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**Synthesis and Characterization of Polymethacrylates
Containing Chiral and Fluorescent
o-Terphenyl Moiety**

by

Valérie Grand

Ingénieur Chimiste (Montpellier, France)

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

The Department of Chemistry

Carleton University

Ottawa, ON Canada

August, 1998

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A handwritten signature in black ink, appearing to read "G. Buchanan", written over a horizontal line.

Dr. G. Buchanan, Chairman

A handwritten signature in black ink, appearing to read "Z. Y. Wang", written over a horizontal line.

Dr. Z. Y. Wang, Thesis Supervisor

Carleton University

August, 1998

Abstract

Helical structures are important in many fields such as chemistry, biology and physics. Carbohelicenes have received much attention due to their particular structures and chiroptical properties. Owing to their symmetry and rigid spatial arrangement functionalized helicenes are potentially useful as chiral auxiliaries and catalysts.

In the course of studying correlations between structures and chiroptical properties of helical *o*-terphenyl derivatives, a new chiral *o*-terphenyl anhydride precursor was synthesized and resolved by chiral chromatography at 22 °C. The new characteristic of this molecule is the *o*-propylene units between biphenyl moieties.

A series of polymethacrylates were derived from this chiral anhydride by free radical polymerization. The methacrylate monomer and polymers were fully characterized by NMR and IR spectroscopy, and UV-vis spectrophotometry. Glass transition temperatures of polymers were determined by DSC and ranged from 132 to 171 °C. Onset temperatures for 5% weight loss of these polymethacrylates were determined by TG and ranged from 236 to 346 °C in nitrogen.

Fluorescent properties of chiral anhydride and polymers were also investigated with an emission band observed at 430 nm.

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Following my happiness and my excitement when I was still in France ready to come and study in Canada, I had to face many different events. First of all, my hard time in the plane (I think I have never been in such a bad shape before!), my lonely first night in Renfrew House and my English nightmare. Since then I have learned more English and chemistry (!), patience and perseverance thanks to my work in the lab. I also met thousands of friends who helped me not to be homesick and with whom I discovered the beauty of Canada and had unforgettable moments.

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Symbols and Abbreviations

Å	Angstrom
$[\alpha]$	Specific optical rotation ($\text{deg.mL.dm}^{-1}.\text{g}^{-1}$)
δ	Chemical shift
λ	Wavelength
λ_{em}	Emission wavelength
λ_{exc}	Excitation wavelength
λ_{max}	Maximum peak wavelength
η_{inh}	Inherent viscosity
2D	Two-dimensional
AIBN	2,2'-azobisisobutyronitrile
calcd	Calculated
COSY	H-H COrrrelated SpectroscopY
CSP	Chiral stationary phase
DMF	N,N-dimethylformamide
DSC	Differential scanning calorimetry
FW	Formula weight
GC	Gas chromatography
GPC	Gel permeation chromatography
HETCOR	Heteronuclear correlation spectroscopy
HPLC	High performance liquid chromatography
HRMS	High resolution mass spectrometry

Hz	Hertz
IR	Infrared
J	Coupling constant
MMA	Methyl methacrylate
MS	Mass spectrometry
MW	Molecular weight
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
NMR	Nuclear magnetic resonance
^1H NMR	Proton nuclear magnetic resonance
^{13}C NMR	Carbon nuclear magnetic resonance
NOESY	Nuclear overhauser enhancement spectroscopy
PMMA	Poly(methyl methacrylate)
ppm	Parts per million
RBF	Round-bottomed flask
rt	Room temperature
TCE	1,1,2,2-tetrachloroethane
TG	Thermogravimetry
TLC	Thin layer chromatography
TMS	Tetramethylsilane
T_g	Glass transition temperature
T_m	Melting temperature
T_d	Onset temperature for 5% weight loss

UV-vis	Ultraviolet-Visible
d	Doublet
dd	Doublet of doublet
dt	Doublet of triplet
m	Multiplet
mp	Melting point
q	Quintet
s	Singlet
sx	Sextuplet
t	Triplet

Chapter I. Introduction

I.1. Helical Molecules in Organic Chemistry

Screw structures or helices (helix: greek = winding, convolution, spiral) are encountered in various variations in nature. Propeller-shaped, helical structures play an important role in architecture, physics, astronomy and biology. Screw-shaped macromolecular skeletons of nuclei acids, proteins and polysaccharides are important structural elements in biochemistry. Their helix turns often are stabilized through H-bonds, metal cations, disulfide linkages, and hydrophobic interactions¹.

α -Amylose was the first helix postulated for a natural macromolecule (Figure I.1).

Figure I.1. Simplified structure of the α -Amylose helix.

One of the most important natural compounds with a helical structure is deoxyribonucleic acid (DNA). Hydrogen bonds between complementary bases allow the

legendary "double-helix structure", which is stabilized also by hydrophobic interactions between facing bases (Figure I.2).

Figure I.2. Double helix of DNA.

Helicity is a geometric structural property. Cahn, Ingold and Prelog² described and defined the helix as follows: "a helix is characterized by a helical sense, a helical axis and a pitch. Thus helicity is a special case of chirality".

A helix is considered to wind starting from the viewer's eye to a point distant from the viewer. The screw sense is right (P)- or left (M)-handed according to the turns (Figure I.3).

Figure I.3. Cylindrical helices.

I.2. Helicenes

Helicenes are benzologues of phenanthrene in which a regular cylindrical helix is formed through an all-ortho annellation of the aromatic rings resulting in a highly conjugated molecule. The helical structure is a consequence of the repulsive steric overlap of the terminal aromatic nuclei.¹

This is an attractive class of compounds because of the unique combination of interesting properties in a single molecule: they bear an inherent chiral chromophor and exhibit very high specific optical rotations¹ (1,000° to 10,000°) depending on gross structure, fine geometry, electronic interactions, etc...

Carbohelicenes contain only carbon atoms in their skeleton and are also called all-benzene helicenes. Newman et al³ were the first to synthesize hexahelicene in 1956. The IUPAC name of hexahelicene is phenanthro[3,4-d]phenanthrene. Newman introduced a

simplified nomenclature by setting in brackets the number of annellated aromatic rings before the helicene name. Thus hexahelicene became [6]helicene (Figure I.4).

Figure I.4. (+)-P- and (-)-M-Hexahelicene.

The specific optical rotations of carbohelicenes increase with increasing number of benzene rings (-1670° for M[5]helicene and -9310° for M[11]helicene), but the increments become continuously smaller (-9620° for [13]helicene).¹ Along with this increase in the number of benzene rings, the terminal facing aromatic rings become more and more coplanar. For example in [11]helicene the interplanar angle of the facing terminal benzene rings (representation in Figure I.8) is only 4° they are therefore arranged nearly parallel to each other (Figure I.5). It could be therefore concluded that there should be a relationship between conjugation and chiroptical properties: the higher the conjugation, the higher the optical rotation value.

All carbohelicenes fluoresce and show a well-defined fluorescence band which shifts to longer wavelengths as the number of benzene rings increases.

Figure I.5. [11]Helicene (stereo view).

I.3. Helical *o*-Terphenyl Derivatives

[5]Helicene is the smallest one among all known carbohelicenes. From a pseudo [5]helicene derivative, 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**I-1**)⁴, a series of helical *o*-terphenyl derivatives^{4,5} were made (Figure I.6) and chiroptical properties⁶ were determined (Table I.1).

All of these molecules have a helical structure can be deduced from the crystal structures of compounds **1-2**⁴ and **1-3**⁶ (Figure I.7). It is interesting to note that some optical rotation values are as high as that of [5]helicene ($[\alpha]_{578} = -1624$ for compound **I-3**). Furthermore, the observed optical rotation values at a lower wavelength are even higher ($[\alpha]_{436} = -7100$ for compound **I-3**) than that of [5]helicene ($[\alpha]_{436} = -4950$).

Table I.1. Chiroptical properties of *o*-terphenyl derivatives **I-3/5** and [5]helicene.

	$[\alpha]_{589}$	$[\alpha]_{578}$	$[\alpha]_{546}$	$[\alpha]_{436}$	$t_{1/2}$ min (°C)	E_a kcal/mol (°C)
I-3 ⁶	-1518	-1624	-1998	-7100	2340 (49.8)	27.7 (25.0)
I-4 ⁶	+1011	N/A	N/A	N/A	N/A	N/A
I-5 ⁶	-1099	-1322	-2356	N/A	3600 (49.8)	N/A
[5]helicene ¹	N/A	-1670	-2025	-4950	62.7 (57.0)	23.5 (57.0)

Figure I.6. 5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic anhydride (I-1) and its helical o-terphenyl derivatives I-2/5.

Figure I.7. Crystal structures of compounds I-2⁴ and I-3⁶.

As opposed to [5]helicene, these derivatives do not consist of five fused aromatic rings. A different helical shape is therefore observed in the crystal structure. Different angles can be measured to describe the geometrical orientation of the molecule. The interplanar angle assigns the angle between the two terminal benzene rings of the helix (Figure I.8, angle between planes II and III). In [5]helicene and *o*-terphenyl derivatives, a twisted angle is also measured. This twisted angle or dihedral angle corresponds to the atoms of the inner helix: the angle refers to the first four atoms. Basically this is the angle between the middle ring and the external ring (Figure I.9, dihedral angle).

Figure I.8. Interplanar angle representation.

Figure I.9. Twisted angle representation.

When carbohelicenes were studied, the most intriguing observation was the unexpected ease with which these compounds racemize thermally.⁷ A direct inversion is involved in the pathway for thermal racemization (Scheme I.1). The “relatively” low potential barriers for these racemizations were justified in the conformational process by the fact that the necessary molecular deformations (bond torsion, bond bending, bond stretching, etc.) are spread over a large number of bonds.⁸ The important conclusion was that the helicenes are dramatically more flexible than expected.

Scheme I.1. Reversible inversion of the helical structure ($M \leftrightarrow P$) via a conformational pathway.

By looking at the racemization half-life time $t_{1/2}$, there should be some analogy between these *o*-terphenyl derivatives and carbohelicenes in the conformational process involved in the racemization. We can see that with the 1-substitution of the aromatic ring the $t_{1/2}$ time increases. Indeed the steric hindrance created by the 1-substitution causes the inversion $M \leftrightarrow P$ process to occur more slowly. Furthermore the larger the substituent the longer the racemization half-life time because the steric hindrance is increased ($t_{1/2}$ =2340 and 3600 min for compounds I-3 and I-5 respectively).

I.4. Hypotheses and Rationale of the Project

As previously discussed, *o*-terphenyl derivatives possess a helical structure whose conformation is closely related to the chiroptical properties. In order to get high optical properties, we think that the conjugation within the molecule and its helical shape are of major importance. *O*-terphenyl derivatives of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**I-1** in Figure I.10) had interesting chiroptical properties⁶ especially high optical rotations. Functionalization of compound **I-1** was also performed⁹ as well as the synthesis of several [5]helicene containing polyimides by chemical and thermal transformation.¹⁰

The objective of this thesis work was to synthesize a similar molecule as anhydride **I-1**, 5,6,7,10,11,12-hexahydrodi(benzocyclohepta)[6,5-*a*:5',6-*c*]benzene-8,9-dicarboxylic anhydride (**I-6**), whose interesting feature is the 7-membered ring in the molecule (Figure I.10).

Figure I.10. 5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic anhydride (**I-1**) and 5,6,7,10,11,12-Hexahydrodi(benzocyclohepta)[6,5-*a*:5',6-*c*]benzene-8,9-dicarboxylic anhydride (**I-6**).

Due to the longer flexible propylene units that link biphenyl moieties in **I-6** the terminal benzene rings would be more overlapped thus inducing the helical shape and the

chirality. However the three aromatic rings would be less coplanar because of the biphenyl twisting.

If **I-6** has chiral and fluorescent features it is desirable to incorporate this unit into the polymer backbone, which should lead to a new class of materials. Furthermore the non-coplanar, spiral shape of the monomeric units should warrant a good solubility of the polymer by preventing the polymer chains from close packing.

