



Highly Isotactic Optically Active Methacrylate Polymers By Free Radical Cyclopolymerization

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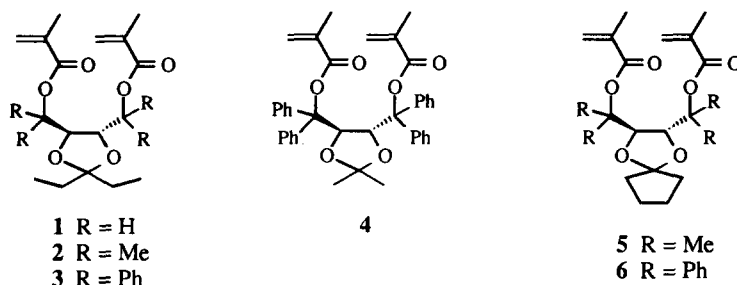
Abstract: Isospecific free radical cyclopolymerization of tartrate-based monomers gives polymers with very high optical rotations. Circular dichroism and polarimetric measurements suggest the polymers are rigid and ordered. Their high resistance to solvolysis suggests potential applications in chiral chromatography.
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Introduction

Free radical polymerization is one of the most versatile methods for polymer synthesis. It is applicable to a large variety of monomers and requires less stringent conditions compared to ionic and step-growth polymerization methods. This, together with the fact that polymer properties depend partly on their stereochemistry,¹ stimulated research directed to control of stereochemistry in free radical polymerization. In fact, efforts in this area date back to Staudinger who first suggested that tertiary carbons in vinyl polymer backbones could assume two different configurations.² The early efforts were uniformly unsuccessful,³ but confirmed the notion that stereochemical control of free radical reactions might be generally more problematic than that of other types of reactions even in small molecule synthesis.⁴ This is illustrated for free radical polymerization of methyl methacrylate where the ratio of rate constants for syndiotactic and isotactic placements, k_s/k_i , is only 1.1 at 0 °C.^{5a} The unsuccessful early attempts in stereospecific free radical polymerization led Pino and Suter to conclude that stereochemical control in free radical polymerization was not promising and could only be realized in the solid state by formation of inclusion complexes which has been quite successful in obtaining highly stereoregular polymers.^{5,6} Although the advent of high resolution NMR spectroscopy has also stimulated extensive research into understanding the stereochemistry of polymers,^{7,8} significant stereochemical control of free radical polymerization has not been achieved until recently.⁹⁻¹⁵ However, with the exception of Porter's chiral auxiliaries,^{15,16} many of the examples of isospecific free radical polymerization in solution are confined to systems involving bulky methacrylates.¹⁰⁻¹⁴

Cyclopolymerization,¹⁷ an alternating intramolecular cyclization and intermolecular propagation, offers an attractive alternative approach since cyclization reactions are generally more stereoselective than acyclic ones.¹⁸ In fact, the past decade has witnessed an unparalleled development of stereochemical control in polymer synthesis via cyclopolymerization leading to well-defined macromolecular architectures not only in free radical but also in anionic, cationic, Ziegler-Natta and group transfer polymerizations.¹⁹⁻³¹ Examples include polymerization of diolefins using Ziegler-Natta catalysts;²⁰ cationic polymerization of divinyl ethers,²¹ bisoxazolines,²² diepoxides,²³ and divinyl acetal;²⁴ group transfer polymerization,²⁵ and free radical polymerization²⁶⁻²⁸ of (meth)acrylates; Ni- or Pd-mediated polymerization of diisocyanides;²⁹ and free radical polymerization of templated styrene monomers.^{30,31}

Chart 1



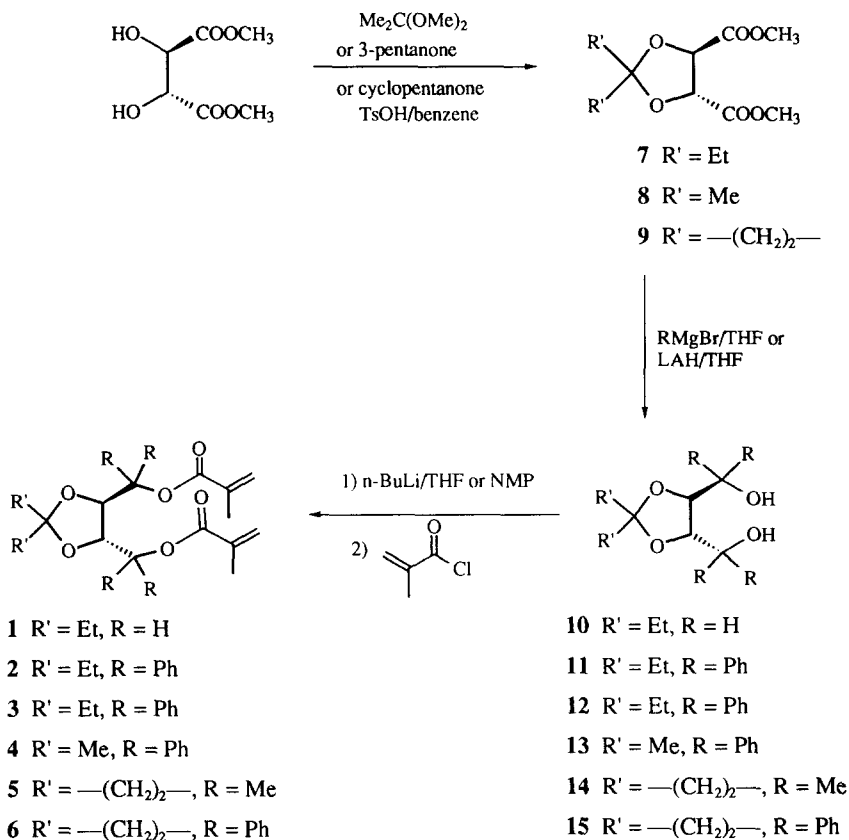
As part of our continuing effort to control polymer architecture, we have been studying the cyclopolymerization of racemic and optically active methacrylates in which we have incorporated asymmetric templates.^{25,26} Earlier preliminary results from our laboratory suggested that cyclopolymerization could be used to obtain optically active and, possibly, helical polymers.²⁶ Such polymers have potential applications for molecular recognition and chiral catalysis.^{14,32} We report herein the detailed synthesis and free radical cyclopolymerization of optically active monomers **1** - **6** (Chart 1) that incorporate tartrate-based templates. The objectives are to use templates to induce stereochemistry into vinyl polymers, elucidate the various factors that affect stereochemical control in template-assisted cyclopolymerization, and lay the ground work for a rational design of chiral polymers from vinyl monomers. Monomers **1** - **3** which contain the same acetal protecting group but α -substituents of varying sizes will permit examination of the influence of steric bulkiness on the course of the reaction. A similar design is shown in monomers **5** and **6**. Monomers **3**, **4**, and **6** contain identical α -substituents but different acetal protecting groups and hence, together with **2** and **5**, will help determine if the protective group has any effect on stereochemical control of the reaction. Additionally, the bulkiness of the ester groups in monomers **2** - **6** are expected to facilitate faster intramolecular cyclization relative to intermolecular propagation thereby preventing crosslinking.

