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Cationic Ring Opening Cyclopolymerization of Bis(oxazolines). Synthesis of Chiral Polymers Containing Pendent Heteromacrocycles

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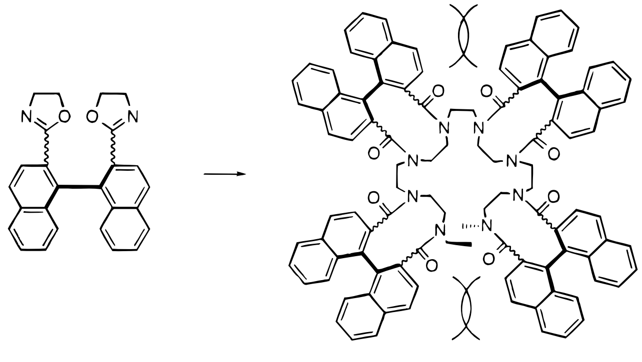
ABSTRACT: Novel biphenyldiylbis(oxazoline) and both racemic and optically active and binaphthyldiylbis(oxazolines) (**1**−**4**) have been cationically cyclopolymerized to give polymers that contained pendent heteromacrocyclic metal receptors. The optically active cyclopolymers showed very high specific optical rotations per repeat unit that varied between $[\alpha]_D^{25}$ −248° and $[\alpha]_D^{25}$ −321° depending upon the solvent. Circular dichroism spectra and optical rotation showed dependence on molecular weight. The cyclopolymers are thermally robust with decomposition temperatures >400 °C and glass transition temperatures (T_g) between 200 and 302 °C. The polymers were reduced with AlH_3 to give polymers with pendent nitrogen-containing heteromacrocycles. Dichloromethane solutions of the reduced polymers were used to extract $Cu(NO_3)_2$ from aqueous solutions to give complexes whose stoichiometry varied from 3−4 Cu^{2+} ions per five reduced repeating units. The Cu^{2+}-containing cyclopolymers gave higher T_g (100−180 °C) than obtained for the reduced polymers (72−138 °C) which in turn gave much lower T_g than did the corresponding unreduced polymers.

Introduction and Rationale

Chiral polymers have been of considerable interest for many years.[1,2] They have found uses in such applications as catalysts for asymmetric induction in organic synthesis,[1−3] chiral chromatographic separations,[4] and ferroelectric and nonlinear optical applications.[5] The types of synthetic chiral polymers that have been reported include the following: (1) the first are polymers that adopt helical conformations such as poly(chloral), poly(isocyanates), poly(isocyanides), and poly(triarylmethyl methacrylates). These polymers are obtained via the so-called "helix-sense-selective" polymerization from achiral monomers using either a chiral initiator or catalyst.[2] (2) The second are polymers whose optical activity is derived either from main chain or side chain chirality. They are obtained by cyclopolymerization of diolefins,[6] diisocyanides,[7] divinyl ethers,[8,9] bis(styrenes),[1,9] dimethacrylates,[10,11] and diepoxides.[12] The second class has not received as much detailed effort as the first one, and in the few reports that have appeared, none adequately addressed the conformations of the chains. In a preliminary report from our laboratory, cyclopolymerization has been used to form ordered materials.[11b,c] For example, cyclopolymerization of (−)-*trans*-4,5-bis((methacryloyloxy)diphenylmethyl)-2,2-dimethyl-1,3-dioxacyclopentane gave rise to polymers with very high specific optical rotations. CD and polarimetric studies of the polymers having different tacticity distributions suggested that the polymers were ordered and, possibly, helical.

As part of our continuing investigation into the use of cyclopolymerization to control polymer architecture and prepare optically active polymers, the cyclopolymerization of biaryldiylbis(oxazolines) was investigated as a route into polymers that contain pendent receptors for different types of guests.[13] For example, polymers containing nitrogen heteromacrocycles may be prepared simply by reduction of the amide groups in the poly(oxazoline) backbone (Scheme 1). Therefore, with the appropriately designed monomers, the technique may serve as a route into polymeric "azacrown" ethers that can serve as ion channels, catalysts, and hosts for different types of guests. Such polymeric hosts will possess a higher density of active sites than is possible through grafting since each repeat unit constitutes the receptor.[14,15]

Scheme 1



A major complicating reaction in cyclopolymerization is cross-linking, which results from the competing linear intermolecular propagation.[16] Scheme 2 outlines the essential steps of bis(oxazoline) cyclopolymerization. M denotes the polymerizable group in the monomer which upon reaction becomes M*, P* represents the quaternary monocyclic oxazolinium propagating species, and P_c* is the quaternary bicyclic oxazolinium propagating species. For a successful cyclopolymerization, it is critical that P* closes faster to form P_c* than it reacts with another M to form P′*. Formation of P′* must be prevented or at least minimized in order to avoid cross-linking. It is quite straightforward to show that the fraction, X_c, of cyclization relative to linear intermolecular propagation is given by the expression

$$X_c = \frac{k_c}{k_c + 2k'_p[M]} \qquad (1)$$

where k_c is the unimolecular rate constant for the

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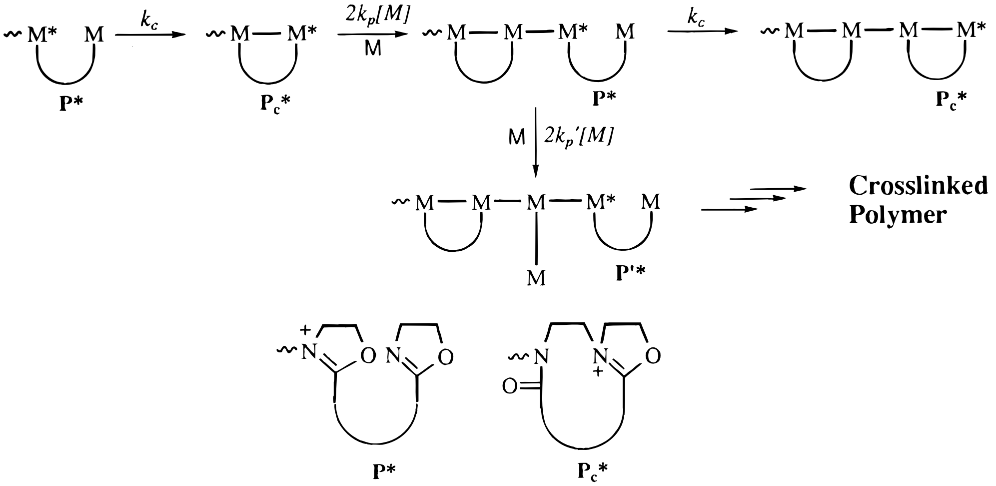
Scheme 2



intramolecular cyclization and k_p' is the linear bimolecular propagation rate constant for the formation of P′*. Taking the reciprocal of the above expression gives

$$\frac{1}{X_c} = 1 + \frac{2k_p'[M]}{k_c} \qquad (2)$$

from which it follows that k_c must be much greater than $2k_p'[M]$ in order to obtain high X_c (i.e., $X_c \rightarrow 1$).

There are several approaches for fulfilling this condition. One is to design the monomer in such a way that it cyclizes very fast. In order to accomplish this, we chose the biaryl groups that, due to the restricted rotation of the two aryl groups, are convergent and the two oxazoline groups are maintained in close proximity to each other. The second approach entails working at low monomer concentrations. However, if [M] is excessively low it will slow down not only the formation of P′* but also that of P*; that is, reduce $k_p[M]$, the desired intermolecular propagation rate. One way to avoid this, is for P_c* to react with another monomer faster than P* does ($k_p > k_p'$) so that the decrease in $k_p[M]$ caused by using low [M] is less than that in $k_p'[M]$. As can be seen in Scheme 2, P_c* is a bicyclic oxazolinium ion and, all other things being equal, the ring strain introduced upon its formation, especially in the case of smaller rings, should increase its rate of ring opening over that of P*. In this paper, we report the details of how the above factors are balanced in order to successfully effect cyclopolymerization of biphenyldiyl- and binaphthyldiyl-bis(oxazolines). The polymerization characteristics, application to the synthesis of optically active polymers with pendent heteromacrocyclic receptors, chiroptical and thermal properties of both unreduced and reduced polymers, and implications of the results for chain conformations are described.

