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**SYNTHESES AND CHIROPTICAL STUDIES OF OPTICALLY ACTIVE
POLYMETHACRYLATES AND POLYISOCYANIDES**

by

JIAN PING CHEN, B.Sc.

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

Department of Chemistry

Carleton University

Ottawa, Ontario

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

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ABSTRACT

A series of optically active block polymethacrylates, azo-containing random polymethacrylates, azo-containing polyisocyanides and [5]helicene-based polyisocyanides were synthesized by atropogenic (screw-sense-selective) polymerization. A film of trityl methacrylate-*block*-methyl methacrylate copolymer containing 1 wt% of diphenyl-*p*-tolylsulfonium triflate can undergo a partial racemization upon UV (254 nm) irradiation and baking (125 °C). Under the similar conditions, a film cast from cyclohexyldiphenylmethyl methacrylate-*block*-methyl methacrylate copolymer can undergo a complete racemization catalyzed by photogenerated acid. These results have demonstrated that the chemical process initiated by irradiation (writing) involves the photogeneration of an acid which catalyzes thermal cleavage of the bulky ester groups. The permanent change in optical rotation of these polymer films can be detected (reading). Photoisomerization of some optically active, azo-containing random polymethacrylates and polyisocyanides in solution indicated that configurational change of side-chain azo chromophore (*trans* to *cis*) under UV (300 nm) irradiation could induce conformational change of the polymer backbone to a certain extent. The main-chain chirality of a [5]helicene-based polyisocyanide was achieved by a chiral transfer from a remote chiral side group during polymerization of a chiral [5]helicene-based isocyanide.

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LIST OF ABBREVIATIONS AND SYMBOLS

<i>P</i>	plus, right-handed
<i>M</i>	minus, left-handed
DNA	deoxyribonucleic acid
TrMA	triphenylmethyl methacrylate or trityl methacrylate
PTrMA	poly(trityl methacrylate)
<i>n</i> -BuLi	<i>n</i> -butyllithium
MBMA	α -methylbenzyl methacrylate
(+)-DDB	(<i>S,S</i>)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane
(-)-DDB	(<i>R,R</i>)-(-)-2,3-dimethoxy-1,4-bis(dimethylamino)butane
(+)-PMP	(<i>S</i>)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine
CHDPMMA	cyclohexyldiphenylmethyl methacrylate
PCHDPMMA	poly(cyclohexyldiphenylmethyl methacrylate)
MMA	methyl methacrylate
<i>t</i> -BuMA	<i>tert</i> -butyl methacrylate
<i>n</i> -BuMA	<i>n</i> -butyl methacrylate
PMMA	poly(methyl methacrylate)
FILi	9-fluorenyllithium
FILi-(+)-DDB	chiral complex of FILi and (+)-DDB
TrMA- <i>co</i> -MMA	random copolymer of TrMA and MMA
TrMA- <i>co-t</i> -BuMA	random copolymer of TrMA and <i>t</i> -BuMA

St	styrene
St- <i>b</i> -TrMA	block copolymer of styrene to TrMA
TrMA- <i>b</i> -MMA	block copolymer of TrMA to MMA
TrMA- <i>b</i> - <i>t</i> -BuMA	block copolymer of TrMA to <i>t</i> -BuMA
TrMA- <i>b</i> - <i>n</i> -BuMA	block copolymer of TrMA to <i>n</i> -BuMA
CHDPMMA- <i>b</i> -MMA	block copolymer of CHDPMMA to MMA
CHDPMMA- <i>b</i> - <i>n</i> -BuMMA	block copolymer of CHDPMMA to <i>n</i> -BuMA
DPTST	diphenyl- <i>p</i> -tolylsulfonium triflate
PAM	4-phenylazophenyl methacrylate
PAEM	2-(4-phenylazophenoxy)-ethyl methacrylate
PAHM	6-(4-phenylazophenoxy)-hexyl methacrylate
TrMA- <i>co</i> -PAEM	random copolymer of TrMA and PAEM
TrMA- <i>co</i> -PAHM	random copolymer of TrMA and PAHM
HPLC	high performance liquid chromatography
UV/vis	ultra-violet/visible
CD	circular dichroism
IR	infrared spectroscopy
λ	a symbol for wavelength
Å	angstrom unit
psi	pounds per square inch
^1H NMR	proton nuclear magnetic resonance
^{13}C NMR	carbon nuclear magnetic resonance

COSY	two-dimensional ^1H NMR COrrrelated SpectroscopY
MS	mass spectroscopy
GPC	gel permeation chromatography
M_n	number average molar mass
M_w	weight average molar mass
PDI	polydispersity index (M_w/M_n)
α	optical rotation in degree
$[\alpha]_D$	specific rotation at 589 nm (degree.mL.g⁻¹.dm⁻¹)
$[M]$	molar optical rotation (degree.mL.mol⁻¹.dm⁻¹)
DSC	differential scanning calorimeter
TGA	thermogravimetric analysis
T_g	glass transition temperature
T_m	polymer melting temperature
T_d	thermal decomposition temperature

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Chapter 1. Introduction

1-1. Helical Polymers

Macromolecules exist in a variety of conformational forms. These forms range from randomly coiled chains to more spatially ordered structures. Of particular interest are those polymers which adopt screw structures or helices (Greek for winding, convolution, spiral). A helix is a consequence of an orderly repetition of internal rotational angles along the polymer backbone and is encountered in both natural and synthetic polymers.¹ It is characterized by a helical sense, a helical axis, and a pitch. A right-handed helix is symbolized by *P* (Plus), a left-handed helix by *M* (Minus).² A helical polymer could be optically active if one of the helices is energetically favorable, because *P* and *M* helices are regarded as a pair of atropisomers. Chirality of an atropisomer arises from asymmetry of its helical conformation rather than that of central, axial or planar configuration.

One of the most important natural compounds with a helical structure is deoxyribonucleic acid (DNA). The B-conformation of DNA is formed in the presence of NaCl or LiCl under conditions of highly relative humidity. Figure 1.1 shows the structure of B-DNA conformation.³ In this structure, two sugar-phosphate chains, situated in anti-parallel fashion, are wound about a common, central axis into a right-handed helical screw. The two strands are joined by hydrogen bonds between complementary base pairs which occupy the internal regions of the helix. B-DNA is an optically active polymer due to its one-handed helix, which is stabilized mainly by hydrogen bonds. B-DNA is characterized by 10_1 helical symmetry, with a pitch length of 34 Å and each perpendicular

base rising some $3.4 \text{ \AA}$ along the helical axis. If water is stripped from B-DNA, caused through higher ion concentrations, A-DNA is formed, which is only hydrated at the strongly polar phosphate groups. This A-DNA possesses 28_3 helical symmetry with 9.33 nucleotides per turn. Its pitch length is $28.2 \text{ \AA}$ and each nucleotide repeat unit against the helical axis is $3.3 \text{ \AA}$.⁴

Figure 1.1. Double helix of B-DNA. Here P means phosphate diester,

S means deoxyribose, A=T is the adenine-thymine pairing,

and G=C is the guanosine-cytosine pairing.

In contrast to the natural helical polymers, most synthetic macromolecules lack the secondary bonding forces to stabilize a helical order in solution. For these polymers, helicity is generally limited to the solid state where crystalline packing forces dictate conformational geometry. A helical arrangement of the polymer backbone is highly favored in the solid state, because extended helices can be easily incorporated into a regular crystalline lattice. For example, crystallographic studies have shown that isotactic vinyl polymers of the form $-(CH_2-CHX)_n-$ possess a helical order. Helix symmetry is governed by the relative size of X, ranging from 3_1 for polypropylene to the larger 7_2 and 4_1 arrangements for poly(1-hexene) and poly(vinyl cyclohexane), respectively.¹

Some synthetic polymers do have stable helical conformations in solution, such as polyisocyanides and poly(triphenylmethyl methacrylate) (PTrMA). The main-chain helicity is stabilized by the rigid polymer backbone (an imino group for polyisocyanides) or bulky side group (a triphenylmethyl group for PTrMA). Both poly(*t*-butyl isocyanide)⁵ and PTrMA⁶ have been resolved by chromatography on an optically active column to give *P* and *M* atropoisomers with opposite optical rotations. Their optical activities arise exclusively from one-handed helical backbone.

It is challenging to obtain an optically active macromolecule whose chirality arises from one-handed helical conformation from an achiral molecule by asymmetric polymerization.

1-2. Asymmetric Polymerization

Asymmetric polymerization refers to a reaction process which produces an optically active polymer from an optically inactive (racemic or prochiral) monomer. It can be classified into three categories: (1) enantiogenic polymerization, (2) enantio-selective polymerization, and (3) atropogenic (Greek for helix-sense-selective or screw-sense-selective) polymerization.

In enantiogenic polymerization, an optically inactive prochiral monomer and an optically active auxiliary are copolymerized to give a polymer with configurational main-chain chirality. This type of polymerization has been reported for several bifunctional monomers including methacrylates,⁷ diisocyanides,⁸ and styrene derivatives.⁹ Figure 1.2 shows the radical copolymerization of styrene and a styrene derivative bearing a chiral template.¹⁰ The copolymer was converted into polystyrene by removal of chiral templates and boron groups. The resulting polystyrene showed optical activity ($[\alpha]_{365}^{30}$ -0.5 to -3.5°), attributed to the existence of chiral monomeric diads separated by atactic sequences. The chiral styrene monomer undergoes cyclopolymerization, in which the two double bonds are incorporated into the polymer chain one after another through the formation of a 19-membered ring. A further monomer (e.g. styrene) can then only react with this cyclized chiral styrene segment, resulting in the formation of a chiral diad with *S,S*-configuration. In general, the polymer obtained from this type of asymmetric polymerization has a low optical rotation.

Figure 1.2. Enantiogenic Polymerization of Styrene
in the Presence of a Chiral Template.

In enantio-selective polymerization, one antipode of a racemic monomer is preferentially polymerized to give an optically active polymer. In this process, kinetic resolution of the racemic monomer is attained. Okamoto and his co-workers reported that in the presence of a chiral initiator, the complex of *n*-BuMgCl and (-)-sparteine, (*R,S*)- α -methylbenzyl methacrylate (MBMA) was polymerized in toluene at -78 °C to give optically active poly(MBMA) ($[\alpha]_D^{20} = -93.9^\circ$ in toluene) with a highly isotactic configuration (Figure 1.3).¹¹ In this case, (*S*)-MBMA was preferentially polymerized over (*R*)-MBMA in an enantiomeric excess of 75%. The unreacted monomer was recovered

after polymerization which contains mainly (*R*)-MBMA in an enantiomeric excess of 84.8% ($[\alpha]_D^{20} = +45.0^\circ$ in toluene). This result indicates that the chiral complex can prefer one enantiomer to the other during polymerization, leading to the formation of optically active polymer whose chirality arises from the chiral ester side group. Due to the lack of secondary structure such as one-handed helical conformation, these polymers do not have very high optical rotations.

Figure 1.3. Enantio-selective Polymerization of (*R,S*)-MBMA.

In atropogenic polymerization, an optically active polymer whose chirality is based on a helical conformation with an excess of single-screw sense is produced. In the absence of any optically active moiety such as optically active initiator, *P* and *M* helices are energetically equivalent, and, therefore are equally probable during polymerization. If one of the two helices is preferentially synthesized, the polymer can be optically active.

A predominance of one of the helical screw directions can be achieved through (1) a complete or partial resolution of a pair of helical screws or (2) the use of optically active initiating species which preferentially induce the formation of one helical screw sense over the other.

Drenth and co-workers employed a chiral chromatographic column, which was packed with optically active insoluble poly[(*S*)-*sec*-butyl isocyanide], to partially resolve racemic poly(*t*-butyl isocyanide).⁵ This process gave four fractions of poly(*t*-butyl isocyanide) with specific rotations of +4.7°, +2.9°, 0°, and -10.2°, respectively, at 578 nm.

The preparation of an optically active polymer whose chirality arises solely from macromolecular asymmetry requires the formation of a tight helical chain which is incapable of undergoing conformational inversion. Such synthetic polymers maintain stable helical structures in solution, as DNA does, but are very few. To date, only a few examples of such helical polymers are known, namely, polyisocyanides,¹²⁻¹⁷ polychlorals,^{18,19} polyisocyanates,^{20,21} and bulky poly(methacrylates).^{6,22}

In 1970, Yuki et al. found that polymerization of TrMA using *n*-BuLi in THF or toluene produces a highly isotactic polymer.²³ This regular structure was ascribed to the bulky triphenylmethyl (trityl) groups which force the polymer chain to take a helical conformation. Under this condition, *P* and *M* helices are formed in equal amounts.

Figure 1.4. Polymerization of TrMA with *n*-BuLi.

In 1979, Okamoto et al. reported that in the presence of a chiral initiator, polymerization of TrMA in toluene gave a highly isotactic, optically active polymer with one-handed helical structure (Figure 1.5).²²

Figure 1.5. Atropogenic Polymerization of TrMA.

This polymer is the first example of an optically active vinyl polymer whose chirality arises exclusively from its stable helical conformation of the backbone. Bulky trityl groups prohibit uncoiling of the growing helical chain during the polymerization. The optical activity of PTrMA is lost when the trityl ester is converted into the methyl ester, demonstrating that the helical conformation is maintained by sterical repulsion of bulky trityl groups.²⁴

Optically active one-handed PTrMA can also be obtained by asymmetric polymerization of TrMA using the complexes of achiral organolithiums and optically active ligands such as (*S,S*)-(+)- and (*R,R*)-(-)-2,3-dimethoxy-1,4-bis(dimethylamino)butanes [(+)- and (-)-DDB], (*S*)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine

$[(+)\text{-PMP}]$.²⁵ In all cases, PTrMA showed high optical activity and possessed high isotacticity, indicating the existence of the one-handed helical structure.

Optically active polymethacrylates having a helical conformation have also been obtained by atropogenic polymerization of methacrylates containing bulky ester groups other than trityl group using the above chiral initiators. Their helical conformations again were stabilized by bulky ester groups. The critical bulkiness of an ester group suitable to afford a helical polymethacrylate has been studied, based on the polymerizations of cyclohexyldiphenylmethyl methacrylate (CHDPMMA), cyclobutyldiphenylmethyl methacrylate (CBDPMMA) and cyclopropyldiphenylmethyl methacrylate (CPDPMMA).^{26,27} The polymer derived from CHDPMMA was highly isotactic and optically active, indicating that this polymer possessed a one-handed helical conformation. In contrast, CPDPMMA afforded an atactic, almost optically inactive polymer under the same polymerization conditions. On the other hand, the polymer obtained at $-78\text{ }^{\circ}\text{C}$ from CBDPMMA having a medium-size ester group, showed a large rotation value ($[\alpha]_{435}^{78} +670^{\circ}$), but the optical activity decreased to the value around zero measured at $-40\text{ }^{\circ}\text{C}$ or higher temperatures. It seems that the poly(CBDPMMA) possessed the helical conformation with prevailing helical sense at $-78\text{ }^{\circ}\text{C}$, and it changed into a random coil conformation at higher temperatures because of its low stability. This suggests that the cyclobutyldiphenylmethyl group is of critical bulkiness for the formation of one-handed helical polymethacrylate in solution.

Optically active PTrMA and its analogues prepared by atropogenic polymerization have been used as chiral stationary phases. Many racemic compounds thus have been

resolved through a chiral PTrMA-based column by high performance liquid chromatography (HPLC).²⁸ The resolution is effected by using a polar eluent like methanol, rather than nonpolar eluents. This suggests that the hydrophobic interaction between the nonpolar group, probably triphenylmethyl group, of chiral PTrMA and the nonpolar groups of enantiomers plays an important role in resolution.

Polyisocyanides have a structural type in which each carbon atom of the main chain has a double bond to a nitrogen atom. The double bond brings about a restricted rotation about the C-C single bond of the main chain and hence results in the formation of stable, rigid helices.¹⁵

Millich was the first one to develop a catalytic system for the polymerization of isocyanides, introducing a combination of an acid-treated glass and a radical initiator or air.¹³ Nolte et al. discovered that simple nickel (II) salts (NiCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) are very efficient catalysts for polymerizing a wide variety of aliphatic and aromatic isocyanides.¹⁶

The polymerization of isocyanides proceeds very rapidly at room temperature, which is remarkable given the fact that so much steric bulkiness is introduced during the chain propagation. For the polymerization catalyzed by nickel (II) chloride, a Merry-Go-Round mechanism has been proposed (Figure 1.6).^{15,16}

The first step in the reaction is the formation of a square-planar nickel complex. Polymerization starts when a nucleophile attacks one of the coordinated isocyanide molecules. This nucleophile may already be present in the solution (e.g. a molecule of water or the counterion of Ni^{2+}), or may have been intentionally added, e.g. an amine. The reaction then continues as a succession of insertion steps in the same direction around the

Ni center. This eventually leads to the formation of a very tight helical structure, since the isocyanide units on the nickel ion are in the desired geometrical arrangement. The insertion reaction can proceed in either a clockwise or a counterclockwise direction, giving rise to a mixture of *P* and *M* 4_1 helices. However, the formation of a regular helix for polyisocyanides has been questioned by some researchers.^{29,30}

Figure 1.6. Ni(II) Catalysed Polymerization of Isocyanide.

Optically active polyisocyanides having a single-screw-sense can be obtained by atropogenic polymerization of bulky achiral isocyanides using Ni(II) salts in the presence of optically active amines,³¹ or using chiral Ni catalysts.³² It is assumed that chiral ligands

coordinating with a metal catalyst could favour, for example, a preferential attack of C^1 on C^2 rather than on C^4 (Figure 1.6), resulting in unequal amounts of *P* and *M* helices. Although the magnitude of asymmetric induction was moderate to high (83% for the highest one), specific rotations of these polyisocyanides were low ($[\alpha]_D^{20} < 100^\circ$ in absolute value). More recently, a living chiral helical oligoisocyanide was employed to induce the atropogenic copolymerization of achiral isocyanides (Figure 1.7).³³ The optically active helical oligomer can act as an effective living macro-initiator to induce atropogenic polymerization of the second achiral isocyanide, which eventually forms one-handed helical polymer.

Figure 1.7. Atropogenic Living Block Polymerization of Isocyanides.

An interesting copolymerization of achiral and chiral isocyanides has been reported.³⁴ Phenyl isocyanide and methyl (*S*)-2-isocyanoisovalerate were polymerized using nickel chloride to produce an optically active polymer incorporating ca. 30% of optically active monomer (Figure 1.8).

Figure 1.8. Atropogenic Copolymerization of Phenyl Isocyanide with a Chiral Isocyanide.

The specific rotation of this copolymer was hundreds of degrees measured at a wavelength of 589 nm. The prevailing helix sense of the copolymer was *P*, while that of the homopolymer of methyl (*S*)-2-isocyanoisovalerate was *M* as assigned based on their CD shapes.³⁴ Their different helical senses were explained on the basis of polymerizability of the monomers. The polymerizability of the optically active monomer is much less than that of the achiral monomer because of steric hindrance arising from the bulky side group. In the copolymerization, phenyl isocyanide preferentially polymerizes in the early stage to afford a mixture of *P*- and *M*-helical propagating chains, and the optically active monomer is incorporated preferentially into the *M*-helical growing chain. As a result, the propagation rate of the *M*-helical chain greatly decreases and the *P*-helix consisting mainly of phenyl isocyanide is the major component in the polymer. Many other achiral less bulky

alkyl and aromatic isocyanides have been copolymerized with this chiral isocyanide, and polyisocyanides with high optical rotations have been obtained, depending on the monomer ratio and monomer polymerizability.³⁴

1-3. Chiroptical Change in Azo-Containing Helical Polymers

Chiroptical change (e.g. optical rotation, ellipticity of CD) of a helical polymer triggered by a certain external stimulus is one of many means that could possibly be used in an information storage system.³⁵ The external stimulus could be light, heat, chemical reaction and electric field.

Light irradiation of polymers containing photochromic groups, which isomerize and change their shape by absorption of light, may induce conformational changes of the polymer backbone.³⁶ The polymer having such properties may be a suitable model for an optical switch device. Accordingly, azobenzene and other photochromic compounds have been incorporated into helical polymers.^{35,36}

1-3-1. Azobenzene Chromophores

Azobenzene and many of its derivatives are characterized by reversible transformations. Upon irradiation with UV or visible light, the generally more stable trans form is converted to the less stable cis form. The photostationary composition is wavelength and temperature dependent (Figure 1.9).³⁶

Figure 1.9. Photoisomerization of Azobenzene.

Photoinduced isomerization of azobenzene produces a large structural change as reflected in the dipole moment and geometry. The distance between the 4,4' carbon atoms in azobenzene is from 9.0 Å in the trans form to 5.5 Å in the cis form. Likewise, the dipole moment of the nonplanar cis-azobenzene is higher than that of the trans-azobenzene. Azo aromatic molecules are also characterized spectroscopically by $n-\pi^*$ and $\pi-\pi^*$ bands in the electronic spectra. The differences between the cis and trans isomers are revealed by the λ_{max} of these absorbances. Thus, the cis-trans isomerization of some azo groups can be monitored by intensity changes in the electronic spectra.