Results and Discussion

Monomer Synthesis and Polymerizations. All monomers were synthesized from the corresponding diols³³ by reaction with methacryloyl chloride in the presence of *N*-methylpyrrolidone (NMP) (monomer **1**)^{27b} or *n*-BuLi (monomers **2** - **6**)³⁴ (Scheme 1) in isolated, chromatographically pure yields of 57-74 % (Table 1). Conventional synthetic routes to esters, such as basic conditions in the presence of triethylamine, pyridine, 4-dimethylamino pyridine, sodium hydride, or AgCN,³⁵ failed to give the desired products, possibly due to steric congestion. It is interesting to note that whereas **3**, **4** and **6** with α -phenyl

substituents gave negative optical rotations similar in magnitude and dependent upon the solvent, **2** and **5** with α -methyl substituents gave positive optical rotations which appeared to be independent of solvent. Compound **1** with the lowest chiral barrier also gave the lowest optical rotation.

Scheme 1



Polymerization was performed in toluene at 60 °C with AIBN as initiator under an argon atmosphere. The conditions and results are summarized in Table 2. The entire polymerization system in each case was homogeneous and the resulting polymer was isolated as a white powder in good yields. The polymers were all soluble in common organic solvents such as chloroform, toluene, and THF. This, coupled with the absence of unreacted pendent vinyl groups in the ^1H NMR spectra (Figure 1), was taken as evidence for the polymerization occurring exclusively via cyclization. The characteristic signals of the methacrylate vinyl groups in the 5-6 ppm region completely disappeared in the polymer's spectrum (Figure 1B).

Monomer **1** polymerized only at low initial monomer concentrations. At higher monomer concentration (0.10 M), the polymer contained traces of unreacted pendent vinyl groups. This result is similar to that reported for the polymerization of bis((methacryloyloxy)methyl)-1,1'-binaphthyl which also contained no α -substituents.²⁵ In contrast, the monomers with sterically hindered α -substituents polymerized cleanly even at higher concentrations. Thus, monomer **3** gave polymer without any evidence of unreacted pendent vinyl groups at initial concentrations between 0.05 - 0.20 M in both toluene and THF.

Table 1. Yields and optical rotations of monomers **1** - **6**.

Monomer No.	% Yield	$[\alpha]^{25}_D$ (CHCl ₃ , c 1.0)	$[\Phi]^{25}_D$ (CHCl ₃ , c 1.0) ^a	$[\alpha]^{25}_D$ (THF, c 1.0)
1	60	-3	-10	ND ^b
2	66	+34	+130	ND ^b
3	57	-105	-662	-123
4	74	-102	-615	-129
5	67	+57	+217	+55
6	66	-109	-685	-128

^a Molar rotation. ^b Not determined.

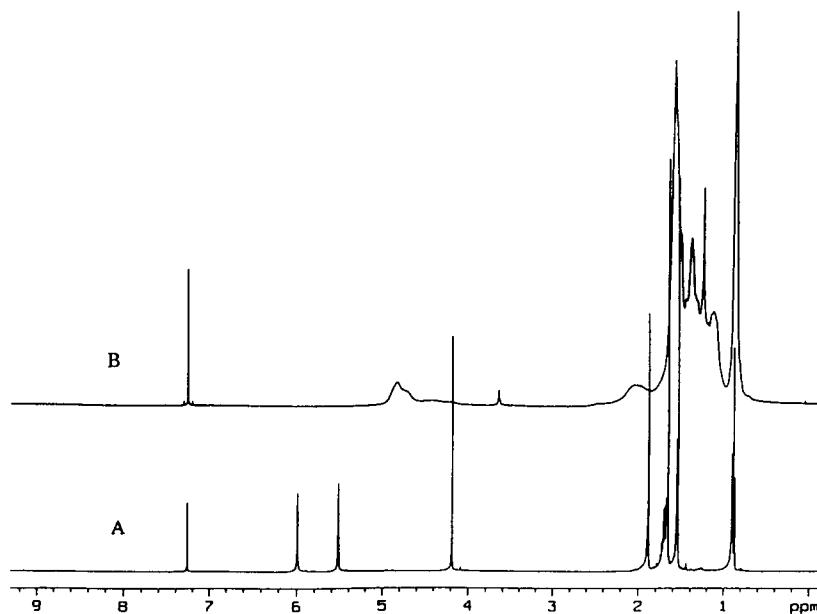


Figure 1. 400 MHz ¹H NMR spectra of (A) monomer **2** and (B) poly-**2** in CDCl₃.

These results, together with our earlier finding that **4** could be polymerized at concentrations up to 0.43 M, an unusually high concentration for the polymerization of a difunctional monomer,²⁶ suggest that the sterically hindered α -substituents impose adequate convergence on monomers **2** - **6**, enabling them to undergo faster intramolecular cyclization relative to intermolecular propagation. The relative effectiveness of the substituents in facilitating ring closure could be determined from the extent to which each one induced stereochemistry into the corresponding polymers as discussed below.

Table 2. Conditions and results of cyclopolymerization of monomers **1** - **6** in toluene.^a

Poly-	[M] ₀ (M)	Yield (%)	M _n x 10 ⁻³	M _w x 10 ⁻³	[α] ²⁵ _D (CHCl ₃ , c 1.0)	[Φ] ²⁵ _D ^b (CHCl ₃ , c 1.0)	[α] ²⁵ _D (THF, c 1.0)
1 ^d	0.10	71	31.5	127.3	+38	+124	ND ^c
	0.025	62	47.6	93.8	+40	+131	ND ^c
2	0.20	72	36.4	99.0	+16	+61	ND ^c
3	0.20	71	11.6	50.0	-210	-1325	-236
3 ^e	0.05	63	9.2	18.9	-196	-1236	-205
3 ^f	0.20	86	16.1	39.0	-199	-1255	-217
4 ^g	0.05	36	7.1	11.5	-211	-1272	-223
5	0.05	64	7.5	20.0	-3	-11	-1
6	0.10	81	4.3	28.6	-176	-1107	-198

^a Polymerization time 24 h; poly-**2** and **5** were precipitated from methanol; others were precipitated from hexane. ^b Molar rotation. ^c Not determined. ^d Polymer contained trace amounts of unreacted pendent vinyl groups. ^e Reaction time 41 h. ^f Reaction in THF. ^g Reaction time 10 h.

Stereochemistry. The stereochemistry of the polymers was determined from ¹H NMR (400 MHz) analyses of PMMA derived from the original cyclopolymer. Poly-**1**, poly-**2** and poly-**5** were hydrolyzed by *t*-BuOK/H₂O in dry THF,³⁶ while poly-**3**, poly-**4**, and poly-**6** were hydrolyzed by concentrated H₂SO₄ in methanol.²⁶ The poly(methacrylic acid) obtained in each case was methylated using diazomethane.³⁷ The tacticity composition was determined by the measurement of isotactic (mm), heterotactic (mr), and syndiotactic (rr) triads using the α -methyl proton resonances at δ 1.2, 1.0, and 0.8 ppm, respectively, and the results are summarized in Table 3.

The triad tacticity distribution of poly-**1** (mm/mr/rr = 15/51/34) (Figure 2B) is similar to the reported value of 12/49/39 for a similar bismethacrylate monomer (R' = Me, R = H).^{27a} The observed isotacticity increased with increasing bulkiness of the monomer, suggesting that the larger the α -substituent the more effective it is in enforcing the *cis* geometry during ring closure. Thus, poly-**3**, poly-**4**, and poly-**6** with α -phenyl groups showed higher isotacticity than did poly-**2** and poly-**5** both of which contained α -methyl groups and, in turn, showed higher isotacticity than poly-**1**. As the polymer became more isotactic, signals for the diastereotopic methylene protons became better resolved indicating that these protons are adjacent to a chiral center of one predominant configuration (Figure 2A). The high *meso* dyads obtained for poly-**3**, poly-**4** and poly-**6** suggest

that cyclization is stereospecifically *cis* and intermolecular addition occurs preferentially in a *meso* fashion. This is incidentally the highest isotacticity obtained in a free radical cyclopolymerization and represents the first example of free radical isospecific cyclopolymerization. The nearly identical triad tacticities for the polymers having the same protective acetal groups (poly-3, poly-4, and poly-6; poly-2 and poly-5) suggest that the acetal protecting groups in the monomers are too far removed from the reactive centers to have any effect on the stereochemistry of the polymers. Hence, through a rational monomer design, free radical cyclopolymerization has been used to prepare highly isotactic polymers.

