

Asymmetric Anionic and Free-Radical Polymerization of 10,10-Dimethyl- and 10,10-Dibutyl-9-phenyl-9,10-dihydroanthracen-9-yl Methacrylate Leading to Single-Handed Helical Polymers

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(Received October 16, 2000; Accepted December 12, 2000)

KEY WORDS Asymmetric Anionic Polymerization / Free-Radical Polymerization / Tacticity / Helix / Conformation / Triphenylmethyl Methacrylate / 1-Phenyldibenzosuberyl Methacrylate /

The asymmetric anionic polymerization of the bulky methacrylates^{1–4} including triphenylmethyl methacrylate (**TrMA**)⁵ and 1-phenyldibenzosuberyl methacrylate (**PDBSMA**)⁶ leads to isotactic polymers having a single-handed helical conformation which show high optical activity based on the conformation. **TrMA** and **PDBSMA** also afford isotactic polymers by free-radical polymerization^{7–10} unlike the conventional methacrylates such as **MMA**.¹¹ During the radical polymerization, **PDBSMA** results in a nearly complete isotactic configuration regardless of condition^{7–9} while isotactic specificity during the radical polymerization of **TrMA** significantly depends on the reaction conditions.⁹ This suggests that the fused (bridged) ring structure including the seven-membered ring of **PDBSMA** with its two phenyl groups tied to each other at the ortho position may be important for realizing the highly effective stereoregulation during the radical polymerization. However, we have also reported that 9-phenylfluoren-9-yl meth-

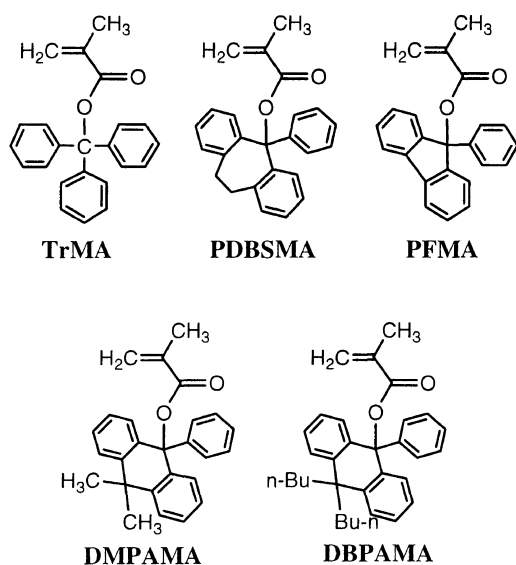
acrylate (**PFMA**) having a fused system involving a five-membered ring leads to only poor stereoregulation during anionic polymerization.¹²

In the present study, in connection with the above background, two novel triarylmethyl methacrylates having *fused ring structures including a six-membered ring, namely*, 10,10-dimethyl-9-phenyl-9,10-dihydroanthracen-9-yl methacrylate (**DMPAMA**), and 10,10-dibutyl-9-phenyl-9,10-dihydroanthracen-9-yl methacrylate (**DBPAMA**), were polymerized under anionic and radical reaction conditions. The radical polymerization of **PFMA** was also performed. The results provided valuable information about the effects of the side chain on the polymerization stereochemistry and also on the chiroptical properties of the helical polymers.

EXPERIMENTAL

PFMA¹² and optically active neomenthanethiol¹⁰ were available from our recent studies. 10,10-Dimethylanthrone was synthesized according to the literature.¹³ This ketone was reacted with PhMgBr to yield 10,10-dimethyl-9-phenyl-9,10-dihydroanthracen-9-ol (mp = 145.5–146.5°C). **DMPAMA** was obtained from a potassium alkoxide of this alcohol and methacryloyl chloride (mp = 165.5–166.3°C). 10,10-Dibutylanthrone was synthesized according to the literature¹³ with modifications. The reaction of this ketone with PhMgBr yielded 10,10-dibutyl-9-phenyl-9,10-dihydroanthracen-9-ol (mp = 110.5–111.5°C). **DBPAMA** was prepared from a potassium alkoxide of this alcohol and methacryloyl chloride (mp = 133.5–134.8°C). The structures of the monomers were identified by ¹H NMR and IR spectroscopies, FD mass spectrometry, and elemental analysis.

