DESIGN, SYNTHESIS, CHARACTERIZATION AND POTENTIAL
APPLICATIONS OF PHOTSENSITIVE ACETYLENE AND
DIACETYLENE-CONTAINING POLYMERS

by

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in partial fulfillment of the requirements for the degree of
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In memory of my mother Verginica

Abstract

The primary focus of this thesis work is to design, synthesize and characterize a series of polymers that meet some of the specific requirements for optical waveguide applications such as adjustable refractive index, low birefringence, good thermal resistance, photo-cross-linkable and patternable and can be processed easily without the use of photoresists. The second objective of this dissertation is to demonstrate the feasibility of a new photo-cross-linkable system that is based on the metal-catalyzed photochemistry of acetylenes and consists of an ethynyl-containing polymer and $W(CO)_6$ as initiator.

A series of linear and hyperbranched diacetylene-containing polymers were synthesized. All the polymers showed typical amorphous diffraction patterns, good solubility in organic solvents, good film-forming capability and good thermal stability. The linear polymers were readily cross-linkable upon exposure to UV at 254-450 nm at ambient temperatures and could also be cured at elevated temperatures. The in-plane and out-of-plane refractive indices of these polymers varied from 1.5454 to 1.6313 and from 1.5329 to 1.6283 at 1550 nm, respectively, according to the monomer ratios in the feed. The birefringence at 1550 nm was significantly reduced from 1.25% to 0.3% by incorporating the cardo fluorenyl and ether linkages into the polymer backbone. The optical properties of the photo-cross-linked linear polymers varied only slightly while thermal curing induced drastic changes in both refractive index and birefringence.

The optical properties, refractive index and birefringence of the hyperbranched polymers were also adjustable by varying the amounts of monomers incorporated into the polymers. The values of in-plane and out-of-plane refractive indices at 1550 nm varied

from 1.5454 and 1.6313 and from 1.5329 to 1.6283, respectively. An increase in branching in the polymers resulted in a considerably reduced birefringence to as low as 0.2×10^{-2} . Although being photosensitive, a poor photo-definition was observed when these polymers were irradiated at 254-450 nm. A significant improvement in photo-definition and photo-cross-linking was achieved when a small amount of $W(CO)_6$ was doped in these polymers and irradiation was done at 320-390 nm. The optical properties of the photo-cross-linked polymers varied slightly causing a decrease in the refractive index values of 0.4×10^{-3} to 6.5×10^{-3} .

To demonstrate the efficiency of the new photo-cross-linking system based on an ethynyl-containing polymer and $W(CO)_6$ as the initiator, a series of polyacrylates containing ethynyl pendent groups were synthesized. Irradiation at 320-390 nm induces the cross-linking through the formation of polyene-type structures. Studies showed that the photocuring process depends mainly on the amounts of ethynyl moieties and initiator, and the curing temperature and it follows first-order kinetics.

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Symbols and Abbreviations

λ	Wavelength
n	Refractive index
n_{TE}	In-plane refractive index
n_{TM}	Out-of-plane refractive index
Δn	Birefringence
$dn/d\lambda$	Refractive index dispersion
$[\eta]$	Inherent viscosity
BPO	Benzoyl Peroxide
CP/MAS	Cross Polarization/Magic Angle Spinning
DMAc	<i>N,N</i> -Dimethylacetamide
DMSO	Dimethylsulfoxide
DMF	<i>N, N</i> -Dimethylformamide
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared
GPC	Gel Permeation Chromatography
IR	Infrared
k	Rate constant
LB	Langmuir-Blodgett
M_w	Weight-average molecular weight
M_n	Number-average molecular weight
NMP	<i>N</i> -Methyl-2-pyrrolidinone
NMR	Nuclear Magnetic Resonance

PFCB	Perfluorocyclobutane
R^2	Regression coefficient
RT	Room temperature
SEM	Scanning Electron Micrograph
T_d	Decomposition temperature
T_g	Glass transition temperature
T_{max}	Peak temperature of the exotherm
TBAB	Tetrabutylammonium Bromide
TCE	<i>1,1,2,2</i> -Tetrachloroethane
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TMEDA	<i>N,N,N',N'</i> - Tetramethylethylenediamine
UV	Ultraviolet
WAXD	Wide Angle X-ray Diffraction
WVASE	Woollam Variable Angle Spectroscopic Ellipsometry
<i>x</i>	Conversion of ethynyl moiety

CHAPTER I. INTRODUCTION

I.1. Polymeric Materials for Optical Waveguides

The demand for high-speed computing and communication is overpowering the current electronics performance in many applications. To overcome such a barrier, photonics has started to be implemented and proved to outperform electronics in many areas. Photonics refers to the technology of generating and harnessing light and other forms of radiant energy whose quantum unit is the photon, such as lasers, photodetectors, optical modulators and amplifiers. Waveguide devices, optoelectronic and photonic integrated circuits, devices for optical communications, switching, networking and signal processing are typical photonic devices. Photonics offers advantages of handling an extremely large-capacity information (very broad bandwidth), very low transmission loss and heat generation, are immune to crosstalk and electromagnetic interference, and are lightweight and smaller size compared to electronics. Photons do not interact linearly when multiple waves propagate in optical medium, and thus allow parallel processing of different wavelengths. Photonics also plays a complementary role to electronics in many application domains such as broadband communications, high-capacity information storage, large-screen and portable information displays.¹

Broadband communications (telecom and datacom) can be realized by free-space optics or guided-wave optics. Free-space optics, also called free-space photonics, refers to the transmission of modulated visible or infrared beams through the atmosphere to obtain broadband communications. These systems can function over distances of several

kilometers but nevertheless they have limitations due to environmental conditions such rain, dust and fog that can block the transmission path. An optical waveguiding element instead conveys light from one point to another through an optically transparent elongated structure by modal transmission, total internal reflection and consists of a material with higher refractive index than that of the surrounding material (Figure I.1.). These waveguides can be made as thin films or as a filament usually circular in the cross section.

Figure I.1. Wave propagation in an optical waveguide

The planar optical waveguide allows the fabrication of planar optical components and integration into planar optical circuits, similar to the integrated electronic circuits. The planar optical waveguides could be in the form of films or strips which can be formed by depositing a thin layer of material (core material) with a high refractive index on a lower index substrate and covering with an additional low-index (cladding) layer (Figure I.2.).

Although the basic technologies for the design and production of several integrated optical waveguide devices have been demonstrated,² there is still no commercial material that can meet both the technical requirements and economic criteria. The materials currently used in optical waveguide devices are mainly metal oxides (e.g.,

lithium niobate and silica) and semiconductor materials (e.g., III-IV semiconductors and silicon). However, the device processing is complicated and expensive.

Figure I.2. Schematic representation of an optical channel waveguide

Polymers have emerged as attractive materials for use in waveguide devices due to their good processibility, low cost and adequate performance. Polymers can be structurally designed to achieve the desired properties that meet specific and strict requirements for optical waveguide applications and at the same time offer a choice to be processed by either photolithographic or non-lithographic method. They are suitable for use as a medium for high-frequency electro-optic modulation and optical amplification. In all the potential applications, the polymeric materials act as passive medium for light transmission and/or as a matrix for active chromophores for electro-optic modulation and rare-earth metal ions for optical amplification. Thus, passive optical polymers refer to those used for light transmissions, in which there are no nonlinear optical process, no electro-optic and electrical conversions.³

I. 1. 1. Characteristics of Optical Polymers

Some of the important properties required for optical polymers to be used as waveguide components include precise refractive index, low absorption at the

wavelength of interest (e.g. 1310 and 1550 nm), low scattering loss and polarization dependence, good processibility and good environmental stability.

a. Refractive index

According to the device design and waveguide geometry, the polymer used as the core material must have a refractive index higher than that of the cladding polymer. The difference in refractive index between the core and cladding material depends on the dimension of the waveguide structure and the wavelength of the light.

The refractive index (n) of a material is defined as the ratio between the speed of light in vacuum, $c_0 = 3.00 \times 10^9$ m/s, and the speed of light through the material, c (Equation I.1).

$$n = \frac{c_0}{c} \quad (\text{Equation I.1.})$$

The refractive index is also determined by the polarizability (Q) and density (ρ), according to the Lorentz-Lorentz relationship (Equation I.2).

$$\frac{(n^2 - 1)}{(n^2 + 2)} = \frac{4\pi}{3} Q \quad (\text{Equation I.2.})$$

Polarizability (Equation I.3) represents the concentration of molecules, N/V with polarization, α where N is the number of molecules in a given volume V .

$$Q = \frac{N}{V} \alpha = \frac{\rho}{M} N_A \alpha \quad (\text{Equation I.3.})$$

Therefore the Lorentz-Lorentz equation I.2 can be written as:

$$\frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} = \frac{4\pi}{3} N_A \alpha$$

From this relation it can be seen that there are two material-related factors that determine the refractive index of a material: free volume (packing density) and the polarizability of the material.⁴ Usually dense packing or large polarizability (electronic, atomic and dipole orientation) results in an increase in refractive index. At optical frequencies only polarizability due to electronic orientation occurs and as a result the refractive index can be tuned through structural modification, physical aging, and guest doping. Therefore, aromatic polymers have a higher refractive index than aliphatic polymers due to both higher packing density and larger electronic polarizability. For example, the incorporation of highly π -conjugated dyes will raise the refractive index of the polymer. Substitution of hydrogen atoms with fluorine atoms in polymer decreases the refractive index of the material. The fluorine atom has a larger steric volume relative to hydrogen and therefore can interfere with efficient chain packing. Second, the electronic polarizability of C-F bond is lower than C-H bond.

Refractive index dispersion represents the variation of the refractive index with wavelength. Many photonic applications rely on having no wavelength-dependent effects except for those geometrically designed into the system and therefore materials' optical dispersion is to be avoided. There are different methods of determining the refractive index dispersion of a material such as prism-coupling technique, the immersion method, ellipsometry, critical angle and interference methods.⁵ The optical dispersion can be expressed numerically as $dn/d\lambda$,⁶ Abbe number,⁷ or modified Abbe number.⁸

Birefringence or double reflection is defined as the resolution or splitting of a lightwave into two unequally reflected waves by an optically anisotropic medium. Birefringence is an indication of optical anisotropy of a material and can be measured

from the difference between the transverse refractive index (n_{TE}) and transverse magnetic refractive index (n_{TM}) (Figure I.3.).

Figure I.3. Optical birefringence phenomenon

Unlike silica glass, whose birefringence is solely the result of stress formed during processing, the birefringence of polymeric materials comes mainly from the preferred orientation of rigid groups and polymer chains. However, the orientation may be induced also by stress during film formation. Some aromatic polymers, such as polyimides, exhibit high birefringence (up to 0.24) that is attributed to the strong preference of aromatic moieties to align in a plane parallel with the film surface.⁹ The birefringence can be also extremely low (10^{-5} to 10^{-6}) in polymers that undergo little molecular orientation during processing, such as in highly cross-linked polymers.¹⁰

b. Optical loss

Absorption and scattering are the main cause for optical loss at the telecom wavelength (1310 nm and 1550 nm) in optical polymers. Absorption loss in polymeric materials could be due to electronic and vibrational absorptions. Electronic absorptions in

polymers are very unlikely to contribute significantly to optical loss at the major telecom wavelengths. In the range of 1300 to 1600 nm, major absorption occurs due to the overtones of fundamental molecular vibrations.¹¹ The C-H and O-H overtones are highly absorptive in the telecom windows (relative intensity 7.2×10^{-2}), while C-F overtones show extremely low absorption in this range (6.4×10^{-6} to 6.4×10^{-9}).¹²

Scattering loss in optical materials is induced by extrinsic and/or intrinsic factors. Extrinsic factors are large defects within the polymer film such as particles, voids, dust, dissolved bubbles or unreacted monomer. Elimination of scattering loss due to extrinsic factors requires the use of clean room facility in the preparation of polymer solutions and films. Intrinsic scattering results from density fluctuations and compositional inhomogeneities, which occur at very short length scales (less than 0.1 μm). To minimize scattering loss in polymer waveguides, direct photo-patterning processes are preferred over the reactive etching methods when high roughness surfaces are formed.

Polarization dependent loss is defined as the maximum difference of attenuation between any of the two polarization states. For planar waveguides this loss is the difference between the TE and TM loss and is caused by processing induced stress in material or edge roughness of the core vertical walls.

c. Processibility

Another requirement for polymers to be used as waveguide materials is good processibility.

Thermal and mechanical stabilities have to be taken into account when polymers are processed for waveguide applications. The processed polymers in waveguide devices

must be stable to temperatures in the range of $-40\text{ }^{\circ}\text{C}$ to $85\text{ }^{\circ}\text{C}$ at a relative humidity of 85%, as required by telecom industry.¹²

Figure I.4. Waveguide fabrication process: (a) conventional process using a photoresist; (b) simplified process using a photosensitive optical polymer

The good solubility of polymers in organic solvents and their good film-forming capability allow for a low-cost, simple spin-coating fabrication process for making polymer waveguides. Polymer films with the desired thickness, in the range of $0.1\text{--}100\text{ }\mu\text{m}$, can be obtained by controlling the concentration of polymer solution and the spinning rate. A wide range of rigid or flexible substrates can also be used, including quartz, oxidized silicon and flexible polymer films. The conventional fabrication process involves multiple steps such as photoresist deposition, pattern formation, pattern transfer

and etching and finally removal of the photoresist (Figure I.4.a). One way to reduce the production cost is to use a photosensitive polymer as shown in Figure I.4.b.

Several classes of polymers have been extensively studied for waveguide applications and will be briefly discussed in the next section.

I.1.2. Fluorinated Polyimides

Aromatic polyimides are high-temperature resistant polymers that have excellent thermal and mechanical resistance, good dielectric properties and adhesion. These properties made them suitable for extensive use in semiconductor, aerospace and electronic industries.¹³ However, conventional polyimides used in the semiconductor industry have inadequate properties for photonic applications.

Among these are high optical loss caused by defects and chain ordering in the polyimides. Polyimides have poor solubility and require the use of the soluble polyamic acid precursors and subsequent thermal imidization. This curing process takes place usually above 300 °C, produces water by-product and tends to generate voids or pinholes in the polymer film. Furthermore, chain ordering can lead to refractive index fluctuations by producing scattering centers and also favors the formation of charge-transfer complexes that increases linear absorption of the polymer.

Another major difficulty encountered with aromatic polyimides is their high birefringence caused by the orientation of phenyl and imide rings during imidization conversion of polyamic acid and film casting on the substrate.

Methods of reducing the chain ordering include the use of amorphous fluorinated polyimides¹⁴ and annealing the free-standing polyimide film.¹⁵ In the past decade, several

types of fluorinated polyimides¹⁶ were developed that display low optical loss, desired refractive index and good thermal resistance (Figure I.5.).

Figure I.5. Refractive index and birefringence of fluorinated polyimides

Optical measurements are done at the wavelength of 850 nm and 1310 nm and in the visible region and have only recently been directed towards the current telecommunication wavelength of 1550 nm. The large birefringence and polarization

dependent loss that result from the aromatic chain ordering are still problematic and difficult to avoid for polyimides.

I.1.3. Acrylic Polymers

Acrylate polymers are another series of optical materials that have been extensively studied for waveguide applications. Deuterated and halogenated acrylates are particularly suitable for optical devices due to their very low stress induced loss and extremely low birefringence. Because of the high photosensitivity of the acrylic moiety, these polymers are photocurable and can serve as a negative type photoresist. There are two approaches to achieving cross-linked polymer networks. The first one uses mixtures of diacrylate monomers and oligomers¹⁷ (Figure I.6) and the second involves the use of reactive groups presented in the polymer chain¹⁸ (Figure I.7).

Figure I.6. Fluorinated diacrylate monomers¹⁶

These methods also allow tuning of the refractive index through blending or copolymerization, although it can be difficult to simultaneously achieve a required refractive index and low intrinsic absorption. The large number of acrylate monomers

makes possible to achieve a wide range of refractive indices, between 1.3 and 1.6, with optical loss for highly halogenated acrylates as low as 0.07 dB/cm at 1550 nm.

Although acrylate polymers have demonstrated some desirable properties, they do not possess the required thermal stability for direct on-chip applications, as required typically at temperatures above 300 °C.

Figure I.7. Halogenated acrylate copolymers¹⁸

I.1.4. Poly(arylene ether)s

Poly(arylene ether)s are high-performance engineering thermoplastics and are known to meet the requirements for applications in the aerospace and electronics industries.¹⁹ They tend to be less birefringent than polyimides, due to the presence of the flexible ether and ketone moieties. Among the fluorinated aromatic poly(arylene ether)s, many contain the hexafluoroisopropylidene units. These polymers have good solubility,

high thermal stability and glass transition temperatures, and relatively low crystallinity, dielectric constant and moisture uptake.

Figure I.8 gives some examples of these polymers for waveguide device applications. Ethynyl moieties at the chain ends are used to induce thermal cross-linking.²⁰

Figure I.8. Fluorinated poly(arylene ether)s

A very low optical loss of 0.2 dB/cm was reported for these uncured polymers, but it was found that the birefringence increases drastically with the increase of curing temperatures. Cross-linking can be performed at lower temperatures by using thermal initiators or by introducing UV-sensitive cross-linkers such as the vinyl pentafluorophenyl moiety.²¹

I.1.5. Other optical polymers

Other polymers that were investigated for optical waveguide applications include Cytop® from Asahi Glass Co.,²² (Figure I.9.a.) Teflon AF (Figure I.9.b.),²³ the cross-linked polymers derived from perfluorocyclobutane aromatic polyethers (PFCB)²⁴ (c in Figure I.9) and Cyclotene (BCB) developed by Dow Chemical Company (Figure I.9.d.).²⁵

These polymers possess excellent optical properties for optical applications at telecommunication wavelength and also have high durability and chemical resistance. Due to the presence of only of C-F, C-C and C-O bonds they have low refractive indices and thus are suitable for use as cladding materials. However, one of the draw back is their poor adhesion to the substrate, which makes them difficult to be integrated in multilayer device structure.