Experimental Details

Reagents. Common reagents were purchased from Aldrich. Anhydrous grade *o*-dichlorobenzene (ODCB) was stirred over CaH_2 under N_2 at 100 °C overnight and fractionally distilled under vacuum. This procedure was repeated twice after which the solvent was stored in a drybox. Benzonitrile (99+% grade) was stirred over P_2O_5 at 50 °C under N_2 overnight and fractionally distilled under vacuum. This procedure was repeated twice after which the solvent was stored in a drybox. Dimethylformamide (DMF, HPLC grade) was dried over freshly activated 3 Å molecular sieves, fractionally distilled under vacuum onto new 3 Å sieves, and, after 1 day, transferred by canula onto new 3 Å sieves. This was repeated twice followed by a final fractional vacuum distillation. Acetonitrile (MeCN, HPLC grade) was refluxed for 1 day and fractionally distilled twice from CaH_2. Methyl triflate (MeOTf) was transferred from the ampoule into an inert atmosphere storage bottle under N_2 and stored in a drybox. Methyl tosylate (MeOTs) was fractionally distilled under N_2 twice and kept in a drybox. *N*-Methyl-2-phenyl-2-oxazolinium triflate was prepared by adding 1 equiv of MeOTf to dry 2-phenyl-2-oxazoline (distilled from CaH_2) in ether, followed by filtration of the salt under N_2 in a Schlenk filter. The resulting solid was extremely susceptible to static charges. The salt was dried under vacuum and transferred into a drybox.

General Data. ^{1}H NMR spectra were recorded on either a Varian XL-200 spectrometer operating at 200.057 MHz or Varian XL-400 spectrometer operating at 399.952 MHz with TMS or chloroform as internal standards. ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer operating at 100.577 MHz with TMS or chloroform as internal standards. IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrophotometer on KBr plates or in KBr pellets. Matrix assisted laser desorption time of flight (MALDI-TOF) mass spectroscopy was carried out on a Finnigan Lasermat 2000. Gel permeation chromatography (GPC) was carried out on either a Viscotek GPC system with 222c HPLC pump, Model 200 differential refractometer/viscometer, and two linear mixed bed and one 500 Å American Polymer Standards 10 μm columns or on a GPC system with a Waters M510 HPLC pump, UKG manual injector, PL gel columns (5 μm) 100, 500, 1000 Å, and mixed C in a Waters column heating compartment at 40 °C, Viscotek 110 differential viscometer, and Milton Roy differential refractometer. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA7. Differential scanning calorimetry (DSC) was performed with a Mettler DSC 30 with a TC10A controller. Alternatively, thermal analysis was carried out on a Seiko 5200 thermal analysis system with TG/DTA 220 and DSC 220C under N_2. Optical rotation was measured on a Perkin-Elmer 241 polarimeter with a 1.0 mL cell with 10 cm path length. Circular dichroism was recorded on a Jobin Yvon Autodichrograph Mark V interfaced with an Apple IIGS computer running CDSoft v 3.1 software using a 0.01 or 0.1 cm cell. A separate solvent run preceded each sample run. The solvent spectrum was subtracted from the sample spectrum to correct for solvent and cell contributions. Elemental analysis was carried out by Oneida Research Labs.

Monomer Synthesis. Monomers **1** and **2** were synthesized by alkylation of commercially available 2-methyl-2-oxazoline in high purity and yields following procedures previously described.[17] Monomer **3**, which has no spacer between the oxazoline ring and the binaphthalene group and, hence, could not be synthesized by an alkylation method, was prepared using Ullmann coupling. Monomer **4**, which has an α-CH_2 but oxygen in the place of β-CH_2, was prepared by condensation of the appropriate dicarboxylic acid with ethanolamine.

Procedures and experimental details are reported in ref 17.

Polymerizations. A typical polymerization procedure is as follows: Inside a drybox, a 50-mL round-bottom flask, equipped with a wide bore Rotaflo stopcock and a magnetic stirring bar, was charged with (±)-**2** (0.22 g, 0.49 mmol) and ODCB (9.0 mL). A solution of MeOTs (0.25 mL, 0.036 M, 0.54 mmol) in ODCB was then added. The flask was stoppered, removed from the drybox, and heated in an oil bath at 100 °C for 5 days. The reaction was quenched with *tert*-BuOH or MeOH and evaporated in vacuo. The crude polymer was dissolved in $CHCl_3$ (4.0 mL) and added dropwise to CH_3CN (200 mL). The resulting mixture was vigorously stirred and filtered through a 4−8 μm sintered glass filter to give 0.21 g (95%) of poly-(±)-**2** as an off-white powder. ^1H NMR (200 MHz, $CDCl_3$): δ 1−4 (br, 8H), 6.5−8.5 (br, 12H). IR (KBr): 1644 (s), 1422 (s) cm^{-1}. Note: Low molecular weight polymers from **1** and **2** were precipitated from ethanol/hexanes (1/1, v/v) instead of CH_3CN.

Typical Procedure for AlH_3 Reduction Illustrated with Poly-2. AlH_3 was prepared by adding concentrated H_2SO_4 (0.32 mL, 3.84 mmol) to a mixture of $LiAlH_4$ (12 mL, 1 M in THF, 12 mmol) and THF (6 mL) at 0 °C. The AlH_3 solution (4 mL, 2.6 mmol) was added at 0 °C to the binaphthyl polymer (poly-(±)-**2**, 0.3 g, 0.7 mmol repeat units) in THF (10 mL). The reaction was quenched with 0.5 mL of THF/water (1/1, v/v) after 23 h and treated with aqueous NaOH (0.13 g in 1 mL of water) to coagulate the precipitate. The resulting precipitate was filtered and dried over Na_2SO_4. Yield: 0.26 g (99%). The procedure was applied to the reduction of the other polymers.

Reduced poly-(±)-**2** (poly-(±)-**2r**): IR (KBr): 1647 (w), 1457 (s) cm^{-1}. Anal. Calcd for $0.5(C_{30}H_{32}N_2).0.5(C_{30}H_{28}N_2O_2)$ (50% reduction): C, 82.95; H, 6.91; N, 6.45. Found: C, 82.95; H, 7.23; N, 6.05.

Reduced poly-(*S*)-**2** (poly-(*S*)-**2r**): IR (KBr): 1667 (w), 1455 (s) cm^{-1}. Anal. Calcd for $0.7(C_{30}H_{32}N_2).0.3(C_{30}H_{28}N_2O_2)$ (70% reduction): C, 83.99; H, 7.24; N, 6.53. Found: C, 83.79; H, 8.00; N, 5.92.

Reduced poly-**1** (poly-**1r**): IR (KBr): 1648 (w), 1448 (s) cm^{-1}. Anal. Calcd for $0.7(C_{22}H_{28}N_2).0.3(C_{22}H_{24}N_2O_2)$ (70% reduced): C, 80.01; H, 8.12; N, 8.48. Found: C, 80.90; H, 7.28; N, 8.45.

Interactions of Cu^{2+} Ions with the Reduced Polymers. Typical Procedure Illustrated with Poly-(*S*)-2r: Poly-(*S*)-**2r** (54 mg) was dissolved in CH_2Cl_2 (7 mL). Then an aqueous $Cu(NO_3)_2{\cdot}2.5H_2O$ solution (7 mL, 260 mg/mL) was added, and the mixture was stirred for 3 days. Some emulsion formed, which was discarded. The methylene chloride layer was separated and evaporated. The residue was dried under vacuum to yield 49 mg (90%) of a green powder. Anal. Calcd for $5(C_{30}H_{32}N_2){\cdot}3\{Cu(NO_3)_2\}{\cdot}2(C_{30}H_{28}N_2O_2)$: C, 70.79; H, 6.11; N, 7.86. Found: C, 70.55; H, 6.24; N, 7.17.

Extraction with poly-(±)-**2r**: Anal. Calcd for $5(C_{30}H_{32}N_2){\cdot}4\{Cu(NO_3)_2\}{\cdot}5(C_{30}H_{28}N_2O_2)$: C, 70.58; H, 5.93; N, 7.68. Found: C, 70.58, H, 5.35, N, 6.79.

Extraction with poly-**1**: Anal. Calcd for $5(C_{22}H_{28}N_2){\cdot}3\{Cu(NO_3)_2)\}{\cdot}2(C_{22}H_{24}N_2O_2)$: C, 64.62; H, 6.62; N, 9.79. Found: C, 64.82; H, 6.72; N, 8.27.