1-3-2. Light-induced Helical Change in Azo-Containing Polymers

The occurrence of helical formation in the secondary structure of polypeptides is a well known phenomenon. The incorporation of photoresponsive azobenzene moieties in these polymers might effect light-induced conformational changes of the helix. After the pioneering work by Goodman on (phenylazo)phenylalanine polymers,³⁷ Ueno and co-workers reported a change in the chiroptical properties of polyaspartates by the trans-cis isomerization of azobenzene units in the side chains.³⁸ A copolymer consisting of β -benzyl L-aspartate and β -(*m*-benzylazo)benzyl L-aspartate formed an *M* helix in the all trans configuration (Figure 1.10).

Figure 1.10. Helix Inversion of a Polypeptide.

Upon irradiation below 400 nm to induce the trans-cis isomerization of azobenzene, the content of the *P* helix reached to 100% in 1,2-dichloroethane. The reverse isomerization to the trans azobenzene was effected by photo-irradiation above 400 nm, giving rise to a concomitant change in helicity. This reversal in helical nature can be monitored by the large change in optical rotation, in principle, offering a method for readout in optical recording. During the photoisomerization, the molecular geometry of the azo group changes from the extended planar trans configuration to the skewed configuration of the cis isomer. In addition, its polarity and hydrophobicity dramatically change, since the trans isomer is practically nonpolar, and the cis form is polar with a high dipole moment. Therefore, the trans-cis isomerization causes a change of polarity in the local environment around the polypeptide backbone. Both the geometry and polarity factors can be the driving forces responsible for the helix inversion.

Ciardelli et al. also noted small conformational changes in chiral copolymers derived from the methacrylates functionalized with azobenzenes and (-)-L-menthyl

methacrylate.³⁹ Conversions between *P* and *M* helices have been found in optically active azo-containing helical polyisocyanates.⁴⁰ The rather low energy barrier between right-helix and left-helix transitions facilitates the conformational change upon azo photoisomerization.

To date, all studies on optically active azo-containing helical polymers have only been carried out in solutions. In the solid state, the conformations of the backbone of chiral azo polymers could not be changed by irradiation.

1-4. Hypotheses and Rationale

In this study, optically active helical polymethacrylates and polyisocyanides were investigated. In order to evaluate the feasibility of chiroptical change triggered by light or acid in solution and in the solid state, these two types of polymers must be modified or functionalized. Also, the chirality of [5]helicene-based polyisocyanides will be investigated.

Hypothesis 1: The loss of a bulky ester group caused directly or indirectly by an external stimulus should result in a racemization of one-handed helical PTrMA and PCHDPMMA, leading to the formation of optically inactive polymer.

To achieve such a racemization in the solid state, an optically active polymer should be available as a flexible film. Thus, PTrMA and PCHDPMMA should be chemically modified by introducing a flexible segment into the helical chain, to improve the solubility in organic solvents. Copolymerization of TrMA, CHDPMMA with methyl methacrylate (MMA), *tert*-butyl methacrylate (*t*-BuMA) and *n*-butyl methacrylate (*n*-BuMA) should also be a convenient way to obtain polymers which would be less rigid and could be cast into films. To this end, both random and living block polymerizations should be attempted.

Any optically active helical copolymer with a good film formability should be candidate for studying the feasibility of racemization in the solid state. In the presence of a photoacid generated, it is expected that the acid-labile ester groups of optically active polymethacrylates should be cleaved upon UV photoirradiation. Due to the partial or complete loss of the bulky ester groups, the optical activity would decrease or completely

vanish, which would demonstrate the feasibility of an irreversible optical data storage system based on such a chiral polymeric material.

Hypothesis 2: Photoisomerization of the azobenzene moiety in the side chain of a polymer might regulate the conformational change of the helical polymer backbone, in solution or in the solid state.

The azobenzene chromophore can be covalently incorporated into optically active helical polymers, such as polymethacrylates and polyisocyanides. The conformational change of helical polymer backbone triggered by azo photoisomerization could be detectable in terms of an optical rotational change and a CD change. If this change is reversible and is repeatable in many cycles, this type of polymers could be used as a reversible optical data storage system.

Optically active azo-containing polymethacrylates may be produced by copolymerization of TrMA and azo-containing methacrylates in the presence of an optically active initiator. The optical activity of the resulting azo polymethacrylates will be decreased due to the incorporation of the less rigid azo comonomer. However, the solubility and film formability could be improved.

Similarly, copolymerization of a series of achiral azo-containing isocyanides and (*S*)-2-isocyanoisovaleric methyl ester should also afford optically active azo-containing polyisocyanides in which the azo monomer could be the major component. It is known that the polyisocyanide backbone is very rigid and the energy barrier for the helix-helix transition is very high, in comparison with polyisocyanates.⁴¹ Therefore, it would be

interesting to see if azo photoisomerization could induce a conformational change in the rigid backbone of polyisocyanide.

Hypothesis 3: In polymerization of the [5]helicene-based isocyanide bearing a remote chiral group, the chirality from the chiral group could be transferred to the isocyano reactive center.

In order to study a possibility of such chirality transfer, a [5]helicene-based isocyanide bearing a remote chiral group should be prepared. A pseudo [5]helicene, 5,6,9,10-tetrahydro-[5]helicene-7,8-dicarboxylic anhydride, could be chosen as a starting material. This compound could be aromatized, nitrated and imidized. Thus, it would be possible to obtain an isocyanide bearing a remote chiral group separated by the [5]helicene (Figure 1.11).

Figure 1.11. A Route to [5]Helicene-based Isocyanide Bearing a Chiral Group.

This isocyanide could be polymerized in the presence of a Ni(II) salt, provided there is no steric hindrance. Furthermore, the chirality transfer from the chiral group to the isocyano reactive center during polymerization might happen and this could be easily confirmed by studying the chiroptical properties such as CD Cotton effect and optical rotation in the resulting polymer.

Chapter 2. Copolymethacrylates Derived from TrMA, CHDPMMA with MMA, *n*-BuMA and *t*-BuMA

2-1. Random Copolymerizations

Optically active PTrMA has a stable helical conformation in solution at room temperature or even in refluxing in chloroform for a few days.²⁴ This stability is mainly due to the bulky trityl group which can prevent the helix chain from uncoiling. On the other hand, in the presence of a strong acid such as hydrochloric acid, the ester group will be hydrolyzed, resulting in a conformational change of the polymer from helix to random coil.²⁴ The chiroptical change (the loss of optical rotation) by the acid suggests a potential information storage system in which writing (acid-catalyzed hydrolysis) and reading (difference of optical rotations) can be carried out in solution. However, to achieve such racemization, it is essential for the practical use in the solid state. Thus, optically active PTrMA must be cast into a flexible film. High molecular weight PTrMA [degree of polymerization (DP) > 50] is highly crystalline and insoluble in common organic solvents.²⁴ On the other hand, low molecular weight PTrMA (DP < 50) can only be cast into a brittle film.⁴²

It has been reported that atropogenic copolymerization of TrMA with MMA, benzyl methacrylate (BzMMA) and diphenylmethyl methacrylate (DPMMA) in the presence of chiral anionic complex initiators produces optically active copolymethacrylates.⁴³ The match of TrMA with MMA of the smaller methyl ester group favors the formation of the copolymer having higher specific rotation as compared with

BzMMA and DPMMA. Thus, random copolymerizations of TrMA with MMA and *t*-BuMA were carried out in this study to cast optically active TrMA-based flexible films (Figure 2.1). The flexible segments derived from MMA or *t*-BuMA are thought to disrupt the rigid helical main-chain in the random copolymer, thus improving its solubility and even film formability, while maintaining its high optical rotation.

Copolymerization of TrMA with MMA and *t*-BuMA was carried out by using the complex of 9-fluorenyllithium and (+)-DDB [F⁺Li-(+)-DDB] as a chiral initiator in toluene at -78 °C.²⁵ The results are summarized in Table 2.1.

Figure 2.1. Random Copolymerization of TrMA and MMA.

Table 2.1. Characterization of Random Copolymethacrylates.

No.	Polymer	Yield (%)	Composition ^a (TrMA:MA)	Mn ^b	[α] _D ^c
2.1	TrMA- <i>co</i> -MMA	95	7.0:1.0	9,600	+200°
2.2	TrMA- <i>co</i> -MMA	95	2.5:1.0	8,800	+130°
2.3	TrMA- <i>co</i> -MMA	95	1.0:2.0	25,000	0°
2.4	TrMA- <i>co</i> - <i>t</i> -BuMA	85	4.5:1.0	13,000	+77°
2.5	TrMA- <i>co</i> - <i>t</i> -BuMA	95	2.0:1.0	7,500	+31°

a: molar ratios, estimated from monomer feeding and ¹H NMR integration.

b: GPC analysis using CHCl₃ as an eluent and polystyrene standards.

c: in CHCl₃ at 22 °C.

All copolymerizations gave nearly quantitative yields and the copolymer compositions could be estimated from their monomer feedings and by ^1H NMR (Figure 2.2). Specific rotations of TrMA-*co*-MMA largely depended on the polymer compositions. High fractions of MMA in polymerization resulted in low or even no optical activity. This is because the MMA segment does not form a stable one-handed helix and it also cuts the TrMA segment so that the copolymer does not form a stable helix or a helix long enough to contribute to a large value of optical rotation. A similar result was also obtained in the copolymerization of TrMA with *t*-BuMA. Although *t*-BuMA has a relatively bulky ester group, there is still no clear indication that *t*-BuMA segment can contribute to optical activity of the TrMA-*co-t*-BuMA copolymer.

All optically active copolymers, TrMA-*co*-MMA and TrMA-*co-t*-BuMA, have improved solubilities. However, they could not be cast into flexible films, probably due to a high remaining fraction of the rigid TrMA helical segments. Thus, these copolymers were not suitable for use in studying photodriven racemization in film.

Figure 2.2. ^1H NMR (200 MHz, CDCl_3) of the TrMA-co-MMA Copolymer 2.2.

2-2. Living Block Copolymerizations

Previous results revealed that the optically active TrMA-based random copolymethacrylates could not be cast into flexible films. To obtain a more soluble polymer, block copolymerization may be feasible in which a long flexible segment is linked to the rigid helical TrMA or CHDPMMA segment. Such a long flexible segment could be polystyrene or poly(methyl methacrylate) (PMMA) which imparts the solubility and improves the film formability of the block copolymer.

It was well-documented that styrene (St) can undergo living anionic polymerization to produce polystyrene with a very narrow polydispersity index because of the absence of a chain transfer and other side reactions.⁴⁴ It was reported that, in the presence of a chiral initiator, such living species can initiate TrMA to produce an optically active block copolymer St-*b*-TrMA whose chirality solely arises from a one-handed TrMA helical block (Figure 2.3).⁴⁵

Figure 2.3. Living Block Polymerization of Styrene Macromonomer to TrMA.

Unfortunately, this method does not allow the preparation of the polymer with appreciably high molecular weight, which would allow the possible formation of a flexible film for the purpose of this study.

Polymerization of TrMA in the presence of a chiral anionic initiator has been suggested to have a living nature.⁴⁶ Since the TrMA oligomers or macromonomers prepared by atropogenic polymerization with the repeat units of 20-30 already display large specific rotations,²² attaching flexible methacrylate blocks with small ester groups to the helical chains would be possible in such a living polymerization system. Thus, optically active copolymers containing flexible methacrylate blocks could be produced simply by introducing a second monomer after the complete formation of the helical TrMA oligomers (Figure 2.4). Similarly, a block copolymer derived from a block polymerization of the subsequent addition of a second monomer (MMA or *n*-BuMA) to the living CHDPMMA macromonomer could also be obtained.

According to the literature procedures,²⁵ living TrMA or CHDPMMA blocks were synthesized using FILi-(+)-DDB in toluene at -78 °C. Optically active helical blocks remained soluble in toluene when the initial molar ratio of a monomer to an initiator was adjusted to about 20 to 1 for TrMA and 40 to 1 for CHDPMMA. After most of the first monomer was consumed (1 h for TrMA and 7-8 h for CHDPMMA), the second monomer, MMA, or *n*-BuMA, or *t*-BuMA of predetermined amount, was introduced into the reaction system. The reaction solution became very viscous rapidly, indicating the progress of living block polymerization. Figure 2.5 shows the GPC curves of the CHDPMMA helical block (dashed line) and the CHDPMMA-*b*-MMA copolymer 2.5

(solid line). The curve shifted from lower molecular weight (longer retention time) to higher molecular weight (shorter retention time) after the addition of a second monomer MMA, further indicating the formation of a block copolymer.

Figure 2.4. Living Block Polymerization of the TrMA Macromonomer to MMA.

Figure 2.5. GPC Curves of the Helical Block CHDPMMA (dashed line) and the CHDPMMA-*b*-MMA Copolymer 2.5 (solid line).

For block polymerizations with MMA, *n*-BuMA and *t*-BuMA, the TrMA helical block could also initiate the polymerization of the second monomer, as evidenced by an increase in reaction solution viscosity and a shift of GPC traces before and after adding the second monomer. Figure 2.6 shows the GPC profiles of the helical block TrMA (solid line) and the TrMA-*b*-MMA copolymer 2.8 (dashed line). Addition of MMA results in a peak shift from low molecular weight to high molecular weight and a further broadening of the peak distribution. However, for the living helical TrMA block and the TrMA-*b*-MMA copolymer, bimodal molecular weight distributions were observed. They may be explained by the mechanism proposed for the atropogenic polymerization of TrMA in the presence of FILi-(+)-DDB.²⁵ Oligomer anions in the early stage of polymerization consist of species of different activity. The highly active oligomer anion predominantly propagates. Once an isotactic oligomer anion grows to DP ~7, reaction of the anion with TrMA monomer is accelerated to afford an optically active, one-handed helical polymer, while the less active species remain as oligomers until completion of polymerization.²⁵

Block polymerizations of CHDPMA, TrMA living macromonomers to MMA and *n*-BuMA could produce polymers in almost quantitative yields, whereas that of TrMA living macromonomer to *t*-BuMA could only give polymers in low yields (60%). The low reactivity of *t*-BuMA due to the bulky *tert*-butyl group, as compared with methyl group in MMA or *n*-butyl group in *n*-BuMA, may be the main reason for the low yield.

Figure 2.6. GPC Profile of the Helical TrMA Block (solid line)
and the TrMA-*b*-MMA Copolymer 2.8 (dashed line).

Table 2.2 summarises the results of the living block copolymerizations. Increasing the content of a small alkyl methacrylate improved the solubility and film formability of the copolymer. All the copolymers 2.5-2.13 were readily soluble in THF, dichloromethane, and chloroform. But a free-standing, flexible film could only be obtained from polymers 2.5, 2.9, and 2.10 by solution casting. Specific optical rotations of the copolymers ranged from $+198^\circ$ to $+973^\circ$ at 365 nm or $+50^\circ$ to $+230^\circ$ at 589 nm, depending on the amount of bulky methacrylates in the polymer chain. There is an apparently linear relationship

between specific rotation of TrMA-*b*-MMA block copolymers and the weight percentage of the helical TrMA blocks (Figure 2.7). Polymers 2.8, 2.12 and 2.13 had similar compositions and had similar optical rotations, suggesting the second blocks, even the *t*-BuMA block, did not contribute to any optical activity. Thus, the optical activity arises solely from the one-handed CHDPMMA or TrMA helical block. Both CHDPMMA and TrMA block copolymers do not contain a chromophore which absorbs beyond 320 nm. The optical activity was found to increase progressively as the wavelength of the plane-polarized light decreased. This agrees with the theory of optical rotational dispersion (ORD).⁴⁸ The ratios of specific rotations at 365 nm and 589 nm, $[\alpha]_{365}/[\alpha]_{589}$, for these copolymers were in the range of 3-5. Ideally, for the same helical block copolymers, they should have almost the same ratios of $[\alpha]_{365}/[\alpha]_{589}$, since they have the same helical block with the same length which contributes to the optical activity. The discrepancy here may arise from the reaction conditions not being ideal for the living polymerization. An ideal living polymerization should produce a polymer with a unimodal GPC trace with the polydispersity index close to 1.0.

Figure 2.8 shows the CD spectrum of the TrMA-*b*-MMA copolymer 2.8. The strong CD Cotton effects result from the molecular interactions of aromatic and carbonyl chromophores in the one-handed helical TrMA block. Due to solvent absorption and the limitation of instrument, CD bands could not be measured below 250 nm where even stronger excitons are expected.⁴⁶

Figure 2.9 shows the ¹H NMR spectrum of the TrMA-*b*-MMA copolymer 2.8. The peaks at a low field are assigned to aromatic protons in the helical block. The rigidity

of the helical block results in a poor resolution. The absence of the vinyl proton peaks around 6 ppm precludes the existence of unreacted monomers.

Table 2.2. Characterization of Optically Active Block Polymers.

Polymer	Composition	Helix ^a (wt%)	M_n^b	$[\alpha]_{589}^c$	$[\alpha]_{365}^c$	$[\alpha]_{365}/[\alpha]_{589}$	Film
2.5	CHDPMMA- <i>b</i> -MMA ^d	46	23,000	+64°	+198°	3.1	flexible
2.6	CHDPMMA- <i>b</i> - <i>n</i> -BuMA	58	10,000	+94°	+290°	3.1	brittle
2.7	TrMA- <i>b</i> -MMA ^e	67	7,500	+230°	+973°	4.2	brittle
2.8	TrMA- <i>b</i> -MMA	45	11,000	+150°	+550°	3.7	brittle
2.9	TrMA- <i>b</i> -MMA	23	12,600	+72°	+296°	4.7	flexible
2.10	TrMA- <i>b</i> -MMA	19	15,600	+50°	+236°	4.7	flexible
2.11	TrMA- <i>b</i> - <i>t</i> -BuMA	52	8,900	+165°	+677°	4.1	brittle
2.12	TrMA- <i>b</i> - <i>t</i> -BuMA	37	8,100	+115°	+446°	3.9	brittle
2.13	TrMA- <i>b</i> - <i>n</i> -BuMA	35	9,700	+120°	+492°	4.1	brittle

a: The weight percentage of CHDPMMA or TrMA in the block polymer, estimated from monomer feeding or ¹H NMR integration. b: GPC analysis on the higher molecular weight peak. c: in CHCl₃ at 22 °C. d: Specific rotation of pure CHDPMMA block = 610° at 365 nm; e: Specific rotation of pure TrMA block = 1300° at 365 nm or 340° at 589 nm.

Figure 2.7. Specific Rotation Dependence on the TrMA-*b*-MMA Composition.

Figure 2.8. CD Spectrum of the TrMA-*b*-MMA Copolymer 2.8 in CHCl₃ at 22 °C.

Figure 2.9. ¹H NMR (400 MHz, CDCl₃) of the TrMA-*b*-MMA Copolymer 2.8.

2-3. Photodriven Racemization of Optically Active Block Polymer Films

PCHDPMMA²⁶ and poly[(*S*)-diphenyl(1-methylpyrrolidin-2-yl)methyl methacrylate]²⁷ can undergo a helix-helix transition (stereomutation) at variable temperatures, resulting in a significant change of optical rotation. PMMA derived from optically active helical PTrMA by acid-catalyzed hydrolysis and methylation showed no optical activity (helix-coil transition), due to loss of the bulky trityl group.²⁴ In the solid state, chiroptical change stimulated by a certain external stimulus has been reported in a few limited cases.^{49,50} A stereomutation of optically active regioregular 3-substituted polythiophene as a thin film has been observed and modulated via heating and cooling cycles.⁴⁹ However, multiple heating-cooling cycles in air led to a rapid deterioration of the polythiophene. It was also reported that achiral stereoregular poly[(4-carboxyphenyl)acetylene] can change its structure into a prevailing one-handed helix upon complexation with chiral amines in a film state cast from solution.⁵⁰ The chiral complexation between the carboxylic acid group and the chiral amine plays an important role in inducing a prevailing helical conformation accompanied by induced CD (ICD). However, a very high ratio of a chiral amine to the polyacetylene (typically 50 to 1) was required in order to achieve the induction of the chiral helical conformation.

Conceivably, if removal of the bulky ester group in the solid state can be triggered by light, optically active polymethacrylates should be able to undergo a facile conformational randomization and can, in principle, be used as irreversible optical storage materials.⁵¹ To cleave the acid-labile trityl ester and its analogues, it is highly appropriate to adopt the photoresist chemistry where a triarylsulfonium salt is used as a photoacid

precursor. It has been shown that a catalytic amount of the photogenerated acid is enough to catalyze the de-*tert*-butylation of poly(*tert*-butyl methacrylate) and the liberation of isobutylene gas.⁵²

The thermal behavior of optically active TrMA- and CHDPMMA-based copolymers was investigated in order to probe the thermal-chiroptical relationship. Figure 2.10 shows the DSC and TG curves of block copolymer 2.10. A broad endothermic peak with the onset temperature at 238 °C was observed in the first DSC scan, demonstrating the presence of a crystalline TrMA helical block. A wide glass transition (onset T_g = 133 °C) was also detected, due to the presence of amorphous MMA segment. However, such a wide glass transition (from 133 °C to 155 °C) may suggest quite different phase behavior between the rigid helical TrMA block and flexible MMA one and a possible phase separation.⁵³ Thermal decomposition of copolymer 2.10 occurred right after melting (ca. 245 °C), with 5% weight loss as assessed by TG in nitrogen. Thus the other endothermic peaks shown above 245 °C in DSC are apparently due to decomposed fragments. The thin film of copolymer 2.10 did not change its optical activity upon heating to below decomposition temperature. Similar thermal behaviors were observed for all copolymers. Obviously, the helical conformation stabilized by the bulky ester group is thermally stable and does not undergo thermal racemization in the solid state.