Figure I.9. Fluorinated optical polymers

All these classes of polymers have been tested and used in fabrication of optical components. The choice of material dictates the technique necessary to make the waveguides. High molecular weight polymers, thermo- or photocurable oligomers or combinations of both can be used. As mentioned previously, photosensitive optical polymers are preferred to achieve the desired patterns as they offer the advantage of a reduced number of processing steps, high-yield manufacture and therefore cost efficiency.

There are numerous technologies that can be applied in the multilayer fabrication process of polymer optical waveguides.

I.2. Photosensitive Polymers

Photosensitive polymers or photopolymers encompass those that upon interaction with electromagnetic radiation undergo chemical reactions. Usually ultraviolet (UV), visible or infrared light are utilized to initiate photochemical reactions, but higher energy sources at a shorter wavelength, such electron-beam irradiation have also been utilized. There are a wide range of practical applications of photopolymers, such as optical adhesives, coatings, and inks.²⁶

The technological applications of photosensitive polymers can be divided, based on the exposure mode into imaging and non-imaging systems. The largest world-wide uses are in non-imaging applications where the polymer is given an overall or non-patterned exposure, typically for photosensitive protective and decorative coatings, adhesive and sealants. The “high-value use” of photosensitive polymers is in the imaging applications, in which a polymer is irradiated to form a pattern (e.g., film and liquid resists, printing plates).

All the applications of photosensitive polymers rely on the formation of detectable changes in organic materials following exposure to electromagnetic radiation, such as increase or decrease in solubility and adhesion, and as well the change in color, electrical conductivity and refractive index. These changes could be achieved by using two different methods photopolymerization or photo-cross-linking.

I.2.1. Photopolymerization

The photoinitiated polymerization of multifunctional monomers and oligomers is one of the most efficient methods to synthesize cross-linked polymer networks. This requires the use of a small amount of photoinitiator, which generates reactive species, free radicals or ions upon UV exposure. Depending on the polymerization mechanism these photopolymer systems can be divided in three major classes: radical, cationic and addition photoinitiated polymerization.

Photoinitiated radical polymerization

Radical polymerization is generally applied to mono and multifunctional vinyl containing monomers or oligomers and requires the presence of an initiator which generates reactive radicals upon UV irradiation that starts the chain reaction (Scheme I.1).

The most ubiquitous photoinitiated radical polymerizations are applied to acrylates. This is due to the ready availability of a large choice of monomers and their good reactivity. However quenching of the polymerization process by oxygen or radicals represents drawbacks of this method.

Scheme I.1. Schematic representation of photoinitiated radical polymerization

Photoinitiated cationic polymerization

This type of photoinitiated polymerization have been developed for epoxy and vinyl ether based monomers or oligomers which are inactive towards radical species.²⁷ The photoinitiators used are mainly diaryliodonium or triarylsulfonium salts that can generate strong Brønsted acids such as HPF_6 , HSbF_6 , HBF_4 , HAsF_6 when they are exposed to UV irradiation (Scheme I.2).

Scheme I.2. Schematic representation of photoinitiated cationic polymerization

The advantages of cationic photopolymerization are the excellent mechanical properties of the resulting film and the fact that the polymerization can continue even in

the absence of light. However, some of the problems encountered are the poor solubility of the catalyst (onium salts) in the usual cationic monomers, such epoxies and vinyl ethers and the limited range of epoxies available.

Photoinitiated addition polymerization

This class of photoinitiated polymerization reactions applies mainly to diacetylene monomers and is a lattice controlled topochemical reaction that yields macroscopic single crystals containing extended, conjugated polymer chains. Topochemical polymerization requires that the chain reaction propagates within the solid state of the organic crystals and requires precise geometry and close approach of the reactive functional groups.²⁸ The polymerization of a linear array of diyne monomers is shown schematically in Scheme I.3.

I.3.

Scheme I.3. Schematic representation of the solid state polymerization of disubstituted diynes: (a) diyne monomers with reactive packing and a unique polymerization direction; (b) polydiacetylene product.

The arrangement of the monomer units can be characterized by the separation of the monomers in the direction of closest contact d , and the angle between the axis of the

diyne units and the polymerization direction γ . The distance which determines whether the reaction is possible is the separation of the 1 and 4' carbons, D and must be less than 4 Å.

Although the requirements for solid state reactivity of diynes are quite strict, there is some leeway which indicates that polymerization is possible in less ordered environments. Examples are the Langmuir-Blodgett (LB) films,²⁹ copolymers containing diynes³⁰ and liquid crystalline phases.³¹ Among these, only the first two are situations in which the packing of the diacetylene units can be close to that encountered in single crystals.

This type of polymerization has been extensively studied for various disubstituted diynes. Although this polymerization yields well ordered products, the stringent stereochemical requirements imposes serious restrictions regarding structural tailoring to optimize the properties.³²

1.2.2. Photo-Cross-Linking

Photo-cross-linking refers to the process whereby light (UV, visible or IR light) is used to induce bond cross-linking in oligomers and polymers. The process involves the irradiation of polymers carrying more than two reactive groups per chain and of blends with a photoinitiator or a sensitizer. Photo-cross-linkable polymers can be classified as polymers that crosslink through photoinitiated radical reactions and photo-cycloaddition reactions.

Photoinitiated radical reactions involve the use of a photoinitiator, which is added to the polymer or grafted onto the polymer chains.³³ The photoinitiator under UV light yields reactive radicals which initiate subsequent chain reactions in the polymer and produce cross-links between macromolecular chains. The polymer by itself can be cross-

linked but the presence of even a very small quantity of an initiator can accelerate considerably the cross-linking reaction.³⁴ Acrylate-based resins are examples of radical photoinitiated cross-linking systems. A typical formulation contains three basic components: an aromatic ketone that generates free radicals by photolysis, an acrylate terminated oligomer (e.g., polyurethane, polyester and polyether) that constitutes the backbone of the three dimensional network and an acrylate monomer which acts as a reactive diluent.³⁵

Polymers that crosslink through photocycloaddition reactions are those that contain cinnamate, chalcone, bismaleimides, anthracene²⁷ or diacetylene^{25a} moieties in the main chain or as a pendent group. One of the most studied systems is the one based on photodimerization of cinnamate and cinnamate analogues and represents a classic example of negative working resists.³⁶ Scheme I.4 shows the cross-linking of a polymer containing the cinnamic groups through photocyclodimerization that forms the cyclobutane moiety linking the two polymeric chains.

Scheme I.4. Schematic representation of photo-cross-linking by cyclodimerization of cinnamic pendent groups of polymers³⁷

Diacetylene-containing polymers such as polyesters,³⁸ polyurethanes,³⁹ polycarbonates,⁴⁰ and polyamides⁴¹ were noted shortly after Wegner's reports on polymerization of single crystals of diacetylene monomers.⁴² Cross-linking takes place in these polymers via intermolecular or interchain 1,4-addition reactions of diacetylene groups, producing a fully extended conjugated polydiacetylene networks.⁴³

I.3. Rationale and Objectives

This thesis work was undertaken to search for new optical polymers potentially useful for waveguide applications. As mentioned above, various classes of polymers have been investigated as optical materials but the search for new optical polymers is still ongoing.

The requirements for optical polymers to be investigated in this work include *adjustable refractive index, low birefringence, good thermal resistance, and good processibility, photo-cross-linkable and patternable.*

I.3.1. Design of New Optical Polymers

In order to achieve the good thermal stability, the polymer should ideally have an aromatic backbone such as polyimide. The hexafluoroisopropylidene moiety needs to be incorporated in the polymer to minimize the optical loss as well to improve its solubility. Incorporation of ether linkages and bulky or branched units in the main chain are also required, as they are expected to decrease the birefringence characteristic to the polyimides. The photosensitivity of these polymers will be accomplished by including the diacetylene moieties in the main chain, since these groups can be cross-linked by UV

irradiation and do not evolve volatile small molecules as by-products when being cured. In this work diacetylene moiety refers to disubstituted 1,3-butadiyne.

The synthesis of these diacetylene-containing polymers is based on the oxidative coupling method developed by Hay.⁴⁴ This method will also allow the achievement of adjustable refractive indices through copolymerization of two different ethynyl monomers.

Through the incorporation of a bulky diphenylfluorenyl moiety⁴⁵ or a branched triphenylethane moiety (Figure I.9.) in the ethynyl end-capped ether monomer, further decrease in polymers' birefringence and increase in solubility are expected.

Figure I.9. Proposed subunits to be incorporated into diacetylene polymers

I.3.2. Design of a New Photo-Cross-Linking System

The ethynyl moieties have been incorporated into polyimides,⁴⁶ poly(aryl ether sulfones),⁴⁷ polyphenylenes,⁴⁸ polyesters⁴⁹ and poly(phenylquinoxalines)⁵⁰ to induce thermal cross-linking. Heating at temperatures above 150 °C induces cross-linking through cyclotrimerization and coupling reactions of the ethynyl moieties.⁵¹ However, photo-initiated cross-linking of polymers containing ethynyl pendent groups has not been reported to date.

Alkyl- and aryl-substituted acetylenes are known to be polymerized by light in the presence of group VI metal carbonyls [e.g., Cr(CO)₆, Mo(CO)₆ and W(CO)₆] in

halogenated solvents, ^{52a-c} and some other group VI metal complexes.⁵³ A variety of Lewis acids (e.g., SiCl₄ and GeCl₄) are effective co-catalysts for polymerization of various acetylenes in non-halogenated solvents.⁵⁴ Among the metal catalysts, tungsten hexacarbonyl, molybdenum hexacarbonyl⁵⁵ and metal carbonyls of general structure M(CO)_xL_y⁵⁶ are widely used for making high molecular weight polyacetylenes.

Therefore, it is conceivable that by applying the metal-catalyzed photochemistry of acetylenes to a polymer that contains ethynyl groups, one could develop a new photo-cross-linkable polymer system.

Such a photo-cross-linkable polymer system requires the use of only a small amount of W(CO)₆ or other metal VI carbonyls and is in principle applicable to any polymers that contain the ethynyl moiety in the main chain, side chain or chain ends.

To demonstrate the applicability of this new system, a series of acrylate polymers containing pendant ethynyl groups as well as the branched diacetylene polymers containing ethynyl end-groups should be prepared and tested.

Accordingly, the overall objectives of this thesis work are:

1. To design, synthesize and characterize novel diacetylene polymers that have the following characteristics:
 - a. adjustable refractive index
 - b. low birefringence
 - c. good thermal resistance
 - d. photopatternable
2. To develop and test a new photocuring system involving ethynyl-containing polymers and W(CO)₆;

3. To investigate the kinetics and various factors of the photocuring process.

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CHAPTER II. LINEAR POLYMERS CONTAINING DIACETYLENE MOIETIES

II.1. Introduction

As outlined in the previous chapter, the specific optical properties required for polymers as waveguide materials may be realized through copolymerization. Poly(ether imide)s are usually synthesized by the nucleophilic displacement of bishaloimides¹ and bisnitroimides² with a bisphenol in dipolar solvents (Scheme II.1) or by the classic method of polyimide synthesis involving a tetracarboxylic acid dianhydride having an ether bridging group and a diamine (Scheme II.2).

Scheme II.1. Synthesis of poly(ether imide)s by nucleophilic substitution polymerization.

Scheme II.2. Synthesis of poly(ether imide)s by nucleophilic self-condensation polymerization

Alternately, poly(ether imide)s can be synthesized by one-step imide-amine interchange reaction³ of a bis(ether imide) with an aromatic diamine (Scheme II.3).

Scheme II.3. Synthesis of poly(ether imide)s by imide-amine interchange reaction

Meanwhile, polyethers⁴ and polyimides^{5,7} containing diacetylene moieties can be synthesized in high yields by Hay's oxidative polymerization.⁶ This self-condensation reaction of α,ω -ethynyl end-capped monomers occurs under mild conditions, in the presence of an amine-Cu(I) complex.⁷ According to Hay, the cupric complex is

catalytically active and is in fact the oxygen-carrying intermediate in the oxidation of the ethynyl compounds to the self-condensed products. Scheme II. 4 displays the catalyst formation and intermediates involved in the oxidative coupling reaction of mono-substituted acetylenes.

Scheme II.4. Catalyst and intermediates involved in the oxidative coupling reaction of alkynes

This versatile polymerization method has been also used to synthesize polymers such as polyesters,⁸ polyamides,⁹ polyurethanes,¹⁰ polysiloxanes¹¹ and polycarbonates.¹² Therefore, in this work it is used for the synthesis of poly(ether imide)s. The diacetylene moieties will form upon polymerization and also serve as reactive sites for photo-cross-linking.

The two ethynyl end-capped monomers used to synthesize poly(ether imide)s are the aromatic ether monomer **II-3** and the fluorinated imide monomer **II-7** (Figure II.1)

Figure II.1. Proposed ethynyl end-capped monomers

II.2. Monomer Synthesis and Characterization

The synthesis of monomer **II-3** was accomplished in a one step reaction starting from 9,9-bis(4-hydroxyphenyl)fluorene **II-1** and propargyl bromide **II-2** (Scheme **II.5**). The reaction was carried in an aqueous solution of sodium hydroxide in the presence of a small amount of tetra-*n*-butylammonium bromide as a phase transfer catalyst.¹³ The incorporation of propargyl moieties was indicated by IR through the appearance of the characteristic absorption of the ethynyl at 3289 cm⁻¹ for ≡C-H and at 2119 cm⁻¹ for -C≡C- and complete disappearance of phenolic -OH at 3399 cm⁻¹. The structure of monomer **II-3** was confirmed through ¹H NMR (400 MHz) and ¹³C NMR. Two characteristic peaks for acetylenic carbons were found in the ¹³C NMR spectrum at 75.44 ppm and 78.64 ppm. The ¹H NMR spectrum indicated the ethynyl proton as a triplet at 2.47 ppm.

The fluorinated diimide monomer **II-7** is a known compound which was prepared using a modified literature procedure¹⁴ involving a two-step method starting from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride **II-4** and propargylamine **II-5**.

Scheme II.5. Synthesis of ethynyl end-capped ether **II-3** and imide **II-7** monomers

The first step is the reaction of a tetracarboxylic acid dianhydride with 2 equivalents of an ethynylated amine to form an amic acid, which is further imidized with the aid of acetic anhydride at 110 °C to afford the imide monomer. The formation of the monomer **II-7**

was monitored by FTIR. The incorporation of propargyl moiety was indicated through the appearance of the $\equiv\text{C-H}$ absorption stretch at 3281 cm^{-1} and $-\text{C}\equiv\text{C}-$ at 2110 cm^{-1} . The complete imidization was judged to be complete once the amic acid absorption band was replaced with that of the imide group at 1779 cm^{-1} and 1721 cm^{-1} . The structure was further confirmed by ^1H NMR (400 MHz) and ^{13}C NMR. In the ^1H NMR the ethynyl proton was present as a triplet at 2.78 ppm and in the ^{13}C NMR the ethynyl carbons were observed at 78.3 ppm and 72.89 ppm (Figure II.2)

Figure II.2. (a) ^1H NMR spectrum (400 MHz, CDCl_3) and (b) ^{13}C NMR (100 MHz, CDCl_3) spectrum of monomer II-3

II.3. Polymer Synthesis and Characterization

The syntheses of polymers **II-8a-II-8e** were carried out according to Scheme **II.6**, using the oxidative coupling method developed by Hay.¹⁵ The catalyst system consisted of copper (I) chloride and N,N,N',N'-tetramethylethylenediamine as the chelating group activated *in situ* by bubbling oxygen in the reaction mixture. N,N,N',N'-Tetramethylethylenediamine has been shown to be one of the most effective ligands in the oxidative coupling polymerizations.¹⁶ The synthesis of polyether **II-8a** was carried out in *o*-dichlorobenzene at 70 °C, while that of **II-8e** was done in DMSO at room temperature. Polyimide **II-8e** is a known polymer whose spectral data correspond to the literature values. Copolymerization was first attempted in *o*-dichlorobenzene and small molecular weight polymers were obtained. By using nitrobenzene as the copolymerization solvent, high molecular weight polymers were isolated as white fibrous materials and purified by reverse precipitation. As mentioned previously, water is a byproduct in the oxidative coupling polymerizations and thus potentially can hydrolyze the imide units. To avoid this, polymerizations were done at low monomer concentrations ranging from 6.2 to 5.7 % wt/vol. However, polymerization in dilute solutions favors the formation of cyclic oligomers.¹⁷ Thus the low molecular weight polymers and cyclics formed during polymerization were removed by reverse precipitation, which resulted in lower yields for the isolated polymers ranging from 69 % (polymer **II-8a**) to 51 % (polymer **II-8d**). The GPC chromatograms of polymer **II-8d** before and after reverse precipitation are shown in Figure **II.3**.

