2d. 5-(Fluorophenyl)-sulfonamidobenzocyclobutenone.....	68
III.2.2e. N-(2-Hydroxypropane)-5-aminobenzocyclobutenone.....	69
III.2.2f. 5-Isocyanatobenzocyclobutenone.....	71
III.2.2g. 5-Hydroxybenzocyclobutenone.....	72

III.3. Ring-Opening Temperature.....	73
III.3.1. Substituent Effect.....	73
III.3.2. Catalysts.....	77
III.3.2a. Metal Catalysts.....	77
III.3.2b. Nucleophilic Catalyst.....	80
III.4. Kinetic Studies.....	81
III.4.1. Mathematical Tool.....	83
III.4.2. Results.....	83
III.5. Conclusion.....	87
III.6. Experimental Section.....	87
III.7. References.....	95
 IV. Benzocyclobutenone : Applications to Polymer Systems	
IV.1. Introduction.....	98
IV.2. Application to Polyurethane Synthesis.....	99
IV.2.1. BCBO End-Capped Diisocyanates.....	100
IV.2.1a. Thermal Analysis of BCBO End-Capped Diisocyanates.....	101
IV.2.2. Polymer Curing.....	103
IV.3. Poly(imide ester)s.....	105
IV.3.1. Bis-Imide-BCBO.....	106
IV.3.1a. Thermal Analysis of Bis-Imide-BCBO.....	107
IV.3.2. Chain Extension.....	108
IV.3.2a. Structural Characterization.....	109
IV.3.2b. Thermal Properties of Poly(imide ester)s.....	109
IV.3.3. AB Monomer.....	110
IV.3.3a. Monomer Synthesis.....	110
IV.3.3b. Polymerization.....	112
IV.4. Poly(ethylene glycol)-Grafted-Polystyrene.....	114
IV.4.1. Monomer Synthesis.....	114
IV.4.2. Polymerization.....	116

IV.4.3. Polymer Characterization.....	116
IV.4.4. Polymer Grafting.....	119
IV.4.5. Characterization of PS-g-PEG.....	120
IV.5. Conclusion.....	122
IV.6. Experimental Section.....	122
IV.7. References.....	134
 V. Cyclobutenedione: A Ketene Precursor in Poly(aryl ether ketone)s	
V.1. Introduction.....	136
V.1.1. Cyclobutenedione.....	136
V.1.1a. Synthesis of Cyclobutenedione.....	136
V.1.1b. Reactions of Cyclobutenedione.....	137
V.1.2. Poly(aryl ether)s.....	140
V.1.3. Polymer Transformation.....	141
V.1.4. Potential Uses of Cyclobutenedione in Polymer Chemistry.....	145
V.2. Design and Synthesis of the Monomer.....	146
V.2.1. Monomer Design.....	148
V.2.2. Monomer Synthesis.....	149
V.2.3. Stability of the Monomer.....	151
V.2.4. Reactivity of the Monomer.....	152
V.2.4a. HMO Calculation.....	152
V.2.4b. From ^1H NMR Measurement.....	154
V.2.4c. From ^{13}C NMR Measurement.....	154
V.2.4d. From ^{19}F NMR Measurement.....	155
V.3. Polymerization.....	156
V.3.1. Model Reaction.....	156
V.3.2. Homopolymerization.....	157
V.3.2a. Characterization of Homopolymers.....	159
V.3.2b. Characterization of Polymer Gels.....	162
V.3.3. Copolymerization.....	165

V.4. Polymer Transformation.....	167
V.4.1. Thermal Transformation.....	168
V.4.1.a. Model Reaction.....	169
V.4.1.b. Polymer Transformation.....	170
V.4.2. Photochemical Transformation.....	171
V.4.2.a. Model Reaction.....	172
V.4.2.b. Polymer Transformation.....	173
V.5. Conclusion.....	174
V.6. Experimental Section.....	175
V.7. References.....	188

List of Tables

II.1.	Pyrolysis of o-toluoyl chloride at different temperature and pressure.....	36
II.2.	Reaction of benzocyclobutenone with alcohols.....	43
III.1.	Ring-opening temperature of 1-substituted benzocyclobutene.....	73
III.2.	Ring-opening and melting temperature of 5-substituted BCBO.....	75
III.3.	Ring-opening and melting temperature of bis-imide-BCBO.....	76
III.4.	Ring-opening temperature of bis-imide-BCBO IV-5a in the presence of metal catalyst.....	79
III.5.	Activation energies calculated for substituted BCBO with and without poly(4-hydroxystyrene).....	86
IV.1.	Film property and decomposition temperature of IV-3 and IV-4	105
IV.2.	Elemental analysis results for IV-5a and IV-5b	107
IV.3.	Thermal analysis of bis-imide-BCBO IV-5	107
IV.4.	Type of copolymer in function of the reactivity ratio of the monomers.....	115
IV.5.	Thermal properties of copolymer IV-12	117
IV.6.	Decomposition temperature of grafted copolymers.....	121
V.1.	NMR data obtained for V-1	151
V.2.	Solubility of polymers V-3a-d	159
V.3.	Viscosity at various concentrations and GPC data for polymers V-3b-d	160
V.4.	Thermal analyses of polymers V-3b-d	161
V.5.	Characterization of polymers V-4a-d	166
V.6.	Thermal properties of polymers V-4a-d	167
V.7.	Comparison of the precursor (V-4c) and the derivative polymers (V-7).....	171

List of Schemes

L1.	Polyimides from polyamic acid precursor.....	3
L2.	One component heat-curing polyurethane.....	4
L3.	Curing reaction of acetylene.....	5
L4.	Thermolysis of paracyclophane.....	5
L5.	Thermal reactions of benzocyclobutene.....	6
L6.	Crosslinking reaction with biphenylene.....	6
L7.	Resonance structure of ketene.....	8
L8.	Routes to ketene formation.....	11
L9.	[2+2] Cycloaddition of ketenes with unsaturated compounds.....	13
L10.	[4+2] Cycloaddition of ketene.....	14
L11.	Proposed mechanism for [2+2] cycloaddition.....	14
L12.	Nucleophilic addition to ketenes.....	16
L13.	Electrophilic addition to ketenes.....	17
L14.	Reaction of hydroxyl radical with ketene.....	17
L15.	Ketene precursors to be investigated for polymer curing.....	18
L16.	Disubstituted cyclobutenedione: a derivative of squaric acid.....	20
II.1.	Synthesis of benzocyclobutene by electrocyclization.....	29
II.2.	Synthesis of cyclobutenone by electrocyclization.....	30
II.3.	Reaction of ketene with alkenes and alkynes.....	30
II.4.	First synthesis of benzocyclobutenone.....	31
II.5.	Synthesis of benzocyclobutenone via benzyne.....	31
II.6.	Synthesis of benzocyclobutenone by pyrolysis.....	32
II.7.	Thermal degradation products of benzocyclobutenone.....	36
II.8.	Ring-opening of benzocyclobutenone.....	38
II.9.	Reaction of benzocyclobutenone with unsaturated substrates.....	38
II.10.	Ring-opening of benzocyclobutenone with hydroxide ion.....	39

II.11.	Dimerization of benzocyclobutene derivatives.....	39
II.12.	Dimerization of benzocyclobutenone derivatives.....	40
II.13.	Dimerization of benzocyclobutenone.....	41
II.14.	Dimerization of vinyl ketene.....	41
II.15.	Thermal reaction of BCBO with alcohols.....	42
II.16.	Photochemical reaction of benzocyclobutenone with alcohols.....	46
II.17.	Proposed mechanism of addition of alcohol to ketene.....	49
II.18.	Acid catalyzed addition of alcohol.....	50
II.19.	Hydration of ketene.....	51
III.1.	Anticipated and observed substitutions with electrophiles.....	65
III.2.	Nitration of benzocyclobutenone.....	65
III.3.	Synthesis of 5-aminobenzocyclobutenone.....	67
III.4.	Synthesis of 5-acetylamidobenzocyclobutenone.....	67
III.5.	Synthesis of 5-succinylimidobenzocyclobutenone.....	68
III.6.	Synthesis of 5-(fluorophenyl)-sulfonamidobenzocyclobutenone.....	69
III.7.	Synthesis of N-(2-hydroxypropane)-5-aminobenzocyclobutenone.....	69
III.8.	Hydrogen bonding in product III-6	71
III.9.	Synthesis of 5-isocyanatobenzocyclobutenone.....	71
III.10.	Reaction of triphosgene with amino-BCBO.....	72
III.11.	Synthesis of 5-hydroxybenzocyclobutenone.....	73
III.12.	Synthesis of bis-imide-BCBO.....	76
III.13.	Preparation of quinone from cyclobutenedione.....	77
III.14.	Proposed mechanism for the catalyzed ring-opening of benzocyclobutenone.....	78
III.15.	Proposed mechanism of tributyl phosphine catalyst.....	80
III.16.	Proposed mechanism of tributyl phosphine with BCBO.....	81
III.17.	Substituted BCBO and alcohol used for the kinetic study.....	82
IV.1.	Preparation of BCBO end-capped diisocyanates.....	101

IV.2.	Curing of BCBO end-capped diisocyanates with diols.....	103
IV.3.	Reaction of liberated isocyanate with urethane.....	104
IV.4.	Synthesis of bis-imide-BCBO IV-5	106
IV.5.	Chain extension of IV-5 with polyester diol.....	109
IV.6.	Synthesis of AB monomer IV-9	111
IV.7.	Polymerization of monomer IV-9	112
IV.8.	Synthesis of benzocyclobutenone vinyl monomer IV-11	115
IV.9.	Copolymerization of monomer IV-11 with styrene.....	116
IV.10.	Grafting polymer IV-12b with poly(ethylene glycol) methyl ether.....	120
V.1.	Synthesis of cyclobutenedione by [2+2] cycloaddition.....	137
V.2.	Synthesis of cyclobutenedione from ketone.....	137
V.3.	Synthesis of substituted naphthoquinones from benzocyclobutenedione....	138
V.4.	Formation of quinone via a maleoylcobalt complex.....	139
V.5.	Synthesis of quinone via addition of an organolithium.....	139
V.6.	Alkenyl cyclopentenedione from cyclobutenedione.....	140
V.7.	Reaction of cyclobutenedione with nucleophiles.....	140
V.8.	Poly(aryl ether)s containing fused benzene rings.....	142
V.9.	Preparation of high molecular weight polybenzophenone.....	143
V.10.	Polymer precursor to heterocyclic poly(aryl ether)s.....	144
V.11.	Possible tranformation of cyclobutenedione containing polymer.....	146
V.12.	Electrophilic route to poly(aryl ether)s.....	147
V.13.	Nucelophilc route to poly(aryl ether)s.....	148
V.14.	Synthesis of 3,4-bis(4-fluorophenyl)-cyclobut-3-ene-1,2-dione (V-1).....	150
V.15.	Model reaction for the polymerization.....	157
V.16.	Polymerization of monomer V-1	158
V.17.	Zwitterionic species formed during polymerization.....	162
V.18.	Copolymerization of monomer V-1 with 4,4;-difluorophenyl sulfone.....	165
V.19.	Synthesis of 3,4-diphenyl cyclobut-3-ene-1,2-dione (V-5).....	168
V.20.	Thermal reaction of nucleophiles with four-membered ring cyclic enones..	168

V.21.	Thermal reaction of diphenylcyclobutenedione with alcohol.....	169
V.22.	Thermal polymer transformation with 1-octanol.....	170
V.23.	Photochemical reactions of cyclobutenedione.....	172
V.24.	Photochemical reaction of V-1 with 1-octanol.....	173
V.25.	Photochemical transformation of polymer V-3c with 1-octanol.....	174

List of Figures

I.1.	Molecular orbitals of ketene.....	8
I.2.	Benzocyclobutenone: a derivative of benzocyclobutene.....	20
II.1.	Pyrolysis apparatus.....	35
II.2.	¹ H NMR spectrum of the reaction mixture of II-3b	45
II.3.	Conversion of alcohols by reaction with benzocyclobutenone.....	46
II.4.	Conversion of alcohol for various benzocyclobutenone ratio.....	48
II.5.	Conversion of alcohol by acid catalyzed reaction with benzocyclobutenone.....	50
III.1.	¹ H NMR spectrum of III-6	70
III.2.	Plot of T _{RO} versus σ_m with T _{max} and T _{onset} for III-4	75
III.3.	DSC trace of III-4 with a heating rate of 50 °C/min, showing T _m , T _{max}	84
III.4.	and T _{onset} of the exothermic peak.....	
	Plot of log β versus 1/T for III-3	85
IV.1.	DSC traces of BCBO prepolymer IV-1 with and without PEG-600.....	102
IV.2.	TG and DTA curves of IV-5a	108
IV.3.	¹ H NMR spectra (400 MHz, CDCl ₃) of IV-9 , IV-10 and II-2	113
IV.4.	IR spectra of monomer IV-11 and polymer IV-12b	118
IV.5.	DSC traces of copolymer IV-12b	118
IV.6.	IR spectra of polymer IV-12b and grafted polymer IV-12b-550	121
V.1.	Grafting methods.....	145
V.2.	Resonance structures of cyclobutenedione.....	148
V.3.	Calculated charge density for difluoro monomers.....	153
V.4.	Chemical shifts of the proton ortho to the reactive group.....	154

V.5.	Chemical shifts of the fluorine-bearing carbons relative to TMS.....	155
V.6.	Chemical shifts of fluorine relative to CCl ₃ F.....	156
V.7.	IR spectra of diphenylcyclobutenedione and its aluminum chloride complex.....	163
V.8.	IR spectra of the gel and polymer from V-3a.....	164

Symbols and Abbreviations

6FDA	4,4'-(Hexafluoroisopropylidene)diphthalic anhydride
BCB	Benzocyclobutene
BCBO	Benzocyclobutenone
BPA	4,4'-isopropylidenediphenol
BPDA	3,3',4,4'-Biphenyltetracarboxylic dianhydride
δ	Chemical shift (ppm)
DMAc	N,N-dimethylacetanamide
DMF	N,N-dimethyl formamide
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
GC	Gas chromatography
GPC	Gel permeation chromatography
HRMS	High resolution mass spectroscopy
IR	Infrared spectroscopy
J	Coupling constant
MS	Low resolution mass spectroscopy
MW	Molecular weight
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
NMP	1-Methyl-2-pyrrolidinone
NMR	Nuclear magnetic resonance
TG	Thermogravimetry
THF	Tetrahydrofuran
PMDA	Pyromellitic dianhydride
TMS	Tetramethyl silane
T_g	Glass transition temperature
T_m	Melting temperature

$T_{\max}$	Temperature at maximal peak height
T_{RO}	Ring-opening temperature
T_{onset}	Onset temperature
VOC	Volatile organic compound
d	Doublet
dd	Doublet of doublet
m	Multiplet
mp	Melting point
q	Quintet
s	Singlet
t	Triplet

Chapter I

Polymer Curing and Ketenes Chemistry

The term curing comes from cure (= solidification). This terminology is based on the change in physical properties of the material during the process; before curing the material is “soft” and becomes “hard” during cure. Curing refers to the process during which a polymer is transformed and can take place during or after the processing. Several reactions can take place during polymer curing; these are chain extension, grafting, dehydration, crosslinking to name a few. Curing leads to the formation of insoluble and infusible polymers. The polymer chains are connected at several points (crosslinks), hence forming a three dimensional network. A crosslinked network is obtained from either linear polymer containing functional group capable of reacting with itself, or functionalized polymer and crosslinking agent. Crosslinked polymers may also be obtained from monomer with an average functionality greater than two.

Infusible materials obtained from polyfunctional and low molecular weight materials are mostly used in adhesives, paints and compression molding. However, linear polymers with reactive functional group are first processed (extrusion or compression molding) and then cured to obtain an infusible material; typical examples are the vulcanization of rubber and the preparation of glass fibers.

The need for polymers with high thermal stability and good mechanical properties at high temperature greatly increased with their applications in aerospace and electronics.

The polymers meeting such stringent requirements are aromatic rigid-rod polymers, whose main drawback is their poor solubility and infusibility due to high glass transition (T_g) or melting temperature (T_m). Introduction of flexible linkage such as ether, methylene, or small pendant group improved the processability of the polymer. However the glass transition temperature was also depressed by the present of flexible groups, hence lowering the use temperature. The decomposition temperature was lowered by the presence of aliphatic groups.

Polymer curing allows the combination of the most desirable properties for the preparation of thermally stable polymer. The introduction of a crosslinking site at the end chain of oligomers has received much attention because of the higher melt-flow properties of the oligomer compared to high molecular weight polymer. In addition, the cured polymer showed the same or improved properties compared to that of the linear high molecular weight polymer (i.e. thermal stability, mechanical properties and resistance to solvent).¹

The curing system has to meet several requirements. First of all, the curing agents have to remain inactive during polymerization. The reaction should also take place above the T_g of the polymer, but below its decomposition temperature. Furthermore, the product of reaction should have a thermal stability comparable or higher than the initial polymer. Finally, the curing reaction has to be specific and proceed rapidly.

I.1. Curing Chemistry

The curing chemistry relies on the presence of functional groups that would not

react during polymerization, but would under different conditions (i.e. higher temperature or irradiation). Other systems using "masked" functional groups have also been developed for functional groups that are too reactive (i.e. isocyanate). In such a system the masking agent is liberated before the desired reaction takes place. The last type of curing system is based on the presence of a latent group in the polymer. The curing chemistry will be presented here with respect of the evolution or not of by-products during the curing reaction.

I.2.1. Curing Systems With Volatile By-Products

Polyimides are known for their high thermal stability and their poor processability. The typical synthesis of polyimides is by reacting a dianhydride with a diamine. A polyamic acid is first obtained. The polyimide is then obtained by evolution of water to form the imide groups. The polyimide precursor (polyamic acid) are more easily processed than polyimides. Thus polyimide materials can be obtained by condensation of a polyamic acid. However the evolution of water during the reaction could lead to the presence of voids in the material which would impair its mechanical properties.

Scheme I.1. Polyimides from polyamic acid precursor.

Polyurethanes are traditionally prepared from a diisocyanate and a diol; this constitutes a two-component heat-curing polyurethane. The two components have to be kept separately because of the high reactivity of isocyanate towards alcohol. One component heat-curing polyurethanes have been developed by masking the isocyanate group with a phenol or an oxime. The resulting urethane is not thermally stable, thus upon heating the isocyanate is regenerated and then reacts with the alcohol. However the main drawback with this system is the release of toxic by-products during the curing reaction.

Scheme I.2. One component heat-curing polyurethane.

Polyimides² and poly(aryl ether)s³ have been crosslinked with triazene terminated polymers. The dimethyl phenyl triazene end-group decomposes to an aryl radical, nitrogen and an aminyl radical. The aryl radical reacts with an aromatic ring of the oligomer to form a σ -complex that reacts with the aminyl radical to produce a crosslink and liberate dimethylamine.

I.2.2. Curing System Without Volatile By-Products

I.1.2a. Carbon Based Systems

Several carbon-based curing systems have been developed. The curing results from self coupling reaction of the crosslinking end-group. Acetylene has been used to crosslink

polyimides.⁴ However, it has not been determined unambiguously whether the curing reaction proceeded by cyclotrimerization⁵ or polymerization⁶ of the acetylene group (Scheme I.3).

Scheme I.3. Curing reaction of acetylene.

Upon thermolysis, paracyclophane ring-opened to a diradical which can then polymerize or dimerize (Scheme I.4).⁷ Paracyclophane has been used to crosslink poly(aryl ether)s⁸ and polyquinolines.⁹

Scheme I.4. Thermolysis of paracyclophane.

Thermal activation of benzocyclobutene (BCB) generated a highly reactive diene (o-quinodimethane), which could then enter into a wide variety of reactions such as dimerization, oligomerization and Diels-Alder cycloaddition (Scheme I.5). Benzocyclobutene group has been introduced as an end group¹⁰ or a pendant group.¹¹ Thus, it has been incorporated into high-performance polyimides,¹² aromatic polyamide,¹³ poly(arylene ether)s¹⁴ and polystyrene.¹⁵

Scheme I.5. Thermal reactions of benzocyclobutene.

Biphenylene has been used for the crosslinking of polyquinolines.¹⁶ However, the degree of crosslinking was not always high enough to change the polymer properties.¹⁷ This is due to the fact that dimerization of biphenylene leads only to chain extension. Crosslinking was obtained only from the reaction of biphenylene with quinoxaline. Better results were obtained when a mixture of acetylene- and biphenylene-terminated polymer led to a crosslinked material via the formation of phenanthrene group (Scheme I.6).¹⁸

Scheme I.6. Crosslinking reactions with biphenylene.

I.1.2a. *Non-Carbon Based Systems*

Polyimides and polyamides have been thermally crosslinked by trimerization of nitriles¹⁹ and cyanamides.²⁰ The resulting cured material showed higher thermo-oxidative stability than that cured with norbornene. This was due to the presence in the cured material of methylene groups when cured with norbornene.

Epoxides react with a wide variety of functional groups (i.e. amine, alcohol, carboxylic acid or anhydride and with itself). The reaction with primary amines is used to produce crosslinked networks. The epoxide is introduced in the polymer at the end-chain or as a pendant group, and an amine or a diamine is used as the crosslinking agent.

The curing chemistry leading to void-free materials is mostly based on self coupling or polymerization of the crosslinking agents and Diels-Alder reaction. The only crosslinking agent that reacts with nucleophiles is the epoxide. Since the thesis work investigates the use of ketenes as a curing agent, a brief overview on the preparation and the reactivity of ketenes is necessary.

I.2. Ketenes

Ketene ($\text{C}=\text{C}=\text{O}$) is a linear moiety. The $\text{C}=\text{O}$ bond length is 1.16 Å, which is shorter than the length of $\text{C}=\text{O}$ bond (1.22 Å) for aldehyde and ketone. The $\text{C}=\text{O}$ bond length corresponds to the length of the $\text{C}=\text{O}$ bond in carbon dioxide. The shorter $\text{C}=\text{O}$ bond in ketene implies an increase of the “triple bond” character.²¹ This increase in triple bond character arises from the relative importance of the resonance structure A over the

two others (B and C) (Scheme I.7).

Scheme I.7. Resonance structure of ketene.

Ketene reactivity can be rationalized from the HOMO and LUMO geometry.²² The LUMO has been determined to be in the ketene plane with a higher coefficient on C_α , whereas the HOMO is perpendicular to the ketene plane with a higher coefficient on C_β (Figure I.1). This implies that nucleophilic attack will occur on C_α ²³ and electrophilic attack on C_β of the ketene.

Figure I.1. Molecular orbitals of ketene.

I.2.1. Preparation of ketenes

Ketenes can be prepared in numerous ways as shown in Scheme I.8. Most ketenes cannot be isolated due to their instability. Hence, ketene formation is usually demonstrated via a trapping experiment and by isolating the products from its reactions with alcohol and cyclopentene.²³⁻⁴⁷

The dehalogenation of 2-haloacyl halides in the presence of activated zinc is the oldest²⁴ and the most widely used method to generate ketenes.²⁵ The first ketene, diphenyl ketene, was prepared by Hermann Staudinger using dehalogenation of α -

bromodiphenylacetyl bromide.²⁴ This method gives excellent yields for stabilized ketenes. Metal anions such as $\text{Mn}(\text{CO})_5^-$ and $\text{Cr}(\text{CO})_4\text{NO}^-$ have also been shown to be effective in dehalogenation.²⁶

Dehydrohalogenation of acyl halides involved the elimination of hydrogen halide using a tertiary amine.²⁷ The initial step of the reaction is the formation of an acylammonium salt.²⁸ However, the use of tertiary amine may lead to other products.²⁹ Monoalkylketenes cannot be prepared by this method since they dimerize in the presence of triethylamine hydrochloride. The dehydrochlorination of acyl chloride is also affected with a metal catalyst.³⁰

The preparative value of the Wolf rearrangement reaction arises from the reactivity and ready accessibility of α -diazocarbonyl. The rearrangement can be triggered either thermally,³¹ photochemically³² or by metal catalysts.³³ The Wolf rearrangement provides a very versatile method for the preparation of ketenes with a wide variety of structural types. However, side reactions such as C-H insertion by the carbene intermediate³⁴ or fragmentation of the ketene³⁵ is more likely to occur in a thermal or catalyzed reaction than in a photochemical one.

Alkylketenes can be obtained by reaction of carboxylic acid over alkali metal-exchange zeolite.³⁶ Direct dehydration of carboxylic acid also leads to the formation of ketene.³⁷ Alkylketenes³⁸ and the parent ketene³⁹ are also produced by pyrolysis of acid anhydride. Photochemical decomposition of cyclic ketones provides ketenes via a biradical.⁴⁰ Most of the reactions are carried out in alcoholic solvents, and as a result the ketene is converted to the ester.⁴¹ However, the formed ketene may further react to yield

Ketenes are obtained by thermolysis of alkynyl ethers.⁴³ The main drawback of this route is the availability and stability of the alkynyl ether under the reaction conditions.⁴⁴

Ketene is also produced by reverse [2+2] or [4+2] Diels-Alder reaction. Thermal decomposition of cyclobutane-1,3-dione (ketene dimer) regenerates ketene. The photochemical decomposition also leads to ketene but lower yields are obtained due to side reactions.⁴⁵ Cyclobutanone and cyclobutenone produces ketenes by thermolysis⁴⁶ or photolysis.⁴⁷ The cleavage is thought to proceed via a biradical, but alternative paths cannot be excluded.⁴⁸

- Dehalogenation

- Dehydrohalogenation

- Wolf rearrangement

- Dehydration of carboxylic acid

- Decomposition of acetic anhydride

- Decomposition of cyclic ketone

- Decomposition of alkynyl ether

- From cyclobutanone

Scheme L8. Routes to ketene formation.

I.2.2. Reactions of ketenes

Ketenes are very reactive towards both unsaturated compounds and nucleophiles.⁴⁹ However, the [2+2] cycloaddition of ketene is by far the most synthetically useful reaction of ketenes. Additions of alcohol, amine or acid are not usually used in synthesis as the corresponding ester, amide or anhydride can be obtained by simpler routes.

I.1.2a. *Cycloadditions*

Ketenes react with unsaturated compounds to produce the [2+2] cycloadduct. Ketenes react even with carbon-carbon double⁵⁰ and triple⁵¹ bond to form cyclobutanone and cyclobutenone. Ketenes also react with carbonyl,^{52,53} imine^{25,54} and azo compound⁵⁵ to yield four-membered ring 2-oxetanones, 2-azetidinones and diazetidinones, respectively (Scheme I.9). The cyclobutanones from the reaction of ketene with cyclopentadiene were found to be a versatile intermediate.⁵⁶ They are used to produce tropones which are precursors to colchine.⁵⁷ Ring contraction of α -halocyclobutanone produces cyclopropanes.⁵⁸ Decarbonylation of β -lactone yields alkenes.⁵⁹

The [2+2] cycloaddition is the preferred reaction of ketenes. However, in few cases ketene is the dienophile in [4+2] cycloaddition of some dienes or β -unsaturated ketones.⁶⁰ The [4+2] cycloaddition is a more common reaction for vinyl-⁶¹ and oxo-⁶² ketene (Scheme I.10). The [4+2] cycloaddition of acyl ketene is used in the synthesis of compounds with herbicidal activity⁴² and an HIV protease inhibitor.⁶³

According to the Woodward-Hoffman rules, thermal [2+2] cycloadditions are forbidden since the total number of electrons is not $4n+2$, but $4n$. Hence, the

photochemical [2+2] cycloaddition is allowed. Thus, the suprafacial cycloaddition, [$\pi 2_s + \pi 2_s$], is ruled out, but the antarafacial, [$\pi 2_s + \pi 2_a$], reaction is allowed. Even though the [$\pi 2_s + \pi 2_s$] cycloaddition is allowed, it has not been observed for ordinary alkenes. However, it occurs with ketenes and other linear molecules in which steric hindrance is minimal.

- Alkene

- Alkyne

- Carbonyl

- Imine

- Azo compound

Scheme I.9. [2+2] Cycloaddition of ketenes with unsaturated compounds.

Scheme I.10. [4+2] Cycloaddition of ketene.

Although the [2+2] cycloaddition of ketene with alkene has been widely studied the mechanism still causes some controversy.⁶⁴ From the higher reactivity of *Z* alkenes over *E* alkenes, it was determined that the ketene approaches the alkene perpendicularly.⁶⁵ Two mechanisms have been proposed, a concerted reaction and a mechanism via a dipolar intermediate, and there is evidence supporting both mechanisms (Scheme I.11). The retention of the alkene stereochemistry supports the concerted reaction or a two step reaction in which no free bond rotation is possible in the intermediate. On the other hand, partial loss of stereochemistry was observed with some *E* alkenes was thought to be the result of a two-step mechanism.⁶⁶

Concerted mechanism

Mechanism via a dipolar intermediate

Scheme I.11. Proposed mechanism for [2+2] cycloaddition.

I.1.2b. Nucleophilic Additions

Ketenes also react with nucleophiles like hydride,⁶⁷ water,⁶⁸ alcohols,⁶⁹ amine⁷⁰ and amide⁷¹ to give the corresponding enol, acid, ester, amide or imide (Scheme I.12). Intramolecular hydride attack occurs in 4-methyl-vinyl ketenes to form the corresponding aldehyde.⁷² The addition of alcohol was synthetically useful in the preparation of unsaturated ester from vinyl ketene.⁷³ Reaction with amines was used in the synthesis of indolizidine and quinolizidine.⁷⁴

The nucleophilic attack also occurs at the C_α of the ketene. Electronic and steric effects of the ketene substituents were rationalized by an in-plane attack.²³ When amine was used as a nucleophile, a zwitterionic intermediate was observed by NMR spectroscopy.⁷⁵

- Hydride

- Water

- Alcohol

- Amine

- Amide

Scheme I.12. Nucleophilic addition to ketenes.**I.1.2c. Electrophilic Additions**

The electrophilic addition on ketenes occurs with protons⁷⁵ and metal alkoxides⁷⁶ (Scheme I.13). Addition of carboxylic acid,⁷⁷ phosphoric acid⁷⁸ and sulfonic acid⁷⁹ to ketenes produces mixed anhydrides.