Figure 2.10. DSC and TG (insert) Spectra of the TrMA-*b*-MMA Copolymer 2.10.

Since cyclohexyldiphenylmethyl and trityl esters are acid labile, the ester cleavage can be achieved in the solid state by a photoacid such as the triarylsulfonium salts used in photoresist chemistry. Triarylsulfonium salts constitute a new class of thermally stable, nontoxic materials that produce protonic acids upon irradiation (Figure 2.11).⁵⁴

Figure 2.11. Mechanism of Photoacid Generation.

The mechanism involves a homolytic cleavage of a phenyl group leading to a resonance stabilized intermediate. Radical recombination occurs and a proton is lost with aromatization to yield the triflic acid.

To demonstrate the feasibility of the photodriven racemization of optically active polymethacrylates, a small amount (1.0 wt%) of diphenyl-*p*-tolylsulfonium triflate (DPTST) was blended into copolymers 2.5 and 2.10 (Table 2.2). The methyl group on the phenyl ring was included in order to impart a greater solubility to the DPTST salt. This addition would reduce the possibility of the salt crystallizing out of solution during the film casting. Transparent films (0.030–0.090 mm thickness) were obtained by casting 10–15%

w/w chloroform solutions on circular glass plates (18 mm x 0.2 mm) and drying at 100 °C. Initial optical rotations of films were measured at 365 nm and ranged from +0.15° to +0.33° (Table 2.3). The films were then subjected to irradiation (UV lamp centered at 254 nm) for 2 min. Optical rotations of the irradiated films were taken before and after baking at 120-130 °C for 10 min. No change in optical rotation was detected from the samples being irradiated but without baking or baking alone without irradiation, indicating that both irradiation and baking are necessary for racemization.

As for the cleavage of poly(*tert*-butyl methacrylate), a catalytic amount of the photoacid is sufficient to split off the acid-labile cyclohexyldiphenylmethyl group from PCHDPMMA in the solid state. Indeed, optical rotations (+0.16 to +0.33°) of the films cast from copolymer 2.5 containing 1.0 wt% of DPTST (molar ratio of CHDPMMA/DPTST: 60/1) vanished completely after 2 min of being exposed to light, followed by 10 min of heating. Although the physical appearance and UV absorption of the irradiated film showed no visible change, a broad weak band around 3200 cm⁻¹ and a weak shoulder peak at 1710 cm⁻¹ due to COOH were detected by IR, indicating that the ester cleavage had taken place at some of the CHDPMMA units. After extensive photolysis and thermolysis (3.0 wt% of DPTST, 5 min irradiation and 10 min baking at 130 °C), the CHDPMMA-*b*-MMA film displayed strong peaks due to COOH. The catalytic nature of the ester cleavage is evidenced by isolation of diphenylmethylenecyclohexane, as expected, from deprotonation of the cyclohexyldiphenylmethyl cation (Figure 2.12).

The results have demonstrated that partial loss of the bulky ester groups can result in conformational randomization of helical blocks, which in turn leads to a significant change in optical rotation of optically active solid films. At the microscopic level, the system clearly behaves as an irreversible optical-optical molecular switching device. The chemical process initiated by irradiation (writing) involves the photogeneration of an acid, the acid-catalyzed thermal cleavage of the cyclohexyldiphenylmethyl ester, and the formation of the regenerated acid catalyst (Figure 2.12).⁵⁵ In magneto-optical data recording system,⁵⁶ recording is accomplished by using laser to heat a magnetized rare earth-transition metal medium, reading is based on the rotation of polarization of reflection light (Kerr effect), the direction of rotation depending on the domain orientation. The amount of signal available depends on the magnitude of this rotation (typically 0.2-1.0°). In our system, a permanent change in optical rotation (about 0.2-0.3°) of these polymer films is comparable to the Kerr angle and, therefore, should be detectable by similar optical means (reading). While the photochemical writing can be carried out at the UV region (< 300 nm), this system may allow for the written data to be safeguarded or locked with nondestruction during the reading process with light at 365 nm or higher. The photodriven racemization of optically active CHDPMMA-*b*-MMA flexible film has been clearly demonstrated, however, since the magnitude of optical rotation is associated with the film thickness, the thinner the film is, the lower the optical rotation will be. Therefore, a thinner film will result in a smaller change in optical rotation upon racemization. Thus, it is challenging to design a system and to obtain a flexible thinner film which has inherently high optical rotation.

Table 2.3. Racemization of Optically Active Block Polymethacrylates.

copolymer	composition ^a	thickness (mm)	α_1^b (365 nm)	α_2^c (365 nm)
2.5	CHDPMMA- <i>b</i> -MMA	0.050	+0.16°	0.00°
		0.070	+0.26°	0.00°
		0.090	+0.33°	0.00°
2.10	TrMA- <i>b</i> -MMA	0.030	+0.15°	+0.04°
		0.050	+0.28°	+0.15°

a: containing 1.0 wt% of DPTST.

b: initial optical rotation of the film before irradiation.

c: optical rotation of the film after 2 min irradiation at 254 nm and 10 min baking at 120-130 °C.

Figure 2.12. Photodriven Racemization of the CHDPMMA-*b*-MMA Copolymer 2.5.

In the case of optically active flexible TrMA-*b*-MMA film, a stoichiometric amount of the acid seems to be needed for complete hydrolysis of all the trityl ester in the TrMA helical block, since no acidic proton is available from the trityl group. However, the

irradiated films of TrMA-*b*-MMA copolymer 2.10 containing a catalytic amount of DPTST (1.0 wt%) turned yellow after baking and showed a moderate decrease in optical rotation (Table 2.3). UV absorption of this yellow film displayed a new peak at 435 nm which is attributed to the trityl cation $[(C_6H_5)_3C^+]$ produced by the photogenerated acid hydrolysis. The formation of the trityl cation was further confirmed by the isolation of trityl alcohol after bleaching the yellow film with water-chloroform. Since the molar ratio of TrMA to the sulfonium salt was about 30:1, only the limited trityl groups could be eliminated from the helical chain during the baking process. Therefore, conformational randomization of one-handed helical TrMA block took place to a certain extent and so did the decrease of optical rotation. It was noticed that the yellow color of the treated TrMA-*b*-MMA film gradually faded while its optical activity remained unchanged. Interestingly, the yellow color or the trityl cation resumed when reheating the film and the optical rotation further decreased. This suggests that the trityl cation and the carboxyl group in the polymer can recombine back to the ester and the acid is regenerated (Figure 2.13).⁵⁵ The acid then continues to hydrolyze the other part of one-handed helical TrMA block during the consecutive baking, which causes a further decrease in optical rotation. Thus, photo-induced cleavage of the trityl ester group causes defects in one-handed helical block which can undergo facile racemization upon slight heating.

Figure 2.13. Photodriven Racemization of the TrMA-*b*-MMA Copolymer 2.10.

2-4. Experimental Section

Materials

Toluene was first distilled from calcium hydride and re-distilled from sodium under nitrogen before use. Tetrahydrofuran (THF) was distilled from calcium hydride under nitrogen. Methylmethacrylate (MMA), *t*-butylmethacrylate (*t*-BuMA) and *n*-butylmethacrylate (*n*-BuMA) were distilled from calcium hydride under vacuum and stored under nitrogen in a refrigerator. Fluorene was recrystallized from ethanol and dried under vacuum overnight. (*S,S*)-(+)-2,3-Dimethoxy-1,4-bis(dimethylamino)butane [(+)-DDB] was distilled from calcium hydride under vacuum (b.p. 62.0–64.0 °C/3mmHg, $[\alpha]_D^{20} = +14.5^\circ$, neat). *n*-Butyllithium was titrated using 2,5-dimethoxybenzyl alcohol as self-indicator in dry toluene at room temperature under nitrogen.⁵⁷ Diphenyl-*p*-tolylsulfonium triflate (DPTST) was prepared by reaction of diphenyl sulfoxide with toluene in triflic acid and trifluoroacetic anhydride.⁵³ CHDPMMA (m.p. 73.6–74.6 °C; lit.²⁶ 73.6–74.6 °C) was synthesized from methacryloyl chloride and cyclohexyldiphenyl methanol according to known procedure.²⁶ Triphenylmethyl chloride and methacryloyl chloride were used as purchased from Aldrich Chemical Co.

Monomer Synthesis

Trityl Methacrylate (TrMA).

Method 1.⁵⁸ Triphenylmethyl chloride (2.77 g, 10.00 mmol) and methacrylic acid (1.00 mL, 12.00 mmol) were dissolved in dichloromethane (50 mL). Then triethylamine (1.70 mL, 12.00 mmol) was added dropwise. The reaction was run at room temperature for 1 h. The

reaction mixture was washed with distilled water three times until pH was 6-7. The organic layer was separated and solvent was removed. The crude product was recrystallized from hexane in the presence of activated charcoal three times. The crystals were dried at 80 °C under vacuum for 2 days. Yield was 2.33 g (70%); m.p. 102.0-103.0 °C (lit.²³ 102-103 °C); IR (KBr) 3028, 1726, 1492, 1449, 1207, 1154 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.35 (m, 15H), 6.15 (s, 1H), 5.61 (s, 1H), 2.00 (s, 3H); ¹³C NMR (50.3 MHz, CDCl₃) δ 165.1, 143.3, 137.4, 128.2, 127.7, 127.2, 125.6, 89.9, 18.5.

Method 2.⁵⁹ To a three-necked, round-bottomed flask equipped with a stirring bar and an addition funnel were added Ca(OH)₂ (10.00 g, 0.13 mol) and 50 mL of distilled water and stirred for few minutes. The methacrylic acid (11.00 mL, 0.13 mol) was added dropwise for 5 min. To this solution was added AgNO₃ (40.00 g, 0.23 mol) in 40 mL of water. The solution was stirred for 2.5 h and silver methacrylate precipitated as a gray solid. The silver methacrylate was filtrated and yield after recrystallized from water was 17.10 g (70%). A solution of triphenylmethyl chloride (11.70 g, 42.00 mmol) in dry ether was stirred with silver methacrylate (10.00 g, 55.00 mol) at room temperature overnight. AgCl was filtrated off and ether filtrate was concentrated. The crude TrMA was recrystallized from ether (100 mL) three times and yield was 10.00 g (75%).

Chiral Initiator

9-Fluorenyllithium (FLi) was made by treating a solution of fluorene in toluene with a stoichiometric amount of *n*-BuLi at room temperature. After 5 min, 1.2 mol equiv

of (+)-DDB was introduced to the FILi solution to form deep brown chiral initiator, FILi-(+)-DDB complex.²⁵

Random Copolymerization

A typical random copolymerization of TrMA and MMA is as follows: TrMA (3.28 g, 1.00 mmol) and MMA (0.53 mL, 0.40 mmol) were placed in a flame-dried flask under N₂ and the system was evacuated and purged with nitrogen alternatively three times. Toluene (30 mL) was added via double-tipped needle and the flask was then immersed into dry ice/acetone bath (-78 °C) for ten min. The chiral initiator FILi-(+)-DDB (0.05 mmol) was added quickly via a syringe into the reaction flask with strong stirring and the reaction continued for 3 h. Then, the temperature of the solution gradually increased to room temperature and the polymer was precipitated out by pouring into methanol (100 mL). The solid after filtration was further purified by re-dissolving in chloroform (10 mL) and precipitating into methanol (100 mL). The copolymer TrMA-*co*-MMA was filtrated and dried around 70 °C under vacuum overnight. The yield was 3.59 g (95%).

Other random copolymerizations of TrMA and MMA or *t*-BuMA with different monomer feed were carried out in the same way and the yields were quantitative.

Living Block Polymerization

A typical living block polymerization of TrMA to MMA is as follows: TrMA (3.28 g, 1.00 mmol) was placed in a flame-dried flask under N₂ and the flask was evacuated and purged with nitrogen alternatively three times. Toluene (30 mL) was added via a double-

tipped needle and the flask was then placed into a dry ice/actone bath (-78 °C) for 10 min. The chiral initiator FILi-(+)-DDB (ca. 0.05 mmol) in dry toluene was added quickly via a syringe into the reaction flask with stirring. The reaction proceeded 1 h. Second monomer MMA (8.48 mL, 8.00 mmol) was then added with vigorous stirring and the solution became very viscous immediately. The reaction continued for 3 h and the reaction temperature gradually increased to room temperature. The reaction was quenched by addition of a small amount of methanol (1 mL) and the polymer was then precipitated into large amount of methanol (100 mL). After filtration, the block polymer was further purified by re-dissolving in chloroform (10 mL) and precipitating into methanol (100 mL). The copolymer after filtration was dried at 70 °C under vacuum overnight. The yield was 11.76 g (95%).

The other block copolymerizations of TrMA or CHDPMMA to MMA, *t*-BuMA or *n*-BuMA with a variable amount of the second monomer were carried out in the same way.

Irradiation of Block Copolymer Films

A small amount (1.0 wt%) of DPTST was blended into block copolymer TrMA-*b*-MMA or CHDPMMA-*b*-MMA. Transparent films (0.030-0.090 mm thickness) were obtained by casting 10-15% w/w chloroform solutions on circular glass plates (18 mm x 0.2 mm) and drying at 100 °C. Initial optical rotations of films were measured at 365 nm and films were then subjected to irradiation (UV lamp centered at 254 nm) for 2 min. Optical rotations of the irradiated films were taken after baking at 120-130 °C for 10 min.

Measurement

^1H and ^{13}C NMR spectra were recorded on a Germini-200 spectrometer at 200 MHz and/or a Bruker AMX-400 spectrometer at 400 MHz in CDCl_3 using tetramethylsilane as an internal reference, at room temperature. UV spectra were recorded on a Perkin-Elmer Lambda UV/Vis spectrometer in CHCl_3 at room temperature. Optical rotations were measured on a Perkin-Elmer 141 polarimeter at the mercury (365 nm) line and the sodium line (589 nm), respectively. GPC analysis was performed on a Perkin Elmer 900 using CHCl_3 as eluent at a rate of 1 mL/min and polystyrene as standard calibration. CD spectra were measured with a JASCO-6000-CD apparatus equipped with a computerized data processor. Thermal analysis was performed on a differential scanning calorimeter (DSC) Seiko 5200 at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen (50 mL/min) and a thermogravimetric analyzer (TGA) Seiko 5200 at a heating rate of 20 $^{\circ}\text{C}/\text{min}$ under nitrogen (150 mL/min), respectively. UV irradiation was done using mercury lamps (16 x 8 w) centered at 254 nm in a Rayonet photochemical reactor.

Chapter 3. Azo-Containing Polymethacrylates

3-1. Random Copolymerizations

A convenient way to prepare optically active polymers having a side chain photochromic group is to copolymerize achiral vinyl or acrylic monomers bearing a photochromic moiety and an optically active group. Copolymers of (-)-L-menthyl acrylate with 4-phenylazophenoxy acrylate have been prepared by free radical polymerization.⁶⁰ This copolymer displayed two dichroic bands associated with the $n\text{-}\pi^*$ and $\pi\text{-}\pi^*$ electronic transitions of the azobenzene chromophore in the trans configuration. Photoisomerization of azobenzene moieties from trans to cis causes a significant change of the dichroic bands. This behavior was attributed mainly to an isolated azobenzene chromophore rather than to conformational change of the whole macromolecules. This is a consequence of a substantial absence of stereoregularity in the main chain, which implies the lack of ordered secondary structures.

It has been shown in the previous chapter that copolymerization of TrMA with other methacrylate monomers can produce an optically active polymer with main-chain chirality in the presence of a chiral initiator. Therefore, copolymerization of TrMA with azo-containing methacrylates should also produce optically active polymers under the same reaction conditions (Figure 3.1). Thus an azobenzene chromophore can be introduced into polymer side-chains by random copolymerization.

Figure 3.1. Random Polymerization of TrMA and Azo-containing Methacrylate.

Therefore, the solubility and film formability of resulting polymers will be effected by the length of a spacer between an azobenzene chromophore and an ester group in the side chain and also by the ratio of TrMA to an azo comonomer.

In this study, three azo methacrylates chosen, PAM, PAEM and PAHM, are structurally related to each other. The azobenzene moiety is attached to the ester group via no spacer or an ethylene or hexamethylene spacer. Accordingly, moving the azo group away from the reactive alkenyl center would affect the formation of a helical segment. It is accepted that four monomeric units of TrMA can form one helical turn in a TrMA

homopolymer.⁶¹ Azo comonomers have less rigid side ester group, therefore, the monomer feeding of TrMA to an azo comonomer should be kept over 1 molar ratio in order to maintain certain helical moieties for optical activity in the copolymer.

Copolymerizations of TrMA with PAM and PAEM, respectively, were run at -78 °C in toluene using FLi-(+)-DDB as an initiator, while the copolymerization with PAHM had to be carried out at room temperature, due to the low solubility of PAHM in toluene at low temperature. It was expected that during the random copolymerization, the magnitude of chirality transferred from the one-handed TrMA segment to the configurationally irregular azo chromophore side chain of the azo comonomer part would follow the order of TrMA-*co*-PAM > TrMA-*co*-PAEM > TrMA-*co*-PAHM. Unfortunately, no polymer was obtained in the copolymerization of TrMA and PAM, probably due to a side reaction which destroys the initiator.⁶² On the other hand, all copolymerizations between TrMA and PAEM or PAHM gave almost quantitative yields. The polydispersities of these copolymers were fairly narrow compared with that of TrMA homopolymer prepared from atropogenic polymerization.

The results of random copolymerization are summarized in Table 3.1. The compositions of all the azo-containing polymers were estimated from the ¹H NMR spectra based on the integration of the aromatic protons and the protons of the -OCH₂- group. Figure 3.2 shows the ¹H NMR spectrum of the TrMA-*co*-PAHM copolymer 3.3.

The UV/Vis absorptions for all the azo copolymers 3.1, 3.2, 3.3, 3.4, 3.5 and 3.6 were measured in CH₂Cl₂. All copolymers had three maximum absorptions, 240 nm, 340 nm and 435 nm. The peak at 240 nm was due to the absorption of carbonyl groups and

phenyl rings. The peak at 340 nm was due to trans transition of $\pi\text{-}\pi^*$ in the azo group, while a weak, broad peak at 435 nm was from cis transition of $n\text{-}\pi^*$ in the azo group. From the random copolymerization of TrMA with PAHM or PAEM in the presence of FILi-(+)-DDB, the resulting copolymers showed dextrotations which were consistent with the results in which polymerization of TrMA in the presence of FILi-(+)-DDB gives (+)-PTrMA, while that in the presence of FILi-(-)-DDB gives (-)-PTrMA.²⁴ Their specific rotations ranged from +50° to +312° at 589 nm (Table 3.1). Optical activity was found to decrease as the azo content increases in the copolymers, especially for the copolymer with PAHM having a longer flexible spacer $\text{-(CH}_2\text{)}_6\text{-}$. Figure 3.3 shows specific optical rotation dependence on composition in TrMA-co-PAHM copolymers. Once the copolymer contains TrMA in high content, it always shows high optical rotation. This optical rotation dependence on composition indicates that the azo part, due to its size in the side chain, could not contribute to the optical activity which was ascribed to the rigid, single-sense helical chain. However, the regular helical TrMA segment was randomly separated by the azo-containing sequence. For the TrMA-co-PAHM copolymers, optical rotations were recorded at 589 nm, 578 nm and 546 nm, respectively. It was found that the optical rotation increased as the wavelength decreased and the ratio of $[\alpha]_{589} : [\alpha]_{578} : [\alpha]_{546}$ was 1:1.05:1.20. Such constant ratio is observed because these azo-containing copolymers have similar electronic structures.⁶³ Optical rotations at 365 nm could not be measured for all azo copolymers due to strong absorption. No clear exciton couplet was observed in the azo absorption region from the CD spectrum of the TrMA-co-PAHM copolymer, indicating that the azo chromophore was not in a chiral helical environment, probably

caused by the long separation of a flexible spacer. Similarly, the azobenzene chromophore from TrMA-*co*-PAEM copolymers was not in a chiral helical environment, based on a CD experiment.

Solubility and film formability were improved through copolymerization. The TrMA-*co*-PAHM copolymer containing only a small amount of PAHM (e.g., 6.5 wt% for copolymer 3.1) already formed a brittle film, indicating that random copolymerization with achiral azo methacrylates effectively disrupts the regularity of the helical chain and reduces the crystallinity of the resulting polymers.

Table 3.1. Characterization of Optically Active Azo-Containing Copolymethacrylates.

Copolymer	Composition	Molar ratio	Azo ^a (wt %)	Mn	[α] ₅₈₉ ^b	Film
3.1	TrMA- <i>co</i> -PAHM	16:1	6.5	14,000	+312°	brittle
3.2	TrMA- <i>co</i> -PAHM	10:1	10	9,400	+164°	brittle
3.3	TrMA- <i>co</i> -PAHM	4.4:1	20	4,800	+85°	flexible
3.4	TrMA- <i>co</i> -PAHM	3.2:1	26	8,500	+37°	flexible
3.5	TrMA- <i>co</i> -PAEM	11.3:1	7.7	4,200	+322°	brittle
3.6	TrMA- <i>co</i> -PAEM	2.8:1	25	4,000	+50°	brittle

a: The weight percentage of azo methacrylates in feed as well as in the random copolymer, as assumed on the basis of nearly quantitative conversion.

b: in chloroform at 22 °C.