Results and Discussion

Polymerization of Racemic Monomers. The cationic ring opening cyclopolymerization was performed using MeI, MeOTs, MeOTf, and *N*-methyl-2-phenyl-2-oxazolinium triflate as initiators. Progress of the reaction was monitored by ^1H NMR spectroscopy and GPC until signals due to monomer completely disappeared and the molecular weight remained constant. Typical polymerization conditions and results are summarized in Table 1. In general, high reaction temperatures (>100 °C) and long reaction times (several hours to days) were necessary to obtain soluble polymers in high yields partly due to the low monomer concentrations (≤50 mM) required to obtain cross-linked-free polymers and partly due to the inherently slow nature of oxazoline polymerizations.[18]

Table 1. Polymerization Results of 1−4 in *o*-Dichlorobenzene at 100 °C[a]

run no.	mon	init[b]	M:I[c]	time (h)	yield (%)	M_n[d] calc	M_n[e] GPC	M_p[e] GPC	PDI
1	**1**	A	12	24	92	3800	1200	5300	3.6
2	**1**	A	56	140	93	18100	10500	20000	1.7
3	**1**	A	158	408	89	48900	28900	43700	2.2
4	**1**	A	260	440	89	76000	47000	84300	3.8
5	**1**	MeI	51	118	47	8300	6300	7100	1.5
6	**1**	B	38	118	91	12000	14100	24900	1.7
7	(±)-**2**	A	13	24	91	5300	3700	9000	1.5
8	(±)-**2**	A	48	118	94	20200	7900	19300	2.1
9	(±)-**2**	A	138	288	99	61800	26700	40800	1.5
10[f]	(±)-**2**	C	50	24	94	21100	19200	23200	1.3
11[g,h]	(±)-**2**	C	47	36	78	16400	36000	47000	1.4
12[i]	(±)-**2**	C	45	48	59	11900	11300	13900	1.3
13	(±)-**3**	C	50	48	80	17900	*j*	*j*	*j*
14[g]	(±)-**4**	C	47	24	80	16400	7300	16000	1.8

[a] Scale: 100−300 mg. $[M]_o = 50$ mM. [b] Initiators: A = MeOTs; B = *N*-methyl-2-phenyl-2-oxazolinium triflate; C = MeOTf. [c] Molar ratio. [d] Calculated M_n corrected for conversion. [e] GPC in THF with PS standard: M_p = peak MW. [f] $[M]_o = 10$ mM. [g] $[M]_o = 40$ mM. [h] Scale: 1.4 g. Temperature: 130 °C. [i] In benzonitrile. [j] Polymer insoluble after isolation.

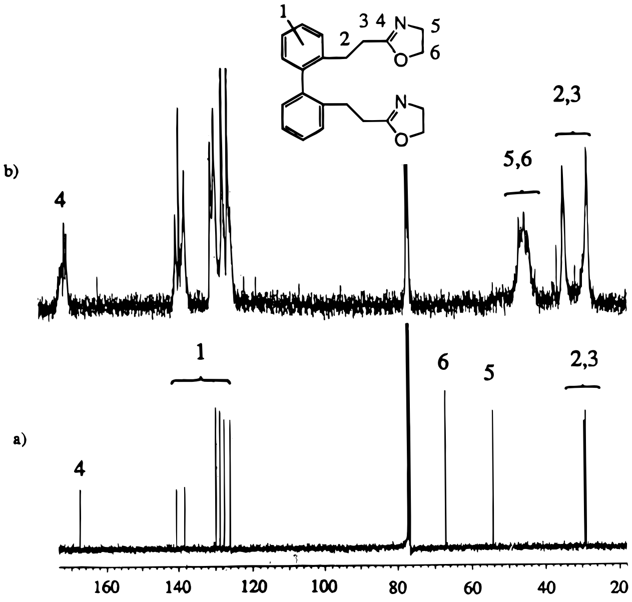
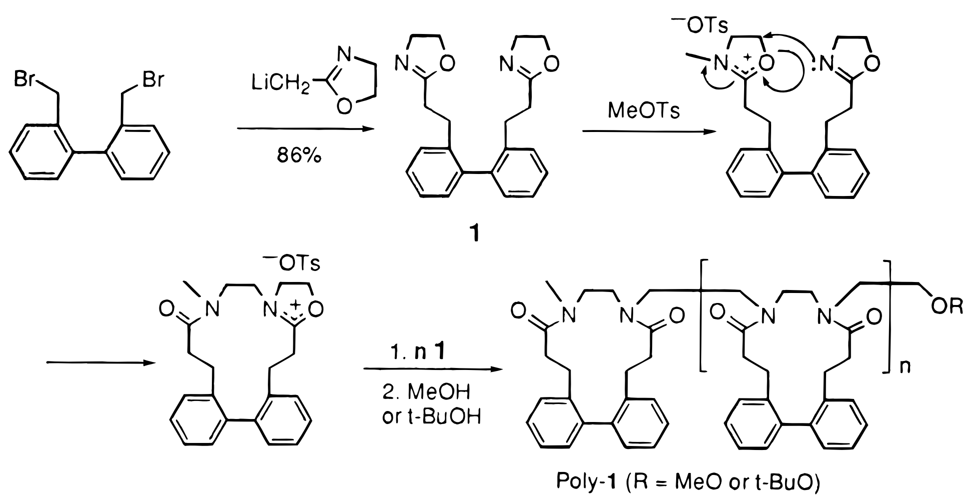


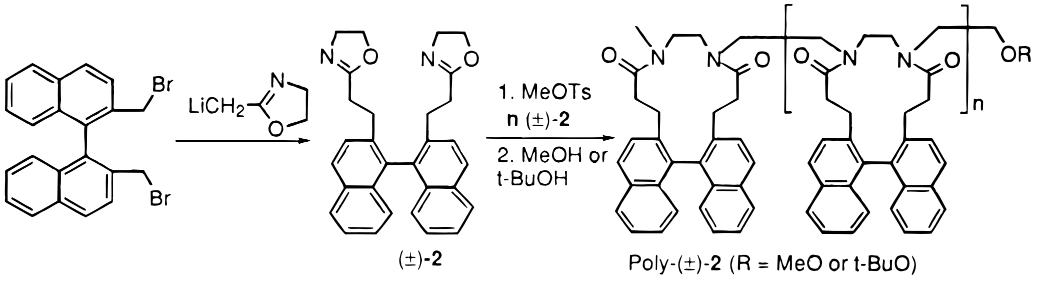
Figure 1. ^{13}C NMR (100.6 MHz) spectra of (a) monomer **1** and (b) poly-**1** recorded on a Varian XL-400 spectrometer ($CDCl_3$, internal standard).

Figure 1 compares the ^{13}C NMR spectra of monomer **1** and poly-**1**. The monomer signals at 54 (C-5), 67 (C-6) and 168 (C-4, C=N) ppm are absent in the spectrum of the polymer (Figure 1b). The corresponding polymer signals from C-5 and C-6 shifted upfield while that from C-4 shifted downfield and broadened, consistent with the oxazoline ring being opened. This was further confirmed by ^1H NMR spectroscopy.[19] The polymers were extremely soluble in solvents such as $CHCl_3$, CH_2Cl_2, THF, DMF, ODCB, and benzonitrile but insoluble in MeCN, methanol, acetone, diethyl ether, and hexanes. The high isolated yields (Table 1), the high solubility, and the complete absence of monomer signals in both proton and carbon NMR spectra support the cyclopolymerization mechanism as outlined for poly-**1** in Scheme 3. For poly-**1** (Table 1, runs 1−6), the molecular weight (MW) increased with increasing monomer:initiator molar ratio (M:I). However, at a very high M:I ratio (260:1), the GPC trace showed the presence of a small amount of higher MW material which may indicate the presence of side reactions.[20] For

Scheme 3



Scheme 4



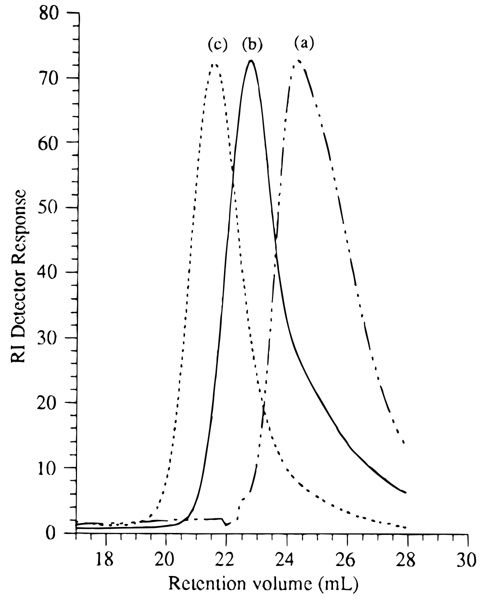


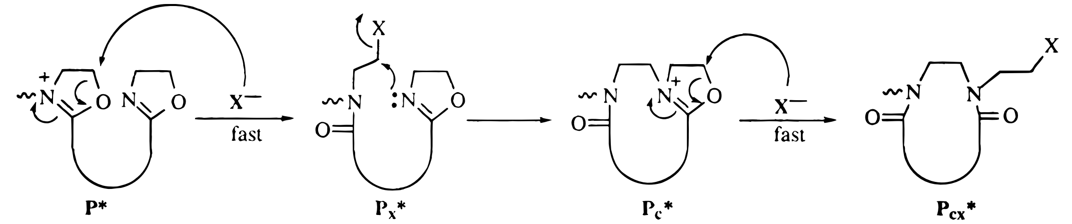
Figure 2. Gel permeation chromatograms of poly-(±)-**2** for different monomer:initiator molar ratios: (a) 13:1 (Table 1, run 7); (b) 48:1 (Table 1, run 8); (c) 138:1 (Table 1, run 9).