- Protonation

- Reaction with metal alkoxides

Scheme I.13. Electrophilic addition to ketenes.

I.1.2d. Radical Reactions

Radical additions to ketenes have been studied with the hydroxyl radical.⁸⁰ The hydroxyl radical addition occurs on either carbon of the ketene and is followed by bond cleavage (Scheme I.10).

Scheme I.14. Reaction of hydroxyl radical with ketene.

I.3. Rationale and Objectives

To our knowledge ketene has not been used in polymer chemistry. However, ketenes are valuable intermediates in natural product synthesis, where the [2+2] cycloaddition is extensively used. But the reaction of ketenes with nucleophiles is not synthetically useful since esters and amides can be prepared by simpler routes.

Both the cycloaddition and nucleophilic addition could be used in polymer synthesis. The cycloaddition reaction of ketene with an unsaturated substrate could be used in unsaturated polymers, or polymers with a reactive end-group. This curing system

would be too similar to the ones described previously (Section I.1.1), providing for little opportunity to break new ground in research. However, the reaction of ketenes with nucleophiles would be of great value to the hydroxy or amine containing polymers, since the reaction of ketenes with alcohol or amine leads to the formation of an ester or amide without producing any by-product.

The only existing curing systems that exhibit the same features are epoxides and isocyanates. Both systems require the use of a masking agent since the reaction will take place as soon as the isocyanate or epoxide are in the presence of an alcohol or an amine. The major drawback associated with the masking agent is that a toxic product is liberated during cure.

The ketene system will be of great value only if the generation of the ketene occurs without releasing any by-product. The only volatile organic compound (VOC)-free route to alkyl ketene is by irradiation of cyclic ketones. Vinyl- and bis-ketenes are easily prepared by electrocyclic ring-opening of cyclobutenone⁸¹ and cyclobutenedione,⁸² respectively (Scheme I.15).

Scheme I.15. Ketene precursors to be investigated for polymer curing.

Our ultimate goal is to develop a versatile, environment friendly curing chemistry which can be used in a wide variety of polymer systems that need to be cured. This curing reaction will be based on the ketene reaction with alcohol. However, ketenes are too

reactive to be present in prepolymers, thus they have to be introduced as a latent group. This ketene precursor has to survive the polymerization and remain inactive until triggered by heat or irradiation. Furthermore, the whole curing reaction (i.e. generation of ketene and its reaction) should not produce any by-products.

In order for this ketene system to be applicable to a wide variety of polymer systems, the ketene precursor has to be functionalized and then incorporated into a polymer. Furthermore, the cure should take place under a wide range of reaction conditions, in order to accommodate various type of polymers.

The ketene precursors, once introduced into a polymer, would generate ketenes, which then react with alcohol or amine containing polymers. This could be used for branching, chain extension and crosslinking.

I.3.1. Benzocyclobutenone

Benzocyclobutenone (BCBO) was chosen as a vinyl ketene precursor. Its structure is very close to that of benzocyclobutene (BCB) (Figure I.2), which has been functionalized and successfully introduced as a crosslinking agent in various polymer systems. However, the BCB chemistry is based on dimerization and Diels-Alder reactions. Benzocyclobutenone, like BCB, undergoes cycloaddition, but this would not make use of the full potential of BCBO. Indeed for the Diels-Alder reaction, the presence of a ketone on the cyclobutene ring would not provide any advantage over the existing BCB system.

Figure I.2. Benzocyclobutenone: a derivative of benzocyclobutene.

In order to evaluate the use of BCBO as a ketene precursor for curing purposes, the reaction with alcohol will be investigated so as to find the best reaction conditions. BCBO will then be functionalized to be introduced in polymer systems. Finally, BCBO containing material will be prepared and cured with alcohols to obtain extended linear polymer and branched polymers.

I.3.2. Cyclobutenedione

The cyclobutenedione will be used as a bis-ketene precursor in poly(aryl ether)s. The cyclobutenedione unit will be introduced in the difluoro monomer. The cyclobutenedione moiety should be sufficiently electron withdrawing to activate the monomer. The difluoro monomer can be prepared from squaric acid (Scheme I.16). The cyclobutenedione unit introduced in the polymer backbone should generate a bis-ketene and subsequently produce a diester by reaction with alcohols, hence producing a branched polymer.

Scheme I.12. Disubstituted cyclobutenedione: a derivative of squaric acid.

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Chapter II

Benzocyclobutenone: Synthesis and Reactions

II.1. Synthesis of Benzocyclobutenone

II.1.1. Introduction

For synthetic purposes, benzocyclobutenone may be considered a derivative of either benzocyclobutene or cyclobutenone. Benzocyclobutene (BCB) ring-opens to give *o*-quinodimethane which can be trapped with maleic anhydride.¹ The ring-opening has been shown to be reversible.² BCB has indeed been obtained from *o*-quinodimethane generated by the pyrolysis of 1,3-dihydroisothionaphthene-2,2-dioxide.³ The first synthesis of BCB was achieved via electrocyclization of *o*-quinodimethane.⁴ Since then, BCB and several derivatives have been prepared by 1,4-elimination of hydrogen halide or dihalide, followed by ring closure (Scheme II.1).

Scheme II.1. Synthesis of benzocyclobutene by electrocyclization.

Cyclobutenones also undergo ring-opening upon thermolysis to yield a vinyl ketene. Early attempts to utilize the reverse reaction for the synthesis of cyclobutenone proved unsuccessful. Treatment of unsaturated acids with thionyl chloride in acetic acid did not yield the cyclobutenone.^{10,11} On heating of 2-chloro-3-phenyl-3-butenic acid (1) in acetic anhydride, a vinyl ketene was generated which did produce 2-chloro-3-phenyl cyclobutenone in 20 to 30% yield (Scheme II.2).¹¹ The pyrolysis of 1-ethoxypentachloro-1,3-butadiene (2) produced perchlorocyclobutenone in 85% yield.¹² Wolf rearrangement of diazoketone (3) generated a vinyl ketene which underwent intramolecular cycloaddition to form a cyclobutenone in moderate to high yield.¹³

Scheme II.2. Synthesis of cyclobutenones.

However, cyclobutanone and cyclobutenone are more commonly prepared by [2+2] cycloaddition of a ketene with an alkene¹⁴ or an alkyne¹⁵ (Scheme II.3).

Scheme II.3. Reaction of ketene with alkenes and alkynes.

II.1.2. Synthesis of Benzocyclobutenone

The synthesis of benzocyclobutenone (BCBO) was first reported by Cava *et al.* in 1960 (Scheme II.4).¹⁶ Reaction of 1-bromo-benzocyclobutene (4) with silver trifluoroacetate produced benzocyclobutenyl trifluoroacetate (5). Hydrolysis of 5 gave benzocyclobutenol (6). Finally, BCBO (II-1) was obtained by oxidation of 6 with chromic

acid anhydride in pyridine. To date, many synthetic routes have been reported for the preparation of BCBO.¹⁶⁻²³ The synthesis of BCBO can be achieved through either solution or gas phase chemistry. The solution chemistry often proceeds via a benzyne. Whereas in the gas phase, benzocyclobutenone is made by reverse electrocyclization of a vinyl ketene.

Scheme II.4. First synthesis of benzocyclobutenone.

Most of the BCBO syntheses in solution involved the *in situ* formation of a benzyne. The four-membered ring was then formed by [2+2] cycloaddition with an activated alkene (Scheme II.5). Benzyne was generated either from anthranilic acid (7),¹⁷ bromobenzene (9)¹⁸ or *o*-iodo benzene triflate (10).¹⁹ The four-membered ring was formed by [2,2] cycloaddition of benzyne with either 1,1-dichloroethylene¹⁷ or methyl ketene acetal.^{18,19} Benzocyclobutenone was finally obtained by hydrolysis of 1,1-dichloro- or 1,1-dimethoxy benzocyclobutene (11 or 12).

Scheme II.5. Synthesis of benzocyclobutenone via benzyne.

Benzocyclobutenone has been synthesized via electrocyclization of a vinyl ketene intermediate (Scheme II-6). *o*-Quinoid ketene was generated by pyrolysis of 1,2-indandione (**13**),²⁰ homophthalic anhydride (**14**),²¹ bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic anhydride (**15**)²² and *o*-toluoyl chloride (**16**).²³ The pyrolysis was accompanied by evolution of carbon monoxide, carbon dioxide or hydrochloric acid. The yield of benzocyclobutenone varied from 11 to 54%.

Scheme II.6. Synthesis of benzocyclobutenone by pyrolysis.

In this work both the solution and gas phase synthesis of benzocyclobutenone were investigated. First, the solution chemistry.

II.1.2a. Solution Chemistry

Benzocyclobutenone (**II-1**) was prepared from vinylidene chloride and anthralinic acid. Benzyne was generated *in situ* by decomposition of the diazonium salt (**8**). Hydrolysis of 1,1-dichloro benzocyclobutenone (**11**) with 3% sulfuric acid then afforded **II-1**. The yield obtained (55%) was similar to the reported one (60%).¹⁷ The moderate yield of this reaction was due to the high reactivity of benzyne. In the absence of a nucleophile, benzyne can dimerize to biphenylene. Biphenylene is indeed a common by-

product in reactions proceeding via benzyne. Thus, vinylidene chloride had to be used in excess in order to reduce the dimerization of benzyne. Furthermore, vinylidene chloride is volatile and slowly evaporates during the reaction even under efficient recovering conditions.

The reaction was also attempted using diethyl ketene acetal. Diethyl ketene acetal was prepared by dehydrobromination of ethyl bromo acetaldehyde.²⁴ White solids appeared in the distillate flask upon standing, which was the polymerization product of diethyl ketene acetal. Indeed, ¹H NMR did not exhibit any vinyl proton. Diethyl ketene acetal does polymerize readily in the presence of trace amounts of an acid. The acidity of the inner surface of the glass container is sufficient to initiate the polymerization.²⁵ Reaction of diethyl ketene acetal with bromobenzene in the presence of sodium nitrite gave a brown solid. Hydrolysis of that brown solid yielded only a trace amount of **II-1**.

II.1.2b. Gas Phase Chemistry

Even though benzocyclobutenone could be prepared in large scale by solution chemistry, with easy experimental procedures. The diazonium salt intermediate is explosive when dry, hence much care has to be taken when handling this product. Furthermore, the yields of **II-1** from anthranilic acid and vinylidene chloride were reproducible and acceptable (overall yield 55%). However, this process is not environmentally friendly. This synthetic route necessitated large quantities of solvent (1.5 liters of chlorinated solvent and 2 liters of diethyl ether for 80 g of BCBO) and produced large amounts of solid wastes. On the other hand, the gas phase reaction is cleaner as there

is no solvent involved and the intermediate is not a diazonium salt. However, the reported yield of BCBO by pyrolysis was low to moderate (10 to 50%) depending on the starting material (Scheme I.6). Starting materials **13**, **14**, **15** (Scheme II.6) are not commercially available; multistep syntheses render their use less favorable for large scale synthesis. However, *o*-toluoyl chloride is easily obtained from *o*-toluic acid, which is derived from petrochemicals.

Thermal elimination of hydrochloric acid occurred readily with *o*-alkyl substituted acyl chlorides.²⁶ Schiess used this thermal elimination on *o*-toluoyl chloride to prepare BCBO and some derivatives.²⁷ The flash vacuum pyrolysis was carried out under 14 torr and with a furnace temperature of 630 °C and BCBO was obtained in 28% yield.²⁷ The yield increased to 60-70% when a second methyl group was in ortho position of either the methyl or the acyl chloride. The same procedure was used to prepare a pyridine analogue of BCBO.²⁸ The BCBO synthesis by pyrolysis of *o*-toluoyl chloride was also investigated in detail in our laboratory.

The pyrolytic apparatus was set up like a vacuum distillation system in which the condenser was replaced by a quartz tube filled with quartz beads. The tube was placed in a tube furnace. The receiving flask was placed in a cold ice bath. The hydrochloric acid evolved was trapped in a column packed with potassium hydroxide pellets (Figure II.1). It was found that the pyrolysis was sensitive to many parameters. The starting material should vaporize before entering the hot quartz tube. Then it should stay in the hot zone long enough to allow the formation of vinyl ketene intermediate. However, this reactive intermediate and the final product should be removed from the hot quartz tube right away

to prevent any further reaction or degradation. Consequently, the pressure and temperature in the system must be finely tuned in order to warrant a high-yield production. The reaction rate is related to the furnace temperature, while pressure governs the time the reactant and product spend in the hot zone. Changes in pressure or temperature may have dramatic effects on the reaction yield.

Figure II.1. Pyrolysis apparatus.

The yields of benzocyclobutenone obtained under different conditions (i.e. pressure and temperature) are summarized in Table II.1. A yield of 28% was obtained at a temperature of 630 °C and a pressure of 14 torr.²⁷ Here, the experiments were carried out at higher temperatures in order to increase the reaction rate and at lower pressures so as to shorten the time the products spend in the hot zone, hence reduce the amount of degradation or side products.

Table II.1. Pyrolysis of *o*-toluoyl chloride at different temperature and pressure.

Run	1	2	3	4	5	6	7	8
Column Temperature (°C)	630	780	780	780	780	780	800	800
Pressure (Torr)	5	5	5	1.75	1.25	0.5	1.75	0.5
Yield of BCBO (%)	53	59	60	35	27	80	32	75

Overall, the yields of BCBO obtained were higher than the one reported by Schiess. A significant improvement in the yield was observed when the pressure was decreased from 14²⁷ to 5 torr (run 1) with a temperature of 630 °C. The lower the pressure is, the fewer the by-products are produced. Some of the degradation products of BCBO have been identified to be benzocyclopropene (17)²⁹ resulting from the loss of carbon monoxide, fulveneallene (18)^{29,30} a rearrangement product of benzocyclopropene,¹¹ and ethynylcyclopentadiene (19)²⁹ (Scheme II-7). An increase in the column temperature from 630 to 780 °C, had little effect on the yield (runs 2-3). A decrease of the pressure in the system, at 780 °C, did not in this case increase the yield as it did at 630 °C, but rather lowered it (runs 4-5). However, a significant increase in the yield (80%) was observed when the pressure was set at 0.5 torr (run 6) while keeping the temperature at 780 °C. At higher temperature, 800 °C, the yield was slightly lower than it was at 780 °C (runs 7-8). As proven in runs 2 and 3, the results obtained were reproducible.

Scheme II.7. Thermal degradation products of benzocyclobutenone.

The product obtained was characterized by spectroscopic analysis. The IR spectrum showed the characteristic bands at 1781 and 1758 cm^{-1} (lit.³¹ 1775 and 1755 cm^{-1}). The ^1H NMR spectrum exhibited the expected singlet at 3.97 ppm for the methylene group. The ^{13}C NMR spectrum showed eight peaks corresponding to the eight chemically non-equivalent carbons of BCBO.

II.2. Reactions of Benzocyclobutenone

Conversion of cyclobutene to butadiene has been shown to be an unimolecular reaction.³² This conversion is also valid for benzocyclobutene and its derivatives. Benzocyclobutenone has been reported to undergo electrocyclic ring-opening upon thermolysis^{33,34} or photolysis^{33,35} to give *o*-quinoid ketene (20) (Scheme II.8). The *o*-quinoid ketene (20), when generated at low temperature (77 K), regenerated benzocyclobutenone (II-1) upon warming up of the solution.³⁶ The loss of carbon monoxide was observed, when *o*-quinoid ketene was generated by pyrolysis or photolysis with a mercury lamp. Benzocyclopropene (17) and its rearrangement product, fulveneallene (18), were then formed.^{33,37} Ketenes have been reported to lose carbon monoxide when irradiated at 212 nm³⁸ and 308 nm.³⁹

Scheme II.8. Ring-opening of benzocyclobutenone.

The resulting vinyl ketene (**20**) undergoes [4+2] cycloaddition with unsaturated substrates to yield six-membered rings (Scheme II.9). The cycloaddition does not only take place with unsaturated carbon-carbon bonds, such as dimethyl fumarate (**21**),⁴⁰ dimethyl acetylenedicarboxylate (**22**),⁴⁰ naphthoquinone (**23**)⁴⁰ and C_{60} ,⁴¹ but also with carbonyls, such as chloral (**24**)^{40a} and diethyl azodicarboxylate (**25**).^{40a}

Scheme II.9. Reaction of benzocyclobutenone with unsaturated substrates.

Cyclobutanone⁴² and cyclobutenone⁴³ are not stable in presence of hydroxide ion. Nucleophilic attack of the hydroxide at the carbonyl carbon, followed by bond cleavage produced a carboxylic acid. Treatment of benzocyclobutenone with hydroxide ion

produced two carboxylic acids. Each of them resulted from a different bond cleavage of **26** (Scheme II.10).⁴⁴

Scheme II.10. Ring-opening of benzocyclobutenone with hydroxide ion.

II.2.1. Self Coupling Reaction

II.2.1a. Dimerization of Benzocyclobutene

Benzocyclobutene derivatives dimerized upon thermolysis or photolysis to an eight-membered ring and/or [4+2] cycloadduct (Scheme II.11). Benzocyclobutene dimerized to either products **27** or **28** depending on the reaction temperature.⁴⁵ At low temperatures (-78 to 0 °C), *o*-quinodimethane dimerized to the [4+2] cycloadduct **27**. When *o*-quinodimethane was generated thermally the dimerization product was the eight-membered ring **28**. However, at temperature higher than 300 °C only BCB was observed.

Scheme II-11. Dimerization of benzocyclobutene derivatives.

II.2.1b. Dimerization of Benzocyclobutenone

Similar eight-membered rings were obtained from BCBO derivatives (Scheme II.12). The eight-membered ring **29** was produced in trace amount by photooxidation of 1,1'-bis(benzocyclobutenyllidene).⁴⁶ Treatment of BCBO with sodium hydroxide generated an enolate anion, which attacked the carbonyl group of another BCBO, leading to the cleavage of the four-membered ring. Rearrangement and acidic aqueous work-up afforded the eight-membered ring **30**.⁴⁷ Thermolysis of 1,1-dimethoxy- benzocyclobutene yielded the eight membered ring **31** as well as the [4+2] cycloadduct **32**.⁴⁸

Scheme II.12. Dimerization of benzocyclobutenone derivatives.

The dimerization of BCBO upon thermolysis was investigated in this thesis work. Thermolysis of BCBO, done in a sealed tube at 250 °C and under an inert atmosphere, produced the coumarin **II-2** in 60% yield along with some unidentified oligomers (Scheme II.13). The same coumarin was isolated in 40% yield from the reaction of *o*-(trimethylsilyl)benzoyl chloride with cesium fluoride in refluxing acetonitrile, in which a vinyl ketene was also formed.⁴⁹ The vinyl ketene underwent a [4+2] cycloaddition with the carbonyl of a second vinyl ketene to form the six-membered ring. The resulting

cycloadduct **33** was stabilized by an intramolecular 1,5-hydrogen shift⁵⁰ producing **II-2**.

Scheme II.13. Dimerization of benzocyclobutenone.

The dimerization of benzocyclobutenone did not yield the eight membered ring due to the formation of the vinyl ketene intermediate. The dimerization of other vinyl ketene also produced a coumarin derivative (**34**)⁵¹ or a β -lactone (**35**)⁵² (Scheme II.14). The vinyl ketene thus acted as the dienophile and the diene in the dimerization reaction.

Scheme II.14. Dimerization of vinyl ketene.

The coumarin **II-2** was characterized and the spectroscopic data agreed well with the literature values; the IR spectrum showed the presence of an ester and carbonyl peak at 1727 cm^{-1} . The ^1H NMR spectrum exhibited a singlet at 2.53 ppm corresponding to the methyl group and a singlet at 6.62 ppm attributed to the olefinic proton. Finally, MS gave the expected molecular ion peak at m/e 236.

II.2.2. Reaction of Benzocyclobutenone with Alcohols

II.2.2a. *Thermal Reaction with Alcohols*

Prior to this thesis work, the thermal reaction of BCBO with alcohols was not

studied. As our intention was to use this reaction for curing polymers, the reaction temperature and other parameters that might influence the reaction must be first investigated. In addition, the reaction of vinyl ketene with alcohols has to prevail over its dimerization in order to be effective in curing. It would be also of interest to study the relative reactivity of alcohols towards ketene.

In the presence of an alcohol, heating BCBO at relatively lower temperatures (170-200 °C) yielded the corresponding 2-methylbenzoates (**II-3**) in good or even quantitative yields (Scheme II.15). Both aliphatic and aromatic diols of low or high molecular weights reacted with BCBO, giving the corresponding bis-benzoates (**II-4**) in quantitative yields.⁵³ The reaction were run in a sealed tube placed in an oil bath. The reaction conditions and the results are summarized in Table II.2.

Scheme II.15. Thermal reaction of BCBO with alcohols.

Table II.2. Reactions of benzocyclobutenone with alcohols.

Run	Alcohol	Amount (meq) ^a	Temp. (°C)	Time (h)	Product	Yield (%) ^b
1	1-octanol	4.0	200	21	II-3a	94.0
2	1-octanol	1.0	200	30	II-3a	79.3
3	2-octanol	1.0	200	26	II-3b	80.5
4	2-octanol	12	170	56	II-3b	83.3
5	3-ethyl-3-pentanol	1.0	170	19	(II-3c)^c	100
6	benzyl alcohol	1.0	180	5	II-3d	100
7	4- <i>t</i> -butyl phenol	1.0	200	2	II-3e	100
8	ethylene glycol	0.5	200	18	II-4a	100
9	bisphenol A	0.5	200	2	II-4b	100
10	poly(ethylene glycol) ^d	0.5	190	18	II-4c	100

^a Molar equivalent to **II-1**. ^b Isolated yield based on **II-1**. ^c Only 2-toluic acid and 3-ethyl-2-pentene were obtained. ^d Mw = 600.

Comparing the reaction time and yields, aromatic and benzylic alcohols reacted with BCBO more readily than aliphatic alcohols. Among aliphatic alcohols, the secondary alcohol reacted more slowly than the primary one (runs 1 and 3). The reaction rate was slower with one equivalent alcohol than when an excess was used (runs 1 and 2). Increasing the reaction temperature increased the reaction rate (runs 3 and 4). This was rationalized by the decrease of the ratio BCBO/*o*-quinoid (**20**) with increasing temperature. In run 5 with a tertiary alcohol, 2-toluic acid and 3-ethyl-2-pentene were obtained quantitatively. Under the same conditions (170 °C, 24 hours), thermolysis of a mixture of BCBO and water afforded *o*-toluic acid, but 3-ethyl-3-pentanol did not dehydrate to 3-ethyl-2-pentene after 24 hours at 170 °C. Therefore, ester **II-3c** was

formed but thermally decomposed to give 2-toluic acid and 3-ethyl-2-pentene since carboxylate is a better leaving group than hydroxide. The higher reactivity of aromatic alcohols was also observed in runs 8 and 9. For all alcohols, the esterification went to completion using a stoichiometric amount of alcohol (Table II.2) and the reaction was clean (Figure II.2).

II.3.2b. Photochemical Reaction with Alcohols

It is known that irradiation of BCBO generates a vinyl ketene that reacts with alcohol at low temperature (-78°C).³⁵ The photochemical reaction of BCBO with alcohol could be used in the formulation of photoresists and coatings. But more details on the reaction itself need to be known. Thus, the effects of the amount and the nature of the alcohol on the addition reaction need to be investigated. BCBO could potentially be used as a new reagent for the protection of alcohol. Since the reaction is done in neutral media, this reaction would be of great value for acid or base labile alcohols.

The UV spectrum of BCBO showed two absorption peaks at 242 and 288 nm. Accordingly, the photo-reactions were carried out at a wavelength centered at 300 nm. The experiments were first carried out with an excess of BCBO (Scheme II.16).

Figure II.2. ^1H NMR spectrum of the reaction mixture of **II-3b**.

Scheme II.16. Photochemical reaction of benzocyclobutenone with alcohol.

A methylene chloride solution of alcohol and an excess of BCBO was introduced into a quartz cell and irradiated in a UV reactor equipped with 300 nm lamps. The reaction was monitored by gas chromatography (GC), every 30 minutes, until all the alcohol reacted. The percent conversion of alcohol into ester was calculated from the peak area of the alcohol and the ester on the GC curve and shown in Figure II.3.

Figure II.3. Conversion of alcohol in the reaction with BCBO.

The reaction was carried out with both aliphatic and aromatic alcohols. With the aromatic alcohol it proceeded very slowly. A small ester peak was detected by GC after 65 minutes. This is likely due to the absorption of the UV light by the phenol instead of being used for the ring-opening of BCBO. Among the aliphatic alcohols, the primary alcohols reacted faster than the secondary ones. No reaction was observed with a tertiary alcohol. Furthermore, the percent conversion obtained with the primary alcohols was above 90%, whereas a percent conversion was only 75% with the secondary alcohols. This result seemed to indicate a steric effect on the approach of the alcohol.⁵⁴ The selectivity of alcohols in their reaction with ketenes has been studied by Luning;⁵⁵ the primary alcohol reacted faster than the secondary alcohol with ketene and the reaction with the tertiary alcohol was very slow. This selectivity, rationalized in terms of steric hindrance, was valid with and without a base catalyst.

The effect of the concentration of alcohol on the reaction rate was examined as well. The reaction was carried out at 40 °C, with one equivalent and an excess of 1-octanol, respectively (Figure II.4). Using one molar equivalent of alcohol, the reaction rate decreased after 60% conversion; after 350 minutes, the conversion was only 75%. When an excess of alcohol was used, the reaction was completed after 200 minutes without a decrease in the reaction rate.

Figure II.4. Conversion of 1-octanol for various benzocyclobutenone ratio.

The fact that the reaction rate decreased with increasing conversion of alcohol indicated that the reaction order in alcohol was greater than one. Furthermore, the rate started to decrease after 60% conversion. This is in accord with the presence of several alcohol molecules in the transition state.⁵⁶ Yet, this mechanism still raises some controversy. The reaction was first thought to proceed via a cyclic transition state involving an alcohol dimer (36) or trimer (37) (Scheme II.17).⁵⁷ However, more recent studies tend to favor a two-step mechanism. The ketene first reacts with one alcohol to give a small amount of 38. The tautomerization of 38 is catalyzed by a second alcohol, to produce 39.⁵⁸ This second mechanism is preferred as the hydration of ketene follows a same mechanism. Even though there is a disagreement regarding the exact nature of the transition state, it has been determined that two or three alcohol molecules are involved. The reaction has also been shown to be catalyzed by either acid⁵⁶ or base.⁵⁹

Scheme II.17. Proposed mechanism of addition of alcohol to ketene.

II.3.2c Acid Catalysts

In our study, adipic acid, methanesulfonic acid, and an acidic Dowex resin were tested. Dowex resin was treated with concentrated HCl, rinsed with distilled water until neutral washings were obtained and dried under vacuum at 40 °C prior use. The reaction was performed with 1.1 to 1.3 molar equivalent of BCBO and 5% wt of acid. The reaction was initiated photochemically and was followed by use of GC.

The plot of % conversion versus time was linear when methanesulfonic acid was used (Figure II.5). Thus the reaction rate was constant throughout the reaction. However, the reaction stopped after 200 minutes, as no BCBO was left. Up to 60% conversion of 2-octanol, the curves obtained for the other acids (a and c) were similar to the one obtained without catalyst (d), and the reaction rate was relatively constant. Past 60% conversion, the reaction rate decreased significantly when no catalyst was used and the conversion did not exceed 75%. When the Dowex resin was used, the reaction rate decreased gradually and a conversion of 83% was obtained. With adipic acid as a catalyst the reaction rate dropped only after 87% conversion was reached.

Figure II.5. Conversion of 2-octanol by acid catalyzed reaction with BCBO.

The acid catalyzed addition of alcohol to ketene has been studied using carboxylic acids. Kinetic studies indicated that one acid and one alcohol were present in the transition state. Furthermore, it has been shown not to proceed via an anhydride.⁶⁰ Satchell observed that the reaction rate increased with decreasing pK_A value of the acid.⁶¹ A complex such as **40** cannot lead to catalysis of the nucleophilic attack of the oxygen (Scheme II.18), since the acceptance of proton by the acid should be much more effective. Thus, the mechanism was thought to proceed via a cyclic transition state (**41**) similar to that of the uncatalyzed reaction (**37**).

Scheme II.18. Acid catalyzed addition of alcohol to ketene.

Hydration of ketenes in acidic media proceed by attack of a proton at C_β leading to an acylium ion (42) (Scheme II-19).⁶² The acylium ion was detected in the gas phase reaction.⁶³

Scheme II.19. Hydration of ketene.

II.3. Conclusion

Regarding the BCBO synthesis, the solution chemistry gave reproducible yields (54%), in a 80 g scale. This procedure is suitable for laboratory experiments. If however BCBO finds any application in polymer chemistry it would have to be synthesized in a large scale. The pyrolysis of *o*-toluoyl chloride should then be more appropriate; pyrolysis does not necessitate the use of organic solvents and the amount of waste is minimal. Furthermore, the high yield (80%) obtained in batch process could be improved and the synthesis could be done in a continuous process. But this is more of an engineering challenge than a chemistry one.

Regarding the reaction of BCBO with alcohols, it was found that the reaction with tertiary alcohol did not proceed very well; the thermal reaction led to the formation of an acid instead of an ester and the photochemical reaction did not occur. The reaction with aromatic alcohol was fast when done thermally whereas the photochemical proceeded very slowly. Thus the reaction condition will dictate which alcohol to use (i.e., primary, tertiary or aromatic). This difference in selectivity between the thermal and photochemical reaction may be taken advantage of to prepare two different materials from the same starting

materials by simply changing the curing conditions.

