Asymmetric Radical Cyclopolymerization of *N*-Allyl-*N*-phenylmethacrylamide in the Presence of $SnCl_4$ and L-Menthol

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ABSTRACT: Asymmetric induction was examined in the cyclopolymerization and cyclocopolymerization of *N*-allyl-*N*-phenylmethacrylamide (PAMA) with dimethyl 2,2′-azobis(isobutyrate) in benzene in the presence of L-menthol and $SnCl_4$. Optical activity ($[\alpha]_D = -0.3$ to -5.6) was observed for poly(PAMA)s formed in the radical polymerization of the PAMA/$SnCl_4$/L-menthol system. The PAMA monomer unit was incorporated exclusively as a five-membered ring into the highly cyclized poly(PAMA)s (degree of cyclization (DC) = 95−98%) obtained. The radical copolymerization of PAMA with methyl methacrylate in the presence of L-menthol and $SnCl_4$ also gave optically active copolymers, the PAMA units of which were similarly highly cyclized (DC = 90−94%) as a five-membered ring. The $[\alpha]_D$ value of the copolymer increased up to $[\alpha]_D = -15.2$ with increasing PAMA concentration in the feed. The much lower DC values (25−68%) of the PAMA monomer unit were observed for the copolymers formed in the copolymerization of the PAMA/styrene/L-menthol/$SnCl_4$ system. However, the copolymers showed a considerable optical activity ($[\alpha]_D = -9.1$ to -11.8).

Introduction

Recently, much attention has been paid to asymmetric inductions in the radical polymerization, the steric course of which is much more difficult to control compared to the polymerizations via other mechanisms such as cationic, anionic, coordination, and metathesis ones. Traditional approaches to the asymmetric induction in radical polymerization are the alternating copolymerization of 1,2-disubstituted monomers[1−3] and the homo- and copolymerizations of substituted conjugated diene monomers[4−7] under adequate chiral conditions.

Wulff suggested the arrangement of a monomer sequence to show an optical activity in vinyl polymers.[8,9] The sequence suggested by Wulff can be formed by a simultaneous diastereoselective addition during propagation. Cyclopolymerization is an effective method to accomplish such a sequence. This was proven to be true by the cyclocopolymerization of nonconjugated diene monomers having a chiral template with styrene (St)[10,11] or methyl methacrylate (MMA).[12] The resulting copolymers still show an optical activity even after removing the chiral template.

On the other hand, *N*-phenyl-*N*-allylmethacrylamide (PAMA) was reported to yield highly cyclized polymers by radical homo- and copolymerizations.[13−15] Such cyclopolymerizations are also expected to produce asymmetric centers in the resulting polymers. Cyclopolymerization of 1,5-pentadiene with an optically active metallocene catalyst was found to yield optically active polymer.[16,17]

In an earlier paper we studied the effect of $SnCl_4$ on the radical cyclopolymerization of PAMA.[15] Recently we have tried to cause asymmetric induction by cyclohomo- and cyclocopolymerizations of PAMA in the presence of $SnCl_4$ and L-menthol as a chiral compound. The present paper describes the results observed in the asymmetric polymerizations of PAMA where dimethyl 2,2′-azobis(isobutyrate) (MAIB) was used as initiator.

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Experimental Section

Materials. PAMA was prepared by the reaction of *N*-allylaniline with methacryloyl chloride according to the literature procedure.[18] MAIB (from Wako Pure Chemicals) was recrystallized from methanol. $SnCl_4$ (guaranteed reagent, Wako Pure Chemicals) was used in an N_2 atmosphere in a polyethylene bag without further purification. L-Menthol (guaranteed reagent, Wako Pure Chemicals) was used without further purification. MMA and St were purified by distillations after being washed with a 5 wt % aqueous NaOH solution and then with water. Solvents were purified by the usual methods.

Polymerization Procedures. Homopolymerization and copolymerization of PAMA were carried out in a degassed and sealed glass tube with shaking. A merry-go-round type apparatus was used for photopolymerization of PAMA where a 400 W high-pressure mercury lamp was applied as the light source. The resulting polymers were isolated by pouring the polymerization mixture into a large amount of methanol. The precipitate was filtrated, dried in vacuo, and weighed. The degree of cyclization of the polymers and the composition of copolymers were determined from their ^{1}H-NMR spectra.