The objectives of this thesis research are to functionalize compound **I-6** and to incorporate it into a polymer.

Chapter II. *O*-Terphenyl Building Block

II.1. Synthesis

Compound **I-1** was prepared from α -tetralone through the process of a pinacol reaction, dehydration of diols, Diels-Alder reaction with maleic anhydride and aromatization of the middle ring.^{4,11}

Although compounds **I-1** and **I-6** are similar, their synthesis processes are not identical. Some changes to the synthetic route and reaction conditions were necessary (Scheme II.1).¹²

Scheme II.1. Synthesis of anhydride **I-6**.

The pinacol reaction^{12,13} was done for a large scale preparation by starting with benzosuberone (500 g), which is the 7-membered ring analogue to α -tetralone used for

the synthesis of compound I-1. The extractions of the product from the acidic solution yielded a yellow solid suspension. No further purification was attempted therefore the yield was not determined. However meso isomer was isolated from the mixture (meso, dl diols) as a white solid.

The diene synthesis consisting of a dehydration of the pinacols under acidic conditions^{13,14} did not work so well: even after distillation to remove low boiling impurities a brown residue was obtained. However a GC-MS analysis confirmed the presence of the diene with the expected molecular weight of 286 g/mol. No further purification was carried on.

The Diels-Alder reaction¹⁵ needed also special attention. Indeed after completion of the reaction when the solution was poured into boiling water, a green gel was obtained. The gel was washed with hot water then triturated in hexane and methylene chloride, and a white precipitate was obtained. Two spots were seen on TLC that might correspond to the endo and exo isomers.¹⁶ The yield was 8% from benzosuberone. This poor yield could be explained by the relative difficulties encountered in each intermediate reaction. Crystals were never isolated. Instead, suspension, residue or gel were obtained. The diene product was difficult to handle because it was a hard solid at room temperature and a viscous liquid when melted. Most of the sample was also probably lost during the purification of the Diels-Alder product by crystallisation and washing. This Diels-Alder cycloaddition with maleic anhydride was thought to be unexpected¹⁷ because the diene need to be sufficiently planar for the addition to take place and the resulting strained adduct has to be stable.

For the synthesis of compound I-1 the aromatization of the middle ring was done overnight at room temperature with 2.5 equivalent of bromine in chloroform and acetic acid solution.⁴ For compound I-6, the aromatization of the central ring did not work using elemental bromine in chloroform and acetic acid. Brominated by-products were formed and the reaction was never complete even after three days. When lead tetraacetate was used as reported before in the literature^{11,18} aromatization was successful yielding I-6 in 48% yield. Pure product was obtained by crystallization from methylene chloride and acetone. The melting point (288 °C) determined by DSC is in agreement with the reported value (284-285 °C)¹¹, indicating a high purity. The overall yield from benzosuberone was only 4% due to the low yield for the Diels-Alder product.

II.2. Characterization

II.2.1. Spectroscopic Characterization

The ¹H and ¹³C NMR data are reported in Table II.1 and Table II.2 and spectra are shown in Figure II.1 and Figure II.2. These assignments were supported by COSY and HETCOR experiments. NOESY experiment was also used to allow an unambiguous assignment of aromatic protons: a NOE crosspeak between the aromatic H4 and the aliphatic H6 was detected. The diamagnetic anisotropy effect of the benzene ring shielded protons H1 and H2. Because of the spatial arrangement of the molecule, these two protons (H1 and H2) are located above the benzene ring therefore their signals are upfield shifted. The ¹³C NMR spectrum displayed the expected 13 lines for each of the representative carbon atoms. Carbon C11 from the anhydride function was easily assigned at 163.47 ppm. The four aromatic carbons in the region of 125-130 ppm and the

three aliphatic carbons below 30 ppm were also well seen in the spectrum. The five other small peaks arise from the aromatic quaternary carbons.

Table II.1. ^1H NMR assignments of anhydride I-6.

^1H NMR	δ , ppm		J, Hz
H 1	6.42	2 H, d	7.68
H 2	6.90	2 H, dt	1.04, 7.44
H 3	7.20	2 H, dt	1.11, 7.46
H 4	7.28	2 H, d	7.44
H 6	2.60, 2.77	2 H, m, 2 H, m	
H 7	2.25	4 H, m	
H 8	3.92, 2.15	2 H, m, 2 H, m	

Table II.2. ^{13}C NMR assignments of anhydride I-6.

^{13}C NMR	δ , ppm
C 1	130.52
C 2	125.83
C 3	128.48
C 4	128.10
C 6	30.95
C 7	31.48
C 8	24.91
C 11	163.47
C 5, 9, 10, 12, 13	147.79, 140.60, 139.98 136.92, 126.40

Figure II.1. ^1H NMR spectrum (400 MHz, CDCl_3) of anhydride I-6.

Figure II.2. ^{13}C NMR spectrum (100 MHz, CDCl_3) of anhydride I-6.

The IR spectrum confirmed the presence of anhydride carbonyl groups at 1765 and 1838 cm^{-1} , aromatic rings at 3069 and 3025 cm^{-1} (CH stretch) 1450 cm^{-1} (C=C stretch) and alkyl groups at 2939 and 2831 cm^{-1} (CH stretch).

The HRMS gave the expected mass (380.14 g/mol). The mass spectrum displayed the $(M+1)^+$ peak ($m/e = 381$) as well as a peak due to the loss of CO ($m/e = 352$).

The structure of anhydride **I-6** was also characterized by UV-vis. The UV-vis spectrum of compound **I-6** displayed two maximum absorption peaks at 335.8 and 269.2 nm (Figure II.3). The highest peak at 269.2 nm comes from the benzene rings absorption. Among the three electronic transitions that usually take place in benzene, the secondary band at 255 nm is shifted to a longer wavelength (269.2 nm) as it often happens in polycyclic aromatic compounds.¹⁹ The smallest peak at 335.8 nm arises from the carbonyl groups absorption conjugated with the aromatic ring. This UV-vis spectrum is characteristic of an α,β -unsaturated carbonyl derivative (presence of a high intensity $\pi \rightarrow \pi^*$ band between 220 and 260 nm and a low intensity $n \rightarrow \pi^*$ band around 320 nm).²⁰

Figure II.3. UV-vis spectrum (2.34×10^{-5} mmol/mL, chloroform) of anhydride **I-6**.

Substances which possess delocalized electrons formally present in conjugated double-bonds generally display significant fluorescence.²¹ Because a π -conjugated system is present in the *o*-terphenyl moiety, fluorescent properties are expected for these molecules.²² Indeed a fluorescence band was observed at 430 nm for anhydride I-6 (1.32×10^{-4} mmol/mL, chloroform); the longest wavelength radiation (335 nm) was chosen for excitation of the sample. The Stokes' shift is observed with a reemission of less energetic photons that have a longer wavelength than the absorbed photons.²¹

II.2.2. Crystal Structure

The crystal structure (Figure II.4) was obtained from orthorhombic crystal. The helical shape of the molecule is clearly visible. The rings are not coplanar because there is a large twisted angle (56.7°). Indeed the terminal rings can flip or twist more freely and they are actually pushed away from each other: they turn towards the outer side of the helix. This conformation is obviously more stable than the one in which the terminal benzene rings overlap and are coplanar with the central benzene. This is probably because in the latter conformation, there are more steric hindrance and repulsion between terminal π -systems.

Figure II.4. Crystal structure of anhydride I-6.

II.2.3. Chiral Chromatographic Separation

One of the foremost chromatographic methods to separate enantiomers is high-performance liquid chromatography technique using a chiral stationary phase (CSP).²³ The most widely used CSP depends on a combination of hydrogen bonding, π - π interactions, dipole-dipole interactions and steric interactions.²⁴ In general terms a chiral moiety is bonded via a non-chiral spacer, to silica. The Whelk-O1 column is well suited to semi preparative separation due to its lower cost compared with other chiral phases.²⁵

As the compound has a helical conformation shown by its crystal structure, it should therefore have two isomers (M and P). Indeed the compound was successfully resolved into M and P enantiomers using chiral Whelk-O1 column. The solvent used was 1.25% isopropanol/hexane at the elution rate of 1 mL/min with the UV detector lamp at 254 nm. As opposed to anhydride I-1 that displayed only one peak (not resolved), this compound displayed two well-separated peaks: the first one being the left-handed M

enantiomer and the second one being the right-handed P enantiomer (Figure II.5). The successful resolution means that the enantiomer is stable at room temperature (22 °C). In the case of compound I-1, the racemization process is too fast to allow any resolution at room temperature.

Figure II.5. Chiral chromatographic separation of anhydride I-6.

In order to measure the specific optical rotations and to study the racemization process, pure fractions of each enantiomers were needed. On this purpose, after each injection five different fractions were collected along the variation of the absorbance values (Figure II.5). Because isomers are more stable in a solid form than in solution towards racemization, those fractions were evaporated after two consecutive collections

at room temperature with a rotary evaporator. The first and the last fraction are considered as the purest ones.

II.2.4. Determinations of Optical Rotation and of Racemization Half-life Time

The optical rotation of a chemical substance at a single wavelength is an important physical property for the study of a chiral system.²⁶

As specific optical rotation depends on the concentration, an accurate determination of the sample concentration is needed. For this purpose, a UV-vis calibration curve of anhydride I-6 was established at 335.8 nm at 22 °C (Figure II.6).

Figure II.6. UV-vis calibration curve (335.8 nm) of anhydride I-6 (chloroform, 22 °C).

The first fraction was used to measure the specific optical rotations at room temperature. The results are listed in Table II.3. Optical angles were measured at four different wavelengths. M-I-6 chloroform solution was then diluted to determine the initial concentration by UV readings. It found to be 0.127 g/100 mL at 22 °C. To check the

purity of the sample, the solution was further injected into the HPLC/chiral column system. Only one peak was observed, therefore the sample is pure made of 100% of the left-handed enantiomer because the observed rotation angle was negative.²⁷

Table II.3. Specific optical rotation values of M-I-6.

λ (nm)	$[\alpha]^{22}$
436	-349
546	-94
578	-67
589	-55

The low optical rotation values can be explained by the low degree of π -conjugation due to the large twisted angle between aromatic rings. It was demonstrated before that high optical rotation could be related to the degree of conjugation in the molecule.¹ Compared to the highly optically active 1-nitro compound **I-3** ($[\alpha]_{436} = -7100$), having the three benzene rings not in complete conjugation (twisted angle of 37.4° for the carbon bearing the nitro substituent), this new anhydride **I-6** has a large twisted angle (56.7°), which results in a dramatic change in optical activity.

The term racemization describes the process by which one optically active compound is irreversibly transformed into the optically inactive racemic mixture. Racemization has also been defined as the loss of optical activity of a substance over a period of time.²⁸ The rate constant (k_{rac}) refers to the process by which 50% of the molecule of the starting enantiomer is converted into the other enantiomer. The half-life time of racemization ($t_{1/2}$) is defined as the time during which the enantiomeric purity of a chiral sample is reduced from 100 to 50% enantiomeric excess.²⁹

Racemization studies were done at room temperature with the last fraction (#5) dissolved in chloroform. This solution was regularly injected into the HPLC/chiral column system within two days. For each chromatogram, the percentage of each peak was determined by cutting the weighing paper and by weighing the two cuts. The relative percentage of the P-enantiomer over the racemic mixture was plotted versus the time in minutes (Figure II.7). The racemization half-life time was then determined for 75% of the initial value (84.6%), i.e. for 63.5%, and was found to be 1100 min at 22 °C.

Figure II.7. Determination of racemization half-life time of anhydride I-6.