the polymers with high polydispersity index (PDI = M_w/M_n), calculated MWs agreed better with peak molecular weights (M_p) than with M_n obtained by GPC (PS standard). This is because M_n is influenced by low molecular weight polymers whose presence in poly-**1** is evidenced by the long tailing in the low MW regions of the GPC plots.[19]

Scheme 4 depicts the polymerization of (±)-**2**. As can be seen from Figure 2, the MW of poly-(±)-**2** also increased with increasing M:I ratio (Table 1, runs 7–9). However, at a high M:I ratio (Table 1, run 9) the agreement between the calculated and observed MWs was less than observed for poly-**1** especially with MeOTs as the initiator. When MeOTf was used as the initiator (Table 1, run 10), the reaction became faster (took only 24 h compared to 5–7 days for MeOTs) and gave poly-(±)-**2** with narrow molecular weight distribution (MWD) (PDI = 1.3–1.4) in 94% yield. This is remarkable because [M] was only 10 mM for run 10 which is only one-fifth of that used for the MeOTs-initiated reactions. Except for the reaction performed on a 5- to 14-fold scale (Table 1, run 11), the calculated MWs correlated well with the observed M_n rather than with M_p (Table 1, Runs 10 and 12). A similar result was obtained when N-methyl-2-phenyl-2-oxazolinium triflate was used for polymerization of **1** (Table 1, run 6). However, the MWD was broader than observed for the MeOTf-initiated polymerizations of (±)-**2**. These results should be contrasted with the results obtained when MeI was used as initiator. The reaction was slow and gave only 47% yield of polymer after 5 days (Table 1, run 5).

The better results obtained with (±)-**2** compared to **1** is attributed to the more convergent nature of the binaphthyl group. This is due to the fact that the dihedral angle for **2** is restricted to values varying from 60–120° while unsubstituted biphenyl can assume dihedral angles from 0–180°. The more convergent the monomer is the closer the two polymerizable groups will be to each other. This will promote faster cyclization in the more convergent monomer. Furthermore, use of highly convergent groups should also minimize the entropic penalty that usually results from both bond localization (loss of internal rotation degrees of freedom) during cyclization, especially for formation of large rings, and loss of translational and rotational degrees of freedom. Consequently, the expected decrease in activation entropy will be less for cyclization than for linear intermolecular propagation.[16b,c] Hence, in the cyclopolymerization of the biaryldiylbis(oxazolines) the

Scheme 5



cyclization will predominate over linear propagation. This effect will be more pronounced for the more convergent binaphthyl monomers than for the biphenyl ones as has been observed above.

As stated in the Introduction and Rationale, participation of the bicyclic oxazolinium ion in the reaction as the propagating living end should increase k_p (due to ring strain release) relative to k_p' (Scheme 2) in order to compensate for reduction in rates under low [M] conditions. Maintaining ionic mechanism requires the use of the appropriate initiator. In ring opening cationic polymerization of oxazolines, ionic mechanism usually predominates if initiators that form relatively non-nucleophilic counterions, such as triflate and tosylate, are used.[18] If the counterion is very nucleophilic then it will compete effectively with the monomer for the quaternary oxazolinium ion. This is illustrated in Scheme 5: The competing counterion X^- reacts with P* to form the covalent species P_x* which can ring close to form P_c*. Once the ring-strained P_c* is formed it will react very fast with X^- to form P_{cx}* as the propagating species. Because P_{cx}* is a neutral species and unstrained, it will propagate more slowly than P_c*. Hence, halides, such as I^- and Br^-, should favor formation of covalent species as the propagating living end. As a result, the polymerization will be generally slower.[18] The results we obtained with the various initiators are consistent with the above rationalization. Triflate, the least nucleophilic anion, gave the fastest cyclopolymerization while I^-, the most nucleophilic, gave the slowest. Thus, through a combination of monomer convergence and a judicious choice of initiator, we have been able to successfully effect cyclopolymerization of bis(oxazolines).

It must be pointed out that even though the MWs obtained from GPC vs PS standard in THF were consistent among all samples tested and the GPC peak molecular weights corresponded closely to the expected molecular weights, PS might not be an appropriate MW standard for these polymers. Our efforts to obtain more accurate MWs by using universal calibration (UNICAL) with an on-line viscometer were not successful. The viscosities were very low (0.03−0.09 dL/g), possibly due to absorption of the polymers onto the walls of the viscometer. Consequently, the measured molecular weights varied widely. Efforts to obtain absolute molecular weights using GPC with on-line laser light scattering detector (LLS) gave very high M_w's that were 2−3 times higher than M_w's obtained by universal calibration but with low PDIs. For example a poly-**1** sample that gave $M_w = 35\ 000$ by UNICAL gave $M_w = 100\ 000$ (PDI 1.1) by the GPC/LLS method. Preliminary results obtained by varying the temperature suggested that the polymers might be aggregating in THF (*vide infra*).

MALDI-TOF techniques were used to obtain further MW information.[21] The spectrum (Figure 3) shows a broad peak and a low MW rise, both of which consisted of individual peaks interspaced by exactly one repeat unit mass. Analysis of the broad peak gave apeak maximum molecular weight $M_m = 54\ 000$ and M_n 79 800 (PDI 1.3). GPC performed on the same sample gave $M_p = 47\ 000$ and M_n 36 000 (PDI 1.4). The peak MWs differ by only 10−13% which suggests that GPC underestimates the M_n by about a factor of 2 as a result of the severe low MW tailing in the chromatogram, especially for samples with broad MWD. Therefore, the M_p's in the tables must be quite close to the actual MWs. The low MW species in the MALDI-TOF spectrum could be due to decomposition during the ionization process because very high laser power had to be employed in order to obtain any signal. A similar behavior has been reported for polymers with high PDIs.[22,23] In addition, it has been recognized that hydrophobic polymers desorb very poorly. All these factors combined to make the MW determination not straightforward. Further work is needed before we can fully understand these effects.

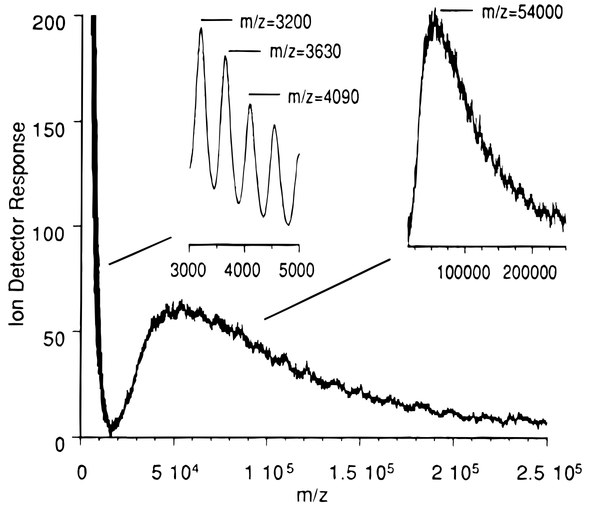
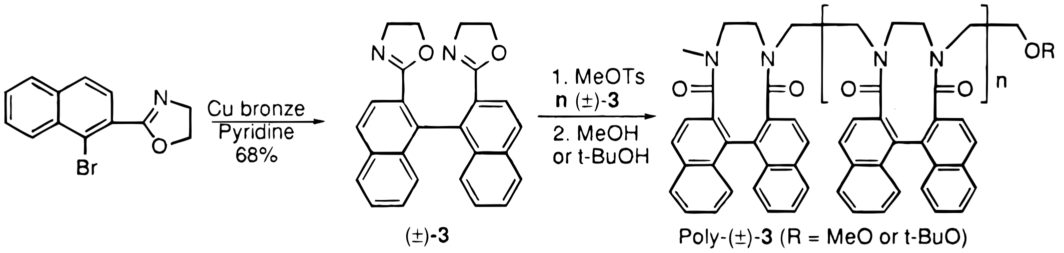


Figure 3. MALDI-TOF mass spectroscopic analysis of poly-(±)-**2** (Table 1, run 11). Insets: low and high molecular weight regions. The spectrum was obtained on a Finnigan Lasermat 2000 a using 2,5-dihydroxybenzoic acid matrix with NaBr added to the sample solutions.