Scheme II.6. Synthesis of linear diacetylene polymers

All the polymers were characterized IR, NMR, GPC, DSC and TGA (Table II.1). No residual ethynyl protons due to the presence of ethynyl end-groups were observed by IR spectroscopy. The characteristic $\equiv\text{C-H}$ stretches at 3289 cm^{-1} (II-3) and 3281 cm^{-1} (II-7) and $\text{-C}\equiv\text{C-}$ stretching vibrations at 2119 cm^{-1} (II-3) and 2138 cm^{-1} (II-7) completely disappeared upon polymerization. The ^{13}C NMR spectra also showed that the terminal ethynyl carbons were transformed by polymerization to 1,3-butadiyne carbons. Two 1,3-butadiynic carbons ($\text{-C}\equiv\text{C-C}\equiv\text{C-}$) at 74.71 and 70.99 ppm for polymer II-8a replaced the two ethynyl carbons at 78.64 and 75.44 ppm of monomer II-3. For polymers II-8b, c and d, the significant changes in the ^{13}C NMR spectra were the appearance of six new 1,3-butadiynic carbons

Figure II.3. GPC chromatograms of polymer II-8d: (a) “as prepared” polymer; (b) after reverse precipitation

The peaks at 74.67 and 70.97 ppm correspond to the symmetric 1,3-butadiynic carbons of the ether fragments and those at 73.71, 72.72, 71.81, and 70.91 ppm are the 1,3-butadiynic carbons due to the heterogeneous coupling between imide and ether units.

The molar percent (%) incorporation of monomer **II-3** in poly(ether imides) was calculated by NMR using the methylenic protons at 4.6 ppm ($\text{OCH}_2\text{-C}\equiv\text{C-}$) and 4.4 ppm ($\text{NCH}_2\text{-C}\equiv\text{C-}$) (Appendix 2). The incorporation of monomer **II-3** in the final polymers were readily controlled and were found to be very close to the feed ratios.

All the polymers displayed excellent solubility in chlorinated hydrocarbons, DMF, NMP, DMAc and THF. Transparent, tough, flexible films could be cast from TCE or DMF.

Table II.1. Characterization of polymers **II-8a-e**

Polymer	II-3 Feed ^a (% mol)	II-3 Incorporated ^b (% mol)	M_w^c ($\times 10^{-4}$)	M_n^c ($\times 10^{-4}$)	M_w/M_n^c	T_d^d ($^{\circ}\text{C}$)	T_{max}^e
II-8a	100	100.0	23.5	20.2	1.2	334	230
II-8b	75	75.6	7.0	3.9	1.8	351	239
II-8c	50.0	50.2	4.6	4.1	1.1	364	244
II-8d	25	25.3	4.2	3.9	1.1	383	258
II-8e	0	0	N/A ^f	N/A	N/A	414	262

a- Mol % ratio of **II-3** in the monomer feed;

b- Mol % ratio of **II-3** incorporated in polymers determined by ^1H NMR;

c- Measured by GPC relative to polystyrene standards;

d- Decomposition temperature as calculated at 5% weight loss in N_2 ($10^{\circ}\text{C}/\text{min}$);

e- Peak temperature of the exotherm, as assessed by DSC under nitrogen at $10^{\circ}\text{C}/\text{min}$.

f- Not recorded due to polymers' poor solubility in DMF.

The onset temperatures for 5% weight loss ranged from 334 to 414 °C. As expected, higher thermal stability was found for the copolymers with a higher molar % incorporation of imide monomer **II-7**. DSC analyses showed that they all undergo an exothermic reaction with values of the onset temperatures higher than 170 °C. The peak temperature of the exotherms varies from 230 to 262 °C, being higher for the polymers with higher imide content (Figure **II.4**).

Gel permeation chromatography (GPC) measurements, relative to polystyrene standards, showed a decrease in molecular weight as the content of imide monomer **II-7** increased in poly(ether imides). The weight-average molecular weights were found to range from 235300 to 42400 with a polydispersity index of 1.1-1.8 (Table **II.1**).

Figure **II.4**. DSC traces of polymers **II-8a-e**

II. 4. Polymer Cross-Linking

Thermal and photochemical cross-linking of diacetylene polymers **II-8a-II-8e** were studied and compared. Typically, after 40 min of exposure to UV light at 254-450 nm, all the polymer films became insoluble and changed color from transparent to yellow. Clearly, the changes in color and solubility are attributed to cross-linking of the diacetylene moieties.¹⁸

To study the photoinduced structural changes, ¹³C CP/MAS NMR experiments were carried out on polymer **II-8a**. Figure **II.5** displays the ¹³C CP/MAS NMR spectra of polymer **II-8a** cured for 40 min at 254 - 450 nm and that of a nonirradiated sample. Characteristic peaks in the nonirradiated sample were observed at 55 ppm (methylene carbon atoms in -CH₂-O-), 60 ppm (tertiary aliphatic carbon), 70-85 ppm (1,3-butadiynic carbons), 100-140 ppm (aromatic carbons) and 150-160 ppm (aromatic =C-O). For the cured sample, the relative intensity of peaks at 74.7 ppm decreased and a small shoulder at 110 ppm appeared, corresponding to the C=C carbon that is formed from the 1,4-addition reaction of diacetylene. Two new peaks also appeared after photo-cross-linking for a tertiary aliphatic carbon at 28.7 ppm (from CP/MAS dipolar dephasing experiment) and a carbonyl carbon at 173.5 ppm, suggesting that another type of reaction also occurs simultaneously or sequentially during photo-cross-linking.

IR studies of thin polymer films on a sodium chloride plate also indicated the structural changes at the ethynyl moiety. The intensity of the $\equiv\text{C}-\text{C}$ stretching vibration band at 916-948 cm⁻¹ decreased (Figure **II.6.b**), along with the appearance of two new peaks: at 1751 cm⁻¹ (carbonyl group) and at 3550 cm⁻¹ (hydroxyl group).

Figure II.5. Changes in ^{13}C NMR spectra of polymer II-8a: (a) in CDCl_3 before irradiation, (b) ^{13}C CP/MAS NMR spectrum before irradiation, (c) ^{13}C CP/MAS NMR spectrum after UV irradiation for 40 min and (d) ^{13}C CP/MAS NMR spectrum after thermal treatment at 210 °C for 3 hours

These results suggest that the $-\text{CH}_2\text{O}-$ linkages were also involved in photocuring to a certain extent, and are responsible for the formation of the new carbonyl and hydroxyl groups in the cross-linking process.

Figure II.6. IR spectra of polymer **II-8a**: (a) before irradiation, (b) after UV irradiation for 20 min and (c) after thermal treatment at 210 °C for 3 hours

In a comparative experiment, thermal curing of polymer **II-8a** was carried out at 210 °C and induced a drastic change in color from transparent to a dark red and in the film quality (insoluble and brittle). The ^{13}C CP/MAS NMR spectrum (Figure II.5.d) confirmed extensive reactions involving the dicetylene and methyleneoxy groups, as the peaks at 70-85 ppm (1,3-butadiynic carbons) and at 50 ppm ($-\text{CH}_2\text{O}-$) almost completely disappeared. IR spectra of the thermally cured polymer (Figure 4c) showed also the presence of a peak at 1655 cm^{-1} for the newly formed alkene bonds, a newly formed hydroxyl group at 3560 cm^{-1} , and a carbonyl group at 1736 cm^{-1} , suggesting that a

Claisen rearrangement reaction had taken place to yield the fragments structurally similar to a phenol and ketone.¹⁹

II. 5. Optical Properties

As mentioned in the previous chapter optical materials with different refractive indices are required as a core and a cladding part of an optical waveguide. The core material must have a higher refractive index than the cladding material. The larger the difference in the refractive indices of the core and the cladding, the larger the numeric aperture of the light guide and a better high-density optical guide. Since the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices and birefringence of an optical polymer are important parameters of waveguide devices, the optical properties of polymers **II-8a-e** were determined by ellipsometry at 1550 nm at room temperature.

Polymer films were prepared by spin coating the polymer solution in TCE (3.5-5 wt. %) onto a silicon wafer in a two-step process, first at 500 rpm and then at 1800 rpm, followed by drying under vacuum (5 mmHg) at 80 °C for 6-8 hours.

Polymer thin films in 400 nm to 800 nm thickness were used to determine the refractive indices at room temperature (Table **II.2**). Polyether **II-8a** with the highest index of refraction of 1.6313 contains a large number of aromatic rings, which have large polarizability²⁰ and therefore a tendency to induce high density packing, factors that are accountable for this high value. Polyimide **II-8e** instead has the lowest refractive index due to the high fluorine content that has a significant low polarizability and increases polymer's free volume. The values of the refractive indices of polymers **II-8b-d** are therefore determined by the molar ratio of the two co-monomers.

As shown in Figure II.7, the refractive indices of our polymers could be controlled by varying the molar ratio of the two monomers and were found to vary between 1.5454 and 1.6313 for the in-plane (TE) polarization ($\Delta n_{TE} = 0.0859$) and from 1.5329 to 1.6283 for the out-of-plane (TM) polarization ($\Delta n_{TM} = 0.0954$).

Table II.2. Refractive index values for polymers **II-8a-e**

Polymer	% mol monomer II-3 ^a	n_{TE} ^b	n_{TM} ^c	Δn ^d
II-8a	100	1.6313	1.6283	0.0030
II-8b	75.6	1.6145	1.6097	0.0048
II-8c	50.2	1.5945	1.5878	0.0067
II-8d	25.3	1.5796	1.571	0.0086
II-8e	0	1.5454	1.5329	0.0125

a- mol % ration of **II-3** incorporated in polymers determined by 1H NMR;

b- in-plane refractive index determined by ellipsometry;

c- out-of-plane refractive index determined by ellipsometry;

d- Birefringence calculated as the difference between n_{TE} and n_{TM}

The values of the refractive indices decreased as the amount of the fluorocarbon content in the polymer (mol %, monomer **II-7**) increased. The n_{TE} and n_{TM} reached maximum values (1.6313 and 1.6283) for polymer **II-8a** derived solely from monomer **II-3**. Photo-cross-linking induced only a small decrease in the refractive index, typically about 0.4×10^{-3} to 6.5×10^{-3} for n_{TE} and 0.4×10^{-3} to 6.2×10^{-3} for n_{TM} . In contrast, thermal cross-linking resulted in a slightly larger increase in refractive index of about 0.3×10^{-2} for n_{TE} and 1.8×10^{-2} for n_{TM} .

Figure II.7. Plot of refractive index and birefringence versus mol % of monomer II-3 in polymers II-8a- e

The optical dispersion property of all the polymers was also determined by ellipsometry (Figure II.8) as another important parameter for waveguide devices.²¹ The dispersion values were calculated as $dn/d\lambda$ in the wavelength range of interest, for the three typical telecommunication wavelengths (810 nm, 1310 nm, and 1550 nm). These values were larger at 840 nm, varying from -4×10^{-5} to $-6 \times 10^{-5} \text{ nm}^{-1}$ and smaller at 1310 and 1550 nm, ranging from -1×10^{-5} to $-2 \times 10^{-5} \text{ nm}^{-1}$.

Figure II.8. Refractive index dispersion of polymers II-8a-e

Figure II.9. Refractive index dispersion of polymer II-8a: (a) uncured, (b) UV irradiated and (c) thermally treated sample at 210 °C for 3 hours

The dispersion displayed no change upon UV cross-linking at all the wavelength of interest. A large change in dispersion was observed at 840 nm upon thermal cross-linking, as the values almost doubled and reached $-12 \times 10^{-5} \text{ cm}^{-1}$. At longer wavelength

the dispersion values increased up to only $-2 \times 10^{-5} \text{ cm}^{-1}$. Figure II.9 displays the optical dispersion of polymer II-8a before and after thermal and photo-cross-linking.

The difference between n_{TE} and n_{TM} defines the birefringence (Δn) of the polymer films. Optical anisotropy expressed by the birefringence value must be low for most waveguide applications, as large anisotropy may cause problems such as near-coupled-noise due to crosstalk in the performance of the device.²² The birefringence of polymers II-8a-e were found to be directly related to the content of monomer II-3 in the polymer ranging from 1.25×10^{-2} to 3×10^{-3} . Polymer II-8a has the lowest birefringence which can be attributed to the fluorenyl group that is oriented perpendicularly to the polymer mainchain. This finding is also supported by the analysis of energy minimized molecular model of monomer II-3, using a commercial modeling software package (SPARTAN). The calculated dihedral angle between the fluorene moiety and phenyl groups was 89.84 (Figure II.10). This bulky cardo moiety therefore prevents the polymer chains from packing and hence hinders the in-plane orientation process. The flexible hexafluoroisopropylidene and ether linkages also contribute to lowering the film birefringence, by increasing the chain mobility and decreasing the chain packing.

Figure II.10. AM1 optimized molecular conformation of monomer II-3

The photo-cross-linking process is believed to involve 1,4-addition reactions of diacetylene moieties and the formation of small conjugated domains of double and triple bonds. The degree of conversion is however small as observed from the relevant peak intensities by spectroscopic means. For the polymers having a higher molar ratio of monomer **II-3** the cross-linking does not affect tremendously the chain packing density (due to the presence of the bulky fluorene moieties) as the observed variation in film thickness was small (typically about 1 %). However, the increase of molar ratio of monomer **II-7** in the polymers allowed for denser chain packing, as demonstrated by higher variations in film thickness to as much as 16% for polymer **II-8e**. This can explain the observed lower birefringence of 2.3×10^{-3} for polymer **II-8a** and the high value (1.5×10^{-2}) for polymer **II-8e**.

In comparison with the photo-cross-linking process, the thermal cross-linking process induced significant structural changes in polymers. The variation in film thickness was larger, varying from 9.6% for polymer **II-8a** to 18.9% for polymer **II-8e**, demonstrating a greater packing density upon thermal treatment. These are the factors that induced a higher birefringence in the polymers, to as high as 2.87×10^{-2} . The presence of newly formed hydroxyl and ketone groups also explain an increase in the refractive index values, as these groups are known to have larger polarizabilities than the ether groups.

In order to determine if small range ordering occurs upon cross-linking powder wide-angle X-ray diffraction analysis of these polymers was performed. All the polymers of the series are amorphous as shown using polymer **II-8-a**, a representative example of the series. Powder wide-angle X-ray diffraction of the polymer before and after

photoirradiation (Figure II.11.a and b), indicates that the cross-linking process should not increase the optical loss caused by scattering due to the formation of the crystalline domains.

Figure II.11. WAXD of polymer **II-8a**: (a) uncured, (b) UV irradiated and (c) thermally treated at 210 °C for 3 hours

However, X-ray diffraction analysis of the thermally cross-linked polymer **II-8a** (Figure II.11.c) indicated the formation of small ordered domains. Similar behaviors were observed for polymers **II-8b**, **II-8c** and **II-8d**. This kind of short-range ordering in polymer waveguides is expected to induce a propagation loss and birefringence due to scattering. Therefore, long-time heating above 210 °C should be avoided when making a polymer waveguide from polymers **II-8a-d**.

To demonstrate the photopatterning capability of our polymers, thin polymer films were spin-coated on silicon wafers and exposed to UV irradiation through a photomask for 40 min. Figure II.12 shows a typical scanning electron micrograph (SEM) of a patterned film produced by direct irradiation using a 3500 mW/cm² light source. The top view shows that the features are very well-defined (Figure II.12.a). The

cross section of one of the ridges of approximately 12 μm width reveals a rough, wrinkled surface, which was likely the result of the nonoptimized etching or washing process. Optimization of film processing, cross-linking, and etching is required in order to achieve a high-quality ridge waveguide.

Figure II.12. SEM images of photopatterned film of polymer **II-8a**: (a) top view and (b) cross section

II.6. Conclusions

The design and synthesis of novel poly(ether imide)s polymers containing diacetylene moieties allowed for the correlation of structure with their optical properties (refractive index and birefringence). The increase in the molar content of the bulky ether monomer **II-3** incorporated in the polymers induced an increase of the refractive index of the polymer while the birefringence decreased noticeably to as low as 0.3×10^{-2} .

Photoinduced cross-linking of all the polymers produced fine patterns when patterned using a photomask. The optical properties of the photo-cross-linked polymers varied only slightly causing a decrease in the refractive index values of typically 0.4×10^{-3} to 6.5×10^{-3} . In comparison, thermally cured polymers underwent drastic changes inducing a high increase in both refractive index and birefringence. Moreover, thermal treatment causes the formation of small crystalline domains within the polymer film that could induce high optical loss when used in optical applications.

II.7. Experimental Section

Materials

All the reagents and solvents were obtained from Sigma-Aldrich Canada and were used as received unless otherwise specified. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride was purchased from Chriskev Co. Inc. Cuprous chloride (BDH Chemicals Ltd.) was purified by dissolution in concentrated HCl followed by precipitation in water, filtration, washing with ethanol and diethyl ether and drying under vacuum (5 mmHg) at 100 °C. Dipropargyl 4,4'-(hexafluoroisopropylidene)diphthalimide (monomer **II-7**) was prepared according to a known procedure and its physical and spectral data (m.p., ^1H NMR, ^{13}C NMR) are in accord with the literature.¹¹ Mp=150 °C; ^1H NMR(400 MHz, acetone- d_6): δ (ppm) 8.08 (1H, d, $J=8.4$ Hz), 8.02 (1H, d, $J=8.4$ Hz), 7.81 (1H, s), 4.47 (2H, d, $J=2.5$ Hz), 2.80 (1H, t, $J=2.5$ Hz); ^{13}C NMR(100 MHz, CDCl_3): δ (ppm) 166.58, 166.50, 139.18, 137.07, 134.11, 133.71, 125.23, 124.77, 78.34, 72.89, 66.50, 29.89, 27.68.

Measurements

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker-400 MHz and Bruker-100 MHz instrument using tetramethylsilane as an internal reference. Infrared (IR) spectra were obtained with a Bomem Michelson 120 FTIR spectrometer. Melting points were obtained from a Fisher-Johns melting apparatus and were uncorrected. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) relative to polystyrene standards, using N,N-dimethylformamide (DMF) at 50 °C at a flow rate of 1.0 mL/min. Differential scanning calorimetry (DSC) was performed with a Seiko SSC/ 5200 DSC instrument at a heating rate of 10 °C/min in nitrogen.