Measurements. ^{1}H-NMR spectra were measured with Hitachi R-24B (60 MHz) and JEOL-EX-400 (400 MHz) spectrometers in $CDCl_3$ containing tetramethylsilane (TMS) as an internal standard. The weight-average molecular weight (M_w) of the resulting polymers was determined by gel permeation chromatography (GPC) with a TOSO HLC-802A apparatus at 38 °C using tetrahydrofuran (THF) as eluent. The calibration curve was obtained using poly(St) standards. FT-IR spectra were recorded on a Perkin-Elmer model 1600 spectrometer. The samples were prepared as KBr pellets. The specific rotation ($[\alpha]_D$) of the resulting polymers was measured by using a JASCO-DIP-360 digital polarimeter at room temperature.

Results and Discussion

Radical Polymerization of PAMA in the Presence of L-Menthol. At first, the additive effect of L-menthol on the radical polymerization of PAMA was investigated. The polymerization of PAMA with MAIB was carried out at 60 °C in benzene in the presence of L-menthol. The polymerization proceeded homogeneously.

Table 1 lists the obtained results. The degree of cyclization (DC) was determined by comparing the peak area of pendant unsaturation protons (4.8−6.5 ppm)

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Table 1. Polymerization of PAMA in the Presence of L-Menthol with MAIB in Benzene[a]

no.	[L-menthol]/[PAMA]	time (h)	yield (%)	DC[b] (%)	$[\alpha]_D^{rt}$ [c] (deg)
1[d]	2.3	15.5	30.4	99	0
2[e]	4.4	20	37.5	98	0

[a] [PAMA] = 1.20 mol L^{-1}, [MAIB] = 5.00 × 10^{-2} mol L^{-1}. [b] Degree of cyclization. [c] c = 1.0, THF, l = 1.0 dm. [d] By photoirradiation at room temperature. [e] At 60 °C.

Table 2. Polymerization of PAMA with MAIB in Benzene in the Presence of $SnCl_4$/L-Menthol at Room Temperature by Photoirradiation[a]

no.	[L-menthol]/[PAMA]	time (h)	yield (%)	$10^{-4}\bar{M}_w$	DC[b] (%)	$[\alpha]_D^{rt}$ [c] (deg)
1	1.0	36	0.3			
2	3.0	30	9.9	5.1	98	−0.5
3	5.0	30	19.9	6.0	99	−0.5

[a] [PAMA] = [$SnCl_4$] = 0.50 mol L^{-1}, [MAIB] = 5.00 × 10^{-2} mol L^{-1}. [b] Degree of cyclization. [c] c = 0.75−1.0, THF, l = 1.0 dm.

with that of *N*-methylene protons (3.0−4.0 ppm) by ^{1}H-NMR. Protons of unreacted olefin were little detected in the ^{1}H-NMR spectra (DC = 98−99%). The resulting poly(PAMA) was soluble in the usual organic solvents. The cyclic structure of poly(PAMA)s was confirmed to be a five-membered ring by IR spectroscopy. The same cyclic structure was also contained in the polymers formed in the homopolymerizations of PAMA without any additives and in the presence of $SnCl_4$ alone.[15]

The specific rotation of the resulting polymers was measured in THF at room temperature. As shown in Table 1, the polymers showed no optical activity. Thus, the presence of L-menthol alone was found to cause no asymmetric induction in the radical polymerization of PAMA.

Radical Polymerization of PAMA in the Presence of $SnCl_4$ and L-Menthol. Next, the polymerization of PAMA with MAIB was performed in the presence of $SnCl_4$ and L-menthol. As reported in the earlier paper,[15] the presence of $SnCl_4$ was observed to cause an appreciable change in the reactivity of PAMA in its homo- and copolymerization, where the 1:1 and 1:2 complexes between $SnCl_4$ and PAMA were confirmed to be formed by ^{1}H-NMR spectroscopy.[15]