This relative low racemization half-life time is probably the result of the large twisted angle (56.7°) that pushes apart the benzene rings. As shown in Scheme I.1, racemization of helicene is supposed to occur via a symmetrical intermediate state in which the terminal rings are parallel to each other.^{8,30} Because of the geometric similarity of *o*-terphenyl derivatives with [5]helicene, this class of compounds may behave the same way with an identical transition state. In compound I-6 the terminal rings turn

towards the outer side of the helix hence there is not too much steric hindrance to prevent racemization to occur and the switch from M to P form is made quite easily. The configuration of this molecule (I-6) is actually almost the same as the postulated transition state occurring during the racemization process of helicenes. Indeed the two terminal benzene rings are almost parallel. Therefore the racemization occurs easily and rapidly. Furthermore the flexibility of the propylene linkage can also promote the interconversion between the two conformational enantiomers because the rings can move more freely hence faster.

Chapter III. Monomers Containing *o*-Terphenyl Moiety

III.1. Nitration of Anhydride **I-6** and its Imide **III-1**

The goal was to synthesize an AB-type polyimide as it was successfully done before from anhydride **I-1** by a selective mononitration followed by an hydrogenation and polymerization in *m*-cresol.⁴ Compound **I-6** needed to be transformed into an AB monomer bearing the two reactive groups (anhydride and amine) in the same molecule. From a synthetic point of view this is an interesting monomer for the production and the process of polyimides because the stoichiometry balance between the two monomers is maintained.

In order to get this AB monomer, a selective mononitration has to be done followed by a reduction of nitro group into amino group and then the polymerization can be carried on (Scheme III.1).

Scheme III.1. Proposed synthetic route to polyimide containing *o*-terphenyl moiety.

As the two terminal benzene rings have the same reactivity toward nitration, a selective mononitration is therefore difficult to achieve. Different conditions were used at room temperature (22 °C) all in chloroform and acetic acid with a mixture of nitric and sulfuric acid in acetic acid as the nitrating agent (Table III.1).

Table III.1. Conditions used for nitrations of anhydride I-6.

Run	Anhydride	CHCl ₃	Acetic acid	HNO ₃	H ₂ SO ₄	Acetic acid	Time products ^a
1	0.1 g	3 mL	1 mL	1.5 g	0.9 g	1 mL	ON; SM+M
2	0.5 g	16.5 mL	5 mL	3.5 g	4.3 g	8.5 mL	4 d, M+D
^b	0.1 g	3,3 mL	1 mL	0.7 g	0.85 g	1.7 mL	4 d, M+D
3	0.263 g	8 mL	2.5 mL	3.6 g	4.33 g	4.3 mL	2 d, M+D
^b	0.1 g	3 mL	0.95 mL	1.37 g	1.65 g	1.64 mL	2 d, M+D
4	0.1 g	3 mL	1 mL	3 g	0.9 g	2 mL	ON; D
5	0.1 g	2 mL	1 mL	6.9 g	3.45 g	none	4 hrs; D

^a significance of abbreviations: ON=overnight, d=days, hrs=hours, SM=starting material, M=mononitro, D=dinitro.

^b recalculated for 0.1 g of anhydride.

First of all no mononitrated compound was isolated alone. If the first three reactions are compared, the compromise of the ratio between nitric acid and sulfuric acid as well as the time of the reaction is clearly seen. The first run (#1) was not long enough and there was still some starting material. When reactions are run to completion up to four days, a mixture of mononitro and dinitro products was obtained. By increasing the amount of sulfuric acid the reaction was a little bit faster and complete after two days (run 3). The control of the nitration reaction to get desired substituted products is therefore not easy. As opposed to the difficulty of getting mononitrated compounds, the dinitration is simple and faster (four hours in the case of run 5). The reaction was made quicker by using more nitrating agent and less solvent (more concentrated mixture).

When the reduction of nitro groups into amino groups was done a self condensation between the amine and the anhydride group was observed. Unfortunately this intra molecular reaction avoids the polymerization to be run. Protection of the anhydride group was therefore needed. For this purpose, an imide was synthesized prior to the nitration/reduction reactions (Scheme III.2). This reaction was easy to work out with a 77% yield.

Scheme III.2. Synthesis of the imide **III-1**.

The compound was fully characterized by spectroscopic means. The IR showed two strong absorptions at 1754 and 1703 cm^{-1} corresponding to the carbonyl groups. If the absorption of the anhydride group is compared between imide **III-1** and anhydride **I-6**, a shift to lower frequencies is observed due to the imide transformation. A strong absorption due to alkyl group is also observed at 2932 and 2859 cm^{-1} .

The ^1H and ^{13}C NMR spectra and assignments are reported in Appendix A and B. The ^1H NMR spectrum showed very well the signals from the alkyl chain with the expected splitting and multiplicities. The deshielding effect of the nitrogen is observed on proton H14 whose signal is shifted to a lower field compared to proton H15. The ^{13}C NMR spectrum displayed the expected 17 chemically non-equivalent carbons. The peak intensities between carbons C14 to C17 from the alkyl chain and the aliphatic carbons C6

to C8 are different. The peak intensity is decreased by half because carbons C14 to C17 are two times less abundant than the other aliphatic carbons in the molecule.

HRMS also confirmed the correct molecular mass (435.22 g/mol). The fragmentation of the alkyl chain is well seen in the mass spectrum with the loss of a methyl radical ($m/e = 420$), an ethyl radical ($m/e = 406$), and a propyl radical ($m/e = 392$).

The nitration reaction was then carried on in order to get dinitro products (Figure III.1). The desired product was the 3,3' substituted compound (III-2). However only the 2,2' and the 2,3' substituted products were obtained (III-3 and III-4 respectively).

Figure III.1. Aromatic nitrations of imide III-1.

The analysis of the splitting, the coupling constants and proton intensities from the ^1H NMR spectrum allowed the unambiguous assignment for each aromatic substituted positions (Figure III.2).

The IR spectrum still showed the two strong absorptions at 1761 and 1704 cm^{-1} corresponding to the carbonyl groups (imide) as well as absorptions due to aromatic CH stretch (3069 and 3026 cm^{-1}), alkyl CH stretching (2934 and 2862 cm^{-1}) and aromatic C=C stretch at 1453 cm^{-1} . The two strong bands at 1521 and 1346 cm^{-1} indicated the presence of the nitro groups.

Figure III.2. ^1H NMR spectra (aromatic region) of nitro compounds **III-3** and **III-4**.

The HRMS confirmed the correct molecular mass for the dinitrated compound (525.19 g/mol). The mass spectrum clearly showed one of the alkyl chain fragmentation with the loss of a propyl radical ($m/e = 482$). However the fragmentation due to the loss of nitro group (NO^+ or NO_2^+) gave very weak peaks.

The reduction of nitro groups into amino groups was successful by hydrogenation using PtO_2 in THF at room temperature. The IR spectrum confirmed the presence of the primary amine groups with absorption at 3438 and 3375 cm^{-1} . However as the control of the nitration reaction as well as the isolation of each isomers were difficult to achieve, this project was not carried on anymore. Instead as the anhydride group is easily functionalized, the synthesis of a methacrylate monomer from **I-6** was attempted.

III.2. Synthesis of Methacrylate Monomer

The synthesis of methacrylate monomer **III-6** is a two-step process (Scheme III.3). The first step is imidization with ethanolamine to give compound **III-5**. The next reaction is esterification with methacryloyl chloride to yield the methacrylate monomer **III-6**. The imidization was a fast reaction and easy to handle, giving the product in a high yield (90%) without any purification. Triethylamine was used in the esterification reaction to capture the formed hydrogen chloride. Monomer **III-6** was purified by recrystallization from acetonitrile and obtained as a white powder in 47% yield.

Scheme III.3. Synthesis of monomer **III-6**.

III.3. Characterization

The intermediate imide **III-5** was fully characterized by spectroscopy. The IR spectrum showed the carbonyl stretching at 1754 and 1701 cm^{-1} , alcohol stretch at 3488 and 3439 cm^{-1} as well as aromatic CH stretch (3062 and 3025 cm^{-1}), aromatic C=C stretch (1450 cm^{-1}) and alkyl CH stretch (2936 and 2859 cm^{-1}).

The ^1H and ^{13}C NMR spectra and assignments are reported in Appendix C and D. If the ^1H and ^{13}C NMR spectra of imide **III-1** and imide **III-5** are compared they are alike. However the oxygen from the terminal alcohol in the imide **III-5** deshields both hydrogen H15 and carbon C15. The carbon C15 is even more shifted to lower field (61.64 ppm) than carbon C14 (40.79 ppm). The ^{13}C NMR spectrum displayed the expected 15 carbon atoms.

HRMS confirmed the exact mass (491.21 g/mol). In the mass spectrum a medium peak (relative intensity 40.2%) is allocated due to the loss of $\text{CH}_2=\text{OH}^+$ ions ($m/e = 392$).

Concerning the monomer **III-6**, the IR spectrum showed separately the ester carbonyl stretching (1721 cm^{-1}) from the two other carbonyl vibrations (1754 and 1703 cm^{-1}). The ester vibration is shifted to lower frequencies due to conjugation of the carbonyl with the double-bond.

The ^1H and ^{13}C NMR data are reported in Table III.2 and Table III.3 and spectra are shown in Figure III.3 and Figure III.4. In the ^1H NMR spectrum the hydrogen H15 is even more deshielded than in imide **III-5** due to the ester function. The two unequivalent protons from the double-bond (H19a and H19b) give two different signals at 6.12 and 5.56 ppm respectively. The methyl signal (H18 at 1.92 ppm) is also deshielded compared to hydrogen H17 in imide **III-5** (0.90 ppm) due to the conjugated ketone-alkene system. The ^{13}C NMR spectrum displayed the expected 19 chemically non-equivalent carbons. The carbon C16 from the carbonyl ester group is assigned at 167.18 ppm. Its intensity is smaller than for carbon C11 (carbonyl from imide) because carbon C11 is present twice in the molecule. Carbons C17 and C19 are displayed in the lower field region of alkene (136.03 and 126.08 ppm) due to the conjugated ketone-alkene system.

Table III.2. ^1H NMR assignments of monomer **III-6**.

^1H NMR	δ , ppm		J, Hz
H 1	6.39	2 H, dd	1.00, 7.68
H 2	6.85	2 H, dt	1.28, 7.54
H 3	7.14	2 H, dt	1.23, 7.44
H 4	7.23	2 H, dd	0.94, 7.50
H 6	2.71, 2.61	2 H, m, 2 H, m	
H 7	2.18	4 H, m	
H 8	4.05, 2.05	2 H, m, 2 H, m	
H 14	4.05	2 H, m	
H 15	4.39	2 H, t	5.40
H 18	1.92	3 H, s	
H 19a	6.12	1 H, m	
H 19b	5.56	1 H, m	

Table III.3 ^{13}C NMR assignments of monomer **III-6**.

^{13}C NMR	δ , ppm	^{13}C NMR	δ , ppm
C 1	130.66	C 11	168.83
C 2	125.66	C 14	36.59
C 3	127.97	C 15	62.16
C 4	127.89	C 16	167.18
C 6	31.13	C 17	136.03
C 7	31.39	C 18	18.26
C 8	24.46	C 19	126.08
C 5, 9, 10, 12, 13	145.76, 140.11, 138.51 137.65, 126.91

Figure III.3. ^1H NMR spectrum (400 MHz, CDCl_3) of monomer **III-6**.

Figure III.4. ¹³C NMR spectrum (100 MHz, CDCl₃) of monomer **III-6**.

The ^1H NMR spectrum of **III-6** is somehow unexplained for the methacrylate part concerning the splitting. If this spectrum is compared with the proton spectrum of methyl methacrylate (MMA)³¹, the chemical shifts of each significant proton match well (Table III.4). However the multiplicity of each signal looks different. The alkene protons in MMA as well as in the monomer give a complex series of lines. However the methyl signal in the monomer **III-6** is a singlet although it is a doublet in MMA which upon expansion shows a more complex pattern.

Table III.4. Proton chemical shifts in ppm of monomer **III-6** and MMA.

III-6		MMA
	a	1.92	1.95
	b	5.56	5.57
	c	6.12	6.10

HRMS confirmed the exact mass (491.21 g/mol). The alpha-cleavage of the ester results in two molecular ions from the alkoxy group and the acylium ion. The mass spectrum clearly showed the fragment peak ($m/e = 422$) due to the loss of the radical $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}=\text{O}^\cdot$.