Thermal stability, as measured by 5% weight loss of the polymer samples, was determined using a Seiko TG/DTA 220 analyzer at a heating rate of 10 °C/min, in nitrogen.

All the polymer films were spin-coated on aprox. 1 cm² surfaces of clean silicon wafer. Cleaning of the silicon wafer was achieved by sonication for 1 h in isopropanol at room temperature followed by immersion in a dilute hydrofluoric acid solution (20% in water), rinsing with distilled water and acetone and blow dried with a nitrogen gun. Drying was completed by heating the silicon wafer in a vacuum oven at 100 °C for 2h. Polymer solutions of 3.5-5 wt. % in TCE were filtered using a 4.5 µm and a 2 µm pore size Teflon filter. Spin coating of the polymer solutions on silicon wafers was done in a two-step process, first at 500 rpm and then at 1800 rpm. All the polymer films were dried under vacuum (5 mmHg) at 80 °C for 6-8 hours.

UV curing of polymer films was done using an Ultracure 100SS Plus/Novacure system as a source with a 250-450 nm filter at a light intensity of 3500 mW/cm². Thermal curing of polymer films was carried out in a vacuum oven at 210 °C for three hours. Photopatterns imaged by scanning electron microscopy were prepared from polymer films (approximately 2 µm thickness) on silicon wafers. After exposure to UV light through a photomask for 40 min at room temperature, the pattern was developed by immersing the sample consecutively in a TCE bath for 30 s and a chloroform bath for 1 min. The films were further dried in a vacuum oven at 70 °C overnight. SEM images were taken using a JEOL-JSM-6400 scanning microscope.

Refractive index, refractive index dispersion and birefringence measurements were done using a WVASE 32TM ellipsometer (J.A. Woolam Co., Inc.).

Monomer Synthesis

Monomer II-3

In a three-neck, round-bottomed flask equipped with a condenser, sodium hydroxide solution (500 mL, 20 wt%), 9,9-bis(4-hydroxyphenyl)fluorene (10.00 g, 28.5 mmol) and tetra-*n*-butylammonium bromide (1.37 g, 4.20 mmol) were mixed for 1 h at room temperature. Propargyl bromide (10.15 g, 85.2 mmol) was then added, and the reaction mixture was heated to 50-55 °C. After 5 h the reaction was stopped, and the product was extracted with ethyl acetate (3 × 200 mL). The organic layer was washed three times with water and then with a saturated NaCl solution. After drying over anhydrous sodium sulfate and removal of the solvent, the crude product was recrystallized twice from MeOH/EtOAc (3.5/1, v/v) to give large light yellow crystals: 7.75 g (63.7 % yield); mp 155-156 °C; IR (KBr, cm⁻¹): 3289 (≡C-H), 2119 (-C≡C-); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.73 (2H, d, *J*= 5.44Hz), 7.30 (6H, m), 7.11 (2H, d, *J*= 8.97 Hz), 7.11(4H, dd, *J*= 9.9 Hz), 6.8 (4H, d, *J*= 9.9 Hz), 4.6 (4H, d, *J*= 2.3 Hz), 2.47 (2H, t, *J*= 2.4 Hz). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 156.35, 151.57, 139.95, 138.95, 129.19, 127.69, 127.39, 126.03, 120.18, 114.43, 78.64, 75.44, 64.15, 55.75.

Polymer Synthesis

Polymer	% Mol II-3 Incorporated
II-8a	100
II-8b	75.6
II-8c	50.2
II-8d	25.3

Polymer II-8a

To a dried three-neck, round-bottomed flask were added CuCl (0.0115 g, 0.11 mmol), *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (0.014 g, 0.12 mmol), pyridine (0.185 g, 2.35 mmol) and 6.6 mL of anhydrous 1,2-dichlorobenzene. To the flask was attached a water condenser and an inlet and outlet for oxygen. The reaction mixture was warmed up to 75 °C while oxygen was bubbled through. After 1 h, monomer **II-3** (1.000 g, 2.34 mmol) in 10 mL of 1,2-dichlorobenzene was added to the catalyst mixture. After 3 h, 5 mL of 1,4-dioxane was added to the viscous solution and the polymer was then precipitated in 400 mL of methanol containing 2% HCl. The fibrous white polymer was filtered, reverse precipitated using DMF and dried under vacuum at 60 °C (69 % yield).

$M_w = 235300$; $M_w/M_n = 1.2$; $\eta_{inh} = 0.565$ dL/g (DMF, 30°C); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.7 (1H, d, $J=7.42$ Hz), 7.34 - 7.17 (3H, m), 7.08 (2H, d, $J=8.7$ Hz), 6.72 (2H, d, $J=8.7$ Hz), 4.58 (2H, s); ^{13}C NMR(100 MHz, CDCl_3): δ (ppm) 156.18,

151.47, 139.91, 139.12, 129.23, 127.75, 127.44, 126.02, 120.18, 114.40, 74.69, 70.98, 64.13, 56.13, 29.71.

Polymer II-8b

The above procedure was followed using CuCl (0.013 g, 0.13 mmol), TMEDA (0.014 g, 0.12 mmol), pyridine (0.185 g, 2.350 mmol), monomer **II-3** (0.639 g, 1.50 mmol), monomer **2** (0.259 g, 0.50 mmol) and 16 mL of nitrobenzene. The polymerization was carried out at 70 °C and the white fibrous polymer **II-8b** was obtained 67 % yield.

$M_w = 69800$; $M_w/M_n = 1.8$; IR (NaCl, cm^{-1}): 1718.6, 1729.0 (C=O); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.92- 7.71 (7H, m), 7.35- 7.21 (12H, m), 7.09 (6H, d, $J = 8.52$ Hz), 6.74 (6H, d, $J = 7.92$ Hz), 4.60 (8H, s), 4.49 (2H, s); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 165.53, 165.35, 156.18, 151.47, 139.91, 139.13, 138.97, 135.86, 132.77, 132.47, 129.23, 127.73, 127.43, 126.02, 125.16, 124.04, 120.16, 114.40, 74.67, 73.71, 72.72, 71.81, 70.97, 70.91, 67.64, 64.12, 56.14, 56.05, 27.91.

Polymer II-8c

The same procedure as for polymer **II-b** was used, employing CuCl (0.019 g, 0.19 mmol), TMEDA (0.023 g, 0.19 mmol), pyridine (0.278 g, 3.52 mmol), monomer **II-3** (0.639 g, 1.49 mmol), monomer **II-7** (0.777 g, 1.49 mmol) and 24 mL of nitrobenzene. The white fibrous polymer was obtained in 55 % yield.

$M_w = 46000$; $M_w/M_n = 1.1$; IR (NaCl, cm^{-1}): 1718.6, 1729.0 (C=O); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.92- 7.71 (4H, m), 7.35- 7.21 (4H, m), 7.09 (2H, d, $J = 8.00$ Hz), 6.74 (2H, d, $J = 7.92$ Hz), 4.62 (2H, s), 4.48 (2H, s); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm)

165.55, 165.37, 156.17, 151.45, 139.91, 139.13, 138.99, 135.88, 132.77, 132.46, 135.88, 132.77, 132.46, 129.23, 127.73, 127.43, 126.02, 125.15, 124.71, 124.05, 121.85, 120.16, 114.38, 74.65, 73.69, 72.72, 71.80, 70.96, 70.90, 67.62, 64.11, 56.15, 56.05, 27.01, 27.86.

Polymer II-8d

The above procedure was followed using CuCl (0.013 g, 0.13 mmol), TMEDA (0.015g, 0.13 mmol), pyridine (0.180 g, 2.35 mmol), monomer **II-3** (0.213 g, 0.5 mmol), monomer **II-7** (0.777 g, 1.5 mmol) and 16 mL of nitrobenzene. The white fibrous polymer was obtained in 51 % yield.

$M_w = 42000$; $M_w/M_n = 1.1$; IR (NaCl, cm^{-1}): 1718.6, 1729.0 (C=O); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.94- 7.72 (10H, m), 7.38- 7.24 (4H, m), 7.09 (2H, d, $J = 8.6$ Hz), 6.74 (2H, d, $J = 8.4$ Hz), 4.63 (2H, s), 4.49 (6H, s); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 165.52, 165.35, 156.20, 151.48, 139.93, 139.19, 139.01, 135.89, 132.80, 132.49, 129.24, 127.73, 127.43, 126.44, 126.03, 125.16, 124.03, 120.16, 114.40, 74.69, 73.72, 72.74, 71.83, 70.96, 70.91, 67.62, 64.14, 56.20, 56.10, 27.93.

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CHAPTER III. HYPERBRANCHED POLYMERS CONTAINING DIACETYLENE MOIETIES

III.1. Introduction

Dendritic and hyperbranched polymers have attracted a lot of attention in polymer chemistry during the past decade. They possess a range of interesting properties due to their highly branched structure, globular shape and multiple functional groups located at the periphery.¹ In comparison to their linear analogues, dendritic polymers possess significant differences in terms of their crystallinity and solubility. Hawker et al. have shown that the linear analogue of a fifth generation dendritic polyether is highly crystalline and possesses low solubility in common solvents, whereas the corresponding dendrimer is fully amorphous and highly soluble.² Hyperbranched polymers are irregularly branched, polydispersed macromolecules whose synthesis involves a one-step polymerization process. In comparison, dendrimers are “perfectly” branched monodisperse structures and are synthesized in a step-wise manner through divergent³ or convergent⁴ approaches. Hyperbranched polymers are therefore much more readily available at lower costs than dendrimers.

Due to their amorphous nature as well as their numerous functionalizable end-groups, hyperbranched polymers can be used to achieve materials with controlled refractive indices and low optical loss, essential properties of optical materials. Based on these characteristics, Pitois⁵ has developed a highly fluorinated aryl-ether hyperbranched polymer with a low birefringence, controlled refractive index and low optical loss (Figure

III.1.a). Another hyperbranched polymer synthesized and tested for its optical properties is a perfluorocyclobutane (PFCB) polymer with silane linkages⁶ (Scheme **III.1.b**) that proved to have low optical losses at 1310 nm and 1550 nm, of 0.30 dB/cm and 0.45 dB/cm respectively.

In the previous chapter, it was demonstrated that the birefringence of linear polyimides can be reduced through the incorporation of bulky cardo moieties in the main chain, which interfere with polymer chain packing. The tree-like structure of hyperbranched polymers allows for significant interactions between chain ends, rather than inter-chain interactions.⁷ This lack of interaction between polymer chains can be used to restrict the preferred planar packing of linear polyimides and therefore decrease their birefringence. In order to probe the efficiency of a branched structure in reducing polymer birefringence, the incorporation of a triethynyl-substituted ether monomer (Figure **III.2**) in the polymer structure will be examined.

a

$$(n_{TE} = 1.515-1.608; n_{TM} = 1.512-1.607; \Delta n = 0.001-0.003)_{1550\text{nm}}$$

Figure III.1. Hyperbranched polymers as optical materials

An $[A_2+B_3]$ oxidative coupling polymerization approach of the diethynyl-imide A_2 -type monomer (**II-7**) and a triethynyl-ether B_3 -type monomer (Figure **III.2**) will be used. Copolymerization using different ratios of the ether and imide monomers will also allow for control of the polymers' refractive indices, which is important for optical materials.

Figure **III.2**. Proposed triethynyl-ether monomer

III.2. Monomer Synthesis and Characterization

The trifunctional monomer **III-3** [1,1,1-tris(4-propargyloxyphenyl)ethane] (Scheme **III.1**) was prepared from propargyl bromide (**III-2**) and 1,1,1-tris(4-hydroxyphenyl)ethane (**III-1**) in an aqueous solution of sodium hydroxide in the presence of a small amount of tetrabutylammonium bromide (TBAB).⁸ This compound was characterized by IR, ^1H NMR and ^{13}C NMR. The IR spectrum of monomer **III-3** showed the disappearance of the phenol precursor absorptions and the appearance of characteristic absorptions for ethynyl $\equiv\text{C-H}$ at 3289 cm^{-1} and $-\text{C}\equiv\text{C}-$ at 2121 cm^{-1} groups. The structure was confirmed by ^{13}C NMR and ^1H NMR. ^1H NMR spectrum showed the ethynyl proton as a triplet at 2.51 ppm (Figure **III.3.a**). Two characteristic peaks for

ethynyl carbons were found in the ^{13}C NMR spectrum at 78.72 and 75.43 ppm (Figure III.3.b).

Scheme III.1. Synthesis of monomer **III-3**

Figure III.3. NMR spectra of monomer III-3: (a) ¹H NMR and (b) ¹³C NMR

III.3. Polymer Synthesis and Characterization

The preparation of hyperbranched polymers **III-4a-e** was carried according to the method shown in Scheme **III.2**. An $[A_2 + B_3]$ type of oxidative coupling polymerization was employed using the diethynyl-imide A_2 -type monomer (**II-7**) and a triethynyl-ether B_3 -type monomer (**III-3**) in different ratios. The catalyst was copper (I) chloride ligated to a diamine and was activated by bubbling oxygen into the reaction mixture.⁹ Polymer **III-4a** is a hyperbranched polyether and polymers **III-4a-e** are hyperbranched copolymers with different molar ratios of the ether/ imide units. Polymer **III-4f** is a known polymer whose spectral characteristics correspond to the literature values.¹⁰

A few trials for the synthesis of polymer **III-4a** were carried out to establish the optimum conditions for the polymerization reactions. In the first attempt to synthesize polymer **III-4a**, a one-pot addition of the monomer mixture to the catalyst solution was done while maintaining the reaction temperature at 60 °C. Within an hour, the gel point was reached and the polymer became insoluble. Tests done on small samples isolated prior to reaching the gelation point did not indicate high molecular weight polymers, as the film capabilities were extremely poor. To circumvent this problem, sequential additions of the monomer mixture to the catalytic solution was performed, while maintaining the temperature of the catalytic solution between 30 and 40 °C. Polymerizations carried out at monomer concentration higher than 2.5% or in other solvents such *o*-dichlorobenzene led to the formation of cross-linked polymer gels within an hour. The optimum conditions for the polymerization reaction was determined to be 2.5% (0.06 M) monomer concentration, with a molar ratio of $\text{CuCl} : \text{TMEDA} : \text{Py} = 0.1 :$

0.1 : 0.14. The polymerization temperature and time varied according to the feed ratio of the two comonomers.

Scheme III.2. Synthesis of the hyperbranched diacetylene polymers

Recent findings¹¹ showed that in the synthesis of hyperbranched poly(aryl ether)s the final concentration of monomers in the polymerization of A₂ with B₃ monomers should not exceed 0.08 M to avoid gelation. However, polymerizations carried out at the total concentration of monomers **II-7** and **III-4** lower than 0.053 M resulted in gelation within several hours. The gels formed within 1.5 hours when the monomer ratio was 1:1, and in few hours when the concentration of monomer **II-7** was higher. This can be attributed to the higher backbone rigidity of our polymers when compared to poly(aryl ether)s. A lower monomer concentration would therefore be required to avoid gelation.

The synthesis of hyperbranched copolymers containing a higher molar ratio of monomer **II-7** could be carried out at temperatures up to 70 °C and monomer molar concentrations below 0.53 mol/L without reaching the gelation point. The polymerization time was shorter for polymers **III-4a** and **III-4b** (1.5 hours) and longer for polymers **III-4c** to **III-4e** (3-5 hours). Low monomer concentrations and slow addition of the monomers were used in the synthesis of polymers **III-4a-e**, which create a quasi-high dilution condition, favoring intramolecular cyclization reactions.¹² The low molecular weight polymers and cyclic oligomers were then removed by reverse precipitation, which explains the lower yields for the isolated polymers, ranging from 71 % (polymer **III-4a**) to 38 % (polymer **III-4d**). The reactions were stopped by precipitating the polymers into acidified solutions of methanol when the viscosities of the reaction mixtures increased rapidly.

The ¹H NMR, ¹³C NMR and IR spectra of the polymers were consistent with the assigned structures. The ¹³C NMR spectra showed a high degree of conversion of the terminal ethynyl carbons. Two diacetylenic carbons at 74.7 ppm and 70.9 ppm in

polymer **III-4a** replaced the two ethynyl carbons at 78.6 ppm and 75.4 ppm which were formed in the spectrum of monomer **III-3**. For polymers **III-4b**, **c**, **d** and **e** the significant changes in the NMR spectra were the appearance of six new ethynyl carbons. The peaks at 71.8 ppm and 67.6 ppm, having the greatest intensity, correspond to the symmetric 1,3-butadiynic carbons of the imide fragments and the ones at 73.8, 72.7, 71.9 and 70.8 ppm are the 1,3-butadiynic carbons formed by the heterogeneous coupling between imide and ether monomers.

The molar ratio of the two monomers incorporated in the copolymers was calculated using ^1H NMR by integrating the aromatic protons at 7.96-7.77 ppm (monomer **II-7**) and at 6.98-6.79 ppm (monomer **III-3**) (Appendix 3). The calculated ratios of monomer **III-3**/ monomer **II-7** varied from 0.9/1 for polymer **III-4b** to 18.5/1 for polymer **III-4e**. It was found also that the mol % incorporation of monomer **II-7** was, in all cases, lower than the corresponding feed ratios. This indicated a higher reactivity of monomer **III-3** compared to monomer **II-7**.

All of the polymers were isolated as white fibrous materials and displayed excellent solubility in chlorinated hydrocarbons, N,N'-dimethylformamide, N-methyl-2-pyrrolidinone and N,N'-dimethylacetamide. Free standing, tough, flexible, transparent films could be cast from 1,1,2,2 tetrachloroethane.