Table 2 presents the results observed in the photopolymerization of PAMA with MAIB at room temperature in benzene in the presence of $SnCl_4$ and L-menthol. The L-menthol concentration was changed from 1 to 5 times the monomer concentration, keeping [PAMA] = [$SnCl_4$] = 0.50 mol L^{-1} constant. When $SnCl_4$ was added to a benzene solution of L-menthol, the solution turned orange with heat evolution, indicating the interaction between $SnCl_4$ and L-menthol. The preceding paper described that no polymerization of PAMA proceeded when the molar ratio of $SnCl_4$ to PAMA was more than 0.7.[15] As shown in Table 2, the addition of L-menthol of 0.50 mol L^{-1} could only slightly restore the polymerization inhibited by $SnCl_4$. However, when [L-menthol]/[PAMA] (=[$SnCl_4$]) was 3.0 and 5.0, the polymerization proceeded homogeneously to yield colored (pink or light brown) polymers that were highly cyclized (DC = 98−99%) as described below. The yield and molecular weight of polymer increased with increasing L-menthol. The resulting poly(PAMA)s showed a specific rotation of $[\alpha]_D$ = −0.5. ^{1}H-NMR spectra of the polymers did not show any presence of L-menthol residues.

Table 3 summarizes the results obtained in the photopolymerization at room temperature where the

Table 3. Polymerization of PAMA with MAIB in Benzene in the Presence of $SnCl_4$/L-Menthol at Room Temperature by Photoirradiation[a]

no.	[L-menthol]/[PAMA]	time (h)	yield (%)	$10^{-4}\bar{M}_w$	DC[b] (%)	$[\alpha]_D^{rt}$ [c] (deg)
1	0	6	50.6	10.0	98	0
2	0.3	10	32.0	6.0	98	−0.5
3	0.5	12	22.3	4.3	98	−0.3
4	0.6	25	22.0	4.0	99	−1.5
5	0.7	36	11.2	3.5	97	−2.6
6	0.8	36.5	5.1	3.4	97	−5.1
7	0.9	21	trace			
8	1.0	10	trace			

[a] [PAMA] = 1.00 mol L^{-1}, [MAIB] = 5.00 × 10^{-2} mol L^{-1}, [$SnCl_4$] = [L-menthol]. [b] Degree of cyclization. [c] c = 0.75−1.0, THF, l = 1.0 dm.

Table 4. Polymerization of PAMA with MAIB in Benzene in the Presence of $SnCl_4$/L-Menthol at 60 °C[a]

no.	[L-menthol]/[PAMA]	time (h)	yield (%)	$10^{-3}\bar{M}_w$	DC[b] (%)	$[\alpha]_D^{rt}$ [c] (deg)
1	0	20	59.3	9.6	<100	0.0
2	0.2	6	9.1	7.1	98	−0.3
3	0.25	6	7.7	6.5	98	−0.4
4	0.4	12	18.4	5.0	96	−1.0
5	0.6	15	10.5	4.8	96	−2.3
6	0.75	21	1.5	4.2	95	−5.6

[a] [PAMA] = 1.00 mol L^{-1}, [MAIB] = 5.00 × 10^{-2} mol L^{-1}, [$SnCl_4$] = [L-menthol]. [b] Degree of cyclization. [c] c = 0.2−1.0, THF, l = 1.0 dm.

L-menthol concentration was varied, fixing the molar ratio of [L-menthol]/[$SnCl_4$] = 1, and the PAMA concentration was kept constant at 1.00 mol L^{-1}. Although the polymerization mixture turned from yellow to brown with time, the polymerization proceeded homogeneously. All the obtained polymers were again soluble in the usual organic solvents.

The polymer yield decreased with increasing $SnCl_4$ concentration. No polymer was formed at $SnCl_4$ concentrations above 0.9 mol L^{-1}. The molecular weight of poly(PAMA) also decreased with the $SnCl_4$ concentration. On the other hand, the specific rotation of polymer showed a tendency to increase with increasing $SnCl_4$ concentration. The poly(PAMA) formed at [$SnCl_4$] = [L-menthol] = 0.8 mol L^{-1} showed a maximum $[\alpha]_D$ value of −5.1.

We have also examined the usual radical polymerization of PAMA with MAIB at 60 °C in benzene in the presence of $SnCl_4$ and L-menthol. Similarly to the above photopolymerization, the concentrations of L-menthol and $SnCl_4$ were varied at a fixed molar ratio of [L-menthol]/[$SnCl_4$] = 1 and the monomer concentration was constant at 1.00 mol L^{-1}. As can be seen from Table 4, the same tendencies were observed for the polymerization rate, the molecular weight, and specific rotation of resulting poly(PAMA) as in the photopolymerization at room temperature. Poly(PAMA) obtained at [$SnCl_4$]/[PAMA] = 0.75 showed $[\alpha]_D$ = −5.6. ^{1}H-NMR spectra of the polymers did again not show any presence of L-menthol residue.