Table 3. Tacticity of PMMA derived from the original cyclopolymer.

Polymer	Triad Tacticity (%)			<i>meso</i> dyad ^a	First-Order Markov Probabilities		
	<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>f_m</i>	<i>P</i> (<i>m/r</i>)	<i>P</i> (<i>r/m</i>)	ΣP
1	15	51	34	0.41	0.63	0.43	1.06
2	25	48	27	0.49	0.49	0.47	0.96
3	83	12	5	0.89	0.07	0.55	0.62
4	84	10	6	0.89	0.06	0.45	0.51
5	24	44	32	0.46	0.48	0.41	0.89
6	82	13	5	0.89	0.87	0.57	0.64

$$^a f_m = f_{mm} + 0.5f_{mr}.$$

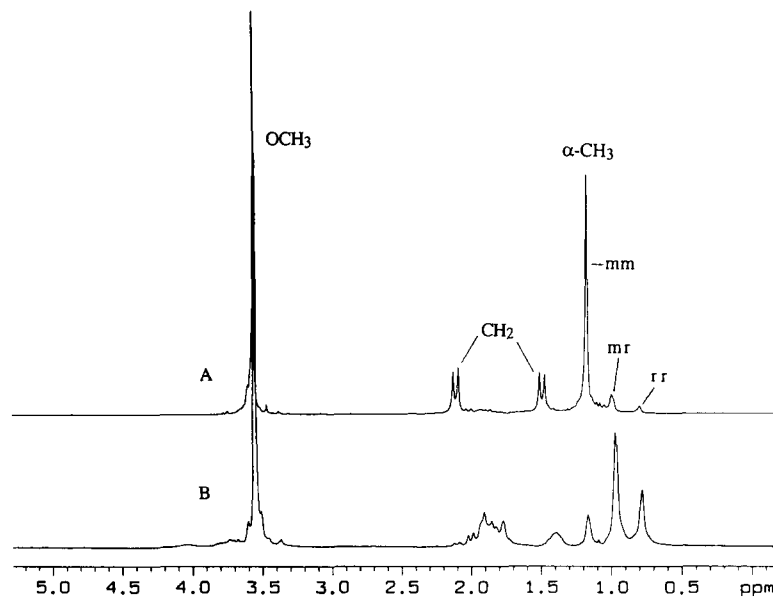


Figure 2. 400 MHz ¹H NMR spectrum of PMMA derived from (A) poly-6 and (B) poly-1 in CDCl₃.

In order to gain further insight into the nature of the stereochemical control, first order Markov probabilities ($P(mr)$ and $P(rm)$) were calculated. As can be seen from Table 3, the sum of the probabilities (ΣP) is close to unity for poly-1 and poly-2 and deviates slightly from unity for poly-5, suggesting that the stereochemical control in the less hindered systems is Bernoullian and, therefore, independent of the nature of the penultimate monomer unit. In contrast, the values for poly-3, poly-4 and poly-6 deviate significantly from unity, suggesting that the stereochemical control is dependent on the penultimate unit and possibly on the conformation of the backbone.

Table 4. Tacticity of poly-3 obtained under various conditions.

Temp (°C)	[M] (M)	Solvent	Triad Tacticity (%)		
			<i>mm</i>	<i>mr</i>	<i>rr</i>
80	0.2	Toluene	86	10	4
60	0.2	Toluene	83	12	5
45	0.2	Toluene	85	11	4
30	0.2	Toluene	86	11	3
60	0.2	THF	85	11	4
60	0.05	Toluene	86	10	4

Okamoto *et al.* found significant effects of solvent, monomer concentration and temperature on the tacticity in the free radical polymerization of trityl methacrylate (TrMA).¹² To explain their findings, they suggested the participation of at least two types of helical propagating radicals having different probabilities of *meso* monomer addition. In contrast, we found that solvent, concentration, and temperature exerted no influence on tacticity in the cyclopolymerization (Table 4). One possible explanation is that the propagating radicals in the cyclopolymerization are too rigid to assume the type of different structures postulated for TrMA polymerization. Kamachi *et al.* have studied the polymerization of TrMA by ESR spectroscopy and suggested that the isotactic placement might be controlled by the rigidity of the bulky TrMA radical.³⁸ The structural similarity among monomers 3, 4, 6 and TrMA and the high isotacticity obtained in our system are consistent with such a postulate. As observed in free radical polymerization of TrMA, the bulkiness of the ester groups prevented syndiotactic placements and forced the addition mode of the monomer to be more favorable for an isotactic propagation.

Chiroptical Properties. The chiroptical properties and secondary structures of the polymers were probed by optical rotation measurements (Tables 1 and 2) and circular dichroism (CD) spectroscopy. The polymers from the bulky monomers showed higher optical rotations than did their corresponding monomers. In contrast, poly-2 showed lower optical rotation than its monomer while poly-1 and poly-5 gave optical rotations opposite in sign to those of their corresponding monomers. The bulkier and the more rigid the polymer is, the higher is the rotation. Thus, poly-3, poly-4 and poly-6, the bulkiest and the most highly isotactic polymers,

gave the highest optical rotations with molar rotations, $[\Phi]^{25}_D$, varying between -1100 and -1325. High optical rotation and isotacticity can be an indication of secondary structures.

Figure 3 shows the CD spectra of poly-3, poly-4 poly-6 and their corresponding monomers. The spectra of the polymers are quite similar which, coupled with the fact that the polymers also have similar high tacticities, suggests that all these polymers adopt similar conformations in solution. The similarity among the spectra of the polymers and among those of the monomers provide further evidence that the acetal protecting groups in the structures have no effect on the stereochemistry and conformation of the polymers. Based on the observed chiroptical properties and the high isotacticity, poly-3, poly-4 and poly-6, indeed appeared to be rigid and ordered. Moreover, since the steric bulkiness of these monomers is similar to that of TrMA which has been reported to give one-handed helical polymers,³⁹ it is likely that poly-3, poly-4 and poly-6 also assume helical conformations. Further studies regarding the presence of secondary structures in poly-3, poly-4 and poly-6 employing copolymerization with achiral monomers, computer modeling and dynamics simulations are in progress and will be published subsequently.

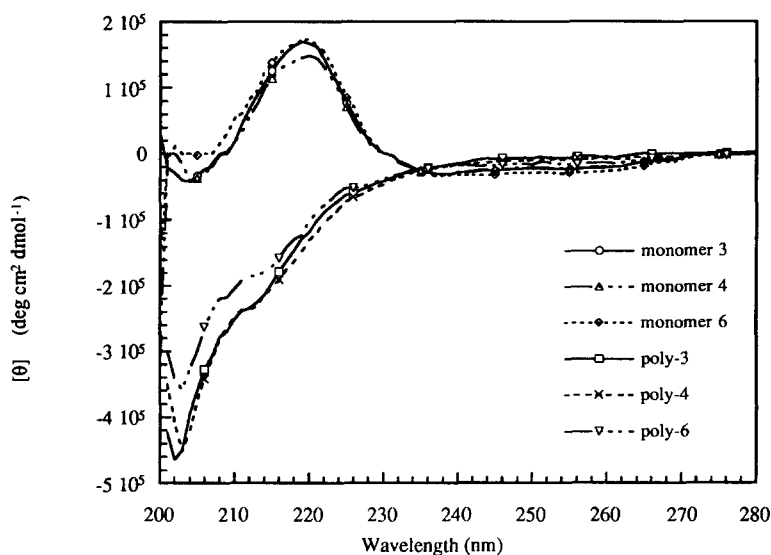


Figure 3. CD spectra of monomers and polymers in THF.