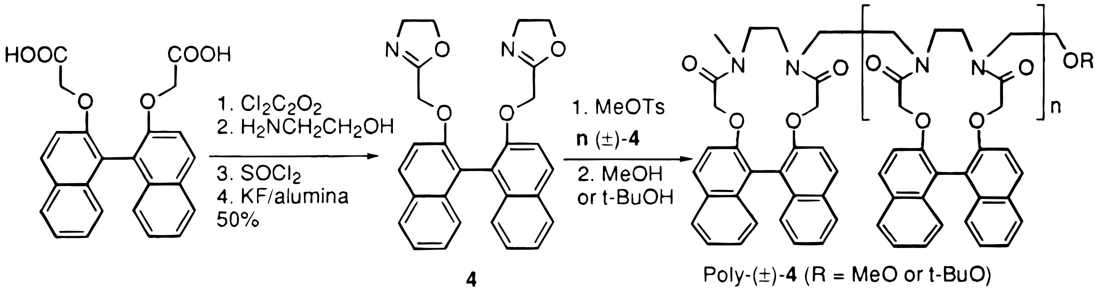
The reactivity of P_c* due to the increased ring strain will depend on the size of the ring formed during the cyclopolymerization. This in turn is determined by the length of the spacer between the two polymerizable groups. In order to determine the influence of the spacer between the aromatic nucleus and the oxazoline group on the reaction, monomer (±)-**3** (Scheme 6) was subjected to the same polymerization conditions using MeOTf as initiator (Table 1, run 13). The polymer remained soluble throughout the course of the reaction. However, upon precipitation from acetonitrile it became completely insoluble in all solvents tested. There are two possible explanations for these observations: (a) either a cross-linked polymer had formed or (b) the polymer was rigid and had a very high MW.

Examination of CPK molecular models revealed that the oxazoline groups in **3** are less convergent than those

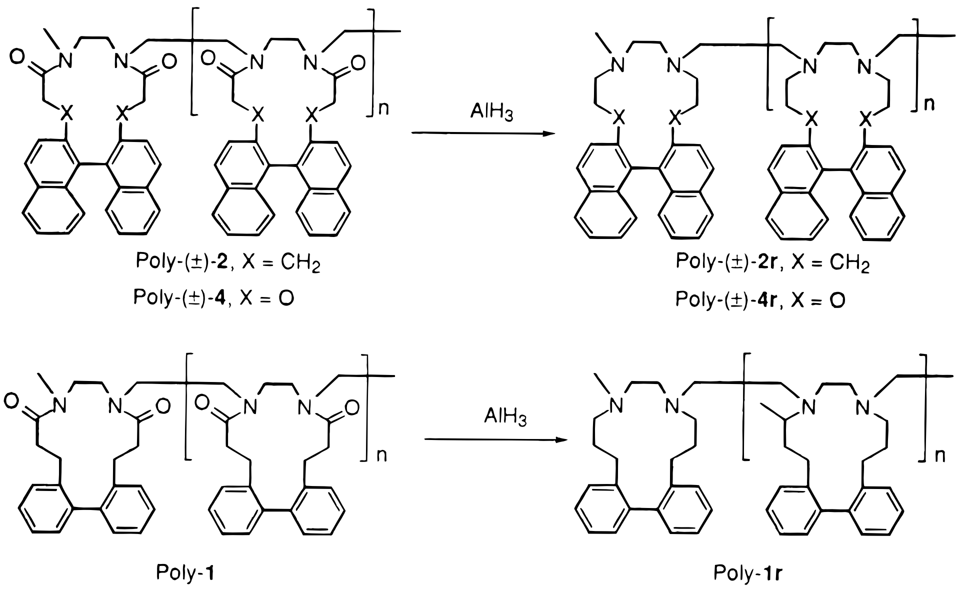
Scheme 6



Scheme 7



Scheme 8



in **2** due to steric congestion. Therefore, it is possible that this imposed further strain on the system especially during the cyclization which made the latter difficult and, consequently, not competitive with the linear intermolecular propagation. This would render $k_p'[M] > k_c$, a favorable condition for the formation of polymer with pendent unreacted monomer groups (P′*, Scheme 2) and cross-linking. However, because the ring-opening process required drastic conditions (high temperature, strong Lewis acids, or electrophiles), any cross-linking involving oxazoline cationic ring opening would more likely occur under the reaction conditions rather than under the neutral conditions and the ambient temperature used for the workup.

A more plausible cause for the insolubility may be formation of high MW and rigid polymer. Due to the increased ring strain as a result of the absence of a spacer (10-membered vs 14-membered macrocycle), the living bicyclic oxazolinium ion (P_c*, Scheme 2) would become more reactive and $k_p[M]$ would be much higher than $k_p'[M]$. This, in conjunction with the expected absence of chain transfer reactions due to **3** not having α-hydrogens,[20] would lead to a very high MW polymer. In addition, the absence of the flexible spacer should enhance the rigidity of the resulting polymer. These factors would combine to make the polymer insoluble in common organic solvents. The broad NMR spectra obtained for all the polymers described herein may indeed be a manifestation of their rigidity.

The influence of the spacer was further demonstrated by the results for the polymerization of a more flexible monomer ((±)-**4**, Scheme 7) which gave a soluble polymer (Table 1, run 14). The ^{1}H NMR spectrum of poly-(±)-**4** was extremely broad, suggesting that the polymer may be rigid.[19] This polymer is a precursor to a polymer whose repeating unit is a binaphthyl-containing aza-crown ether that may find applications as a metal ion receptor, a chiral host for organic compounds, and a packing material for chiral chromatographic separations.

The long reaction times and the very high temperatures necessitate that we determine if the reaction had any living character and to what extent it might be living. The most valid test for livingness is the dem-

Table 2. Three-Stage–One-Pot Reaction of 1 in *o*-Dichlorobenzene at 100 °C[a]

run no.	M:I[b]	time (h)	yield (%)	M_n[c] calcd	M_p[d] GPC	M_n[d] GPC	PDI
1	50	132	88	15400	20500	8300	2.1
2	100	312	94	32700	31500	11800	2.4
3	150	408	90	47000	52700	34200	2.4
4	158	408	89	48900	43700	28900	2.2

[a] Scale: 100–300 mg. Initiator: MeOTs. $[M]_0$: 50 mM. [b] Molar ratio. [c] Calculated M_n corrected for conversion. [d] GPC in THF with PS standard: M_p = peak MW.

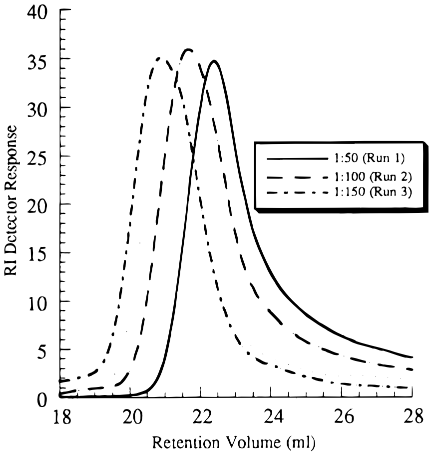


Figure 4. Gel permeation chromatograms (THF, PS standard) of homotriblock poly-**1** prepared by sequential monomer feed in a livingness test. The data are taken from Table 2, runs 1–3.