II.3. Experimental section

Materials: Anthranilic acid, vinylidene chloride, propylene oxide, bromoacetaldehyde diethyl acetal, potassium t-butoxide, n-butanol, 3-ethyl-3-pentanol, phenol were received from Aldrich Chemical Co. and used without purification. Bisphenol A was recrystallized from toluene. 1-Octanol, 2-octanol and benzyl alcohol were purchased from Fisher Scientific Co. and were used as received.

Characterization: Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Infrared measurements were performed on a Bomem-FTIR Michelson series instrument with a resolution of 4 cm^{-1} , the spectra were recorded after 2 scans. The ^1H NMR and ^{13}C NMR spectra were recorded on either a Varian Gemini-200 or a Bruker-400 instruments and results are reported in ppm from tetramethylsilane on the δ scale. The coupling constants were assigned by assuming first order spectrum obtained. Low resolution mass spectra were obtained on a DuPont 21-492B spectrometer. The photochemical reactions were performed in a Rayinet photochemical reactor with 16 UV lamps.

Benzocyclobutenone (II-1)

From anthranilic acid: In a 2 L beaker, anthranilic acid (41.5 g) was dissolved in absolute

ethanol (495 mL). Once the solution was cooled down in an ice bath, concentrated hydrochloric acid (33 mL) and isoamyl nitrite (82 mL) were added to the magnetically stirred solution. After the mixture was stirred for 15 minutes, diethyl ether (495 mL) was added and the solution was stirred for another 10 minutes. The resulting 2-carboxybenzodiazonium chloride was isolated by vacuum filtration and rinsed with diethyl ether (165 mL). The product was dried first for 30 minutes with suction filtration. It was placed in a desiccator under reduced pressure (water pump) in the presence of phosphorus pentoxide, the pump was then turned off and the product can be kept in the desiccator overnight (**Caution! The salt is explosive when too dry**). The yield of the first step was 87 %. 2-Carboxybenzodiazonium chloride (52.6 g), propylene oxide (39.5 mL) and freshly distilled vinylidene chloride (187 mL) were placed in a dry 2 L round-bottom-flask equipped with a condenser and a nitrogen inlet/outlet. The reaction mixture was refluxed for 20 hours (heating mantle temperature 40-50 °C), cooled down to room temperature and the tan precipitate was removed by filtration. The brown filtrate containing the crude 2,2-dichlorobenzocyclobutene was concentrated to an oil. Vacuum distillation gave the pure dichlorobenzocyclobutenone: IR (NaCl, cm^{-1}) 2942 (C-H), 683 (C-Cl); ^1H NMR (200 MHz, CDCl_3) δ 7.38 (m, 3H), 7.28 (d, 1H, $J_{\text{H-H}} = 26$ Hz), 4.14 (s, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 198.63, 132.22, 129.31, 124.25, 120.75, 57.63; MS (EI, m/e, relative intensity %) 172 (M^+ , 28.1), 137 ($\text{M}^+ - \text{Cl}$, 100), 102 ($\text{M}^+ - 2\text{Cl}$, 50).

The crude dichloro compound was refluxed for 24 hours with aqueous sulfuric acid (3 %wt). Once the reaction mixture was cooled down to room temperature, the crude organic product was extracted with diethyl ether (4 x 80 mL). The organic layers were

pooled together and washed with saturated KHCO_3 (80 mL), and dried over magnesium sulfate. The diethyl ether solution was filtered and concentrated. The resulting oil was distilled under vacuum to give benzocyclobutenone as a colorless liquid (18.5 g, 54.8 %): $\text{bp}_{0.05}$ 35-37 °C; IR (NaCl, cm^{-1}) 1781, 1758, 1585, 958; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (m, 2H), 7.40 (dt, 1H, $J_{\text{H-H}} = 7.9$ Hz, $^4J_{\text{H-H}} = 0.8$ Hz), 7.33 (d, 1H, $J_{\text{H-H}} = 7.6$ Hz), 3.97 (s, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 188.54, 151.28, 147.97, 135.17, 128.70, 123.71, 120.48, 52.34; UV (λ_{max} , nm, CH_2Cl_2) 242, 288; MS (EI, m/e, relative intensity %) 118 (M^+ , 96), 90 ($\text{M}^+ - \text{CO}$, 100).

From diethyl ketene acetal: Bromoacetaldehyde diethyl acetal (12.55 g, 63.7 mmol) was added to a solution of potassium *t*-butoxide (1.0M, 63mmol) in *t*-butanol under nitrogen in a flask equipped with a Vigreux column and a distillation head. As the reaction temperature increased, KBr precipitated out. *t*-Butanol was first distilled off at 85 °C with a distillate ratio of 1:6. Once all *t*-butanol was removed, the temperature was lowered and the system was placed under vacuum (130 mmHg). Diethyl ketene acetal was then distilled as a colourless liquid (3.81 g).

Freshly distilled bromobenzene (1.29 g, 8.2 mmol) and sodium amide (0.66 g, 16.9 mmol) were introduced into the flask containing diethyl ketene acetal as well as some polymeric products. Upon addition of sodium amide a white foam was formed, which disappeared slowly with increasing temperature. The solution was stirred overnight at 80 °C (oil bath temperature). The solution was then cooled with an ice bath, and water (5 mL) was added. The mixture was extracted three times with diethyl ether (10 mL). The organic layers were dried over magnesium sulfate and the solvent evaporated to yield a

viscous brown liquid. This liquid was stirred with an acidic THF solution (THF 5 mL, water 1 mL, HCl 2 drops) overnight at 50 °C. Thin layer chromatography showed only a trace amount of benzocyclobutenone was formed.

Coumarin (II-2)

Heating benzocyclobutenone on its own at 250 °C in a sealed tube under nitrogen. The product was purified by column chromatography using ethyl acetate/hexane (20/80): mp 84-85 °C, IR (KBr, cm^{-1}) 3019, 1727, 1643, 1216, 1063; ^1H NMR (400 MHz, CDCl_3) δ 8.36 (d, 1H, $J_{\text{H-H}} = 7.82$ Hz), 7.75 (dt, 1H, $J_{\text{H-H}} = 7.59$ Hz, $^4J_{\text{H-H}} = 1.25$ Hz), 7.53 (m, 3H), 7.37 (t, 1H, $J_{\text{H-H}} = 7.50$ Hz), 7.30 (d, 2H, $J_{\text{H-H}} = 7.60$ Hz), 6.62 (s, 1H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.94, 162.56, 155.69, 137.55, 136.82, 134.83, 132.85, 131.09, 129.83, 129.67, 129.23, 128.25, 126.11, 126.02, 125.84, 105.91, 20.75; MS (EI, m/e , relative intensity %) 236 (M^+ , 30.4), 208 ($\text{M}^+ - \text{CO}$, 24.5), 193 (208 - CH_3 , 6.6), 119 ($\text{M}^+ - \text{PhCH}_3$, 29.3).

General procedures for thermal and photochemical reaction with alcohol

Thermal Reaction: Benzocyclobutenone and an alcohol were placed in a sealed tube under

nitrogen and reduced pressure (20 mmHg). The sealed tube was immersed in an oil bath at 180-210 °C. The same reaction mixture was placed in a test tube with a stopper so as to follow the reaction. After cooling, the sealed tube was broken and the solution was analyzed by NMR without any purification.

Photochemical Reaction: An alcohol and an excess of benzocyclobutenone were placed in a quartz cuvette. The product were diluted with methylene chloride. The quartz cuvette was covered with a stopper and placed in a UV reactor equipped with 300 nm lamps. At the end of the reaction the solution was evaporated and analyzed by GC.

Characterization of the products obtained with

1-Octanol, II-3a: Colourless liquid; IR (NaCl, cm^{-1}) 2930, 1720, 1255; ^1H NMR (200 MHz, CDCl_3) δ 7.91 (dd, 1H, $J_{\text{H-H}} = 8.0$ Hz, $^4J_{\text{H-H}} = 1.5$ Hz), 7.40 (dt, 1H, $J_{\text{H-H}} = 7.3$ Hz, $^4J_{\text{H-H}} = 1.7$ Hz), 7.25 (m, 2H), 4.30 (t, 2H, $J_{\text{H-H}} = 6.6$ Hz), 2.60 (s, 3H), 1.77 (q, 2H, $J_{\text{H-H}} = 7.8$ Hz), 1.30 (bs, 10H), 0.89 (t, 3H, $J_{\text{H-H}} = 6.7$ Hz); ^{13}C NMR (50 MHz, CDCl_3) δ 168.03, 140.27, 132.05, 131.90, 130.77, 130.25, 125.92, 65.18, 65.18, 32.07, 29.48, 29.01, 26.39, 22.92, 22.03, 14.37; MS (EI, m/e, relative intensity %) 248 (M^+ , 8.0), 136 ($\text{M}^+ - \text{C}_8\text{H}_{14}$, 100), 119 ($\text{M}^+ - \text{OC}_8\text{H}_{15}$, 66.6), 91 (119 - CO, 48.2).

2-Octanol, II-3b: Colourless liquid; IR (NaCl, cm^{-1}) 2924, 1718, 1256; ^1H NMR (400 MHz, CDCl_3) δ 7.91 (dd, 1H, $J_{\text{H-H}} = 8.1$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz), 7.40 (dt, 1H, $J_{\text{H-H}} = 7.5$ Hz, $^4J_{\text{H-H}} = 1.3$ Hz), 7.26 (t, 2H, $J_{\text{H-H}} = 7.3$ Hz), 5.17 (h, 1H, $J_{\text{H-H}} = 6.3$ Hz), 2.62 (s, 2H), 1.7 (m, 2H), 1.36 (d, 3H, $J_{\text{H-H}} = 6.3$ Hz), 1.3 (m, 8H), 0.90 (t, 3H, $J_{\text{H-H}} = 6.9$ Hz); ^{13}C NMR

(100 MHz, CDCl_3) δ 167.43, 139.80, 131.64, 131.60, 130.52, 130.36, 125.65, 71.54, 36.11, 31.76, 29.19, 25.48, 22.60, 21.74, 20.10, 14.07; MS (EI, m/e, relative intensity %) 248 (M^+ , 7.1), 163 ($\text{M}^+ - \text{C}_6\text{H}_{13}$, 1.2), 136 ($\text{M}^+ - \text{C}_8\text{H}_{16}$, 96.8), 119 ($\text{M}^+ - \text{C}_8\text{H}_{17}\text{O}$, 100), 91 ($\text{M}^+ - \text{C}_9\text{H}_{17}\text{O}_2$, 41.8); HRMS Calculated for $\text{C}_{16}\text{H}_{24}\text{O}_2$: 248.1770, Found: 248.1749.

3-Ethyl-3-pentanol, II-3c: Toluic acid and 3-ethyl-2-pentene were obtained instead of the ester. Toluic acid: IR (KBr, cm^{-1}) 2920, 1692; ^1H NMR (200 MHz, CDCl_3) δ 8.12 (dd, 1H, $J_{\text{H-H}} = 8.2$ Hz, $^4J_{\text{H-H}} = 1.5$ Hz), 7.48 (td, 1H, $J_{\text{H-H}} = 7.5$ Hz, $^4J_{\text{H-H}} = 1.5$ Hz), 7.31 (t, 2H, $J_{\text{H-H}} = 7.3$ Hz), 2.70 (s, 3H); 3-Ethyl-2-pentene: ^1H NMR (200 MHz, CDCl_3) δ 5.17 (q, 1H, $J_{\text{H-H}} = 6.6$ Hz), 2.04 (quintet, 4H, $J_{\text{H-H}} = 7.7$ Hz), 1.60 (d, 3H, $J_{\text{H-H}} = 7.0$ Hz), 1.00 (t, 3H, $J_{\text{H-H}} = 7.4$ Hz), 0.97 (t, 3H, $J_{\text{H-H}} = 7.6$ Hz).

The reaction of **II-1** with water yielded toluic acid.

Benzyl alcohol, II-3d: Liquid; IR (KBr, cm^{-1}) 1716 (C=O), 1251; ^1H NMR (CDCl_3 , 400 MHz) δ 7.95 (dd, 1H, $J_{\text{H-H}} = 8.2$ Hz, $^4J_{\text{H-H}} = 1.3$ Hz), 7.20 to 7.45 (m, 8H), 5.33 (s, 2H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.34, 140.34, 136.11, 132.06, 131.69, 130.67, 129.69, 128.57, 128.18, 126.97, 125.70, 66.49, 21.80.

Phenol, II-3e: Liquid; IR (KBr, cm^{-1}) 1737 (C=O), 1244; ^1H NMR (CDCl_3 , 200 MHz) δ 8.18 (dd, 1H, $J_{\text{H-H}} = 8.2$ Hz, $^4J_{\text{H-H}} = 1.5$ Hz), 7.50 to 7.20 (m, 8H), 2.7 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 166.13, 151.19, 141.61, 133.01, 132.25, 131.45, 129.76, 128.83, 126.20, 126.11, 122.12, 22.25; MS (EI, m/e, relative intensity %) 212 (M^+ , 1.2), 119 (M^+

- OPh, 100).

n-Butanol, II-3f: Colourless liquid; IR (NaCl, cm^{-1}) 2960 (C-H), 1719 (C=O), 1255 (C-O), 1082, 737; ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, 1H, $J_{\text{H-H}} = \text{Hz}$), 7.38 (dt, 1H, $J_{\text{H-H}} = \text{Hz}$, $^4J_{\text{H-H}} = \text{Hz}$), 7.24 (m, 2H), 4.30 (t, 2H, $J_{\text{H-H}} = \text{Hz}$), 2.60 (s, 3H), 1.75 (q, 2H, $J_{\text{H-H}} = \text{Hz}$), 1.48 (h, 2H, $J_{\text{H-H}} = \text{Hz}$), 0.98 (t, 3H, $J_{\text{H-H}} = \text{Hz}$); ^{13}C NMR (100 MHz, CDCl_3) δ 167.82, 140.02, 131.82, 131.66, 130.52, 130.01, 125.68, 64.64, 30.80, 21.75, 19.36, 13.77; MS (EI, m/e, relative intensity %) 192 (M^+ , 24.8), 136 ($\text{M}^+ - \text{C}_4\text{H}_8$, 66.4), 119 ($\text{M}^+ - \text{C}_4\text{H}_9\text{O}$, 100), 91 ($\text{M}^+ - \text{C}_5\text{H}_9\text{O}_2$, 52.9); HRMS Calculated for $\text{C}_{12}\text{H}_{16}\text{O}_2$: 192.1146, Found: 192.1136.

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Chapter III

Ring-Opening Temperature of Benzocyclobutenone

III.1. Introduction

The ring-opening temperature of BCBO is an important factor for polymer curing, and therefore should be studied in detail. In its reaction with alcohol, BCBO first ring-opens to generate an *o*-quinoid ketene (vinyl ketene) which then reacts with the alcohol.

Our goal is to be able to introduce BCBO into any polymer system and to thermally cure the polymer in bulk. Since the reaction temperature depends on the melting and decomposition temperature of the polymer, the curing temperature would vary with the polymer system used. BCBO chemistry could be used in any polymer system if there is a way to tune its ring-opening temperature. Therefore, the sensitivity of the ring-opening temperature to both the nature of the substituent on the aromatic ring and the use of a catalyst was investigated. Kinetic parameters were also obtained for some BCBO derivatives.

III.2. Functionalization of Benzocyclobutenone

In order to introduce benzocyclobutenone to polymer systems, it first has to be functionalized. Benzocyclobutenones with substituents such as methyl, methoxy, chloro groups on the benzene ring, have been prepared from the corresponding substituted anthranilic acid.¹ The presence of substituents like hydroxy, amino or nitro groups would be

useful for the incorporation of BCBO into polymers. However, the synthesis of substituted BCBO can only be done by solution chemistry, as the presence of substituent would provide additional degradation pathways. In addition, hydroxy- or amino-BCBO cannot be prepared from the corresponding anthranilic acid as the functional group would react with the benzyne intermediate. Since benzocyclobutenone is readily available (Chapter II), the direct functionalization of BCBO seems to be the best route.

III.2.1. Nitration

Electrophilic nitration of BCBO was expected to produce only one product (Scheme III.1). The methylene group favors the ortho and para substitutions and the carbonyl is a meta directing group. Thus, the cyclobutenone unit will direct the electrophilic substitution at positions 3 and 5. However, the 3-substituted BCBO should be only a minor product. Indeed the electrophilic substitution of benzocyclobutene (BCB) was predicted to occur at positions 3 and 4, but only substitution at position 3 was observed.² This differs greatly from the prediction made with *o*-xylene which is comparable to BCB from a steric and electronic point of view. Biphenylene, which also has a four-membered ring, was substituted only at the 3 position with electrophilic substituents.³

Scheme III.1. Anticipated and observed substitutions with electrophiles.

Nitration of benzocyclobutenone (**II-1**) (Scheme III.2) was first carried out in concentrated sulfuric acid. The nitration gave only mono nitrated products when carried out between -20 and 0 °C. The 5-nitrobenzocyclobutenone (nitro-BCBO **III-1**) was the major product of the reaction. Varying the reaction temperature from -20 to 0 °C did not affect the reaction in any way. After work up and recrystallization from methanol, **III-1** was obtained in 83 % yield.

The nitration was also done using nitric acid in acetic anhydride/chloroform. Under these conditions, the nitrating agent was milder. This resulted in the reaction being slower (24 hours) than when concentrated sulfuric acid was used (20 minutes). Pure nitro-BCBO **III-1** was obtained in 73 % yield after a simple work up.

Scheme III.2. Nitration of benzocyclobutenone.

Nitro-BCBO **III-1** was fully characterized by spectroscopic means. The IR spectrum showed the presence of the ketone carbonyl (1785 cm^{-1}). There were as well two strong bands at 1342 and 1522 cm^{-1} indicating the presence of the nitro group. The ^1H NMR spectrum displayed the pattern of a mono-substituted BCBO. The ^{13}C NMR spectrum exhibited only seven peaks. However the intensity of one the quaternary carbon peak was unusually high, implying the overlapping of two quaternary carbon peaks. The high resolution mass spectrum also confirmed the molecular mass of **III-1**.

III.2.2. Aminobenzocyclobutenone and its Derivatives

Aminobenzocyclobutenone is a key compound for the introduction of BCBO in polymers. Amino-BCBO itself can be introduced into polymers with carboxylic acid, acyl chloride or anhydride, and isocyanate groups, for which amido- and imido- BCBO are the model compounds. In addition, isocyanate can be prepared from the reaction of amine with phosgene. Isocyanato-BCBO would allow the incorporation of BCBO in polymers with active hydrogens (i.e. alcohols and amines). Finally, the amino group can be substituted by other nucleophiles via a diazonium salt.

III.2.2a. *5-Aminobenzocyclobutenone*

Reduction of nitro-BCBO (**III-1**) in aqueous ethanol with iron and hydrochloric acid yielded 5-aminobenzocyclobutenone (amino-BCBO, **III-2**) in good yield (Scheme III.3). The reaction slowed down with time due to the evaporation of hydrochloric acid. The

reaction speeded up when a few drops of hydrochloric acid were added regularly (every 15 minutes). The reaction was then complete within one hour.

Scheme III.3. Synthesis of 5-aminobenzocyclobutenone.

The amino-BCBO was fully characterized. First, the IR spectrum showed a ketone carbonyl at 1744 cm^{-1} as well as the N-H vibrations of a primary amine at 3466 and 3362 cm^{-1} . The ^1H NMR spectrum exhibited a singlet at 3.83 ppm which corresponded to the methylene group. The aromatic protons had an integration area of three and their pattern was in accord with the mono-substituted BCBO. The ^{13}C NMR spectrum displayed 8 peaks, each corresponding to the chemically non-equivalent carbons. Finally, the mass for **III-2** found in the high resolution mass spectrum (133.0527) compared well with the calculated one (133.0526).

III.2.2b. 5-Acetylamidobenzocyclobutenone

Reaction of amino-BCBO with an excess of acetic anhydride produced 5-Acetylamidobenzocyclobutenone (amido-BCBO, **III-3**) (Scheme III.4). After heating the solution for one hour at $90\text{ }^{\circ}\text{C}$, no more **III-2** was present in the reaction mixture. The amido-BCBO was obtained as yellow crystals after recrystallization from chloroform.

Scheme III.4. Synthesis of 5-acetylamidobenzocyclobutenone.

The IR spectrum displayed the absence of the primary amine; only one peak for N-H stretch was present at 3336 cm^{-1} . In addition to the peak of the ketone carbonyl at 1744 cm^{-1} , another one was present at 1692 cm^{-1} corresponding to the amide carbonyl. In addition to the BCBO peaks, the ^1H NMR spectrum exhibited an additional peak for the acetyl group at 2.06 ppm. The ^{13}C NMR spectrum confirmed the presence of an additional methyl and carbonyl in **III-3**. High resolution mass spectrum gave a mass for **III-3** of 175.0631 which was in accord with the calculated one (175.0617).

III.2.2c. 5-Succinylimidobenzocyclobutenone

A solution of succinic anhydride and amino-BCBO in 1,2-dichlorobenzene was refluxed for 3 hours. Crystals of 5-succinylimidobenzocyclobutenone (imido-BCBO, **III-4**) were obtained upon cooling the reaction mixture (Scheme III.5).

Scheme III.5. Synthesis of 5-succinylimidobenzocyclobutenone.

III.2.2d. 5-(4-Fluorophenyl)-sulfonamidobenzocyclobutenone

Reaction of amino-BCBO (**III-2**) with 4-fluorophenyl sulfonyl chloride in pyridine at room temperature, produced 5-(4-fluorophenyl)-sulfonamidobenzocyclobutenone (**III-5**) (Scheme III.6). The product **III-5** was recrystallized from aqueous methanol.

Scheme III.6. Synthesis of 5-(4-fluorophenyl)-sulfonamidobenzocyclobutenone.

The IR spectrum showed the presence of the sulfonamide group at 1162 cm^{-1} , in addition to the peak of the ketone carbonyl at 1759 cm^{-1} . The ^1H NMR spectrum exhibited two additional peaks in the aromatic region corresponding to the fluorosulfonyl moiety. The MS gave a molecular ion at m/e 291 as well as the loss of carbon monoxide (m/e 263) and 4-fluorophenyl sulfonyl group (m/e 132).

III.2.2e. *N*-(2-Hydroxypropane)-5-aminobenzocyclobutenone

The title compound (**III-6**) was obtained by reacting amino-BCBO (**III-2**) with propylene oxide according to the literature procedure (Scheme III.7).⁴ The solution was stirred at room temperature. Product **III-6** was purified from the starting amino-BCBO and the disubstituted product (**III-7**) by column chromatography.

Scheme III.7. Synthesis of *N*-(2-Hydroxypropane)-5-aminobenzocyclobutenone.

The ^1H NMR spectrum of product **III-6** exhibited aliphatic peaks in addition to the pattern of 5-substituted-BCBO (Figure III.1). The additional aliphatic peaks were a singlet at 1.29 ppm corresponding to the methyl group, a multiplet at 4.06 ppm for H and an AB

Figure III.1. ^1H NMR spectrum of III-6.

system for H_a and H_b. Hydrogen bonding between the hydroxyl and the amine formed a five-membered ring in which the two protons of the methylene are magnetically non-equivalent (Scheme III.8).

Scheme III.8. Hydrogen bonding in product **III-6**.

III.2.2f. 5-Isocyanatobenzocyclobutenone

An isocyanate functionalization was obtained by reacting the amine with phosgene (Scheme III.9).⁵ The reaction was first carried out with a solution of phosgene in toluene. To the phosgene solution was added **III-2** in toluene/dichloromethane. Upon addition of the amine, the corresponding amine hydrochloride (**43**) precipitated as a white product. The precipitate disappeared upon heating to form the isocyanate.

Scheme III.9. Synthesis of 5-isocyanatobenzocyclobutenone.

Due to the difficulties of the handling of phosgene, triphosgene was also used for the reaction. Triphosgene is a crystalline compound and only an equimolar amount is used in contrast to phosgene.⁶ Triphosgene reacts with nucleophiles like phosgene which is produced as an intermediate (Scheme III.10).

Scheme III.10. Reaction of triphosgene with amino-BCBO.

The IR spectrum showed a complete lack of the amine stretch but the presence of the isocyanate group at 2273 cm^{-1} . The ^1H NMR spectrum had the pattern of a mono-substituted BCBO. The ^{13}C NMR spectrum exhibited nine peaks corresponding to the chemically non-equivalent carbons as expected.

III.2.2g. 5-Hydroxybenzocyclobutenone

The hydroxyl group was introduced by substitution of the diazonium generated *in situ* by water (Scheme III.8). Amino-BCBO was first treated with sodium nitrite to generate the diazonium salt which then reacted with water to produce 5-hydroxybenzocyclobutenone (hydroxy-BCBO, **III-5**).

Scheme III.11. Synthesis of 5-hydroxybenzocyclobutenone.

The IR spectrum showed the presence of an hydroxy group at 3267 cm^{-1} in addition to the carbonyl ketone at 1733 cm^{-1} . The ^1H NMR spectrum also exhibited the peak for the hydroxy proton at 8.84 ppm, in addition to the peaks of a 5-substituted BCBO pattern.

III.3. Ring-Opening Temperature

III.3.1. Substituent Effect

Benzocyclobutenone (BCBO) undergoes electrocyclic ring-opening like all cyclobutene derivatives. Benzocyclobutenone is closely related to benzocyclobutene since upon ring-opening the aromaticity is lost.

Benzocyclobutene (BCB) can be easily functionalized on the benzene ring as well as on the four-membered ring. The presence of a functional group on the four-membered ring influenced significantly the ring opening temperature of benzocyclobutene (Table III-1).⁷

Table III.1. Ring-opening temperature of 1-substituted benzocyclobutene.

R	NH ₂	OH	NH-CO-R	CO-R	CH ₂ -R	H
T _{RO} (°C)	24	80	110	150	180	200

The presence of a ketone on the four-membered ring in the BCBO increased the ring-opening temperature by 50 °C (250 °C) compared to that of BCB (200 °C). However, the substituent effect on BCBO has not been reported. The nature of the substituent on the four-membered ring is expected to affect the ring-opening temperature in a similar manner as for BCB, cyclobutene and cyclobutenone, but it will not be examined here.

The nature of the substituent on the benzene ring of BCB did not affect the ring-opening temperature according to its electronic structure. Indeed, the relation between the Hammett parameter of the substituent and the ring-opening temperature was not linear.⁸ However, the effect of substituent position had a significant effect; the presence of a substituent at the 4 position had little effect on the ring-opening temperature (T_{RO} 220-250 °C) compared to that of the parent BCB.⁸⁻⁹ However, the ring-opening temperature increased by about 100 °C when the substituent was moved from the 2 position to the 3 position (T_{RO} 320-390 °C).¹⁰ This increase in the ring-opening temperature was explained in terms of steric hindrance. The ring-opening temperature of 5-substituted BCBO has been examined and our findings are discussed below.

The ring-opening temperatures (T_{RO}) were obtained from first DSC trace of 5-substituted-BCBO. The ring-opening temperature were recorded at the maximum height of the exotherm peak (Table III.2).

Table III.2. Ring-opening and melting temperature of 5-substituted-BCBO.

R	H	NO ₂	NH ₂	NHCOMe	imide	NHSO ₂ R	OH	SO ₂ NHR
T _{RO} ^a (°C)	250 ^b	202	225	267	288	222	242	234
T _m ^a (°C)	N/A	126	92	184	190	146	131	220

^a Measured at the maximum height of the exotherm peak on the DSC trace obtained with a heating rate of 10 °C/min and under a nitrogen flow of 50 mL/min. ^b Onset temperature.

There was no apparent linear relationship between T_{RO} and σ_m (Hammett parameter,¹¹ obtained from the pK_a ratio between a substituted benzoic acid and benzoic acid) (Figure III.2). The value of T_{RO} for amino-BCBO and hydroxy-BCBO may not reflect the effect of the substituent as these two groups react with the generated vinyl ketene. The result obtained with isocyanato-BCBO was not included either because of the interfering reaction of the isocyanate group. Finally, the Hammett parameter for an imido group was not reported, hence no comparison could be made for the imido-BCBO.

Figure III.1. Plot of T_{RO} versus σ_m with T_{max} and T_{onset} for III-4.

The 5-substituted-BCBO compared above all melted before reaching ring-opening temperature. Several bis-imide-BCBO have been prepared (Scheme III.12). The synthesis and characterization of **IV-5 a-c** is reported in Chapter IV. The ring-opening of **IV-5a** and **IV-5b** was about 100 °C higher than that of bis-imide-BCBO **IV-5c** (Table III.3). The steric and electronic effects were similar for all three bis-imide-BCBO. Hence, only the fact that **IV-5a** and **IV-5b** did not melt seemed to explain such a high T_{RO} . The same effect of the melting temperature on T_{RO} has also been observed on the benzocyclobutene series.¹

Scheme III.12. Synthesis of Bis-imide-BCBO.

Table III.3. Ring-opening and melting temperatures of bis-imide-BCBO.^a

	IV-5a	IV-5b	IV-5c
T_m (°C)	N/O ^b	N/O	242
T_{RO} (°C)	325	323	274

^a Measured by DSC at 10 °C/min and under a nitrogen flow of 100 mL/min. ^b Not observed.

The nature of the substituent on the aromatic ring affected the ring-opening temperature to a certain extent; a ring-opening temperature range of 90 °C and centered at

250 °C was obtained. However, the substituents likely to result from the incorporation of BCBO into a polymer are amide and imide and their ring-opening temperatures were the highest of those tested. The implications of this result is that BCBO should remain inert during polymerization but it can be incorporated only into polymers that can withstand such temperatures (250-300 °C). To extend this curing chemistry to as wide a range of polymers as possible, our efforts were directed toward lowering the ring-opening temperature of BCBO. The high temperature needed for the ring-opening of BCBO is due to the large activation energy required to overcome the loss of aromaticity. The use of a catalyst may induce a further decrease of the ring-opening temperature of BCBO.