In order to investigate the stability of the secondary structure, specific optical rotations were measured as a function of temperature and time. Representative results are shown for poly-3 in Figures 4 and 5. No significant change in the optical rotation was observed up to 60 °C in THF. Hence, unlike the one-handed helical poly(diphenyl-2-pyridylmethyl methacrylate) which showed remarkable mutarotation over time due to conformational change,⁴⁰ the cyclopolymers maintain conformational integrity in solution. This is further corroborated by the fact that the optical rotations at room temperature did not change with time (Figure 5). As expected for a random coil, the specific optical rotation of the unordered poly-2 did not show any time-

dependence either (plots not shown). Cram and Sogah reported the preparation of helical methacrylate polymers using optically active crown ether complexes as templates.⁴¹ However, these polymers lost helicity in solution by uncoiling since the ester groups were not sterically hindered enough to maintain a helical conformation in solution. Our results confirm the earlier finding of Okamoto and coworkers that bulky ester groups are essential for the formation and stability of helical structures.¹⁴ Furthermore, it appears that the rigidity of the cyclic repeat units also contributes to the conformational stability of the polymers described herein.

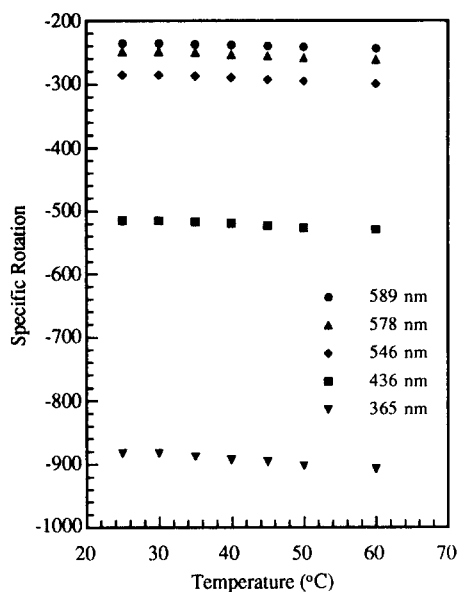


Figure 4. Optical rotations at different wavelengths versus temperature for poly-3 (*c* 1.0, THF)

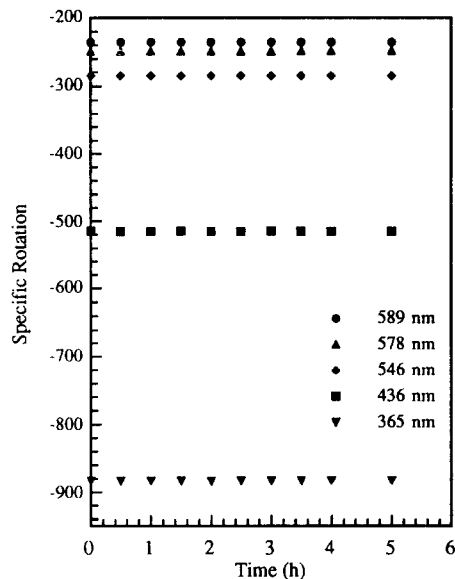


Figure 5. Optical rotations at different wavelengths versus time for poly-3 (*c* 1.0, THF, 25 °C).

Figures 6 and 7 show the CD spectra of the less sterically hindered polymers. Monomer 1 and poly-1 showed similar spectral patterns (Figure 6). The polymer showed a broad negative Cotton effect around 205–220 nm while the monomer showed a broad negative Cotton effect near 220 nm. Both spectra are structureless and consistent with poly-1 being completely unordered. In contrast, the CD spectra of 2 and poly-2 are substantially different from each other (Figure 7). The spectrum of monomer 2 is characterized by a negative Cotton effect at 218 and a small positive one at 250 nm whereas that of poly-2 is characterized by a negative Cotton effect at 207 nm and a broad shoulder at 220 nm suggesting that the polymer is partially ordered. Poly-5 which is structurally similar to poly-2 gave quite a similar CD spectrum implying that these polymers have similar conformations in solution. Hence, the results of our chiroptical properties as well as stereochemical studies indicate that the tendency to adopt ordered conformations decreases with steric bulkiness: poly-3 >>> poly-2 > poly-1. These results are consistent with our design postulate stated earlier.

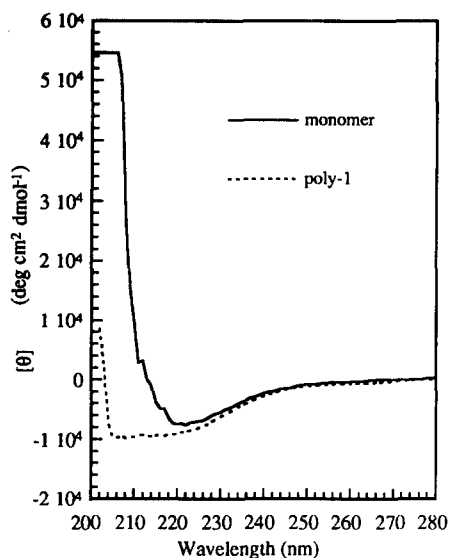


Figure 6. CD spectra of monomer 1 and poly-1 in THF at 25 °C.

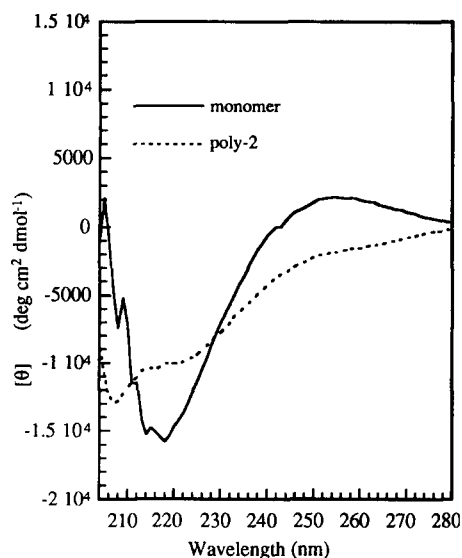


Figure 7. CD spectra of monomer 2 and poly-2 in THF at 25 °C.

Thermal Properties. Thermal properties for the various polymers are summarized in Table 5. The decomposition temperatures (T_d) were determined by TGA. With the exception of poly-1 which showed only one T_d at 353 °C, all the polymers underwent a two-stage decomposition with $T_{d1} = 300$ °C and $T_{d2} = 420$ °C which correspond to both side-chain and main-chain decomposition. Hence, as the polymers became bulkier, side-chains began to decompose before the main-chain. The T_d of poly(TrMA) was reported to be 280 °C which is substantially lower than the T_d 's for the cyclopolymers.⁴² Therefore, the rigidity of the cyclic repeat units in the polymer main chain imparts some degree of thermal stability to these polymers.

Table 5. Thermal properties of the polymers.