These polymers have high molecular weights as proved by their inherent viscosities which varied from 0.216 to 1.126 dL/g (Table III.1). They have a good thermal stability, as their decomposition temperatures for 5% weight loss in N_2 varied from 364°C (polymer **III-4a**) to 414 °C (polymer **III-4f**) as assessed by TGA (at a heating rate of 10 °C). The thermal stability increased when a higher molar percent of

monomer **II-7** was incorporated into polymers. Differential scanning calorimetry revealed that these polymers thermal reaction with a maximum exothermic peak between 224 °C and 262 °C (Figure **III.4**), according to the content of the imide in the polymers.

Table III.1. Characterization of polymers **III-4a-f**

Polymer	II-7 Feed ^a (% mol)	II-7 Incorporated ^b (% mol)	[M] ^c (mol/L)	Yield ^d (%)	[η] ^e (dL/g)	T _d ^f (°C)	T _{max} ^g (°C)
III-4a	0	0	0.060	71	0.204	363	130 ; 240
III-4b	50	46.5	0.053	66	1.126	364	224
III-4c	91	90.4	0.049	63	0.216	389	237
III-4d	93	91.9	0.048	38	0.596	389	257
III-4e	95	94.9	0.048	55	0.365	389	260
III-4f	100	100	0.17	60	0.361	414	262

a- Mol % ratio of **II-7** in the monomer feed;

b- Mol % ratio of **II-7** incorporated in polymers determined by ¹H NMR;

c- Concentration of the monomers in the feed;

d- % Yield of polymer obtained after reverse precipitation;

e- Inherent viscosity measured in DMF at 30 °C;

f- Decomposition temperature as calculated at 5% weight loss in N₂ (10° C/min);

g- Peak temperature of the exotherm, as assessed by DSC under nitrogen at 10° C/min.

A different behavior was observed for polymer **III-4a** which displayed a sharp exotherm at 130 °C and a second, broader at 262 °C. The broad exotherms observed for all the polymers were likely to be caused by reaction of the diacetylene moieties. The sharp exotherm observed in the case of polymer **III-4a** was most likely due to the reaction of ethynyl end groups¹³ present at the periphery of the polymer in a greater

number than in any of the other copolymers. Thermal cross-linking of monoacetylenes involves coupling and trimerization reactions, which are known to take place around 150 °C.¹⁴

Figure III.4. DSC traces of polymers III-4a-f

III.4. Polymer Cross-Linking

The photochemically induced cross-linking reactions of the diacetylene polymers III-4a-e were studied and compared. Exposure of thin polymer films to UV light 250-420 nm for 40 min caused obvious changes in solubility and color. The UV-cured polymers were found to be slightly soluble in TCE and insoluble in chloroform and changed from transparent colorless to light yellow. These changes can be attributed to cross-linking of the diacetylene moieties in the polymer backbone, through 1,4-addition type reactions.¹⁵

From the ^{13}C CP MAS studies was determined that there are residual diacetylene moieties that did not react upon UV irradiation. These groups can be used further cured thermally at temperatures typically above 200 °C. However, thermal cross-linking resulted in further coloring to dark red and film brittleness.

To study the structural changes that occur during the photoinduced cross-linking process, several experiments were carried out on polymer **III-4e**. ^{13}C CP/MAS NMR studies were performed on polymer **III-4e**. Figure **III.5** displays the ^{13}C CP/MAS NMR spectra of polymer **III-4e** that was irradiated for 40 min at 254-450 nm and that of a nonirradiated sample. The characteristic peaks observed for the nonirradiated polymer are the methylene carbons ($-\text{CH}_2-$) at 28 ppm, 1,3-butadiyne carbons ($-\text{C}\equiv\text{C}-$) at 67 ppm and 74 ppm, aromatic carbons at 124, 133 and 138 ppm and carbonyl carbons of the imide groups at 166 ppm. For the cured sample, significant changes were observed for the ethynyl and aromatic carbons. The relative intensity of the peak at 67 ppm decreased while the intensity of the peak at 72 ppm increased, confirming the photoinduced conversion of the diacetylene groups.

The changes observed for the aromatic and carbonyl carbons proved that the imide group also reacted upon UV irradiation. This can be explained by the presence of a large number of phthalimide units in the polymer backbone, which is known to undergo a photochemical reaction with γ -hydrogen abstraction involving the carbonyl group.¹⁶

Figure III.5. Polymer III-4e: (a) ^{13}C NMR spectrum in CDCl_3 (400 MHz); (b) ^{13}C CP/MAS NMR spectrum before irradiation; (c) ^{13}C CP/MAS NMR spectrum after irradiation for 40 min at 254-450 nm

FTIR studies performed on thin polymer films showed that changes occurred at both ethynyl and imide units (Figure III.6). The intensity of the $\equiv\text{C}-\text{C}$ stretching vibration band at 937 cm^{-1} decreased, as did the $\equiv\text{C}-\text{H}$ deformation vibration band of the terminal ethynyl groups at 628 cm^{-1} . The appearance of a small hydroxyl peak at 3600 cm^{-1} and the changes in the C-N stretching vibration band of the imide at 1350 cm^{-1} proved that photoinduced reactions involving the imide groups occurred also.

Figure III.6. IR spectra of polymer III-4e: (a) before irradiation, (b) after irradiation for 40 min at 254-450 nm and (c) after thermal treatment at $210\text{ }^{\circ}\text{C}$ for 3 hours

To test the photopatterning capability of the hyperbranched polymers, films in $2\text{ }\mu\text{m}$ thickness were spin-coated on silicon wafers and exposed at 254-450 nm light for 40 min. The irradiated area of the polymer films became less soluble to TCE and chloroform

due to cross-linking of diacetylene moieties. However, the low conversion of these reactive groups resulted in a poor photo-definition and needed further improvement.

In a comparative experiment, thermal curing of polymer **III-4e** was performed at 210 °C and induced a significant change in color (from transparent to dark red) and in the film quality (insoluble and brittle). IR data showed that thermal induced reactions involved the ethynyl groups and aryl ether groups. The formation of a large hydroxyl peak at 3670 cm^{-1} , a carbonyl group at 1870 cm^{-1} and changes in the C=C aromatic stretching vibration band at 1527 cm^{-1} suggest that a Claisen rearrangement reaction had taken place to yield fragments structurally similar to a phenol and ketone.¹⁷ The thermal induced reaction of the diacetylene groups is suggested by the changes in the intensity of the peaks at 941 cm^{-1} ($\equiv\text{C}-\text{C}$ stretching vibration band) and 628 cm^{-1} ($\equiv\text{C}-\text{H}$ deformation vibration band of terminal ethynyls).

It is known that the absorption overtones of hydroxyl group in the near-IR are the source for polymers' optical loss and therefore the use of this functional group is to be avoided in an optical material. Due to the appearance of large hydroxyl groups upon thermal treatment, as indicated by IR, and the poor quality of the cured films, studies on thermal curing were not carried out.

Further investigations were needed in order to improve the photoinduced cross-linking of these polymers. We have demonstrated previously that $\text{W}(\text{CO})_6$, a catalyst used to generate high molecular weight polyacetylene can be used to induce efficiently solid-state photo-cross-linking of polyacrylates containing ethynyl pendent groups by irradiation at wavelengths between 320 and 390 nm.¹⁸ Due to their branched structures, polymers **III-4a-e** have a large number of ethynyl groups at the periphery and thus should

be readily photochemically cross-linked in the presence of $W(CO)_6$, which should improve the photo-definition.

Polymer **III-4e** was used as a representative to demonstrate the increased photosensitivity of these polymers in the presence of $W(CO)_6$. The first test was carried out on two sample solutions in TCE at 320-390 nm (100 mW/cm^2 intensity), one containing 2 wt % of $W(CO)_6$ and the other with no initiator. The blank sample (vial 1, Figure **III.7a** and **b**), containing only polymer solution did not yield cross-linked polymer while the one containing $W(CO)_6$ (vial 2, Figure **III.7**) resulted in complete gelation within 30 s.

Figure III.7. Photoinduced cross-linking of polymer **III-4e** carried out in solution: (a) before irradiation; (b) after UV irradiation at 320-390 nm for 30s.

A second test was performed on thin polymer films that were cast on NaCl pellets and exposed to UV light (320-390 nm, 3500 mW/cm^2). Polymer **III-4-e** doped with 2 wt. % of $W(CO)_6$ was irradiated for 40 minutes. The cured film became completely insoluble in TCE or chloroform. UV exposure for 60 min of the undoped polymer resulted only in slight cross-linking as the polymer film was still soluble in TCE.

The last test performed was to prove that this system could be used successfully for photopatterning. Thus, polymer **III-4e** films containing 2 wt. % $W(CO)_6$ were spin-coated onto silicon wafers and exposed to UV light (3500 mW/cm^2) through a contact mask. Figure **III.8** shows a scanning electron micrograph (SEM) of a pattern in an approximately $2 \mu\text{m}$ thick film. The silicon wafer was clean and the top of the polymer film was quite smooth. The cross-section view (Figure **III.8.b**) of an $8 \mu\text{m}$ feature showed the residual polymer that could not be removed by washing with TCE.

Figure III.8. SEM images of photopatterned film of polymer **III-4e**: (a) top view and (b) cross section

Infrared spectroscopy was used to monitor the structural changes that occurred during irradiation of the polymer films. Following the spectral changes of the carbonyl absorption of $W(CO)_6$ it was observed that these findings are similar to our previous ones for the acrylate polymers having pendent ethynyl groups. The initial IR spectrum of $W(CO)_6$ doped into a thin polymeric film showed a sharp peak at 1974 cm^{-1} with a small shoulder at 2015 cm^{-1} (Figure **III.9.2.a**). UV photolysis at 320-390 nm for 30 sec at ambient temperature generated the formation of alkyne pentacarbonyl derivatives having

three characteristic bands at 1936 cm^{-1} (medium), 1967 cm^{-1} (strong) and 2091 cm^{-1} (weak). The peak values and relative intensities of these features correspond to the reported alkyne- $\text{W}(\text{CO})_5$ fragments.¹⁹ According to Marshall's²⁰ results, these pentacarbonyl complexes lose another CO group and coordinate with another alkyne molecule forming a tetracarbonyl complex that initiates the photocatalytic polymerization of the alkynes. These intermediates could not be determined in our IR study, due to the known fact that they have a very short lifetime at ambient temperatures. Prolonged irradiation ($> 1000\text{ sec}$) of the polymer films resulted in the nearly complete loss of CO ligands from the tungsten carbonyl species.

The presence of pentacarbonyl intermediates is noteworthy in that they represent the first stage of the photopolymerization mechanism of alkynes by $\text{W}(\text{CO})_6$, and potentially the mechanism by which cross-linking occurred.

The IR analysis showed also that the photo-initiated cross-linking induced by $\text{W}(\text{CO})_6$ takes place mainly at the 1,3-butadienic and ethynyl groups, and no major changes were observed for the imide functional group. The intensity of the $\equiv\text{C}-\text{C}$ stretching vibration band at 939 cm^{-1} decreased, as did the $\equiv\text{C}-\text{H}$ deformation vibration band of the terminal ethynyl groups at 628 cm^{-1} (Figure III.9.2.b). This suggests that both diacetylene and terminal ethynyl groups reacted upon photoirradiation.

Figure III.9. FTIR spectral changes of polymer **III-4e** doped with 2% wt $\text{W}(\text{CO})_6$ after irradiation at 320-390 nm: (1) carbonyl peak of $\text{W}(\text{CO})_6$ during the first 5 min of irradiation and (2) fingerprint region: (a) before UV irradiation and (b) after UV irradiation for 40 min

These changes could also be observed in the ^{13}C CP/MAS NMR spectra of polymer **III-4-e**. Figure **III.10** displays the ^{13}C CP/MAS NMR spectra of polymer **III-4e** doped with 2 wt % of $\text{W}(\text{CO})_6$ and cured for 40 min and a nonirradiated sample. Characteristic peaks were observed at 20-34 ppm (methylene carbons), 65-75 ppm (ethynyl carbons), 120-140 ppm (aromatic carbon atoms) and 160-175 ppm (carbonyl carbon atoms). No change was observed for the carbonyl, aromatic and methylene carbons, which excludes the involvement of the imide groups in the cross-linking process. The relative intensity of the peak at 67 ppm decreased and the peak at 72 ppm increased with slight shift to 74 ppm, which demonstrates the high degree of reaction of the diacetylene and ethynyl end groups. This result is consistent with the hypothesis that gelation/cross-linking involves a chemical transformation of the ethynyl groups to polyene-type structure induced by the $\text{W}(\text{CO})_6$ initiator. However, the formation of new peaks corresponding to the alkene carbons was not observed, as they might be overlapped by the aromatic $\text{C}=\text{C}$ peaks. At the same time, the degree of cross-linking is low since there are still some ethynyl groups left in the cross-linked polymers.

Figure III.10. Comparison of ^{13}C NMR spectra: (a) ^{13}C NMR spectrum of polymer **III-4e** in CDCl_3 , (b) CPMAS ^{13}C NMR spectrum of polymer **III-4e** before irradiation and (c) CPMAS ^{13}C NMR spectrum of polymer **III-4e** doped with 2% of $\text{W}(\text{CO})_6$ after 40 min of irradiation at 320-390 nm

III.5. Optical Properties

As mentioned in Chapter I the basic requirement for optical waveguiding is a relatively high difference between the refractive indices of the waveguides' core and cladding. A higher refractive index is required for the core and a lower refractive index for the cladding. The optical properties of polymers such as in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices, birefringence and optical dispersion are important parameters of waveguide devices. The optical properties of all the polymers of the series **III-4a-f** were determined by using ellipsometry, at room temperature.

Polymer films were prepared by spin-coating the polymer solution in TCE (3.5-5 wt. %) onto a silicon wafer in a two-step process, first at 500 rpm and then at 1800 rpm, followed by drying under vacuum (5 mmHg) at 80 °C for 6-8 hours. Thin polymer films with thickness between 400 nm and 800 nm thickness were used to determine the refractive indices, at room temperature (Table **III.2**). The values of the refractive indices decreased as the amount of the fluorocarbon content in the polymer (mol %, monomer **II-7**) increased. The n_{TE} and n_{TM} reached maximum values (1.6169 and 1.6167) for polymer **III-4a**. Figure **III.11** shows that the refractive indices were between 1.5454 and 1.6313 for the in-plane (TE) polarization and 1.5329 to 1.6283 for the out-of-plane (TM) polarization. These values could be controlled by varying the ratio of the two diethynyl monomers.

Table III.2. Refractive indices for polymers III-4a-f

Polymer	% mol monomer II-7 ^a	n_{TE} ^b	n_{TM} ^c	Δn ^d
III-4a	0.0	1.6169	1.6167	0.0020
III-4b	46.5	1.6069	1.601	0.0059
III-4c	90.4	1.5653	1.55	0.0103
III-4d	91.9	1.5611	1.5459	0.0152
III-4e	94.9	1.5518	1.5348	0.0170
III-4f	100.0	1.5454	1.5329	0.0125

a- Mol % ratio of II-7 incorporated in polymers determined by 1H NMR;

b- In-plane refractive index determined by ellipsometry;

c- Out-of-plane refractive index determined by ellipsometry;

e- Birefringence calculated as the difference between n_{TE} and n_{TM}

Figure III.11. Plot of refractive index and birefringence versus mol % of monomer II-7 in polymers III-4a-f

The optical dispersions of all the polymers was determined (Figure III.12), as another important parameter for waveguide devices.²¹ The dispersion values were calculated as $dn/d\lambda$ in the wavelength range of interest, for the three typical telecommunication wavelengths (810 nm, 1310 nm and 1550 nm). These values were larger at 840 nm, varying from -3×10^{-5} to $-5 \times 10^{-5} \text{ nm}^{-1}$, smaller at 1310 nm, ranging from -1×10^{-5} to $-2 \times 10^{-5} \text{ nm}^{-1}$ and negligible at 1550 nm with values of 0 to -1×10^{-5} .

Figure III.12. Refractive index dispersion of polymers III-4a-f

The dispersion values did not change upon UV cross-linking at all the wavelengths of interest. A large change in dispersion was observed at 840 nm upon thermal cross-linking, as the values almost reached -10×10^{-5} . At 1310 nm the dispersion values increased up to only -3×10^{-5} , while no change was observed at 1550 nm.

Figure III.13. Refractive index dispersion of polymer **III-4e**: (a) uncured, (b) UV irradiated and (c) thermally treated sample at 210 °C for 3 hours

The difference between n_{TE} and n_{TM} defines the birefringence (Δn) of the thin polymer film and is an indication of the optical anisotropy of the material. The birefringences of polymers **III-4a-e** were found to be directly related to the content of monomer **II-7** in the polymer. These values ranged from 1.25×10^{-2} to 2×10^{-3} . The six fold decrease in birefringence could be explained by the highly branched structure and by the presence of bulky hexafluoroisopropylidene moieties. The branched structures induce smaller chain interactions which reduces the planar orientation characteristic of linear aromatic polyimides. This finding is also supported by the analysis of an energy minimized molecular model of monomer **III-3**, using a commercial modeling software package (SPARTAN) as the calculated dihedral angle between the phenyl groups were 124.26, 69.83 and 55.83 respectively (Figure **II.14**). The bulky hexafluoroisopropylidene units reduced the birefringence also by increasing the polymer's free volume. The polymers with a higher molar ratio of monomer **III-3** have a smaller birefringence which

can be attributed to the higher degree of branching and also to the larger amount of flexible ether linkages.