Thus, asymmetric induction was observed to occur in the radical cyclopolymerization of PAMA in the presence of L-menthol and $SnCl_4$.

Structure of Poly(PAMA) Formed in the Presence of L-Menthol and $SnCl_4$. Figure 1 illustrates the ^{1}H-NMR spectrum of the poly(PAMA), which showed the maximum specific rotation ($[\alpha]_D$ = −5.6) (no. 6 in Table 4), together with that of olefin protons of the PAMA monomer. Comparison of spectra of polymer ((A) and (B)) with that of monomer (C) reveals that intact

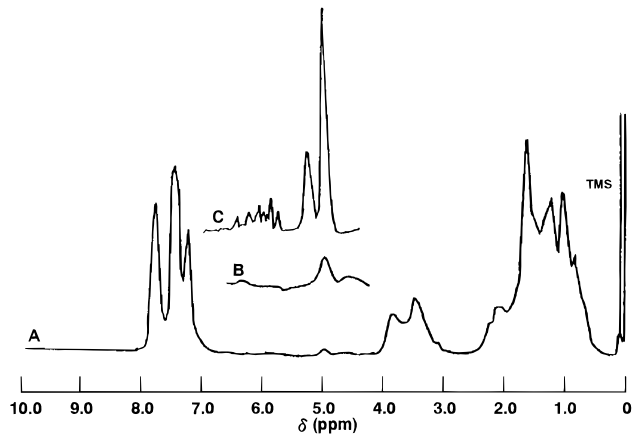


Figure 1. ^{1}H-NMR spectra. (A) Poly(PAMA) formed in the polymerization in the presence of $SnCl_4$/L-menthol; [PAMA] = 1.00 mol L^{-1}, [MAIB] = 5.00×10^{-2} mol L^{-1}, [$SnCl_4$] = [L-menthol] = 0.75 mol L^{-1}. (B) Same polymer, but measured in an increased gain. (C) Olefin protons of PAMA monomer.

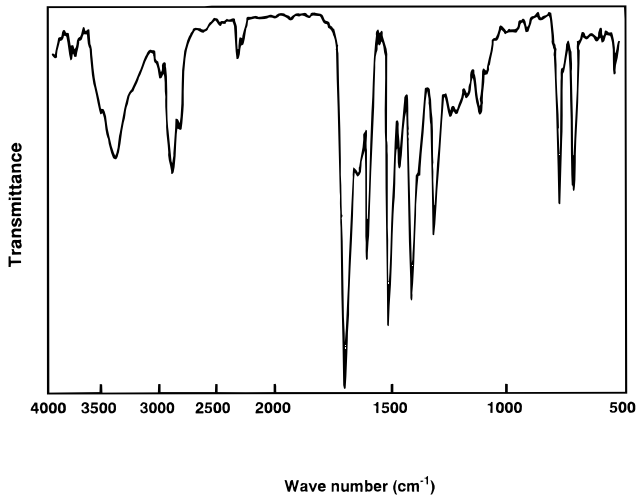


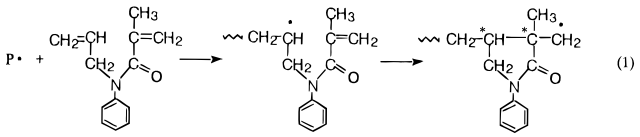
Figure 2. IR spectrum of poly(PAMA) formed in the polymerization of PAMA in benzene in the presence of $SnCl_4$/L-menthol at 60 °C.

unsaturations are mainly the methacryloyl group. It indicates that the allyl group of PAMA is first attacked and then cyclized to propagate in the present polymerization system.

DC of the polymers was estimated in the same manner described above. The obtained results are listed in Tables 2−4. Thus all the poly(PAMA)s formed in the presence of $SnCl_4$ and L-menthol were found to be highly cyclized (DC = 95−100%). As shown in Table 4, the DC value decreased slightly with increasing $SnCl_4$ concentration. A similar tendency was also observed in the radical polymerization of PAMA in the presence of $SnCl_4$ alone.[15]

Figure 2 shows the IR spectrum of the same polymer as in Figure 1. The stretching vibrations of C=O double bonds of five- and six-membered lactams are known to appear at 1690 and 1650 cm^{-1}, respectively.[19] The strong absorption at 1690 cm^{-1} in Figure 2 shows that the cyclic structure is a five-membered ring. All the polymers formed in the polymerization of PAMA/$SnCl_4$/L-menthol were confirmed to contain exclusively five-membered rings in the main chain.