III.3.2. Catalysts

II.3.2a. Metal Catalysts

Highly substituted quinones have been obtained from cyclobutenedione (Scheme III.13). Cyclobutenediones first reacted with a transition metal to yield methaloyl metal complexes (44), which were isolated.¹² Stoichiometric reaction of the transition metal carbonyl complexes with an alkyne produced benzoquinone or benzoquinone complexes in good yields.^{13,14}

Scheme III.13. Preparation of quinone from cyclobutenedione.

The metal insertion between the two carbonyls produced a reactive intermediate that reacted with alkynes at 80 °C^{13,15} instead of 150 °C for the bis-ketene. Since the

decrease in temperature was significant in the case of the cyclobutenedione moiety, the effect of catalysts on the ring-opening temperature of BCBO was investigated. The reaction of BCBO with alcohol in the presence of a metal catalyst would proceed as follows; the metal catalyst would first be inserted between the carbonyl and the methylene group of the BCBO moiety to form the pseudo acyl chloride **III-10**. The reactive intermediate **III-10** should then react with alcohol to produce *o*-toluate (Scheme III.14).

Scheme III.14. Proposed mechanism for the ring-opening of benzocyclobutenone.

The effect of the metal complexes on the reaction of benzocyclobutenone with alcohols was examined. The experiments were not carried out with BCBO itself but with bis-imide-BCBO **IV-5a**. This bis-imide-BCBO was chosen because of it had the highest ring-opening temperature among all BCBO derivatives prepared. The ring-opening temperature (recorded at the maximum of the exothermic peak on the DSC trace) of bis-imide-BCBO **IV-5a** was determined to be 325 °C. Hence the effect of the catalyst on the ring-opening temperature would be more significant.

An excess of 1-octanol was used. The reaction temperature was raised by about 10 °C every 30 min or 1 hour. Due to the insolubility of bis-imide-BCBO in most organic solvent, the reaction was monitored by IR spectroscopy. In the IR spectrum, the ketone (1760 cm⁻¹) and the ester (1720 cm⁻¹) peaks were well separated. The reaction was said to occur when an ester peak was detected by IR. The results obtained are summarized in table III.4.

Table III.4. Ring-opening temperature of bis-imide-BCBO IV-5a in the presence of metal catalyst.

Catalyst	T _{RO} (°C)	Catalyst	T _{RO} (°C)
No catalyst	220	Pd on charcoal	220
CuCl ₂	230	Ni(II) acetyl acetonate	180
Pt black	220	Ru(III) Cl ₃ , H ₂ O	160
Ni(II) Cl ₂	230	Cr(III) acetyl acetonate	160

The ring-opening temperature of bis-imide-BCBO IV-5a (220 °C) was found to be 115 °C lower in solution than when measured by DSC (325 °C). This result was rationalized by the fact that bis-imide-BCBO was in solution and not in a solid state as for the DSC measurement. A similar decrease in the ring-opening temperature was observed for bis-imide-BCBO IV-5c which melted before its ring-opening. It can be seen that most metal complexes have no effect whatsoever on the ring opening temperature of the bis-imide-BCBO IV-5a. When Ru(III)Cl₃, Cr(II)acetyl acetonate and Ni(II)acetyl acetonate were used, the reaction took place at a lower temperature (160-180 °C).

In an attempt to isolate and identify the intermediate, BCBO was reacted with the three metal catalysts without alcohol. In light of the temperature decrease observed with bis-imide-BCBO IV-5a, the ring-opening temperature was expected to be lowered by about 60 °C. However, the reaction did not proceed as expected. No ester was obtained before the reaction temperature reached 170 °C, which was the reaction temperature without catalyst. Since the three metal complexes did not act as a catalyst for the reaction of BCBO with 1-octanol, the results obtained with bis-imide-BCBO IV-5a became

questionable and the search for a metal catalyst to lower the ring-opening temperature was not pursued any further.

III.3.2b. Nucleophilic Catalyst

As the use of metal catalyst was not conclusive, the use of a nucleophilic catalyst was examined as the ring-opening of cyclobutenone has been reported to be catalyzed by tributylphosphine.¹⁶ The products resulted from the 1,2- or the 1,4-addition of alcohol to the corresponding vinyl ketene.

Nucleophiles have been shown to attack the cyclobutenone at the carbonyl carbon.¹⁷ However, tributylphosphine did not attack at the carbonyl carbon but at the carbon 3 (Scheme III.15). Tributylphosphine was believed to attack the carbon 3 according to the Michael addition of tributylphosphine to electron-poor olefins.¹⁸ The enolate formed upon addition of the phosphine gave the symmetric cyclobutanone upon protonation. Addition of the alkoxide to the carbonyl carbon of the four-membered ring ketone was followed by ring cleavage, thus forming the 1,2-addition product.

Scheme III.15. Proposed mechanism of tributylphosphine catalyst.

With BCBO as a substrate, tributylphosphine can attack at either carbon 1 or 8. The attack on carbon 8 would produce an intermediate in which the aromaticity is lost.

This renders the attack on carbon 8 less favorable than in cyclobutenone. On the other hand, the attack on carbon 1 does not involve the aromatic ring (Scheme III.16), hence this attack should be favored. Furthermore, with a mechanism similar to that of the reaction of BCBO with hydroxide, the intermediate **45** could be formed. Reaction of **45** with alcohol would produce the *o*-toluate.

Scheme III.16. Proposed mechanism of tributylphosphine with BCBO.

Benzocyclobutenone was stirred at room temperature with 1-octanol (1.1 mol eq) in toluene (1 mL) in the presence of tributylphosphine (8.5 mol %). After 20 days, only a small ester peak was visible on the IR spectrum, while the ketone peak was still very strong.

Tributylphosphine clearly did not act as a catalyst. This may be due to the presence of the benzene ring in benzocyclobutenone. The addition of tributylphosphine on the carbon opposite to the carbonyl disrupts the aromatic ring. The loss of aromaticity is not favorable to the reaction.

III.4. Kinetic Studies

From a practical point of view, it is useful to consider the kinetic of the ring-opening of BCBO in the presence or absence of an alcohol. The kinetic parameters are

useful for the determination of the time for the reaction to take place at a given temperature. The reaction of ketenes with alcohol can take place at a low temperature ($-78\text{ }^{\circ}\text{C}$).¹⁹ Thus, the actual rate determining step in the reaction with alcohol is assumed to be the ring-opening of benzocyclobutenone. Similar assumption was made for the kinetic study of cyclobutenone to vinyl ketene.²⁰ From the activation energy obtained by *ab initio* calculation it was deduced that the ring-opening of cyclobutenone was nearly thermoneutral.²¹ But since the calculations considered that the molecule was in the gas phase, the result may be not apply to the DSC results since the mixture were in the liquid phase. Thus the exothermic peak observed on the DSC trace corresponded to the formation of *o*-quinoid ketene followed by its dimerization or reaction with alcohol. The kinetic experiments were performed on amido-BCBO (**III-3**), imido-BCBO (**III-4**) and sulfonamide-BCBO (**III-10**)²² alone and in presence of poly(4-hydroxystyrene) (Scheme III.17). The activation energies of the overall reactions were determined from DSC experiments at several heating rates.

Scheme III.17. Substituted BCBO and alcohol used for the kinetic study.

A Seiko DSC 220C Calorimeter was operated from room temperature to $300\text{ }^{\circ}\text{C}$ and purged with nitrogen flowing at 50 mL/min . The instrument temperature and sensitivity

were calibrated with indium and tin. A 5 mg samples were used to obtain the DSC traces. The first scan showed a melting endotherm and an exothermic peak due to the ring-opening and subsequent reaction of BCBO.

III.4.1. Mathematical Tool

Ozawa and Flynn correlated the activation energy with the heating rate as shown in equation 1.²³ Even though it was first established for thermogravimetric analysis, it is applicable to any properties measured by thermal analysis, using constant heating rates.²⁴ Standard methods for the determination of kinetic constant have been published.²⁵

The temperature at maximum the maximum peak height ($T_{\max}$ in Kelvin) is first recorded for several heating rates. Then $\log \beta$ is plotted against $1/T$, where β is the heating rate and T the temperature in Kelvin. The activation energy can then be calculated as follows, provided that a linear relationship was obtained:

$$E_a = -2.19 \times R \times [d \log \beta / d (1/T)] \quad (\text{eq. 1})^{24}$$

where R is the gas constant.

III.4.2. Results

DSC traces were recorded for **III-3**, **III-4** and **III-6** with heating rates of 0.5, 2, 5, 10 and 50 °C, with a nitrogen flow of 100 mL/min. The temperature at which the peak reached a maximum ($T_{\max}$) and the onset temperature (T_{onset}) were directly taken from the graph (Figure III.3). The onset temperature was recorded at the intersection of the tangents of the baseline and of the peak.

Figure III.3. DSC trace of **III-3** with a heating rate of 10 °C/min, showing T_m , T_{max} and T_{onset} of an exothermic peak.

The plot of $\log \beta$ versus $1/T$ showed a linear relationships for both T_{max} and T_{onset} (Figure III.5). The correlation coefficient (r) was greater than 0.99 for T_{max} except for **III-10** (0.96) and 0.98 for T_{onset} . Linear regression was used to determine the slope, which was used to calculate the activation energies with equation 1. The results are summarized in Table III.4.

Figure III.4. Plot of $\log \beta$ versus $1/T$ for **III-3**.

The activation energies obtained from the onset temperatures were somewhat higher than when calculated from the maximum temperatures. However, the same order of magnitude was obtained for both. Furthermore, the activation energy obtained from the maximum temperature are probably more accurate as the standard method uses the maximum temperature and not the onset temperature. The reading of T_{onset} itself was somewhat arbitrary as it depended on which point of the exotherm the tangent was taken for its determination. The activation energy of all three substituted BCBO was of the same order, with a value slightly higher for **III-10**.

Table III.5. Activation energies^a calculated for substituted BCBO with and without poly(4-hydroxy-styrene).

BCBO	without poly(4-hydroxystyrene)		with poly(4-hydroxystyrene)	
	T _{onset}	T _{max}	T _{onset}	T _{max}
III-3	133	123	107	109
III-4	142	121	N/M ^b	N/M
III-10	191	149	175	144

^a in KJ/mol. ^b Not measured.

The activation energies were also calculated in presence of alcohol in order to see how the presence of alcohol would affect the activation energy. Poly(4-hydroxy-styrene) was used and TG showed that it was stable up to 300 °C. In addition, its DSC trace was flat in the temperature range of the ring-opening temperature of substituted BCBO. The DSC traces were first obtained from a mixture of substituted BCBO and poly(4-hydroxystyrene) but the results were not consistent. This was explained by a lack of mixing between the two reactants. The two starting materials had to be thoroughly mixed so as to minimize self coupling of BCBO and favor the reaction with alcohol. Mixing of the two starting materials was achieved by dissolving them in the same solvent, followed by evaporation of the solvent. The kinetic study was then carried out with the resulting mixture.

The first observation was the decrease of the activation energy in presence of poly(4-hydroxystyrene) (Table III.4). The decrease in activation energy was consistent the lower value of *k* for the reaction with ketones compared to that with an excess of alcohol.²⁶ The decrease in the case of **III-10** was not as significant as for **III-3**. This may be due to the fact that the starting materials were not soluble in a common solvent and resulted in a poor mixing between **III-10** and poly(4-hydroxystyrene).

III.5. Conclusion

The ring-opening temperature depends on the nature of the substituent on the benzene ring, but the ring-opening could not be correlated with the electronic effect (Hammett parameter) of the substituent. Thus, the ring-opening temperature of new 5-substituted BCBO cannot be predicted. Furthermore, the BCBO moiety does not ring-open in the solid state, but does when the compound was in a liquid form (melted or in solution). Since the glass transition temperature (T_g) of a polymer is the temperature above which the polymer chains are mobile. Thus, the ring-opening temperature will not occur below T_g , when the polymer is in a glassy state, but above it. This implies that in a polymer with high T_g , the ring-opening temperature for the BCBO moiety is likely to be higher than in a polymer with low T_g .

The metal and nucleophilic catalysts examined did not lower the ring-opening temperature. The kinetic studies showed that the dimerization of 5-substituted BCBO had a similar activation energy regardless of the substituent. Furthermore, the reaction with alcohol had lower activation energy than the dimerization, thus the curing reaction will preferentially occur by addition of alcohol than by dimerization.

III.5. Experimental Section

Materials: Sulfuric acid, nitric acid (70%), nitric acid (90%), iron powder, acetic anhydride were purchased from Anachemia. Phosgene solution in toluene (20%), Lithium perchloride, propylene oxide were purchased from Aldrich Chemical Co. and were used as received.

Characterization: The polymer samples were analyzed using thermal analysis techniques: thermogravimetry (TG) and differential Scanning Calorimetry (DSC). A Seiko TG/DTA 320 was used with a heating rate of 10 °C/min. The system was permanently purged with 200 mL/min of dry nitrogen. A Seiko DSC 220 was used with a heating rate of 10 °C/min. The system was purged with 50 mL/min of nitrogen. The temperature of both instruments was calibrated using indium and tin.

5-Nitrobenzocyclobutenone (III-1)

sulfuric acid - nitric acid (70 %): Benzocyclobutenone (**II-1**) (10.10 g, 85.6 mmol) was added slowly to a strongly stirred concentrated sulfuric acid (25 mL), the temperature was maintained between -10 and -5 °C. The resulting solution was cooled to -10 °C. The nitration mixture (70 % nitric acid (8.75 g, 97.2 mmol) in sulfuric acid (5 mL)) which was cooled down in an ice bath, was added to the reaction mixture at such a rate that the solution temperature remained between -10 °C and -5 °C. After addition of nitrating solution, the solution was stirred for another 10 min at that temperature. The reaction mixture was then slowly poured into an ice slurry (150 g of ice in 30 mL of water) with strong stirring. A yellow product was formed, it was collected by suction filtration and washed with water twice, aqueous sodium carbonate solution (10%) twice, and water until the rinsing became neutral. The solid product was recrystallized from methanol to give fine white crystals: 3.44 g (83.1%).

Nitric acid (90 %) - chloroform: Benzocyclobutenone (**II-1**) (20.02 g, 169.6 mmol) was dissolved in chloroform (20 mL) in a round bottom flask. Acetic anhydride (40 mL) was added to the stirring solution. The flask was maintained at room temperature with a water bath. Nitric acid 90% (24 mL, mmol) was then slowly added to the stirring solution over a 20 minute period. The temperature was carefully kept below 30 °C. The precipitate was filtered off, rinsed with water and dried under vacuum. A white precipitate (13.39 g, 48.5%) was obtained. More product could be recovered from the filtrate. The washings and the filtrate were combined and poured into iced water. The mixture was then extracted with water until washings were neutral and then with chloroform. The organic solution was then dried and the solvent evaporated to give an additional 7.35g of yellowish precipitate (75% overall yield). mp 126-127 °C; IR (KBr, cm^{-1}) 1785, 1522, 1342; ^1H NMR (400 MHz, CDCl_3) δ 8.46 (dd, 1H, $J_{\text{H-H}} = 8.1$ Hz, $^4J_{\text{H-H}} = 1.9$ Hz), 8.18 (dd, 1H, $^4J_{\text{H-H}} = 1.8$ Hz, $^5J_{\text{H-H}} = 0.8$ Hz), 7.75 (dd, 1H, $J_{\text{H-H}} = 8.1$ Hz, $^5J_{\text{H-H}} = 0.8$ Hz), 4.11 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.58, 157.02, 149.04, 129.90, 124.70, 115.85, 52.69; UV (λ_{max} , nm, CH_2Cl_2) 231, 267; MS (EI, m/e, relative intensity %) 163 (M^+ , 99.3), 135 ($\text{M}^+ - \text{CO}$, 39.3), 89 (135 - NO_2 , 100); HRMS Calculated for $\text{C}_8\text{H}_5\text{O}_3\text{N}$: 163.04475, Found: 163.02594.

5-Aminobenzocyclobutenone (**III-2**)

A suspension of 5-nitrobenzocyclobutenone (**III-1**) (5.06 g, 31.0 mmol) and iron powder (5.08 g) in aqueous ethanol (1:1 ratio, 50 mL) was gently refluxed. The acidic

aqueous ethanol (1:1 ratio with 6 drops of concentrated hydrochloric acid) was then added to the reaction mixture. A vigorous reflux was maintained for 90 minutes (the reaction mixture should not exceed 3 hours). Addition of hydrochloric acid (2 drops) every 20 minutes was necessary to maintain the reaction rate. Once the reaction was complete, the solution was treated with sodium carbonate (2 g), and was allowed to cool down to room temperature. The reaction mixture was passed through a pad of Celite and the iron oxide paste rinsed thoroughly with ethanol. The filtrate was concentrated and the product a yellow-brown solid was collected by filtration, rinsed with water and dried under vacuum: 1.88 g (92.4%); mp 92-93 °C; IR (KBr, cm^{-1}) 3466, 3362, 1744, 1620; ^1H NMR (400 MHz, CDCl_3) δ 7.30 (d, 1H, $J_{\text{H-H}} = 7.9$ Hz), 6.85 (dd, 1H, $J_{\text{H-H}} = 7.9$ Hz, $^4J_{\text{H-H}} = 2.0$ Hz), 6.62 (d, 1H, $J_{\text{H-H}} = 1.6$ Hz), 3.83 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 188.78, 148.89, 147.46, 141.45, 124.21, 123.04, 104.90, 50.96; UV (λ_{max} , nm, CH_2Cl_2) 240, 351; MS (EI, m/e, relative intensity %) 133 (M^+ , 31.2), 105 ($\text{M}^+ - \text{CO}$, 100); HRMS Calculated for $\text{C}_8\text{H}_7\text{ON}$: 133.0526, Found: 133.0527.

5-Acetylamidobenzocyclobutenone (III-3)

A solution of 5-aminobenzocyclobutenone (III-2) (0.178 g, 1.34 mmol) in acetic anhydride (3 mL) was heated up to 90 °C for 1 hour. The acetic anhydride and acetic acid were removed by vacuum distillation. The residue was then recrystallized twice from chloroform yielding yellow crystals (0.080 g, 34%): mp 184-185 °C; IR (KBr, cm^{-1}) 3336

(N-H), 1744 (C=O, ketone), 1692 (C=O, amide); ^1H NMR (400 MHz, DMSO- d_6) δ 10.17 (s, 1H), 7.73 (s, 1H), 7.64 (dd, 1H, $J_{\text{H-H}} = 8.0$ Hz, $^4J_{\text{H-H}} = 1.7$ Hz), 7.60 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz), 3.92 (s, 2H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 188.13, 168.62, 147.59, 145.75, 140.12, 126.63, 124.31, 109.75 (d), 51.35, 23.98; UV (λ_{max} , nm, CH_2Cl_2) 235, 317; MS (EI, m/e, relative intensity %) 175 (M^+ , 38.8), 147 ($\text{M}^+ - \text{CO}$, 34.4), 105 ($\text{M}^+ - \text{C}_3\text{H}_2\text{O}_2$, 100); HRMS Calculated for $\text{C}_{10}\text{H}_9\text{O}_2\text{N}$: 175.0631; Found: 175.0617.

5-Succinylimidobenzocyclobutenone (III-4)

A mixture of succinic anhydride (0.5 g) and 5-aminobenzocyclobutenone (III-2) in 1,2-dichlorobenzene (10 mL) was refluxed with stirring for 3 hours. The solution was cooled down. The crystals formed upon cooling were collected and washed with ethanol and dried under vacuum to produce white crystals (0.9 g, 79%): mp 190 °C.

5-(4-fluorosulfonamino)-benzocyclobutenone (III-5)

To a stirring solution of 5-aminobenzocyclobutenone (III-2) (0.33 g) in dry pyridine (2 mL) at room temperature was added 4-fluorobenzene sulfonyl chloride (0.50 g) in one portion. The solution was stirred overnight. The resulting red solution was poured into water (10 mL). To this suspension, methanol was added until a clear solution was obtained.

On standing at room temperature, the product recrystallized out. After filtration, washing with aqueous methanol (30% by volume) twice and drying in vacuo, the product **III-5** was obtained (0.71 g, 98%): mp 146 °C; IR (KBr, cm^{-1}) 3243 (N-H), 1759 (C=O), 1162 (SO_2); ^1H NMR (200 MHz, CDCl_3) δ 7.81 (m, 2H), 7.45 (dd, 1H), 7.35 (br s, 1H), 7.29 (dd, 1H), 7.14 (br t, 2H), 3.92 (s, 2H); MS (EI, m/e, relative intensity %) 291 (M^+ , 27), 263 ($\text{M}^+ - \text{CO}$, 39), 132 ($\text{M}^+ - \text{SO}_2\text{PhF}$, 39), 104 (133 - CO, 100).

N-(2-hydroxypropane)-5-aminobenzocyclobutenone (**III-6**)

Lithium perchlorate (1.624 g, 15.3 mmol) was dissolved in a solution of propylene oxide (0.907 g, 15.6 mmol) in acetonitrile (2 mL). Once the salt was completely dissolved, the 5-aminobenzocyclobutenone (**III-2**) (1.332 g, 10.0 mmol) was added at once. The resulting brown solution was stirred until no more starting material was present in the reaction mixture. The solution was then diluted to 100 mL with water and was extracted twice with diethyl ether (5 mL). The ether extracts were dried over magnesium sulfate, and the solvent evaporated to produce a mixture containing amino-BCBO (**III-2**), the product (**III-6**) and the disubstituted product (**III-7**). A short column was run on the mixture using 50% ethyl acetate in hexane as the eluting solvent. Pure **III-6** was obtained as a viscous brown liquid: ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, 2H, $J_{\text{H-H}} = 8.0$ Hz), 6.85 (dd, 2H, $J_{\text{H-H}} = 8.0$, $^4J_{\text{H-H}} = 2.1$ Hz), 6.55 (d, 2H, $J_{\text{H-H}} = 1.8$ Hz), 4.06 (m, 1H), 3.84 (s, 2H), 3.21 (dd, 1H, $J_{\text{H-H}} = 12.8$ Hz, $^4J_{\text{H-H}} = 3.2$ Hz), 3.00 (dd, 1H, $J_{\text{H-H}} = 12.8$ Hz, $J_{\text{H-H}} = 8.3$ Hz), 1.29 (d,

3H, $J_{\text{H-H}} = 6.3$ Hz); ^{13}C NMR (400 MHz, CDCl_3) δ 188.96, 149.38, 148.85, 140.95, 124.18, 122.56, 101.82, 66.27, 51.55, 50.96, 21.07.

5-Isocyanato-benzocyclobutenone (III-8)

Using phosgene: Phosgene solution (10 % in toluene, 20 mL) was placed in a flame dried flask equipped with a nitrogen inlet, a condenser and a dropping funnel. A solution of 5-aminobenzocyclobutenone (III-2) (0.287 g, 2.16 mmol) in dry toluene/dichloromethane was placed into the dropping funnel. The amine solution was added slowly with strong stirring. A precipitate was formed. Once the addition was complete, the solution was refluxed overnight. The solvent was distilled off under reduced pressure and the residue extracted with hexane. The solution was concentrated and the product recrystallized from hexane to give pale yellow needles (0.085 g, 26 %).

Using tri-phosgene: Tri-phosgene (1.083 g, 3.65 mmol) in dry toluene (10 mL) was added over 20 minutes, to a stirring solution of 5-aminobenzocyclobutenone (III-2) (1.116 g, 8.39 mmol) in dry toluene. The solution was then heated to 80-90 °C overnight. Toluene was distilled off and the residue was recrystallized from hexane to yield 0.770 g (58 %) of pale yellow needles: mp 91-93 °C; IR (KBr, cm^{-1}) 2266 (N=C=O), 1764 (C=O); ^1H NMR (200 MHz, CDCl_3) δ 7.48 (d, 1H, $J_{\text{H-H}} = 7.8$ Hz), 7.22 (d, 1H, $J_{\text{H-H}} = 7.8$ Hz), 7.07 (s, 1H), 3.94 (s, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 187.29, 149.43, 148.60, 134.80, 131.89, 125.18,

116.57, 112.58, 52.23; MS (EI, m/e, relative intensity %) 159 (M^+ , 27.7), 131 ($M^+ - CO$, 30.8), 105 (100).

5-Hydroxybenzocyclobutenone (III-9)

To a cold solution of phosphoric acid (75%, 1.788 g), were added 5-aminobenzocyclobutenone (0.502 g), sulfuric acid (0.20 g) and water (10 mL). A solution of sodium nitrite (0.196 g) in water (1 mL) was then added with good stirring. After stirring for 10 minutes, a small amount of urea was added to the resulting pink solution. The reaction mixture was heated up to 30 °C for 10 minutes. The dark solution was cooled to room temperature and saturated with sodium chloride. After standing overnight, the mixture was filtered and the filtrate was extracted eight times with diethyl ether (50 mL). The ether extracts were combined and concentrated under reduced pressure. The product was isolated from the residue by preparative thin layer chromatography (15% ethyl acetate in hexanes) as yellow solids (64 mg, 13%): mp 131 °C; IR (KBr, cm^{-1}) 3267 (OH), 1733 (CO); ^1H NMR (200 MHz, acetone- d_6) δ 8.84 (s, 1H), 7.46 (dd, 1H), 7.77 (dd, 1H), 7.10 (dd, 1H), 3.78 (s, 2H); MS (EI, m/e, relative intensity %) 134 (M^+ , 65), 106 ($M^+ - CO$, 100).

General procedure for the reaction of IV-5a with 1-octanol with metal catalysts

The bis-imide-BCBO IV-5a (100 mg) and 1-octanol (1 mL) were placed in a test tube along with the catalyst to be tested (5% wt). The test tube was then heated in a sand

bath. The temperature was raised by 10 °C every 30 to 60 minutes, starting at 150 °C and the reaction was followed by IR.

Sample preparation for kinetic studies with poly(4-hydroxystyrene)

The substituted BCBO and poly(4-hydroxystyrene) were dissolved in chloroform and the solvent was evaporated. This procedure was repeated twice. The DSC was then run with the resulting mixture.

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Chapter IV

Application of Benzocyclobutenone Chemistry to Polymer Synthesis

IV.1. Introduction

The curing reactions include chain extension, grafting or crosslinking, which may be achieved thermally or photochemically. Photochemical transformation is mostly performed on thin films, whereas thermal curing is used in bulk and reaction injection molding (RIM).

Crosslinking leads to insoluble and infusible polymers. The polymer chains are connected at several points (crosslinks). As a result, all the chains are linked to each other, forming a three dimensional network. A crosslinked network is obtained from either linear polymer containing functional group capable of reacting with itself, or functionalized polymer and crosslinking agent. Crosslinked polymers may also be obtained during polymerization providing the presence of monomer with a functionality greater than two.

The curing reaction has to meet several requirements. First of all, the moieties responsible for the crosslinking should remain non-reactive during polymerization. Furthermore, the curing reaction has to take place above the T_g of the polymer, but below the decomposition temperature of both the starting and resulting polymer. Ideally, the reaction should be specific and proceed rapidly and without the production of volatile by-products.

BCBO does not generate a significant amount of *o*-quinoid ketene (vinyl ketene) below 180 °C, hence remain inactive in this temperature range. Vinyl ketene has also been

observed at 20 K upon irradiation of BCBO.¹ Once the vinyl ketene is produced from BCBO, it undergoes a variety of reactions: with itself, unsaturated compounds and nucleophiles. BCBO was used in the present work for the preparation of a one-component heat-curing polyurethane, chain extension of poly(imide ester)s and the grafting of polystyrene.

IV.2. Application to Polyurethane Synthesis

Polyurethanes were first prepared by O. Bayer in 1937. Their commercial importance was realized in early 1950's with polyurethane elastomers and foams. Since then, the applications of polyurethanes have been extended to fibers, surface coatings, elastomers, adhesives and sealants. Today, because of the known structure-property relationship and the large variety of starting materials, polyurethanes may be tailored for specific applications. Urethane is not usually the major functional group present in polyurethanes. Essentially any polymer containing urethane groups will be referred as a polyurethane. The chemical composition of polyurethanes includes a large variety of functional groups such as ester, ether, amide and urea.

Polyurethanes are conventionally prepared from a diol and a diisocyanate. Since alcohol reacts with isocyanate at room temperature, they must be kept separate. These two monomers are mixed in equimolar amount just before curing. Recently, much effort has been directed towards the development of a one-component heat-curing polyurethane. Some such polyurethanes exist in which the isocyanate group is masked. The diisocyanate is first reacted with phenol or an oxime to form the corresponding urethane which is chemically inert to alcohol. Upon heating, the masking agent is liberated and the resulting

isocyanate could then react with a diol to produce a polyurethane. The disadvantage of these masking agents is that during cure toxic phenol and oxime are liberated. There is a need for the development of a one-component heat-curing system which does not liberate any volatile organic compounds during the curing process (VOC free curing system).

It has been shown in previous chapter that ketene reacts rapidly with nucleophiles without generating any by-product. Hence, if a ketene is formed under curing conditions it would react with the alcohol to produce the polyurethane. Ketenes can be produced by several routes (Chapter I). However, the ketene precursor has to be chosen so that it does not react with alcohol. If the ketene formation does not liberate any by-product there will be an additional advantage, as the material properties would not be impaired by the presence of gas or other small products trapped.

Functionalized benzocyclobutenone could be used to cap the diisocyanate. BCBO does not react with alcohol below 150 °C, but at higher temperature a vinyl ketene is generated and readily reacts with alcohol to produce the polymer. If satisfactory, this one-component heat-curing polyurethane would not only be a VOC free curing system but a system that would not produce *any* by-product.