Polymer	T_g (°C)	$T_{d1, onset}$ (°C)	$T_{d2, onset}$ (°C)
poly-1	170	353	—
poly-2	170	284	423
poly-3	NO ^a	298	410
poly-4	NO ^a	303	422
poly-5	170	289	422
poly-6	NO ^a	296	427

^a Not observed

The results of DSC measurements (Table 5) showed that poly-3, poly-4, and poly-6 showed no T_g below their decomposition temperatures. We attribute this partly to their high rigidity and partly to the cyclic nature of the repeat units. In contrast, the less sterically hindered and more conformationally mobile poly-1, poly-2 and poly-5 showed the same T_g at 170 °C which reflects their similar structures and less ordered conformations.

Resistance to solvolysis and implications for applications in chiral separations. One of the major uses for poly(TrMA) has been in the preparation of chiral HPLC columns for enantiomeric resolutions.³² Such columns are extremely valuable especially in the pharmaceutical industry where the need to obtain biologically active compounds as single enantiomers is very critical. However, poly(TrMA) has been reported to decompose in methanol with cleavage of the trityl group.⁴³ Such a tendency toward decomposition has limited the application of poly(TrMA) as a chiral separation medium and shortened the shelf-life of columns prepared from them. We found that, unlike poly(TrMA), the highly rigid and isotactic optically active polymers showed remarkable resistance to solvolysis. Thus, all attempts to either selectively hydrolyze the acetal protecting groups or completely remove the ester groups in poly-3, poly-4 and poly-6 under mild acidic conditions, such as using either HCl, H₂SO₄, TFA or triflic acid in THF/MeOH, were completely unsuccessful. Only under very severe acidic conditions, such as using concentrated sulfuric acid in methanol, were we able to successfully hydrolyze them. We attribute this solvolytic resistance to their high steric hindrance and the cyclic nature of the polymer repeat unit. The results suggest that these optically active cyclopolymers should find use as superior packing materials for chiral columns with much longer shelf lives for chromatographic enantiomeric separations.

Summary and Conclusions

Through a rational monomer design, we have successfully carried out isospecific free radical cyclopolymerization of optically active tartrate-based monomers **1** - **6**. We found that the bulkier the divinyl monomer, the more readily it polymerized to give soluble polymers with no unreacted pendent vinyl groups and totally devoid of cross-links. The α,α' -substituents conferred enough convergence on the monomers for faster cyclization relative to intermolecular propagation. The effectiveness of the α -substituents in facilitating ring closure decreased in the following manner: Ph >>> Me > H. The ring closure was stereospecifically *cis* while the intermolecular addition was predominantly *meso* leading to very high isotacticity which decreased with decreasing steric hindrance: poly-6 $\approx$ poly-4 $\approx$ poly-3 >>> poly-2 $\approx$ poly-5 > poly-1. The distal acetal protecting groups had no effect.

Results of polarimetric and CD spectroscopic measurements suggest that the polymers from the bulkiest monomers assume ordered and rigid conformation with very high average molar rotation/repeat unit ($[\Phi]_D \approx 1100$ -1325°) in chloroform. The polymers did not mutarotate with either temperature or time suggesting that they are conformationally stable. In analogy with poly(TrMA), which was shown to adopt one-handed helical conformation in solution, the rigid structures of the polymers described herein, especially poly-3, poly-4 and poly-6 with α,α' -phenyl groups, may also be helical. Further studies to confirm these are in progress. Their

high rigidity is reflected in the polymers having no T_g and being thermally robust with decomposition temperatures between 300 and 430 °C. Poly-2 and poly-5 having α,α' -methyl substituents appeared to be conformationally flexible and only partially ordered while poly-1 was totally unordered both giving $T_g \approx 170$ °C. We further found that the polymers exhibited higher hydrolytic and thermal stability than poly(TrMA) and should, therefore, find use as superior chiral packing materials for enantiomeric separations.

Experimental Details

Measurements. ^1H NMR spectra were recorded with chloroform as an internal standard on either a Varian XL-200 spectrometer operating at 200 MHz or a Varian XL-400 spectrometer operating at 400 MHz. ^{13}C NMR spectra were recorded with chloroform as an internal standard on a Varian XL-400 spectrometer operating at 100.6 MHz. Gas chromatographic analysis was carried out on a Hewlett Packard 5980A gas chromatograph equipped with a methylsilicone column and a TCD detector. Melting points were measured with an Electrothermal 9100 melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin Elmer 241 digital polarimeter with a 10-cm pathlength cell. GPC analysis was performed using three American Polymer Standard columns connected in series with THF as eluent and a Viscotek RI/viscometric detector. The molecular weight was calculated on the basis of universal calibration using polystyrene standards. Circular dichroism (CD) spectra were recorded in THF at 30 °C on a Jobin Yvon Autodichrograph Mark V spectrometer with a 0.01-cm or 0.10-cm pathlength cell and solution concentration of 0.5 mg/mL. IR spectra were recorded on a Perkin Elmer 16PC FTIR instrument on KBr plates. TGA/DSC analyses were performed on a Seiko Instrument. TGA data were obtained between 30 and 550 °C at a heating rate of 20 °C/min. DSC data were obtained from a second heating cycle at 10 °C/min. Mass spectroscopy (FAB) was carried out at the University of Illinois Mass Spectroscopic facility. Elemental analysis was carried out by Oneida Research Services, Inc.

Materials. Common reagents were purchased from Aldrich and solvents from Fisher Scientific. Azobis(isobutyronitrile) (AIBN) was recrystallized from diethyl ether at low temperature and dried in a vacuum oven with phosphorus pentoxide (P_2O_5) at room temperature. Methacryloyl chloride was distilled under nitrogen. *n*-Butyllithium was obtained from Aldrich and titrated in toluene with 1,10-phenanthroline as indicator. *N*-Methylpyrrolidinone (NMP) was distilled over calcium hydride under nitrogen. THF and diethyl ether were distilled from sodium benzophenone immediately before use. Toluene was distilled over potassium under nitrogen before use.

Dimethyl-(2R, 3R)-1,4-dioxaspiro[4.4]nonane-2,3-dicarboxylate (9). In a 500 mL round-bottomed flask equipped with a Dean-Stark trap, a mixture of dimethyl L-tartrate (50 g, 0.28 mol), cyclopentanone (62 mL, 0.70 mol), *p*-toluenesulfonic acid monohydrate (0.80 g, 4.2 mmol), and 250 mL of benzene was heated at reflux for 164 h. The reaction was then cooled to room temperature, and *p*-toluenesulfonic acid was neutralized by the addition of 1.6 g of K_2CO_3 . Solvent and unreacted cyclopentanone were removed under reduced pressure, and the brown residue was vacuum distilled to give a light yellow oil (43.2 g, 86% yield). B.p. 154–156 °C/0.2 mmHg. GC purity, > 96%. $[\alpha]_{\text{D}}^{25}$ -29.1, $[\alpha]_{\text{D}}^{25}$ -92.4 (c 1.0, CHCl_3). ^1H NMR (CDCl_3) δ : 1.67–1.97 (m, 8H), 3.79 (s, 6H), 4.74 (s, 2H). ^{13}C NMR (CDCl_3) δ : 23.37, 36.43, 52.69, 123.31, 169.95. IR (film, KBr): 2957, 1763, 1438, 1337, 1205, 1124 cm^{-1} . MS (FAB): 245.1 (MH^+). HRMS (FAB): Calcd. for $\text{C}_{11}\text{H}_{17}\text{O}_6$ (MH^+), 245.1025; found 245.1023.