Figure III.14. AM1 optimized molecular conformation of monomer **III-3**

The photo-cross-linking of the undoped polymers involves 1,4-addition reactions of diacetylene moieties and induces the formation of small conjugated domains of double and triple bonds. However, the degree of conversion of these moieties is small (5% as observed from their peak intensities by spectroscopic means) and therefore they do not have a significant influence on the chain packing density. This was observed in particular for the polymers having a higher degree of branching induced by increasing the amount of monomer **III-3**. The observed variation in film thickness upon UV irradiation was small (typically about 3 %). However, the increase of molar ratio of monomer **II-7** in the polymers allowed for better chain packing, as demonstrated by higher variations in

film thickness to as much as 10% for polymer **III-4e**. At the same time, a slight decrease of typically 0.1% was observed for both in-plane and out-of plane refractive indices.

Meanwhile, polymers **III-4a-e** doped with 2 wt of % $W(CO)_6$ and cured for 40 min at 320-390 nm showed similar optical properties to the undoped polymers. The variation in refractive index was only at the third decimal (± 0.002), while maintaining the same birefringence.

In comparison to photo-cross-linking, thermal cross-linking induced more drastic structural changes in polymers. The variation in film thickness was larger, varying from 2.1% for polymer **III-4-a** to 14.9% for polymer **III-4e**, demonstrating a greater packing density upon thermal treatment. Although the variation in thickness was relatively large, an unexpected decrease in the birefringence values was observed, the highest value being only 0.96 %.

We have also carried out wide-angle X-ray diffraction experiments that can provide additional structural information regarding ordering within the polymer. Short range ordering within the polymer can increase a polymer's scattering optical loss. Polymer **III-4e** revealed structureless WAXD patterns (Figure **III.15.a**). Three broad diffraction peaks were observed: the first at 15.64° , the second at 26.10° and the third at 41.00° . Similar patterns were observed for all the polymers, which indicate amorphous morphologies without short range ordering.

Figure III.14. WAXD of polymer **III-4e**: (a) uncured and (b) UV irradiated

III.7. Conclusions

A series of photosensitive hyperbranched poly(ether imides) containing diacetylene moieties with adjustable refractive indices and small birefringences were designed and synthesized. An increased degree of branching within the polymers resulted in a considerably reduced birefringence to as low as 0.2×10^{-2} .

These polymers are photosensitive but the photo-definition of the irradiated samples at 254–450 nm was poor. Photoinduced cross-linking of all the polymers was greatly enhanced by doping with small amounts of $W(CO)_6$ and irradiation at 320–390 nm using a photomask produced fine patterns.

The optical properties of the photo-cross-linked polymers varied only slightly causing a decrease in the refractive index values to 0.4×10^{-3} to 6.5×10^{-3} . In comparison,

thermally cured polymers underwent drastic changes inducing a high increase in both refractive index and birefringence.

III.8. Experimental Section

Materials

All reagents and solvents were obtained from Aldrich Chemical Co. and used as received unless otherwise specified. 4,4'-(Hexafluoroisopropylidene)diphtalic anhydride was purchased from Chriskev Company, Inc. Cuprous chloride (BDH Chemicals LTD.) was purified by dissolution in conc. HCl followed by precipitation in water, filtration, washing with ethanol and diethyl ether and dried under vacuum at 100 °C.

Polymer films were prepared by spin-coating TCE solutions (3.5 wt %) onto a silicon wafer using a two step spinning rate process, first at 500 rpm and then at 1800 rpm, followed by drying under vacuum at 80 °C for 6-8 h. The film thickness varied from 700 to 1000 nm.

N,N'-Dipropargyl(4,4'-hexafluoroisopropylidene)bispthalimide (**II-7**) is a known compound, whose spectral data (FTIR, ^1H NMR, ^{13}C NMR) agreed with literature values.²² Polymer **III-4f** is a known polymer whose spectral characteristics (FTIR, ^1H NMR, and ^{13}C NMR) agreed with the reported values.

Measurements

The monomers and polymers were measured as outlined in Chapter II (pg. 54). The inherent viscosity of the polymers were determined using an Ubbelohde viscometer for 0.5 g/dL DMF solution at 30 °C. UV curing of thin polymer films was performed using an Ultracure 100SS Plus/ Novacure system with a 254-450 nm and 320-390 nm filter at a light intensity of 3500 mW/cm².

Polymer thin films and photopatterns were prepared and measured as presented in Chapter II (pg. 55).

Monomer Synthesis

Monomer III-3

In a three-neck, round-bottomed flask equipped with a condenser, were added sodium hydroxide (250 mL, 20%), 1,1,1-tris(4-hydroxyphenyl)ethane (5.00 g, 16.0 mmol) and tetrabutylammonium bromide (0.77 g, 2.4 mmol). The solution was mixed for one hour at room temperature to form the corresponding sodium phenolate. Propargyl bromide (5.71 g, 48.0 mmol) was added and the reaction mixture was heated up to 60 °C. After 5 h, the reaction was stopped and the product extracted with ethyl acetate. The organic layer was washed three times with water and then washed with a saturated NaCl solution. After drying over anhydrous sodium sulfate and removal of the solvent, the product (yellow solid) was recrystallized twice from ethanol to give large yellow crystals: 4.05 g (59 % yield); mp: 74-76 °C. IR (KBr, cm⁻¹): 3289 (≡C-H), 2121 (-C≡C-); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.99 (6H, d, *J*= 9.8 Hz), 6.85 (6H, d, *J*=9.8 Hz), 4.65 (6H, d, *J*= 2.3 Hz), 2.51 (3H, d, *J*= 2.36 Hz), 2.1 (3H, s); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 155.68, 142.49, 129.65, 114.03, 78.72, 75.43, 55.80, 50.71, 30.73.

Polymer Synthesis

Polymer	% Mol II-7 Incorporated
III-4a	0
III-4b	46.5
III-4c	90.4
III-4d	91.9
III-4e	94.9
III-4f	100

Polymer III-4a

To a dried three-neck round bottomed flask were added copper (I) chloride (0.012g, 0.11 mmol), N,N,N',N'-tetramethylethylenediamine (TMEDA) (0.015g, 0.13 mmol), Py (0.01g, 0.12 mmol) and 10 mL of anhydrous nitrobenzene. To the flask was attached a water condenser and an inlet and outlet for O₂. The flask was warmed up to 40

°C while oxygen was bubbled through the reaction mixture. 1,1,1-Tris(4-propargyloxyphenyl)ethane (**III-3**) (0.500 g, 1.20 mmol) was dissolved in 10 mL nitrobenzene and added drop wise, after 1h to the catalyst mixture. The reaction was stopped after one and a half hours. The viscous solution was precipitated in 400 mL of acidified methanol (2% HCl in MeOH). The fibrous white polymer was filtered, reverse precipitated and dried under vacuum at 50 °C (yield 71 %).

$\eta_{inh} = 0.204$ dL/g (DMF, $c = 0.5$ g/dL, 30 °C); IR (NaCl, cm^{-1}): 3299 ($\equiv C-H$); 1H NMR(400 MHz, $CDCl_3$) δ (ppm): 6.99 (s, br, aromatic CH), 6.85 (m, br, aromatic CH), 4.66 (m, br, CH_2), 2.50 (s, br, $\equiv C-H$), 2.1 (s, br, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 155.67, 155.51, 142.66, 142.60, 142.41, 142.35, 129.70, 129.64, 114.03, 114.01, 78.72, 75.47, 74.76, 71.00, 56.20, 55.77, 50.71, 30.73.

Polymer **III-4b**

The above procedure was followed using CuCl (0.01 mg, 0.10 mmol), TMEDA (0.07 g, 0.06 mmol), Py (0.01g, 0.14 mmol), **III-3** (210.28mg, 0.5 mmol), **II-7** (259.20 mg, 0.5 mmol) and 18.8 mL nitrobenzene. The polymerization was carried out for one hour at 50 °C yielding a white fibrous polymer soluble in common organic solvents (yield 66 %).

$\eta_{inh}=1.126$ dL/g (DMF, $c = 0.5$ g/dL, 30 °C); IR (NaCl, cm^{-1}): 3304 ($\equiv C-H$), 1781, 1728 ($C=O$); 1H NMR(400 MHz, $CDCl_3$): δ (ppm) 7.94 (s, br, aromatic CH), 7.84- 7.78 (m, aromatic CH), 6.97 (s, br, aromatic CH), 6.80 (s, br, aromatic CH), 4.67 (s, br, CH_2), 4.50 (s, br, CH_2), 2.95 (s, br, $\equiv C-H$), 2.88 (s, br, $\equiv C-H$), 2.50 (s, br, $\equiv C-H$), 2.24 (s, br, $\equiv C-H$), 2.08 (s, br, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.75, 165.56, 165.39,

155.67, 155.49, 142.60, 142.36, 138.99, 135.88, 132.87, 132.77, 132.55, 132.48, 129.69, 125.15, 124.73, 124.05, 121.86, 113.99, 78.72, 75.47, 74.75, 73.80, 72.74, 71.97, 71.81, 70.98, 70.89, 67.65, 57.73, 56.20, 56.10, 55.77, 50.70, 31.25, 29.73, 28.37, 27.93, 27.33.

Polymer III-4c

The same procedure was applied using CuCl (0.005 mg, 0.005 mmol), TMEDA (0.006 g, 0.005 mmol), Py (0.007 g, 0.008 mmol), **III-3** (21.028 mg, 0.050 mmol), **II-7** (259.2 mg, 0.500 mmol) and 11.2 mL nitrobenzene. The polymerization was carried out at 50°C for three hours, yielding a white powdered polymer soluble in common organic solvents (yield 63 %). $\eta_{inh} = 0.216$ dL/g (DMF, $c = 0.5$ g/dL, 30 °C); IR (NaCl, cm^{-1}): 3298 ($\equiv C-H$), 1781, 1728 (C=O); 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94 (s, br, aromatic CH), 7.84- 7.78 (m, aromatic CH), 6.97 (s, br, aromatic CH), 6.80 (s, br, aromatic CH), 4.67 (s, br, CH_2), 4.50 (s, br, CH_2), 2.95 (s, br, $\equiv C-H$), 2.88 (s, br, $\equiv C-H$), 2.50 (s, br, $\equiv C-H$), 2.24 (s, br, $\equiv C-H$), 2.08 (s, br, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.76, 165.56, 164.32, 155.53, 142.62, 139.02, 138.94, 135.91, 132.90, 132.81, 132.55, 132.58, 132.50, 129.70, 125.16, 124.74, 124.04, 121.88, 114.02, 73.82, 72.75, 71.96, 71.83, 70.89, 67.63, 56.26, 56.14, 55.81, 50.73, 30.72, 27.89, 27.35

Polymer III-4d

The same procedure was applied using CuCl (0.010 mg, 0.010 mmol), TMEDA (0.012 g, 0.01 mmol), Py (0.011g, 0.015 mmol), **III-3** (31.54mg, 0.075 mmol), **II-7** (518.4 mg, 1 mmol) and 22 mL nitrobenzene. The polymerization was carried out at 40°C for three hours and then at 60°C for another two hours, yielding a white fibrous

polymer soluble in common organic solvents (yield 38 %). $\eta_{inh} = 0.596$ dL/g (DMF, $c = 0.5$ g/dL, 30°C); IR (NaCl, cm^{-1}): 3298 ($\equiv\text{C-H}$), 1781, 1728 (C=O); ^1H NMR(400 MHz, CDCl_3): δ (ppm) 7.94 (s, br, aromatic CH), 7.84- 7.78 (m, aromatic CH), 6.97 (s, br, aromatic CH), 6.80 (s, br, aromatic CH), 4.67 (s, br, CH_2), 4.50 (s, br, CH_2), 2.95 (s, br, $\equiv\text{C-H}$), 2.88 (s, br, $\equiv\text{C-H}$), 2.50 (s, br, $\equiv\text{C-H}$), 2.24 (s, br, $\equiv\text{C-H}$), 2.08 (s, br, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 165.76, 165.56, 164.32, 155.53, 142.62, 139.02, 138.94, 135.91, 132.90, 132.81, 132.55, 132.58, 132.50, 129.70, 125.16, 124.74, 124.04, 121.88, 114.02, 73.82, 72.75, 71.96, 71.83, 70.89, 67.63, 56.26, 56.14, 55.81, 50.73, 30.72, 27.89, 27.35

Polymer III-4e

The above procedure was used employing CuCl (0.010 mg, 0.010 mmol), TMEDA (0.011 g, 0.010 mmol), Py (0.008 g, 0.014 mmol), **III-3** (21.028 mg, 0.050 mmol), **II-7** (518.4 mg, 1.000 mmol) and 21.5 mL nitrobenzene. The polymerization was carried out at 70°C for three and a half hours yielding a white powdered polymer soluble in common organic solvents (yield 55 %). $\eta_{inh} = 0.365$ dL/g (DMF, $c = 0.5$ g/dL, 30°C); IR (NaCl, cm^{-1}): 3298 ($\equiv\text{C-H}$), 1781, 1729 (C=O); ^1H NMR(400 MHz, CDCl_3): δ 7.96- 7.77 (m, aromatic H); 6.98- 6.79 (m, aromatic H), 4.65 (s, br, CH_2); 4.51 (s, br, CH_2); 2.97 (s, $\equiv\text{C-H}$), 2.89 (s, $\equiv\text{C-H}$), 2.85 (s, $\equiv\text{C-H}$), 2.09 (s, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ 165.52; 165.36; 155.51; 142.60; 139.00; 135.91; 132.79; 132.48; 129.68; 127.59; 125.15; 124.72; 124.03; 121.86; 119.00; 113.99; 73.80; 72.75; 71.95; 71.82; 70.87; 67.60; 56.12; 49.44; 30.68; 29.59; 27.87; 17.67.

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CHAPTER IV. A NEW PHOTO-CROSS-LINKING SYSTEM CONSISTING OF POLYMERS WITH PENDENT ETHYNYL GROUPS AND $W(CO)_6$

VI.1. Introduction

The development of materials for photonic applications that can be rapidly and efficiently processed at low cost is an important and expanding area of research. An easy and cost effective approach to achieving specified requirements would be to use the existing polymers with or without small amounts of additives. At present, there is high demand for photosensitive polymers for fabrication of optical waveguides in a simple process without the use of a photoresist. Therefore, it would be of great interest to develop a versatile formulation based on the known polymers that can be transformed to become photosensitive.

The ethynyl moiety has been used as a reactive group in thermal cross-linking of many different classes of polymers including polyimides,¹ poly(aryl ether sulfone)s,² polyphenylenes,³ polyesters⁴ and poly(phenyl quinoxaline)s.⁵ One of the main advantages of the ethynyl group is that no volatile byproducts are formed during cure. However, to date there are no reports on the photoinitiated cross-linking of polymers containing the ethynyl moiety.

Aromatic and aliphatic mono-substituted acetylenes are known to undergo catalytic photo-polymerization to yield the corresponding polyacetylenes in the presence of group VI metal carbonyls [e.g., $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$] in halogenated

solvents,^{6a-c} and some other group VI metal complexes.⁷ A variety of Lewis acids (e.g., SiCl_4 and GeCl_4) are also effective co-catalysts for polymerization of various acetylenes in non-halogenated solvents.⁸

Early studies by Higashimura have demonstrated that the active catalysts in the thermal polymerization of acetylenes by metal VI complexes are carbene or alkylidene complexes.⁹ Geoffroy et al. later proposed a mechanism for the photocatalytic polymerization of 1-acetylenes in the presence of W(CO)_6 .^{6c} This catalytic cycle proceeds according to Figure IV.1 and involves the formation of a pentacarbonyl tungsten acetylene complex $[(\eta^2\text{-RC}\equiv\text{CH})\text{W(CO)}_5]$ (**I**) which rearranges itself to a vinylidene complex $[\text{R(H)C}=\text{C}=\text{W(CO)}_5]$ (**II**). This step was proven to be the initiation step in the polymerization of acetylenes. Prolonged irradiation with UV light and coordination to another acetylene molecule resulted in the formation of tungsten tetracarbonyl species (complex **III**), which triggered the photocatalytic cycle. The next step involves the insertion of another acetylene molecule through a metallocyclobutene intermediate **IV**. Continuation of this cycle leads to the polymerization product. Marshall et al.¹⁰ elucidated this reaction mechanism and especially the formation of the unstable complexes **I** and **II** by the use of matrix-isolation techniques to prove spectroscopically the photochemical transformations that occurred.¹¹

Figure IV.1. Proposed mechanism of the photoinduced polymerization of acetylenes by metal (VI) hexacarbonyl^{6c}

Based on the efficiency of metal (VI) hexacarbonyls in promoting the photoinduced polymerization of acetylenes, the author proposes the use of $W(CO)_6$ as initiator in the photo-cross-linking of polymers containing ethynyl moieties. In this work, a series of acrylate polymers containing pendent ethynyl groups will be synthesized and the photoinduced chemical transformations of these polymers will be studied in the presence of $W(CO)_6$. The structure of the monomer that will be investigated is presented in Figure IV.2.

Figure IV.2. Propargyl acrylate (monomer IV-3)

IV.2. Monomer Synthesis and Characterization

Propargyl acrylate (monomer **IV-3**) was prepared according to the method shown in Scheme IV.1, from acryloyl chloride (**IV-1**) and propargyl alcohol (**IV-2**) in the presence of triethylamine using a modified procedure developed by Murray.¹² This is a one step reaction which proceeded with 59 % yield. This compound was characterized by IR, ¹H NMR and ¹³C NMR. The FTIR showed the characteristic absorption for the $\equiv\text{C-H}$ at 3296 cm^{-1} and for the $-\text{C}\equiv\text{C}-$ at 2135 cm^{-1} and the hydroxyl peak of the alcohol precursor was absent. The structure was confirmed by ¹³C NMR and ¹H NMR. ¹H NMR spectrum showed the ethynyl proton as a triplet at 3.05 ppm. Two characteristic peaks for acetylenic carbons were found in the ¹³C NMR spectrum at 78.77 and 76.38 ppm.