IV.2.1. BCBO-End Capped Diisocyanates

Several diisocyanates have been end capped with 5-aminobenzocyclobutenone. Two proprietary diisocyanate oligomers (Desmodur and Baytec) from Bayer were used. End-capped diisocyanates were obtained by reacting the diisocyanate with a slight excess (2.1

molar equivalent) of 5-aminobenzocyclobutenone. The products precipitated out of solution and were isolated as beige powders.

Scheme IV.1. Preparation of BCBO end capped diisocyanates.

The IR spectra of the products showed the presence of the ketone (1764 cm^{-1}) and urea carbonyl (1630 cm^{-1}). The NMR spectra confirmed the presence of the BCBO moiety in **IV-1** and **IV-2**.

IV.2.1a. Thermal Analysis of BCBO-End Capped Diisocyanates

The thermal stability and the ring-opening of the BCBO in **IV-1** and **IV-2** were then examined. The decomposition temperature for 5% weight loss of **IV-1** and **IV-2** were 270 and 244 °C, respectively, although both started to degrade at 200 °C. The DSC scans were run up to 230 °C and the onset of an exotherm peak was observed at 170 °C. This exotherm was due to either the ring-opening of BCBO or the degradation of the oligomer. The DSC on the mixture **IV-1**/alcohol (BPA, hexanediol or PEG-600) was run up to 250 °C as the degradation started at a higher temperature. The DSC obtained with a mixture of **IV-1** and PEG-600 clearly exhibited an exothermic peak indicating that a reaction and not degradation took place (Figure IV.1). The exotherm started at the same temperature in both

cases. However, in the presence of an alcohol, the peak was sharper and the peak maximum was detected between 213 to 223 °C. This difference in the exotherm peak due to the presence of an alcohol may be explained in terms of reactivity.

Figure IV.1. DSC traces of BCBO prepolymer IV-1 with and without PEG-600.

At elevated temperatures the equilibrium between benzocyclobutenone and *o*-quinoid ketene (vinyl ketene) is shifted towards the vinyl ketene. In the absence of an alcohol the vinyl ketene can either dimerize or eject carbon monoxide. The release of carbon monoxide explains the weight loss observed by TG. But, in the presence of an alcohol, the vinyl ketene readily reacts to give the ester instead of the dimer (Chapter II). The variation in the peak position was due to the higher temperatures required for the dimerization than for the nucleophilic addition of alcohol.

It could also be noticed that in the presence of PEG-600, the melting point of IV-1 was decreased by 20 °C. This decrease in melting point was due to a plasticizing effect of the alcohol.

IV.2.2. Polymer Curing

The BCBO-end capped diisocyanates were reacted with small diols (i.e. BPA and hexanediol), and poly(ethylene glycol)s of different molecular weights (Scheme IV.2). Equimolar amounts of **IV-1** and one of the listed diols were placed on a glass plate sitting on a hot plate. The mixture became homogeneous with stirring at about 150 °C (surface temperature of the hot plate). The temperature was then raised up to 230-240 °C. At this temperature, the mixture became more viscous and turned brown. The glass plate was then removed from the hot plate and allowed to cool to room temperature. The polymer film was then peeled off for characterization.

Scheme IV.2. Curing of BCBO-end capped diisocyanates with diols.

None of the polymer films were soluble in organic solvents which hampered full characterizations. The insolubility and coloration of the polymer film indicated that other reaction occurred during cure. The urea bond is not thermally stable, it decomposes to an

amine and an isocyanate. As a consequence crosslinking results from the production of allophanate, a product of the reaction between isocyanate and urethane (Scheme IV.3).

Scheme IV.3. Reaction of liberated isocyanate with urethane.

The IR spectrum was not obtained by transmission as the film was too thick. Hence, only the surface of the polymer film was analyzed by reflection. The IR spectrum showed that on the surface of the film the ketone of the BCBO unit was replaced by an ester group. The films of **IV-3a** and **IV-4a** were thin enough to run a transmittance IR. In this case the bulk of the film was analyzed and some ketone was still present.

Thermal analyses showed that the decomposition temperature of **IV-3** and **IV-4** seemed to depend only on the diol used. In addition, the 5% weight loss of the film matched the 5% weight loss of the diol alone. This indicate that unreacted diol was present in the film in the case of hexanediol and BPA, whose weight loss was due to sublimation. The decomposition temperature matched that of the PEG used. Assuming that the reaction was incomplete as with BPA, the polymer contained free PEG end group and the polymer degradation would result from the same reaction. However, analysis of the thermolysis product would be necessary to support this explanation.

Table IV-1. Film property and decomposition temperature of IV-3 and IV-4.

	Aliphatic Polyisocyanate IV-3		Aromatic Polyisocyanate IV-4	
alcohol	film	T _d ^a (°C)	film	T _d ^a (°C)
a	not flex.	240	not flex.	241
b	flex.	263	not flex.	268
c	flex. elast.	334	flex. elast.	312
d	N/M ^b	N/M	flex. elast.	303

^a Measured by TG at 10 °C/min, under a nitrogen flow of 200 mL/min. ^b Not Measured.

IV.3. Poly(imide ester)s

Polyimides are high temperature engineering materials with superior properties. The main drawback associated with polyimides is their poor processability or insolubility. The solubility increases when pendant groups² and bents³ are introduced in the polymer backbone to disrupt the chain packing. To be processed the temperature must be higher than the T_g of the polymer. However, polyimides have a very high T_g preventing them from being melt processed. The chain mobility of polyimide increases, T_g decreases, when flexible groups are placed in the polymer backbone.

Poly(imide ester)s are usually prepared in three steps. Poly(imide ester)s can be prepared by reaction of a bis-imide BCBO with a diol. The resulting polymer is expected to be stable at the reaction temperature. Thus, no degradation or crosslinking should occur during the reaction, unlike in the case of polyurethanes. Hence, this polymer system should be more suited to demonstrate the chain extension.

IV.3.1. Bis-Imide-BCBO

Three bis-imide-BCBO (**IV-5**) were prepared from commercial dianhydrides (i.e. PMDA, BPDA and 6FDA) and amino-BCBO (**III-2**) (Scheme IV.4). The dianhydride and **III-2** were refluxed in anhydrous DMAc for 2 hours. The product precipitated out of solution and was obtained as a beige powder in 58 to 77% yield.

Scheme IV.4. Synthesis of bis-imide-BCBO **IV-5**.

Bis-imide-BCBO **IV-5a** and **IV-5b** were not soluble in common organic solvents including chloroform and DMSO, thus preventing NMR characterization. The IR spectra of all Bis-BCBO exhibited carbonyl peaks for the imide and ketone. Elemental analyses of **IV-5a** and **IV-5b** gave percentages of C, N and H that matched well the calculated values (Table IV.2). Bis-BCBO **IV-5c** was soluble in chloroform and hence was characterized by NMR. Finally, MS could not be obtained for **IV-5a** and **IV-5b**, since they did not desorb. However, it confirmed the molecular mass of **IV-5c** at 674, the main fragmentation products resulted from the loss of carbon monoxide.

Table IV.2. Elemental analysis results for IV-5a and IV-5b.

	IV-5a			IV-5b		
	%C	%N	%H	%C	%N	%H
Found	71.40	5.11	2.85	60.30	6.25	2.48
Calculated	71.74	5.07	2.92	60.64	6.25	2.68

IV.3.1a. Thermal Analysis of Bis-Imide-BCBO

Thermal analyses were performed on bis-imide-BCBO IV-5 so as to find their thermal stability (T_d) and determine their ring-opening temperature (T_{RO}) (Table IV.3). The decomposition temperatures of IV-5 were quite high (430–470 °C). For example, the TG trace of IV-5a (Figure IV.2) showed a small weight loss (1%) that occurred at the same time as its ring-opening (exotherm). This weight loss could be attributed to the loss of carbon monoxide from the vinyl ketene. However, the weight percent of carbon monoxide in IV-5a, IV-5b and IV-5c was calculated to be 10.1, 12.5 and 8.3%, respectively. This implies that only few BCBO units released carbon monoxide and the majority dimerized. The measured decomposition temperature was not the one of the bis-imide-BCBO but that of the resin formed by BCBO self-coupling which occurred at about 300 °C.

Table IV.3. Thermal analysis of bis-imide-BCBO IV-5.

	IV-5a	IV-5b	IV-5c
T_d^a	430	477	437
T_{RO}^b	325	323	274

^a Measured by TG at 10 °C/min, under a nitrogen flow of 200 mL/min. ^b Measured by DSC at 10 °C/min, under a nitrogen flow of 50 mL/min.

The first DSC scan of IV-5 exhibited a large exotherm peak. The exotherm of IV-5c occurred at much lower temperature than either one of IV-5a or IV-5b. This may be explained by the fact that IV-5c melted but not IV-5a and IV-5b. DSC analyses were also run on the mixture of IV-5 and polyester diol (Desmophen). As for polyurethanes, the peak maximum appeared at a lower temperature than for IV-5 alone. This was especially obvious with IV-5a and IV-5c (15-40 °C).

Figure IV.2. TG and DTA curves of IV-5a.

IV.3.2. Chain Extension

It has been shown in the previous chapter that the thermal reaction of BCBO with alcohol gave an ester quantitatively. The reaction of bis-BCBO IV-5 with a diol or hydroxy-terminated prepolymer would thus lead to chain extension.

Chain extension was performed with a polyester diol (Desmophen), provided by Bayer Co. The equimolar amount of polyester diol was calculated from its hydroxy number.

The polymerization was carried out under nitrogen in phenyl ether at 220 °C for **IV-5a** and **IV-5b** and at 160 °C for **IV-5c** (Scheme IV.5). The high boiling solvent was removed by repetitive precipitation of polymers **IV-6** in methanol.

Scheme IV.5. Chain extension of **IV-5** with polyester diol.

IV.3.2a. Structural Characterization

Except for polymer **IV-6c** which could not be completely freed of phenyl ether, the polymers were fully characterized. The IR spectra showed a complete absence of a ketone peak. The formation of the ester peak was not detected by IR due to the presence of the ester peak from the polyester. The ^{13}C NMR spectra showed only the presence of ester and imide carbonyls. The reaction of the BCBO moiety with Desmophen was best seen in ^1H NMR where the methylene group of BCBO at about 4 ppm disappeared and was replaced by a peak at 2.6 ppm corresponding to the methyl group of the *o*-toluate.

IV.3.2b. Thermal Properties of Poly(imide ester)s

The decomposition temperatures of polymers **IV-6a** and **IV-6b** were the same as that of Desmophen (polyester diol). Both polymers had very low T_g , -34 and -44 °C for **IV-6a** and **IV-6b** respectively. These low T_g values were expected as both polymer behaved as

elastomers at room temperature. The elastomeric nature of the film results from the presence of long flexible chains (i.e. polyester diol) as well as structures that can pack easily (i.e. imide moiety).

IV.3.3. AB Monomer

The high molecular weight obtained with the bis-imide-BCBO and polyester diol did not prove that only the reaction of BCBO with alcohol occurred. Dimerization of the BCBO unit might have occurred to a low extent even though it was not detected by NMR spectroscopy. The formation of dimers would not have influenced the molecular weight too much as the molecular weight of the starting polyester diol was $M_n = 2000$. However, the presence of dimer in the polymer obtained from a low molecular weight AB monomer would be more easily detected.

IV.3.3a. *Monomer Synthesis*

Amino-BCBO and trimellitic anhydride were heated in DMAc at 120 °C for 3 hours to produce **IV-7** (Scheme IV.6). The resulting **IV-7** precipitated out of solution and was recrystallized from DMAc. The purity of **IV-7** influenced greatly the yield of **IV-8**. Pure **IV-7** provided **IV-8** in quantitative yields. The acid chloride **IV-8** was obtained by refluxing **IV-7** in thionyl chloride. The acid chloride **IV-8** precipitated out of solution and was used directly for the next step. Characterization of **IV-8** was performed on a sample recrystallized from toluene. The IR spectrum showed the presence of the three carbonyl peaks for the ketone, imide and acyl chloride. The ^1H NMR spectrum exhibited a singlet for

the methylene group as well the patterns of two 1,2,4-trisubstituted benzene (s, d, and dd). The ^{13}C NMR spectrum had 17 peaks for each chemically non-equivalent carbons of IV-8. Reaction of IV-8 with hexanediol in methylene chloride afforded the AB monomer IV-9 in 87% yield.

Scheme IV.6. Synthesis of AB monomer IV-9.

AB-Monomer IV-9 was fully characterized by spectroscopic means. The IR spectrum showed the presence of the free hydroxy group. The ^1H NMR spectrum showed the presence of the aliphatic chain. The formation of the ester was confirmed by different chemical shift for H_{18} and H_{23} (Figure IV.3). In addition, the ^{13}C NMR spectrum exhibited four carbonyl peaks corresponding to the different carbonyl groups in the product.

The first DSC trace run on IV-9 showed a melting endotherm at 118 °C, and a broad exotherm starting at 180 °C. The second scan, which was that of the curing product of IV-9, exhibited a small T_g at 98 °C. No exotherm was observed on the second scan, meaning that all BCBO moieties reacted during the first scan.

IV.3.3b. Polymerization

Monomer **IV-9** was polymerized in diphenyl ether at 240 °C for 24 hours (Scheme IV.7). After reaction the solution was left standing for two days. Two phases were obtained and the yellow top layer containing mostly diphenyl ether was decanted. The remaining brown viscous layer was diluted with chloroform and precipitated into methanol. This procedure was repeated until no more diphenyl ether was seen on the GPC trace of polymer **IV-10**.

Scheme IV.7. Polymerization of monomer **IV-9**.

The IR spectrum of polymer **IV-10** exhibited an ester peak which was overlapped with the symmetric stretching bands of the imide. The ^1H NMR spectrum showed that the BCBO unit reacted with the hydroxy group (Figure IV.3). The BCBO moiety reacted as the peak due to the methylene of BCBO (4.05 ppm, 2H) was replaced by a methyl group at 2.65 ppm. The addition reaction between the free hydroxy group of **IV-9** and BCBO was demonstrated by the shift of the peak from 3.67 ppm (H_{23} , **IV-9**) to 4.31 ppm (H_{23} , **IV-10**).

The molecular weight of polymer **IV-10** was low ($M_w = 6260$, as determined by GPC). This low molecular weight was due to an incomplete reaction; some small peaks are still present at 4.05 and 3.67 ppm. However, no side reaction (i.e. dimerization) was observed. The olefinic proton of the dimer **II-2** was not present in the ^1H NMR spectrum of polymer **IV-10**.

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113

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IV.4. Poly(ethylene glycol)-Grafted-Polystyrene

Poly(ethylene glycol) (PEG) is used to modify polymer surfaces for biomedical applications.⁴ Poly(ethylene glycol)-grafted-polystyrenes (PS-g-PEG) are widely used as solid support in the preparation of peptide libraries.⁵ PS-g-PEG fulfills both solubility and biocompatibility with enzymes and cells. A wide variety of functional groups have been introduced onto polystyrene either by direct electrophilic substitution or from lithiated polystyrene.⁶ PS-g-PEG was prepared from lithiated polystyrene and ethylene oxide.³ Friedel-Crafts alkylation of polystyrene with propylene oxide in the presence of a Lewis acid catalyst introduced a hydroxy group onto polystyrene.⁷ The hydroxy polystyrene then reacted with ethylene oxide to form a PS-g-PEG.

The grafting of polystyrene has been achieved by first introducing a hydroxy group onto the polymer followed by polymerization of ethylene oxide. This is the “graft from” method (Section V.1.3) and the problem usually associated with the incorporation of the hydroxy group onto the polystyrene is the formation of polysubstituted benzene ring. The “graft onto” method does not have this drawback. Thus, a poly(ethylene glycol) will be reacted with a complementary functional group of the polymer.

IV.4.1. Monomer synthesis

The design of the monomer used for the copolymerization with styrene depends on the type of copolymer wanted. The type of copolymer (i.e. block, alternating) to be produced can be predicted from the reactivity ratio of each monomer (r_1 and r_2 for monomer M_1 and M_2 , respectively) (Table IV.4). The reactivity ratio quantifies the likelihood of the monomer

to react with itself instead of with the other monomer. Hence, a random copolymer with only few units of BCBO-monomer at the time will be obtained if the value of r_{styrene} is in the range of 1-3, and that of BCBO-monomer (r_{BCBO}) between 0.1 and 0.3.

Table IV.4. Type of copolymer in function of the reactivity ratio of the monomers.

type of copolymer	block	alternating	random
r_1	10	0.1	3
r_2	10	0.1	3

For the couple styrene and N-substituted acrylamide, the relative reactivities are about 1.5-2 for r_{styrene} , and 0.25-0.54 for $r_{\text{acrylamide}}$.⁸ Hence, with this two monomers a copolymer with the acrylamide will be introduced between small blocks of polystyrene. Furthermore, an acrylamide monomer can be prepared from amino-BCBO.

The vinyl monomer (IV-11) was synthesized by condensation of methacryloyl chloride with amino-BCBO (III-2) in the presence of a triethyl amine in anhydrous THF (Scheme IV.8). Monomer IV-11 was obtained as yellow flakes after recrystallization from ethanol/cyclohexane.

Scheme IV.8. Synthesis of benzocyclobutenone vinyl monomer IV-11.

The structure of monomer IV-11 was verified by spectroscopic means. The IR spectrum showed the presence of the cyclobutenone unit ($\text{C=O } 1745 \text{ cm}^{-1}$) as well as that of

the amide group ($\text{C}=\text{O}$ 1766 cm^{-1} , N-H 3357 cm^{-1}). The ^1H NMR spectrum showed the presence of two vinylic protons and a methyl group in addition to the peaks from the BCBO unit. The mass spectrum exhibited a molecular mass of 201, as well as the fragmentation product resulting from the loss of carbon monoxide.

IV.4.2. Polymerization

Two copolymers were prepared using different ratios of monomer **IV-11** and styrene (Scheme IV.9). The copolymers were prepared by radical polymerization using AIBN as a radical initiator. A THF solution of monomer **IV-11**, styrene and AIBN was first deoxygenated with nitrogen, placed in a sealed vessel and heated at $60\text{ }^{\circ}\text{C}$ for 24 hours. The resulting polymer was precipitated in hexane. The remaining unreacted monomer was removed by successive precipitation in methanol, and monitored by GPC.

Scheme IV.9. Copolymerization of monomer **IV-11** with styrene.

IV.4.3. Polymer Characterization

The effective incorporation of monomer **IV-11** into polymer **IV-12a** and **IV-12b** was indicated by the presence of two carbonyl peaks at 1762 cm^{-1} for the ketone and 1680

cm⁻¹ for the amide in their IR spectra (Figure IV.4). The ¹H NMR spectrum also proved the incorporation of monomer IV-11 into the copolymers. Despite the overlap of most peaks corresponding to monomer IV-11 by that of polystyrene, the characteristic methylene peak at 3.9 ppm was clearly identified. However, not one but three singlets were present at 3.9 ppm. These three singlets were due to the presence of three different diads, each corresponding to a different magnetic environment in the polymer.

Monomer ratios in polymers IV-12 were calculated from the peak integration of the ¹H NMR spectrum. Comparing these results with the feed ratio, it was determined that 80% of monomer IV-11 was incorporated into polymer IV-12a and 97% into polymer IV-12b.

The results of the thermal analyses on polymers IV-12 are summarized in Table IV.5. The decomposition temperature of both copolymers was identical to that of polystyrene. Thus, the presence of monomer IV-11 did not influenced the thermal stability of the polymer.

Table IV.5. Thermal properties of copolymer IV-12.

	BCBO content	T _d ^a (°C)	T _g ^b (°C)	T _{max} (°C)	T _g (°C) 2nd scan
Polystyrene	0	378	100	N/A	N/A
IV-12a	0.04	375	108	300	97
IV-12b	0.097	375	118	298	111

^a Measured by TG at 10 °C/min, under a nitrogen flow of 200 mL/min. ^b Measured by DSC at 10 °C/min, under a nitrogen flow of 50 mL/min.

The T_g is usually measured on the second DSC scan. However, as the polymer contained BCBO units, after the first scan a partly crosslinked polymer could be obtained.

Figure IV.4. IR spectra of monomer IV-11 and polymer IV-12b.

Figure IV.4. DSC traces of copolymer IV-12b.

Therefore, oscillating DSC was used to determine the T_g of polymer **IV-12** in the first run. The T_g values of the polymers **IV-12** were slightly higher than that of polystyrene, increasing with the amount of monomer **IV-11**. However, the difference was not significant enough to draw any further conclusions. The first DSC curves also exhibited an exotherm peak at about 300 °C due to the ring-opening of the BCBO units (Figure IV.5). On the second scan, the T_g was lower than for the first scan. This was somewhat surprising as partly crosslinked polymers generally have a higher T_g than non-crosslinked ones. The T_g remained lower for **IV-12a** than for **IV-12b**.

IV.4.4. Polymer Grafting

The copolymers were grafted using poly(ethylene glycol) methyl ether with two different molecular weights (550 and 2000). Furthermore, poly(ethylene glycol) methyl ether was used in order to prevent crosslinking (Scheme IV.10). Polymer **IV-12** was heated under nitrogen at 300 °C with a large excess of poly(ethylene glycol) methyl ether for four hours. The polymer was precipitated in water or methanol. The remaining polyol in the polymer was extracted in a Soxhlet extractor overnight with water or methanol. The resulting grafted-polymers are named according to the starting copolymer (i.e. **IV-12a-**, **IV-12b-**) and the molecular weight of poly(ethylene glycol) methyl ether (i.e. **-550**, **-2000**) they were grafted with.

Scheme IV.10. Grafting polymer IV-12 with poly(ethylene glycol) methyl ether.

IV.4.5. Characterization of PS-g-PEG

The complete reaction of the BCBO moiety in copolymers IV-12 with poly(ethylene glycol) methyl ether was proved by IR and NMR spectroscopy. In the IR spectrum (Figure IV.6), the ketone peak of polymer IV-12 was replaced by an ester peak at 1720 cm^{-1} . The ester peak was the result of the reaction between the BCBO moieties and PEG methyl ether. An ether peak (1109 cm^{-1}) was also present in the IR spectrum, proving the incorporation of PEG side chain in the polymer.

Figure IV.6. IR spectra of polymer **IV-12b** and grafted-polymer **IV-12b-500**.

The results obtained from thermogravimetric analyses of the graft-polymers are reported in table IV.6. The decomposition temperature was not related to the BCBO ratio but rather seemed to depend on the length of the poly(ethylene glycol) side chain. Polymers **IV-12-550** had a lower decomposition temperature than **IV-12-2000**. The higher decomposition temperature of **IV-12a-2000** and **IV-2b-2000** may be due to their higher overall molecular weights. Indeed, the properties of low molecular weight polymers strongly depend on their molecular weights. However, once the molecular weight is high enough, the polymer properties become independent of it.

Table IV.6. Decomposition temperature of grafted copolymers.

	IV-12a-550	IV-12b-550	IV-12a-2000	IV-12b-2000
T_d^a (°C)	335	327	363	369

^a Measured by TG at 5% weight loss, with a heating rate of 10 °C/min, under a nitrogen flow of 200 mL/min.

The DSC traces obtained for the grafted polymers exhibited a very broad transition for the T_g from -50 to -30 °C. This is a common phenomenon for branched polymer. However, in the second DSC run, **IV-12b-2000** exhibited a T_g at -49 °C, a melting point at 42 °C and a small T_g transition at 134 °C (Figure IV.7). The first T_g was associated to the branched PEG. The melting point at 42 °C was due to the PEG side chains. The small transition at 134 °C may be associated with the T_g of polystyrene, but the temperature was higher than that of T_g of polystyrene alone which is at 90-100 °C. The DSC curve of **IV-12a-2000** did not have a melting endotherm. This was justified by the fact that there was less PEG branching along the polystyrene backbone and therefore the PEG side chain could not pack enough to form a regular structure.

IV.5. Conclusion

BCBO was introduced into polyurethanes, polyimides and polystyrene and upon curing with a diol; a cured material, linear polymer and grafted polymer, were obtained. The polymer transformation in the case of polyimides and polystyrene was performed in solution to prepare a linear and branched polymer. The same reaction can be achieved in melt. The use of a polyfunctional alcohol or amine would produce a crosslinked material.

IV.6. Experimental Section

Materials: Benzene tricarboxylic anhydride, thionyl chloride, methacryloyl chloride, AIBN and styrene were purchased from Aldrich Co. and were used as received. Desmodur N-

3300, Baytec MP-100 and Desmophen 2001 KS were graciously provided by Bayer Co. THF was dried over sodium metal and distilled prior to use.

Characterization: FT-ATR were performed on a Bomem-FTIR Michelson series instrument with a resolution of 4 cm^{-1} . A crystal of ZnSe with a dimension of 50x20x2mm and $\theta\ 45^\circ$, was used.

End-capped Desmodur (IV-1)

Desmodur isocyanate prepolymer (1.004 g, 2.52 mmol), amino-BCBO (**III-2**) (0.671 g, 5.05 mmol) and freshly distilled NMP (9 mL) were introduced in a flame dried flask under nitrogen. The solution was stirred and heated up to $80\text{ }^\circ\text{C}$ until no more isocyanate could be detected by IR. The solution was then cooled down to room temperature, diluted with acetone (3 mL) and precipitated in an acetone/water solution (10/90). During the precipitation, the solution was stirred with a spatula to get only a fine precipitate and to prevent the formation of sticky product as would happened if a magnetic stirring was used. The precipitate was then filtered and dried under vacuum at $80\text{ }^\circ\text{C}$. The end-capped Desmodur was obtained as a beige powder: 1.278 g (55% yield); mp $147\text{ }^\circ\text{C}$ (DSC); decomposition temperature $267\text{ }^\circ\text{C}$ (TG); IR (KBr, cm^{-1}) 3362, 3313, 1763 (C=O, ketone), 1689 (C=O, urethane); ^1H NMR (400 MHz, DMSO- d_6) δ 8.62 (s, 2H), 7.54 (s, 2H), 7.50 (d, 2H, $J_{\text{H-H}} = 7.8\text{ Hz}$), 7.44 (dd, 2H, $J_{\text{H-H}} = 7.8\text{ Hz}$, $J_{\text{H-H}} = 1.7\text{ Hz}$), 6.19 (t, 2H, $J_{\text{H-H}} = 5.5\text{ Hz}$), 3.87 (s, 4H), 3.07 (d, 1H, $J_{\text{H-H}} = 6.4\text{ Hz}$), 3.05 (d, 1H, $J_{\text{H-H}} = 6.4\text{ Hz}$), 1.54

(s, 2H), 1.41 (s, 2H), 1.28 (s, 12H); ^{13}C NMR (MHz, DMSO- d_6) δ 188.14, 155.04, 148.83, 147.62, 143.64, 141.54, 125.56, 124.05, 108.05, 51.01, 42.07, 29.48, 27.10, 25.90, 25.77.

End-capped Baytec (IV-2)

Baytec (1.583 g, 1.83 mmol), amino-BCBO (**III-2**) (0.487 g, 3.66 mmol) and freshly distilled NMP (7.5 mL) were introduced in a flame dried flask under nitrogen. The solution was stirred and heated up to 80 °C until no more isocyanate could be detected by IR. The solution was then cooled down to room temperature, diluted with acetone (3 mL) and precipitated in a methanol/water (5:4) solution. During the precipitation, the solution was magnetically stirred but the end of the pipette had to be in the solution to prevent the formation of sticky product and form a nice precipitate. The precipitate was then filtered and dried under vacuum at 80 °C. The end-capped Baytec was obtained as a beige powder: 0.872 g (77% yield); no melting point was observed on DSC, decomposition at 244 °C (TG); IR (KBr, cm^{-1}) 3297, 1764 (C=O, ketone), 1642 (C=O, urethane); ^1H NMR (400 MHz, DMSO- d_6) δ 9.43 (s, 2H), 8.83 (s, 2H), 8.65 (s, 2H), 7.58 (s, 2H), 7.55 (d, 2H, $J_{\text{H-H}} = 8.0$ Hz), 7.52 (dd, 2H, $J_{\text{H-H}} = 8.1$ Hz, $^4J_{\text{H-H}} = 1.6$ Hz), 7.35 (m, 6H), 7.11 (d, 2H, $J_{\text{H-H}} = 8.4$ Hz), 7.08 (d, 2H, $J_{\text{H-H}} = 8.5$ Hz), 3.89 (s, 4H), 3.46 (m, H), 1.03 (d, H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 188.03, 152.51, 147.71, 144.46, 140.70, 137.31, (137.16), 135.20, 128.88, 128.83, 128.75, 126.11, 124.23, 118.55, 118.49, 118.29, 108.79, 74.63, 74.54, 74.43, 72.37, 72.17, 51.15, 17.19.

Polymer curing (IV-3 and IV-4)

An equimolar amount of IV-1 or IV-2 and diol was placed on a glass plate and heated with a hot plate. The mixture was stirred while the temperature was increased. The hot plate temperature was raised up to 230-240 °C. The glass plate was then removed from the hot plate and allowed to cool down to room temperature. The film was peeled off the glass plate for characterization.

General procedure for the synthesis of bis-imide-BCBO (IV-5)

Dianhydride (2 mmol) and amino-BCBO (III-2) (4 mmol) in anhydrous DMAc (7 mL) were refluxed for two hours. The product precipitated out from solution and thoroughly rinsed with methanol. The precipitate was then dried under vacuum.

IV-a

Yellow powder (71% yield); Solubility test (5 mg in 0.5 mL): insoluble in DMAc, DMF, NMP, chloroform, chloronaphthalene; soluble in hot DMSO and precipitated on cooling; soluble in hot m-cresol; no melting point (DSC); decomposition at 430 °C (TG, 5% loss); IR (KBr, cm^{-1}) 1759 (C=O, ketone), 1725 (C=O, imide), 1646 (C=O, ketone); elemental analysis $\text{C}_{33}\text{H}_{16}\text{N}_2\text{O}_7$: %C: calcd 71.74, found 71.40; %N: calcd 5.07, found 5.11; %H: calcd 2.92, found 2.85.