Other experimental details including the polymerization and analysis of the obtained polymers are the same as those in our previous reports.^{5,6,10}



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Table I. Polymerization of **DMPAMA** and **DBPAMA** using anionic and radical initiators in toluene for 24 h^a

Run	Monomer	Polymerization mode	Initiator	[M]/[I]	Temp. °C	Yield ^b %	[α] ₃₆₅ ^c deg	DP ^d	M_w/M_n ^d	Tacticity ^e /%		
										mm	mr	rr
1	DMPAMA	Anionic	PMP-DPEDA-Li	20	-78	6	n.d. ^f	322 ^g	1.36 ^g	>99	<1	0
2	DMPAMA	Anionic	DDB-DPEDA-Li	20	-78	88	n.d. ^f	76	1.92	>99	<1	0
3	DMPAMA	Anionic	DDB-DPEDA-Li	7	-78	85	+125	13	1.47	>99	<1	0
4	DMPAMA	Anionic	Sp-DPEDA-Li	20	-78	1	n.d. ^f	30 ^h	1.38 ^h	>99	<1	0
5	DBPAMA	Anionic	PMP-DPEDA-Li	20	-40	82	+183 ⁱ	52 ^j	1.17 ^j	>99	<1	0
6	DMPAMA	Radical	AIBN ^j	50	60	86		428	1.53	>99	<1	0
7	DMPAMA	Radical	(<i>i</i> -PrOCCO) ₂	50	40	37		468	1.39	>99	<1	0
8	DBPAMA	Radical	AIBN ^j	50	60	57		700	5.07	91	6	3
9	DBPAMA	Radical	(<i>i</i> -PrOCCO) ₂	50	40	61		506	6.60	94	3	3
10	DBPAMA	Radical	BPO-DMA ^k	50	0	66		974	3.25	98	1	1
11	DBPAMA	Radical	BPO-DMA ^k	50	-20	69		563	3.40	99	1	~0
12 ^l	DBPAMA	Radical	BPO-DMA ^k	50	0	43	+74	76	1.52	99	1	~0
13 ^l	DBPAMA	Radical	BPO-DMA ^k	50	0	45	-53	114	1.54	99	1	~0
14	PFMA	Radical	AIBN ^j	50	60	92		80	1.89	33	49	18
15	PFMA	Radical	AIBN ^j	50	40	80		89	1.80	38	44	18

^a Conditions: monomer 0.2 g, toluene 6 mL (runs 1–4); monomer 0.3 g, toluene 6 mL (runs 5); monomer 0.2 g, toluene 1.6 mL (runs 6, 7); monomer 0.2 g, toluene 0.8 mL (runs 8–13); monomer 0.5 g, toluene 8 mL (runs 14, 15). ^b MeOH-insoluble part. ^c In CHCl₃ (runs 3) or THF (runs 5, 12, and 13). ^d Determined by SEC analysis of the PMMAs derived from the original polymers. ^e Determined by 400 MHz ¹H NMR analysis of the PMMAs derived from original polymers. ^f Not Determined because the polymer was not completely soluble in THF or CHCl₃. ^g Additional oligomeric products (DP=3) were formed. ^h Additional oligomeric products (DP=4) were formed. ⁱ Properties of methanol-benzene (1/2)-insoluble part of the products (56 w% of the methanol-insoluble polymer). The methanol-insoluble polymer ([α]₃₆₅+171°) contained oligomers of low DP. ^j AIBN= α,α' -azobisisobutyronitrile. ^k BPO=benzoyl peroxide, DMA=*N,N*-dimethylaniline. [DMA]/[BPO]=20. ^l In the presence of (+)-NMT (run 12) or (-)-NMT (run 13). [M]=0.55 M, [I]=0.01 M, [NMT]=0.03 M.

RESULTS AND DISCUSSION

Asymmetric Anionic Polymerization of **DMPAMA** and **DBPAMA**

The results of the anionic polymerization of **DMPAMA** and **DBPAMA** are summarized in Table I, runs 1–5. The polymerization was carried out with the complexes of *N,N'*-diphenylethylenediamine monolithium amide (**DPEDA-Li**) with (-)-sparteine (**Sp**), (+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (**DDB**), and (+)-1-(2-pyrrolidinylmethyl)pyrrolidine (**PMP**) at low temperature. The two monomers gave nearly perfectly isotactic polymers. The high isotactic specificity implies that the polymers have helical conformation similar to that of poly(**TrMA**) and its analogues.

DMPAMA afforded polymers in high yield by polymerization using **DDB** as the chiral ligand while polymers were obtained only in low yields when **PMP** and **Sp** were used as ligands (runs 1–4). The poly(**DMPAMA**)s were poorly soluble in the common solvents including tetrahydrofuran and chloroform. A polymer with a relatively low DP (13) (run 3) was obtained using **PMP** at [M]/[I]=7, and this polymer was completely soluble in chloroform. This polymer showed a much lower optical activity compared with the single-handed helical poly(**TrMA**) ([α]₃₆₅~1500°)⁵ and poly(**PDBSMA**) ([α]₃₆₅1780°).¹⁰ However, this may not immediately mean a low helix-sense excess of the poly(**DMPAMA**) as will be discussed later.