Figure 3.2. ^1H NMR (200 MHz, CDCl_3) of the TrMA-*co*-PAHM Copolymer 3.3.

Figure 3.3. Specific Rotation Dependence on the TrMA-co-PAHM Composition.

3-2. Photoisomerization of Optically Active Azo-Containing Polymethacrylates

Azobenzene and its analogues exist as *trans* and *cis* isomers and can undergo *trans*-*cis* transition by irradiation with 300 nm light (*trans* to *cis*) or heating (*cis* to *trans*). Isomerization of azo groups of helical copolymers by external stimuli might induce the helix-helix transition or racemization process in solution.³⁸ The azo group in the copolymer as prepared is usually in the thermally favored *trans* form which has a strong absorbance at around 340 nm due to the π - π^* transition of the *trans* azo group. However, no significant change in optical rotation was observed by irradiating a film of the optically active TrMA-*co*-PAHM copolymer 3.3 with light (300 nm wavelength) over two hours. It may be due to the fact that there exists a very high energy barrier for isomerization of azo chromophore from *trans* to *cis* in this frozen state. However, significant changes in optical rotation and UV/vis absorption were observed when the photoisomerization of azo-containing helical copolymers were carried out in CH₂Cl₂ at 15 °C. Figure 3.4 shows the UV/Vis absorption spectra of the TrMA-*co*-PAEM copolymer 3.6 in CH₂Cl₂ before and after irradiation for up to 20 min. The peak intensity at around 340 nm decreased as the irradiation time was increased, indicating the conversion of the *trans* azo to the *cis* azo. The specific optical rotation of the polymer decreased dramatically after irradiation. The copolymer 3.6 was racemized after 20 min exposure to light at 300 nm. This is because, during the photoisomerization, the molecular geometry of the azo group changes from the extended planar *trans* configuration to the skewed configuration of the *cis* isomer. In addition, the polarity of the azo chromophore dramatically changes, since the *trans* isomer

is practically nonpolar, whereas the *cis* form is characterized by a high dipole moment. The *trans-cis* isomerization causes a change in polarity around the backbone. Both the geometry and the group polarity can be the driving forces responsible for the conformational racemization of the helix.

For the TrMA-*co*-PAHM copolymer 3.1 containing a much lower content of the azo moiety, the change in optical rotation took place much slower and was less significant. This indicates that *trans-cis* azo isomerization and the azo content play a key role in the helix-helix or helix-coil transformation. High content of PAHM may also cut the length of the helical TrMA segment and reduce the rigidity of the copolymer, and thus make TrMA-*co*-PAHM copolymer undergo conformational change in the backbone. Similar photochemical behavior was observed for the TrMA-*co*-PAHM copolymer 3.3 (Figure 3.4). Optical rotation decreased after 20 min exposure to light at 300 nm (Figure 3.5). GPC indicated that the irradiation did not cause the degradation of the polymer chains.

Figure 3.4. UV/vis Spectra of the TrMA-*co*-PAHM Copolymer 3.3 (left) and the TrMA-*co*-PAEM Copolymer 3.6 (right) in CH_2Cl_2 .

Figure 3.5. Specific Rotations for the TrMA-*co*-PAHM Copolymer 3.3 and the TrMA-*co*-PAEM Copolymer 3.6 at Different Irradiation Times.

3-3. Experimental Section

Materials and Measurements

Triethylamine and tetrahydrofuran (THF) were dried by distillation over CaH_2 under N_2 . 4-Phenylazophenol, diglyme, 2-chloro-1-ethanol, methacryloyl chloride and 6-chloro-1-hexanol were obtained from Aldrich Co.

Specific rotations were measured on Perkin-Elmer 141 polarimeter at 546 nm, 578 nm and 589 nm, respectively. UV irradiation was carried out using mercury lamps (16 x 21 w) centered at 300 nm in a Rayonel photochemical reactor. For all other measurements, refer to Experimental Section 2.4, Chapter 2.

Monomer Synthesis

2-(4-Phenylazophenoxy)-1-Ethanol.⁶² 4-Phenylazophenol (10.00 g, 0.050 mol), anhydrous K_2CO_3 (15.00 g, 0.11 mol) and KI (0.50 g) were dissolved into 50 mL of diglyme by heating and stirring. Toluene (75 mL) and 2-chloro-1-ethanol (5.00 mL, 0.070 mol) were added and the solution was refluxed at 168 °C for 6 h. The mixture was cooled to room temperature and inorganic salts were removed by filtration. The filtrate was concentrated under rotatory water pump vacuum at 70 °C and the crude product was precipitated into a large amount of distilled water (500 mL). After filtration, the product was redissolved in toluene (100 mL) and washed with aq. NaOH solution (0.1 M, 2 x 200 mL) and distilled water (2 x 200 mL). The solvent was removed under rotatory water pump vacuum at 70 °C and the product was recrystallized three times from hexane. Yield of 2-(4-phenylazophenoxy)-1-ethanol was 0.50 g (41%); m.p. 100.0-102.0 °C; IR (KBr) 3294,

2924, 1602, 1496, 1251 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 4.00 (t, 2H), 4.18 (t, 2H), 7.05 (d, 2H), 7.50 (m, 3H), 7.91 (m, 4H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 161.0, 152.7, 147.2, 130.4, 129.0, 124.7, 122.6, 114.7, 69.4, 61.3; MS (EI, m/z , %) 242 (M^+ , 49); HRMS for $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2$: found 242.1047, calcd. 242.1056.

2-(4-Phenylazophenoxy)ethyl Methacrylate (PAEM).⁶² 2-(4-Phenylazophenoxy)-1-ethanol (2.00 g, 8.26 mmol) and dry triethylamine (5.00 mL, 36.00 mmol) were dissolved in dry THF (50 mL) and cooled in ice/water bath under N_2 . Methacryloyl chloride (2.00 mL, 20.00 mmol) dissolved in dry THF (50 mL) was added dropwise. The solution was stirred for 3 h at room temperature. The mixture was filtrated and the solvent was removed under rotatory water pump at 40 $^\circ\text{C}$. The product was recrystallized three times from absolute ethanol. Yield of PAEM was 1.00 g (40%); m.p. 71.0-73.0 $^\circ\text{C}$; IR (KBr) 2947, 1716, 1600, 1501 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 1.97 (s, 3H), 4.30 (t, 2H), 4.55 (t, 2H), 5.61 (m, 1H), 6.18 (s, 1H), 7.05 (d, 2H), 7.50 (m, 3H), 7.91 (m, 4H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 167.5, 161.2, 153.0, 147.7, 136.3, 130.7, 129.3, 126.5, 125.0, 122.8, 115.1, 66.4, 63.1, 18.6; MS (EI, m/z , %); 310 (M^+ , 5); HRMS for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_3$: found 310.1334, calcd. 310.1318; UV/Vis (CHCl_3) λ_{max} 343, 430 (w) nm.

6-(4-Phenylazophenoxy)-1-Hexanol.⁶² It was prepared from 4-phenylazophenol and 6-chloro-1-hexanol as for preparation of 2-(4-phenylazophenoxy)-1-ethanol. Yield was 70%; m.p. 87.0-89.0 $^\circ\text{C}$; IR (KBr) 3250, 2938, 1602, 1498, 1248, 1142, 1008 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.90 (m, 4H), 7.45 (m, 3H), 7.00 (d, 2H), 4.05 (t, 2H), 3.64

(t, 2H), 1.40-1.90 (m, 8H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 161.3, 152.7, 146.8, 130.3, 129.0, 124.7, 122.5, 114.7, 68.2, 62.8, 32.6, 29.1, 25.9, 25.3.

6-(4-Phenylazophenoxy)hexyl Methacrylate (PAHM).⁶² It was prepared from 6-(4-phenylazophenoxy)-1-Hexanol and methacryloyl chloride as for preparation of PAEM. Yield was 67%; mp. 86.0-87.0 °C; IR (KBr) 2947, 2865, 1705, 1605, 1256, 1182 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.88 (m, 4H), 7.47 (m, 3H), 6.98 (d, 2H), 6.09 (s, 1H), 5.53 (m, 1H), 4.15 (t, 2H), 4.02 (t, 2H), 1.93 (s, 3H), 1.50-1.80 (m, 8H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 167.7, 161.8, 152.6, 147.0, 136.9, 130.3, 129.0, 125.2, 124.7, 122.5, 114.6, 68.1, 64.6, 29.1, 28.5, 25.7, 18.3; UV/Vis (CHCl_3) λ_{max} 348, 430 (w) nm.

4-Phenylazophenyl Methacrylate (PAM).⁶⁴ 4-Phenylazophenol (18.00 g, 0.090 mol) was dissolved in an excess of aq. NaOH (5%, w/v, 100 mL) solution. The solution was cooled in an ice-water bath and methacryloyl chloride (10.00 g, 0.16 mol) was added in 10 min with stirring. The reaction continued for additional 30 min at room temperature. The resulting ester was collected by filtration and recrystallized three times from absolute ethanol. Yield was 7.00 g (30%); mp. 117.0-118.0 °C (lit.⁶⁴ 113 °C); ^1H NMR (200 MHz, CDCl_3) δ 7.91 (m, 4H), 7.52 (m, 3H), 7.30 (d, 2H), 6.44 (s, 1H), 5.82 (s, 1H), 2.15 (s, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 165.2, 153.1, 152.4, 150.1, 136.0, 131.1, 129.1, 127.7, 124.1, 122.9, 122.3, 18.4.

Copolymerization of TrMA with azo comonomer

Random copolymerization (TrMA-*co*-PAEM). TrMA(2.77 g, 1.00 mmol) and PAEM (1.10 g, 0.36 mmol) were placed in a flame-dried flask under N₂. The flask was evacuated and purged by nitrogen-vacuum cycling three times. Dry toluene (30 mL) was added via double-tipped needle and the flask was then submerged into dry ice/acetone bath (-78 °C) for 10 min. The chiral initiator FILi-(+)-DDB (0.05 mmol) in dry toluene (1 mL) was added quickly into the reaction flask with strong stirring and the reaction continued for 3 h. Then, the temperature of the solution gradually increased to room temperature and the polymer was precipitated out by pouring into methanol (100 mL). The solid was further purified by redissolving in chloroform (10 mL) and precipitating into methanol (100 mL). The azo-containing copolymer was filtrated, washed and dried around 70 °C under vacuum. The yield was 4.30 g (95%).

Random copolymerization of TrMA and PAHM was carried out under similar conditions for the preparation of TrMA-*co*-PAEM except that it was run at room temperature. No polymer was obtained from copolymerization of TrMA and PAM.

Photoirradiation

A quartz flask equipped with a condenser containing a solution of TrMA-*co*-PAHM copolymer **3.3** (1.40×10^{-4} g/mL in CH₂Cl₂) was placed in a photochemical radiator. The solution temperature was controlled at 15 °C by an ethanol-circulating cooler system. Photochemical radiation was carried out at wavelength of 300 nm with ca.

336 w. UV/vis spectra and specific rotations were measured at different irradiation times (0 min, 1 min, 5 min, 10 min and 20 min).

Photochemical radiation for the TrMA-*co*-PAHM copolymers 3.1, 3.2, 3.4 and the TrMA-*co*-PAEM Copolymers 3.5, 3.6 was carried out in the same way.

A yellow film (0.050 mm thickness) of the TrMA-*co*-PAHM copolymer 3.3 cast from CH₂Cl₂ solution (20 mg/mL) was dried under vacuum at 70 °C overnight and then photoirradiated at 300 nm (ca. 336 w) in a photoradiator at ca. 30 °C. Optical rotations were measured before and after 2 h irradiation.

Chapter 4. Azo-Containing Helical Polyisocyanides

4-1. Monomer Synthesis

Isocyanides have the general structure: $R-N^+ \equiv C^-$.⁵ The synthesis of isocyanide has been extensively reviewed by Ugi.⁶⁵ A few methods have been used to prepare a variety of isocyanides. The most popular pathway is to convert primary amines into *N*-formamides, followed by dehydration (Figure 4.1).⁶⁶ The conversion of primary amines into formamides is straightforward. Phosphorous oxychloride is often used rather than phosgene for the dehydration of formamides for the preparation of most alkyl and some aryl isocyanides. An excess of a tertiary amine is often used to promote the α -elimination from the imine chloride intermediate and to consume the resulting hydrogen halide.

Figure 4.1. General Synthesis of Isocyanides from Amines.

Accordingly, methyl (*S*)-2-isocyanoisovalerate and a series of azo-containing isocyanides have been prepared in good yields (Figure 4.2). The starting amines for the chiral isocyanide and isocyanides 4.1 and 4.2 are commercially available. The azo-containing amines for the syntheses of isocyanides 4.3, 4.4 and 4.5 were prepared (Figure 4.3).⁶⁷ The key step is the azo coupling reaction. If the amino group on aniline is protected, the coupling reaction occurs at its para position. The protection group can be

removed by hydrolysis under basic condition (aqueous NaOH solution). The resulting compound, after filtration, can be acidified with hydrochloric acid to afford 4'-amino 1-phenylazobenzoic acid. This acid can then be esterified in the acid condition (H_2SO_4) with three different alcohols, methanol, ethanol and 1-butanol, respectively, to produce three primary amines (4.3a, 4.4a and 4.5a) with different ester substituents on the azobenzene (Figure 4.3).

Figure 4.2. Isocyanides Prepared in This Work.

Figure 4.3. Synthesis of Aminoazobenzene Compounds.

By using the same method (Figure 4.3), two other amino azobenzene derivatives (4.6a and 4.7a) have also been prepared. However, these two primary amines could not be converted into the corresponding isocyanides 4.6 and 4.7 (Figure 4.2) by the method described above (Figure 4.1).

Therefore, Hoffmann's carbylamine reaction was adopted.⁶⁸ In this reaction, a primary amine is treated with chloroform and a strong base (e.g., NaOH) in the presence of a phase transfer reagent (Figure 4.4). Dichlorocarbene is generated *in situ* from the reaction of hydroxide ion and chloroform, which then attacks the amine, followed by β -elimination of one of hydrogen chloride and α -elimination of another. Isocyanides 4.6 and 4.7 thus were prepared in good yields by using this method.

Figure 4.4. Hoffmann's Carbylamine Reaction.

All these isocyanides were characterized by IR and ¹H NMR experiments. A typical IR peak due to the isocyano stretching was found at around 2120 cm⁻¹ for the azo-containing isocyanides and at 2153 cm⁻¹ for the chiral isocyanide. The conjugation between the isocyano group and the azobenzene chromophore in the azo-containing

between the isocyano group and the azobenzene chromophore in the azo-containing isocyanides reduced the frequency of the isocyano absorption. Figures 4.5 and 4.6 show the IR and ^1H NMR spectra of the isocyanide 4.4, respectively.

Figure 4.5. IR Spectrum of the Isocyanide 4.4.

Figure 4.6. ¹H NMR (400 MHz, CDCl₃) Spectrum of the Isocyanide 4.4 at 22 °C.

4-2. Homopolymerization

All azo-containing isocyanides can be polymerized in the presence of NiCl_2 in quantitative yields. Figure 4.7 shows the IR spectra of the monomer 4.1 and its homopolymer. The infrared peak at 2119 cm^{-1} due to $\text{N}^+\equiv\text{C}^-$ group disappears after polymerization and a new peak at 1591 cm^{-1} due to imino double bond appears, indicative of the quantitative polymerization. Figure 4.8 shows the electronic spectra of the monomer 4.1 and its homopolymer. The polymer shows broad and extended absorption in the visible region, suggesting that conjugations exist in the backbone and between the backbone $\text{N}=\text{C}$ groups and the azo side groups. Similar results were also obtained from polymerization of other azo monomers. High molecular weight polymer was obtained from polymerization of the monomer 4.5, because the resulting polymer had a good solubility during polymerization. On the other hand, the polymers derived from monomers 4.6 and 4.7 could not be characterized for their molecular weights by GPC analysis because of strong adsorption of the polymers having sulfate groups onto the GPC column. These two polymers were soluble in alcoholic solvents and partially soluble in water due to their sulfate groups.

DSC analyses on these azo-containing polyisocyanides revealed that there were neither glass transitions nor melting points prior to thermal decompositions. This may be due to the tightly helical conformations of these polymers.¹⁴ Thermogravimetric analyses of these polymers showed 5% weight loss over wide temperature ranges (150 to 400 °C).

A racemic polyisocyanide is a mixture of *P* and *M* helices in equal amounts. In an attempt to obtain optically active one-handed polyisocyanide, monomers 4.1 and 4.2 were

homopolymerized with NiCl_2 and (-)-sparteine. It was hoped that one enantiomeric polyisocyanide (e.g., *P* helix) was prepared predominately over the other (e.g., *M* helix) in the presence of (-)-sparteine. Unfortunately, the resulting polymers were all optically inactive after purification by removing the chiral (-)-sparteine. Probably, these two isocyanides were reactive and were therefore not sensitive to a slight difference in activation energy between the formation of the screw senses. As reported, only those achiral isocyanides with bulky side groups (e.g., *t*-butyl isocyanide) could undergo asymmetric polymerizations to afford optically active one-handed polyisocyanides in the presence of a chiral amine additive³¹ or a chiral initiator.³² Isocyanides studied here had less bulky side groups and thus the reactive center in the growing polymer chains was lacking chiral discrimination, resulting in the same propagation rates for both *P* and *M* helices.

Figure 4.7. IR spectra of Monomer 4.1 (top) and Its Homopolymer (bottom).

Figure 4.8. UV/vis Spectra of Monomer 4.1 (solid line) and
Its Homopolymer (dashed line) in CHCl_3 at 22 °C.

4-3. Optically Active Azo-Containing Polyisocyanides

Optically active polyisocyanides, with an excess of a one-handed helical conformation, can be obtained by a direct polymerization of a chiral isocyanide¹³ or a copolymerization of a slow polymerizing chiral isocyanide and a fast polymerizing achiral isocyanide.³⁴ The latter approach can produce polyisocyanides with very high optical rotation and high degree of achiral monomer in composition. It is this last approach which is preferred when obtaining optically active azo-containing helical polyisocyanides.

Therefore, a chiral isocyanide, methyl (*S*)-2-isocyanoisovalerate ($[\alpha]_D^{22} = +5.5^\circ$ in CHCl_3) (Figure 4.2), was chosen. When it copolymerized with other fast polymerizing achiral isocyanides, polymers with high optical rotations were always obtained.³⁴ Thus, copolymerizations of this chiral isocyanide with a series of azo-containing achiral isocyanides (4.1-4.7) (Figure 4.2) were carried out according to known procedures.³⁴ The results are summarized in Table 4.1. In all cases, polymers had a majority of azo monomer component, while oligomers consisted of a majority of the chiral monomer component. This composition difference was due to the different polymerizability between the azo monomers and the chiral isocyanide.³⁴ Copolymers derived from monomers 4.1, 4.3, 4.4, 4.5 and 4.6 were optically active, while those derived from monomers 4.2 and 4.7 were optically inactive. The very small optical rotation ($[\alpha]_D^{22} = -16^\circ$) of polymer 4.11 derived from the isocyanide 4.2 was simply due to the residual side groups of the chiral monomer. Because CD experiment revealed that this polymer did not have any Cotton effect related to the imino backbone interaction. A possible reason for the latter case is that the monomer 4.2 having a methyl group ortho to the isocyano group was not a fast

polymerizing monomer. Kinetic studies on homopolymerizations of monomers 4.1 and 4.2 revealed that at an early stage (ca. ≤ 60 min), monomer 4.1 polymerized much faster than monomer 4.2 (Figure 4.9, see the experimental section for the measurement). The rate of polymerization of an achiral monomer is quite important, since a faster polymerizing monomer will favor this type of atropogenic polymerization.³⁴

Figure 4.9. Dependence of the Propagation Rate on Polymerization Time
for Monomers 4.1 and 4.2.

For optically active polymers, there exist some discrepancies for optical activities based on the same or nearly the same monomer feed and ratio of monomers to catalyst. As

can be seen in Table 4.1, polymers 4.9 and 4.10, prepared in almost the same conditions, have quite different specific rotations as well as polymer compositions and molecular weights. Similar results have also been obtained with other optically active polymers (4.13 and 4.14) derived from monomers 4.4. This may be mainly due to the heterogeneous polymerization as the polymer precipitated out from reaction medium. Nevertheless, chiralities of these polymers were further confirmed from CD experiments.

Figure 4.10 shows the electronic and CD spectra of polymer 4.8. The UV spectrum shows a maximum at 340 nm which extends to the visible region. This is due to the $n-\pi^*$ transition of the $N=C$ groups in the polymer backbone and the $\pi-\pi^*$ transition of the azobenzene chromophore in the side chain. According to reference interpretation, the $n-\pi^*$ transition is responsible for the CD spectrum in the region of 250-500 nm.³⁴ However, the peak at 340 nm is almost at the zero crossing point of the CD spectrum. Since the azobenzene chromophore is directly linked to the $N=C$ backbone, and the UV absorption is actually due to the overlapping of the $N=C$ double bond and the azobenzene chromophore, it thus could be assumed that the azobenzene chromophore interacted electronically in this helical chiral environment to a certain degree. According to this result the interplay of the helical polymer main-chain and the azo chromophore side-chain as well as the chiral side group was rather complex. The $N=C$ chromophores in the helical main-chain were the major source of the chiral information, so they determine the preference for *P* or *M* helix of the main-chain.