Table 3. Polymerization Results of (*S*)-2 and (*R*)-2 with MeOTs at 100 °C in ODCB

run no.	mon[a]	[mon] (mM)	M:I[b]	yield (%)	M_n[c] Calc	M_n[d] GPC	M_p[d] GPC	PDI	$[\alpha]_D^{25}$ [e] (deg)
1	(*S*)-**2**	50	102	84	38400	15800	24700	1.5	−300
2	(*S*)-**2**	50	44	97	19100	13000	26700	1.8	−273
3	(*S*)-**2**	30	20	92	8200	3500	11200	2.2	−250
4	(*S*)-**2**	10	1	99	500	1200	3000	2.0	−161
5	(*R*)-**2**	20	50	67	15000	8400	16000	1.6	+290
6	(*R*)-**2**	50	44	72	14200	7600	21900	2.3	+253

[a] Monomer. [b] Molar ratio. [c] Calculated M_n corrected for conversion. [d] GPC in THF with PS standard: M_p = peak MW. [e] Specific rotation per repeat unit in THF; $c = 1$).

onstration of a successful polymerization of block copolymers via sequential addition of monomers. However, because different monomers and their corresponding living polymers may have different reactivities toward one another, we chose to perform the livingness test by preparing different segments of the same homopolymer by sequential addition of several monomer batches and making sure that each monomer addition went to complete conversion. In this regard, a three-stage-one-pot synthesis of a *homotriblock* polymer was carried out using monomer **1** and MeOTs (Table 2) as follows: After the first batch of the monomer was completely polymerized, half of the reaction mixture was removed and quenched (Table 2, run 1). To the remaining half was added the appropriate amount of monomer, and the reaction mixture was allowed to polymerize to complete conversion (Table 1, run 2). The procedure was repeated to give the data for run 3. In every case a near-quantitative yield of the polymer was obtained. Despite the very long reaction times (5–17 days), the observed MWs agreed quite well with calculated ones. The MW increased as the M:I ratio increased, and as can be seen from the GPC plots in Figure 4, each homoblock disappeared completely in the chromatogram of the next higher homoblock. Furthermore, the MW characteristics of the final polymer (Table 2, run 3) resembled those of the polymer obtained in a continuous single batch polymerization using approximately the same M:I ratio (Table 2, run 4). Hence, it can be concluded that the cationic ring opening cyclopolymerization of bis(oxazolines) has living character.

Polymerization of Optically Active Monomer 2 and Its Chiroptical Properties. One important reason for selecting the 2,2′-disubstituted-1,1′-binaphthyl group in our monomer design is that it is known to remain optically and thermally stable up to 290 °C for many hours.[24] This is important for our goal toward the preparation of optically active polymers, especially since the oxazoline cyclopolymerization required high temperatures and long reaction times. Indeed, when optically active bis(oxazoline) monomers (*S*)-**2** and (*R*)-**2** were subjected to the same conditions used for the racemic monomers, soluble optically active polymers were obtained in high yields (Table 3). Their *mean residue* specific rotation (rotation per repeat unit) in THF were extremely high and appeared to be molecular weight dependent. For example, oligo-(*S*)-**2** (M_n 1200; approximate degree of polymerization, DP = 3) gave mean residue specific optical rotation $[\alpha]_D^{25} = -161°$ (Table 3, run 4), but the polymer with M_n of 15 800 (DP = 35) gave $[\alpha]_D^{25} = -300°$ (Table 3, run 1). The monomer showed a very low rotation in the same solvent ($[\alpha]_D^{25}$ +4°, THF, $c = 0.8$).[17]

The most important factors likely to influence optical activity in synthetic polymers are (1) the chirality of the repeat units and (2) the presence of a secondary structure, such as a helix. The extent to which each one contributes to the observed rotations of the polymers may be determined from the dependence of the *mean residue* rotation on molecular weight. If there is no contribution from a secondary structure, then the observed mean residue rotation will be independent of molecular weight. End group contribution to the optical rotation, which can be significant in oligomers that contain asymmetric carbons,[1] may be ignored because the chirality of the repeating unit of the cyclopolymers is derived from restricted rotation. The dihedral angle, which is the main factor controlling the optical activity of biaryl compounds, is not expected to depend on the MW of the polymer. Therefore, the fact that the observed rotation is MW dependent suggests that the optical rotations are influenced by some secondary structure, perhaps, in addition to the influence of the chirality of the repeat unit. The high optical rotations observed and their dependence on MW led us to conclude that the cyclopolymers adopt an ordered conformation, possibly a helix. This may partly account for the broad NMR spectrum obtained for the polymers. Even though the formation of ordered helical conformation was not directly observed, there are also not many other possible secondary structures available to synthetic polymers containing no hydrogen bonding functional groups that can contribute to the polymer's optical activity. Furthermore, there is evidence in the literature that suggests that appropriately substituted chiral poly(oxazolines) and their derivatives could adopt helical conformations.[25,26] The propensity to form ordered structures, such as helices, should be enhanced by the presence of the cyclic amide linkages in the cyclopolymer backbone. The cyclic amides should also increase the rigidity of the polymers, which should be further

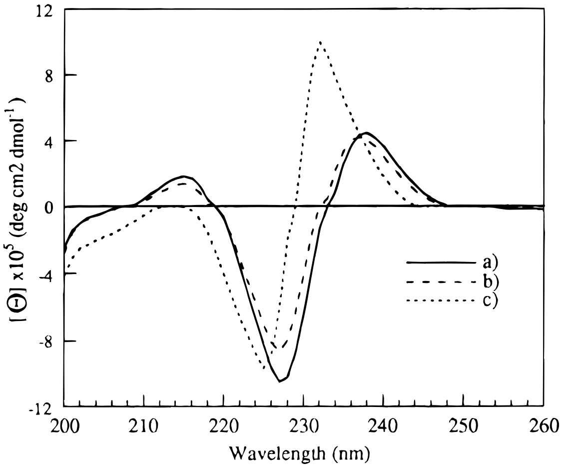


Figure 5. Circular dichroism spectra in THF of (a) poly-(*S*)-**2** (Table 3, run 1), (b) oligo-(*S*)-**2**, and (c) monomer (*S*)-**2**. Molar ellipticities were recorded per repeat unit at ambient temperature and sample concentration of 30 mg/dL. Cell path length: 0.01 cm.

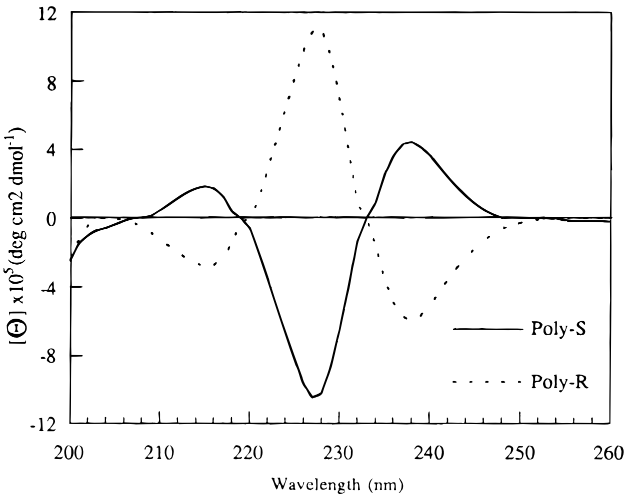


Figure 6. Circular dichroism spectra in THF of (a) poly-(*S*)-**2** and (b) poly-(*R*)-**2**. Molar ellipticities were recorded per repeat unit at ambient temperature and sample concentration of 30 mg/dL. Cell path length: 0.01 cm.

reinforced by the high rigidity and the steric bulk of the binaphthyl group. More work is, however, needed in order to establish the conformations of these novel cyclopolymers.

We attempted to obtain further information on the conformation of the polymers using circular dichroism (CD) spectroscopy.[27,28] Figure 5 shows the CD spectra of (*S*)-**2**, oligo-(*S*)-**2**, and poly-(*S*)-**2**. The spectrum of the monomer shows a negative Cotton effect at 225 and a positive one at 232 nm. The same Cotton effects in the spectrum of the polymer underwent slight bathochromic shifts to 228 and 238 nm, respectively, with the high wavelength peak showing a decrease in its mean residue molar ellipticity (ellipticity per repeat unit). The spectra of oligo-(*S*)-**2** ($[\alpha]_D^{25}$ −161°) and poly-(*S*)-**2** ($[\alpha]_D^{25}$ −300°) showed an additional positive Cotton effect at 215 nm attributed to the amide chromophore. The similarity among the overall profiles of the three spectra suggests that the absorption of the binaphthyl group is so strong as to dominate the spectra. Hence, either CD spectroscopy is not discriminative enough in these special cases to significantly distinguish between the conformations of the oligomer (DP = 7 from M_p or 3 from M_n) and the polymer (DP = 55 from M_p or 35 from M_n), or the oligomer is long enough to assume the same predominant conformation as the polymer. That the maximum molar ellipticity of the negative Cotton effect ($\lambda = 228$ nm) of the polymer increased by almost 25% over that of the oligomer may be an indication of the existence of an ordered conformation. The bathochromic shifts are very likely due to changes in the binaphthyl dihedral angle in going from the monomer to polymer. Upon cyclopolymerization of (*S*)-**2** the repeat units are 14-membered macrocycles which might lead to a reduction in the dihedral angle from the maximum of 120° available to the monomer to calculated values of 90−110°. The enantiomeric relationship between the conformations of poly-(*S*)-**2** and poly-(*R*)-**2** was confirmed by their CD spectra which showed the same Cotton effects but opposite in sign (Figure 6). This indicates that the cyclopolymerization occurred in a similar fashion for the two enantiomers giving polymers of the same but opposite sense conformation.