The UV-vis absorption spectra of anhydride **I-6** and monomer **III-6** are shown in Figure III.5. Both spectra are alike with the two maximum absorptions of monomer **III-6** at 339.0 and 265.0 nm. The smallest peak is shifted to a longer wavelength due to the conjugation of the carbonyl with the double-bond. The introduction of the alkene brings a

new chromophore within the molecule therefore a higher intensity was observed at 265 nm.

Figure III.5. UV-vis spectra of anhydride **I-6** (2.34×10^{-5} mmol/mL, chloroform) and monomer **III-6** (1.78×10^{-5} mmol/mL, chloroform).

Theis two-step process yielded the monomer in good yield and high purity. With this pure monomer at hand the polymerizations were then carried out.

Chapter IV. Polymethacrylate Containing *o*-Terphenyl Moiety

IV.1. Free Radical Polymerization

The match of monomer **III-6** and MMA of the smaller methyl ester group favours the formation of copolymers. Copolymerizations were run at 80°C in benzene with AIBN as an initiator (0.1% weight). Four different molar ratios between **III-6** and MMA were experimented as well as the homopolymerization (Figure IV.1). The molar composition of the two monomers in the copolymer was determined by UV calibration of monomer **III-6** at 339.0 nm (Figure IV.2 and Table IV.1).

The resulting polymers, as white fibrous solids, were isolated by precipitation into methanol, and purified by reverse precipitation to remove small amounts of oligomers. Polymers were dried overnight in a vacuum oven (50 °C, 5 mmHg).

Figure IV.1. Structures of homopolymer **IV-1** and copolymers **III-6:MMA**.

Figure IV.2. UV-vis calibration curve (339.0 nm) of monomer **III-6** (chloroform, 22 °C).

Table IV.1. Compositions of copolymers (molar percentage).

Copolymers	IV-2	IV-3	IV-4	IV-5
x in polymer ^a	0.09	0.15	0.38	0.45
x in feed ^b	0.10	0.17	0.50	0.89

^a mole fraction of monomer **III-6** in polymers determined by UV-vis calibration of monomer **III-6**.

^b mole fraction of monomer **III-6** in feed.

Because of a difference in the reactivity of the monomers, the composition of copolymers is different from that of the feed mixture.³² Indeed a decrease of monomer **III-6** content in copolymers is observed compared to the reactant mixture. This effect occurred more specifically when the monomer **III-6** content in the feed mixture is high. The reactivity of monomers is characterized by the reactivity ratios r_1 and r_2 . These parameters measure the relative preference that the polymer radicals $A^\bullet$ and $B^\bullet$ have for the two monomers A and B. When $r_1 < 1$, the polymer radical $A^\bullet$ reacts more

preferentially with the monomer B than the monomer A. Conversely when $r_1 > 1$, the polymer radical $A^\bullet$ reacts more preferentially with the monomer A than the monomer B. As stated above the content of copolymers **IV-2/5** is richer in MMA (poorer in monomer **III-6**) compared to the feed mixture composition. Therefore MMA is the most reactive monomer: MMA is more reactive than monomer **III-6** toward both propagation species. The radical from MMA preferentially adds monomer MMA instead of monomer **III-6** ($r_{\text{MMA}} > 1$) and the radical from monomer **III-6** preferentially adds monomer MMA than monomer **III-6** ($r_{\text{monomer III-6}} < 1$).³³

IV.2. Characterization

IV.2.1. Spectroscopic Characterization

NMR analyses were done with homopolymer **IV-1** and copolymer **IV-3**. ^1H and ^{13}C NMR spectra were not always well resolved and broad lines were displayed. However by running HETCOR experiment most of the peaks were assigned. The ^1H and ^{13}C NMR data are reported in Table IV.2 and Table IV.3 for homopolymer **IV-1** and in Table IV.4 and Table IV.5 for copolymer **IV-3**. The spectra can be seen Figure IV.3 and Figure IV.4 for homopolymer **IV-1** and Figure IV.5 and Figure IV.6 for copolymer **IV-3**.

The transformation of monomer **III-6** into homopolymer **IV-1** is seen by the disappearance of the two protons H_{19a} and H_{19b} from the double bond, and the presence of a new peak in the alkyl region at 1.85 ppm. The carbon NMR also confirmed the chemical transformation of carbons C_{17} and C_{19} : both carbon signals are shifted to higher field (44.75 and 53.83 ppm) because the double bond reacted to give a simple carbon-carbon bond. In the proton spectrum some impurities appeared below 1 ppm correlated to

the 19.05 and 17.26 ppm peaks in the carbon spectrum. The peak at 1.56 ppm in the proton spectrum is unexplained as this signal has no proton-carbon correlation in the molecule (no crosspeak appeared in the HETCOR experiment).

Table IV.2. ^1H NMR assignments of homopolymer IV-1.

^1H NMR	δ , ppm	^1H NMR	δ , ppm
H 1	6.27	H 8	3.91, 2.00
H 2	6.72	H 14	3.91
H 3	7.00	H 15	4.03
H 4	7.08	H 18	1.26
H 6	2.54	H 19	1.85
H 7	2.00		

Table IV.3. ^{13}C NMR assignments of homopolymer IV-1.

^{13}C NMR	δ , ppm	^{13}C NMR	δ , ppm
C 1	130.64	C 11	168.33
C 2	125.51	C 14	35.98
C 3	127.72	C 15	61.43
C 4	127.72	C 16	176.10
C 6	31.12	C 17	44.75
C 7	31.39	C 18	29.70
C 8	24.32	C 19	53.83
C 5, 9, 10, 12, 13	145.33, 140.11, 138.06 137.72, 127.04

Figure IV.3. ^1H NMR spectrum (400 MHz, CDCl_3) of homopolymer IV-1.

Figure IV.4. ^{13}C NMR spectrum (100 MHz, CDCl_3) of homopolymer IV-1.

Table IV.4. ^1H NMR assignments of copolymer IV-3.

^1H NMR	δ , ppm	^1H NMR	δ , ppm
H 1	6.40	H 14	3.59
H 2	6.85	H 15	4.20
H 3	7.14	H 18	1.00
H 4	7.22	HD	0.82
H 6	2.67	H 19	1.87
H 7	2.17	HE	1.80
H 8	4.00, 2.03	HA	3.59

Table IV.5. ^{13}C NMR assignments of copolymer IV-3.

^{13}C NMR	δ , ppm	^{13}C NMR	δ , ppm
C 1	130.67	C 15	61.83
C 2	125.65	C 16/B	177.79, 176.96
C 3	127.91	C 17/C	44.94, 44.60
C 4	127.91	C 18	18.87
C 6	31.13	CD	16.64
C 7	31.42	C 19	54.16
C 8	24.47	CE	54.41
C 11	168.72	CA	51.77
C 14	35.99	C 5, 9, 10, 12, 13	145.74, 140.16, 138.45 137.71, 126.91

Figure IV.5. ^1H NMR spectrum (400 MHz, CDCl_3) of copolymer IV-3.

Figure IV.6. ^{13}C NMR spectrum (100 MHz, CDCl_3) of copolymer IV-3.

In copolymer IV-3 NMR spectra, each monomer showed separate signals for the same chemical carbon or proton. In ^1H NMR spectrum there is a distinction between protons H_{18} and H_{D} as well as protons H_{19} and H_{E} . In ^{13}C NMR spectrum two peaks are displayed for carbons $\text{C}_{\text{B}}/\text{C}_{16}$, $\text{C}_{\text{E}}/\text{C}_{19}$ and $\text{C}_{18}/\text{C}_{\text{D}}$. By comparison of the chemical shifts between homopolymer IV-1 and copolymer IV-3, the signals due to monomer III-6 can be assigned. It is interesting to notice that the signal intensities for monomer III-6 are smaller than the one for MMA. However this was expected as the composition of copolymer IV-3 is 14.9% of monomer III-6.

In both ^{13}C NMR spectra, two of the aromatic carbons (C_3 and C_4) are overlapped. At 127.91 ppm, only one peak is seen but in the HETCOR experiment (Figure IV.7), the peak is correlated to two different proton signals (H_3 and H_4).

Figure IV.7. HETCOR 2D spectrum of copolymer IV-3 (aromatic region).

These NMR analyses indicated the expected presence of the two monomers in the copolymers.

The IR spectra of copolymers indicated the presence of the carbonyl groups (1760 and 1707 cm^{-1}) as well as the ester (1734 cm^{-1}). It could be seen that the carbonyl ester stretching is shifted back to its usual frequency as the carbonyl group is no longer in conjugation with the double bond (the double bond reacted to give a simple carbon-carbon bond). It is interesting to notice that these carbonyl vibrations varied with the composition of the copolymers. Indeed when the molar percentage of monomer **III-6** increases in the copolymer (when the percentage of MMA decreases), the ester carbonyl peak from MMA reduced in intensity (Figure IV.8). When the molar ratio of MMA in the copolymer is up to 91.4%, the carbonyl ester peak is so strong that it overlaps one of the other carbonyl peak.

Figure IV.8. IR spectra (carbonyl stretching vibrations) of monomer III-6 and polymers IV-2,-5.

Polymers with saturated C-C bonds in the main chain exhibit fluorescent properties if a π -conjugated system is present in their side groups (aromatic or heterocyclic substituents).³⁴ Therefore the synthesized polymers should be fluorescent. Furthermore they contain a fluorophore unit (fluorescence substance) from the anhydride I-6.

The goal was to study the fluorescence of homopolymer and copolymers to approach the effect of the concentration of the fluorophore in these molecules. For very dilute solutions, the relation between fluorescence and concentration is comparable to Beer's law in spectrophotometry. Thus a plot of fluorescence versus concentration should be linear.³⁵ This linear response was observed with four different concentrations of copolymer IV-3 in chloroform at 22 °C (Figure IV.9). The excitation wavelength was at 335 nm and the emission wavelength was observed at 430 nm as with the anhydride I-6.

Figure IV.9. Dependence of fluorescence on the concentration of copolymer IV-3 (chloroform, 22 °C).

Dilute solutions of each polymer were then studied in order to see the effect of the fluorophore III-6 on the fluorescence properties of the polymers (Table IV.6). The same excitation and emission wavelengths as above were used to collect data.

Table IV.6. Fluorescence intensities of polymers **IV-1/5** (chloroform, 22 °C).

Polymers	x in polymer ^a	Concentration (x 10 ⁻⁴ mg/mL)	Fluorescence intensity (%) at 430 nm
IV-1	1	3.26	56
IV-2	0.09	3.23	36
IV-3	0.15	3.23	37
IV-4	0.38	3.23	66
IV-5	0.45	3.20	66

^a mole fraction of monomer **III-6** in polymers determined by UV-vis calibration of monomer **III-6**.

As all polymer solutions have the same concentration, the percentage of monomer **III-6** in polymers may be considered as a “concentration effect”. Between copolymers **IV-2,-3** and **IV-4,-5** the increase in monomer **III-6** percentage is well seen with an increase in the fluorescence intensity. However the fluorescence response is not sensitive enough to see a difference between copolymers **IV-2** and **IV-3** as well as copolymers **IV-4** and **IV-5**; the percentage of monomer **III-6** between polymers needs to be large enough in order to notice a change in the fluorescence intensity.