As a conclusion, the propagation of the present polymerization proceeds according to eq 1 to generate chiral carbons in the polymer main chain. Either or both of the two asymmetric centers contribute to the optical activity of resulting



(P · : Propagating Polymer Radical * : Chiral Center)

poly(PAMA)s observed in Tables 2−4.

Copolymerization of PAMA and MMA in the Presence of $SnCl_4$ /L-Menthol. As reported in the preceding paper,[15] the presence of $SnCl_4$ changed the monomer reactivity ratios in the copolymerization of PAMA and MMA because $SnCl_4$ complexed not only PAMA but also MMA.[15]

The copolymerization of PAMA (M_1) and MMA (M_2) with MAIB was examined at 60 °C in benzene in the presence of $SnCl_4$ and L-menthol, where the total monomer concentration was fixed at 1.00 mol L^{-1}, keeping an equimolar ratio of PAMA, $SnCl_4$, and L-menthol ([PAMA] = [$SnCl_4$] = [L-menthol]). The observed results are listed in Table 5. The copolymerization proceeded homogeneously. The polymerization mixtures became yellow to brown during polymerization depending on the $SnCl_4$ concentration. The copolymerization rate and the molecular weight of the copolymer gradually decreased with increasing PAMA concentration in feed. All the copolymers formed were soluble in the usual organic solvents.

The composition of copolymer was estimated by ^{1}H-NMR spectroscopy (Figure 3), where the signal intensities of *N*-methylene protons of PAMA and methoxy protons of MMA (3.6−4.5 ppm) were compared with those of phenyl protons of PAMA (6.8−7.8 ppm). Figure 4 shows the copolymer composition curves for the systems of PAMA/MMA/$SnCl_4$/L-menthol, PAMA/MMA/$SnCl_4$,[15] and PAMA/MMA.[15] The monomer reactivity ratios of the PAMA/MMA/$SnCl_4$/L-menthol system were calculated to be $r_1 = 0.08$ and $r_2 = 3.42$ according to a curve-fitting method.[20] In Figure 4, the copolymer behavior of the PAMA/MMA/$SnCl_4$/L-menthol system is rather similar that of the PAMA/MMA system than that of the PAMA/MMA/$SnCl_4$ system.[15]

The DC value of PAMA units in the copolymer was determined to be 90−94% in the same manner described above. This high DC value is also similar to that of the PAMA/MMA system (DC = ∼99%),[15] comparing with that of the PAMA/MMA/$SnCl_4$ system (DC = 63−78%).[15] As can be seen from Figure 3, the methacryloyl group (4.5−6.5 ppm) was alone detected as the pendant unsaturation group in the copolymer. The same result was also obtained in the PAMA/MMA system,[15] whereas the allyl group was much more frequently observed than the methacryloyl group in the copolymers formed in the PAMA/MMA/$SnCl_4$ system.[15]

These findings suggest that L-menthol disturbs the interactions among PAMA, $SnCl_4$, and MMA. The complex between PAMA, MMA, and $SnCl_4$ was considered to play an important role in leaving the allyl group intact and in DC decreasing in the PAMA/$SnCl_4$ /MMA system in the earlier paper.[15] The presence of L-menthol weakens the ternary interaction. The complex of $SnCl_4$ and L-menthol interacts more strongly with PAMA as amide than with MMA as ester in the PAMA/$SnCl_4$/MMA/L-menthol system. Consequently, the cyclopolymerizability and copolymerization behavior of PAMA in the PAMA/MMA/$SnCl_4$/L-menthol system were rather similar to that in the PAMA/MMA system than that of the PAMA/$SnCl_4$/MMA system.