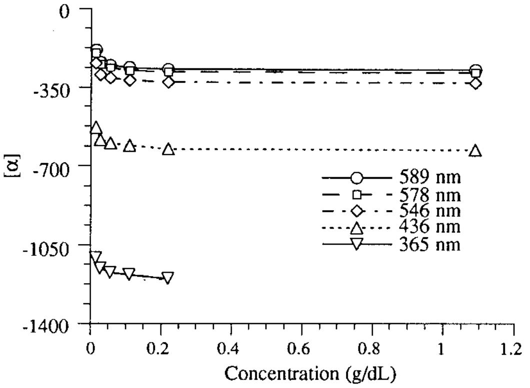


Figure 7. Plots of specific rotation [α] vs concentration (g/dL) for poly-(*S*)-**2** in THF at various wavelengths at 25 °C.

Table 4. Optical Rotations (deg) $[\alpha]_D^{25}$ ($c = 1$) of Poly-(*S*)-2 and Poly-(*R*)-2 in Different Solvents

wavelength	poly-(*S*)-**2**				poly-(*R*)-**2**[b]
(nm)	DMF	THF/MeOH[a]	THF	ODCB	THF
589	−249	−267	−258	−321	+253
578	−261	−280	−271	−325	+264
546	−302	−323	−313	−375	+307
436	−576	−614	−596	−715	+586

[a] Ratio: 5/1 (v/v). [b] $c = 0.25$.

Concentration and Solvent Effects. The specific rotations at all wavelengths appeared to be dependent on substrate concentration in THF (Figure 7) especially in the very low concentration range (<0.05 g/dL). This raises again the question as to whether or not the polymers were forming aggregates even though the effect was observed only at extremely low concentrations. Because one can not *a priori* predict the critical concentration for onset of aggregation, formation of aggregates could still occur even at the low concentrations used especially since the polymers have an outer hydrophobic aromatic shell.

Aggregation can be affected by the polarity of solvents. Table 4 shows specific rotations measured in different solvents at four different wavelengths. The specific rotations were very high in each solvent and appeared dependent on solvent polarity. Thus, ODCB gave the highest observed optical rotation ($[\alpha]_D^{25}$ −321°) while the most polar solvent DMF gave the lowest ($[\alpha]_D^{25}$ −248°). It is noteworthy that DMF, which is more compatible with the polar *N*-acylethylene imine backbone of the polymer and, therefore, should promote

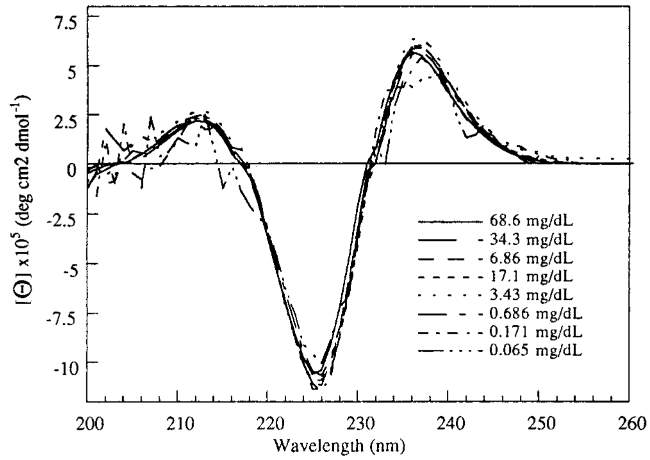


Figure 8. Circular dichroism spectrum of poly-(*S*)-**2** recorded in THF at different concentrations. Molar ellipticities were recorded per repeat unit at ambient temperature and sample concentration of 30 mg/dL. Cell path length: 0.01 cm.

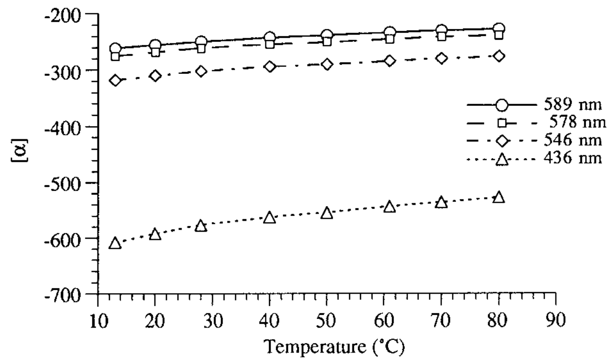


Figure 9. Plots of specific rotation [α] vs temperature at various wavelengths for poly-(*S*-**2** (Table 3, run 2). (c = 1.16 g/dL, DMF).

Table 5. Thermal Properties of Polymers 1−4

polymer	M_n[a] GPC	PDI	T_{onset}[b] (°C)	T_g[c] (°C)
poly-**1**	5500	1.3	419	207
poly-(±)-**2**	4500	1.5	417	278
poly-(±)-**2**	36000	1.4	415	292
poly-(*S*)-**2**	17800	1.5	422	302
poly-(±)-**3**	ND[d]	ND[d]	423	*e*
poly-(±)-**4**	7300	1.8	370	250

[a] GPC in THF with PS standard. [b] Onset of decomposition temperature under N_2 (TGA, 20 °C/min). [c] From DSC (10 °C/min). [d] Not determined. [e] No T_g below 420 °C.

aggregation less than the apolar ODCB, also gave the lowest rotation. This concentration dependence disappeared completely when the rotation was measured in THF/MeOH (5/1, v/v) although the rotation still remained high (Table 4, column 3). The results are not inconsistent with aggregate formation and suggest that any aggregation occurring in THF was broken by the addition of a strongly hydrogen bonding solvent.

In order to probe further the above effects, we performed CD measurements on solutions of poly-(***S***)-***2*** at concentrations varying from 70 μg/dL to 69 mg/dL in THF. This concentration range overlaps sufficiently well with that used for optical rotation measurements (10−1100 mg/dL)). As can be seen in Figure 8, the CD spectra remained unchanged over the entire concentration range.[29] Even though it is tempting to conclude that the CD results suggest no aggregation, the results are more likely a consequence of the CD spectra of the polymers being controlled by the dihedral angle of the binaphthyl group, which should not be affected by aggregation.

Effect of Temperature. The temperature dependence of the optical rotations of the polymers obeyed the simple second order polynomial equation normally used to describe the temperature dependence.[30] Over the temperature range studied in DMF (Figure 9) no abrupt changes in the optical rotations were observed, which indicates that no heat-induced conformational changes in the polymer occurred over the temperature range studied. The temperature was kept below 100 °C because we observed that when solutions of the optically active polymer were kept at elevated temperatures for prolonged periods of time they showed some discoloration and loss of optical activity. For example, when the polymer sample with $[\alpha]^{25}_{D}$ −321° was heated in ODCB at 130 °C for 15 days the optical rotation decreased irreversibly to −246°. In addition, a considerable portion of the sample became insoluble suggesting that some decomposition might have occurred.

Reduction of Poly-1 and Poly-2 and Interactions with Cu^{2+} Ions. In order to prepare materials with receptors for metal ions and investigate how complexation and the absence of the backbone cyclic amides will affect the polymers' chiroptical properties and conformations, we reduced the bis(oxazoline) cyclopolymers using AlH_3.[31−33] The intensity of the C=O absorption in the IR spectrum (not shown) decreased significantly upon reduction but did not disappear completely suggesting incomplete reduction. Elemental analyses suggested that the extent of reduction varied from 50−70%. The optical rotation of the reduced polymer was significantly lower than that of the unreduced material. For example, poly-(***S***)-**2** with $[\alpha]^{25}_{D}$ −273° (c = 1, THF) gave $[\alpha]^{25}_{D}$ −172° (c = 1, THF) upon reduction. This is consistent with the chain becoming flexible as a result of reducing the amides. A more flexible chain is less likely to adopt an ordered conformation in solution. Hence, any prior contribution of secondary structure to the optical activity of the original polymer will be lost, and the observed rotations will be lower since the chirality of the repeat unit will be the main contributor to the reduced polymers optical activity, if not the only one.