The smaller fluorescence response for homopolymer **IV-1**, when compared to that of copolymers **IV-4** or **IV-5**, may be explained by fluorescence quenching due to concentration. Fluorescence quenching refers to any process that decreases the fluorescence intensity of a given substance. A variety of processes can result in quenching. These include excited state reactions, energy transfer, complex formation and collisional quenching.³⁶ Fluorescence intensity is proportional to the molar absorptivity: the more highly absorbing the substance, the greater its fluorescence. But when the absorption is too large, no light can pass through to cause excitation. This type of concentration quenching causes a fluorescence loss that is called the inner-cell effect: the fluorescence decreases at high concentrations. Concentration quenching can also take the

form of energy transfer between molecules of the sample. An important formation of concentration quenching involves excimer quenching. The excimer has a different electron orientation and a longer emission wavelength. As the instrument monitors the fluorescence at one wavelength, the emission at the longer wavelength is not detected. So the observed fluorescence will decrease with increasing concentrations.³⁵ Thus when the polymer contains a lot of fluorophore – high percentage of monomer **III-6** – the fluorescence intensity is decreased. This is well observed in homopolymer **IV-1** but also in copolymers **IV-3,-4** where the fluorescence intensity should be a little bit higher than 36% depending on the monomer **III-6** percentage.

In many fields such as nuclear power engineering, biology and medicine, ionizing radiation detections are used very often. One of the methods which holds great promise is the scintillation method. Along with monocrystal and liquid scintillators, plastic scintillators are much used. Plastic scintillators are composed of a polymer base and an organic luminescent compound. Of the inactive polymer bases, poly(methyl methacrylate) is most popular owing to its good physical and mechanical properties and high transmission. However, because of the absence in the repeat unit of PMMA of π -conjugation, PMMA based scintillators have low scintillation efficiency.³⁷ The copolymerization of MMA with monomer **III-6** may contribute to a higher π -conjugation hence a better scintillation efficiency.

IV.2.2. Molecular Weight Determination

The molecular weight of a polymer is of prime importance in its synthesis and application. Important aspects such as thermal and mechanical properties are all dependent on the molecular weight. In general, as the molecular weight increases, the

physical properties improve until they reach a plateau value at which point further increase in the molecular weight will have only limited effect on the properties.

GPC showed that high molecular weight products relative to polystyrene standards were obtained. The apparent weight-average molecular weight of polymers ranged from 140,300 to 214,600 g/mol (Table IV.7). All GPC traces were monomodal with polydispersity indexes (M_w/M_n) varying between 1.43 and 2.57.

Table IV.7. Molecular weights and inherent viscosities of polymers IV-1/5.

Polymers	x in polymers ^a	$M_w^b \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n	$\eta_{inh} \text{ (dL/g)}^c$
IV-1	1	14.03	9.81	1.43	0.21
IV-2	0.09	15.04	7.62	1.97	0.37
IV-3	0.15	21.46	8.33	2.57	0.45
IV-4	0.38	16.40	7.55	2.17	0.26
IV-5	0.45	14.97	7.48	2.00	0.15

^a mole fraction of monomer III-6 in polymers determined by UV calibrations of monomer III-6.

^b relative to polystyrene standards.

^c inherent viscosity (0.5 g/dL in chloroform) measured at 25°C.

One of the most characteristic features of a dilute polymer solution is that its viscosity is considerably higher than that of the pure solvent. This arises because of the large differences in size between polymer and solvent molecules. Most commonly dilute solution viscometry is used to estimate the molecular weight of a polymer.³⁸ In general, providing that the polymers with similar structures are being compared, the higher the viscosity, the higher the molecular weight. This statement is pretty much observed in the present polymers with inherent viscosities ranging from 0.21 to 0.45 dL/g in chloroform (Table IV.6). The highest viscosity (0.45 dL/g) was obtained for the highest molecular weight (214,600 g/mol) and the lowest viscosities (0.15; 0.21 dL/g) were achieved by the

lowest molecular weights (149,700; 140,300 g/mol). However the values are quite low for the high molecular weight polymers synthesized.

IV.2.3. Thermal Properties

Semi-crystalline polymers are characterized by two major types of transition temperatures (Figure IV.10): the crystalline melting temperature (T_m) and the glass transition temperature (T_g). None of these polymers showed any crystalline behavior as assessed by DSC.

Figure IV.10. DSC trace of a semicrystalline polymer.

An amorphous polymer at low temperatures is a hard glassy material which, when heated, melts into a viscous liquid. However before melting it goes through a rubbery state. The temperature at which a hard glassy polymer becomes a rubbery material is termed the glass transition temperature T_g .³⁹ The glass transition temperature is therefore

the temperature at which the amorphous domains of a polymer take on the characteristic properties of the glassy state: brittleness, stiffness, and rigidity.⁴⁰

Given that T_g is a function of rotational freedom, chemical structure is clearly the most important factor in the determination of thermal properties. The flexibility of the polymer chain is dependent upon the free space available for rotation. If the free space is reduced by the presence of large substituents, the T_g value goes up.

Although T_g is independent of molecular weight when it is substantially high, as the molecular weight decreases so does the T_g . This lowering of the T_g is essentially an end-group effect. Polymers of low molecular weight have a greater number of chain ends in a given volume compared to those of high molecular weight. Since chain ends are less restrained, they have a greater mobility at a given temperature. This results in a lower T_g value.

The glass transition temperatures of polymers were observed between 132 and 171 °C depending on their composition (Table IV.8).

Table IV.8. DSC and TGA results for polymers IV-1/5.

Polymers	x in polymer ^a	T_g (°C) ^b	T_d (°C) ^c
IV-1	1	171	346
IV-2	0.09	132	236
IV-3	0.15	136	276
IV-4	0.38	146	294
IV-5	0.45	148	330

^a mole fraction of monomer III-6 in polymers determined by UV calibrations of monomer III-6.

^b second scan at a heating rate of 10 °C/min.

^c onset temperature for 5% weight loss in nitrogen at a heating rate of 10 °C/min.

By looking at the T_g values, it is clearly seen that the introduction of MMA in the polymer chains brings more flexibility to the backbone hence lowers the T_g temperature.

This is especially observed between copolymer **IV-2** and homopolymer **IV-1**. The latter possess a higher Tg due to a large steric hindrance coming from the bulky pendant groups. For copolymer **IV-2** the Tg value is decreased by 40 °C.

In copolymers **IV-3/5** even though the percentage of MMA is higher the decrease in the Tg temperature is not significant. This could be due to the high molecular weight polymers. Indeed there is a compromise between the flexibility ability that MMA brings into the polymer backbone - the higher the flexibility the lower the Tg - and the free space availability for rotation – the higher the molecular weight the higher the steric hindrance then the lower the motion in the polymer.

The plot of monomer **III-6** content in polymers versus the Tg temperature (Figure IV.11; Equation: $y = 42.1x + 129$, $R^2 = 0.998$) is linear therefore copolymers are random copolymers.⁴¹

Figure IV.11. Dependence of the Tg on the composition of random copolymers **IV-1/5**.

Thermogravimetry is widely used for assessing the thermal stability of polymeric materials. However the conclusions drawn with regard to stability are only relevant within the context of the weight loss of the sample. There are reactions that can take place on heating a polymer and which alter drastically the physical properties of the material without an observed change in weight.⁴²

The thermal stabilities of the polymers were assessed by thermogravimetric analysis (TGA) in nitrogen. The onset temperatures for 5% weight loss for these polymers ranged from 236 to 346 °C (Table IV.8).

TG thermograms for copolymers **IV-2** and **IV-3** showed different degradations. Copolymer **IV-2** had three weight losses at 170 °C (99.6% weight loss), 229 °C (95.5% weight loss) and 333 °C (69.7% weight loss). For copolymer **IV-3**, the first weight loss (98.8%) occurred at 245 °C and the second weight loss (68.6%) occurred at 338 °C.

The homopolymer **IV-1** is the most thermal stable polymer as its T_d is the highest one among all polymers. The incorporation of monomer **III-6** into copolymers brings more thermal stability to the polymer. Indeed the higher the ratio of monomer **III-6** versus MMA, the higher the T_d . When this ratio is almost 50:50 (copolymer **IV-5**) the T_d is just 15 °C below the homopolymer's T_d .

Conclusion

Chiral *o*-terphenyl anhydride **I-6** was synthesized in four steps from commercially available products. The spatial arrangement of *o*-terphenyl moiety induced the helical shape of the molecule hence its chirality. The study of the crystal structure and chiroptical properties led to the conclusion that optical rotation is strongly affected by degree of conjugation.

From this chiral anhydride, a methacrylate monomer **III-6** then a series of high molecular weight polymethacrylates **IV-1/5** were synthesized. An interesting feature of these polymers is their fluorescence ability that varies with their composition.

Experimental section

Materials.

Mercury (II) chloride (99.5%), maleic anhydride (99%), lead (IV) acetate (95%), ethanolamine (98%), n-butylamine (99%), triethylamine (99%), methacryloyl chloride (90%), 2,2'-azobisisobutyronitrile (recrystallized from ethanol) were purchased from Aldrich Chemical Co. Methyl methacrylate (99%) was distilled at 20 mm Hg at room temperature then passed through a column packed with silicagel 60, particle size 0.063-0.200 mm, EM Science. Benzosuberone was purchased from Digital Specialty Chemicals Ltd. and used without any purification. Common organic solvents (Aldrich) were reagent grade and used as received. N,N-dimethylformamide was dried over molecular sieves (4Å, Aldrich). Isopropanol and hexane were HPLC grade when used for HPLC separation. Chloroform was spectrograde when used for fluorescence studies.

Characterization.

The ^1H and ^{13}C NMR spectra were recorded on either a Varian Gemini-200 or a Bruker-400 instruments and results are reported in ppm from tetramethylsilane on the δ scale. Infrared measurements were performed on a Bomem-FTIR Michelson series instrument. Low resolution mass spectra were obtained on a DuPont 21-492B spectrometer. The apparent molecular weights of the polymers were determined by gel permeation chromatography using chloroform at ambient temperature at the flow rate 1.0 mL/min on a Perkin-Elmer LC-250 GPC. Molecular calculations were based on polystyrene standards. The elution of the polymers from the column was detected by a

Perkin-Elmer UV-vis spectrophotometric detector set at 254 nm wavelength. Inherent viscosity data were obtained from a Ubbelohde viscometer (size OB114) in 0.5 g/dL chloroform solution at 25 °C. The glass transition temperatures (Tg's) of the polymers were obtained on a Seiko 220C differential scanning calorimeter with a heating rate of 10 °C/min in oscillation mode under nitrogen (50 mL/min). The Tg values were reported from the second scan. The Tg was taken from the midpoint of the change in the slope of the baseline. The weight loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 10 °C/min under nitrogen (200 mL/min). Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. UV-vis spectra were obtained on a Varian Cary 3 Spectrometer, using 1 cm quartz cells. Fluorescence studies were performed on a Perkin-Elmer 204-S Fluorescence Spectrophotometer with a Perkin-Elmer 150 Xenon Power Supply using 1 cm quartz cells.

Aromatic anhydride I-6.

In a 20 L reaction vessel absolute ethanol (0.76 L) and toluene (1.33 L) were placed with mercuric chloride (2.8 g, 10.3 mmol). When benzosuberone (500 g, 3.12 mol) was added to this colourless solution the mixture turned yellow. Under mechanic stirring and heating with a hot plate, aluminum foil (151 g, 5.6 mol) was added time to time in square pieces. The grey solution was refluxed during 5h30 until no more starting material showed on TLC (hexane-acetone). After cooling, ice then diluted HCl solution

(500 mL) were added to this mixture. Without any filtration, diethyl ether was then added. Seven extractions with diethyl ether were performed leading to two different organic extracts: one yellow and the other one white. Both were dried over magnesium sulfate, suction filtered and concentrated with rotary evaporator at 80 °C to yield 454 g of a yellow solid suspension and 45 g of a white solid suspension. From this white suspension, 10 g of pure meso isomer was obtained by suction filtration.

In a 1 L RBF, acetic acid (100 mL) and acetic anhydride (300 mL) were mixed with the previously isolated yellow solid suspension (454 g). With an oil bath, the solution was refluxed during 2h30 until no more starting material showed on TLC (hexane-acetone). The colour of the solution changed from yellow to green then brown. Solvent was removed at 90 °C with rotary evaporator to yield a brown suspension. Distillation (under 0.05 mm Hg, oil bath up to 175 °C) was performed to remove low boiling points products (80 °C). Two other fractions were also collected that contained the product with impurities. Hexane was added to the brown residue (188 g) and the mixture refluxed for 30 minutes, filtered by suction (brown precipitate) and concentrated. A GC-MS confirmed the presence of diene with MW=286 g/mol.