IV-b

Yellow powder (75% yield); Solubility test (5 mg in 0.5 mL): insoluble in DMAc, DMF, NMP, DMSO, chloroform; soluble in hot m-cresol; no melting point (DSC), decomposition at 477 °C (TG, 5% loss); IR (KBr, cm^{-1}) 1762 (ketone), 1722 (imide); elemental analysis $\text{C}_{32}\text{H}_{16}\text{N}_2\text{O}_6$: %C: calcd 69.64, found 60.30; %N: calcd 6.25, found 6.25; %H: calcd 2.68, found 2.48.

IV-c

In a flame dried flask equipped with a condenser and a nitrogen inlet were introduced amino-BCBO (0.766 g, 5.76 mmol), 6FDA (1.278 g, 2.878 mmol) and DMAc (5 mL). The solution was refluxed for 2 hours. The reaction was stopped and the product was precipitated in absolute ethanol. The precipitate was filtered off and dried under vacuum at 60 °C to yield a beige powder (1.135 g, 58.5 %): mp 242 °C (DSC); IR (KBr, cm^{-1}) 1765 (C=O, ketone), 1724 (C=O, imide); ^1H NMR (400 MHz, CDCl_3) δ 8.07 (dd, 1H, $J_{\text{H-H}} = 7.9$ Hz, $^4J_{\text{H-H}} = 9.4$ Hz), 7.94 (s, 1H), 7.92 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz), 7.70 (dd, 1H, $J_{\text{H-H}} = 7.9$ Hz, $^4J_{\text{H-H}} = 0.8$ Hz), 7.59 (dd, 1H, $J_{\text{H-H}} = 7.9$ Hz, $^4J_{\text{H-H}} = 1.7$ Hz), 7.44 (d, 1H, $^4J_{\text{H-H}} = 0.8$ Hz), 4.05 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.85, 165.77, 165.59, 151.07, 148.91, 139.42, 136.14, 133.24, 132.54, 132.25, 132.04, 125.59, 124.75, 124.40, 118.84, 52.30;

UV (λ_{max} , nm, CH_2Cl_2) 236, 294; MS (EI, m/e, relative intensity %) 674 (M^+ , 50.6), 646 ($M^+ - \text{CO}$, 100), 619 ($M^+ + 1 - 2\text{CO}$, 31.4), 309 ($M^+ - 2\text{CO}$, 31.8).

Chain extension of IV-5 with Desmophen (IV-6)

An equimolar amount of bis-imide-BCBO and Desmophen (determined by the number of OH group/g of polymer) were heated in phenyl ether at 260 °C (160 °C for IV-5c). The starting concentration was 15-18 % wt., and the solution was diluted after increasing molecular weight. The polymerization solution was poured in methanol, the polymer formed a gummy product. This gummy product was dissolved in chloroform and the solution poured in methanol. This procedure was repeated until the polymer was free of phenyl ether.

IV-a: brown gummy polymer (purified polymer: 27% yield); GPC $M_w = 78,337$, $M_n = 31,033$, $M_w/M_n = 2.52$; IR (KBr, cm^{-1}) 1782 (small; C=O, imide), 1731 (strong; C=O, ester in Desmophen), 1681 (small; C=O, ketone); ^1H NMR (400 MHz, CDCl_3) δ 8.32 (s, 1H), 8.27 (d, 1H, $J_{\text{H-H}} = 8.7$ Hz), 8.16 (d, 1H, $J_{\text{H-H}} = 7.5$ Hz), 8.04 (s, 1H), 7.51 (t, 1H, $J_{\text{H-H}} = 8.0$ Hz), 7.33 (t, 1H, $J_{\text{H-H}} = 7.9$ Hz), 7.01 (d, 1H, $J_{\text{H-H}} = 8.0$ Hz), 4.27 (s, 10H), 4.09 (broad peak, 14H), 2.67 (s, 3H), 2.34 (broad peak, 26H), 1.67 (broad peak, 42H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.42, 173.17, 166.05, 142.13, 141.16, 136.04, 135.19, 132.88, 132.36, 130.16, 129.87, 129.30, 128.93, 124.96, 124.56, 123.36, 119.04, 63.99, 62.93, 62.25, 33.99, 33.81, 25.59, 25.48, 24.54, 24.48, 24.43, 24.37, 21.74.

IV-b: brown gummy polymer; GPC $M_w = 46,761$, $M_n = 21,336$, $M_w/M_n = 2.19$; IR (KBr, cm^{-1}) 1776 (small; C=O, imide), 1732 (strong; C=O, ester in Desmophen); ^1H NMR (400 MHz, CDCl_3) δ 8.50 (s, 1H), 8.06 (d, 1H, $^4J_{\text{H-H}} = 2.1$ Hz), 7.54 (dd, 1H, $J_{\text{H-H}} = 8.1$ Hz, $^4J_{\text{H-H}} = 2.2$ Hz), 7.44 (d, 1H, $J_{\text{H-H}} = 8.2$ Hz), 7.34 (d, 1H, $J_{\text{H-H}} = 9.6$ Hz), 7.01 (d, 1H, $J_{\text{H-H}} = 8.2$ Hz), 4.27 (s, 13H), 4.09 (broad peak, 13H), 2.68 (s, 3H), 2.34 (broad peak, 13H), 1.68 (broad peak, 21H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.25, 173.02, 166.10, 164.92, 157.28, 137.19, 132.79, 129.82, 129.73, 128.86, 128.62, 123.22, 119.35, 118.90, 63.85, 62.85, 62.11, 33.86, 33.66, 25.33, 24.39, 24.33, 24.29, 24.23.

IV-c: The polymer could not be completely purified and was lost during partial purification; GPC $M_w = 29,730$, $M_n = 16,718$, $M_w/M_n = 1.78$.

BCBO imide acid (IV-7)

In a flame dried flask equipped with a nitrogen inlet and a condenser were introduced amino-BCBO (1.117 g, 8.40 mmol), benzene tricarboxylic anhydride (1.612 g, 8.39 mmol) and anhydrous DMAc (5 mL). The solution was heated at 120 °C for 3 hours. The product precipitated out of solution during the reaction. The solution was poured in water (50 mL). The precipitate was then filtered out, rinsed with diethyl ether. The product was then recrystallized from DMAc to yield a yellowish powder (2.094 g, 81 %): ^1H NMR (400 MHz, CDCl_3) δ 13.72 (b, 1H), 8.42 (dd, 1H, $J_{\text{H-H}} = 7.7$ Hz, $^4J_{\text{H-H}} = 1.4$ Hz), 8.31 (s,

1H), 8.09 (dd, 1H, $J_{\text{H-H}} = 7.8$ Hz, $^4J_{\text{H-H}} = 0.5$ Hz), 7.82 (dd, 1H, $J_{\text{H-H}} = 7.9$ Hz, $^4J_{\text{H-H}} = 0.7$ Hz), 7.69 (dd, 1H, $J_{\text{H-H}} = 7.8$ Hz, $^4J_{\text{H-H}} = 1.6$ Hz), 7.51 (s, 1H), 4.07 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.40, 166.03, 165.72, 151.02, 147.67, 36.54, 135.48, 134.83, 134.48, 132.37, 132.00, 124.59, 123.83, 123.35, 119.33, 51.90. DSC scan showed a melting endotherm at 115 °C and two exotherms peaked at 266 and 284 °C.

BCBO imide acid chloride (IV-8)

In a flask fitted with a condenser and a drying tube, BCBO imide carboxylic acid (0.5 g, mmol) was stirred in thionyl chloride (5 mL) at 80 °C. The product was pure enough for further reactions without recrystallization from toluene. Yield: 0.55 g (100%); IR (KBr, cm^{-1}) 1790, 1783, 1724; ^1H NMR (400 MHz, CDCl_3) δ 8.40 (dd, 1H, $J_{\text{H-H}} = 7.7$ Hz, $^4J_{\text{H-H}} = 1.3$ Hz), 8.29 (s, 1H), 8.07 (d, 1H, $J_{\text{H-H}} = 7.7$ Hz), 7.81 (d, 1H, $J_{\text{H-H}} = 7.8$ Hz), 7.68 (dd, 1H, $J_{\text{H-H}} = 7.8$ Hz, $^4J_{\text{H-H}} = 1.6$ Hz), 7.50 (s, 1H), 4.67 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.44, 166.08, 165.70, 151.06, 147.72, 136.54, 135.52, 134.86, 134.50, 132.41, 132.02, 124.65, 123.90, 123.50, 123.40, 119.36, 51.95; MS (EI, m/e, relative intensity %) 327 ($\text{M}^+ + 2$, 26.4), 325 (M^+ , 79.3), 297 ($\text{M}^+ - \text{CO}$, 100).

AB monomer (IV-9)

BCBO imide acid chloride (0.481 g, 1.48 mmol) and hexanediol (0.399 g, 3.38 mmol) were dissolved in methylene chloride (15 mL). The solution was refluxed overnight. The solvent was removed and the white solid rinsed several times with hot hexane and once with water. After drying a white product (0.521 g, 87% yield) was obtained. The first DSC scan showed the presence of a melting endotherm at 118 °C and two exothermic peak at 228 and 266 °C. The decomposition temperature was found to be 375 °C by TG at 5% loss; IR (KBr, cm^{-1}) 3434 (OH), 1784 (C=O, imide), 1765 (C=O, ketone), 1719 (C=O, imide and ester); ^1H NMR (400 MHz, CDCl_3) δ 8.60 (s, 1H), 8.50 (dd, 1H, $J_{\text{H-H}} = 7.8$ Hz, $^4J_{\text{H-H}} = 1.1$ Hz), 8.04 (d, 1H, $J_{\text{H-H}} = 7.7$ Hz), 7.70 (d, 1H, $J_{\text{H-H}} = 7.9$ Hz), 7.61 (dd, 1H, $J_{\text{H-H}} = 7.9$ Hz, $^4J_{\text{H-H}} = 0.9$ Hz), 7.46 (s, 1H), 4.42 (t, 2H, $J_{\text{H-H}} = 6.7$ Hz), 4.05 (s, 2H, 3.68 (t, 2H, $J_{\text{H-H}} = 6.4$ Hz), 1.84 (q, 2H, $J_{\text{H-H}} = 6.8$ Hz), 1.62 (q, 2H, $J_{\text{H-H}} = 6.7$ Hz), 1.50 (m, 4H); ^{13}C NMR (MHz, CDCl_3) δ 186.91, 166.11, 166.04, 164.60, 150.89, 148.85, 136.67, 136.03, 134.75, 133.25, 132.23, 131.79, 125.03, 124.65, 124.07, 118.81, 66.19, 62.78, 52.28, 32.58, 28.61, 25.87, 25.48; MS (EI, m/e, relative intensity %) 407 (M^+ , 100), 379 ($\text{M}^+ - \text{CO}$, 91).

Polymerization of monomer IV-9 (IV-10)

In a dry flask purged with nitrogen, monomer IV-9 was heated at 240 °C in diphenyl ether overnight. The solution was left standing for two days and phase separation occurred. The top layer was decanted. The brown viscous layer was diluted with chloroform and

precipitated in methanol. A beige precipitate was obtained. The polymer was purified from diphenyl ether by repeated precipitation in methanol, until the diphenyl ether peak disappeared from the GPC trace. GPC $M_w = 6260$, $M_n = 3200$, $M_w/M_n = 1.95$; IR (KBr, cm^{-1}) 1780, 1723, 1376, 1250, 1209; ^1H NMR (400 MHz, CDCl_3) δ 8.53 (d, 1H, $J_{\text{H-H}} = 8.2$ Hz), 8.44 (dd, 1H, $J_{\text{H-H}} = 10.9$ Hz, $J_{\text{H-H}} = 8.0$ Hz), 8.00 (d, 1H, $J_{\text{H-H}} = 5.8$ Hz), 7.47 (s, 1H), 7.38 (d, 1H, $J_{\text{H-H}} = 8.6$ Hz), 4.40 (b q, 2H, $J_{\text{H-H}} = 6.2$ Hz), 4.31 (b q, 2H, $J_{\text{H-H}} = 6.6$ Hz), 2.65 and 2.62 (s, 3H), 1.82 (b, 4H), 1.53 (b, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.21, 164.62, 140.60, 136.39, 135.82, 132.60, 131.85, 130.65, 129.70, 129.22, 128.57, 124.83, 123.89, 66.01, 64.95, 28.59, 25.75, 25.67, 21.58.

Vinyl monomer with BCBO (IV-11)

To a solution of amino-BCBO (2.556 g, 19.2 mmol) in anhydrous THF (10 mL) at room temperature and under nitrogen, was added triethyl amine (2.736 g, 27.1 mmol) in THF (5 mL). The temperature was cooled down to 0 °C and methacryloyl chloride (2.556 g, 32.8 mmol) in THF (10 mL) was added to the solution. The resulting yellow solution was allowed to warm up and was stirred at room temperature overnight. The reaction solution was diluted with diethyl ether (50 mL for 230 mg) and washed with diluted hydrochloric acid three times. Removal of the solvent and subsequent recrystallization of the residue ethanol/cyclohexane afforded the pure amide product as yellow crystalline flakes: (87%

yield); mp 147-148 °C; IR (KBr, cm^{-1}) 3357 (N-H), 2923, 1745 (C=O, ketone), 1666 (C=O, amide); ^1H NMR (200 MHz, CDCl_3) δ 7.85 (b, 1H), 7.71 (dd, 1H, $J_{\text{H-H}} = 8.1$ Hz, $^4J_{\text{H-H}} = 1.8$ Hz), 7.61 (s, 1H), 7.49 (d, 1H, $J_{\text{H-H}} = 7.9$ Hz), 5.83 (s, 1H), 5.498 (s, 1H), 3.94 (s, 2H), 2.06 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 167.00, 147.35, 140.77, 138.99, 128.03, 124.42, 120.71, 112.25, 52.06, 19.01; MS (EI, m/e, relative intensity %) 201 (M^+ , 37.5), 173 ($\text{M}^+ - \text{CO}$, 43.5). DSC showed a melting endotherm peaked at 147 °C and an exotherm beginning at 199 °C in the first scan. The second scan displayed no peak up to 330 °C.

Copolymerization of monomer IV-11 and Styrene (IV-12)

IV-12a (feed ratio: 5% BCBO) To a solution of BCBO-vinyl monomer (0.201 g, 1.0 mmol) in anhydrous THF (6 mL) was added styrene (1.977 g, 19.0 mmol), styrene was passed through a short silica gel column prior use to remove the inhibitor, and AIBN (0.023 g, 0.15 mmol). The solution was degassed with nitrogen and the vessel was sealed. The solution was stirred at 60 °C overnight. The polymer was then precipitated in hexane. The white powder was purified from the monomers by three successive reprecipitations from methanol. The polymer was dried under vacuum. GPC $M_w = 37570$, $M_n = 19680$, $M_w/M_n = 1.91$; IR (KBr, cm^{-1}) 3026, 2924, 1763, 1601, 1493, 1452; ^1H NMR (400 MHz, CDCl_3) δ 7.08 (b), 6.60 (b), 6.48 (b), 3.98, 3.91, 3.86 (3 s), 1.85 (b), 1.45 (b).

IV-12b (feed ratio: 10% BCBO): To a solution of BCBO-vinyl monomer (0.402 g, 2.0 mmol) in anhydrous THF (9 mL) was added styrene (1.879 g, 18.0 mmol) and AIBN (0.023 g, 0.15 mmol). The solution was degassed with nitrogen and the vessel was sealed. The

solution was stirred at 60 °C overnight. The polymer was then precipitated in hexane. The white powder was purified from the monomers by two successive reprecipitations from methanol. The polymer was dried under vacuum. GPC $M_w = 31080$, $M_n = 15300$, $M_w/M_n = 2.03$; IR (KBr, cm^{-1}) 3025, 2923, 1762, 1493, 1452; ^1H NMR (400 MHz, CDCl_3) δ 7.08 (b), 6.60 (b), 3.97, 3.91, 3.85 (3 s), 1.85 (b), 1.45 (b).

Grafting of copolymer IV-12

Polymer IV-12 (150 mg) and poly(ethylene glycol) methyl ether (3 g) were stirred in a dry flask under nitrogen at 300 °C for 4 hours. The reaction mixture was then poured in water or methanol. The resulting solution was centrifuged, filtered and extracted overnight with water or methanol in a Soxhlet extractor. The resulting yellow polymer was then dried at 50 °C under reduced pressure (5 mmHg).

IV-12a-550 (5% BCBO + PEG-550): GPC $M_w = 9,955$, $M_n = 6,010$, $M_w/M_n = 1.66$; IR (KBr, cm^{-1}) 3026, 2924, 1720, 1601, 1493, 1452, 1109; ^1H NMR (400 MHz, CDCl_3) δ 7.10 (b), 6.55 (b), 3.67 (s), 2.61, 2.54, 2.48 (3 s, 3H), 2.10 (b), 1.85 (b), 1.44 (b); ^{13}C NMR (100 MHz, CDCl_3) δ 127.96, 127.65, 125.65, 118.37, 70.59, 40.33.

IV-12b-550 (10% BCBO + PEG-550): GPC $M_w = 4025$, $M_n = 2630$, $M_w/M_n = 1.53$; IR (KBr, cm^{-1}) 2922, 1720, 1601, 1493, 1452, 1102; ^1H NMR (400 MHz, CDCl_3) δ 7.08 (b), 6.59 (b), 6.47 (b), 3.67 (s), 3.40 (s), 2.60, 2.53, 2.48 (3s), 2.28 (b), 1.83 (b), 1.43 (b); ^{13}C

NMR (100 MHz, CDCl_3) δ 127.96, 127.64, 125.65, 125.49, 118.42, 71.94, 70.59, 59.08, 40.28.

IV-12a-2000 (5% BCBO + PEG-2000): IR (KBr, cm^{-1}) 2922, 1720, 1601, 1493, 1452, 1102.

IV-12b-2000 (10% BCBO + PEG-2000): IR (KBr, cm^{-1}) 2922, 1720, 1601, 1493, 1452, 1102.

IV.6. References

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Chapter V

Cyclobutenedione: A Ketene Precursor in Poly(aryl ether)s

V.1. Introduction

V.1.1. Cyclobutenedione

V.1.1a. *Synthesis of Cyclobutenedione*

The four-membered ring of cyclobutenedione has mainly been prepared by [2+2] cycloaddition (Scheme V.1).¹ Phenylcyclobutenedione was the first cyclobutenedione synthesized in 1955.² The four-membered ring was formed from phenylacetylene and trifluorochloroethylene (46); hydrolysis with sulfuric acid produced 3-phenylcyclobut-3-ene-1,2-dione in 75% yield. The four-membered ring was also formed by [2+2] cycloaddition of two molecules of trifluorochloroethylene, followed by reduction with zinc to give hexafluorocyclobutene (47).³ Cyclobutenedione was obtained by hydrolysis of the disubstituted tetrafluorocyclobutenedione (48). Thermolysis of 1-ethoxypentachloro-1,3-butadiene gave perchlorocyclobutenone (49) in 85-90% yield along with chloroethane.⁴ Hydrolysis of 49 with sulfuric acid produced squaric acid (50). Cyclobutenedione was easily obtained by functionalization of squaric acid.⁵ The [2+2] cycloaddition of dichloroketene with substituted acetylene yielded dichlorocyclobutenone (51), which produced cyclobutenedione upon hydrolysis.⁶ Addition of trichloromethane anion to cyclopropanone gave 4,4-dichlorocyclobutenone (51).⁷

Scheme V.1. Synthesis of cyclobutenedione by [2+2] cycloaddition.

More recently, a simple synthesis of cyclobutenedione from ketone has been reported (Scheme V.2).⁸ The ketone was first converted to the enol thioether, which reacted with dichloroketene to give the corresponding cyclobutanone. Elimination of hydrochloric acid and oxidation with *m*-chloroperbenzoic acid yielded the cyclobutenedione in good yield.

Scheme V.2. Synthesis of cyclobutenedione from ketone.

V.1.1b. Reactions of Cyclobutenedione

Cyclobutenediones, as cyclobutene derivatives, undergo electrophilic ring-opening

to produce butadiene-1,4-diones (bis-ketenes). In addition to the reaction of ketene with unsaturated compounds and nucleophiles, bis-ketenes undergo [4+2] cycloadditions and insertion reactions.

The cyclobutenedione unit is a valuable precursor for substituted quinones. Benzocyclobutenedione reacts with electron deficient olefins such as maleic anhydride and naphthoquinone upon photolysis to give the Diels-Alder adducts in 67 and 13% yield, respectively.⁹ The same reaction, attempted with other olefinic and acetylenic substrates, only led to very low yield of the Diels-Alder adducts. The reaction with quinones, despite their low yield, was recognized as being of great utility for the total synthesis of natural products, such as islandicin and digitopurpone (Scheme V.3).¹⁰

Scheme V.3. Synthesis of substituted naphthoquinones from benzocyclobutenedione.

The yield of the Diels-Alder reaction was greatly improved when a transition metal complex was used.¹¹ The metal transition complex reacted with cyclobutenedione to give a maleoyl transition metal complex which reacted with alkynes via an insertion-reductive elimination sequence (Scheme V.4). Among the metals tested (Co, Fe, Ni, Rh), cobalt gave the highest yield. Reaction of cyclobutenedione with ClCo(PPh₃)₃ gave a crystalline maleoyl cobalt complex, which after ligand exchange, reacted with a wide variety of alkynes to provide substituted benzoquinones in a regioselective manner.¹²

Scheme V.4. Formation of quinone via a maleoyl cobalt complex.

Substituted quinones can also be prepared by oxidation of the 4-hydroxyphenol obtained from 4-substituted 4-hydroxycyclobutenone (Scheme V.5).¹³ The 4-substituted 4-hydroxycyclobutenone was obtained in good yield from an alkenyllithium agent and cyclobutenedione. Fused quinones were obtained when using aryllithium.¹⁴ Benzocyclobutenedione monoketal has been used as a precursor in the synthesis of ($\pm$)-4-demethoxydauno-mycinone, a potential antibiotic.¹⁵

Scheme V.5. Synthesis of quinone via addition of an organolithium.

Thermal rearrangement of 4-alkynyl-4-hydroxycyclobutenone was shown to lead to a mixture of quinone and alkynyl cyclopentenediones.¹⁶ Some natural products containing cyclopentenedione show significant biological activity.¹⁷ When the rearrangement took place in the presence of Pd(II), only alkynyl cyclopentenedione was

produced, demonstrating a very good stereochemical control of the double bond (Scheme V.6).¹⁸

Scheme V.6. Alkenyl cyclopentenedione from cyclobutenedione.

Cyclobutenediones also react with nucleophiles (Scheme V.7). Cyclobutenedione has been reported to produce a diester in the presence of ethanol at room temperature after one week.¹⁹ The reaction proceeded more rapidly when the solution was heated (150 °C)²⁰ or irradiated with a mercury lamp.²¹ The cyclobutenedione unit was easily oxidized to the anhydride using oxygen²² or hydrogen peroxide.²³ When cyclobutenedione was irradiated in the presence of isonitrile, an iminodione is obtained.²⁴

Scheme V.7. Reaction of cyclobutenedione with nucleophiles.

V.1.2. Poly(aryl ether)s

Even though poly(aryl ether)s (PAEs) are usually referred to as high temperature resistant thermoplastics, it would be more accurate to classify them as high performance polymers.²⁵ This is due to the fact that applications of PAEs are primarily associated with

their excellent performance at high temperature. PAEs are known to sustain a service temperature as high as 280 °C and retain good mechanical properties at high temperatures. The good thermal behavior of PAEs is associated with their high glass transition temperature (T_g). The glass transition temperature is the temperature below which the polymer is in a glassy state, hence where it retains its mechanical properties.

In addition to their thermal resistance, PAEs also exhibit a good chemical and hydrolytic resistance, low flammability even without flame retardants and resistant against nuclear radiation. PAEs can be injection molded or extruded and therefore are encountered in a wide variety of applications, such as molded automobile parts, domestic appliances, medical equipment, printed circuit boards, glass-fiber and wire coatings.

V.1.3. Polymer Transformation

New polymers are obtained either by polymerization of new monomers or by chemical transformation of existing polymers. Polymer transformation is a very useful way of making new polymers. It is sometimes the only synthetic route to some high molecular weight polymers, especially when the corresponding monomer is not reactive enough or would yield oligomers due to insufficient solubility in the polymerization solvent. Polymer transformation is also a very convenient way to prepare a wide range of polymers starting from a single precursor polymer. The precursor polymer is first synthesized and then the desired derivative polymers may be obtained by reaction at the functional groups present in the precursor.

The lack of monomer reactivity is a problem in the preparation of poly(aryl ether)

by the nucleophilic route, in which the dihalo monomer has to be activated by an electron withdrawing group. For example, the direct syntheses of polymers with fused benzene rings **54** and **58** from the corresponding dihalo monomer **55** and **59** are not feasible. However, polymers **53**²⁶ and **57**²⁷ were prepared in high molecular weights from the corresponding difluoro monomers **52** and **56**. Treatment of the precursor polymers **53** and **57** with Lawesson's reagent yielded the desired polymers **54**²⁶ and **58**²⁷ (Scheme V.8).

Scheme V.8. Poly(aryl ether)s containing fused benzene rings.

Polymerization of crystalline polymers usually produces oligomers as they

precipitate out of the polymerization solution. Higher molecular weight crystalline polymers may be obtained by increasing the reaction temperature or from soluble precursor. Poly(aryl ether ketone)s (PAEKs) readily crystallize and thus precipitate from most organic solvents as their molecular weights increase. PAEKs must be polymerized at 280-340 °C in high boiling arylsulfone solvent in order to keep the polymer in solution and hence to produce a high molecular weight material. Polybenzophenone is a crystalline polymer. Direct polymerization of dichlorobenzophenone using nickel(0) as a catalyst yielded an insoluble, crystalline oligomer. However, the amorphous high molecular weight polymer (61) was obtained from the corresponding imine monomer (60). Hydrolysis of the imine polymer 61 produced the desired high molecular weight polybenzophenone (62) (Scheme V.9).²⁸

Scheme V.9. Preparation of high molecular weight polybenzophenone.

Polyquinoxaline has been prepared, in moderate to high molecular weight, directly from the corresponding quinoxaline monomer.²⁹ The quinoxaline heterocycle was sufficiently electron withdrawing for the etherification to occur. Quinoxaline can be prepared from a 1,2-diketone and 1,2-diaminobenzene.³⁰ Thus, instead of preparing a

whole series of polyquinoxaline from the corresponding monomers, a polymer containing 1,2-diketone moiety could be used as a precursor for the whole series. Polymerization of difluoro benzyl (**63**) with bisphenols gave high molecular weight polymers³¹ which could be used as a precursor to polyquinoxaline (Scheme V.10). Indeed, reaction of the diketone unit in the poly(aryl ether) precursor with substituted 1,2-diaminobenzene should provide a general route to polyquinoxalines.

Scheme V.10. Polymer precursor to heterocyclic poly(aryl ether)s.

Grafting is by far the most important process for chemical transformation of known polymers. Grafted copolymers are prepared by three methods: "grafting from", "grafting onto" and "macromonomer" methods (Figure V.1).³²

The "grafting from" method involves the generation of a reactive species along the polymer backbone. This reactive species may be generated thermally, photochemically or chemically. The reactive sites on the polymer backbone then initiate the polymerization of a comonomer present, thus forming the graft segment. This method yields a random grafted polymer which is often crosslinked. The "grafting onto" method consists of attaching a prepolymer onto the backbone of another polymer. It is achieved by reacting complementary functional groups at the end of the prepolymer and on the polymer

backbone. In the "macromonomer" method, a prepolymer containing one reactive end chain is copolymerized with a low molecular weight monomer.

"Grafting from" method

"Grafting onto" method

"Macromonomer" method

Figure V.1 . Grafting methods.

V.1.4. Potential Uses of Cyclobutenedione in Polymer Chemistry

As discussed earlier (section V.1.1b), cyclobutenedione reacts with a variety of compounds. Therefore, the presence of the cyclobutenedione moiety in a polymer backbone would be of great value as numerous polymer derivatives could be produced from the same parent polymer (Scheme V.11). Grafted polymers could be obtained by reaction with a hydroxy- or amine-terminated polymer as well as with unsaturated polymers. Potentially, any side chain could be introduced on the polymer as long as it contains a hydroxy or an amine group. Furthermore, the polymer transformation could be done thermally or photochemically. A crosslinked network would be produced if more than one functional group was present in the polymer. Another interesting application of a cyclobutenedione containing polymer would be the formation of a redox polymer by

reaction of the cyclobutenedione moiety with alkenes or alkynes.

Scheme V.11. Possible transformations of cyclobutenedione containing polymers.

The objectives of this research are (1) to design and synthesize a monomer containing the cyclobutenedione unit, (2) to synthesize and characterize a series of poly(aryl ether)s containing the cyclobutenedione unit and (3) to investigate the reaction of the cyclobutenedione in the polymer with alcohol to produce grafted polymers.

V.2. Design and Synthesis of the Monomer

The criteria for reactive monomers are different for each polymerization reaction. Thus, before designing a reactive monomer, the polymerization reaction must first be decided upon.

Poly(aryl ether)s have been synthesized by two main methods:^{33,34} the electrophilic and the nucleophilic route. In the electrophilic process, an aromatic acyl chloride reacts with an aromatic ring in the presence of a Friedel-Crafts catalyst (Scheme V.12). However, the purification of the polymer from the Lewis acid catalyst may be difficult. Furthermore, the para substitution is often insufficient as ortho linkages and branching are observed.

Scheme V.12. Electrophilic route to poly(aryl ether)s.