It was reported that poly(*N*-(4′-decyloxybenzyl)ethyleneamine) (obtained from the corresponding poly(oxazoline) by reduction) showed the presence of a liquid crystalline phase upon copper(II) binding.[33] Hence, a methylene chloride solution of our partially reduced polymers was used to extract an aqueous solution of $Cu(NO_3)_2$. The solutions turned dark green within minutes in the case of the reduced polymers. In contrast, the unreduced polymer solutions, in a control experiment, did not show any coloration. This indicates that the Cu^{2+} ions have been bound to the polymer since $Cu(NO_3)_2$ is completely insoluble in methylene chloride. In order to obtain information on the extent of binding, elemental analyses were performed. The stoichiometry of binding was, thus, estimated to be three to four Cu^{2+} ions per five repeat units, assuming that only the reduced segment was responsible for the binding. However, the Cu^{2+}-bound partially reduced polymers showed no evidence of liquid crystallinity when examined by DSC.

Thermal Properties. The thermal properties of the unreduced polymers are summarized in Table 5. The TGA results showed that the polymers are thermally stable with onset of decomposition temperatures be-

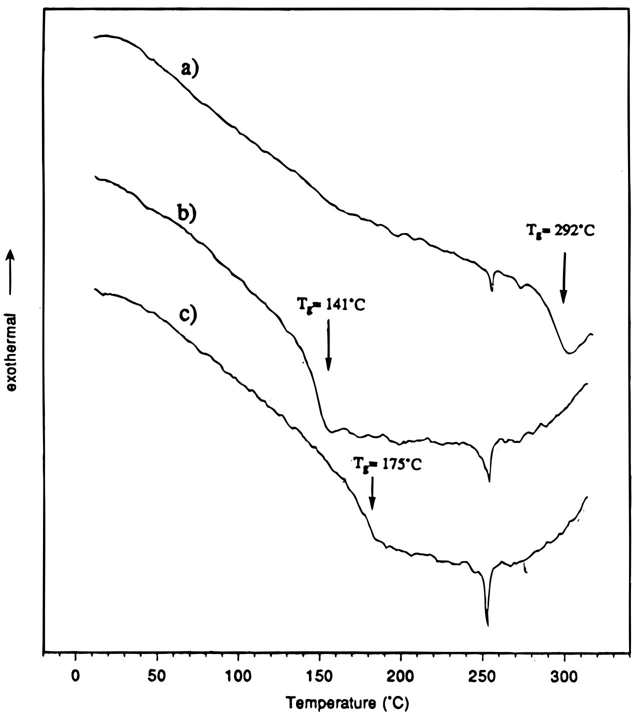


Figure 10. DSC plots for (a) poly-(±)-**2**, (b) poly-(±)-**2r**, and (c) Cu^{2+} complex of poly-(±)-**2r** recorded at 20 °C/min under N_2. Peak at ~255 °C is an instrumental artifact.

tween 400 and 430 °C with the exception of poly-(±)-**4** (T_d 370 °C) which had oxygen atom directly attached to the binaphthyl ring. DSC analyses gave high glass transition temperatures (T_gs) but no melting transition. The T_g increased as the MW increased and the highest T_g recorded for poly-(±)-**2** was 292 °C at $M_n = 36\,000$. The optically active polymer showed slightly higher T_g (302 °C) than that of the polymer from the racemic monomer. The biphenyl polymer (poly-**1**) gave the lowest T_g (207°), which may be attributed to its lower rotational barrier and smaller steric bulk compared to the binaphthyl group. The more flexible poly-(±)-**4** gave T_g at 250 °C while rigid poly-(±)-**3** gave no T_g below 420 °C. Thus, the T_gs decrease in the poly-(±)-**3** >> poly-(*S*)-**2** > poly-(±)-**2** > poly-(±)-**4** > poly-**1**, which reflects the increasing order of flexibility in these polymers.

Figures 10 and 11 show representative DSC and TGA traces for poly-(±)-**2**, poly (±)-**2r** (reduced poly-(±)-**2**), and poly-(±)-**2r**Cu^{2+}. As can be seen from the results summarized in Table 6, the T_gs for all the polymers decreased upon reduction. This is consistent with their expected increased flexibility upon the loss of the rigid amide group from the polymer backbone. In the presence of Cu^{2+} ions, however, the T_g increased again, which implies some decrease in the rotational degrees of freedom due to interactions with the metal ion. The decomposition temperatures of the reduced polymers are lower than those of the unreduced ones (Figure 11). In the presence of Cu^{2+} ions, the reduced polymers showed a slight increase in the onset of decomposition temperatures (except poly-(*S*)-**2r**) which parallels the DSC results.

Summary and Conclusions

We have successfully carried out cationic ring opening cyclopolymerization of biaryl bis(oxazolines) (**1**−**4**) using a variety of electrophilic initiators to give soluble polymers in high yields and without any pendent monomer groups. The choice of monomers and initiators were based on cyclopolymerization principles which call for a judicious balance of different rates. The results of our cyclopolymerizations can be rationalized by the minimization of activation entropy loss due to the rigidity built into our designed monomers. This causes the cyclopolymerization to win over the linear intermolecular propagation. The optically active cyclopolymers showed very high specific optical rotations per repeat unit that varied between $[\alpha]_D^{25}$ −248° and $[\alpha]_D^{25}$ −321° depending upon the solvent. In contrast, the corresponding monomers and oligomers showed much lower specific optical rotations. From the results of circular dichroism spectroscopic studies performed on both oligomers and high molecular weight polymers, the high optical rotation per repeat unit, and its dependence on molecular weight, we conclude that the chiral polymers adopt ordered conformations in solution.

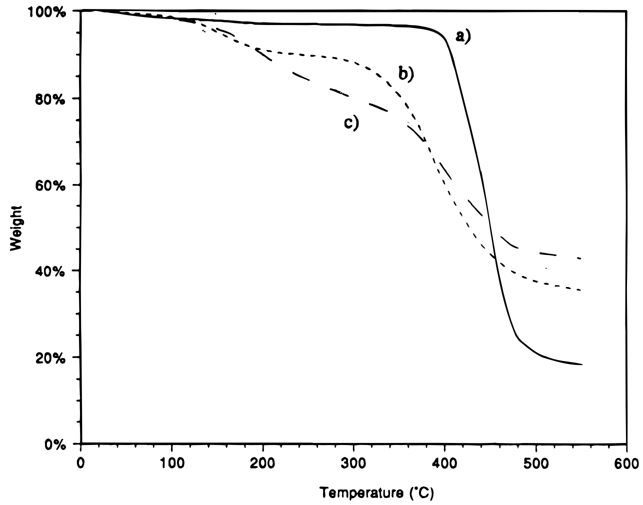


Figure 11. Thermogravimetric analysis (TGA) for (a) poly-(±)-**2**, (b) poly-(±)-**2r**, and (c) Cu^{2+} complex of poly-(±)-**2** recorded at 20 °C/min under N_2.

Table 6. Thermal Properties of the Reduced Polymers and Effect of Cu^{2+}

sample	T_{onset}[a] (°C)	T_g[b] (°C)
poly-**1r**	343	72
poly-**1r**Cu^{2+}	362	100
poly-(±)-**2r**	350	141
poly-(±)-**2r**Cu^{2+}	362	175
poly-(*S*)-**2r**	376	138
poly(*S*)-**2r**Cu^{2+}	350	180

[a] Onset of decomposition temperature under N_2 (TGA, 20 °C/min). [b] From DSC (10 °C/min).

Upon reduction using AlH_3, polymers that are essentially repeating units of nitrogen-containing heteromacrocycles were obtained. Dichloromethane solutions of the reduced polymers readily extracted $Cu(NO_3)_2$ from aqueous solutions to give complexes whose stoichiometry, estimated from elemental analyses, varied from three to four Cu^{2+} ions per five reduced repeating heteromacrocycles. The Cu^{2+}-containing cyclopolymers gave a higher T_g than those obtained for the reduced polymers, which, in turn, gave much lower T_gs than did the corresponding unreduced polymers. The unreduced cyclopolymers are all thermally robust with onset temperatures of decomposition > 400 °C and T_gs between 200 and 302 °C. These are consistent with the expected changes in the relative rigidity of the polymers. Our results suggest that, through a rational monomer design and judicious choice of initiators, cyclopolymerization can be made a viable method for generation of polymeric hosts of controlled structure with high density of binding sites since every repeat unit carries the macrocyclic ionophore. Further work involving preparation of hosts with different ring sizes, detailed complexation studies, mechanistic work especially with respect to chain transfer, evaluation of solution properties, and conformational analyses are in progress.

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Supporting Information Available: Proton NMR spectra (200 MHz) in $CDCl_3$ for monomers **1**−**4** and poly-**1,** poly-(±)-**2**, and poly-(±)-**4** and GPC plots for poly-**1** showing dependence of MW on monomer to initiator molar ratio (5 pages). See any current masthead page for ordering information and Internet access instructions.

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