Maleic anhydride (700.5 g, 7.14 mol) was melted first with an oil bath at 110 °C in a 2 L Erlenmeyer flask. The previously isolated diene melted with heat gun was then added. The reaction was carried out at 100-110 °C and followed by TLC (hexane-acetone). It was stopped after 3 hours. The brown solution was poured into 700 mL of boiling water to give a green gel in an orange-brown solution. Hot water (700 mL) was added again to the isolated green gel and then removed by setting and decanting the solution. The brown solution contained a lot of white-orange water-soluble solid that

could be maleic anhydride plus other impurities but no product. The green gel was triturated in hexane and methylene chloride and a white precipitate came out. The latter was suction filtered and washed with hexane to yield 173 g of product. This white powder was washed with chloroform, filtered and concentrated to yield 90 g of product. After drying in a vacuum oven (100 °C, 20 mm Hg) 47.8 g of product was finally obtained (8% yield from benzosuberone).

The Diels-Alder product (47.8 g, 0.124 mol) was mixed with lead tetraacetate (140.8 g, 0.318 mol) in acetic acid (500 mL) and acetic anhydride (500 mL) in a 3 L RBF with an inner thermometer. The mixture was heated with an heating mantle at 130 °C during 4h30. The colour of the solution changed from milky yellow to a translucent orange. Overnight a yellow powder precipitated in the solution. More lead tetraacetate was added (30 g) and the reaction was carried overnight at 130 °C to yield a black solution. To this cooled solution 3 L of distilled water was added to precipitate a brown fine powder. It was suction filtered, washed with water and dried overnight at room temperature. The following day, the powder was dried 4 hours in a vacuum oven (100 °C, 5 mm Hg). Methylene chloride (700 mL) was added to the crystals and the suspension was suction filtered. The collected white beige precipitate was washed several times with methylene chloride then dried. Acetone (700 mL) was added to the filtrate and the solution was stirred overnight. Pure product (11.7 g) precipitated as a slightly yellow powder and was suction collected then dried. More impure crystals (11.0 g) were also later collected from the filtrate. The final yield was 48% and 4% from benzosuberone.

mp 288 °C (DSC; lit. 284-285 °C); IR (KBr, cm^{-1}) 1765, 1838 (C=O anhydride), 3069, 3025 (aromatic CH), 1450 (C=C), 2936, 2831 (alkyl CH); λ_{max} (2.34×10^{-5}

mmol/mL, chloroform) 269.2, 335.8 nm; λ_{exc} 335 nm, λ_{em} 430 nm (1.32×10^{-6} mmol/mL, chloroform); ^1H NMR (400 MHz, CDCl_3) δ 7.28 (2 H, d, $J = 7.44$ Hz), 7.20 (2 H, dt, $J = 1.11$ Hz, $J = 7.46$ Hz), 6.90 (2 H, dt, $J = 1.04$ Hz, $J = 7.44$ Hz), 6.42 (2 H, d, $J = 7.68$ Hz), 3.92 (2 H, m), 2.77 (2 H, m), 2.60 (2 H, m), 2.25 (4 H, m), 2.15 (2 H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 163.47, 147.79, 140.60, 139.98, 136.92, 130.52, 128.48, 128.10, 126.40, 125.83, 31.48, 30.95, 24.91; MS (EI, m/e , relative intensity %) 380 (M^+ , 100); HRMS calcd for $\text{C}_{26}\text{H}_{20}\text{O}_3$ 380.1413, found 380.14215.

Imide III-1.

Anhydride **I-6** (1.00 g, 2.64 mmol) was dissolved in acetic acid (18 mL) then *n*-butylamine (7.00 mL, 0.07 mol) was added dropwise. The mixture was heated for 24 hours at 160 °C with a glassware adaptor to remove the water. After cool down to room temperature acetic acid was partially removed with a rotary evaporator then the solution was poured into water to precipitate a slightly brown powder. The latter was suction filtered, washed with water and dried overnight in a vacuum oven (80 °C, 5 mm Hg) to give 0.885 g of product (77%).

mp 185-190 °C; IR (KBr, C=O imide) 1754, 1703 cm^{-1} (alkyl CH) 2932, 2859 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.15 (2 H, dd, $J = 1.00$ Hz, $J = 7.48$ Hz), 7.07 (2 H, dt, $J = 1.28$ Hz, $J = 7.46$ Hz), 6.77 (2 H, dt, $J = 1.29$ Hz, $J = 7.55$ Hz), 6.32 (2 H, dd, $J = 1.10$ Hz, $J = 7.70$ Hz), 4.00 (2 H, m), 3.62 (2 H, t, $J = 7.28$ Hz), 2.64 (2 H, m), 2.54 (2 H,

m), 2.12 (4 H, m), 2.04 (2 H, m), 1.62 (2 H, q, $J = 7.37$ Hz), 1.34 (2 H, sx, $J = 7.42$ Hz), 0.90 (3 H, t, $J = 7.36$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 169.31, 145.56, 140.15, 138.22, 137.78, 130.67, 127.89, 127.86, 127.08, 125.63, 37.56, 31.37, 31.16, 30.76, 24.39, 20.23, 13.70; MS (EI, m/e, relative intensity %) 435 (M^+ , 100); HRMS calcd for $\text{C}_{30}\text{H}_{29}\text{NO}_2$ 435.2199, found 435.2194.

Nitrations of Anhydride I-6.

Anhydride I-6 was dissolved in chloroform to which acetic acid was added. The nitrating agent (mixture of 70% nitric acid and concentrated sulfuric acid in acetic acid) was then added to the previous solution. All reactions were carried on at room temperature (22 °C).

Run	Anhydride	CHCl_3	Acetic acid	HNO_3	H_2SO_4	Acetic acid	Time products ^a
1	0.1 g	3 mL	1 mL	1.5 g	0.9 g	1 mL	ON; SM+M
2	0.5 g	16.5 mL	5 mL	3.5 g	4.3 g	8.5 mL	4 d, M+D
3	0.263 g	8 mL	2.5 mL	3.6 g	4.33 g	4.3 mL	2 d, M+D
4	0.1 g	3 mL	1 mL	3 g	0.9 g	2 mL	ON; D
5	0.1 g	2 mL	1 mL	6.9 g	3.45 g	none	4 hrs; D

^a significance of abbreviations: ON=overnight, d=days, hrs=hours, SM=starting material, M=mononitro, D=dinitro.

Most of the time no isolation was performed. Reactions were followed by TLC to check their completion and composition (mononitrated or dinitrated compounds).

Imide III-5.

Anhydride **I-6** (10.21 g, 26.9 mmol) was first dissolved in DMF (50 mL) at 160 °C. Ethanolamine (4 mL, 64.7 mmol) was then added dropwise to this solution. After 15 min almost all the starting material reacted. The reaction was stopped after 30 min. After being cooled to room temperature, the dark orange solution was added dropwise to a solution (200 mL water/200 mL methanol/10 g NaCl) to yield a beige powder. The latter was suction filtered and dried overnight in a vacuum oven (22 °C, 20 mm Hg) to yield 10.28 g (90%).

mp 215-218 °C; IR (KBr, cm^{-1}) 1754, 1701 (C=O imide) 3488, 3439 (OH bonded) 3062, 3025 (aromatic CH) 1450 (aromatic C=C) 2936, 2859 (alkyl CH); ^1H NMR (400 MHz, CDCl_3) δ 7.22 (2 H, d, $J = 7.44$ Hz), 7.14 (2 H, dt, $J = 1.17$ Hz, $J = 7.46$ Hz), 6.85 (2 H, dt, $J = 1.21$ Hz, $J = 7.58$ Hz), 6.39 (2 H, d, $J = 7.68$ Hz), 4.05 (2 H, m), 3.92 (4 H, m), 2.72 (2 H, m), 2.61 (2 H, m), 2.20 (4 H, m), 2.06 (2 H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 169.78, 145.90, 140.10, 138.64, 137.62, 130.65, 128.00, 127.89, 126.84, 125.68, 61.64, 40.79, 31.35, 31.12, 24.49; MS (EI, m/e, relative intensity %) 423 (M^+ , 96.7); HRMS calcd for $\text{C}_{28}\text{H}_{25}\text{NO}_3$ 423.1835, found 423.1833.

Nitration of Imide III-5.

Imide **III-5** (0.885 g, 2.03 mmol) was dissolved in chloroform (5 mL) and acetic acid (5 mL). At room temperature (22 °C) the nitrating agent (10 mL of 70% nitric acid

and 10 mL of concentrated sulfuric acid in 3 mL of acetic acid) was added dropwise to the above solution. The reaction continued for 2 hours. TLC showed the presence of two isomers. The solution was then poured onto crushed ice with vigorous stirring and the product was extracted with chloroform. Combined organic layers were washed with saturated sodium chloride solution, dried over magnesium sulfate and concentrated. The yellow powder was dried under vacuum (22 °C, 20 mm Hg) to yield 0.823 g of sample. The product was further purified by a chromatographic column eluting with ethyl acetate/hexane (10/90): 0.38 g (36%). A preparative TLC plate allowed the characterization (¹H NMR) of the two isomers. However there was not enough sample to get carbon NMR spectra.

mp 98-100 °C; IR (KBr, cm⁻¹) 1761, 1704 (C=O imide) 3069, 3026 (aromatic CH stretch) 3062, 3025 (aromatic CH) 1453 (aromatic C=C stretch) 2934, 2862 (alkyl CH stretch) 1521, 1346 (NO₂ stretch); MS (EI, m/e, relative intensity %) 525 (M⁺, 100); HRMS calcd for C₃₀H₂₇N₃O₆ 525.1901, found 525.1928.

2,2'-sustituted compound III-3.

¹H NMR (400 MHz, CDCl₃) δ 7.97 (2 H, dd, J = 2.36 Hz, J = 8.32 Hz), 7.41 (2 H, d, J = 8.36 Hz), 7.12 (2 H, d, J = 2.40 Hz), 4.11 (2 H, m), 3.65 (2 H, t, J = 7.28 Hz), 2.87 (2 H, m), 2.65 (4 H, m), 2.21 (2 H, m), 1.95 (2 H, m), 1.64 (2 H, q, J = 7.40 Hz), 1.35 (2 H, sx, J = 7.43 Hz), 0.92 (3 H, t, J = 7.36 Hz).

2,3'-sustituted compound III-4.

¹H NMR (400 MHz, CDCl₃) δ 8.13 (1 H, dd, J = 2.36 Hz), 8.00 (1 H, dd, J = 2.36 Hz, J = 8.32 Hz), 7.66 (1 H, dd, J = 2.36 Hz, J = 8.48 Hz), 7.39 (1 H, d, J = 8.36 Hz), 7.14 (1 H, t, J = 2.36 Hz), 6.42 (1 H, d, J = 8.48 Hz), 4.11 (2 H, m), 3.65 (2 H, t, J = 7.28 Hz), 2.86 (2 H, m), 2.64 (2 H, m), 2.20 (4 H, m), 1.92 (2 H, m), 1.63 (2 H, q, J = 7.40 Hz), 1.35 (2 H, sx, J = 7.37 Hz), 0.91 (3 H, t, J = 7.36 Hz).

Monomer III-6.

Imide **III-5** (10.3 g, 24.3 mmol) was first dissolved in chloroform (20 mL) to which triethylamine (20.0 mL, 0.143 mol) was added. Methacryloyl chloride (7.00 mL, 71.6 mmol) dissolved in chloroform (6 mL) was then added dropwise over 10 min. After one hour reaction at room temperature, the orange solution was washed (3×30 mL) with a 5 % potassium carbonate solution, 30 mL of 5 % HCl solution, 30 mL of saturated sodium chloride solution. It was then dried over magnesium sulphate, filtered and the solvent was removed with a rotary evaporator at room temperature. The orange oil was dried with a vacuum oven (22 °C, 20 mm Hg) for 8 hours to yield a yellowish powder.

