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Cyclopolymerization of Optically Active (−)-*trans*-4,5-Bis((methacryloyloxy)diphenylmethyl)-2,2-dimethyl-1,3-dioxacyclopentane through Radical and Anionic Mechanisms Gives Highly Isotactic Polymers

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Cyclopolymerization is an important method of polymer synthesis from the viewpoint of stereocontrolled polymerization since cyclization reactions are generally more stereoselective than acyclic reactions. The effectiveness of this method in stereoregulation has been reported for several bifunctional monomers including methacrylates,[1−3] oxazoline,[4] diolefin,[5] diisocyanides,[6] and styrene derivatives.[7] In certain cases, the monomers are based on a chiral template moiety which controls the cyclization stereochemistry. In this work, we synthesized and polymerized (−)-*trans*-4,5-bis((methacryloyloxy)diphenylmethyl)-2,2-dimethyl-1,3-dioxacyclopentane (**1**),[8] a novel dimethacrylate monomer based on (−)-*trans*-4,5-bis(hydroxydiphenylmethyl)-2,2-dimethyl-1,3-dioxacyclopentane (**2**)[9,10] as a template, under free-radical and anionic conditions. **2** and its derivatives are known to be versatile and excellent chiral ligands for several types of asymmetric syntheses.[9−12] The conditions and results of the free-radical polymerization of **1** are shown in Table 1. The obtained polymers were soluble in CHCl$_3$, tetrahydrofuran, and toluene, and ^{1}H NMR spectral analysis of the polymers showed no clear existence of pendent vinyl groups (Figure 1). These results indicate that the polymerization took place exclusively via a cyclization mechanism where cyclization was faster than propagation. It is interesting to note that cyclization was predominant even at a relatively high monomer concentration in feed ([M]$_0$) (0.43 M) as well as at [M]$_0$ of 0.05 M in the polymerization at 60 °C. In general, a low [M]$_0$ is required for cyclopolymerization in order to avoid a situation where intermolecular propagation is faster than cyclization. For instance, to achieve an effective cyclopolymerization of 2,2′-bis((methacryloyloxy)methyl)-1,1′-binaphthyl (**3**) by a free-radical mechanism,[1] a [M]$_0$ of 0.026 M is reported to be adequate.

The stereochemistry of polymerization was revealed by ^{1}H NMR analysis of the PMMA[13] derived from the original polymer of run 1 by hydrolysis with MeOH−H$_2$SO$_4$ followed by methylation with CH$_2$N$_2$. The polymer had an isotactic structure with the triad distributions of mm/mr/rr = 84/10/6, indicating that intramolecular cyclization as well as the intermolecular propagation took place preferentially in a meso fashion. The two peaks for the methine proton around 6 ppm and the two for the α-CH$_3$ protons in the spectrum of the original poly-**1** (Figure 1A) are consistent with the fact that the methine protons and α-CH$_3$ groups in a repeat unit are diastereotopic in the isotactic polymer.

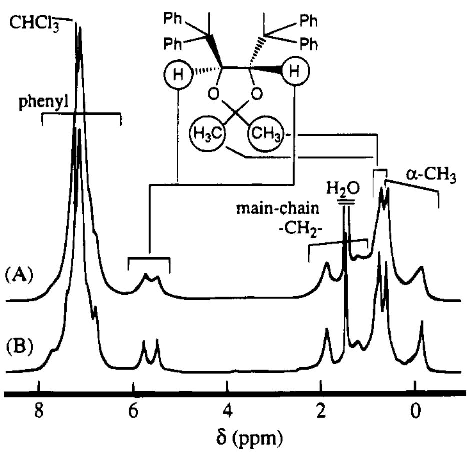


Figure 1. 500 MHz ^{1}H NMR spectrum (CDCl$_3$, 60 °C) of the poly-**1** obtained by free-radical polymerization (run 1 in Table 1) (A) and the poly-**1** obtained by anionic polymerization (B).

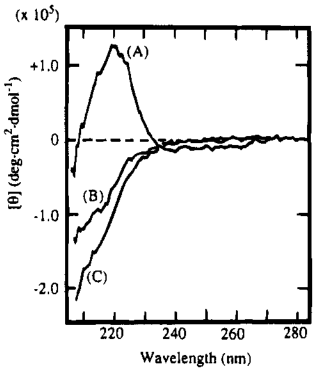
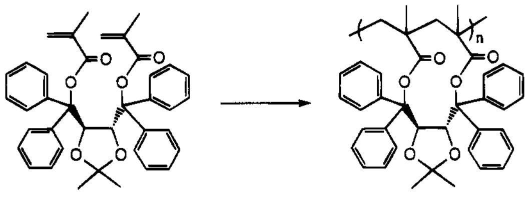


Figure 2. Circular dichroism spectra (THF, 25 °C) of monomer **1** (A), the poly-**1** obtained by free-radical polymerization (run 1 in Table 1) (B), and the poly-**1** obtained by anionic polymerization (C).