For optically active helical polyisocyanides, CD calculations suggest that in the case of a *P* helix the couplet is Z-shaped, and in the case of an *M* helix it is S-shaped.^{5,16}

Thus in its CD spectrum, polymer 4.8 clearly shows a Z-shaped couplet, indicative of a *P* helix. CD spectra also confirmed that negative optical rotations of the other optically active polymers (Table 4.1) were ascribed to right-handed helical structures of their main-chains.

All these optically active azo-containing polyisocyanides had quite stable chiral helical conformations. No significant specific rotational changes were observed when they were refluxed in chloroform for a few hours. Polymer 4.16 (Table 4.1) was cast into a film on a glass substrate. On baking, the optical rotation did not change too much at temperatures below 200 °C, but decreased at temperatures over 200 °C, due to a thermodecomposition (Figure 4.11).

Figure 4.10. UV/vis (top) and CD (bottom) Spectra of Polymer 4.8 in CHCl_3 at 22 °C.

Table 4.1. Screw-Sense Selective Polymerization of Methyl (*S*)-2-Isocyanoisovalerate with Achiral Isocyanide in the Presence of NiCl₂.

polymer	monomer feed (R*NC:RNC)	yield ^a (%)	polymer composition ^b (R*NC:RNC)	Mn ^c (x10 ⁻³)	[α] _D ²² ^d
4.8 ^e	1.91:1	90	1:1.89	10.3	-192°
4.9 ^e	2.93:1	94	1:3.72	9.0	-274°
4.10 ^e	3.08:1	85	1:3.34	5.8	-667°
4.11 ^f	2.84:1	90	1:6.94	4.6	-16°
4.12 ^g	3.98:1	82	1:5.00	2.7	-119°
4.13 ^h	3.00:1	95	1:4.56	4.9	-145°
4.14 ^h	3.00:1	85	1:3.55	8.6	-345°
4.15 ⁱ	3.19:1	78	1:5.67	4.3	-152°
4.16 ⁱ	3.00:1	60	1:3.29	15.1	-189°
4.17 ^j	3.00:1	N/D ^l	N/D	—	-101°
4.18 ^k	3.00:1	N/D	N/D	—	0

a: based on achiral monomer. b: estimated from ¹H NMR calculation. c: molecular weight was determined from GPC analysis using CHCl₃ as eluent and polystyrene standards. d: in CHCl₃ at 22 °C. e: achiral monomer 4.1. f: achiral monomer 4.2. g: achiral monomer 4.3. h: achiral monomer 4.4. i: achiral monomer 4.5. j: achiral monomer 4.6. k: achiral monomer 4.7. l: not determined.

Figure 4.11. Optical Rotation-Temperature Relationship for Polymer 4.16
(film thickness: 0.040 mm, baking: 5 min).

4-4. Photoirradiation on Azo-Containing Polyisocyanides

In the previous chapter, despite the fact that the azobenzene chromophore in the side-chain was not in the helical environment of an optically active polymethacrylate, the configurational change of the azo chromophore triggered by light (300nm) could still induce the conformational change of the main-chain in solution. A series of optically active azo-containing polyisocyanides were prepared by atropogenic polymerization. The azo chromophore was directly attached to the helical backbone in these polymers. CD study revealed that the azo chromophore was in the chiral helical environment. It was the aim of this investigation to test if these polyisocyanides could have the similar or even more pronounced chiroptical change upon photoirradiation both in solution and in the solid state.

Photoisomerization of the azo-containing polyisocyanides was first carried out in solution (dichloromethane) using UV irradiation centered at 300 nm. Azobenzene in polymer 4.9 (Table 4.1) could undergo trans to cis photoisomerization upon irradiation. But the rate was quite slow and the prolonged irradiation (≥ 3 h) resulted in the polymer chain scission, as evidenced by GPC analysis in which a low molecular weight fraction was found and by UV measurement in which a UV curve (after 3 h irradiation) did not pass through an isosbestic point at 291 nm. However, the chiroptical change of the polymer could still be monitored by CD measurement. Figure 4.12 shows UV/vis and CD changes during the irradiation at different times. On increasing the irradiation time, the peak intensity at 340 nm decreases, corresponding to the progress of the trans to cis isomerization in azobenzene chromophores. CD spectra allow detection of changes in

equilibrium between *P* and *M* helices or random coil caused by the photochemical isomerization. Figure 4.12 presents an example, for which the ellipticity and thus the preference for a right-handed conformation, decreased due to the trans to cis isomerization (2h irradiation at 300 nm without any polymer chain scission). The maxima of the bands associated with the chiral helical conformation (negative band centered at 375 nm and positive band centered at 315 nm) remain unchanged during isomerization for the Cotton effects. An explanation of this result should be based on the interaction of the azobenzene chromophore in the side-chain with the chiral helical polymer main-chain. As a helical polyisocyanide has a 4₁ tight helical turn. The polyisocyanide studied here has a majority of azo-containing monomer component and the azo chromophore is directly linked to the helical chain. Since bond conformations are often neighbour dependent along the polymer chain, small free energy differences accumulated in the individual side chain upon trans to cis isomerization could be a driving force to perturb the regularity of the helical skeletal chain, thus decreasing the preference of its *P* helix (Figure 4.13).

As mentioned above, this polymer is tight and has a high fraction of azo chromophores, therefore, this may be the basis on which to explain a slow photoisomerization. In a comparison, a relatively fast photoisomerization of an oligomer with the low fraction of the azo chromophore, which was isolated from the copolymerization of methyl (*S*)-2-isocyanoisovalerate and monomer 4.1 (see experimental section), was observed. The photostationary stage was reached after 20 min irradiation.

In order to study the feasibility of the reversible property which may induce reversible chiroptical change, polymer 4.9 was refluxed in CH₂Cl₂ for 24 h after a 2 h UV

irradiation (300 nm). No cis to trans isomerization was observed by UV/vis measurement. This result indicated that the side-chain cis azo configuration was stable under the current condition.

In order to investigate chiroptical changes of other optically active polyisocyanides (polymers 4.12, 4.13, 4.15 and 4.17) with different azo chromophores, the similar photoirradiation at 300 nm was performed in CH₂Cl₂. The UV/vis absorbance did not change after long irradiation (> 2 h) at 15 °C or at -15 °C, suggesting there was no detectable photoisomerization from trans to cis under the current conditions. This may be due to the fact that not only are these polymer backbones too rigid and side-chains too crowded, but also these azo chromophores have electro-withdrawing groups (i.e. ester or sulfate) which may inhibit the trans to cis isomerization.

Photoirradiation was also attempted in the solid state. Polymer 4.16 could be cast into a film (thickness 0.010 mm, α 0.40°), therefore, this film was irradiated by UV at 300 nm (ca. 30 °C). No change in both UV absorption and optical rotation was observed after irradiation for several hours, indicative of a possible non-photoisomerization from trans to cis of the azo chromophore in the side-chain. This was mainly due to the high energy barrier from the trans to cis isomerization and the limited free volume in the solid state, resulting in no conformational change in the helical backbone.

Figure 4.12. Change of UV/vis (left) and CD (right) Spectra of Polymer 4.9 at Different Irradiation Times in CH_2Cl_2 at 15 °C.

(CD spectra were recorded before and after 2 h irradiation at 300 nm).

Figure 4.13. Chiroptical Change of Polymer 4.9
upon UV Irradiation (300 nm) in CH_2Cl_2 at 15 °C.

4-5. Experimental Section

Materials and Measurements

Methylene chloride and triethyl amine were dried by distillation over CaH_2 under N_2 . L-Valine, thionyl chloride, formic acid (90%), phosphorus oxychloride, 4-aminoazobenzene, 2',3-dimethyl 4-aminoazobenzene, metanilic acid were obtained from Aldrich Co. and were used without further purification.

^1H and ^{13}C NMR spectra were recorded on a Germini-200 spectrometer at 200 MHz and/or a Bruker AMX-400 spectrometer at 400 MHz in CDCl_3 or $\text{DMSO}-d_6$ using tetramethylsilane as an internal reference at 22 °C. For all other measurements refer to Experimental Section 2.4, Chapter 2.

Monomer Syntheses

Methyl L-Isovalerate.⁶⁹

To a 50 mL three-necked flask equipped with a stirring bar, a condenser and an addition funnel was added thionyl chloride (7.9 mL, 0.1 mol) dropwise to absolute methanol (30 mL, 0.8 mol) at -5 °C under N_2 . Then L-valine (5.8 g, 0.05 mol) was added and the reaction was run for 12 h at -5 °C, followed by 12 h at 10 °C. The mixture was warmed to 40 °C for 2 h. Methanol was removed under reduced pressure at 80 °C and the white solid was dissolved into methylene chloride at 0 °C. To this organic solution were added two drops of phenolphthalein. A concentrated aq. NH_3 (ca. 5 mL) solution was then

added dropwise until the aqueous solution became red. The organic layer was separated and the aqueous layer was extracted with methylene chloride (3 x 30 mL). The combined organic phase was dried over MgSO_4 and the solvent was removed under reduced pressure at 22 °C. The residue was further distilled at high vacuum and the colorless liquid product was collected at 24.0 °C/1 mmHg. Yield was 3.9 g (60%); $[\alpha]^{22}_{\text{D}} = +9.7^\circ$ (C = 0.33 mg/mL, CH_3OH); ^1H NMR (200 MHz, CDCl_3) δ 0.8 [2 d, 6H, $\text{C}(\text{CH}_3)_2$], 1.8-1.9 (m, 1H, CH), 3.17(d, 1H, CH on the chiral carbon), 3.62 (s, 3H, OCH_3).

Methyl *N*-Formyl-L-Isovalerate.⁷⁰

Methyl L-isovalerate (3.5 g, 0.03 mol) was mixed with warm formic acid (40 °C, 90%, 2.0 mL, 0.05 mol). To this solution was added acetic anhydride (4.0 mL, 0.04 mol) dropwise over 20 min. After the solution was stirred for an additional 1 h at 60 °C, the formic acid and acetic acid were removed under vacuum. The crude product was recrystallized from CCl_4 . Yield was 3.4 g (80%); $[\alpha]^{22}_{\text{D}} = -28^\circ$ (C = 12 mg/mL, methanol), (lit.³⁴ $[\alpha]^{20}_{\text{D}} = -27.2^\circ$, C = 5.0 mg/mL, methanol); m.p. 61.0-62.0 °C (lit.³⁴ 62.1 °C); IR (KBr) 1664 (NHCHO), 1739 (C=O) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 1.0 [2 d, 6H, $\text{CH}(\text{CH}_3)_2$], 2.3 [m, 1H, $\text{CH}(\text{CH}_3)_2$], 3.85 (s, 3H, OCH_3), 4.7 (2 d, 1 H, CH), 6.16 (s, br, 1H, NH), 8.29 (s, 1H, CHO).

Methyl (*S*)-2-Isocyanoisovalerate.⁷¹

Into a 50-mL three-necked flask were equipped with a stirring bar, an addition funnel and a condenser, at $-40\text{ }^{\circ}\text{C}$, were added methyl *N*-formyl-L-isovalerate (1.0 g, 6.3 mmol), dry methylene chloride (8 mL) and dry triethylamine (5 mL). The phosphorus oxychloride (0.7 mL, 7.5 mmol) in dry methylene chloride (2 mL) was added dropwise to this solution in the course of 10 min. After the mixture was stirred for an additional 1 h, the reaction was stopped by pouring the mixture into ice water (20 mL). The organic phase was separated and the aqueous phase was extracted with methylene chloride (3 x 30 mL). The combined organic phase was washed with aqueous NaHCO_3 (10 mL, 10%) solution, distilled water (3 x 30 mL), and dried over Na_2SO_4 . Methylene chloride was removed under reduced pressure at $22\text{ }^{\circ}\text{C}$ and the residue was further distilled under vacuum to collect the liquid product at $33.0\text{--}34.0\text{ }^{\circ}\text{C}/1\text{ mmHg}$. Yield was 0.5 g (60%); $[\alpha]_{\text{D}}^{22} = +5.5^{\circ}$ ($\text{C} = 25\text{ mg/mL}$, CHCl_3), (lit.³⁴ $[\alpha]_{\text{D}}^{20} = +5.5^{\circ}$, $\text{C} = 3.4\text{ mg/mL}$, CHCl_3); IR (CHCl_3) 2153 (NC) , 1758 (C=O)cm^{-1} ; $^1\text{H NMR}$ (200 MHz, CDCl_3) δ 1.0 [2 d, 6H, $\text{CH (CH}_3)_2$], 2.3 (m, 1H, CH), 3.8 (s, 3H, OCH_3), 4.3 (d, 1H, CH).

4-Formyl aminoazobenzene.⁶⁶

To a flask equipped with a condenser attached with a water separator were added 4-aminoazobenzene (9.0 g, 0.05 mol), toluene (30 mL) and formic acid 90% (5.0 g, 0.1 mol). The mixtures were refluxed at $110\text{ }^{\circ}\text{C}$. After water stopping collecting (2 h), toluene

and formic acid were removed under reduced pressure at 80 °C. The crude product was recrystallized from toluene three times and dried under vacuum at 50 °C overnight. Yield was 8.1 g (80%); m.p. 161.0–162.0 °C; IR (KBr) 1736 (C=O), 1680 (NHCHO) cm^{-1} ; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 8.45 (d, 1H, CHO), 7.35 (s, 1H, NH); ^{13}C NMR (50.3 MHz, $\text{DMSO}-d_6$) δ 165.5 (NHCHO), 157.3, 153.1, 146.6, 134.7, 129.6, 129.2, 127.2, 124.8; MS (EI, m/z , %) 225 (M^+ , 49.6).

4-Isocyanoazobenzene (4.1).⁶⁶

To a 50-mL flask were added 4-formyl aminoazobenzene (5.0 g, 0.02 mol), 40 mL of dry methylene chloride and 20 mL of dry triethylamine at 0 °C. Phosphorus oxychloride (4 mL, 0.04 mol) in 2 mL of dry methylene chloride was added dropwise in course of 10 min and the reaction was continued under N_2 for 1 h. The reaction was quenched by pouring the mixture into ice water (100 mL). The organic layer was separated and washed with aqueous NaHCO_3 (2 x 50 mL, 10%) solution and distilled water (3 x 120 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was washed with hexane (2 x 50 mL) and dried under vacuum at 40 °C overnight. Yield for the yellow solid product was 3.2 g (80%); m.p. 104.0–106.0 °C (lit.⁶⁵ 102.0–104.0 °C); IR (KBr) 2119 (NC) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.5–8.1 (m, aromatic protons); ^{13}C NMR (50.3 MHz, CDCl_3) δ 165.87 (NC), 152.7, 151.7, 131.8, 129.2, 127.3, 123.8, 123.1; MS (EI, m/z , %) 207 (M^+ , 26); UV/Vis (CHCl_3) 240, 324, 445 (br, weak) nm.

2',3-Dimethyl 4-Formyl aminoazobenzene.

This compound was prepared in the same manner as described above for the preparation of 4-formyl aminoazobenzene. The brown product was obtained in 62% yield; m.p. 135.0-136.0 °C; IR (KBr) 1733 (C=O), 1645 (NHCHO) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.0-8.8 (m, 9H, aromatic protons and NHCHO), 2.73 (s, 3H, CH_3), 2.40 (s, 3H, CH_3); ^{13}C NMR (50.3 MHz, CDCl_3) δ 162.58 (NHCHO), 158.9, 131.3, 131.2, 131.0, 130.9, 130.8, 126.4, 125.7, 124.7, 122.3, 119.5, 115.5, 17.9, 17.5; MS (EI, m/z , %) 253 (M^+ , 40).

2',3-Dimethyl 4-Isocyanoazobenzene (4.2).

This isocyanide was prepared in the same manner as described above for the preparation of 4-isocyanoazobenzene 4.1. The brown product was obtained in 91% yield; m.p. 114.0-117.0 °C (lit.⁶⁵ 115.0-118.0 °C); IR (KBr) 2121 (NC) cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.2- 8.0 (m, 7 H, aromatic protons), 2.74 (s, 3H, CH_3), 2.54 (s, 3H, CH_3); ^{13}C NMR (50.3 MHz, CDCl_3) δ 167.53 (NC), 162.6, 161.3, 152.5, 139.0, 135.9, 131.7, 131.4, 127.3, 126.5, 125.0, 121.1, 115.3, 18.8, 17.5; MS (EI, m/z , %) 235 (M^+ , 26); UV/Vis (CHCl_3) 242, 335, 451 (br, weak) nm.

N-Methylene Aniline Sulphonic Acid.

Sodium bisulfite (4.6 g, 44 mmol) was dissolved in 7 mL of water and the solution was heated to 70 °C. To this solution was added 37% of formaldehyde (3.12 g, 38.5 mmol). After 10 min, aniline (3.0 g, 32.3 mmol) was added and the temperature was kept at 70-80 °C for 1 h. After cooling, the product was filtrated off and washed with a saturated NaCl solution (5 x 50 mL). The white crystals were dried at 70 °C under vacuum. The yield was 6.7 g (99%); ¹H NMR (200 MHz, D₂O) δ 7.32 (t, 2H), 6.95 (m, 3H), 4.80 (s, 2H); ¹³C NMR (50.3 MHz, D₂O) δ 149.2, 132.5, 121.8, 116.7, 64.0.

4'-Amino-1-Phenylazobenzoic Acid.

4-Aminobenzoic acid (1.37 g, 10 mmol) was dissolved in 10 mL of distilled water and was diazotised at 0 °C with 6 mL of concentrated hydrochloric acid, 5 g of ice and 0.69 g of 30% NaNO₂ (10 mmol) solution. After stirring for 30 min, the mixture was made very weakly congo acid (pH = 4) with addition of Na₂CO₃ (ca. 10 g), and then NaHCO₃ (1 g). Immediately afterwards *N*-methylene aniline sulphonic acid (1.87 g, 10 mmol) was charged and the solution was kept at 5-10 °C. After 2 h, 5 g of NaCl salt was added and the solution was stirred for 24 h. After filtration, the solid was refluxed in 30% NaOH (10 mL) solution for 2 h, cooled down and the solution was blown into 5 g of ice, 30 mL of water with 5 g of NaCl salt, then filtrated to afford 2.2 g of a solid. This solid was dissolved in 30 ml of water and made definitely Congo acid with concentrated HCl (ca. 2

mL). The product was filtrated, washed with water (2 x 50 mL) and dried under vacuum at 70 °C. Yield of 4'-amino-1-phenylazobenzoic acid was 1.8 g (75%); IR (KBr) 3394, 1692, 1594 cm^{-1} ; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 8.15 (d, 2H), 7.88 (d, 2H), 7.74 (d, 2H), 6.75 (d, 2H); ^{13}C NMR (50.3 MHz, $\text{DMSO}-d_6$) δ 167.2, 155.4, 153.9, 143.2, 131.0, 130.8, 126.1, 121.9, 113.8.

Methyl 4'-Amino-1-Phenylazobenzoate.

4'-Amino-1-phenylazobenzoic acid (0.5 g, 2.1 mmol) was dissolved in methanol (30 mL). To this solution was added the concentrated H_2SO_4 (3 mL) and the mixture was refluxed for 2 h. After cooling, 50 mL of 10% aqueous Na_2CO_3 solution was added dropwise. The precipitate was filtrated off, washed with distilled water (2 x 50 mL), and dried under vacuum at 70 °C to give 0.5 g (95%) of this ester; m.p. 180.0-182.0 °C; IR (KBr) 3463, 3366, 1703, 1630, 1599 cm^{-1} ; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 8.09 (d, 2H), 7.83 (d, 2H), 6.72 (d, 2H), 6.32 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (50.3 MHz, $\text{DMSO}-d_6$) δ 166.1, 155.6, 154.1, 143.2, 130.6, 129.7, 126.2, 122.0, 113.7, 52.5; MS (EI, m/z , %) 255 (M^+ , 27.4).

Methyl 4'-Formamido-1-Phenylazobenzoate.

This compound was prepared from methyl 4'-amino-1-phenylazobenzoate in the same manner as described for the preparation of 4-formyl aminoazobenzene. The yield was

70%; m.p. 245.0-246.0 °C; IR (KBr) 3451, 1728, 1605, 1440, 1280, 1113 cm^{-1} ; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 8.42 (s, 1H), 7.92 (m, 8H), 7.50 (s, 1H), 3.95 (s, 3H); ^{13}C NMR (50.3 MHz, $\text{DMSO}-d_6$) δ 171.2, 165.9, 160.2, 147.6, 136.2, 130.4, 129.9, 128.2, 125.2, 122.9, 58.1; MS (EI, m/z , %) 283 (M^+ , 39.2).

Methyl 4'-Isocyano-1-Phenylazobenzoate (4.3).

This isocyanide was prepared from methyl 4'-formyl-1-phenylazobenzoate in the same method as described for the preparation of 4-isocyanoazobenzene 4.1. The yield was 30%; m.p. 141.0-143.0 °C; IR (KBr) 3448, 2123, 1723, 1281, 1107 cm^{-1} ; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 8.20 (d, 2H), 8.04 (q, 4H), 7.82 (d, 2H), 3.95 (s, 3H); ^{13}C NMR (50.3 MHz, $\text{DMSO}-d_6$) δ 166.6, 165.7, 154.4, 151.7, 132.4, 130.9, 128.2, 124.4, 123.3, 122.7, 52.8; MS (EI, m/z , %) 265 (M^+ , 39.3).