Scheme IV.1. Synthesis of propargyl acrylate **IV-3**

VI.3. Polymer Synthesis and Characterization

Acrylate polymers **IV-5a-e** having pendent ethynyl moieties were synthesized from propargyl acrylate (**IV-3**) and methyl methacrylate (**IV-4**) by radical polymerization in benzene (for **IV-5a-d**) or acetone (for **IV-5e**) initiated by benzoyl peroxide (Scheme IV.2). All of the polymers were isolated by precipitation in hexane as white powders. These polymers displayed excellent solubility in chlorinated hydrocarbons, benzene, DMF, NMP and DMAc.

Scheme IV.2. Synthesis of acrylate polymers IV-5a-e

^1H NMR, ^{13}C NMR and IR spectra of the polymers were consistent with the assigned structures. The IR bands for the ethynyl groups were found at 3300 cm^{-1} ($\equiv\text{C-H}$) and 2132 cm^{-1} ($\text{C}\equiv\text{C}$), while the ester carbonyl peaks were observed at 1736 cm^{-1} . The $\equiv\text{C-H}$ peaks in the ^1H NMR spectra were observed at 2.5 ppm. The ratios of the two comonomers in copolymers IV-5a-d were calculated using the methylene protons at 4.62 ppm ($\text{OCH}_2\text{-C}\equiv\text{C}$ within propargyl acrylate fraction) and at 3.61 ppm (from methyl methacrylate fraction). Methyl methacrylate is more reactive than propargyl acrylate in this radical polymerization reaction as proven by the higher number of methyl methacrylate fragments incorporated in the copolymers. The relative ratio of propargyl acrylate to methyl methacrylate in the copolymers ranged from 1/32.5 to 1/0.8, as determined from the NMR data.

Analyses by gel permeation chromatography indicated that copolymers IV-5a-d had weight-average molecular weights ranging from 54000 to 375000 (Table IV.1). Homopolymer IV-5e could only be obtained in relatively low molecular weight (88000)

with a large polydispersity index (8.3), indicating that chain termination likely caused by side reaction of the ethynyl group.

Table IV.1. Characterization of ethynyl-containing polymers **IV-3a -e**

Polymer	IV-3 Feed ^a (% mol)	IV-3 Incorporated ^b (% mol)	x:y ^c	M _w ^d	M _w /M _n ^d	T _g ^e (°C)	T _d ^f (°C)
VI-5a	5.0	3.0	1:32.5	350000	1.9	115	285
VI-5b	25.0	11.6	1:7.6	375000	2.4	44	287
VI-5c	50.0	34.5	1:1.9	234000	1.5	51	290
VI-5d	75.0	55.5	1:0.8	54000	1.2	37	325
VI-5e	100	100	1:0	88000	8.3	51	335

a- % Mol ratio of **IV-3** in the monomer feed;

b- % Mol ratio of **IV-3** incorporated in polymers determined by ¹H NMR;

c- Molar ratio in the final polymer, as determined from the NMR data;

d- Measured by GPC using polystyrene standards;

e- Taken from the second scan of DSC at a heating rate of 10 °C/min;

f- Onset temperature for 5% weight loss in nitrogen, as assessed by TGA at a heating rate of 10 °C/min.

The onset temperatures for 5% weight loss in nitrogen for all the polymers were determined by TGA to range from 285 °C (**IV-5a**) to 335 °C (**IV-5e**). The thermal stability of the polymers increased when a higher molar percent of monomer **IV-4** was incorporated into their structures. Differential scanning calorimetry (DSC) revealed the glass transition temperatures for all the polymers were in the range of 37 °C (**IV-5d**) to 115 °C (**IV-5a**) (Table IV.1). These ethynyl-containing polymers are thermally reactive or cross-linkable, as their DSC traces displayed one or two exothermic peaks, depending on the molar percent of monomer **IV-4** incorporated into the polymer (Figure IV.3). The polymers having the lowest molar ratio of the ethynyl moieties displayed no exotherm

(e.g. polymer **IV-5a**), while polymer **IV-5-b** exhibited only one exotherm with a maximum at 275 °C. Polymers **IV-5c-e** with over 34.5 molar % of monomer **IV-4** incorporated displayed two exotherms, at approximately 160 °C and 260 °C. The presence of the two exotherms indicates that there are two different cross-linking reactions.¹³ Initially, the coupling reaction of the ethynyl groups to form the ene-yne structures takes place, which thermally cyclize to aromatic and polyaromatic structures.

Figure IV.3. DSC traces of polymers **IV-5a-e**

IV.4. Polymer Cross-linking

To demonstrate photo-cross-linking of these polymers in the presence of $W(CO)_6$, three experiments were carried out using polymer **IV-5c** as a representative example. First, irradiation of a polymer solution in TCE (6.5% wt/v) at 320-390 nm using a 100 mW/cm² intensity beam (Ultracure 100SS Plus/Novacure system) did not yield any

polymer gels after one hour. After doping the polymer solution with 5 mol% of W(CO)_6 and exposure to UV light for 30 sec, a gelation clearly occurred. Polymer films doped with 5 mol% of W(CO)_6 were then irradiated (320-390 nm, 3500 mW/cm^2) for 60 min at 70°C in argon and were found to be completely insoluble in organic solvents. Infrared analysis performed on polymer films that were cast on NaCl plates and exposed to UV light showed that the ethynyl absorption at 3300 cm^{-1} ($\equiv\text{C-H}$) decreased by nearly 67 % after 60 min (Figure IV.4.a. and b). UV exposure of the undoped polymer film after 60 min did not result in any changes in the IR spectrum.

As mentioned previously, Marshall et al.^{10b} demonstrated by spectroscopic means the formation of the intermediates involved in the photopolymerization of acetylenes by W(CO)_6 . The IR bands of all these catalytic intermediates are reported and can be easily assigned.^{11a} In this study, the initial IR spectrum of the W(CO)_6 -doped polymer films showed a sharp peak at 1977 cm^{-1} with a small shoulder at 2016 cm^{-1} (Figure IV.4.b). UV photolysis at 320-390 nm for 40 sec at ambient temperature in nitrogen generated the acetylene pentacarbonyl derivatives having three characteristic bands at 1935 cm^{-1} (medium), 1962 cm^{-1} (strong) and 2089 cm^{-1} (weak). The peak positions and relative intensities are consistent with reported acetylene- W(CO)_5 fragments.⁴ The tungsten tetracarbonyl complexes that are known to be intermediates in the acetylene polymerization¹⁴ could not be detected in our IR study, due to the known fact that they have a very short lifetime at ambient temperatures. Prolonged irradiation ($> 1000 \text{ sec}$) of the polymer films resulted in the nearly complete loss of carbonyl ligands from the tungsten carbonyl species (99 %).

To study in more detail the photoinduced structural changes that occurred upon irradiation, ^{13}C CP/MAS NMR experiments were carried out on polymer **IV-5e**. Figure IV.5 displays the ^{13}C CP/MAS NMR spectra of polymer **IV-5e** doped with 2% $\text{W}(\text{CO})_6$ cured for 60 min at 100°C in nitrogen and the ^{13}C NMR of the nonirradiated sample. Characteristic peaks in the nonirradiated sample were observed at 34 ppm (methylene carbon atoms **1**), 40 ppm (methine carbon atoms **2**), 52 ppm (methylene carbon atoms **4a**), 75 ppm (ethynyl carbon atoms **6a**) and 79 ppm (ethynyl carbon atoms **5a**). In the cured sample the formation of new carbons at 136 ppm (alkene carbon atoms **5b**), 130 ppm (alkene carbon atoms **6b**) and 65 ppm (methylene carbon atoms **4b**) indicated that $\text{W}(\text{CO})_6$ induced an ethynyl to polyene type of reactions upon irradiation.

Figure IV.4. FTIR spectra of polymer IV-5c at different stages of photo-cross-linking for (a) $\equiv\text{C-H}$ stretch 0-350 sec.; (b) $\equiv\text{C-H}$ stretch 5-60 min and (b) carbonyl peaks of W(CO)_6 and acetylene- W(CO)_5 species (0-350 sec.)

Figure IV.5. Changes in ^{13}C NMR spectra of polymer IV-5-a: (a) in CDCl_3 before irradiation and (b) ^{13}C CP/MAS NMR spectrum after UV irradiation for 60 min at 100°C in nitrogen (* spinning side-band)

The DSC analysis of polymer IV-5-c also revealed a significant change in polymer structures before and after UV irradiation (for 60 min at 70°C , in nitrogen), as the photo-irradiated polymer had a broad T_g around 80°C and negligible exotherm at

150 °C (Figure IV.6, trace b). It can be noticed that the second exotherm around 260 °C had only slightly changed while the first exotherm, at 160 °C almost completely disappeared. The absence of the first exotherm on the UV cured sample suggest that the reactivity of structures thermally at lower temperatures (160 °C) and photochemically at ambient temperatures are quite similar and can be further thermally cross-linked at higher temperatures.

Figure IV.6. DSC traces of polymer **IV-5c**: (a) before UV irradiation and (b) after UV irradiation for 60 min at 70 °C

Finally, direct photopatterning of polymer **IV-5-c** (doped with 5 mol% of $\text{W}(\text{CO})_6$) on a silicon wafer was achieved by UV irradiation (3500 mW/cm^2) of an approximately 2 μm -thick film through a contact mask (Figure IV.7), at 75 °C in argon. The darker areas represent the polymer while the lighter color the silicon wafer. In comparison, the undoped polymer films could not be patterned in the same way.

Figure IV.7. SEM micrograph of a patterned film of polymer **IV-5c**

IV.5. Factors Influencing the UV Cure

The efficiencies of the UV curing reaction of polymers **IV-5a-e** were determined by monitoring the decrease in the absorption of the ethynyl $\equiv\text{CH}$ stretch at 3300 cm^{-1} , using time resolved FTIR. The decreased absorption with the curing time indicates that the ethynyl bonds have reacted during UV irradiation. The extent of curing or conversion (x) was calculated using the Lambert-Beer law (Equation IV.1), as the ratio of the absorbance at time t during curing to the absorbance before curing ($t = 0$). The variable thickness of the polymer films required the use of the ester carbonyl bond absorption which does not undergo modification during the curing process. Therefore, the integrated value of the ethynyl $\equiv\text{C-H}$ absorption peak at 3300 cm^{-1} was normalized to the integrated value of the ester C=O absorption peak at 1730 cm^{-1} .

$$x = 1 - \frac{\left(A_{\equiv\text{CH}} / A_{\text{ester C=O}} \right)_t}{\left(A_{\equiv\text{CH}} / A_{\text{ester C=O}} \right)_{t=0}} \quad \text{Equation IV.1}$$

The percentage of cross-linking was calculated according to the amount of ethynyl moieties incorporated into the polymer, by multiplying the conversion (x) of the reactive units with the molar % of monomer **IV-3**.

Influence of the ethynyl content in polymer

Polymer films doped with 10 % mol $W(CO)_6$ per mol of ethynyl were cast on KBr pellets and exposed to a 320-390 nm UV source at room temperature in argon for one hour. The cross-linking density for polymers **IV-5a** and **b** and were only 0.8 % and 1.5 % respectively, after 60 min of irradiation (Figure **IV.8**) which can be attributed to the fact that only 2.9 and 11.6 % molar percent of ethynyl moieties were incorporated in these polymers. Therefore, these polymers possessed a reduced number of curing sites in close vicinity that have restricted mobility and are capable of reacting. With a higher molar % of monomer **IV-3** incorporated into the polymers, the density of cross-linking increased, varying from 5 % for polymer **IV-5c** to 42 % for polymer **IV-5e**. This is probably due to the higher number of reactive sites found in closer vicinity able to react when irradiated. Considering that polymer **IV-5c** has a sufficient number of cross-linked units for patternability, we have used this polymer in our following studies.

Figure IV.8. Percentage cross-linking of polymers IV-5a-e upon UV irradiation

Influence of the amount of $W(CO)_6$ doped into the polymer

Thin films of polymer IV-5c doped with different amounts of initiator (1, 2, 5, 10 and 20 % mol $W(CO)_6$ / mol ethynyl) were irradiated with a UV source (320-390 nm) for one hour, at room temperature in argon. The data points in Figure IV.9 show the extent of curing versus the amount of $W(CO)_6$ at various times, during irradiation. The ethynyl conversion was highest when 10 % mol $W(CO)_6$ was used, and reached a maximum 17.7 % after 60 min. This means that the polymer was actually 5.07 % cross-linked. Interesting to observe was the drastic decrease in polymer cross-linking when the amount of catalyst was increased to 20 %. This was probably due to the reduction of catalytic activity of $W(CO)_6$ at high concentrations.

Figure IV.9. Conversion of ethynyl moieties at different concentrations of initiator

Influence of the curing temperature

Photo-cross-linking of polymer **IV-5-c** films doped with 10 % mol W(CO)₆ was carried out at five different temperatures, in argon. Figure **IV.10** displays the conversion versus time at 25, 50, 70, 90 and 110 °C. The conversion of the ethynyl moieties increased with increasing temperature. At temperatures below the polymer's T_g ($T_g = 51^\circ\text{C}$) a relatively low extent of cure was observed (e.g. 34 % at 50 °C). Low chain mobility and non-uniform distribution of these reactive units in space to reach the reacting distance may explain the low conversion of ethynyl moieties at these temperatures. At temperatures above T_g , the extent of curing drastically increased, reaching up to 90 % within 35 min at 110 °C. Irradiation for an additional 25 min did not yield 100 % conversion. There are two possible reasons that could explain this. First is the so-called topological limit (TL), when the unreacted groups in the network are very

much apart and they cannot meet anymore and secondly an increase in the T_g that can reach or surpass the curing temperature.¹⁵

Figure IV.10. Conversion vs. time at different curing temperatures

Kinetic study of the photo-cross-linking reaction

Plots of $\ln(1-x)$ versus time, where x is the conversion of ethynyl moieties, show that the reaction follows first order kinetics (Figure IV.11). Linear regression analysis using the least squares method was used to fit the data. The kinetic rate constants, k , derived from the slopes of each reaction isotherm, are listed in Table IV.2.

Figure IV.11. Kinetic plot of $\ln(1-x)$ versus time

Table IV.2. Kinetic analysis of the cross-linking reaction

Temperature (°C)	Rate constant $k \times 10^3 \text{ (s}^{-1}\text{)}$	Regression coefficient (R^2)
25	0.05	0.9254
50	0.1	0.9664
70	0.1	0.9359
90	0.7	0.9720
110	0.9	0.9093

From the Arrhenius plot, $\ln k$ versus $1/T$, where k is the rate constant and T is the temperature, the activation energy of the cross-linking reaction was determined (Figure IV.12). The calculated value of 34.08 kJ/mol indicates a temperature dependence of the rate constants of the photo-cross-linking reaction of polymer IV-5c in the presence of $W(CO)_6$. The linearity of the data plot, as determined from the regression coefficient (R^2) is 0.8512 indicating a less perfect fit. By excluding the data point corresponding to 70 °C,

the R^2 value increased to 0.9738. The low rate constant at this temperature and therefore the non-linearity of $\text{Ln}k$ in the Arrhenius plot can be explained by the increase in the polymer's T_g up to 80 °C, as proved by the DSC data, which decreases the chain mobility.

Figure IV.12. Arrhenius plot of the photo-cross-linking reaction of polymer **IV-5c**

A similar kinetic study was carried out on polymer **IV-5b** and it was found that a 93 % conversion of ethynyl moieties occurred (11 % cross-linking) after curing at 100 °C and the activation energy of the cross-linking reaction was 17.7 kJ/mol. This indicates that a lower activation energy is required when the T_g of the polymer is lower ($T_g = 44$ °C).

IV. 6. Conclusions

Efficient photo-cross-linking of polyacrylates having pendent ethynyl groups using $W(CO)_6$ has been demonstrated. The cross-linking process involves the formation of polyene-type structures upon irradiation at 320-390 nm, as determined by IR and NMR studies. The amount of ethynyl moieties incorporated in the polymer, the amount of initiator as well as the temperature were the main factors that influenced the curing process. Kinetic studies have demonstrated that the rate law follows first-order kinetics, with activation energies of 34.08 kJ/mol for polymer **IV-5c** and 17.7 kJ/mol for polymer **IV-5b**.

This work opens a new route to the development of various types of photo-cross-linkable polymers containing ethynyl groups in the mainchain, sidechain and chain ends, in the presence of a small amount of $W(CO)_6$ or other catalysts known to induce acetylene photo-polymerization.

II.7. Experimental Section

Materials

All reagents and solvents were obtained from Sigma-Aldrich Canada and were used as received unless otherwise specified. Methyl methacrylate (Sigma-Aldrich Canada) was purified by flash-chromatography. Benzoyl peroxide was purchased from Fisher Scientific Co. and used as received.

Measurements

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker-400 MHz and Bruker-100 MHz instrument using tetramethylsilane as an internal reference. Infrared (IR) spectra were obtained with a Bomem Michelson 120 FTIR spectrometer. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) relative to polystyrene standards, using chloroform at a flow rate of 1.0 mL/min. A UV detector set at 254 nm and refractive index detector were used for detection. Differential scanning calorimetry (DSC) was performed with a DSC Q100 TA Instruments analyzer at a heating rate of 10 °C/min in nitrogen. Thermal stability, as measured by 5% weight loss of the polymer samples, was determined using a Hi-Res TGA TA Instruments Thermogravimetric Analyzer at a heating rate of 10 °C/min, in nitrogen. UV curing of polymer films was done using an Ultracure 100SS Plus/ Novacure system as a source with a 320-390 nm filter at a light intensity of 3500 mW/cm². Photopatterns imaged by scanning electron microscopy were prepared from polymer films (approximately 2 μm thickness) on silicon wafers. After exposure to UV light through a photomask for 30 min at 75 °C in argon, the pattern was developed by immersing the sample consecutively in an acetone bath for 30 sec and a chloroform bath for 1 min. The films were further dried

in a vacuum oven at 70 °C overnight. SEM images were taken using a Jeol-JSM-6400 Scanning Microscope.