The cyclic structure derived from the PAMA unit in poly(PAMA-*co*-MMA) formed in the PAMA/MMA/$SnCl_4$/

Table 5. Copolymerization of PAMA (M_1) and MMA (M_2) in Benzene in the Presence of $SnCl_4$/L-Menthol at 60 °C[a]

no.	M_1 in feed (mol %)	time (min)	yield (%)	M_1[b] in copolymer (mol %)	$10^{-4}\bar{M}_w$	DC[c] (%)	M[d] (%)	A[e] (%)	$[\alpha]_D^{rt}$[f] (deg)
1	12.5	40	5.9	5.4	2.9	94	5	1	0.0
2	25.0	60	7.8	8.7	2.5	91	6	3	0.0
3	37.5	90	8.2	12.2	1.8	90	6	4	−0.6
4	50.0	150	9.6	19.9	1.4	91	6	3	−1.5
5	62.5	900	8.1	25.5	0.83	92	5	3	−5.0
6	75.0	900	3.1	38.9	0.68	92	4	4	−7.4
7	80.0	960	3.6	43.6	0.77	91	5	4	−9.1
8	87.5	900	0.6	48.6	0.56	94	2	4	−15.2

[a] $[M_1] + [M_2] = 1.00$ mol L^{-1}, $[MAIB] = 5.00 \times 10^{-2}$ mol L^{-1}, $[M_1] = [SnCl_4] =$ [L-menthol]. [b] Determined by ^{1}H-NMR. [c] Degree of cyclization. [d] M = content of pendant methacryloyl group. [e] A = content of pendant allyl group. [f] $c = 0.1-2.1$, $CHCl_3$, $l = 1.0$ dm.

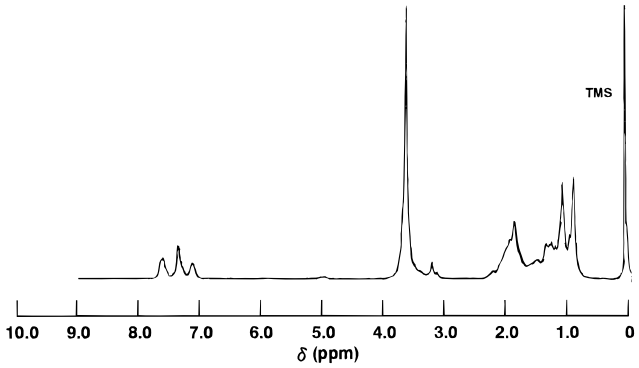


Figure 3. ^{1}H-NMR spectrum of poly(PAMA-*co*-MMA) obtained in the copolymerization of PAMA and MMA in benzene in the presence of $SnCl_4$/L-menthol at 60 °C; $[PAMA] = [MMA] = [SnCl_4] =$ [L-menthol] = 0.50 mol L^{-1}, $[MAIB] = 5.00 \times 10^{-2}$ mol L^{-1}.

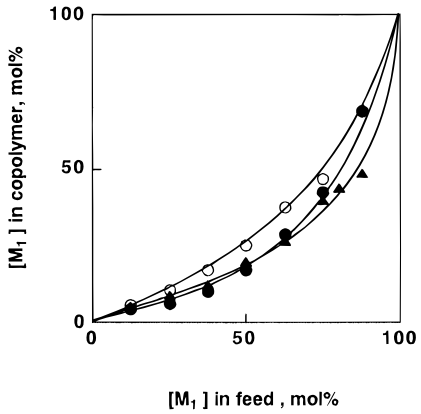


Figure 4. Copolymer composition curves for the copolymerizations of PAMA (M_1)/MMA (M_2) (●), PAMA (M_1)/MMA (M_2)/$SnCl_4$ (○), and PAMA (M_1)/MMA (M_2)/$SnCl_4$/L-menthol (▲) systems in benzene at 60 °C; $[M_1] + [M_2] = 1.00$ mol L^{-1}, $[MAIB] = 5.00 \times 10^{-2}$ mol L^{-1}.

L-menthol system proved to be only a five-membered ring from the IR spectrum.

Table 5 also lists the $[\alpha]_D$ values of the copolymers formed in the PAMA/MMA/$SnCl_4$/L-menthol system. The optical activity was observed for all the copolymers formed at the feed composition of PAMA higher than 37.5 mol %. The $[\alpha]_D$ value increased with increasing feed composition of PAMA and reached −15.2 at the 85 mol % feed composition of PAMA.

Figure 5 illustrates the relationship between the PAMA content and the $[\alpha]_D$ value of copolymer. Thus, the optical activity increased with the PAMA content, but the increment was not proportional to the latter.