The nucleophilic route proceeds via the nucleophilic displacement of an aromatic halogen by a phenoxide by S_{NAr} mechanism (Scheme V.13).³⁵ The nucleophile attacks a vacant π^* orbital and this allows the bonding of the nucleophile to the aromatic ring without displacement of the existing substituent.³⁶ This first step is also the rate determining step of the reaction. The reaction rate is increased by facilitating the attack of the nucleophile; this is achieved by lowering the electron density of the site of the attack. The presence of an electron withdrawing group at the para-position to the attack site lowers the electron density. Typical electron withdrawing groups used for polymerization are sulfone, carbonyl and diazo groups, and their reactivity decreases in that order.

Besides the activation of the monomer, the reaction can be activated by lowering the energy of the Meisenheimer complex intermediate. The Meisenheimer complex is formed when the phenoxide attacks the fluorine bearing carbon of the difluoro-monomer.

The increase in sp^3 character of the fluorine bearing carbon changes geometry of the molecule. The leaving group is either an halogen or a nitro group. The halogens are used more often and their reactivity decrease in the order $F \gg Cl > Br > I$. Thus, only fluorine and chlorine are used. The phenoxide is usually generated *in situ* from a phenol using an alkali metal carbonate.³⁷

Scheme V.13. Nucleophilic route to poly(aryl ether)s.

V.2.1. Monomer Design

In this work, the nucleophilic approach will be used to synthesize poly(aryl ether)s. Due to the wide variety and availability of bisphenols, the cyclobutenedione unit will be introduced in the dihalo-monomer. Furthermore, the resonance structures of cyclobutenedione showed that it is an electron withdrawing moiety (Figure V.2). Thus, it should also stabilize the Meisenheimer complex intermediate. The cyclobutenedione unit itself will be used as the activating group in the dihalo-monomer.

Figure V.2. Resonance structure of cyclobutenedione.

The halogen to be used is fluorine because of its higher reactivity; chlorine is sufficiently activated only when the electron withdrawing group is a sulfone. When the dihalo-monomer is activated by ketone, the use of chlorine leads to a longer reaction time which increases the amount of unwanted side reactions. Furthermore, when chlorine is used, the polymer chain may be terminated by reductive halogenation of chlorine.³⁸

V.2.3. Monomer Synthesis

The designed monomer V-1 was readily synthesized in a one-pot reaction starting from 3,4-dihydroxycyclobut-3-ene-1,2-dione (squaric acid, 64) (Scheme V.14). Squaric acid was first treated with 2 equivalents of thionyl chloride using DMF as a catalyst in fluorobenzene. If an excess of thionyl chloride is used perchlorocyclobutenone will be obtained. The presence of the DMF catalyst was required as squaric acid can be refluxed in thionyl chloride without any reaction occurring.³⁹

The disubstituted cyclobutenedione was obtained when two molar equivalents of aluminum chloride were used.⁴⁰ However, when a catalytic amount or one molar equivalent was used only the monosubstituted product was obtained.³⁹ But, if aluminum chloride was present in excess, 1,2,3,3-tetraphenylcyclobuten-4-one was obtained.⁴¹ Monomer V-1 was prepared from squaric acid via the intermediate 65, according to literature procedure.^{39,40} The dichlorocyclobutenedione 65 was not isolated but used directly in the next step. Addition of two molar equivalents of aluminum chloride to the cooled reaction mixture led to the production of monomer V-1.

Scheme V.14. Synthesis of 3,4-bis(4-fluorophenyl)-cyclobut-3-ene-1,2-dione (V-1).

Pure 3,4-bis(4-fluorophenyl)-cyclobut-3-ene-1,2-dione (V-1) was obtained as yellow needles after two recrystallizations from methanol. Monomer V-1 was fully characterized by spectroscopic means. The IR spectrum exhibited a peak at 1766 cm^{-1} corresponding to the ketones. Diphenyl cyclobutenedione exhibited two carbonyl peaks at 1782 and 1770 cm^{-1} , corresponding to the asymmetric and the symmetric stretch of the two carbonyls. The ^1H NMR spectrum showed only two peaks which were a doublet of doublets and a triplet assigned to the protons at position 4 and 5, respectively (Table V.1). The pattern was due to a coupling between the protons and the fluorine. The coupling constant decreases since they are farther apart from each other. In the ^{13}C NMR spectrum, coupling between the carbons and the fluorine were also present and allowed the assignment of all peaks (Table V.1). The ^{19}F NMR spectrum showed a single peak at -102.78 ppm relative to CCl_3F , which confirmed the symmetry of monomer V-1. The mass spectrum showed the expected molecular ion mass, as well as the peaks derived from two successive losses of carbon monoxide.⁴²

Table V.1. NMR data obtained for V-1.

position	^1H NMR			^{13}C NMR	
	ppm	$J_{\text{H-H}}$ (Hz)	$J_{\text{H-F}}$ (Hz)	ppm	$J_{\text{C-F}}$ (Hz)
1				196.17	
2				186.00	
3				124.73	3.5
4	8.13	8.5	5.4	131.08	9.3
5	7.28	8.5	8.5	117.27	21.9
6				165.57	257

V.2.3. Stability of the Monomer

The cyclobutenedione unit opens by heat, UV irradiation or hydroxide ion.⁴³ Yet, the cyclobutenedione unit in difluoro monomer must remain intact during polymerization in order to produce a linear polymer. The stability of the difluoro monomer was first assessed before carrying out the polymerization. Polyetherifications are carried out in a polar aprotic solvent (i.e. DMAc) at temperature ranging from 150 to 220 °C and the phenoxide is usually generated in situ in the presence of a metal carbonate (i.e. potassium carbonate). Thus, the stability of monomer V-1 under polymerization conditions (i.e. anhydrous DMAc plus potassium carbonate) and towards phenoxides was examined.

The stability of monomer V-1 under polymerization condition was tested by heating V-1 in anhydrous DMAc with an equimolar amount of potassium carbonate plus molecular sieves at 140-150 °C. Monomer V-1 was fully recovered after 2 hours. Thus

the monomer is inert without a bisphenol monomer under polymerization conditions.

In order to check the reactivity of the cyclobutenedione unit towards the phenoxide, diphenyl-cyclobutenedione was heated in the presence of two equivalents of a phenoxide. The phenoxide was prepared from t-butylphenol and potassium carbonate. No reaction occurred after one hour at 140-150 °C, both starting materials were recovered. However, some reaction occurred when the temperature exceeded 150 °C. Thus, no side reaction involving the cyclobutenedione unit and the phenoxide should occur during the polymerization reaction as long as the temperature is maintained at below 140 °C.

V.2.4. Reactivity of the Monomer

The ultimate test for the reactivity of monomer V-1 is the successful synthesis of high molecular weight polymer. However, one would like to be able to predict the reactivity of the monomer before carrying out the polymerization. The reactivity of the difluoro monomer can be assessed by four different methods: the Hückel Molecular Orbital calculations (HMO) which provide the partial charge at the carbon to be attacked, and the chemical shift from the proton, carbon and fluorine NMR spectroscopy.

V.2.4a. *HMO Calculation*

The first method which can be used even before synthesizing the monomer is to calculate the charge density on the fluorine bearing carbon, using HMO calculations.⁴⁴ The net charge on the halogen bearing carbon will give a rough estimate of the reactivity of the designed monomer. The higher the positive charge is, the more reactive the

monomer. The results obtained for monomer V-1 and other monomers are displayed in Figure V.3. The presence of two ketones in the monomer increased slightly the positive charge on the fluorine bearing carbon (66 and 67). However, the 1,2-diketone unit (68) increased the partial charge significantly. The three monomers 66, 67 and 68 have been used to prepare high molecular weight polymers. Comparing the molecular weight obtained and the reaction time it was deduced that monomer 66 is less reactive than 67.⁴⁵ Monomer 68 produced high molecular under mild conditions (150 °C).^{31b}

The cyclobutenedione unit can be seen as a cyclized form of a combination of a carbonyl and a double bond, for which the corresponding linear form would be either 69 or 70. The net charge of the fluorine bearing carbon for the monomer V-1 (0.034) is closer to the one obtained for 70 (0.039) than the one for 69 (0.054). This result could be anticipated since in the monomer V-1, the carbonyl is not directly attached to the phenyl ring. The HMO calculations predicted that the monomer V-1 is not very reactive. However, this method is not always accurate as the method takes only the inductive effects of the substituents into account.

Figure V.3. Calculated charge density of difluoro monomers.

V.2.4b. From ^1H NMR Measurement

The electronic effect of the electron-withdrawing group can also be evaluated by NMR spectroscopy as the chemical shift is influenced by the environment of each nuclei. In the ^1H NMR spectrum, the deshielding of the protons ortho to the activating substituent is indicative of its electron-withdrawing capability.⁴⁶ The stronger the deshielding of the ortho proton is, the more reactive the monomer. Figure V.4 shows the chemical shift of the proton ortho to the electron-withdrawing group for some known reactive monomers as well as for monomer V-1. The aromatic proton ortho to the cyclobutenedione unit has a chemical shift of 8.13 ppm. This value is higher than the one of the proton ortho to the ketone in 4,4'-difluorobenzophenone (7.9 ppm)⁴⁷ or in 4,4'-difluorobenzil (8.08 ppm).⁴⁸ Accordingly, monomer V-1 would be more reactive than 68 which has been shown to be a very reactive monomer.^{31b}

Figure V.4. Chemical shifts of the proton ortho to the activating group.

V.2.4c. From ^{13}C NMR Measurement

The ^1H NMR probes indirectly the reactivity of the difluoro monomer since the evaluation is done at the ortho position of the activating group rather than the reaction site. The reaction center of a given monomer can be assessed directly using ^{13}C NMR spectroscopy. The chemical shifts of some difluoro monomers are reported in Figure V.5. The chemical shift of the fluorine bearing carbon in reactive monomers have a chemical

shift higher than 164.5 ppm relative to TMS.⁴⁹ For comparison, the chemical shift of non-polymerizable fluorobenzene is 162.8 ppm. The chemical shift for monomer V-1 was found to be 165.8 ppm. This makes V-1 more reactive than 4,4'-difluorobenzophenone (66) and 4,4'-difluorophenylsulfone (71).

Figure V.5. Chemical shifts of the fluorine-bearing carbons relative to TMS.

V.2.4d. From ¹⁹F NMR Measurement

In this case, the magnitude of the fluorine chemical shift can be directly related to the electron density at the carbon to which it is attached.⁵⁰ The fluorine is indeed located at the reaction site and its chemical shift is very sensitive to any perturbations of the aromatic ring electron density by the inductive and resonance effects of the substituents. It was found that the correlation between the charge on the fluorine bearing carbon and the chemical shift in the ¹⁹F NMR was stronger than with the ¹³C NMR results. The stronger correlation was attributed to the larger range of chemical shifts in the case of ¹⁹F NMR than in the ¹³C NMR. The reactivity of the difluoro monomer increase with the fluorine chemical shift. Monomer V-1 was predicted to be the most reactive monomer among those reported in Figure V.6.^{51,52} Indeed, the chemical shift of fluorine for monomer V-1 was higher than for the other monomers. Monomer V-1 was even

predicted to be more reactive than 4,4-difluorophenylsulfone (**71**) which is a well-known, widely used monomer. Monomer **71** was found to be more reactive than **66**, based on the molecular weight of the resulting polymer.⁵² The low chemical shift for the fluorine in **72** predicts a low reactivity which has been observed experimentally.⁵³

Figure V.6. Chemical shifts of fluorine relative to CCl_3F .

V.3. Polymerization

V.3.1. Model Reaction

The polymerization reaction was first tested on a model compound, so as to make sure that only the desired reaction occurs and not any other side reaction. In a dry flask under nitrogen, monomer **V-1** and two molar equivalents of *t*-butylphenol were heated up in the presence of potassium carbonate in anhydrous DMAc. The water generated from the formation of the phenoxide was removed azeotropically with toluene at 140-150 °C. The temperature was then maintained at 140-150 °C. The reaction was followed by TLC and was complete in 30 minutes. The model compound **V-2** was isolated in 77% yield (Scheme V.15).

Scheme V.15. Model reaction for the polymerization.

The IR spectrum of V-2 showed the presence of the carbonyls (1777 and 1758 cm^{-1}) and of the ether linkage (1253 cm^{-1}). The ^{13}C NMR spectrum exhibited the expected 12 peaks corresponding to all chemically non-equivalent carbons. The mass spectrum showed the expected molecular mass of V-2 (530.0) as well as the peaks derived from the successive loss of two carbon monoxides. These data clearly proved that the cyclobutenedione unit did not react during the etherification.

V.3.2. Homopolymerization

As the model reaction was successful, polymerization with bisphenols was undertaken. The polymerization was first carried out in a standard fashion; the two monomers were introduced in the reaction flask, followed by potassium carbonate, DMAc and toluene. The water was distilled off azeotropically and the excess of toluene at $130\text{ }^\circ\text{C}$. The temperature was then increased to $140\text{--}150\text{ }^\circ\text{C}$ for the polymerization to take place. As soon as the temperature reached $150\text{ }^\circ\text{C}$, a dark precipitate appeared in the reaction flask and no polymer could be isolated. The dark precipitate was thought to be the result of the cyclobutenedione reaction (ring-opening) when a temperature of $150\text{ }^\circ\text{C}$

was reached.

Since the reaction had to be kept below 140 °C, the polymerization procedure had to be changed so as to prevent the monomer V-1 from reacting. However, a temperature of 140 °C was needed to distilled off the water generated during the formation of the bis-phenoxide. Hence the bis-phenoxide was first formed from the bisphenol and potassium carbonate, and the water was removed azeotropically with toluene (140-150 °C). The reaction temperature was then lowered to 110 °C and monomer V-1 in anhydrous DMAc was added. The temperature was then raised to 130 °C in order for the polymerization to take place. Much care was taken to keep the temperature below 140 °C. The polymerization was carried out using four bisphenols (Scheme V.16).

Scheme V.16. Polymerization of monomer V-1.

In all cases, the polymerization was stopped because of the formation of gel in the reaction flask. The gel could not be prevented by dilution of the polymerization solution. The gel could be partially dissolved by addition of acetic acid and more solvent. In the case of BPA, the gel could not be redissolved.

The structure of the synthesized polymer was characterized by IR, ^1H and ^{13}C

NMR spectroscopy. The IR spectrum of clearly exhibited a carbonyl peak at 1765-1775 cm^{-1} corresponding to the cyclobutenedione unit. Furthermore, the ^{13}C NMR spectrum displayed a peak at 196.5 ppm corresponding to carbonyl of the cyclobutenedione. Thus, the cyclobutenedione unit did not react during the polymerization and was successfully introduced into the polymer backbone.

The fact that polymerization readily took place at temperatures as low as 130-135 °C demonstrated the difluoro monomer **V-1** was indeed very reactive. However, only low molecular weight polymers were obtained. This can be attributed to the formation of gel. Usually, polyetherification is carried out at much higher temperature such as 200 °C⁵⁴ or even 280-340 °C for poly(ether ether ketone) (PEEK).⁵⁵ The high temperatures required for the synthesis of PEEK are not only due to the lack of reactivity of the monomer but also the solubility of the polymer and the phenoxide in the polar aprotic solvent.⁵⁶

V.3.2a. Characterization of Homopolymers

The polymers were soluble in polar aprotic solvents as well as pyridine (Table V.2). In some solvents the polymer partly dissolved with the presence of some gel. This mostly occurred in DMSO and chloroform.

Table V.2. Solubility of polymers **V-3a-d**.^a

Polymer V-3	DMAc	DMF	NMP	DMSO	Pyridine	CHCl_3	cyclohexanone
a	+	+	+	$\pm^b$	+	N/M ^c	N/M
b	+	+	+	$\pm$	+	$\pm$	+
c	+	+	+	-	+	$\pm$	$\pm$
d	+	$\pm$	$\pm$	$\pm$	N/M	-	N/M

^a Measured at 25 °C. ^b Some gel did not dissolve. ^c Not measured.

The recovered polymers were found to be of low molecular weight by GPC (Table V.3). Polymer **V-3b** and **V-3c** were found to be of similar molecular weight. The insolubility of polymer **V-3d** in chloroform prevented the determination of its molecular weight by GPC.

The inherent viscosity in DMAc at 25 °C of polymers **V-3b** and **V-3c** was similar, hence they had similar molecular weights. However, the viscosity of **V-3d** was much higher, indicating that it had a higher molecular weight than **V-3b** and **V-3c**. The inherent viscosity of the polymers was also measured at several concentrations so as to obtain the intrinsic viscosity of the polymers (Table V.3). It can first be noticed that the three polymers did not behave in the same way upon dilution. The inherent viscosity of polymer **V-3d** decreased with decreasing concentration. The inherent viscosity of polymer **V-3c** increased upon dilution. This behavior was typical of polyelectrolytes.⁵⁷ The behavior of polymer **V-3b** was intermediate to that of polymer **V-3c** and **V-3d**. The viscosity first decreased, then jumped drastically at a concentration of 0.25 g/dL, and decreased again with increasing dilution.

Table V.3. Viscosity at various concentrations and GPC data for polymers **V-3b-d**.

	Inherent Viscosity ^a (dL/g)					GPC ^b	
concentration (g/dL)	0.5	0.33	0.25	0.167	0.125	M _n	M _w
V-3b	0.345	0.309	0.813	0.774	0.783	1830	5190
V-3c	0.338	0.814	0.775	4.343	5.719	2170	5750
V-3d^b	0.681	0.659	0.595	0.665	0.630	N/M ^c	N/M

^a Measured in DMAc at 25 °C. ^b Intrinsic viscosity 0.615. ^b In chloroform, relative to polystyrene standards. ^c Not Measured.

The thermal stability of the polymers was assessed by thermogravimetry (TG) (Table V.4). The decomposition temperature (T_d) of the polymers was measured at 5% weight loss. Polymers **V-3b** and **V-3c** had a T_d above 400 °C, and polymer **V-3d** had a T_d of 338 °C. The low T_d obtained for polymer **V-3d** may be due to the ring closure of the phenolphthaleine which liberated water. It is known that the cyclobutenedione ring can open to form a bis-ketene which upon pyrolysis loses carbon monoxide to yield acetylene.⁵⁸ Similarly, the loss of carbon monoxide from the cyclobutenedione moiety in polymers **V-4** was confirmed by TG-IR on polymer **V-4c**. The carbon monoxide was gradually released, starting at 295 °C.

Table V.4. Thermal analyses of polymer **V-3b-d**.

Polymer	TG	DSC - 1st run ^b		2nd run ^b
	T_d ^a (°C)	T_g (°C)	Exotherm (°C)	curve
V-3b	414	193	290	flat
V-3c	406	N/A ^c	354	flat
V-3d	338	N/A	359	flat

^a Measured under nitrogen flow of 200 mL/min, heating rate 10 °C/min. ^b Measured under nitrogen flow of 100 mL/min, heating rate 10 °C/min. ^c Not applicable.

DSC experiments were performed to measure the glass transition temperature (T_g) and detect the exothermic ring-opening of the cyclobutenedione unit. The DSC traces of all polymers **V-3b-d** followed the same trend. In the first run, there was an exotherm at about 300-350 °C, due to the ring opening of the cyclobutenedione units in the polymers. The first DSC trace of polymer **V-3b** also showed a T_g at 193 °C. However, the second DSC trace was completely flat for all polymer **V-3**, indicating a crosslinking which had

taken place during the first run.

V.3.2b. Characterization of Polymer Gels

All polymerization reactions were stopped by the formation of gel. Addition of large amount of solvent to the reaction mixture only postponed the time for gelation. The gel could be partially dissolved upon addition of acetic acid and more solvent at reflux. However, the same gel could not be obtained from the isolated polymer when placed under the same polymerization conditions. The gel was believed to be due to the entanglement of ionic species that were generated during the polymerization. These ionic species were believed to be zwitterions generated by the cyclobutenedione unit upon attack of phenoxide (Scheme V.17). The ionic forces between the polymer chains might lead to entanglement, which caused gelation. Once out of solution the polymer chain stopped growing, which would explain the low molecular weight obtained.

Scheme V.17. Zwitterionic species formed during polymerization.

It has been reported that aluminum chloride could form a complex with tetraphenyl cyclobutenone.⁵⁹ This complex had a delocalized positive charge on the four-membered ring. Thus if a similar complex with diphenylcyclobutenedione was prepared, its IR spectrum could be compared to that of the polymer gel. A match in the carbonyl region would support our hypothesis that the gel was caused by entanglement of ionic

species in the polymer. Diphenylcyclobutenedione gave a yellow solution in methylene chloride. The yellow solution turned greenish upon addition of aluminum chloride. That green color was also observed during polymerization. The IR spectra of diphenylcyclobutenedione and its complex with aluminum chloride are displayed in Figure V.7.

Figure V.7. IR spectra of diphenylcyclobutenedione and its aluminum chloride complex.

Additional evidence for the entanglement of zwitterionic species causing the precipitation of polymers was found in the IR spectra of the gel and isolated polymer. The IR spectrum of the gel from polymer V-3a showed a peak at 1726 cm⁻¹, whereas the ketone peak of cyclobutenedione in polymer V-3b appeared at 1782 cm⁻¹ (Figure V.8). The shift of the ketone peak to a lower wavenumber indicates a decrease in double bond character of the carbonyl, so proving the presence of the zwitterionic species 73 in the polymer.

Figure V.8. IR spectra of the gel and polymer from V-3a.

Since the gel was formed during the polymerization reaction, several reaction parameters were changed in order to see if any had an effect on the formation of gel. First, pyridine and lutidine were tried as a polymerization solvent as could both dissolved the polymers V-3a-c. The polymerization did not take place in pyridine and only oligomers were obtained with lutidine. This was expected, given that these solvents are not polar aprotic solvents, hence not suitable for polyetherification.

The second alteration was to add lithium chloride to the polymerization solution. Lithium chloride is used in making polyamides in order to prevent the gelation.⁶⁰ The addition of small amount of lithium chloride (15 mol %) did not have any effect on the formation of gel. However, the use of an excess of lithium chloride (7 mol equiv.) inhibited the polymerization reaction.

V.3.3. Copolymerization

Since the cyclobutenedione unit appeared to be responsible for the gel formation, higher molecular weight material should be produced if a lower amount of monomer V-1 was used. A decrease of the cyclobutenedione content can simply be achieved by copolymerization with another difluoro-monomer. Less cyclobutenedione in the polymer may not stop completely the formation of gel but would certainly delay it, leading to a higher molecular weight polymer. A range of copolymers were prepared using 4,4'-difluorophenyl sulfone as comonomer (Scheme V.18).

Scheme V.18. Copolymerization of V-1 with 4,4'-difluorophenyl sulfone.

The copolymers were prepared with 5, 10, 25 and 50% of cyclobutenedione unit in the feed ratio. The actual cyclobutenedione content was calculated from the proton NMR spectrum: the ratio between the peak area of the proton ortho to the cyclobutenedione unit and the area of the protons of diphenyl sulfone could be easily determined. For polymers V-4c and V-4d, the IR spectra exhibited a small carbonyl peak

at 1770 cm^{-1} , corresponding to the cyclobutenedione.

The molecular weight determined by GPC increased as the amount of monomer V-1 decreased (Table V.5). This was expected as the gelation was delayed due to the lower monomer content. The viscosity of V-4a and V-4b were very close (0.52 and 0.49 dL/g). However, the higher viscosity of V-4c relative to that of V-4a and V-4b was not due to its higher molecular weight of the polymer, since the higher content of monomer V-1 caused the polymer to gel sooner. The higher viscosity may be rationalized by an increase in ionic forces in the polymer. The very low viscosity (0.20 dL/g) for polymer V-4d was due to a low molecular weight and a different solvent used for the viscosity measurement.

Table V.5. Characterization of polymer V-4a-d.

Copolymer	monomer feed	actual content ^a	M _w ^b	Viscosity ^c (dL/g)
V-4a	0.05	N/M ^d	144 400	0.52
V-4b	0.10	N/M	128 100	0.49
V-4c	0.25	0.21	39 000	1.08
V-4d	0.50	0.39	N/M	0.20 ^e

^a Calculated from ^1H NMR spectrum. ^b Measured by GPC, relative to polystyrene standard. ^c Intrinsic viscosity at 25 °C in chloroform unless stated. ^d Not measured. ^e Intrinsic viscosity measured in DMAc at 25 °C.

Polymers V-4a-d had a higher decomposition temperature (T_d) than polymer V-3c (T_d 414 °C). The greater proportion of monomer V-1 in the polymer did not have any effect on T_d (Table V.6). The first DSC scan exhibited an exotherm peak at about 300-350 °C. For polymers V-4c and V-4d, the T_g increased by 20 and 50 °C, respectively. This increase in T_g , particularly for polymer V-4d, was due to the presence

of crosslinking in the polymer after the first run.

Table V.6. Thermal properties of polymers V-4.

Polymer	TG ^a	DSC ^b (1st run)		DSC ^b (2nd run)
	Td (°C)	Tg (°C)	Exotherm (°C)	Tg (°C)
V-4a	462	190	N/A	203
V-4b	496	N/A ^c	356	205
V-4c	450	199	301	217
V-4d	469	188	344	240

^a Measured under a nitrogen flow of 200 mL/min and a heating rate of 10 °C/min. ^b Measured under a nitrogen flow of 50 mL/min, and a heating rate of 10 °C/min. ^c Not applicable.

V.4. Polymer transformation

Cyclobutenediones react with alcohols via a bisketene to give the corresponding diester. The reaction of diphenylcyclobutenedione may be carried out thermally^{19,20} or photochemically.²¹ Both thermal and photochemical transformation of the polymer were investigated in this work. The transformation of the cyclobutenedione containing polymer will result in a graft polymer.

For characterization purposes, model reactions were carried out with 3,4-diphenyl cyclobut-3-ene-1,2-dione (V-5). Compound V-5 was synthesized according to the same reaction sequence as for V-1, using benzene instead of fluorobenzene (Scheme V.19). Compound V-5 was fully characterized by spectroscopic means. The IR spectrum exhibited a carbonyl ketone at 1770 cm⁻¹ (lit.⁶¹ 1782, 1770 cm⁻¹). The melting point of V-5 was 97-98 °C (lit.² 97-97.2 °C). The ¹³C NMR spectrum showed 6 peaks in total for each chemically non-equivalent carbons.

Scheme V.19. Synthesis of 3,4-diphenyl cyclobut-3-ene-1,2-dione (V-5).

V.4.1. Thermal Reaction of Cyclobutenedione with Alcohol

The reaction of ethanol with cyclobutenedione at room temperature has been reported in 1961.¹⁹ However, the reaction with alcohol at higher temperature has not appeared in the literature. Other four-membered cyclic enones have been shown to produce the corresponding acid or ester presumably via thermal ring-opening (Scheme V.20).⁶²

Scheme V.20. Thermal reaction of nucleophiles with four-membered cyclic enones.

The cyclobutenedione unit formed a bis-ketene upon ring opening.⁶³ The bis-ketene can react with an alcohol to form the corresponding diester. Thus, the cyclobutenedione moiety in polymers V-4 should react with alcohol to produce the corresponding diester.

V.4.1a. Model Reaction

Diphenylcyclobutenedione (V-5) was used to test the reaction with alcohol. An aliphatic high boiling alcohol was used in the model reaction. The cyclobutenedione V-5 was heated at 200 °C with an excess of either 1-octanol or benzyl alcohol, until complete disappearance of the starting material was observed (Scheme V.21).

Scheme V.21. Thermal reaction of diphenylcyclobutenedione with alcohol.

The diesters V-6 were fully characterized by spectroscopic means. The formation of the ester was confirmed by IR, as the carbonyl peak shifted from 1770 cm^{-1} (ketone) to 1720 cm^{-1} (ester). The single carbon-oxygen bond of the ester exhibited a peak at 1210 cm^{-1} . The ^1H NMR spectrum clearly showed the presence of a CH-CO peak at 4.4 ppm, as well as the O-CH_2 peak at 3.8 ppm. The ^{13}C NMR spectrum also showed the transformation of the ketone (196.43 ppm) into the ester (171.82 ppm). The ^{13}C NMR spectra of V-6a and V-6b exhibited 11 and 14 peaks, respectively, corresponding to the number of chemically non-equivalent carbons. The fragmentation peaks in the mass spectra could be explained for both products. HRMS of V-6a gave a molecular mass of 494.3418 that was close to the calculated one (494.3384).

V.4.1b. Polymer Transformation

On the basis of the results obtained from the model reaction, the polymer transformation was carried on copolymer **V-4c** with an excess of 1-octanol at 160 °C in TCE (Scheme V.22).

Scheme V.22. Thermal polymer transformation with 1-octanol.

The properties of polymers **V-4c** and **V-7** were compared (Table V.7). The molecular weight of polymer **V-7**, as determined by GPC, was higher than that of the polymer **V-4c**. This increase in molecular weight was due to the change in the polymer shape. More importantly, the molecular weight did not decrease after the transformation, which indicated that no cleavage of the polymer backbone occurred. The IR spectrum of polymer **V-7** exhibited a peak at 1734 cm^{-1} , indicative of the presence of the ester. In addition, there was no peak at 1776 cm^{-1} , thus all the cyclobutenedione moieties had reacted. Polymer **V-4c** was not soluble in toluene, but after the transformation, the presence of aliphatic side chains, rendered polymer **V-7** soluble in toluene. The thermal analysis of the polymer showed a decrease of 57 °C of the glass transition temperature (T_g). The T_g values were measured on the second scan so the polymer history would not

interfere. However, polymer V-4c showed a broad exotherm on the first run due to the ring-opening of the cyclobutenedione along the polymer backbone. During the first run, bis-ketenes were generated and reacted to form some crosslinks in the polymer. Thus, the T_g of polymer V-4c was in fact the one of the crosslinked polymer in the second run.

Table V.7. Comparison of the precursor (V-4c) and the derivative polymers (V-7).