Time resolved IR experiments were carried using the set-up presented in Figure IV.13. The set-up contains a heating unit made of a quartz tube (6) and a heat conducting nickel coil to which variable potential was applied in order to obtain the desired temperature.

Figure IV.13. Set-up for the time resolved experiments: 1- dark coloured chamber; 2- electric power source; 3- holder; 4- polymer sample on KBr pellet; 5- nickel coil; 6- quartz tube; 7- UV light guide

The polymer samples casted on the KBr pellet (4) were mounted in the heating unit and irradiated with a UV source (7) while recording the IR changes. IR spectra were collected every 5 seconds for the first five minutes and every 5 minutes for the following 35 min. All the experiments were carried in a dark chamber (1) which had an argon inlet and outlet.

Monomer Synthesis

Monomer IV-3

In a flame dried three-neck, round-bottomed flask equipped with a dropping funnel, a stirring bar and a nitrogen inlet/outlet, propargyl alcohol (compound **IV-2**) (22.02 g, 0.4 mol) and triethylamine (40.46 g, 0.4 mol) were added to dried benzene (60 mL) at room temperature. To the stirred solution was added drop-wise a solution of acryloyl chloride (compound **IV-1**) (36.20 g, 0.4 mol) in benzene (40 mL). The excess of hydrochloric acid gas formed that was not combined to form the triethylammonium hydrochloride salt, was trapped outside the reaction vessel in a bubbler containing concentrated sodium hydroxide solution. The reaction was carried out at room temperature and was stopped after 3 hours. The triethylammonium hydrochloride salt formed was separated by collected in a Buchner funnel. The monomer **IV-3** was purified by fractional distillation under vacuum to yield 25.92 g (59.4%) of a clear colourless liquid having a boiling point of 40 °C/ 12 mmHg. Monomer **IV-3** was stored in the presence of t-butyl catechol under nitrogen in the fridge. IR (NaCl, cm⁻¹): 3296 (≡C-H), 2135 (-C≡C-), 1796, 1732 (C=O); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.42 (1H, dd, ³J = 17.2 Hz, ²J = 1.2 Hz), 6.19 (1H, dd, ³J = 17.2 Hz, ³J = 110.4 Hz), 5.96 (1H, dd, ³J = 10.4 Hz, ²J = 1.2 Hz), 4.40 (2H, ⁴J = 2.8 Hz), 3.05 (t, ⁴J = 2.8 Hz) ; ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 165.52, 132.16, 128.67, 78.77, 76.38, 52.39.

Polymer Synthesis

Polymer	% Mol IV-3 Incorporated
IV-5a	3.0
IV-5b	11.6
IV-5c	34.5
IV-5d	55.5
IV-5e	100

Polymer IV-5a

A flame dried ace pressure tube was charged with monomer **IV-3** (0.055 g, 0.5 mmol), monomer **IV-4** (1.001g, 10 mmol), benzoyl peroxide (0.3% wt.) and 2.12 mL benzene. Nitrogen was bubbled through the reaction mixture, then the reaction vessel was sealed and heated at 70 °C for 4 hrs. Chloroform was added to the viscous solution and then the polymer was precipitated in hexane. The fibrous white polymer was filtered and dried under vacuum at 45 °C (yield 12.05%). $M_w = 350,000$; $M_w/M_n = 1.9$; IR (KBr, cm^{-1}): 3302, 3264 ($\equiv\text{C-H}$), 2182 ($-\text{C}\equiv\text{C}-$); 1730 ($-\text{C=O}$); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 4.61 (m, br, $-\text{O-CH}_2-$), 3.59 (d, br, $-\text{COOCH}_3$), 2.50 (s, br, $\equiv\text{C-H}$), 2.06-0.84 (m, br, aliphatic CH); ^{13}C NMR(100 MHz, CDCl_3): δ (ppm) 178.15, 177.86, 177.15, 176.99, 54.45, 54.18, 51.83, 44.89, 44.54, 29.70, 18.72, 16.46.

Polymer IV-5b

The above procedure was followed using monomer **IV-3** (0.275 g, 2.5 mmol), monomer **IV-4** (1.001g, 10 mmol), benzoyl peroxide (0.3% wt.) and 2.55 mL benzene.

The polymer was isolated as white fibrous material, yield 23.0 %. $M_w = 375,000$; $M_w/M_n = 2.4$; IR (KBr, cm^{-1}): 3302, 3265 ($\equiv\text{C-H}$), 2182 ($-\text{C}\equiv\text{C}-$); 1730 ($-\text{C=O}$); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 4.60 (m, br, $-\text{O-CH}_2-$), 3.59 (d, br, $-\text{COOCH}_3$), 2.50 (s, br, $\equiv\text{C-H}$), 2.06-0.84 (m, br, aliphatic CH); ^{13}C NMR(100 MHz, CDCl_3): δ (ppm) 178.15, 177.86, 177.15, 175.11, 75.18, 54.42, 51.83, 45.11, 44.51, 36.75, 34.66, 31.59, 29.70, 22.65, 20.70, 18.70, 18.00, 16.38, 14.13.

Polymer IV-5c

The same procedure as for polymer IV-5-a was used, employing monomer IV-3 (0.549 g, 5 mmol), monomer IV-4 (0.5 g, 5 mmol), benzoyl peroxide (0.3% wt.) and 2.09 mL benzene. The polymer was isolated as white powder, yield 18.8 %. $M_w = 234,000$; $M_w/M_n = 1.5$; IR (KBr, cm^{-1}): 3293, 3272 ($\equiv\text{C-H}$), 2128 ($-\text{C}\equiv\text{C}-$); 1731 ($-\text{C=O}$); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 4.60 (m, br, $-\text{O-CH}_2-$), 3.59 (d, br, $-\text{COOCH}_3$), 2.50 (s, br, $\equiv\text{C-H}$), 2.06-0.84 (m, br, aliphatic CH); ^{13}C NMR(100 MHz, CDCl_3): δ (ppm) 178.01, 176.77, 176.56, 175.57, 75.23, 54.30, 52.12, 51.83, 45.47, 44.51, 39.74, 38.98, 36.83, 29.69, 22.65, 20.85, 19.04, 18.78, 16.66, 16.31.

Polymer IV-5d

The above experimental procedure was used, employing monomer IV-3 (0.826 g, 7.5 mmol), monomer IV-4 (0.25 g, 2.5 mmol), benzoyl peroxide (0.3% wt.) and 2.15 mL benzene. The reaction was stopped after 5hrs. The polymer was isolated as white powder, yield 21.37 %. $M_w = 54,500$; $M_w/M_n = 1.2$; IR (KBr, cm^{-1}): 3293 ($\equiv\text{C-H}$), 2129 ($-\text{C}\equiv\text{C}-$); 1737 ($-\text{C=O}$); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 4.60 (m, br, $-\text{O-CH}_2-$), 3.59 (d, br, $-\text{COOCH}_3$), 2.50 (s, br, $\equiv\text{C-H}$), 2.11-0.85 (m, br, aliphatic CH); ^{13}C NMR(100 MHz,

CDCl₃): δ (ppm) 176.81, 176.63, 175.75, 175.09, 75.27, 52.11, 51.87, 45.61, 44.86, 40.71, 39.66, 38.90, 22.65, 20.93, 18.49, 17.19.

Polymer IV-5e

A similar method was used to synthesize polymer **IV-5-e**. Monomer **IV-3** (1.2g, 11mol) and benzoyl peroxide (0.5% wt.) were added to 4.8 mL of dry acetone. The reaction mixture was warmed up to 80 °C. The reaction was stopped after 31 hrs. The polymer was precipitated in hexane as a white flaky material, yield 28%. $M_w = 10,500$; $M_w/M_n = 8.3$; IR (KBr, cm⁻¹): 3291 ($\equiv$ C-H), 2128 (-C $\equiv$ C-); 1736 (-C=O);); ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.61 (s, br, -O-CH₂-), 2.57 (d, br, $\equiv$ C-H), 1.98-0.86 (m, br, aliphatic CH); ¹³C NMR(100 MHz, CDCl₃): δ (ppm) 178.15, 77.34, 75.55, 52.27, 40.86, 34.72, 29.70.

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Appendix 1

Ellipsometric Measurements and Analyses of Thin Polymer Films

Refractive index, refractive index dispersion and birefringence measurements were done using Variable Angle Spectroscopic Ellipsometry (VASE). VASE is an optical technique that uses polarized light to characterize film thickness, optical constants and microstructural material properties such as surface roughness, thickness uniformity, and refractive index grating with thickness.¹ VASE is an especially attractive method because it is noncontact, is nondestructive, and does not require vacuum.

An optical experiment does not measure directly the sample parameters of interest (thickness, refractive index, etc.) but rather the reflected or transmitted beam intensities or polarization states.² Ellipsometry in particular measures the Fresnel reflection coefficients Psi (ψ) and Delta (Δ), that describe the change in the polarization state of light reflected from the surface of the sample (Equation 1).

$$\rho = \tan(\psi) e^{i\Delta} \quad (\text{Equation 1})$$

These values can be measured over a broad spectral range (200-1800 nm) and several angles of incidence.³ The acquired data is further analyzed by developing a model to simulate the sample (substrate and all thin films) and generate theoretical data for the sample. Further comparison of the experimental data and generated data along with regression analysis are used to vary the fit parameters (unknown film thickness and/or refractive index) to fit the best agreement between model, generated and experimental data.

The ellipsometric measurements of this thesis work involved transparent thin polymer films spin-coated on silicon wafer substrates. The nature of the substrate and

more precisely the index of refraction, dictated the angles at which measurements are performed. These angles, also known as Brewster angle or angle of incidence provides maximal sensitivity to the properties of the sample under test.⁴ For silicon wafer an incidence angle of 65° to 75° was used in order to achieve high measurement sensitivity. The experimental data was acquired for a spectral range of 400 to 1800 nm. Figure 1 represents an example of a set of experimental data graph for the ellipsometric ψ (Figure 1a) and Δ (Figure 1b) for polymer **II-3**.

This data was analyzed by constructing a layer by layer model of the measured sample. The first layer of the model was the silicon layer for which a model is provided with the WVASE 32TM software. Another model layer corresponding to the organic polymer film, of variable thickness, was further attached to the silicon layer model. A Cauchy dispersion relation model was used for the parameterization of the refractive index of the polymer layer. The Cauchy model is generally applied to thin polymer films due to the fact that most of them share the common characteristic of a negligible extinction coefficient in the visible to near infrared (NIR) spectral range.²

A general relation for the refractive index can be written as:

$$n = n_R + i n_I$$

where the refractive n index is a complex number consisting of the index of refraction n_R , and the extinction coefficient n_I ($i^2 = -1$). The real component n_R determines how fast a light wave will propagate in a material, while the extinction coefficient n_I describes how absorptive the material is. Therefore, visible and NIR light will transmit through polymers without losing energy. VASE uses this transparent region to determine film thickness and refractive index.

Figure 1. Ellipsometric experimental data for polymer **II-3** on silicon wafer: (a) ψ and (b) Δ

The Cauchy dispersion equation (Equation 2) describes the behavior of the refractive index as a function of wavelength (λ).

$$n(\lambda) = n_R(\lambda) = A + B/\lambda^2 + C/\lambda^4 \text{ with } n_I(\lambda) = 0 \quad (\text{Equation 2})$$

where $n(\lambda)$ is the index of refraction, λ is the wavelength and A, B and C are the Cauchy parameters.

Since the polymer is transparent ($n_I(\lambda) = 0$) in this spectral range, the refractive index must decrease with increasing the wavelength, and the Cauchy relationship is adequate. However, the Cauchy equation is unable to describe the refractive index in regions with film absorption ($n_I(\lambda) \neq 0$).

Dispersion models can greatly reduce the number of parameters needed to “fit” the data. The model calculates the Fresnel reflection coefficients ψ and Δ to compare with measured values. The Cauchy model requires only three parameters, which are the Cauchy coefficients A, B and C in order to replace a direct “fit” for the index of refraction ($n(\lambda) = n_R(\lambda)$). For example if 100 wavelengths are measured, three Cauchy parameters replace the 100 individual n values. Fits between experimental and calculated ψ and Δ must be close, otherwise the model does not properly represents the physics.³

The fit parameters which are the thickness of the film and Cauchy parameters are optimized using a multiparameter regression analysis to fit the generated data to the experimental data. The regression analysis varies these parameters within the defined limits to minimize a “goodness of fit” function called the mean square method (MSE):

$$MSE = \frac{1}{2N - M} \sum_{i=1}^N \left[\left(\frac{\Psi_i^{Mod} - \Psi_i^{Exp}}{\sigma_{\Psi,i}^{Exp}} \right)^2 + \left(\frac{\Delta_i^{Mod} - \Delta_i^{Exp}}{\sigma_{\Delta,i}^{Exp}} \right)^2 \right] \quad \text{Equation 3}$$

where N is the number of (ψ , Δ) pairs, M is the number of variable parameters in the model, and σ are the standard deviations on the experimental data points. The MSE as shown in Equation 3 represents a sum of the squares of the differences between the

measured and calculated data, with each difference weighted by the standard deviation of that measured data point. For a very noisy measurement, the corresponding standard deviation will be large and that measurement will not be strongly weighted in the fit.

The first parameter to fit was the film thickness. By reducing the spectral range (to 500-1200 nm, for example) the fitting procedure yielded an improved MSE. Further reduction of the spectral range usually to 600-1000 nm yielded a better MSE, and the value of the thickness determined. Although the generated data matched the experimental data qualitatively, the generated and experimental ψ were not very close and further adjustment of the Cauchy parameters did not yield a better fit.

The polymer films were expected to be birefringent and therefore optically anisotropic, so a different model had to be used to better fit the experimental data. VASE data at multiple angles is especially sensitive to optical anisotropy, because different amounts of light interact with the different film directions as the angle changes. A biaxial layer model (BIAXIAL.mat) was used to describe the different optical constants in the plane of the film and perpendicular to the film. To this biaxial model two Cauchy layer models were coupled a Cauchy.mat model to describe the in-plane optical constants and a Cauchy2.mat model describing the out-of-plane optical constants. The fit parameters were in this case the thickness of the biaxial layer and the parameters A_1 , A_2 , B_1 and B_2 of the two Cauchy models. A reduced spectral range of 500-1700 nm was used to fit the data and determine the film thickness. The MSE values obtained for this anisotropic model were better than the ones obtained for the isotropic model, as was seen from the generated and experimental ψ data. Additionally, for some of the polymer films a thickness non-uniformity parameter was included which improved the final best-fit.

Figure 2 displays the best-fit generated (red) and experimental (green) ellipsometric ψ and Δ data with a MSE of 6.969.

Figure 2. Ellipsometric generated and experimental data for polymer **II-3** on silicon wafer: (a) ψ and (b) Δ

A point-by-point fit of the experimental data was also performed, by defining the refractive index (n) and coefficient of extinction (k) as fit parameters. Although

sometimes this fitting method should improve further the MSE, no major changes were observed for most of the polymers covered in our study.

A problem that sometimes arises with Cauchy parameterization is that it can produce unphysical dispersion of the refractive index of the material. As mentioned previously, in a spectral range where the absorption of the material is zero, the index of refractive should decrease monotonically with increasing wavelength. In the case of using only A and B Cauchy parameters, a negative B parameter will always yield unphysical index spectra.

Figure 3 displays the calculated refractive index and the coefficient of extinction for the two Cauchy layers, representing the in-plane optical constants (Figure 3.a) and out-of-plane optical constants (Figure 3.b). These are physically reasonable index dispersion spectra as the refractive index value decreases with wavelength and B1 and B2 have positive values.

Figure 3. Refractive index spectra as predicted by Cauchy dispersion models for the anisotropic polymer film: a- in-plane and b- out-of-plane

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Appendix 2

Integrated ^1H NMR spectrum (400 MHz, CDCl_3) of polymer **II-8b** with a 75.6 % mol ratio of **II-3** incorporated as calculated using the methylenic protons at 4.6 ppm ($\text{OCH}_2\text{-C}\equiv\text{C-}$) and 4.4 ppm ($\text{NCH}_2\text{-C}\equiv\text{C-}$)

Appendix 3

Integrated ^1H NMR spectrum (400 MHz, CDCl_3) of polymer **III-4e** with a molar ratio of **III-3:II-7** = 18.5:1 as calculated using the aromatic protons

CONTRIBUTION TO KNOWLEDGE

1. Linear and hyperbranched poly(ether imides) copolymers with variable refractive indices were obtained by copolymerization of a diacetylene end-capped fluorinated imide with diethynyl and triethynyl end-capped ether monomers.
2. Decrease in polymers birefringence resulted from the incorporation of the bulky cardo fluorenyl group or of the branched structure of the ether monomers.
3. The linear polymers are curable both thermally and by UV irradiation, at 250-450 nm due to the presence of diacetylene moieties.
4. A new photo-cross-linking system based on an ethynyl-containing polymer and $W(CO)_6$ as initiator was developed.
5. The photocuring process depends on the amount of ethynyl moieties, amount of catalyst, and the curing temperature and it follows first-order kinetics.