This product was recrystallized twice from acetonitrile as a white powder. The solid was dried overnight in a vacuum oven (50 °C, 5 mm Hg) and gave 5.55 g (47%).

mp 144–146 °C; IR (KBr, cm^{-1}) 1754, 1703 (C=O imide), 1721 (C=O ester); λ_{max} (1.78×10^{-5} mmol/mL, chloroform) 265.0, 339.0 nm; ^1H NMR (400 MHz, CDCl_3) δ 7.23 (2 H, dd, $J = 0.94$ Hz, $J = 7.50$ Hz), 7.14 (2 H, dt, $J = 1.23$ Hz, $J = 7.44$ Hz), 6.85 (2 H, dt, $J = 1.28$ Hz, $J = 7.54$ Hz), 6.39 (2 H, dd, $J = 1.00$ Hz, $J = 7.68$ Hz), 6.12 (1 H, m), 5.56 (1 H, m), 4.39 (2 H, t, $J = 5.40$ Hz), 4.05 (4 H, m), 2.71 (2 H, m), 2.61 (2 H, m), 2.18 (4 H, m), 2.05 (2 H, m), 1.92 (3 H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 168.83, 167.18, 145.76, 140.11, 138.51, 137.65, 136.03, 130.66, 127.97, 127.89, 126.91, 126.08, 125.66, 62.16, 36.59, 31.39, 31.13, 24.46, 18.26; MS (EI, m/e, relative intensity %) 491 (M^+ , 100); HRMS calcd for $\text{C}_{32}\text{H}_{29}\text{NO}_4$ 491.2098, found 491.2092.

UV-vis calibration curve of monomer **III-6** (chloroform, 22 °C, 339.0 nm; Equation $y = 19.9x + 0.000674$, $R^2 = 0.999$).

Concentration (mg/mL)	Absorbance at 339.0 nm
5.20×10^{-2}	1.04
3.64×10^{-2}	0.72
2.18×10^{-2}	0.44
8.74×10^{-3}	0.17
4.37×10^{-3}	0.087

Random Copolymerization IV-2/5.

A typical random copolymerization of monomer **III-6** and MMA is as follows: in a dried flask monomer **III-6** (1.21 g, 2.46 mmol) was dissolved in the minimum amount of benzene. To this solution was added the initiator AIBN (10.9 μ mol) then the MMA (0.243 g, 2.43 mmol). Nitrogen was bubbled through the solution for 15 minutes to remove the dissolved oxygen. Under stirring, the reaction proceeded 24 hours at 80 °C. The polymer was precipitated out by pouring into a large amount of methanol under vigorous stirring. The solid after filtration was further purified by re-dissolving in chloroform and precipitating into methanol. The copolymer was filtered and dried under vacuum (40 °C, 5 mm Hg) overnight. The yield was 1.08 g (75%).

Copolymer **IV-3**: IR (KBr, cm^{-1}) 1707 (C=O), 1733 (C=O ester); ^1H NMR (400 MHz, CDCl_3) δ 7.22, 7.14, 6.85, 6.40, 4.20, 4.00, 3.59, 2.67, 2.17, 2.03, 1.87, 1.80, 1.00, 0.82; ^{13}C NMR (100 MHz, CDCl_3) δ 177.79, 176.96, 168.72, 145.74, 140.16, 138.45, 137.71, 130.67, 127.91, 126.91, 125.65, 61.83, 54.41, 54.16, 51.77, 44.94, 44.60, 35.99, 31.42, 31.13, 24.47, 18.87, 16.64.

Homopolymer IV-1.

The same procedure as above was used by mixing the monomer **III-6** (0.602 g, 1.23 mmol) in the minimum amount of benzene along with AIBN (4.26 μ g). Centrifugation of the solid may be needed as the products are too small to be suction filtered). The yield was 0.294 g (49%).

IR (KBr, cm^{-1}) 1760, 1708 (C=O imide), 1734 (C=O ester); ^1H NMR (400 MHz, CDCl_3) δ 7.08, 7.00, 6.72, 6.27, 4.03, 3.91, 2.54, 2.00, 1.85, 1.26; ^{13}C NMR (100 MHz, CDCl_3) δ 176.10, 168.33, 145.33, 140.11, 138.06, 137.72, 130.64, 127.72, 127.04, 125.51, 61.43, 53.83, 44.75, 35.98, 31.39, 31.12, 29.70, 24.32.

Fluorescence studies of polymers IV-1/5.

Four different chloroform solutions of copolymer **IV-3** were made and their fluorescence measured at 22 $^{\circ}\text{C}$ with a gain of 2 and different sensitivities. The exciting wavelength was at 335 nm and the emission wavelength was at 430 nm. A plot of the concentration versus the fluorescence intensity was made (Equation $y = 784x + 1.04$, $R^2 = 0.997$).

Concentration (mg/mL)	Sensitivity	Fluorescence intensity (%) at 430 nm
0.05	0.3	40
0.01	1	34
0.005	3	50
0.001	10	24

Same measurements were proceeded on chloroform polymer solutions at 22 °C with exciting wavelength at 335 nm, emission wavelength at 430 nm, gain of 3 and sensitivity of 0.3.

Polymers	Concentrations ($\times 10^{-4}$ mg/mL)	Fluorescence intensity (%) at 430 nm
IV-1	3.26	56
IV-2	3.23	36
IV-3	3.23	37
IV-4	3.23	66
IV-5	3.20	66

Crystal Structure Determination of Anhydride I-6.

The crystal structure determination was performed at the Department of Chemistry, University of Ottawa, Ottawa, Canada. The single crystal was grown from acetic anhydride solution at ambient temperature and cut with dimensions of 0.4 mm x 0.1 mm x 0.1 mm. All the measurements were made on a Nonius diffractometer with CuK α radiation. Data collection were obtained from least-squares refinement using the setting angles in the range $1.14 < 2\theta < 28.74$ corresponded to an orthorhombic cell with dimensions: $a = 35.753(2)$ Å, $b = 14.2245(7)$ Å, $c = 7.5267(4)$ Å, $\alpha = \beta = \gamma = 90^\circ$. For FW = 380.42, the calculated density is 1.320 g/cm³. The space group was determined to

be Pccn. The data were collected at 23 °C. The residuals are as follows: for significant reflections, $R_f = 0.067$, $R_w = 0.133$; for all reflections, $R_f = 0.105$, $R_w = 0.153$. A total of 21719 reflections were collected. The unique set contains 4579 reflections. No absorption correction was made. The hydrogen atoms were calculated assuming a distance C-H of 1.007 Å.

Chiral Chromatographic Separation.

The chiral separations were performed with a Millipore Waters Delta Prep 3000 Preparative Chromatography System coupled with a Merck (S,S)-Whelk-O1 column with (3S,4S)-4-(3,5-dinitrobenzamido)-1,2,3,4-tetrahydrophenanthrene as the chiral selector. The elution of the enantiomers from the column was detected by a Millipore Waters 484 Tunable Absorbance Detector set at 254 nm wavelength.

Anhydride I-6 was dissolved in chloroform and injected through the HPLC apparatus coupled with the chiral column. A mixture of isopropanol/hexane (1.25%) was used as the eluting solvent at the flow rate 1 mL/min. After each injection, five different fractions were collected along the variation of the absorbance values (UV detector lamp was set up at 254 nm): from the "middle" of the first peak to the top of the peak, from the top of the peak to the "middle" of the peak, from the "middle" of the first peak to the "middle" of the second peak, from the "middle" of the peak to the top of the peak, from the top of the peak to almost the baseline.

After two consecutive collections the fractions were evaporated with a rotary evaporator at room temperature. After several injections, collections and concentrations around 5 mg of product was obtained for the first and the last fractions.

Optical Rotation Determination.

The specific optical rotations were determined on a Perkin-Elmer 141 Polarimeter at room temperature (22 °C) using a 1 dm cell.

A calibration curve (absorbance versus concentration) of the anhydride **I-6** in chloroform was first made by UV-vis at the maximum peak wavelength 335.8 nm (Equation: $y = 26.1x + 0.01$, $R^2 = 0.999$). With the polarimeter, the optical rotation was determined at four different wavelengths from a concentrate chloroform solution of the first fraction collected before. This concentrate chloroform solution was diluted two times (dilution 40). The absorbance was 0.842 therefore the concentration was 3.19×10^{-3} g/100 mL hence the initial concentration was 0.127 g/100 mL at 22 °C.

Concentration (mg/mL)	Absorbance at 335.8 nm
5.30×10^{-2}	1.39
3.71×10^{-2}	0.98
2.23×10^{-2}	0.59
8.90×10^{-3}	0.26
4.45×10^{-3}	0.12

λ (nm)	$[\alpha]^{22}$
436	-349
546	-94
578	-67
589	-55

Determination of Racemization Half-life Time.

The last fraction was dissolved in chloroform (the concentration was unknown) and was injected at room temperature through the column regularly within two days. The

percentage determination of each peak was made by using weighing paper: each peak was cut and weigh. For each chromatogram, the relative percentage of the P-enantiomer over the racemic mixture was calculated and plotted versus time in minutes (Equation: $y = -0.0177x + 82.8$, $R^2 = 0.991$). The racemization half-life time is determined at 75% of the initial percentage value (84.6%); for 63.5% $t_{1/2}$ was found to be 1100 min at 22 °C.

Time (min)	Percentage of M : P peaks	Relative % of P enantiomer
0	7.7 : 92.3	84.6
330	15.6 : 84.4	76.9
395	17.4 : 82.6	74.9
455	18.2 : 81.8	74.1
510	19.1 : 80.9	73.2
1340	32.9 : 67.1	59.4
1405	35.1 : 64.9	57.2
1570	36.0 : 64.0	56.3

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Contribution to knowledge

1. Synthesis of *o*-terphenyl derivative and polymers by multi-step reactions with spectroscopic characterizations.
2. Correlation between structures and chiroptical properties: studies of crystal structures, optical activities and thermal racemizations of helical chiral *o*-terphenyl derivatives.
3. Thermal properties of polymers: glass transition temperatures and onset temperatures for 5% weight loss were measured by differential scanning calorimetry and thermogravimetry respectively.

Appendix A. ^1H NMR spectrum (400 MHz, CDCl_3) and assignments of imide III-1

^1H NMR	δ , ppm		J, Hz
H 1	6.32	2 H, dd	1.10, 7.70
H 2	6.77	2 H, dt	1.29, 7.55
H 3	7.07	2H, dt	1.28, 7.46
H 4	7.15	2 H, dd	1.00, 7.48
H 6	2.64, 2.54	2 H, m, 2 H, m	
H 7	2.12	4 H, m	
H 8	4.00, 2.04	2 H, m, 2 H, m	
H 14	3.62	2 H, t	7.28
H 15	1.62	2 H, q	7.37
H 16	1.34	2 H, sx	7.42
H 17	0.90	3 H, t	7.36

Appendix B. ^{13}C NMR spectrum (100 MHz, CDCl_3) and assignments of imide III-1

^{13}C NMR	δ , ppm	^{13}C NMR	δ , ppm
C 1	130.67	C 8	24.39
C 2	125.63	C 11	169.31
C 3	127.89	C 14	37.56
C 4	127.86	C 15	30.76
C 6	31.16	C 16	20.23
C 7	31.37	C 17	13.70
C 5, 9, 10, 12, 13	145.56, 140.15, 138.22 137.78, 127.08

Appendix C. ^1H NMR spectrum (400 MHz, CDCl_3) and assignments of imide III-5

^1H NMR	δ , ppm		J, Hz
H 1	6.39	2 H, d	7.68
H 2	6.85	2 H, dt	1.21, 7.58
H 3	7.14	2H, dt	1.17, 7.46
H 4	7.22	2 H, d	7.44
H 6	2.72, 2.61	2 H, m, 2 H, m	
H 7	2.20	4 H, m	
H 8	4.05, 2.06	2 H, m, 2 H, m	
H 14	3.92	2 H, m	
H 15	3.92	2 H, m

Appendix D. ^{13}C NMR spectrum (100 MHz, CDCl_3) and assignments of imide III-5

^{13}C NMR	δ , ppm	^{13}C NMR	δ , ppm
C 1	130.65	C 7	31.35
C 2	125.68	C 8	24.49
C 3	128.00	C 11	169.78
C 4	127.89	C 14	40.79
C 6	31.12	C 15	61.64
C 5, 9, 10, 12, 13	145.90, 140.10, 138.64 137.62, 126.84

Appendix E. X-ray conditions and data

Table 1. Crystal data and structure refinement for 1.