DBPAMA afforded only trace amounts of oligomers when **Sp** or **DDB** was employed as a ligand while the monomer led to a polymer when the **PMP** ligand was used (run 5). However, due to the slow propagation during the polymerization using **PMP** at -78°C, it was necessary to perform the polymerization at -40°C to achieve a yield of over 80% in 24 h (run 5). Similar to the poly(**DMPAMA**) of run 3, the highly isotactic poly-

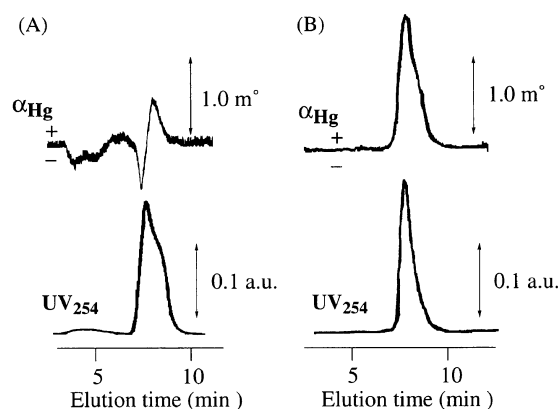


Figure 1. HPLC resolution chromatograms of poly(**DBPAMA**)s measured by polarimetric (top) and UV (bottom) detectors: racemic mixture obtained by radical polymerization (run 11 in Table I) (A) and benzene/methanol (1/2)-insoluble optically active polymer obtained by asymmetric anionic polymerization (run 5 in Table I) (B). Chromatographic experiment was performed with JASCO PU-970 chromatographic pump and 975 UV and OR 990 detectors using a column packed with (+)-poly(**TrMA**)-bonded silica gel¹³ (25 × 0.46 (i.d.) cm) (eluent, THF; flow rate, 0.5 mL min⁻¹; temp, 5°C; injection, 0.10 mg).

(**DBPAMA**) obtained at -40°C showed a much lower optical activity than the single-handed helical poly(**TrMA**) or poly(**PDBSMA**). In order to obtain information on the helix-sense excess in the polymer, chromatographic analysis was performed using a chiral HPLC column based on the single-handed helical poly(**TrMA**)-bonded silica gel¹⁴ (Figure 1). A highly isotactic polymer prepared by radical polymerization (see below), a racemic specimen, was first subjected to the analysis: the sample was resolved into the dextro- and levorotatory fractions under the chromatographic conditions of this study as confirmed from the chromatogram using a polarimetric detector (Figure 1A). The polymer of run 5 was next analyzed. The resolution resulted in only dextrorotatory

fraction, indicating that the polymer does not contain a levorotatory fraction (Figure 1B) and hence, *the polymer is single-handed helical*. The relatively low specific rotation for a single-handed helix may mean that *the reported high optical activity of poly(TrMA) and its analogues is partly based on the single-handed propeller conformation^{15–17} of the triarylmethyl group in the side chain in addition to the helical arrangement of the entire polymer chain*. Such a propeller conformation would be difficult for poly(DBPAMA) because the anthracene moiety in the side chain should have a planar structure. A single-handed helical structure may also be assumed for the highly isotactic poly(DMPAMA) of run 3 whose magnitude of specific rotation is in a range similar to that of the poly(DBPAMA) of run 5.

Circular dichroism (CD) spectrum of the single-handed helical poly(DBPAMA) had a spectral pattern roughly similar to that of the single-handed helical poly(TrMA) though the band intensity was much lower in the spectrum of the poly(DBPAMA). The effect of the side chain propeller conformation on optical activity of helical poly(triarylmethyl methacrylate) discussed above may also be the case for CD absorption.

Radical Polymerization of DMPAMA, DBPAMA, and PFMA

The results of the radical polymerization are shown in Table I, runs 6–15. Radical polymerization of DMPAMA led to a highly isotactic polymer regardless of the reaction temperature (runs 6, 7). This is in stark contrast to the fact that PFMA afforded a polymer with a low stereoregularity by radical polymerization (runs 14, 15). Because the bulkiness of the anthracene moiety in DMPAMA and that of the fluorenyl moiety in PFMA seem similar, steric repulsion based on the two methyl groups on the anthracene ring may be indispensable for the isotactic control. On the other hand, isotactic specificity during the DBPAMA polymerization varied depending on the temperature (runs 8–11). A lower temperature resulted in a higher isotacticity and the mm triad content of nearly 99% was achieved at -20°C . This tendency is opposite to the tacticity-temperature relation during the radical polymerization of TrMA. The isotactic specificity in the DBPAMA polymerization was lower than that in the DMPAMA polymerization in spite of the higher bulkiness of DBPAMA. The excess bulkiness of DBPAMA relative to DMPAMA may affect the conformation of the growing radical and interaction of the growing species with the entering monomer. In addition, molecular aggregation of the growing helical radicals, which is less likely during the DBPAMA polymerization as discussed below, may have a connection with the stereospecificity during the radical polymerization.