(-)-trans-4,5-Bis(hydroxymethyl)-2,2-diethyl-1,3-dioxacyclopentane (10). (+)-Dimethyl-2,3-*O*-(3,3-pentylidene)-L-tartrate **7** was synthesized by protecting hydroxy groups with 3-pentanone according to a literature procedure.^{33c} $[\alpha]_{\text{D}}^{25}$ -16.4 (c 3.35, CHCl_3) (lit. $[\alpha]_{\text{D}}^{25}$ -16.8 (c 3.03, CHCl_3)). LAH (1.6 g, 42 mmol) was suspended in 30 mL of dry ether and refluxed for 0.5 h under argon. The suspension was then cooled to room temperature and tartrate **7** (2.5 g, 10.15 mmol) in 20 mL of dry ether was added slowly to the suspension. The mixture was heated at reflux for 3.5 h, cooled to 0 °C, and quenched successively with 2 mL of water, 5 mL of 4 N NaOH, and 2 mL of water. The white precipitate was filtered off and then extracted overnight with ether using a Soxhlet apparatus. The ether solution from the extraction was combined with the filtrate, and the aqueous layer was extracted with ether three times. The organic phase was washed with brine,

dried over MgSO_4 , and concentrated to yield pure diol (1.8 g, 61% yield). This product was a colorless viscous oil and solidified to opaque crystals upon standing at room temperature. GC purity > 99%. M.p. 43.5–45 °C. ^1H NMR (CDCl_3) δ : 0.91 (t, J = 7 Hz, 6H), 1.64 (q, J = 7 Hz, 4H), 2.25 (s, 2H), 3.65–3.84 (m, 4H), 3.95–3.98 (m, 2H). ^{13}C NMR (CDCl_3) δ : 7.99, 30.31, 62.16, 78.41, 112.95. IR (film on KBr): 3382, 2973, 2941, 2882, 1463, 1201, 1173, 1056 cm^{-1} . $[\alpha]_D^{25} +2.80$, (c 5.0, CHCl_3). MS (FAB): 191.2 (M^+). HRMS (FAB): Calcd. for $\text{C}_9\text{H}_{19}\text{O}_4$ m/z 191.1283; found 191.1285.

(-)-trans-4,5-Bis(hydroxydimethylmethyl)-2,2-diethyl-1,3-dioxacyclopentane (11). A 300 mL three-neck flask was equipped with a condenser, an addition funnel, a nitrogen inlet, and a stirring bar. (+)-Dimethyl-2,3-*O*-(3-pentylidene)-*L*-tartrate **7** (4 g, 16.24 mmol) was placed in the addition funnel and dissolved in 20 mL of dry THF. A solution of CH_3MgBr (2.8 M in ether, 58 mL, 162.4 mmol) was placed in the flask and cooled to 0 °C. The diester **7** solution was added slowly to the flask from the addition funnel. A white precipitate formed after some Grignard reagent was added. The reaction was refluxed for 3 h and then stirred at room temperature for additional 3 h. The precipitate dissolved upon heating. After cooling to 0 °C, the reaction was quenched by a slow addition of saturated aqueous NH_4Cl solution, and a white precipitate formed. More NH_4Cl solution was added until all the precipitate dissolved. The THF solvent was then removed, and the reaction mixture was extracted with ether three times. The combined organic phase was washed with water and brine and then dried over sodium sulfate. The crude crystalline product was recrystallized from hexane. Three crops of crystals were obtained to give a total yield of 2.38 g (59%); M.p. 136.6–138.3 °C. ^1H NMR (CDCl_3) δ : 0.87 (t, J = 7 Hz, 6H), 1.26 (s, 6H), 1.32 (s, 6H), 1.59 (q, J = 7 Hz, 4H), 3.25 (s, 2H), 3.69 (s, 2H). ^{13}C NMR (CDCl_3) δ : 8.07, 23.45, 29.33, 30.23, 70.57, 82.57, 110.40. IR (film, KBr): 3252, 2973, 1465, 1381, 1180, 1075, 1041, 1002 cm^{-1} . $[\alpha]_D^{25} -2.60$ (c 1.0, CHCl_3). MS (FAB): (MH^+) 247.2. HRMS (FAB): Calcd. for $\text{C}_{13}\text{H}_{27}\text{O}_4$ (MH^+), 247.1909; found 247.1912.

(-)-trans-4,5-Bis(hydroxydiphenylmethyl)-2,2-diethyl-1,3-dioxacyclopentane (12). The procedure used to obtain diol **11** was followed. Diester **7** (5.00 g, 20.3 mmol) in 90 mL of dry THF was reacted with PhMgBr solution (3 M in ether, 54 mL, 162 mmol) in 80 mL of dry THF to give a yellow viscous oil. The crude reaction mixture was recrystallized from a mixture of hexane and methylene chloride to yield white crystals (1.2 g). The mother liquor was purified by column chromatography (silica gel, EtOAc:hexane, 10:90, v:v) to give 6.17 g of **12**. Total yield, 62%. M.p. 179–181 °C. ^1H NMR (CDCl_3) δ : 0.65 (t, J = 7 Hz, 6H), 1.27 (q, J = 7 Hz, 4H), 4.21 (s, 2H), 4.43 (s, 2H), 7.23–7.51 (m, 20H). ^{13}C NMR (CDCl_3) δ : 8.27, 29.45, 78.28, 80.29, 112.50, 127.09, 127.16, 127.53, 127.66, 128.07, 128.66, 142.47, 146.14. IR (film, KBr): 3291, 2970, 1495, 1446, 1174, 1083, 1033 cm^{-1} . Optical rotation: $[\alpha]_D^{25} -73.6$ (c 1.06, CHCl_3). Anal. calcd. for $\text{C}_{33}\text{H}_{34}\text{O}_4$: C, 80.13; H, 6.93. Found: C, 79.84; H, 6.90.

(-)-trans-2,3-Bis(hydroxydiisopropyl)-1,4-dioxaspiro[4.4]nonane (14). The procedure used to obtain diol **11** was followed. Diester **9** (11.57 g, 47.37 mmol) in 160 mL THF reacted with CH_3MgBr solution (3 M in ether, 126 mL, 0.38 mol). The crude product was recrystallized from hexane to give white crystals 6.35 g (55% yield); m.p. 157–159 °C. $[\alpha]_D^{25} = -7.3$, $[\alpha]_{365}^{25} = -12.8$ (c 1.0, chloroform). ^1H NMR (CDCl_3) δ : 1.25–1.80 (m, 14H, CH_3 , 6-H, 7-H, 8-H, and 9-H), 2.54 (s, br, 2H, OH), 3.74 (s, 2H, 2-H and 3-H). ^{13}C NMR (CDCl_3) δ : 23.36, 23.91, 28.77, 37.80, 70.62, 82.78, 118.27. MS (FAB): 245.2 (MH^+). HRMS (FAB): calcd. for $\text{C}_{13}\text{H}_{25}\text{O}_4$ (MH^+) 245.1753, found 245.1753.

(-)-trans-2,3-Bis(hydroxydiphenylmethyl)-1,4-dioxaspiro[4.4]nonane (15). The procedure used to obtain diol **11** was followed. Diester **9** (15.1 g, 61.82 mmol) was reacted with PhMgBr solution (3.0 M in ether, 165 mL, 0.50 mol) in 150 mL of dry THF to give a brown oil, which was purified by column chromatography (silica gel, ether:hexane, 15:85, v:v), and then recrystallized from chloroform/pentane to give **15** as white crystals. Yield 18.01 g (59%). M.p. 169–171 °C. $[\alpha]_D^{25} -27.8$, $[\alpha]_{365}^{25} -72.9$ (c 1.0, CHCl_3). ^1H NMR (CDCl_3) δ : 1.30–1.51 (m, 8H), 3.56 (s, br, 2H), 4.69 (s, 2H), 7.18–7.57 (m, 20H). ^{13}C NMR (CDCl_3) δ : 22.83, 36.97, 78.28, 80.96, 119.84, 127.15, 127.35, 127.39, 128.07, 128.37, 143.12, 145.69. Anal. Calcd. for $\text{C}_{33}\text{H}_{32}\text{O}_4$: C, 80.46; H, 6.55. Found: C, 77.62; H, 6.47.