As mentioned above, no polymer was formed in the polymerization at $[PAMA] = [SnCl_4] =$ [L-menthol] = 1.00 mol L^{-1}. So, the $[\alpha]_D$ value of homopoly(PAMA) to

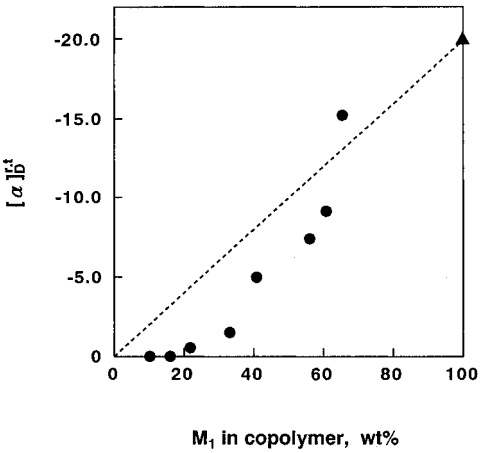


Figure 5. Dependence of specific rotation $[\alpha]_D$ on the composition (wt %) of poly(PAMA-*co*-MMA)s obtained in the copolymerization in the presence of $SnCl_4$/L-menthol; $[M_1] = [SnCl_4] =$ [L-menthol].

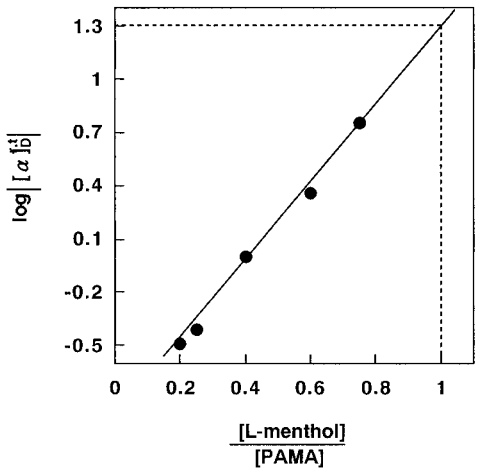


Figure 6. Relationship between specific rotation $[\alpha]_D$ and [L-menthol]/[PAMA] ($[SnCl_4] =$ [L-menthol]).

be formed under such conditions was predicted by extrapolation in Figure 6 obtained from the data in Table 4 in the following manner. Figure 6 shows the plot of $\log(-[\alpha]_D)$ against the molar ratio of [L-menthol]/[PAMA]. Using the linear relationship thus observed, the $[\alpha]_D$ value was estimated to be −20.0 at $[PAMA] = [SnCl_4] =$ [L-menthol] = 1.00 mol L^{-1}.

The dotted line in Figure 5 was obtained using the $[\alpha]_D$ value of −20.0. The observed $[\alpha]_D$ values of the copolymers showed some deviations from the dotted straight line. Such deviations suggest that the asymmetric induction occurs not only on the PAMA unit but also on the MMA one.

Copolymerization of PAMA and St in the Presence of $SnCl_4$ and L-Menthol. The copolymerization

Table 6. Copolymerization of PAMA (M_1) and St (M_2) in Benzene in the Presence of $SnCl_4$ and L-Menthol at 60 °C[a]

no.	M_1 in feed (mol %)	time (min)	yield (%)	hex-insol[b] (%)	M_1 in copolymer[c] (mol %)	$10^{-3}\bar{M}_w$	DC[d] (%)	M^e (%)	A^f (%)	$[\alpha]_D^{rt}$ [g] (deg)
1	37.5	6	7.5	1.1	27.2	2.4	25	69	6	−9.1
2	50.0	10	7.2	2.6	36.2		29	63	8	−11.8
3	87.5	42	8.9	8.9	55.4	2.4	68	27	5	−9.8

[a] $[M_1] + [M_2] = 1.00$ mol L^{-1}, $[MAIB] = 5.00 \times 10^{-2}$ mol L^{-1}, $[M_1] = [SnCl_4] =$ [L-menthol]. [b] Cyclohexane-insoluble fraction of formed polymer. [c] Determined by ^{1}H-NMR. [d] Degree of cyclization. [e] M = content of pendant methacryloyl group. [f] A = content of pendant allyl group. [g] $c = 0.1-2.1$, $CHCl_3$, $l = 1.0$ dm.