Ethyl 4'-Amino-1-Phenylazobenzoate.

This ester was prepared from a reaction of ethanol with 4'-amino-1-phenylazobenzoic acid in the same method as for the preparation of methyl 4'-amino-1-phenylazobenzoate. Yield was 90%; m.p. 151.0-153.0 °C; IR (KBr) 3352, 3238, 1701, 1643, 1599, 1280, 1137 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 8.18 (d, 2H), 7.90 (m, 4H), 6.73 (d, 2H), 4.48 (q, 2H), 4.20 (s, br, 2H), 1.52 (t, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 166.3, 155.6, 150.3, 145.5, 130.9, 130.5, 125.6, 122.1, 114.5, 61.1, 14.3; MS (EI, m/z , %) 269 (M^+ , 25.2).

Ethyl 4'-Formamido-1-Phenylazobenzoate.

This compound was prepared from ethyl 4'-amino-1-phenylazobenzoate in the same manner as described above for the preparation of 4-formyl aminoazobenzene. The yield was 74%; m.p. 195.0-196.0 °C; IR (KBr) 3445, 1745, 1712, 1604, 1277 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 8.45 (s, 1H), 8.19 (d, 2H), 7.94 (q, 4H), 7.73 (d, 2H), 7.40 (s, br, 1H), 4.40 (q, 2H), 1.43 (t, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 161.8, 159.0, 155.1, 137.2, 130.6, 125.1, 124.4, 122.5, 120.0, 118.2, 61.3, 14.3; MS (EI, m/z , %) 297 (M^+ , 35.7).

Ethyl 4'-Isocyano-1-Phenylazobenzoate (4.4).

This isocyanide was prepared from ethyl 4'-formyl-1-phenylazobenzoate in the same manner as described for the preparation of 4-isocyanoazobenzene 4.1. The yield of isocyanide was 85%; m.p. 134.0-135.0 °C; IR (KBr) 3350, 2129 (NC), 1717, 1268, 1100 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 8.20 (d, 2H), 7.97 (t, 4H), 7.55 (d, 2H), 4.42 (q, 2H), 1.45 (t, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 166.6, 165.8, 154.6, 152.0, 139.2, 129.9, 130.6, 127.4, 124.2, 122.9, 61.4, 14.3; MS (EI, m/z , %) 279 (M^+ , 47.6).

n-Butyl 4'-Amino-1-Phenylazobenzoate.

This ester was prepared from a reaction of 1-BuOH and 4'-amino-1-phenylazobenzoic acid in the same method as for the preparation of methyl 4'-amino-1-phenylazobenzoate. After removal of 1-BuOH at 70 °C under reduced pressure, the yield of ester was 50%; m.p. 77.0-78.0 °C; IR (KBr) 3437, 1702, 1597, 1281, 1128 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 8.18 (d, 2H), 7.85 (q, 4H), 6.75 (d, 2H), 4.34 (t, 2H), 3.5 (s, br, 2H), 1.75 (m, 2H), 1.48 (m, 2H), 1.00 (t, 3H); ¹³C NMR (50.3 MHz, CDCl₃) δ 166.6, 156.0, 150.4, 131.1, 130.5, 125.7, 122.0, 121.9, 114.6, 65.0, 30.7, 19.3, 13.8; MS (EI, *m/z*, %) 297 (M⁺, 20.7).

n-Butyl 4'-Formamido-1-Phenylazobenzoate.

This compound was prepared from *n*-butyl 4'-amino-1-phenylazobenzoate in the same manner as described for the preparation of 4-formyl aminoazobenzene. Yield was 95%; m.p. 165.0-166.0 °C; IR (KBr) 3454, 1709, 1601, 1278, 1106 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 8.44 (s, 1H), 8.15 (m, 2H), 7.92 (m, 3H), 7.72 (d, 2H), 7.24 (d, 2H), 4.35 (t, 2H), 1.77 (m, 2H), 1.48 (m, 2H), 1.00 (t, 3H); ¹³C NMR (50.3 MHz, CDCl₃) δ 166.6, 162.3, 159.3, 155.5, 130.6, 125.0, 124.4, 122.6, 120.0, 118.2, 65.2, 30.8, 19.3, 13.8; MS (EI, *m/z*, %) 325 (M⁺, 31.5).

n-Butyl 4'-Isocyano-1-Phenylazobenzoate (4.5).

This isocyanide was prepared *n*-butyl 4'-formyl-1-phenylazobenzoate in the same manner as described for the preparation of 4-isocyanoazobenzene 4.1. The yield was 81%; m.p.

117.0-119.0 °C; IR (KBr) 2118 (NC), 1710 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 8.20 (d, 2H), 7.98 (t, 4H), 7.55 (d, 2H), 4.38 (t, 2H), 1.80 (m, 2H), 1.51 (m, 2H), 1.02 (t, 3H); ^{13}C NMR (50.3 MHz, CDCl_3) δ 166.4, 166.0, 154.6, 152.0, 132.9, 130.6, 127.4, 124.2, 122.9, 122.5, 65.3, 30.8, 19.3, 13.8; MS (EI, m/z , %) 307 (M^+ , 37).

3-Sodium 4'-Amino-1-Phenylazobenzenesulfate.

This amino azobenzene was prepared from a reaction of metanilic acid and *N*-methylen aniline sulphonic acid in the same manner as described above for the preparation of 4-amino-1-phenylazobenzoic acid. The yield of this salt was 70%; IR (KBr) 3407, 1597, 1538, 1396, 1146 cm^{-1} ; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 8.02 (s, 1H), 7.75 (m, 4H), 7.53 (t, 1H), 6.72 (d, 2H), 6.22 (s, 2H); ^{13}C NMR (50.3 MHz, $\text{DMSO}-d_6$) δ 153.3, 152.2, 149.4, 143.0, 128.9, 126.6, 125.5, 123.8, 117.4, 113.7; This salt was acidified with hydrochloric acid to afford 3-sulphonic acid 4'-amino-1-phenylazobenzene. MS (EI, m/z , %) 277 (M^+ , 8.3).

3-Tetra-*n*-butylammonium 4'-Amino-1-Phenylazobenzenesulfate.

3-Sodium 4'-amino-1-phenylazobenzenesulfate (1.1 g, 3.8 mmol) was dissolved in 10 mL of water and tetra-*n*-butylammonium bromide (1.2 g, 3.8 mmol) was dissolved in 10 mL of water. Then, these two solutions were mixed each other and the resulting cloudy

solution was stirred at 22 °C for 10 min. The product was extracted with dichloromethane (3 x 90 mL) and the combined organic phase was washed with distilled water (2 x 50 mL). The organic solution was dried over anhydrous MgSO_4 . After removal of methylene chloride, the yield of product was 1.8 g (91%); IR (KBr) 3425, 2957, 1601, 1474, 1139, 1031 cm^{-1} ; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 8.15 (s, 1H), 7.68 (q, 4H), 7.50 (t, 1H), 6.80 (d, 2H), 6.34 (s, 2H), 3.20 (br, 8H), 1.65 (br, 8H), 1.30 (m, 8H), 0.92 (t, 12H); ^{13}C NMR (50.3 MHz, $\text{DMSO}-d_6$) δ 153.5, 152.2, 149.6, 142.9, 128.9, 126.3, 125.3, 123.5, 117.7, 113.7, 57.9, 23.4, 19.4, 13.7.

3-Tetra-*n*-butylammonium 4'-Isocyano-1-Phenylazobenzenesulfate(4.6).

3-Tetra-*n*-butylammonium 4'-amino-1-phenylazobenzenesulfate (1.5 g, 2.9 mmol) was dissolved into 20 ml of CH_2Cl_2 . To this solution were added CHCl_3 (3.0 mL, 37.5 mmol) and benzyltriethylammonium chloride (0.1 g, 0.4 mmol). 50% Aqueous NaOH solution (3.0 g, 75 mmol) was added in one portion. After an induction period of about ten minutes, the solution became warm and the mixture was stirred for 24 h. The reaction mixture was diluted with water (20 mL) and the isocyanide was extracted with methylene chloride (2 x 20 mL). The combined organic phase was washed with water (2 x 20 mL), and dried over MgSO_4 . Yield after vaporation of solvent was 0.9 g (60%); IR (KBr) 3450, 2950, 2875, 2122 (NC), 1600, 1476, 1211; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 7.6-8.3 (m, 8H), 3.15 (br, 8H), 1.65 (br, 8H), 1.33 (br, 8H), 0.97 (t, 12H); ^{13}C NMR (50.3

MHz, DMSO- d_6) δ 166.3 (NC), 151.9, 151.6, 150.1, 129.5, 128.2, 125.5, 124.1, 118.2, 117.5, 113.7, 57.8, 55.2, 23.3, 19.8, 13.8.

3-Tetra-*n*-butylammonium 2'-Methoxy-4'-Amino-1-phenylazobenzenesulfate.

This compound was prepared in the same method as described above for the preparation of 3-tetra-*n*-butylammonium 4'-amino-1-phenylazobenzenesulfate. Yield was 85%; ^1H NMR (200 MHz, DMSO- d_6) δ 7.94 (s, 1H), 7.4-7.8 (m, 5H), 6.37 (d, 1H), 6.26 (br, 2H), 3.89 (s, 3H), 3.15 (br, 8H), 1.56 (br, 8H), 1.31 (m, 8H), 0.92 (t, 12H); ^{13}C NMR (50.3 MHz, DMSO- d_6) δ 159.9, 155.3, 152.8, 149.6, 132.8, 128.7, 126.0, 124.0, 117.9, 117.1, 106.9, 96.4, 57.8, 55.6, 23.3, 19.5, 13.8.

3-Tetra-*n*-butylammonium 2'-Methoxy-4'-Isocyano-1-phenylazobenzenesulfate(4.8).

This isocyanide was prepared in the same method as described above for the preparation of 3-tetra-*n*-butylammonium 4'-isocyano-1-phenylazobenzenesulfate. Yield was 90 %; IR (KBr) 3444, 2954, 2123 (NC), 1601, 1471, 1210 cm^{-1} ; ^1H NMR (200 MHz, DMSO- d_6) δ 8.34 (s, 1 H), 8.06 (t, 1H), 7.92 (dt, 1H), 7.83 (dt, 1H), 7.66 (s, 1H), 7.60 (m, 1H), 7.28 (dd, 1H), 4.05 (s, 3H), 3.25 (br, 8H), 1.58 (br, 8H), 1.30 (m, 8H), 0.95 (t, 12H); ^{13}C

NMR (50.3 MHz, DMSO- d_6) δ 165.9 (NC), 157.2, 152.1, 149.9, 141.4, 129.3, 129.1, 125.7, 119.1, 117.8, 117.6, 112.2, 79.5, 57.8, 23.3, 19.5, 13.7.

Polymerization

1. Homopolymerization Using NiCl₂

Poly [methyl (*S*)-2-isocyanoisovalerate]. Methyl (*S*)-2-isocyanoisovalerate (1.0 g, 7.1 mmol) was polymerized neat with anhydrous NiCl₂ (93 mg, 10 mol%) at 22 °C for five days. The polymer was precipitated from a mixture of methanol (15 mL) and water (5 mL) and filtrated. The yellow polymer was dried at 40 °C under vacuum for 24 h. Yield was 0.15 g (15%); $[\alpha]_D^{22} = -110^\circ$ (C = 1 mg/mL, CHCl₃); IR (KBr) 1743, 1646 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 3.5 (br, -OCH₃), 1.0 (br, *i*-C₃H₇ and -CH); UV/Vis (CHCl₃) 250-500 (br) nm; T_d (5% weight loss in N₂) = 190 °C; Mn 1850, PDI 1.7.

General Procedures for the Polymerizations of Isocyanides 4.1-4.5.

Polyisocyanide from isocyanide 4.1. Isocyanide 4.1 (1.0 g, 5.0 mmol) was polymerized in a mixture of methanol (3 mL) and chloroform (3 mL) with anhydrous NiCl₂ (13.1 mg, 2 mol%) at 22 °C for five days. The polymer was precipitated in a large amount of methanol (50 mL), collected by filtration and dried under vacuum. Yield was 0.9 g (90%); IR (KBr) 3444, 1636, 1591 cm⁻¹; UV/Vis (CHCl₃) $\lambda_{\max}$ 335 nm; ¹H NMR (CDCl₃, 200 MHz) δ 7.5 (br, aromatic protons); T_d (5 % weight loss in N₂) 358 °C.

Polyisocyanide from isocyanide 4.2: 90%; IR (KBr) 2890, 1592 cm⁻¹; T_d (5% weight loss in N₂) = 357 °C.

Polyisocyanide from isocyanide **4.3**: 90%; IR(KBr) 3446, 2949, 1720, 1590, 1276 cm^{-1} ; T_d (5% weight loss in N_2) = 171 $^{\circ}\text{C}$; M_n 2,700, PDI 4.3.

Polyisocyanide from isocyanide **4.4**: 90%; IR(KBr) 3426, 2923, 1718, 1590, 1273 cm^{-1} ; T_d (5% weight loss in N_2) = 289 $^{\circ}\text{C}$; M_n 6,700, PDI 2.9.

Polyisocyanide from isocyanide **4.5**: 90%; IR(KBr) 3431, 2953, 2874, 1716, 1593, 1275 cm^{-1} ; T_d (5% weight loss in N_2) = 280 $^{\circ}\text{C}$; M_n 12,000, PDI 2.2.

Polyisocyanide from isocyanide **4.6**. The polymerization of isocyanide **4.6** (1.0 g, 1.9 mmol) was carried out in methanol (5 mL) at 22 $^{\circ}\text{C}$ with anhydrous NiCl_2 (5 mg, 2 mol%) for five days. Polymer was precipitated from a large amount of diethyl ether (100 mL) after solution was concentrated. Yield was 0.95 g (95%); IR (KBr) 3437, 2956, 2873, 1642, 1598, 1476, 1210, 1032 cm^{-1} ; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 7.4-8.4 (br, aromatic protons), 3.05 [br, $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$], 1.40 [br, $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$], 1.20 [br, $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$], 0.74 [br, $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$]; UV/Vis (CHCl_3) λ_{max} 350 nm; M_n could not be determined from GPC because of strong adsorption on column; T_d (5% weight loss in N_2) = 234 $^{\circ}\text{C}$.

Polyisocyanide from isocyanide **4.7**. Polymerization of isocyanide **4.7** was carried out in same manner as described above for polymerization of isocyanide **4.6**. Yield was 95%; IR

(KBr) 3443, 2948, 1592, 1469, 1208, 1030 cm^{-1} ; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 7.7-8.3 (br, aromatic protons), 3.27 [br, OCH_3 and $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$], 1.22 [br, $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$], 0.82 [br, $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$]; ^{13}C NMR (CDCl_3) δ 153.0 (br), 149.2 (br), 129.1 (br), 58.3 [OCH_3 and $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$], 23.8 [$\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$], 19.6 [$\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$], 13.6 [$\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$]; UV/Vis (CHCl_3) λ_{max} 377 nm; M_n could not be determined from GPC because of strong adsorption onto column; T_d (5% weight loss in N_2) = 221 $^\circ\text{C}$.

2. Homopolymerization Using NiCl_2 and (-)-Sparteine

Polyisocyanide from isocyanide 4.1. Isocyanide 4.1 (1.0 g, 5.0 mmol) was dissolved in a mixture of methanol (3 mL) and chloroform (3 mL). To this solution was added (-)-sparteine (1 mL). After stirring for 5 min, NiCl_2 (13.1 mg, 2 mol%) was introduced and polymerization was carried at 22 $^\circ\text{C}$ for five days. The polymer was precipitated in a large amount of methanol (50 mL), collected by filtration and dried under vacuum. Yield was 0.95 g (95%); $[\alpha]_D^{22} = 0^\circ$ in CHCl_3 ; IR (KBr) 3450, 1591, 1484 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.4-7.9 (br, aromatic protons); UV/Vis (CHCl_3) λ_{max} 335; T_d (5% weight loss in N_2) = 336 $^\circ\text{C}$.

Polyisocyanide from isocyanide 4.2. Polymerization of isocyanide 4.2 was carried in the same manner as for isocyanide 4.1. Yield was 90%; $[\alpha]_D^{22} = 0^\circ$ in CHCl_3 ; IR (KBr) 3450, 2900, 2850, 1581 cm^{-1} .

3. Atropogenic Polymerization

A typical atropogenic polymerization is as follows:

Polymer 4.9. Methyl (*S*)-2-isocyanoisovalerate (360 mg, 2.55 mmol) was mixed with isocyanide 4.1 (180 mg, 0.87 mmol) in 4 mL of CHCl_3 and 2 mL of CH_3OH and polymerized with anhydrous NiCl_2 (4 mg, 0.9 mol%) at 22 °C. After five days, methanol (20 mL) was added to the reaction mixtures. The polymer was collected by filtration and purified by redissolving into CHCl_3 (2 mL) and precipitated in methanol (15 mL). The oligomer was recovered from filtrate and purified by using methanol (3 x 30 mL) to wash away the unreacted chiral monomer. Yield for the polymer 4.9 was 200 mg (94% based on isocyanide 4.1). IR(KBr) for the polymer 4.9: 3422, 1742 (C=O), 1640, 1593 (N=C) cm^{-1} , for the oligomer: 3375, 2962, 1744 (C=O), 1600 (weak, N=C), 1203 cm^{-1} ; UV/Vis (CHCl_3) for the polymer: λ_{max} 340 nm, for the oligomer: λ_{max} 340 nm; $[\alpha]_{\text{D}}^{22} = -274^\circ$ for the polymer in CHCl_3 , $[\alpha]_{\text{D}}^{22} = -28^\circ$ for the oligomer in CHCl_3 .

Polymers 4.8, 4.10–4.16 were prepared in the similar manner as described above. Polymer 4.17 and 4.18 were obtained in the similar way as for polymer 4.9, excepting for omitting chloroform in the reaction media, because monomers were soluble in methanol. A typical work-up is as follows: after polymerization (five days), polymer was precipitated into a large amount of diethyl ether. After filtration, the polymer was redissolved into a small amount of methanol and precipitated into a large amount of diethyl ether. The polymer obtained was deep brown.

Kinetic Measurement

Isocyanide **4.1** (1.0 g, 5.0 mmol) was polymerized in a mixture of methanol (3 mL) and chloroform (3 mL) with NiCl_2 (13 mg, 2 mol%) at 22 °C. Kinetic data were obtained by periodically (0 min, 1 min, 5 min, 10 min, 20 min, and 60 min) removing an aliquot (5.00 μL) from polymerization solutions, diluting into CHCl_3 (1.00 mL), and then recording the peak intensity of the isocyanide stretch (2119 cm^{-1}) of the unreacted monomer by IR spectroscopy. The kinetic curve was obtained by plotting $\log(A_0/A_t)$ vs. reaction time (t), where A_0 and A_t were the intensities at 2119 cm^{-1} before and after reaction, respectively.

Similarly, kinetic data for the polymerization of monomer **4.2** were obtained. The peak (2121 cm^{-1}) intensity before and after reaction was obtained from IR spectra.

Photoirradiation

A quartz flask equipped with a condenser containing a solution of polymer **4.9** (1.00×10^{-4} g/mL in CH_2Cl_2) was placed in a photochemical radiator. The solution temperature was controlled at 15 °C by an ethanol-circulating cooler system. Photochemical radiation was carried out at 300 nm with ca. 336 W. UV/vis spectra were measured at different irradiation times (0 min, 30 min, 60 min, 90 min, 120 min and 180 min) and CD spectra were recorded before and after 120 min irradiation.

Photoirradiation of polymers **4.12**, **4.13**, **4.15** and **4.17** in methylene chloride was carried in the similar way as described for polymer **4.9**. But irradiation was also carried out at -15 °C.

Polymer 4.16 (5 mg) was cast into a film on a glass substrate from CH_2Cl_2 (5 mL). Thus, a film with a thickness of 0.010 mm and an α of 0.40° was obtained after removal of the solvent under vacuum at 40°C overnight. The film was irradiated in UV at 300 nm for at least 3 h. Optical rotation and UV were then measured.

An oligomer isolated from the copolymerization of methyl (*S*)-2-isocyanoisovalerate and monomer 4.1 was also used for photoirradiation in CH_2Cl_2 under similar conditions as for polymer 4.9. UV/vis spectra were recorded at different irradiation times (0 min, 5 min, 10 min and 20 min). The photostationary stage was reached after the solution was exposed to the light (300 nm) for 20 min.

Chapter 5. [5]Helicene-based Polyisocyanides

5-1. Monomer Syntheses

[5]Helicene and 5,6,9,10-tetrahydro[5]helicene-based isocyanides were prepared from 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride. The synthesis of 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride, a pseudo [5]helicene derivative, has been reported.⁷² This compound can be functionalized by nitration, imidization, aromatization, etc.