Identification code	ww001
Empirical formula	C ₂₆ H ₂₀ O ₃
Formula weight	380.42
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pccn
Unit cell dimensions	a = 35.753(2) Å alpha = 90 deg. b = 14.2245(7) Å beta = 90 deg. c = 7.5267(4) Å gamma = 90 deg.
Volume, Z	3827.8(3) Å ³ , 8
Density (calculated)	1.320 Mg/m ³
Absorption coefficient	0.085 mm ⁻¹
F(000)	1600
Crystal size	0.40 x 0.10 x 0.10 mm
Theta range for data collection	1.14 to 28.74 deg.
Limiting indices	-42 ≤ h ≤ 46, -18 ≤ k ≤ 12, -10 ≤ l ≤ 7
Reflections collected	21719
Independent reflections	4579 [R(int) = 0.0431]
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4577 / 0 / 262
Goodness-of-fit on F ²	1.168
Final R indices [I > 2σ(I)]	R ₁ = 0.0668, wR ₂ = 0.1329
R indices (all data)	R ₁ = 0.1050, wR ₂ = 0.1535
Largest diff. peak and hole	0.215 and -0.170 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	1115(1)	1252(1)	7846(2)	60(1)
O(2)	1717(1)	1312(1)	7001(3)	74(1)
O(3)	530(1)	1619(1)	8662(2)	68(1)
C(1)	1442(1)	1736(2)	7381(3)	52(1)
C(2)	1360(1)	2749(2)	7508(3)	43(1)
C(3)	1584(1)	3518(2)	7130(3)	44(1)
C(4)	1982(1)	3443(2)	6469(3)	54(1)
C(5)	2270(1)	3789(2)	7825(3)	60(1)
C(6)	2172(1)	4736(2)	8657(3)	59(1)
C(7)	1999(1)	5413(2)	7372(3)	50(1)
C(8)	2191(1)	6196(2)	6732(4)	63(1)
C(9)	2032(1)	6784(2)	5497(4)	71(1)
C(10)	1680(1)	6609(2)	4855(4)	68(1)
C(11)	1480(1)	5850(2)	5497(3)	56(1)
C(12)	1634(1)	5252(2)	6762(3)	45(1)
C(13)	1420(1)	4413(2)	7372(3)	41(1)
C(14)	1055(1)	4504(1)	8083(2)	39(1)
C(15)	902(1)	5437(1)	8600(3)	41(1)
C(16)	1091(1)	5995(2)	9828(3)	55(1)
C(17)	936(1)	6836(2)	10391(3)	65(1)
C(18)	599(1)	7130(2)	9718(3)	63(1)
C(19)	409(1)	6581(2)	8527(3)	50(1)
C(20)	552(1)	5727(2)	7964(3)	42(1)
C(21)	336(1)	5102(2)	6726(3)	48(1)
C(22)	173(1)	4243(2)	7662(3)	53(1)
C(23)	434(1)	3821(2)	9061(3)	47(1)
C(24)	829(1)	3707(2)	8393(3)	41(1)
C(25)	991(1)	2843(2)	8067(3)	41(1)
C(26)	833(1)	1891(2)	8265(3)	50(1)

Table 3. Bond lengths [Å] and angles [deg] for 1.

O(1)-C(26)	1.393(3)
O(1)-C(1)	1.402(3)
O(2)-C(1)	1.187(3)
O(3)-C(26)	1.191(2)
C(1)-C(2)	1.473(3)
C(2)-C(3)	1.384(3)
C(2)-C(25)	1.392(3)
C(3)-C(13)	1.414(3)
C(3)-C(4)	1.509(3)
C(4)-C(5)	1.531(3)
C(5)-C(6)	1.526(3)
C(6)-C(7)	1.498(3)
C(7)-C(8)	1.393(3)
C(7)-C(12)	1.404(3)
C(8)-C(9)	1.374(4)
C(9)-C(10)	1.371(4)
C(10)-C(11)	1.382(3)
C(11)-C(12)	1.390(3)
C(12)-C(13)	1.492(3)
C(13)-C(14)	1.414(3)
C(14)-C(24)	1.412(3)
C(14)-C(15)	1.488(3)
C(15)-C(16)	1.393(3)
C(15)-C(20)	1.402(3)
C(16)-C(17)	1.385(3)
C(17)-C(18)	1.372(3)
C(18)-C(19)	1.369(3)
C(19)-C(20)	1.385(3)
C(20)-C(21)	1.500(3)
C(21)-C(22)	1.527(3)
C(22)-C(23)	1.530(3)
C(23)-C(24)	1.509(2)
C(24)-C(25)	1.380(3)
C(25)-C(26)	1.474(3)
C(26)-O(1)-C(1)	109.8(2)
O(2)-C(1)-O(1)	120.0(2)
O(2)-C(1)-C(2)	132.6(2)
O(1)-C(1)-C(2)	107.4(2)
C(3)-C(2)-C(25)	122.3(2)
C(3)-C(2)-C(1)	130.1(2)
C(25)-C(2)-C(1)	107.6(2)
C(2)-C(3)-C(13)	116.4(2)
C(2)-C(3)-C(4)	123.8(2)
C(13)-C(3)-C(4)	119.9(2)
C(3)-C(4)-C(5)	113.1(2)
C(6)-C(5)-C(4)	113.7(2)
C(7)-C(6)-C(5)	113.4(2)
C(8)-C(7)-C(12)	118.3(2)
C(8)-C(7)-C(6)	122.3(2)
C(12)-C(7)-C(6)	119.3(2)
C(9)-C(8)-C(7)	121.2(2)
C(8)-C(9)-C(10)	120.6(2)
C(9)-C(10)-C(11)	119.5(2)
C(10)-C(11)-C(12)	120.8(2)
C(11)-C(12)-C(7)	119.6(2)
C(11)-C(12)-C(13)	119.8(2)
C(7)-C(12)-C(13)	120.5(2)
C(3)-C(13)-C(14)	121.0(2)

C(3)-C(13)-C(12)	117.8(2)
C(14)-C(13)-C(12)	121.1(2)
C(24)-C(14)-C(13)	121.0(2)
C(24)-C(14)-C(15)	117.5(2)
C(13)-C(14)-C(15)	121.4(2)
C(16)-C(15)-C(20)	119.5(2)
C(16)-C(15)-C(14)	120.2(2)
C(20)-C(15)-C(14)	120.1(2)
C(17)-C(16)-C(15)	120.0(2)
C(18)-C(17)-C(16)	120.1(2)
C(19)-C(18)-C(17)	120.2(2)
C(18)-C(19)-C(20)	121.2(2)
C(19)-C(20)-C(15)	118.8(2)
C(19)-C(20)-C(21)	121.4(2)
C(15)-C(20)-C(21)	119.8(2)
C(20)-C(21)-C(22)	112.6(2)
C(21)-C(22)-C(23)	113.4(2)
C(24)-C(23)-C(22)	112.6(2)
C(25)-C(24)-C(14)	116.5(2)
C(25)-C(24)-C(23)	123.2(2)
C(14)-C(24)-C(23)	120.3(2)
C(24)-C(25)-C(2)	122.5(2)
C(24)-C(25)-C(26)	129.7(2)
C(2)-C(25)-C(26)	107.8(2)
O(3)-C(26)-O(1)	120.2(2)
O(3)-C(26)-C(25)	132.3(2)
O(1)-C(26)-C(25)	107.5(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1.
 The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	67(1)	48(1)	65(1)	-1(1)	-8(1)	2(1)
O(2)	70(1)	63(1)	88(1)	-11(1)	0(1)	22(1)
O(3)	62(1)	62(1)	81(1)	9(1)	2(1)	-19(1)
C(1)	54(1)	56(1)	47(1)	-4(1)	-7(1)	7(1)
C(2)	40(1)	49(1)	40(1)	-2(1)	-6(1)	5(1)
C(3)	32(1)	58(1)	40(1)	-2(1)	-2(1)	3(1)
C(4)	38(1)	65(2)	60(1)	-1(1)	7(1)	9(1)
C(5)	33(1)	80(2)	68(2)	13(1)	-2(1)	4(1)
C(6)	39(1)	82(2)	57(1)	4(1)	-8(1)	-10(1)
C(7)	37(1)	61(2)	52(1)	-1(1)	3(1)	-4(1)
C(8)	39(1)	73(2)	75(2)	-1(1)	5(1)	-14(1)
C(9)	56(1)	63(2)	93(2)	16(2)	15(1)	-8(1)
C(10)	54(1)	67(2)	83(2)	23(1)	9(1)	4(1)
C(11)	38(1)	64(2)	66(2)	10(1)	1(1)	2(1)
C(12)	33(1)	53(1)	48(1)	0(1)	6(1)	0(1)
C(13)	31(1)	52(1)	39(1)	1(1)	-3(1)	0(1)
C(14)	30(1)	49(1)	39(1)	-1(1)	-2(1)	0(1)
C(15)	35(1)	47(1)	41(1)	-4(1)	6(1)	-4(1)
C(16)	43(1)	66(2)	55(1)	-9(1)	0(1)	-9(1)
C(17)	72(2)	63(2)	60(2)	-21(1)	6(1)	-16(1)
C(18)	71(2)	53(2)	65(2)	-10(1)	18(1)	2(1)
C(19)	49(1)	54(1)	49(1)	2(1)	13(1)	5(1)
C(20)	37(1)	49(1)	39(1)	1(1)	7(1)	-1(1)
C(21)	38(1)	59(1)	46(1)	-2(1)	-5(1)	2(1)
C(22)	32(1)	64(2)	61(1)	-4(1)	0(1)	-4(1)
C(23)	36(1)	54(1)	52(1)	3(1)	8(1)	-4(1)
C(24)	33(1)	52(1)	37(1)	0(1)	-2(1)	-2(1)
C(25)	38(1)	47(1)	38(1)	1(1)	-5(1)	-4(1)
C(26)	53(1)	52(1)	45(1)	3(1)	-9(1)	-3(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1.

	x	y	z	U(eq)
H(4A)	2006(1)	3809(2)	5388(3)	65
H(4B)	2034(1)	2792(2)	6179(3)	65
H(5A)	2293(1)	3324(2)	8762(3)	72
H(5B)	2511(1)	3840(2)	7244(3)	72
H(6A)	2000(1)	4633(2)	9633(3)	71
H(6B)	2398(1)	5014(2)	9142(3)	71
H(8A)	2430(1)	6322(2)	7148(4)	75
H(9A)	2164(1)	7305(2)	5093(4)	85
H(10A)	1576(1)	6999(2)	3993(4)	82
H(11A)	1239(1)	5738(2)	5079(3)	67
H(16A)	1321(1)	5802(2)	10270(3)	66
H(17A)	1060(1)	7202(2)	11227(3)	78
H(18A)	499(1)	7704(2)	10072(3)	76
H(19A)	180(1)	6786(2)	8089(3)	61
H(21A)	500(1)	4894(2)	5778(3)	57
H(21B)	134(1)	5461(2)	6194(3)	57
H(22A)	116(1)	3766(2)	6780(3)	63
H(22B)	-61(1)	4420(2)	8229(3)	63
H(23A)	436(1)	4225(2)	10100(3)	57
H(23B)	338(1)	3212(2)	9420(3)	57

IMAGE EVALUATION TEST TARGET (QA-3)

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