(-)-trans-4,5-Bis(methacryloyloxymethyl)-2,2-diethyl-1,3-dioxacyclopentane (1).^{27b} Diol **10** (2.9 g, 15.24 mmol), methacryloyl chloride (6 mL, 61.0 mmol), and phenothiazine (30 mg) were

dissolved in 90 mL of dry NMP. The reaction was stirred at room temperature under nitrogen for 23 h. Solvent was removed, and the oily residue was partitioned between ether (300 mL) and saturated aqueous NaHCO_3 solution (100 mL). The ether layer was washed with saturated aqueous NaHCO_3 solution twice and water once, and dried over MgSO_4 . After removal of the solvent, the resulting yellow oil was purified by column chromatography (silica gel, ether:hexane, 15:85, v:v) to yield a light yellow oil (4.13 g, 60% yield). GC purity > 99%. ^1H NMR (CDCl_3) δ : 0.89 (t, $J = 7$ Hz, 6H), 1.65 (q, $J = 7$ Hz, 4H), 1.94 (s, 6H), 4.11 (m, 2H), 4.26-4.38 (m, 4H), 5.58-5.60 (m, 2H), 6.126-6.130 (m, 2H). ^{13}C NMR (CDCl_3) δ : 3.54, 13.93, 25.99, 59.22, 71.76, 109.18, 121.70, 131.56, 162.39. IR (film, KBr): 2974, 1723, 1638, 1455, 1320, 1295, 1164, 1104 cm^{-1} . $[\alpha]_D^{25}$ -3.7, $[\alpha]_{578}^{25}$ -3.9, $[\alpha]_{546}^{25}$ -4.0, $[\alpha]_{436}^{25}$ -4.0, $[\alpha]_{365}^{25}$ -7.0 (c 1.0, CHCl_3). MS (FAB): (MH^+) 327.3. HRMS (FAB): Calcd for $\text{C}_{17}\text{H}_{27}\text{O}_6$ (MH^+), 327.1808; found 327.1806. Anal. calcd for $\text{C}_{17}\text{H}_{26}\text{O}_6$: C, 62.56; H, 8.03. Found: C, 62.92; H, 8.27.

(-)-trans-4,5-Bis(methacryloyloxy)dimethylmethyl-2,2-diethyl-1,3-dioxacyclopentane

(2). Diol **11** (10.00 g, 40.6 mmol) was dissolved in 110 mL of dry THF, and the solution was cooled to 0 °C. *n*-Butyllithium solution (2.5 M in hexane, 41 mL, 102.5 mmol) was added slowly with a syringe. The reaction mixture was stirred at room temperature for 30 min, cooled to 0 °C, and methacryloyl chloride (20 mL, 203 mmol) was added slowly. White precipitate (LiCl) formed immediately. The reaction was refluxed for 1 h, and stirred at room temperature overnight. After cooling to 0 °C, the reaction was quenched by the addition of saturated aqueous NaHCO_3 . A portion of the THF was removed, and the residue was extracted with ether. The organic phase was washed with aqueous NaHCO_3 solution three times, water and brine once, and dried over MgSO_4 . The crude reaction mixture was purified by repeated column chromatography (silica gel, ether:hexane, 3:97, v:v) to yield a clear viscous oil (9.8 g, 66% yield). GC purity 99.1%. ^1H NMR (CDCl_3) δ : 0.89 (t, $J = 7$ Hz, 6H), 1.54 (s, 6H), 1.66 (s, 6H), 1.67-1.71 (m, 4H), 1.89 (s, 6H), 4.18 (s, 2H), 5.52 (m, 2H), 5.99 (m, 2H). ^{13}C NMR (CDCl_3) δ : 8.52, 18.34, 22.26, 23.68, 29.50, 82.15, 82.86, 113.03, 125.13, 137.48, 166.36. IR (film, KBr): 2978, 1718, 1636, 1457, 1383, 1328, 1178, 1139, 1080 cm^{-1} . $[\alpha]_D^{25}$ +33.9, $[\alpha]_{578}^{25}$ +35.2, $[\alpha]_{546}^{25}$ +40.4, $[\alpha]_{436}^{25}$ +74.9, $[\alpha]_{365}^{25}$ +135.0 (c 1.0, CHCl_3). MS (FAB): (MH^+) 353.3. HRMS (FAB): calcd for $\text{C}_{21}\text{H}_{35}\text{O}_6$ (MH^+) 383.2434, found 383.2431. Anal. calcd for $\text{C}_{21}\text{H}_{34}\text{O}_6$: C, 65.94; H, 8.96. Found: C, 66.05; H, 9.08.

(-)-trans-4,5-Bis((methacryloyloxy)diphenylmethyl)-2,2-diethyl-1,3-dioxacyclopentane

(3). The procedure used to obtain monomer **2** was followed. Diol **12** (6.9 g, 13.95 mmol), fluorene (20 mg, 0.12 mmol) (used as an indicator), *n*-BuLi solution (1.6 M in hexane, 21 mL, 33.6 mmol), and methacryloyl chloride (4.1 mL, 41.96 mmol) in 90 mL of dry THF were used to give the crude product as a brown solid. The crude product was recrystallized from hexane. The crystals contained both mono(methacrylate) and bis(methacrylate). The crude crystals were further purified by column chromatography (silica gel, ether:hexane, 5:95, v:v) to yield white crystals (3.25 g). The mother liquor was also purified by column chromatography to yield more white crystals (1.73 g). Total yield: 57%; M.p. > 175 °C (dec.). ^1H NMR (CDCl_3) δ : 0.50 (t, $J = 7$ Hz, 6H), 0.70-0.77 (m, 2H), 0.85-0.92 (m, 2H), 1.73 (s, 6H), 5.49 (s, 2H), 5.65 (s, 2H), 6.12 (s, 2H), 7.15-7.33 (m, 20H). ^{13}C NMR (CDCl_3) δ : 8.54, 18.33, 29.12, 77.32, 87.78, 113.39, 126.67, 126.81, 127.26, 127.38, 128.70, 138.00, 141.17, 144.40, 166.36. $[\alpha]_{365}^{25}$ -356, $[\alpha]_{436}^{25}$ -220, $[\alpha]_{546}^{25}$ -127, $[\alpha]_{578}^{25}$ -111, $[\alpha]_D^{25}$ -105 (c 1.0, CHCl_3); $[\alpha]_{365}^{25}$ -401, $[\alpha]_{436}^{25}$ -250, $[\alpha]_{546}^{25}$ -146, $[\alpha]_{578}^{25}$ -128, $[\alpha]_D^{25}$ -123 (c 1.0, THF). Anal. calcd for $\text{C}_{41}\text{H}_{42}\text{O}_6$: C, 78.07; H, 6.71. Found: C, 77.79; H, 6.95.