In order to introduce an isocyano functionality on the 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride, nitration may be the one way in which the nitro group could be reduced to an amino group and the amino group could be readily converted into isocyano group by formylation and dehydration according to reference.⁶⁵ Therefore, in this study, 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride was first nitrated to produce a mixture of two mono-nitro compounds, 1-nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (5.1) and 3-nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (5.2), respectively. These two compounds, without separation, were imidized with *n*-butylamine to afford a mixture of *N*-(*n*-butyl)-1-nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic imide (5.3) and *N*-(*n*-butyl)-3-nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic imide (5.4). Without separation, these two compounds having nitro groups were then reduced with SnCl₂ or H₂ in the presence of PtO₂ to afford a mixture of two compounds having amino groups, *N*-(*n*-butyl)-1-amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic imide (5.5) and *N*-(*n*-

butyl)-3-amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic imide (5.6), which could be separated through a silica gel column using acetone and hexane as eluents. Compounds having the amino group (5.5 and 5.6) could be easily converted into the corresponding pseudo [5]helicene-based isocyanides (5.9 and 5.10). The synthesis of isocyanide monomer *N*-(*n*-butyl)-3-isocyano-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic imide (5.10) and its corresponding precursors is shown in Figure 5.1. The structure of isocyanide 5.10 was determined mainly by ^1H NMR, COSY experiments. Figure 5.2 shows the ^1H NMR spectrum of isocyanide 5.10.

In a similar synthetic route, a chiral imide group could be introduced into this type of isocyanide by using (*S*)-(-)- α -methylbenzylamine (Figure 5.1). Thus, isocyanides 5.11 and 5.12 having a chiral imide group were obtained. Structures of isocyanides 5.9, 5.11 and 5.12 are shown in Figure 5.3.

In order to obtain [5]helicene-based isocyanide, 5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride should be aromatized. In this study, a mixture of 1-nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (5.1) and 3-nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic anhydride (5.2) was first aromatized by reaction with bromine, thus producing a mixture of 1-nitro-[5]helicene-7,8-dicarboxylic anhydride (5.13) and 3-nitro-[5]helicene-7,8-dicarboxylic anhydride (5.14). These two compounds, without separation, were then imidized with *n*-butylamine to produce a mixture of two imides (5.15 and 5.16). These two imides containing a nitro group on the [5]helicene, without separation, were reduced with SnCl_2 to afford a mixture of two imides having an amino group on the [5]helicene (5.17 and 5.18). These two compounds were then

separated and purified through a silica gel column. Thus, compounds **5.17** and **5.18** could be converted into the [5]helicene-based isocyanides **5.21** and **5.22**, respectively. Figure 5.4 shows the synthetic route to isocyanide **5.22**. By using (*S*)-(-)- α -methylbenzylamine in imidization (Figure 5.4), [5]helicene-based isocyanide **5.23** having a remote chiral imide group was also obtained. Structures of isocyanides **5.21** and **5.23** are shown in Figure 5.3.

Figure 5.1. Synthesis of 5,6,9,10-Tetrahydro-[5]Helicene-Based Isocyanide **5.10**.

Figure 5.2. ^1H NMR (400 MHz, CDCl_3) of Isocyanide 5.10.

Figure 5.3. Structures of Isocyanides 5.9, 5.11, 5.12, 5.21, 5.23.

Figure 5.4. Synthesis of [5]Helicene-Based Isocyanide 5.22.

5-2. [5]Helicene-based Polyisocyanides

It is advantageous to have a material with a high optical rotation, since chiroptical change will be more sensitive and significant. Helicenes are benzologues of phenanthrene in which the extra ortho-condensed rings give rise to a regular cylindrical helix.^{73,74} The helical structure is a consequence of the repulsive steric overlap of the terminal aromatic nuclei. This inherently dissymmetric property makes helicene possess very high optical rotation if it is resolved.

In this study, [5]helicene- and 5, 6, 9, 10-tetrahydro[5]helicene-based isocyanides were prepared. Homopolymerizations of these isocyanide monomers were carried out by adding 1-4 mol% of NiCl_2 as catalyst.

Monomers **5.10**, **5.12**, **5.22** and **5.23** with isocyano groups at the 3 position on 5, 6, 9, 10-tetrahydro[5]helicene and [5]helicene could be polymerized by NiCl_2 in quantitative yields. The polymers were deep brown solids. In the IR spectra, $\text{N}=\text{C}$ stretching vibrations were visible at $1590\text{--}1620\text{ cm}^{-1}$. Figure 5.5 shows the IR spectra of monomer **5.10** and its homopolymer, respectively. It can be seen that the peak at 2116 cm^{-1} of the isocyano group of the monomer disappears and a new peak at 1600 cm^{-1} due to the imino backbone appears. Figure 5.6 shows the electronic spectra of the monomer **5.10** and its polymer in chloroform. The extended absorption in the visible region (400-500 nm) from the monomer to the polymer indicates that there exists conjugation in the backbone and between the imino group and a phenyl ring on the 5, 6, 9, 10-tetrahydro[5]helicene side group. Figure 5.7 also shows the GPC profile of polymer **5.1** and the unimodal molecular weight distribution was observed for other polymers, **5.2**, **5.3** and **5.4** (Table

5.1). Polydispersity indices for polymers 5.1-5.4 ranged from 1.8 to 2.6. Thermal decomposition temperatures (5 wt%) of these polymers were around 400 °C.

Table 5.1. Polymerizations of Isocyanides 5.10, 5.12, 5.22, and 5.23 with NiCl₂ (1-4 mol%) in a Mixture of Methanol and Chloroform (v/v, 1/1) at 22 °C.

Monomer	Polymer	Yield (%)	M _n ^a	PDI ^a	T _d ^b (°C)	[α] _D ^c	[M] _D ^c
5.10	5.1	91	16,000	2.6	390	—	—
5.12	5.2	95	11,000	1.8	411	+29.0°	+139.0°
5.22	5.3	95	15,000	2.0	420	—	—
5.23	5.4	95	11,100	2.6	426	+48.0°	+228.0°

a: GPC analysis using CHCl₃ as an eluent and polystyrene standards.

b: 5% weight loss in N₂.

c: in CHCl₃ at 22 °C.

Figure 5.5. IR Spectra of Monomer 5.10 (top) and Its Homopolymer (bottom).

Figure 5.6. UV/vis Spectra of Monomer 5.10 (solid line) and Its Homopolymer (dashed line) in CHCl_3 at 22 °C.

Figure 5.7. GPC Curve of Polymer 5.1.

In general, an isocyanide having a chiral side group which is in close vicinity to the isocyanide reactive center could undergo atropogenic polymerization to afford an optically active one-handed polyisocyanide.^{13,34} Polymerization of the monomer **5.12** ($[\alpha]_D^{22} = -53.0^\circ$, $C = 0.54$ mg/mL, chloroform) with a remote chiral imide group separated by 5,6,9,10-tetrahydro[5]helicene still produced an optically active polymer **5.2** ($[\alpha]_D^{22} = +29.0^\circ$, $C = 0.29$ mg/mL, chloroform). The optical rotation of this polymer had an opposite sign to that of the monomer **5.12**. Molar optical rotation ($[M]_D^{22}$)⁷⁵ changed from -254.0° for the monomer to $+139.0^\circ$ for the polymer. The result suggests that the polymer **5.2** had a preferentially one-handed backbone (Figure 5.8). However, the preference of the helical sense at the backbone was induced by the chirality transfer from the remote chiral imide group during the polymerization. Since this chiral group was distal to the isocyanide reactive center, the optical rotation of polymer **5.2** was not high. A similar phenomenon has also been observed in a chiral liquid crystalline system where the chiral center was separated by a mesogen, but still was able to transfer its chirality to the helical chain.⁷⁶

Figure 5.8. Polymerization of Isocyanide **5.12**.

Figure 5.9 shows electronic and CD spectra of the polymer **5.2**. UV/vis spectrum clearly indicates two maximum absorptions at 285 nm and 375 nm with an extension to

500 nm, due to the imino backbone $n\text{-}\pi^*$ transition and the side group $\pi\text{-}\pi^*$ transition. The peak at 285 nm on the UV/vis spectrum is split into two transitions in the CD spectrum at 280 nm and 300 nm, while the broad peak at 375 nm is split into three transitions at 330 nm, 400 nm and 450 nm. The helical sense for the helical backbone is tentatively assigned as an *M* helix based on the succession of the positive band at 330 nm to the negative band at 300 nm.^{5,16} Because these two Cotton effects are much stronger than that of the visible region, therefore, they should be the main sources of the chirality of the helical backbone. The relatively weak couplet between the negative band at 400 nm and the positive band at 450 nm may also arise from the chiral helical backbone.

A similar asymmetric induction was found in the homopolymerization of [5]helicene-based isocyanide **5.23**. The specific rotation increased from -48.0° of the monomer **5.23** ($C = 0.57$ mg/mL, chloroform) to $+48.0^\circ$ of the polymer **5.4** ($C = 0.32$ mg/mL, chloroform). Also, $[M]^{22}_D$ increased from -228.0° of the monomer to $+228.0^\circ$ of the polymer. Figure 5.10 shows UV/vis and CD spectra of homopolymer **5.4**. The peak at 325 nm on UV/vis spectrum may be responsible for the CD couplets of 280 nm, 320 nm and 350 nm, whereas the broad peak at 440 nm is for the weak CD couplets between the negative band at 420 nm and the positive band at 475 nm. As for an unresolved [5]helicene, *P* and *M* helices should be present in equal amounts. Therefore, the unresolved monomer **5.23** should be considered as a mixture of two diastereoisomers, namely (*S,M*) and (*S,P*)-[5]helicenes. This monomer, however, was CD inactive from 260 nm to 600 nm. Thus, Cotton effects observed from polymer **5.4** suggested that optical activity of this polymer was mainly due to a preferentially one-handed helical conformation

of its backbone (Figure 5.11). Obviously, this one-handed helical conformation was induced by a chirality transfer from the remote chiral imide group during polymerization.

However, no polymer was obtained from polymerization of monomers **5.9**, **5.11** and **5.21** with isocyano groups at the 1 position on 5, 6, 9, 10-tetrahydro[5]helicene and [5]helicene because of hindrance.

Figure 5.9. UV (top) and CD (bottom) Spectra of
Polymer 5.2 in CHCl_3 at 22 °C.

Figure 5.10. UV (top) and CD (bottom) Spectra of
Polymer 5.4 in CHCl_3 at 22 °C.

Figure 5.11. Polymerization of Isocyanide 5.23.

5-3. Experimental Section

Materials and Measurements

5,6,9,10-Tetrahydro-[5]helicene-7,8-dicarboxylic anhydride was synthesized according to reference.⁷² *n*-Butylamine, platinum (IV) oxide, tin (II) chloride dihydrate, ethyl formate, bromine, and (*S*)-(-)- α -methylbenzylamine ($[\alpha]_D^{20} = -39^\circ$, neat) were obtained from Aldrich Co. For measurements refer to Experimental Section 2.4, Chapter 2.

Monomer Syntheses

1-Nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Anhydride (5.1) and 3-Nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Anhydride (5.2).

5.1

5.2

5,6,9,10-Tetrahydro[5]helicene-7,8-dicarboxylic anhydride (10.0 g, 28.4 mmol) was dissolved into 1.8 L of methylene chloride with strong stirring at room temperature until the solution became clear. Then 600 mL of acetic acid was added into this solution. To this solution was slowly added a mixture of acids (80 g of nitric acid was added into 90 g of sulfuric acid, then slowly poured into 120 mL of acetic acid at 0 °C), keeping temperature at or below 20 °C. The reaction continued for a week. The reaction solution was poured into a large amount of water (1 L). The organic layer was separated and the

aqueous solution was extracted with methylene chloride (4 x 400 mL). The combined organic phase was washed with water (5 x 500 mL) until pH equal to 7 and dried under MgSO_4 . The solvent was removed under reduced pressure at 40 °C and the products were the mixture of anhydrides **5.1** and **5.2**. The total yield was 10.15 g (90%).

N-(*n*-Butyl)-1-nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Imide (**5.3**) and *N*-(*n*-Butyl)-3-nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Imide (**5.4**).

5.4 **5.3**

A mixture of **5.1** and **5.2** (2.0 g, 5.0 mmol) was dissolved into DMF (10 mL). To this solution was added an excess of *n*-butylamine (2.0 mL, 20.2 mmol). The solution was refluxed for 6 h, cooled down, poured into a large amount of acetic acid (100 mL) and washed with water (4 x 200 mL). The precipitated crude products were filtrated and dried under vacuum at 70 °C. The two major products were separated by recrystallization from a mixture of hexane and acetone (4:1, v:v). Compound **5.3** crystallized and compound **5.4** remained in solution. Yield for **5.3** was 0.8 g; m.p. 170.0-172.0 °C; IR (KBr) 2940, 1704, 1656, 1595, 1503, 1279, 1214 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, 1H), 7.49 (d, 1H), 7.35 (q, 2H), 7.25 (t, 1H), 6.93 (t, 1H), 6.58 (d, 1H), 4.15 (m, 2H), 3.71 (m, 2H), 2.4-3.1 (m, 6H), 1.69 (m, 2H), 1.42 (m, 2H), 0.99 (t, 3H); MS (EI, m/z , %) 452 (M^+ , 14.1). Yield for **5.4** was 1.0 g; m.p. 152.0-153.0 °C; IR (KBr) 2946, 2866, 1759, 1701,

1339 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 8.19 (d, 1H), 7.75 (dd, 1H), 7.28 (m, 3H), 6.95 (m, 2H), 4.15 (m, 2H), 3.69 (t, 2H), 3.10 (m, 4H), 2.50 (m, 2H), 1.65 (m, 2H), 1.35 (m, 2H), 0.99 (t, 3H);

N-(*n*-Butyl)-3-amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Imide (5.6).

5.6

Compound 5.4 (1.0 g, 2.2 mmol) was dissolved into a mixture of distilled THF (50 mL) and 95% ethanol (15 mL). To this solution was added catalyst PtO_2 (60 mg, 0.26 mmol). The solution was purged with H_2 for three times and the reduction reaction was carried out under H_2 atmosphere (50 psi) at room temperature for 5 h. The catalyst was filtrated off and solvents were removed by evaporation. The crude product was purified through a silica gel column (hexane:acetone, 4:1, v:v). Yield of orange product 5.6 was 0.6 g (64%); m.p. 130.0-135.0 $^\circ\text{C}$; IR (KBr) 3438, 2943, 1752, 1696, 1629, 1594 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.2-7.4 (m, 7H), 4.07 (br, 2H), 3.77 (s, 2H, NH_2), 3.66 (t, 2H, $\text{N-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.80 (m, 4H), 2.49 (br, 2H), 1.63 (m, 2H, $\text{N-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.39 (m, 2H, $\text{N-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.95 (t, 3H, $\text{N-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR (50.3 MHz, CDCl_3) δ 169.2, 169.1, 146.6, 141.0, 139.2, 139.0, 138.4, 137.6, 137.1, 134.1, 131.7, 129.8, 127.9, 127.6, 125.7, 124.6, 124.2, 113.3, 112.7, 37.4, 30.8, 28.8, 28.6, 24.4, 34.1, 20.1, 13.8; MS (EI, m/z , %) 422 (M^+ , 100).

N-(*n*-Butyl)-3-formamido-5,6,9,10-tetrahydro-[5]helicene-7,8-dicarboxylic Imide (5.8).

5.8

To a 50-mL flask equipped with a condenser attached with a water separator were added compound 5.6 (380 mg, 0.9 mmol), toluene (20 mL) and formic acid 90% (0.5 g, 10.9 mmol). The solution was refluxed at 110 °C. After water stopping collecting (2 h), toluene and formic acid were removed under reduced pressure at 80 °C. The crude product was purified through a silica gel column (acetone:hexane, 1:4, v:v). Yield of 5.8 was 385 mg (95%); m.p. 155.0-160.0 °C; IR (KBr) 3429, 2943, 1755, 1694, 1522 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 8.75 (d, 1H), 8.42 (s, 1H, NHCHO), 6.6-7.8 (m, 7H, aromatic protons and NHCHO), 4.07 (br, 2H), 3.66 (t, 2H, $\text{N-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.80 (m, 4H), 2.49 (br, 2H), 1.63 (m, 2H, $\text{N-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.39 (m, 2H, $\text{N-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.95 (t, 3H, $\text{N-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$); MS (EI, m/z , %) 450 (M^+ , 14.0).

N-(*n*-Butyl)-3-isocyano-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Imide (5.10).

5.10

To a 50-mL flask were added compound **5.8** (385 mg, 0.86 mmol), dry methylene chloride (10 mL) and dry triethylamine (2 mL) at 0 °C. Phosphorus oxychloride (0.5 mL, 5.0 mmol) in 2 mL of methylene chloride was added dropwise in course of 10 min and the reaction was continued under N₂ for 1 h. The reaction was quenched by pouring the solution into ice water (50 mL). The organic layer was separated and washed with aqueous NaHCO₃ (10%, 4 x 100 mL) solution, distilled water (4 x 100 mL), and dried over Na₂SO₄. Solvent was removed under reduced pressure at 30 °C. The crude product was purified through a silica gel column (acetone:hexane, 1:3, v:v). Yield for **5.10** was 304 mg (82%); m.p. 109.0-111.0 °C; IR (KBr) 3447, 2940, 2116, 1766, 1599, 1434 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.9-7.4 (m, 7H), 4.14 (br, 2H), 3.69 (t, 2H, N-CH₂CH₂CH₂CH₃), 2.92 (m, 4H), 2.52 (br, 2H), 1.63 (m, 2H, N-CH₂CH₂CH₂CH₃), 1.39 (m, 2H, N-CH₂CH₂CH₂CH₃), 0.95 (t, 3H, N-CH₂CH₂CH₂CH₃); ¹³C NMR (50.3 MHz, CDCl₃) δ 168.7, 164.6, 140.6, 139.3, 138.7, 138.0, 136.7, 134.9, 132.9, 131.1, 130.2, 128.8, 128.0, 126.8, 126.1, 126.0, 125.6, 123.7, 123.0, 112.2, 37.6, 30.7, 28.5, 28.4, 24.0, 23.7, 20.1, 13.7; MS (EI, *m/z*, %) 432 (M⁺, 100).

N-(*n*-Butyl)-1-Amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Imide (**5.5**).

5.5

Into a 50-mL round-bottom flask were added **5.3** (452 mg, 1.0 mmol), THF (10 mL) and 95% EtOH (5 mL). To this clear solution was added $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (1.25 g, 5.56 mmol). The solution was refluxed for overnight and poured into cooled water (100 mL). The crude product was extracted with acetal acetate (3 x 100 mL). The combined organic phase was washed with aqueous NaHCO_3 (5%, 2 x 50 mL) solution, distilled water (2 x 50 mL), and dried under MgSO_4 . After filtration, the solvent was removed under reduced pressure and the crude product was purified through a silica gel column using a mixture of acetone and hexane as eluent (1:4, v:v). Yield for compound **5.5** was 380 mg (90%): ^1H NMR (200 MHz, CDCl_3) δ 7.0–7.4 (m, 4H), 6.92 (t, 1H), 6.78 (d, 1H), 6.39 (t, 1H), 4.10 (m, 2H), 3.68 (t, 2H), 3.35 (s, 2H, NH_2), 2.2–3.0 (m, 6 H), 1.66 (m, 2H), 1.39 (m, 2H), 0.96 (t, 3H).

N-(*n*-Butyl)-1-formamido-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Imide (**5.7**).

5.7

Compound **5.5** (380 mg, 0.9 mmol) was dissolved into a mixture of formic acid (5 mL, 90%) and ethyl formate (5 mL) and the solution was refluxed for 6 h. The formic acid and ethyl formate were removed under reduced pressure and the crude product was purified through a silica gel column (acetone:hexane, 1:3, v:v). Yield for **5.7** was 385 mg (95%); m.p. 211–212 °C; IR (KBr) 2940, 2850, 1756, 1700, 1690, 1435, 1400 cm^{-1} ; ^1H NMR

(200 MHz, CDCl_3) δ 7.1–7.7 (m, 7H), 6.74 (t, 1H), 6.45 (t, 1H), 4.09 (m, 2H), 3.68 (t, 2H), 2.3–3.0 (m, 6H), 1.66 (m, 2H), 1.39 (m, 2H), 0.96 (t, 3H); MS (EI, m/z , %) 450 (M^+ , 100).

N-(*n*-Butyl)-1-isocyano-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Imide (5.9).

5.9

This isocyanide was prepared from compound 5.7 in the same manner as described above for the preparation of compound 5.10. Yield was 95%; m.p. 143.0–145.0 °C; IR (KBr) 2960, 2114, 1760, 1702, 1435, 1399 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, 1H), 7.37 (d, 1H), 7.28 (t, 1H), 7.21 (t, 1H), 7.09 (d, 1H), 6.89 (t, 1H), 6.70 (d, 1H), 4.09 (m, 2H), 3.68 (m, 2H), 2.3–3.0 (m, 6H), 1.66 (m, 2H), 1.39 (m, 2H), 0.96 (t, 3H); MS (EI, m/z , %) 432 (M^+ , 98.7).

N-(*n*-Butyl)-3-amino-[5]helicene-7,8-dicarboxylic Imide (5.18) and *N*-(*n*-Butyl)-1-amino-[5]helicene-7,8-dicarboxylic Imide (5.17).