Scheme 1. Cyclopolymerization of 1



1 poly-**1**

The poly-**1** of run 1 showed levorotation, $[\alpha]^{25}_{365}$ −716° and $[\alpha]^{25}_{D}$ −194° (THF, *c* 1.0), which is greater than the specific rotation of the monomer. Further, the poly-**1** showed a spectral pattern of circular dichroism quite different from that of the monomer (Figure 2). These observations along with the isotactic structure may suggest that the polymer structure is somewhat rigid and ordered. Since the steric bulkiness of the monomer is comparable to that of triphenylmethyl methacrylate, which gives a one-handed helical polymer by asymmetric anionic polymerization,[14,15] highly isotactic poly-**1** is expected to be helical. Further experiments are in progress to determine to what extent helical contribution, if any, affects the structure of poly-**1**.

Having established that the free-radical polymerization of **1** gives highly isotactic polymers, anionic polymerization was performed using (9-fluorenyl)lithium in tetrahydrofuran at −78 °C at [M]$_0$ of 0.08 M to see if

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Table 1. Cyclopolymerization of 1 in Toluene Using Radical Initiators[a]

run	initiator[b]	$[M]_0$ (M)	temp (°C)	yield[c] (%)	M_n[d] $\times 10^{-3}$	M_w/M_n[d]	M_n[e] $\times 10^{-3}$	M_w/M_n[e]
1	AIBN	0.05	60	56	6.3[f]	1.40[f]	5.4[f]	1.30[f]
2	AIBN	0.43	60	84	13.5[g]	3.24[g]	10.0[f]	1.63[f]
3	(*i*-PrOCOO)$_2$	0.40	30	74	26.6[g]	3.13[g]	nd[h]	nd[h]

[a] Conditions: monomer, 0.5 g; [monomer]/[initiator] = 15 (runs 1−3); reaction time 24 h. [b] AIBN = α,α′-azobis(isobutyronitrile). [c] The polymer was precipitated in hexane and collected with a centrifuge. The hexane-soluble part of the product was found to consist of unreacted monomer and oligomeric products. [d] Determined by GPC analysis of the original polymers using polystyrene standard examples. [e] Determined by GPC analysis of the PMMAs derived from the original polymers using polystyrene standard samples. [f] Unimodal molecular weight distribution (see note 13). [g] Multimodal molecular weight distribution (see note 13). [h] nd = not determined.

the isotactic content could be further increased. A soluble polymer having no pendent vinyl group was obtained ($M_n = 5.3 \times 10^3$ and $M_w/M_n = 2.02$ as determined by GPC of the original polymer) (Figure 1B), indicating that the anionic reaction also proceeded exclusively through the cyclization mechanism. This is in contrast to the anionic polymerization of **3** at $[M]_0$ of 0.028 M, where a polymer having unreacted vinyl groups or an insoluble polymer was obtained under various conditions.[1] Indeed, the PMMA derived from the poly-**1** obtained by anionic polymerization was almost perfectly isotactic (mm > 99%). This value of triad isotacticity, to the best of our knowledge, is the highest one reported for cyclopolymerization of a dimethacrylate monomer. The poly-**1** obtained by anionic polymerization showed a higher optical rotation, $[\alpha]^{25}_{365}$ −841° and $[\alpha]^{25}_{D}$ −222° (THF, *c* 0.5), than that obtained by radical polymerization, suggesting that the polymer obtained by anionic polymerization is more ordered, possibly with a higher one-handedness of helicity based upon the higher isotacticity than the polymer obtained by the free-radical polymerization. In addition, the intensity of the circular dichroism absorption of this polymer was ca. 1.5 times higher than that of the polymer having a triad isotacticity of mm = 84% (Figure 2); the increase in the circular dichroism intensity was not proportional to the increase in the isotacticity. This may support that the chiroptical properties of the polymers are based more on a conformational chirality rather than a configurational one.

In summary, we have reported the effective cyclopolymerization of the novel monomer **1** by free-radical and anionic mechanisms leading to helical polymers. More detailed analyses of the polymerization stereochemistry and polymer conformation are underway. We are also investigating the chiral recognition ability of the poly-**1** and the polymerization of the derivatives of **1**.

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Supporting Information Available: ^{1}H NMR spectra of the PMMA derived from poly-**1** by free-radical polymerization, of the PMMA derived from poly-**1** by anionic polymerization, and of **1** (3 pages). Ordering information is given on any current masthead page.

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(8) **1** was synthesized from the lithium salt of **2** and methacryloyl chloride in tetrahydrofuran and purified by recrystallization from methanol. Mp 103−104 °C. Anal. Calcd for $C_{39}H_{38}O_6$: C, 77.72; H, 6.35. Found: C, 77.69; H, 6.35. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 0.68 (6H, *s*, CH_3), 1.75 (6H, *s*, α-CH_3), 5.52 (2H, *m*, vinyl-H), 5.78 (2H, *s*, 4-H and 5-H in 1,3-dioxacyclopentane moiety), 6.14 (2H, *m*, vinyl-H), 7.19−7.35 (20H, *m*, ArH). $[\alpha]^{25}_{365}$ −430° ; $[\alpha]^{25}_{D}$ −134° (tetrahydrofuran, *c* 1.00).

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(13) A significant discrepancy is seen between the polydispersities of the poly-**1** of run 2 as determined for the original polymer and the PMMA derived therefrom. This may be because of aggregate formation of the poly-**1** of run 2, similarly, to the observation for one-handed helical poly(diphenyl-2-pyridylmethyl methacrylate), which is known to form aggregates; the degree of association is sensitive to the M_n of the polymer, and aggregation leads to a multimodal, broad molecular weight distribution.[16]

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