	Polymer V-4c	Polymer V-7	Comment
M_n^a	20 200	32 300	No cleavage
IR (C=O) (cm^{-1})	1776	1734	Complete transformation
% monomer V-1	21.2	21.6	Complete transformation
Solubility in toluene	No	Yes	Presence of aliphatic side chains
T_g^b ($^{\circ}\text{C}$)	217	160	Presence of aliphatic side chains

^a Determined by GPC, relative to polystyrene standards. ^b 2nd run DSC trace, at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ and under a nitrogen flow of 50 mL/min.

V.4.2. Photochemical Reaction of Cyclobutenedione

Cyclobutenediones can undergo ring-opening upon irradiation. The bis-ketene has been observed when irradiating cyclobutenedione in methanol at -196°C .⁶⁴ The bis-ketene, from diphenyl cyclobutenedione, reacts with oxygen to give the anhydride (Scheme V.23).⁶⁵ Diphenyl acetylene has been observed among the products in all cases. Irradiation of diphenylcyclobutenedione under nitrogen using a high pressure mercury lamp for 6 hours produced diphenylacetylene in 28% yield along with the starting material.⁶⁶ However, under an oxygen atmosphere it was produced in only 4% yield along with the ring-expanded products. These products are diphenylmaleic anhydride and 9,10-phenanthrolic acid anhydride, resulting from the oxidative cyclization of

diphenylmaleic anhydride. The reaction with isocyanide also leads to ring expansion. The isocyanide, as the oxygen, is inserted between the two carbonyls. Irradiation of cyclobutenedione in the presence of methanol yielded two isomers (meso and dl) of dimethyl diphenylsuccinate.⁶⁷

Scheme V.23. Photochemical reactions of cyclobutenedione.

V.4.2a. Model Reaction

A high pressure mercury lamp emits a wide range of wavelengths. It is also known that the ketene decomposes at 308 nm.⁶⁸ Therefore once it is formed, the bisketene may either return to the cyclobutenedione or dissociate, liberating carbon monoxide. The UV spectrum of V-5 was recorded in dichloromethane, showing two peaks. The first one at 266 nm was due to the absorption of the phenyl ring. The second peak at 325 nm was due to the cyclobutenedione unit. The maximum absorption of the cyclobutenedione unit was at 325 nm. Thus a UV lamp with a wavelength close to 325 nm can be used for the excitation of the cyclobutenedione without any interferences from the aromatic rings. The available UV lamp has a wavelength centered at 300 or 365 nm.

Both lamps were used and the results compared. The reactions were carried out in a quartz cell. Irradiation of compound V-1 with an excess of 1-octanol in dichloromethane with a 300 nm UV lamp produced only dioctyl-di(4-fluorophenyl)succinate (V-8) in three hours (Scheme V.24).

The IR spectrum showed the presence of an ester carbonyl (1731 cm^{-1}). The ^1H NMR spectrum exhibited a singlet at 4.3 ppm corresponding to the PhCH-C=O , as well as peaks for the aliphatic proton of the octyl chain. The ^{13}C NMR exhibited the expected 14 peaks corresponding to the chemically non-equivalent carbons. Finally a mass spectrum provided the expected molecular mass for V-8.

V.4.2b. Polymer Transformation

Polymer V-3c was used for the photochemical transformation with 1-octanol. The UV spectrum of the polymer was first recorded in order to adjust, if necessary, the wavelength of the lamp to be used. Polymer V-3c showed two absorption peaks at 307 and a broad one at 365 nm. Polymers V-3c was irradiated at 300 and 365 nm UV lamp, with and without an alcohol.

A solution of polymer V-3c in chloroform was first irradiated with both UV lamps (300 and 365 nm). The ^1H NMR spectrum of the irradiated polymer was identical to that

of polymer **V-3c**. The IR spectrum of the irradiated polymer showed the presence of the ketone (1763 cm^{-1}), indicating that no reaction or dissociation of the ketene took place.

The transformation of polymer **V-3c** was carried out with an excess of 1-octanol in chloroform, using both UV lamps (Scheme V.25). The ^1H NMR spectrum of the transformed polymer (**V-9**) showed the incorporation of 1-octanol in the polymer. However, by comparing the peak integration, it was clear that only 50% of the cyclobutenedione had reacted. The IR spectrum exhibited two carbonyl peaks for the unreacted ketone (1764 cm^{-1}) and the formed ester (1731 cm^{-1}).

Scheme V.25. Photochemical transformation of polymer **V-3c** with 1-octanol.

V.5. Conclusion

It has been shown that the cyclobutenedione moiety may be used as electron withdrawing group in the difluoro monomer. Monomer **V-1** was found more reactive than difluorobenzyl (**68**). Indeed, monomer **V-1** polymerized at $130\text{ }^{\circ}\text{C}$ compared to 150

°C for **68**. However, due to the formation of gel, only low molecular weight polymer were obtained. These poly(aryl ether)s crosslinked and reacted with 1-octanol. The reaction of cyclobutenedione containing polymer with alcohol is of greater value than its crosslinking. Any side chain may be grafted onto the polymer as long as it has an hydroxy group. Side chains containing diazogroups may be introduce onto a homopolymer to make a photoresponsive polymer, in which case the low molecular weight is an asset. When the the polymer transformation is carried out with a diol instead of a mono alcohol a crosslinked material would be produced. This crosslinking may be applied to the preparation of interpenetrating networks (IPNs).

V.6. Experimental Section

Materials: Squaric acid, thionyl chloride, benzene, fluorobenzene, aluminum chloride (98%), t-butyl phenol, phenol, DMAc (anhydrous) were purchased from Aldrich Chemical Co. and used as received. 1-Octanol, benzyl alcohol were received from Fisher Scientific Co. and used as received. Other common organic solvents are reagent grade unless otherwise stated.

Characterization: Viscosity data were obtained from a Ubbelohde viscometer (size OB114) at 25 °C. Other data were recorded as previously described.

3,4-Bis(4-fluorophenyl)cyclobutenedione (V-1)

A 100 mL round bottom flask equipped with a condenser was flame dried under nitrogen. It was then charged with squaric acid (3,4-dihydroxy-1,2-cyclobutenedione) (18.20 g, 0.160 mol), thionyl chloride (25.5 mL, 0.353 mol), fluorobenzene (80.0 mL) and DMF (4 drops). The solution was heated to reflux until a clear brown solution was formed. After cooling to 0 °C with an ice bath, aluminum chloride (47.23 g, 0.354 mol) was slowly added. The solution was then allowed to warm up to 60 °C and held at this temperature for 36 hours. The reaction solution was cooled down to room temperature and extracted with chloroform (2 x 100 mL). The organic phase was dried and concentrated *in vacuo*. The residual product was then recrystallized twice from methanol, giving the pure 3,4-bis(4-fluorophenyl) cyclobutenedione (27.20 g, 63 %) as yellow needles: mp 175-177 °C; IR (KBr, cm⁻¹) 1766 (C=O); ¹H NMR (400 MHz, CDCl₃) δ 8.13 (dd, 4H, J_{H-H} = 8.9 Hz, J_{H-F} = 5.4 Hz), 7.28 (t, 4H, J_{H-H} = J_{H-F} = 8.5 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 195.61, 185.55, 165.57 (d, J_{C-F} = 257 Hz), 131.08 (d, ³J_{C-F} = 9.3 Hz), 124.73 (d, ⁴J_{C-F} = 3.5 Hz), 117.27 (d, ²J_{C-F} = 21.95 Hz); ¹⁹F NMR (282.23 MHz, DMSO-d₆, relative to CCl₃F) δ -104.15 or (in CDCl₃, relative to CCl₃F) δ -102.78; MS (EI, m/e, relative intensity %) 270 (M⁺, 12.9), 214 (M⁺ - 2CO, 100); HRMS Calculated for C₁₆H₈O₂F₂: 270.0490, Found: 270.0494.

Stability of V-1 under polymerization conditions

Monomer V-1 (0.209 g, 0.776 mmol), potassium carbonate (0.108 g, 0.780 mmol), molecular sieves (1.627 g) and dry DMAc (3 mL) were placed in a flamed dried three necked flask fitted with a nitrogen inlet and a condenser. The solution was heated up to 130 °C for 2 hours. The solution was precipitated in water/HCl. The precipitate and the molecular sieves were filtered off. The precipitate was dissolved in chloroform and the molecular sieves were filtered off. The chloroform solution was dried over magnesium sulfate and concentrated. The yellow-orange residue was analyzed without any further purification. IR (NaCl, cm^{-1}) 1768 (C=O); ^1H NMR (200 MHz, CDCl_3) δ 8.10 (dd, 4H, $J_{\text{H-H}} = 8.9$ Hz, $J_{\text{F-H}} = 5.3$ Hz), 7.25 (t, 4H, $J_{\text{H-H}} = 8.4$ Hz).

Stability of diphenylcyclobutenedione (V-5) in the presence of t-butyl phenoxide

t-Butyl phenol (0.256 g, 1.71 mmol), potassium carbonate (0.151 g, 1.09 mmol), molecular sieves (1.885 g) and freshly distilled DMAc (2 mL) were placed in a flame dried three necked flask equipped with a condenser and a nitrogen inlet. The solution was heated to 140 °C for 15 minutes, and then cool down to 130 °C. V-1 (0.205 g, 0.88 mmol) was added to the reaction flask along with DMAc (1.5 mL). The temperature was maintained at 130 °C for 1 hour. The solution was then precipitated in water/HCl. The yellow-orange precipitate and the molecular sieves were filtered off. The yellow-orange precipitate was dissolved in chloroform and the molecular sieves were filtered off. The chloroform solution was dried over magnesium sulfate and concentrated. The yellow-orange residue (0.356 g, 72 %) was analyzed without any further purification. IR (NaCl,

cm⁻¹) 1772 (C=O); ¹H NMR (200 MHz, CDCl₃) δ 8.08 (dd, 4H, J_{H-H} = 7.8 Hz, ⁴J_{H-H} = 1.7 Hz), 7.56 (m, 6H); ¹³C NMR (50 MHz, CDCl₃) δ 196.49, 187.83, 133.73, 129.63, 128.53, t-butyl phenol: 154.05, 143.12, 126.57, 115.13, 34.30, 31.85.

Model reaction for polymerization (V-2)

In a flame dried three necked round bottom flask equipped with a stirring bar, Dean Stark trap fitted with a condenser and a nitrogen inlet, were introduced V-1 (0.300 g, 1.11 mmol) and t-butyl phenol (0.334 g, 2.22 mmol), DMAc (8.4 mL) and deoxygenated toluene (5 mL) were added to the flask. Grounded potassium carbonate (0.312 g, 3.15 mmol) was then added to the solution. The orange solution was heated up to 130-140 °C to allow the removal of water as an azeotrope with toluene as well as the excess of toluene. The solution was then maintained at this temperature. The solution turned green after 30 min. Half an hour after the change in colour, no more starting material was observed. The reaction was stopped and the solution was precipitated in water (50 mL) to give a orange precipitate. More product was obtained by extraction of the filtrate with diethyl ether. The yellow - orange precipitate (0.492 g, 77.7 %) did not need any further purification: mp 142-143 °C; IR (KBr, cm⁻¹) 2957 (C-H), 1777 and 1758 (C=O), 1591, 1250 (C-O); ¹H NMR (200 MHz, CDCl₃) δ 8.09 (d, 4H, J_{H-H} = 8.8 Hz), 7.44 (d, 4H, J_{H-H} = 9.1 Hz), 7.06 (t, 8H, J_{H-H} = 9.2 Hz), 1.35 (s, 18H); ¹³C NMR (50

MHz, CDCl₃) δ 196.43, 184.98, 162.80, 152.70, 148.34, 130.68, 127.27, 122.70, 120.21, 117.98, 34.78, 31.74; UV (λ_{max} , nm, CH₂Cl₂) 247, 305, 365; MS (EI, m/e, relative intensity %) 530 (M^+ , 1.4), 474 ($M^+ - 2\text{CO}$, 10.4), 459 (474 - CH₃, 4.9), 326 (474 - OPhC₄H₁₁, 1.3), 176 (325 - OPhC₄H₁₁, 0.7), 119 (OPhC₂H₅, 100).

Polymerization - method A

In a flame dried 50 mL round bottom flask equipped with a stirring bar, a Dean Stark trap fitted with a condenser and a nitrogen inlet, were placed 2 (3 mmol), a bisphenol (3 mmol) and grounded potassium carbonate (6 mmol). DMAc (8 mL) and deoxygenated toluene (10 mL) were then added to the flask. The temperature was first increased to 130 °C to remove the water as an azeotrope with toluene. Once all the water and the excess of toluene were removed, the temperature was increased to 160 °C so as to allow the polymerization to take place. More DMAc was added to the flask as the viscosity of the solution increased.

Polymerization - method B

In a flame dried 50 mL round bottom flask equipped with a stirring bar, a Dean Stark trap fitted with a condenser and a nitrogen inlet, were placed the bisphenol (3 mmol) and the grounded potassium carbonate (4.6 mmol). DMAc (4 mL) and deoxygenated toluene (8 mL) were introduced in the flask. The temperature was then increased to 140-150 °C to remove the water as an azeotrope with toluene, as well as the excess of toluene. The solution was then cooled down to 110 °C and the

difluoromonomer **2** (3 mmol) was introduced to the flask along with of DMAc (4 mL). The temperature was increased to 125-130 °C for the polymerization to take place. As the polymerization proceeded, the viscosity of the solution increased. Additional DMAc was introduced to the solution in order to allow stirring.

Work up of polymers

When gels appeared during the polymerization, acetic acid (1 mL) and DMAc (4 mL) were added to the hot solution. Heating the diluted solution with stirring allowed the partial or complete dissolution of the gel. The solution was filtered and the polymer precipitated in acidic methanol (100 mL). The resulting polymer was dissolved in a good solvent and reprecipitated in methanol and dried under vacuum.

Polymer characterization

V-3a: (method A) brown crispy product.

V-3a: (method B) yellow orange powder (0.958 g, 69.7%). The resulting polymer was soluble in DMAc, NMP, DMF, pyridine, sulfuric acid, slightly soluble in DMSO, chlorobenzene, and not soluble in THF, triethyl amine. IR (film, cm^{-1}) 2966, 1766, 1594, 1504, 1244, 1172, 834.

V-3b: (method B) small yellow fibbers (0.8822 g, 52 %). The polymer was soluble in DMF, NMP, pyridine, cyclohexanone, partly soluble in TCE, chloroform, DMSO, acetone, nitromethane, and not soluble in THF and acetonitrile. GPC $M_w = 5750$, $M_n = 2174$, $M_w/M_n = 2.64$; IR (film, cm^{-1}) 1769, 1595, 1504, 1248, 1174, 928, 832;

7.16 (d, 4H, $J_{\text{H-H}} = 8.2$ Hz), 7.10 (d, 4H, $J_{\text{H-H}} = 8.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 196.15, 185.18, 161.16, 156.29, 132.38, 130.81, 129.60, 124.40 (q, $J_{\text{C-F}} = 283$ Hz), 123.76, 119.66, 119.22, 77.48; T_d (5% weight loss) 505 °C; DSC 1st run: $T_g = 200$ °C, exotherm about 350 °C, 2nd run $T_g = 233$ °C.

V-3c: (method B) yellow powder (1.508 g, 86.7 %). The resulting polymer was soluble in DMF, NMP, pyridine, slightly soluble in cyclohexanone, chloroform, sulfuric acid, and not soluble in DMSO, nitromethane, acetonitrile, 4-methyl pentan-2-one; IR (film, cm^{-1}) 1779, 1593, 1499, 1351, 1245, 1169; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CF}_3\text{CO}_2\text{D}$) δ 8.02 (s, 4H), 7.75 (s, 4H), 7.38 (s, 8H), 7.24 (s, 4H), 7.04 (d, 2H, $J_{\text{H-H}} = 4.2$ Hz), 6.93 (s, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 197.06, 185.35, 163.18, 153.69, 150.99, 143.06, 140.33, 131.19, 130.15, 128.18, 126.27, 123.04, 122.13, 120.55, 118.25, 106.05, 64.85; TG (5% weight loss) 462 °C; DSC 1st run: exotherm at 334 °C.

V-3d: (method B) The polymer was soluble in DMAc, partly soluble in DMF, NMP, DMSO and not soluble in TCE, chloroform. IR (film, cm^{-1}); T_d (5% weight loss) 338 °C; DSC 1st run: exotherm 359 °C, 2nd: run no T_g .

General procedure for the copolymerization

In a flame dried 50 mL round bottom flask equipped with a stirring bar, a Dean Stark trap fitted with a condenser and a nitrogen inlet, were placed the bisphenol (3 mmol) the difluorocomonomer (x mmol) and the grounded potassium carbonate (4.6

mmol). DMAc (4 mL) and deoxygenated toluene (8 mL) were introduced in the flask. The temperature was then increased to 140-150 °C to remove the water as an azeotrope with toluene, as well as the excess of toluene. The formation of oligomers was monitored by GPC. When the molecular weight of the oligomers stopped increasing the solution was then cooled down to 110 °C. The difluoromonomer 2 (3-x mmol) was introduced to the flask along with of DMAc (4 mL). The temperature was increased to 125-130 °C for the polymerization to continue. As the polymerization proceeded, the viscosity of the solution increased. Additional DMAc was introduced to the solution in order to allow stirring.

V-4a: yellow fiber (0.5497 g, 33.25 %); GPC $M_w = 144417$, $M_n = 61784$, $M_w/M_n = 2.34$; IR (KBr, cm^{-1}) 1640, 1597, 1500, 1488, 1246, 1174; ^1H NMR (200 MHz, CDCl_3) δ 7.99 (d, 4H, $J_{\text{H-H}} = 8.5$ Hz), 7.40 (d, 4H, $J_{\text{H-H}} = 8.3$ Hz), 7.19 (d, 4H, $J_{\text{H-H}} = 8.8$ Hz), 7.12 (d, 4H, $J_{\text{H-H}} = 8.7$ Hz); ^{13}C NMR (50 MHz, CDCl_3) δ 160.97, 156.23, 136.65, 132.36, 130.24, 129.56, 124.35 (q, $J_{\text{C-F}} = 290$ Hz), 119.53, 119.08; T_d (5% weight loss) 462 °C; DSC 1st run: T_g 190 °C no exotherm, 2nd run: T_g 203 °C; intrinsic viscosity (CHCl_3 , 25 °C) 0.52 dL/g.

V-4b: yellow fibers. GPC $M_w = 128144$, $M_n = 27183$, $M_w/M_n = 1.94$; IR (KBr, cm^{-1}) 2924, 1787; ^1H NMR (200 MHz, CDCl_3) δ 7.90 (d, 4H, $J_{\text{H-H}} = 8.4$ Hz), 7.39 (d, 4H, $J_{\text{H-H}} = 7.6$ Hz), 7.08 (d, 4H, $J_{\text{H-H}} = 8.8$ Hz), 7.01 (d, 4H, $J_{\text{H-H}} = 8.9$ Hz); ^{13}C NMR (50 MHz, CDCl_3) δ 160.69, 155.95, 136.36, 132.08, 129.96, 129.28, 119.25, 118.79; T_d (5%

weight loss) 496 °C; DSC 1st run: no T_g , exotherm 356 °C, 2nd run: T_g 205 °C; intrinsic viscosity (CHCl_3) 0.49 dL/g.

V-4c: yellow fibers (0.595 g, 35.8 %): GPC $M_w = 39022$, $M_n = 20164$, $M_w/M_n = 1.94$; IR (KBr, cm^{-1}) 3045, 1770, 1588, 1498, 1241; ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, 4H - 21%, $J_{\text{H-H}} = 8.8$ Hz), 7.92 (d, 4H - 79%, $J_{\text{H-H}} = 8.6$ Hz), 7.40 (d, 4H - 100%, $J_{\text{H-H}} = 8.3$ Hz), 7.17 (d, 4H - 21%, $J_{\text{H-H}} = 8.6$ Hz), 7.09 (d, 4H - 100%, $J_{\text{H-H}} = 8.7$ Hz), 7.03 (d, 4H - 79%, $J_{\text{H-H}} = 8.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 184.99, 160.74, 156.05, 136.49, 132.51, 132.11, 130.57, 130.00, 129.33, 124.12 (q, $J_{\text{C-F}} = 286$ Hz), 119.28, 118.84; TG (5% weight loss) T_d 450 °C; DSC 1st run: T_g 199 °C exotherm 301 °C, 2nd run: T_g 217 °C; intrinsic viscosity (CHCl_3 , 25 °C) 1.08. The polymer was soluble in DMAc, DMSO, TCE, chloroform, THF, acetone, but not soluble in DMF.

V-4d: yellow polymer (0.2898 g, 17.3 %): IR (KBr, cm^{-1}) 1775, 1595, 1510, 1247, 1173; ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J_{\text{H-H}} = 8.7$ Hz), 7.93 (d, $J_{\text{H-H}} = 8.3$ Hz), 7.62 (d, $J_{\text{H-H}} = 7.1$ Hz), 7.43 (m), 7.19 (d, $J_{\text{H-H}} = 7.7$ Hz), 7.11 (d, $J_{\text{H-H}} = 6.8$ Hz), 7.05 (m); ^{13}C NMR (100 MHz, CDCl_3) δ 195.92, 184.97, 160.90, 160.74, 156.04, 136.47, 132.12, 130.57, 130.57, 130.00, 129.33, 124.14 (q, $J_{\text{C-F}} = 282$ Hz), 123.53, 119.39, 119.28, 118.99, 118.83; TG (5 % loss) T_d 469 °C; DSC 1st run: T_g 188 °C exotherm 344 °C; 2nd run: T_g 235 °C; intrinsic viscosity (DMAc, 25 °C) 0.20 dL/g.

3,4-Bisphenylcyclobutenedione (V-5)

The product was synthesized in the same way as the 3,4-bis(4-fluorophenyl)-cyclobutenedione fluorobenzene was replaced with benzene. 3,4-bisphenyl-cyclobutenedione was obtained as yellow/brown needles in 75 % yield. yellow powder: mp 98-99 °C; IR (KBr, cm^{-1}) 1770 (C=O), 1351; ^1H NMR (400 MHz, CDCl_3) δ 8.08 (dt, 2H, $J_{\text{H-H}} = 6.6$ Hz, $^4J_{\text{H-H}} = 1.5$ Hz), 7.61 (tt, 1H, $J_{\text{H-H}} = 7.3$ Hz, $^4J_{\text{H-H}} = 1.8$ Hz), 7.56 (tt, 2H, $J_{\text{H-H}} = 7.2$ Hz, $^4J_{\text{H-H}} = 1.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 196.43, 187.77, 133.67, 129.59, 128.48, 128.42; UV (λ_{max} , nm, CH_2Cl_2) 266, 325.

Model compounds for thermal polymer transformation**V-6a**

A solution of V-5 (1.000 g, 4.27 mmol) in 1-octanol (1.674 g, 12.8 mmol) was placed in a dry flask equipped with a condenser and a drying tube. The solution was heated at 220 °C until complete disappearance of V-5 (3 hours). The solution was cooled down and solidified. The product was recrystallized from methanol to afford fine ecru needles (0.940 g, 44.5 %): mp 101-102 °C; IR (KBr, cm^{-1}) 2914, 1720 (C=O), 1210 (C-O); ^1H NMR (200 MHz, CDCl_3) δ 7.51 (dd, 4H, $J_{\text{H-H}} = 7.9$ Hz, $^4J_{\text{H-H}} = 1.6$ Hz), 7.34

(m, 6H), 4.38 (s, 2H), 3.79 (m, 4H), 1.20 (m, 24H), 0.87 (t, 6H, $J_{\text{H-H}} = 6.7$ Hz); ^{13}C NMR (50 MHz, CDCl_3) δ 171.82, 136.76, 128.88, 128.74, 128.138, 65.22, 55.43, 32.04, 29.37, 29.33, 28.60, 25.85, 22.93, 14.39; MS (EI, m/e, relative intensity %) 494 (M^+ , 1.8), 364 ($\text{M}^+ - \text{HO}(\text{CH}_2)_7\text{CH}_3$, 47.2), 252 (365 - $(\text{CH}_2)_7\text{CH}_3$, 100), 224 (252 - CO, 62.1); HRMS Calculated for $\text{C}_{32}\text{H}_{46}\text{O}_4$: 494.3384, Found: 494.3418.

V-6b:

A solution of V-5 (0.165 g, 0.707 mmol) in benzyl alcohol (5 mL) was placed in a dry flask equipped with a condenser and a drying tube. The solution was heated at 210 °C until complete disappearance of V-5 (2 hours). The solution was cooled down and the product precipitated in methanol. The precipitate was dissolved in chloroform and reprecipitated in methanol, this procedure was repeated twice. The product can also be recrystallized from methanol. A white powder (fine beige needles were obtained by recrystallization) was obtained (0.137 g, 43.2 %): mp 159 °C; IR (KBr, cm^{-1}) 1725 (C=O), 1138 (C-O); ^1H NMR (400 MHz, CDCl_3) δ 7.49 (dd, 4H, $J_{\text{H-H}} = 6.5$ Hz, $^4J_{\text{H-H}} = 1.9$ Hz), 7.31 (m, 6H), 7.22 (m, 6H), 6.90 (dd, 4H, $J_{\text{H-H}} = 7.8$ Hz, $^4J_{\text{H-H}} = 1.6$ Hz), 4.92 (d, 2H, $J_{\text{H-H}} = 12.4$ Hz), 4.77 (d, 2H, $J_{\text{H-H}} = 12.4$ Hz), 4.49 (s, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.21, 136.04, 135.39, 128.75, 128.56, 128.35, 128.02, 127.96, 127.68, 66.53, 55.09; MS (EI, m/e, relative intensity %) 450 (M^+ , 2.9), 359 ($\text{M}^+ - \text{CH}_2\text{Ph}$, 12.9),

342 (M^+ - HOCH₂Ph, 100), 253 (342 - CHPh, 68.8), 225 (253 - CO, 48.3).

Thermal transformation of polymer V-4c (V-7)

Polymer V-4c was refluxed in 1-octanol for 24 hours. Once the reaction was complete the polymer was precipitated in methanol. The polymer was redissolved in chloroform and precipitated again in methanol. It was then dried under vacuum. GPC M_n = 32,300; IR (KBr, cm⁻¹) 1731, 1587, 1509, 1489, 1248; ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, 4H - 79 %), 7.40 (d, 4H - 100%), 7.09 (d, 4H - 79%), 7.03 (d, 4H - 100%), 3.64 (t, 4H), 1.58 (m, 8H), 1.28 (br, 16H), 0.86 (br, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 160.71, 155.97, 136.38, 132.09, 129.98, 129.29, 119.26, 118.81, 31.64, 29.21, 25.63, 22.65, 11.11.

Model compound for the photochemical transformation (V-8)

A solution of V-2 (0.121 g, 0.448 mmol) and 1-octanol (0.058 g, 0.448 mmol) in dichloromethane (1.5 mL) was placed in a closed quartz cuvette. The solution was irradiated with a 300 nm UV lamp. The disappearance of V-2 was monitored by IR. After 3h the reaction was complete. The solvent was then evaporated and the residue rinsed with methanol to give a white solid: mp 54-55 °C; IR (KBr, cm⁻¹) 2932, 1731 (C=O), 1603, 1509, 1229, 1158 (C-O??); ¹H NMR (400 MHz, CDCl₃) δ 7.46 (dd, 4H, J_{H-H} = 8.8

Hz, $J_{\text{H-F}} = 5.3$ Hz), 7.02 (t, 4H, $J_{\text{H-H}} = 8.7$ Hz, $J_{\text{H-F}} = 8.7$ Hz), 4.30 (s, 2H), 3.81 (m, 4H), 1.28 (m, 8H), 1.13 (m, 12H), 1.01 (bq, 4H), 0.88 (t, 6H, $J_{\text{H-H}} = 7.1$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 171.38, 162.49 (d, $J_{\text{C-F}} = 247$ Hz), 132.06 (d, $^5J_{\text{C-F}} = 3.2$), 130.12 (d, $^4J_{\text{C-F}} = 8.1$), 115.59 (d, $^3J_{\text{C-F}} = 21.4$), 65.15, 54.53, 31.75, 29.11, 29.04, 28.35, 25.59, 22.63, 14.08; MS (EI, m/e, relative intensity %) 530 (M^+ , 0.8), 419 ($\text{M}^+ - \text{C}_8\text{H}_{16}$, 0.2), 400 ($\text{M}^+ - \text{HO}(\text{CH}_2)_7\text{CH}_3$, 13.9), 372 (400 - CO, 2.6), 288 (400 - C_8H_{16} , 34.1), 260 (289 - F, 23.7), 216 (260 - CO_2 , 19), 109 (FPhCH_2 , 100).

Photochemical transformation of polymer V-3c (V-9)

Polymer V-3c (0.031 g) was dissolved in chloroform (3 mL) and the solution was placed in a quartz cuvette. 1-Octanol (0.217 g) was then added to the stirring solution. The solution was then irradiated with a UV lamp. When the reaction was stopped, the solution was concentrated and precipitated in chloroform. The precipitate was filtered, redissolved in chloroform and precipitated again in methanol. The polymer was then dried and characterized. After being irradiated with either UV lamp for 10 minutes, an ester peak was detected on the IR spectrum as well as a decrease in intensity of the ketone peak (1780 and 1765 cm^{-1}). After 82 minutes irradiation no more changes were observed. GPC $M_w = 2928$, $M_n = 1580$, $M_w/M_n = 1.85$; IR (KBr, cm^{-1}) 2926, 1764, 1732, 1596, 1498, 1242; ^1H NMR (400 MHz, CDCl_3) δ 7.75 (br s), 7.38 (br s), 7.16 (s), 6.92 (d), 6.82 (d), 6.71 (br s), 3.81 (br), 1.19 (br), 0.82 (s).

Irradiation of V-3c at 365 nm or 300 nm: The solution was irradiated for 80 minutes.

GPC Mw = 2355, Mn = 1094, Mw/Mn = 2.15; IR (KBr, cm⁻¹) 1765, 1593, 1498, 1243.

V. 7. References

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