5.18

5.17

A mixture of anhydrides **5.1** and **5.2** (2.0 g, 5.0 mmol) was dissolved in 1,2-dichlorobenzene (20 mL) and the solution was heated up to 180 °C. To this solution was added an excess of bromine (1.0 mL, 19.4 mmol) dropwise. After 2 h reaction, the solvent was removed by distillation and the crude products, 1-nitro-[5]helicene-7,8-dicarboxylic anhydride (**5.13**) and 3-nitro-[5]helicene-7,8-dicarboxylic anhydride (**5.14**), were obtained. Without separation, these two crude products were imidized with *n*-butylamine (1.0 mL, 10.0 mmol) in refluxing for 2 h. The solution was poured into a large amount of acetic acid (100 mL) and the products precipitated to afford a mixture of *N*-(*n*-butyl)-1-nitro[5]helicene-7,8-dicarboxylic imide (**5.15**) and *N*-(*n*-butyl)-3-nitro[5]helicene-7,8-dicarboxylic imide (**5.16**). The mixture of **5.15** and **5.16** was dissolved into distilled THF (20 mL). To this solution was added SnCl₂·2H₂O (2.0 g, 8.9 mmol). The solution was refluxed for 3 h and poured into a saturated aq. NaHCO₃ (100 mL) solution. The crude products precipitated and were filtrated, washed with distilled water (2 x 100 mL). After drying, the two isomers, *N*-(*n*-butyl)-1-amino-[5]helicene-7,8-dicarboxylic imide (**5.17**) and *N*-(*n*-butyl)-3-amino-[5]helicene-7,8-dicarboxylic imide (**5.18**), were separated through a silica gel column (hexane:acetone, 3:1, v:v). Compound **5.17** eluted first, followed by a mixture of **5.17** and **5.18**, and compound **5.18** came out last using acetone as an eluent. Yield for **5.18** was 550 mg; m.p. 156.0-158.0 °C; IR (KBr) 3420, 1754, 1693, 1623, 1399 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 8.96 (dd, 2H), 8.41 (d, 1H), 8.12 (d, 1H), 7.95 (dd, 2H), 7.85 (d, 1H), 7.54 (t, 1H), 7.24 (t, 1H), 7.02 (m, 1H), 6.63 (dd, 1H), 4.05 (s, 2H, NH₂), 3.90 (t, 2H), 1.75 (m, 2H), 1.42 (m, 2H), 0.98 (t, 3H); MS (EI, *m/z*, %) 418 (M⁺, 100). Yield for **5.17** was 400 mg; m.p. 112.0-114.0 °C; IR (KBr)

3439, 1754, 1696, 1396 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 9.01 (dd, 2H), 8.11 (d, 1H), 8.06 (d, 1H), 7.96 (t, 2H), 7.60 (t, 1H), 7.52 (t, 1H), 7.44 (d, 1H), 7.23 (t, 1H), 6.68 (d, 1H), 3.62 (t, 2H), 3.38 (s, 2H, NH_2), 1.75 (m, 2H), 1.44 (m, 2H), 0.99 (t, 3H); MS (EI, m/z , %) 418 (M^+ , 65.1).

N-(*n*-Butyl)-3-formamido-[5]helicene-7,8-dicarboxylic Imide (5.20).

5.20

This formamide was prepared from *N*-(*n*-butyl)-3-amino-[5]helicene-7,8-dicarboxylic imide (5.18) in the same manner as for the preparation of compound 5.8. The product was purified through a silica gel column using acetone as an eluent. Yield was 70%; m.p. 234.0-236.0 $^{\circ}\text{C}$; IR (KBr) 3439, 2920, 2850, 1755, 1694, 1539, 1401 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.2-9.2 (m, 13H), 3.82 (t, 2H), 1.75 (m, 2H), 1.42 (m, 2H), 0.98 (t, 3H); MS (EI, m/z , %) 446 (M^+ , 83.4).

N-(*n*-Butyl)-3-isocyano-[5]helicene-7,8-dicarboxylic Imide (5.22).

5.22

This isocyanide was prepared from **5.20** in the same manner as for the preparation of compound **5.10**. The product was purified through a silica gel column (hexane:acetone, 2:1, v:v). Yield was 80%; m.p. 147.0–149.0 °C; IR (KBr) 3439, 2920, 2850, 2123, 1755, 1695, 1398 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 9.10 (dd, 2H), 8.33 (d, 1H), 8.21 (t, 1H), 8.07 (d, 1H), 7.98 (m, 3H), 7.60 (t, 1H), 7.28 (d, 1H), 7.16 (dd, 1H), 3.82 (t, 2H), 1.75 (m, 2H), 1.42 (m, 2H), 0.98 (t, 3H); MS (EI, m/z , %) 428 (M^+ , 54.6).

N-(*n*-Butyl)-1-formamido-[5]helicene-7,8-dicarboxylic Imide (**5.19**).

5.19

N-(*n*-Butyl)-1-amino-[5]helicene-7,8-dicarboxylic imide (**5.17**) (0.6 g, 1.4 mmol) was dissolved into a mixture of 90% formic acid (5 mL) and ethylformate (5 mL). The solution was refluxed for 1 h. The liquid was removed by distillation under reduced pressure and the crude product was purified through a silica gel column using acetone as an eluent. Yield was 0.58 g (90%); m.p. 120.0–122.0 °C; IR (KBr) 3425, 2929, 2860, 1757, 1695, 1396 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.4–9.1 (m, 13H), 3.70 (t, 2H), 1.82 (m, 2H), 1.46 (m, 2H), 0.99 (t, 3H); MS (EI, m/z , %) 446 (M^+ , 19.3).

N-(*n*-Butyl)-1-isocyano-[5]helicene-7,8-dicarboxylic Imide (**5.21**).

5.21

This isocyanide was prepared from *N*-(*n*-butyl)-1-formamido-[5]helicene-7,8-dicarboxylic imide (5.19) in the same manner as for the preparation of compound 5.10. The product was purified through a silica gel column (hexane:acetone, 2:1, v:v) and yield was 90%; m.p. 92.0-94.0 °C; IR (KBr) 3446, 2929, 2860, 2112, 1758, 1700, 1396 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 9.14 (dd, 2H), 8.11 (m, 4H), 7.68 (t, 1H), 7.60 (t, 1H), 7.45 (d, 1H), 7.25 (t, 2H), 3.82 (t, 2H), 1.76 (m, 2H), 1.46 (m, 2H), 0.99 (t, 3H); MS (EI, m/z , %) 428 (M^+ , 100).

N-[(*S*)-(-)- α -Methylbenzyl]-3-amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Imide (5.26) and *N*-[(*S*)-(-)- α -Methylbenzyl]-1-amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Imide (5.27).

5.26

5.27

A mixture of anhydrides 5.1 and 5.2 (2.0 g, 4.0 mmol) with (*S*)-(-)- α -methylbenzylamine (3 mL, 23 mmol) was refluxed in 20 mL of DMF for 2 h. The solution was cooled down and poured into a large amount of distilled water (200 mL). The products precipitated to afford a mixture of *N*-[(*S*)-(-)- α -methylbenzyl]-1-nitro-5,6,9,10-tetrahydro[5]helicene-7,8-

dicarboxylic imide and *N*-[(*S*)-(-)- α -methylbenzyl]-3-nitro-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic imide. Without separation, the mixture was dissolved into 20 mL of distilled THF. To this solution was added $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (2.6 g, 11.5 mmol). The solution was refluxed for 1 h and poured into a saturated aqueous NaHCO_3 (200 mL) solution. The crude products precipitated and were filtrated, washed with distilled water (4 x 100 mL). After drying, the two isomers, *N*-[(*S*)-(-)- α -methylbenzyl]-3-amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic imide (**5.26**) and *N*-[(*S*)-(-)- α -methylbenzyl]-1-amino-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic imide (**5.27**) were separated through a silica gel column (hexane:acetone, 4:1, v:v). Compound **5.27** eluted first, followed by a mixture of **5.26** and **5.27**, and compound **5.26** came out last using acetone as an eluent. Yield for **5.26** was 330 mg; $[\alpha]_D^{22} = -17.0^\circ$ ($C = 1.44$ mg/mL in chloroform); m.p. 80.0-82.0 $^\circ\text{C}$; IR (KBr) 3440, 2930, 2860, 1752, 1696, 1626 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.52 (d, 2H), 7.33 (t, 2H), 7.26 (m, 2H), 7.15 (dt, 2H), 6.94 (m, 2H), 6.58 (d, 1H), 6.24 (dd, 1H), 5.57 (q, 1H), 4.06 (m, 2H), 3.78 (s, 2H, NH_2), 2.83 (m, 4H), 2.46 (m, 2H), 1.96 (d, 3H); MS (EI, m/z , %) 470 (M^+ , 100). Yield for **5.27** was 700 mg; $[\alpha]_D^{22} = -27.5^\circ$ ($C = 2.07$ mg/mL in chloroform); m.p. 102.0-105.0 $^\circ\text{C}$; IR (KBr) 3428, 2930, 2860, 1751, 1699, 1358 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.7-7.6 (m, 11H), 6.35 (d, 1H), 5.60 (q, 1H), 4.15 (m, 2H), 3.32 (s, 2H, NH_2), 2.83 (m, 4H), 2.46 (m, 2H), 1.95 (d, 3H); MS (EI, m/z , %) 470 (M^+ , 100).

N-[(*S*)-(-)- α -Methylbenzyl]-1-formamido-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Imide (**5.28**).

5.28

Compound **5.27** (700 mg, 1.5 mmol) was dissolved into 20 mL of toluene. To this solution was added formic acid (5 mL, 95%). The solution was refluxed for 1 h. After vaporating the liquids, the solid product was purified through a silica gel column using chloroform as an eluent. Yield was 672 mg (90%); $[\alpha]_D^{22} = -64.0^\circ$ (C = 0.69 mg/mL in chloroform); m.p. 264.0-266.0 °C; IR (KBr) 2930, 2860, 1754, 1692, 1346 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.7–8.8 (m, 14H), 5.60 (q, 1H), 4.15 (m, 2H), 2.83 (m, 4H), 2.46 (m, 2H), 1.95 (d, 3H); MS (EL, m/z , %) 498 (M^+ , 100).

N-[*(S)*-(-)- α -Methylbenzyl]-1-isocyano-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Imide (**5.11**).

5.11

This isocyanide was prepared from compound **5.28** in the same manner as for the preparation of compound **5.10**. The crude product was purified through a silica gel column using chloroform as an eluent. Yield was 80%; $[\alpha]_D^{22} = -31.0^\circ$ (C = 1.78 mg/mL

in chloroform); m.p. 116.0–118.0 °C; IR (KBr) 2930, 2860, 2116, 1755, 1701, 1361 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.52 (d, 1H), 7.20–7.45 (m, 8H), 7.08 (d, 1H), 6.86 (t, 1H), 6.68 (d, 1H), 5.60 (q, 1H), 4.15 (m, 2H), 2.83 (m, 4H), 2.46 (m, 2H), 1.95 (d, 3H); MS (EI, m/z , %) 480 (M^+ , 56.3).

N-[*(S)*-(-)- α -Methylbenzyl]-3-formamido-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Imide (5.29).

5.29

Compound 5.26 (330 mg, 0.7 mmol) was dissolved into 20 mL of toluene and 3 mL of 95% of formic acid. The solution was refluxed for 1 h and liquids were removed by distillation. The crude product was purified through a silica gel column using methylene chloride as an eluent. Yield for 5.29 was 331 mg (95%); $[\alpha]_{\text{D}}^{22} = -57.0^\circ$ ($C = 0.72$ mg/mL in chloroform); m.p. 168.0–170.0 °C; IR (KBr) 2930, 2860, 1754, 1697, 1361 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.4–7.7 (m, 14H), 5.60 (q, 1H), 4.15 (m, 2H), 2.83 (m, 4H), 2.46 (m, 2H), 1.95 (d, 3H); MS (EI, m/z , %) 498 (M^+ , 100).

N-[*(S)*-(-)- α -Methylbenzyl]-3-isocyano-5,6,9,10-tetrahydro[5]helicene-7,8-dicarboxylic Imide (5.12).

5.12

This isocyanide was prepared from compound 5.29 in the same manner as for the preparation of compound 5.10. The crude product was purified through a silica gel column using chloroform as an eluent. Yield was 75%; $[\alpha]_D^{22} = -53.0^\circ$ (C = 0.81 mg/mL in chloroform); m.p. 112.0–114.0 °C; IR (KBr) 2930, 2860, 2116, 1755, 1700, 1356 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 6.8–7.6 (m, 12H), 5.60 (q, 1H), 4.15 (m, 2H), 2.83 (m, 4H), 2.46 (m, 2H), 1.95 (d, 3H); MS (EI, m/z , %) 480 (M^+ , 69.7).

N-[*(S)*-(-)- α -Methylbenzyl]-3-amino-[5]helicene-7,8-dicarboxylic Imide (5.30).

5.30

A mixture of anhydrides 5.1 and 5.2 (3.0 g, 6.0 mmol) was dissolved into dichlorobenzene (20 mL) and the solution was heated up to 180 °C. To this solution was added an excess of bromine (1.0 mL, 19.4 mmol) dropwise. The aromatization was continued for 1 h and the solution was then cooled to room temperature to afford a mixture of 1-nitro-[5]helicene-7,8-dicarboxylic anhydride and 3-nitro-[5]helicene-7,8-dicarboxylic anhydride. Without separation, an excess of (*S*)-(-)- α -methylbenzylamine (4.0 mL, 31.0 mmol) was

added to this solution and the solution was refluxed for 1 h. After removing most of the solvent by distillation, the crude products, *N*-[(*S*)-(-)- α -methylbenzyl]-1-nitro-[5]helicene-7,8-dicarboxylic imide and *N*-[(*S*)-(-)- α -methylbenzyl]-3-nitro-[5]helicene-7,8-dicarboxylic imide, were dissolved into 60 mL of distilled THF. To this solution was added $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (2.0 g, 8.8 mmol) and the solution was refluxed for 2 h. After cooling down to room temperature, the solution was poured into a saturated aqueous Na_2CO_3 (100 mL) solution. The precipitated crude products, *N*-[(*S*)-(-)- α -methylbenzyl]-1-amino-[5]helicene-7,8-dicarboxylic imide and *N*-[(*S*)-(-)- α -methylbenzyl]-3-amino-[5]helicene-7,8-dicarboxylic imide (**5.30**), were filtrated, washed with water (4 x 200 mL) and dried over Mg_2SO_4 . These two compounds were then separated through a silica gel column (hexane:acetone, 3:1, v:v). *N*-[(*S*)-(-)- α -Methylbenzyl]-1-amino-[5]helicene-7,8-dicarboxylic imide came out first and *N*-[(*S*)-(-)- α -methylbenzyl]-3-amino-[5]helicene-7,8-dicarboxylic imide (**5.30**) came out later. Yield for **5.30** was 430 mg; $[\alpha]_D^{22} = -40.6^\circ$ ($C = 0.76$ mg/mL in chloroform); m.p. 270.0-272.0 $^\circ\text{C}$; IR (KBr) 3430, 3383, 2930, 1752, 1691, 1628, 1593, 1389 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 9.0 (d, 1H), 8.92 (dd, 1H), 8.38 (d, 1H), 8.10 (d, 1H), 7.92 (q, 2H), 7.77 (d, 1H), 7.55 (m, 4H), 7.25 (m, 7H), 7.02 (d, 1H), 6.62 (dd, 1H), 5.58 (q, 1H), 4.05 (s, NH_2 , 2H), 2.04 (d, 3H); MS (EI, m/z , %) 466 (M^+ , 37.1).

N-[(*S*)-(-)- α -Methylbenzyl]-3-formamido-[5]helicene-7,8-dicarboxylic Imide (**5.31**).

5.31

This formamide was prepared from compound 5.30 in the same manner as for the preparation of compound 5.8. Yield was 100%; $[\alpha]_D^{22} = -40.0^\circ$ (C = 0.81 mg/mL in chloroform); IR (KBr) 3434, 2930, 1755, 1692, 1534, 1367 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.0-9.1 (m, 18H), 5.58 (q, 1H), 2.04 (d, 3H).

N-[(*S*)-(-)- α -Methylbenzyl]-3-isocyano-[5]helicene-7,8-dicarboxylic Imide (5.23).

5.23

This isocyanide was prepared from compound 5.31 in the same manner as for the preparation of compound 5.10. The crude product was purified through a silica gel column using chloroform as an eluent. Yield was 91%; $[\alpha]_D^{22} = -48.0^\circ$ (C = 0.86 mg/mL in chloroform); m.p. 120.0-122.0 $^\circ\text{C}$; IR (KBr) 2923, 2115, 1758, 1700, 1355 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 9.06 (q, 2H), 8.28 (d, 1H), 8.14 (d, 1H), 7.95 (m, 3H), 7.60 (m, 2H), 7.30 (m, 6H), 7.14 (dd, 1H), 5.58 (q, 1H), 2.04 (d, 3H); MS (EI, m/z , %) 476 (M^+ , 59.5).

Polymerization

Polymer 5.1. Isocyanide **5.10** (495.0 mg, 1.1 mmol) was dissolved into chloroform (2 mL). To this solution was added methanol (2 mL). After stirring for 10 min, NiCl₂ (3.0 mg, 2 mol%) was added and polymerization proceeded at room temperature for five days. The polymer was precipitated in a large amount of methanol (30 mL), collected by filtration. Polymer **5.1** was then redissolved into chloroform (2 mL) and precipitated from methanol (20 mL). The polymer was collected by filtration and dried under vacuum at 70 °C: Yield was 450.0 mg (91%); IR (KBr) 2945, 1766, 1704, 1592 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 6.4–7.9 (br, aromatic protons); UV/Vis (CHCl₃) λ_{max} 289 nm, 370 nm; T_d (5% weight loss in N₂) = 390 °C; M_n = 16,000, PDI = 2.6.

Polymer 5.2. Polymerization of isocyanide **5.12** was carried out in the same way as for isocyanide **5.10**. Yield was 95%; [α]_D²² = +29° in CHCl₃; IR (KBr) 3450, 1592, 1484 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.3 (br, aromatic protons, 12H), 5.5 (br, 1H), 1.9 (br, 11H); UV/Vis (CHCl₃) λ_{max} 300 nm, 375 nm; T_d (5% weight loss in N₂) = 411 °C; M_n = 11,000, PDI = 1.8.

Polymer 5.3. Polymerization of isocyanide **5.22** was carried out in the same way as for isocyanide **5.10**. Yield was 95%; IR (KBr) 1756, 1708, 1600 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.0–8.5 (br, aromatic protons, 11H); UV/Vis (CHCl₃) λ_{max} 320 nm, 430 nm; T_d (5% weight loss in N₂) = 420 °C; M_n = 15,000, PDI = 2.0.

Polymer 5.4. Polymerization of isocyanide **5.23** was carried out in the same way as for isocyanide **5.10**. Yield was 95%; $[\alpha]_D^{22} = +48^\circ$ in CHCl_3 ; IR (KBr) 1758, 1704, 1592 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.6 (br, aromatic protons, 16H), 5.6 (br, 1H), 2.0 (br, 3H); UV/Vis (CHCl_3) λ_{max} 335 nm, 440 nm; T_d (5% weight loss in N_2) = 426 $^\circ\text{C}$; $M_n = 11,100$, PDI = 2.6.

SUMMARY

1. A series of optically active block copolymethacrylates (TrMA-*b*-MMA, TrMA-*b*-*t*-BuMA, TrMA-*b*-*n*-BuMA, CHDPMMA-*b*-MMA and CHDPMMA-*b*-*n*-BuMA) were synthesized by living anionic polymerization in the presence of chiral initiator, FILi-(+)-DDB. Their optical activities largely depend on polymer compositions. Polymers with a high fraction of the helical segment, TrMA or CHDPMMA, have high optical rotations. Block polymers with a high fraction of flexible segment MMA could be cast into flexible films. A block TrMA-*b*-MMA polymer film containing 1 wt% of diphenyl-*p*-tolylsulfonium triflate could undergo a partial racemization upon UV (254 nm) irradiation and baking (125 °C). In the similar conditions, a block CHDPMMA-*b*-MMA polymer film could undergo a complete photodriven racemization. The results have demonstrated that the chemical process initiated by irradiation (writing) involves the photogeneration of an acid, the acid-catalyzed thermal cleavage of bulky ester groups. The permanent change in optical rotation of these polymer films should be detectable (reading).

2. Optically active azo-containing copolymethacrylates (TrMA-*co*-PAEM, TrMA-*co*-PAHM) were synthesized by atropogenic copolymerization. The optical activity of these copolymers varies with their compositions. Polymers with a high fraction of azo monomer component have low optical rotation, but have improved solubility and even film formability. Photoisomerization of optically active, high azo-containing random polymethacrylates in solution indicated that configurational change of a side-chain azo chromophore (trans to cis) under UV (300 nm) irradiation could induce a conformational

change of polymer backbone to a certain extent. Configurational change and polarity change of the azo chromophore are the two main driving forces responsible for this main-chain conformational transition. However, no detectable photoisomerization was observed by irradiating polymer film.

3. Optically active azo-containing polyisocyanides were synthesized by copolymerization of a chiral isocyanide and a series of achiral azo-containing isocyanides. Only one type of azo-containing polyisocyanides could undergo a conformational change in the helical chain induced by the azo isomerization in the side chain triggered by UV irradiation at 300 nm in solution. Such chiroptical change was confirmed by the CD changes before and after irradiation, indicating that azo photoisomerization could perturb the chiral helical backbone.

4. New [5]helicene-based polyisocyanides were synthesized, their chiroptical properties were investigated by optical rotation, UV/vis and CD experiments. Optically active one-handed helical polymers were obtained by a chirality transfer from a remote chiral imide group to the polymer main chain during polymerization.

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