(-)-trans-4,5-Bis((methacryloyloxy)diphenylmethyl)-2,2-dimethyl-1,3-dioxacyclopentane

(4). The procedure used to obtain monomer **2** was followed. Diol **13** (5.59 g, 11.98 mmol), fluorene (13.1 mg, 0.079 mmol), *n*-BuLi (1.6 M in hexane, 18 mL, 28.8 mmol), and methacryloyl chloride (3.5 mL, 35.82 mmol) in 50 mL of dry THF were used to give crude product which was purified by column chromatography (silica gel, ether:hexane, 5:95, v:v) to give the product as white crystals (5.37 g, 74% yield). M.p. 105-107 °C. ^1H NMR (CDCl_3) δ : 0.68 (s, 6H), 1.75 (s, 6H), 5.52 (m, 2H), 5.78 (s, 2H), 6.14 (m, 2H), 7.19-7.35 (m, 20H). ^{13}C NMR (CDCl_3) δ : 18.33, 27.40, 77.54, 87.74, 110.02, 126.81, 126.95, 127.34, 127.38, 127.45, 128.85, 137.94, 141.11, 144.11, 166.32. $[\alpha]_{365}^{25}$ -332, $[\alpha]_{436}^{25}$ -208, $[\alpha]_{546}^{25}$ -121, $[\alpha]_{578}^{25}$ -106, $[\alpha]_D^{25}$ -102 (c 1.0, CHCl_3); $[\alpha]_{365}^{25}$ -425, $[\alpha]_{436}^{25}$ -263, $[\alpha]_{546}^{25}$ -153, $[\alpha]_{578}^{25}$ -153, $[\alpha]_D^{25}$ -129 (c 1.0, THF). Anal. calcd for $\text{C}_{39}\text{H}_{38}\text{O}_6$: C, 77.72; H, 6.35. Found: C, 77.91; H, 6.22.

(-)-trans-2,3-Bis(methacryloyloxydimethylmethyl)-1,4-dioxaspiro[4.4]nonane (5). The procedure used to obtain monomer **2** was followed. Diol **14** (6.05 g, 24.76 mmol), fluorene (10 mg), n-BuLi solution (1.65 M in hexane, 37.5 mL, 61.9 mmol), and methacryloyl chloride (7.3 mL, 74.28 mmol) in 90 mL of dry THF were used to give crude product as a brown viscous oil. The crude product was purified by column chromatography (silica gel, ether:hexane, 5:95, v:v) to give the product as a clear viscous oil (6.3 g, 67% yield), which solidified upon standing in a refrigerator. M.p. 65–66 °C. ¹H NMR (CDCl₃) δ: 1.49 (s, 6H), 1.59–1.61 (m, 6H), 1.62 (s, 6H), 1.82–1.84 (m, 2H), 1.88 (s, 6H), 4.16 (s, 2H), 5.53 (m, 2H), 6.03 (m, 2H). ¹³C NMR (CDCl₃) δ: 18.42, 22.17, 22.34, 23.42, 38.90, 82.73, 84.44, 122.46, 125.58, 137.39, 166.61. IR (film, KBr): 2937, 1715, 1330, 1303, 1171, 1135, 1082, 1007 cm⁻¹. [α]_D²⁵₃₆₅ +232, [α]_D²⁵₄₃₆ +129, [α]_D²⁵₅₄₆ +69, [α]_D²⁵ +60, [α]_D²⁵₅₇₈ +57 (c 1.0, CHCl₃); [α]_D²⁵₃₆₅ +222, [α]_D²⁵₄₃₆ +123, [α]_D²⁵₅₄₆ +66, [α]_D²⁵₅₇₈ +57, [α]_D²⁵ +55 (c 1.0, THF). MS (FAB): 380.2 (M⁺). HRMS (FAB): Calcd for C₂₁H₃₂O₆ *m/z* 380.2199, found 380.2191. Anal. calcd for C₂₁H₃₂O₆: C, 66.29; H, 8.48. Found: C, 66.37; H, 8.29.

(-)-trans-2,3-Bis(methacryloyloxydiphenylmethyl)-1,4-dioxaspiro[4.4]nonane (6). The procedure to obtain monomer **2** was followed. Diol **15** (12.35 g, 25.07 mmol), fluorene (37 mg), n-BuLi solution (1.6 M in hexane, 39 mL, 62.68 mmol), and methacryloyl chloride (7.4 mL, 75.21 mmol) in 120 mL dry THF were used to give a brown viscous oil, which was purified by column chromatography (silica gel, ether:hexane, 5:95, v:v) and then recrystallized from hexane to give the product as white crystals (10.45 g, 66% yield). M.p. > 195 °C (dec.). ¹H NMR (CDCl₃) δ: 0.90–0.93 (m, 2H), 1.10–1.13 (m, 2H), 1.39–1.43 (m, 4H), 1.80 (s, 6H), 5.55 (m, 2H), 5.90 (s, 2H), 6.20 (m, 2H), 7.24–7.43 (m, 20H). ¹³C NMR (CDCl₃) δ: 18.28, 22.25, 36.28, 77.54, 87.71, 119.88, 127.27, 127.33, 127.43, 128.82, 130.12, 137.84, 141.10, 144.06, 166.21. IR (film, KBr): 3059, 2959, 1725, 1495, 1447, 1324, 1100, 1009, 982, 909, 732, 700 cm⁻¹. [α]_D²⁵₃₆₅ -345, [α]_D²⁵₄₃₆ -220, [α]_D²⁵₅₄₆ -130, [α]_D²⁵ -114, [α]_D²⁵ -109 (c 1.0, CHCl₃); [α]_D²⁵₃₆₅ -408, [α]_D²⁵₄₃₆ -259, [α]_D²⁵₅₄₆ -152, [α]_D²⁵₅₇₈ -134, [α]_D²⁵ -128 (c 1.0, THF). Anal. calcd. for C₄₁H₄₀O₆: C, 78.32; H, 6.41. Found: C, 78.20; H, 6.46.

General procedure for radical polymerization at 60 °C. Monomer **5** (565 mg, 0.090 mmol) and AIBN (9.6 mg, 0.058 mmol) were placed in a 25 mL round-bottomed flask charged with a stirring bar and capped with a three-way stopcock. The flask was evacuated and refilled with nitrogen three times. Toluene (10 mL) was added with a syringe, and the reaction mixture was heated to 60 °C under argon. After 24 h, the reaction was terminated by cooling to 0 °C and then added dropwise to 450 mL of well-stirred hexane. The polymer was purified by re-precipitation from hexane and dried overnight under vacuum at 60 °C.

Conversion of cyclopolymer to PMMA by hydrolysis with t-BuOK and H₂O. Hydrolysis of the cyclopolymer was done according to a method developed by Gassman.³⁶ A dry 100 mL flask containing poly-**1** (158 mg, 0.484 mmol) and t-BuOK (6.5 g, 58.1 mmol) was fitted with a condenser. The flask was evacuated and refilled with nitrogen three times, and THF (70 mL) and water (130 μL, 7.3 mmol) were added by separate syringes. The reaction was heated at reflux for 6 days under nitrogen. After cooling to room temperature, the solvent was removed. The residue was suspended in 50 mL of methanol and then acidified to pH ~ 2 by addition of concentrated HCl solution. The methanol insoluble part was filtered off and the filtrate was concentrated. The residue was suspended in benzene (5 mL) and treated with CH₂N₂. The benzene insoluble part was filtered off. The crude PMMA was precipitated from 60 mL of hexane, filtered, and dried overnight under vacuum at 60 °C.

Conversion of polymer to PMMA by hydrolysis with concentrated H₂SO₄. Poly-**6** (100 mg) was treated with 3 mL of concentrated sulfuric acid. To this brown suspension was added 2 mL of methanol. The reaction mixture was heated at reflux overnight until it became homogeneous. The sulfuric acid was neutralized by the addition of saturated KOH/methanol solution to pH ~ 9. The reaction mixture was treated with concentrated HCl solution to pH ~ 4. The inorganic salts were filtered off and the filtrate was evaporated to dryness. The residue was suspended in 10 mL of benzene and treated with CH₂N₂. The crude PMMA was purified by reprecipitation from 50 mL of hexane.

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