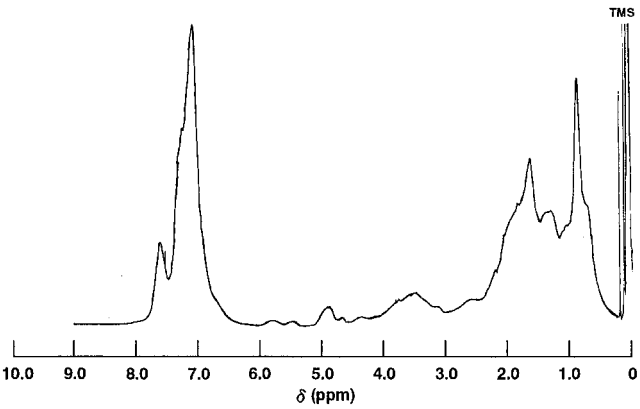


Figure 7. ^{1}H-NMR spectrum of poly(PAMA-*co*-St) obtained in the copolymerization of PAMA and St in benzene in the presence of $SnCl_4$/L-menthol at 60 °C: $[PAMA] = [SnCl_4] =$ [L-menthol] = 0.875mol L^{-1}, $[MAIB] = 5.00 \times 10^{-2}$ mol L^{-1}.

PAMA (M_1) and St (M_2), electron-donating monomer, with MAIB was performed in benzene in the presence of $SnCl_4$ and L-menthol. The total monomer concentration in the feed was kept constant at 1.00 mol L^{-1}, and the concentration of PAMA used in all runs was equal to those of $SnCl_4$ and L-menthol. The homopoly(St) cationally formed by $SnCl_4$ was removed by reprecipitation from the benzene−cyclohexane system. The cyclohexane-insoluble part as copolymer was subjected to measurement.

Figure 7 illustrates the ^{1}H-NMR spectrum of copolymer formed at 37.5 mol % of PAMA in the feed. The copolymer composition was determined by comparing the signal intensities of *N*-methylene protons of PAMA (3.6−4.5 ppm) with those of phenyl protons of PAMA and St (6.8−7.8 ppm). The results obtained are presented in Table 6. The DC value of the copolymer was estimated by comparing the peak area of pendant unsaturation protons with that of *N*-methylene protons. As shown in Table 6, the DC value of the PAMA unit was considerably low, especially in the PAMA feed composition less than 50 mol %. It is noteworthy that the pendant group of copolymer was mainly the methacryloyl group. The absorption at 1697 cm^{-1} in the IR spectrum of the resulting poly(PAMA-*co*-St) showed that the cyclic unit is exclusively a five-membered structure.

In spite of such low DC values, the copolymers were found to show fairly high $[\alpha]_D$ values (−9.1 to −11.8) independently of the PAMA content in the copolymer. ^{1}H-NMR spectra of the copolymers did not show any presence of L-menthol residue.

Conclusion

Optically active polymer was obtained in the radical cyclopolymerization of PAMA in benzene in the presence of L-menthol and $SnCl_4$, whereas the polymerization in the presence of L-menthol alone gave no optically active polymer. The DC value of poly(PAMA) formed in the PAMA/L-menthol/$SnCl_4$ system was very high (97−99%) and the cyclic structure was exclusively five-membered. The interaction between PAMA and L-menthol through $SnCl_4$ causes asymmetric induction in the cyclic main chain of the resulting poly(PAMA). A maximum optical activity ($[\alpha]_D = -5.6$) was observed for the polymer formed in the polymerization at 60 °C at a molar ratio of [PAMA]/[$SnCl_4$]/[L-menthol] = 1/1/0.75.

Copolymerization of PAMA with MMA in the presence of $SnCl_4$ and L-menthol also yielded optically active copolymers. The PAMA unit was incorporated almost exclusively as a five-membered ring into the copolymers (DC = 90−94%). When [PAMA] was 85 mol % in the feed, the resulting copolymer showed a maximum $[\alpha]_D$ value (−15.2). Much lower DC values (25−68%) were observed for copolymers obtained in the copolymerization of PAMA with St in the presence of L-menthol and $SnCl_4$. Pendant unsaturated groups of the copolymers were mainly the methacryloyl group. The copolymers showed $[\alpha]_D$ values of −9.1 to −11.8.

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