It is notable that the poly(DBPAMA)s with relatively high DPs (up to 974) were soluble in THF and chloroform, suggesting that the two butyl groups per unit prevent aggregation of the helical molecules. *This is interesting because helical polymethacrylates with high DPs generally have tendency to form aggregates and become quite insoluble.*^{5a),10} *The good solubility of the poly(DBPAMA)s would make it possible to clarify the solution properties of the high-molecular-weight, helical vinyl*

polymers.

Helix-sense selection was realized during the radical polymerization of DBPAMA at 0°C using optically active neomenthanethiol (NMT) as the chain-transfer agent (runs 12, 13). We have already reported the helix-sense-selective radical polymerization of PDBSMA using NMT and concluded that the helix-sense selection took place through the hydrogen transfer from NMT to a growing radical or the coupling of the thio radical derived from NMT with a growing radical.¹⁰ A similar mechanism is assumed for the present systems. Unlike the PDBSMA polymerization, the optically active poly(DBPAMA)s obtained through the radical polymerization were completely soluble in chloroform and THF: this allowed us to analyze the entire polymer without solvent fractionation. The specific rotation values of the obtained polymers suggest that the helical sense excess (e.e.) is *ca.* 30–40% which is higher than the e.e. observed in the PDBSMA polymerization using NMT (THF-soluble polymer: e.e. 4–8%).

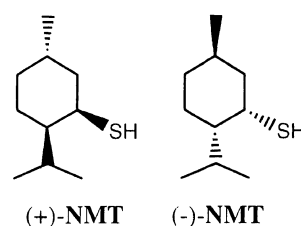


Figure 2 shows the GPC curves of the poly(DBPAMA) of run 12. The polymer consisted of dextrorotatory fractions with higher molecular weight and levorotatory fractions with lower molecular weight. This supports the assumption that the helix-sense selection occurs through radical termination; the helical growing radical producing the (–)-polymer was more readily terminated by NMT or the thio radical derived from NMT than that giving the (+)-polymer with the opposite helical sense.

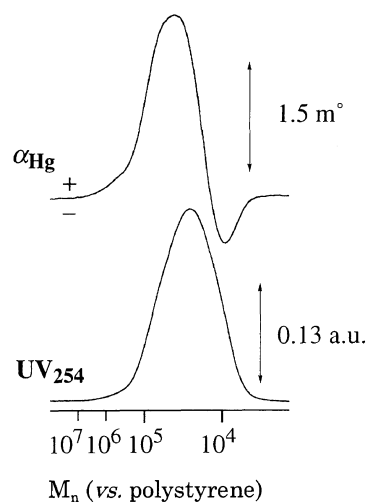


Figure 2. SEC curves measured by polarimetric (top) and UV (bottom) detectors of the poly(DBPAMA) of run 12 obtained by radical polymerization in the presence of (+)-NMT as chain transfer agent. Chromatographic experiment was performed with a Shodex System-21 SEC system equipped with an RI-71S detector using KF-803 and KF-806 F columns connected in series (eluent, THF; flow rate, 1.0 mL min^{-1} ; temp, 40°C).

The change in the ratio of the peak intensities of the polarimetric and UV chromatograms according to molecular weight in the GPC charts indicates that the optical activity of the fractions increased with molecular weight and it was comparable to that of the single-handed helical poly(**DBPAMA**) obtained by the asymmetric anionic polymerization (run 5) in the higher molecular weight range, indicating that the higher-molecular-weight fractions have single-handed helicity. This means that complete helical-sense selection was achieved during the radical polymerization.

CONCLUSIONS

The asymmetric anionic polymerization of **DMPAMA** and **DBPAMA** led to highly isotactic, optically active polymers having a single-handed helical conformation. From a comparison of the optical activity of the polymers with that of poly(**TrMA**), it was suggested that the high optical activity of the poly(triarylmethyl methacrylate)s so far reported may be partly based on the single-handed propeller conformation in addition to the main-chain helix. The radical polymerization of **DMPAMA** and **DBPAMA** resulted in the isotactic polymer formation while **PFMA** gave atactic polymers, suggesting that the polymerization stereochemistry is sensitive to the monomer structure. The helix-sense selection was achieved during the radical polymerization of **DBPAMA** in the presence of an optically active chain-transfer agent. Poly(**DBPAMA**)s with high molecular weight showed much better solubility than the other helical polymethacrylates. This finding opens the way for the examination of the solution properties of helical vinyl polymer with high molecular weights.

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