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Asymmetric Induction in the Free Radical Copolymerization of Isobutyl Vinyl Ether with Maleic Anhydride in *l*-Menthol

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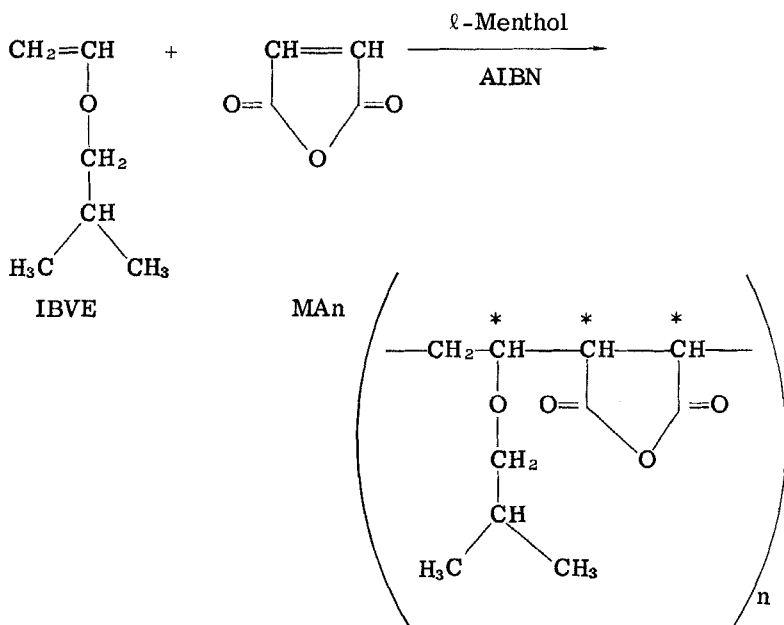
ABSTRACT

The radical copolymerization of isobutyl vinyl ether with maleic anhydride was carried out in the presence of *l*-menthol by using azobisisobutyronitrile. The resulting copolymer was found to be alternating and optically active. The overall activation energy for copolymerization was calculated to be 22.8 kcal/mol in the presence of *l*-menthol and 22.0 kcal/mol in the absence of *l*-menthol. The specific rotation of the copolymer decreased with an increase of the reaction temperature.

INTRODUCTION

During our investigation of the solvent effect on the radical copolymerization of styrene (St) with vinyl monomers having polar groups in various solvents, we found that their monomer reactivity ratios were influenced considerably by the reaction temperature and solvents [1-6]. We have already postulated the hypothesis that this might be caused by the hydrogen-bonding solvation of the polar group of a vinyl monomer in the ground state and the transition state of a propagation step. We found that an optically active copolymer was obtained by the radical copolymerization of St with maleic anhydride (MAN) in ℓ -menthol [7] and that optically active addition products were obtained by the radical reaction of cyclohexanone with 2-octene in ℓ -menthol [8]. We extended our concept to an asymmetric induction in the radical addition of thiols to olefins [9-11].

Thus, with the hope of finding an additional example of asymmetric inductive radical copolymerization, the radical copolymerizations of various vinyl monomers having polar groups were carried out in the presence of several chiral compounds [12]. However, no optically active copolymer was obtained except for the copolymerization of isobutyl vinyl ether (IBVE) with MAN. This article deals with the reinvestigated results of the radical copolymerization of IBVE (M_1) with MAN (M_2) in the presence of ℓ -menthol.



Recently Doiuchi and Minoura reported successful asymmetric polymer synthesis in an interfacial emulsion copolymerization in the presence of lecithin [13-16]. Kataoka and Ando reported asymmetric induction by the radical polymerization of methacrylic acid and sorbic acid in the presence of chitosan [17, 18].

EXPERIMENTAL

Isobutyl vinyl ether (IBVE, M_1) was purified by the usual method. Maleic anhydride (MAN, M_2) was purified by recrystallization from chloroform.

ℓ -Menthol was purified by distillation; $[\alpha]_D^{25} -50.1^\circ$ ($C = 10$, EtOH).

Azobisisobutyronitrile (AIBN) and other reagents were purified by the ordinary methods.

Copolymerization was carried out in degassed ampules. The prescribed amounts of monomers, initiator, solvent, and ℓ -menthol were sealed in vacuo and shaken in a thermostated incubator. After a definite polymerization time the ampule was broken and the contents were added to THF containing hydroquinone. The THF solution was then poured into an excess of n-hexane to isolate the copolymer. All the copolymers were purified by reprecipitation from THF and n-hexane. The copolymers were characterized by infrared (IR) and nuclear magnetic resonance (NMR) spectral analyses and elemental analysis.

Optical rotation measurements were made with a Jasco model J-20 automatic recording spectropolarimeter equipped with a xenon source.

Measurements of IR spectra were taken with a Hitachi model 285 grating IR spectrophotometer.

^1H and ^{13}C NMR spectral measurements were made at 100 and 25 MHz with a Jeol model PS PFT-100 NMR spectrometer.

Ultraviolet (UV) spectra were measured by using a Shimadzu model UV-150-02 spectrophotometer at 25°C : a continuous variation method was adopted to determine the composition of the charge-transfer (CT) complex of IBVE with MAN in the absence and presence of ℓ -menthol.

RESULTS AND DISCUSSION

An optically active copolymer was found to be produced in the radical copolymerization of IBVE (M_1) with MAN (M_2) in the presence of ℓ -menthol (Table 1). It was noted that the reaction proceeded homogeneously in THF but heterogeneously without THF. Figure 1 shows the relationships between the values of the mole ratio of ℓ -menthol to monomers and those of the copolymerization rate (R_p),

TABLE 1. Radical Copolymerization of IBVE (M_1) with MAN (M_2) in the Presence of ℓ -Menthhol at 60°C^a

Run	M_1 (mmol)	M_2 (mmol)	ℓ -Menthhol (mmol)	Solvent (mL)	Time (min)	Yield (%)	R_p (%/min)	$\frac{[m_1]}{[m_1] + [m_2]}$	$[\eta]_{DMF}^{27}$	$[\alpha]_{400}^{25}$ (THF)
0 ^b	23.1	22.9	0.0	THF (10)	27	31.20	1.16	0.45	0.25	0.00
1	23.1	22.9	23.4	None	87	23.37	0.27	0.45	0.63	-0.22
2	23.1	23.2	46.7	None	130	12.52	0.10	0.46	0.50	-0.44
3	23.1	23.0	69.8	None	190	9.34	0.05	0.45	0.37	-0.59
4	23.1	23.1	93.1	None	240	11.04	0.05	0.45	0.34	-0.85
5 ^b	23.1	23.1	23.1	THF	71	10.19	0.14	0.50	-	-0.09
6 ^b	23.1	23.1	47.6	THF	110	9.60	0.09	0.48	-	-0.12

^aRuns 0-4, $[AIBN] = 2.41 \times 10^{-4}$; Runs 5 and 6, $[AIBN] = 1.35 \times 10^{-3}$ mol/L. Total volume: 22 mL.

^bThe reaction proceeded homogeneously.

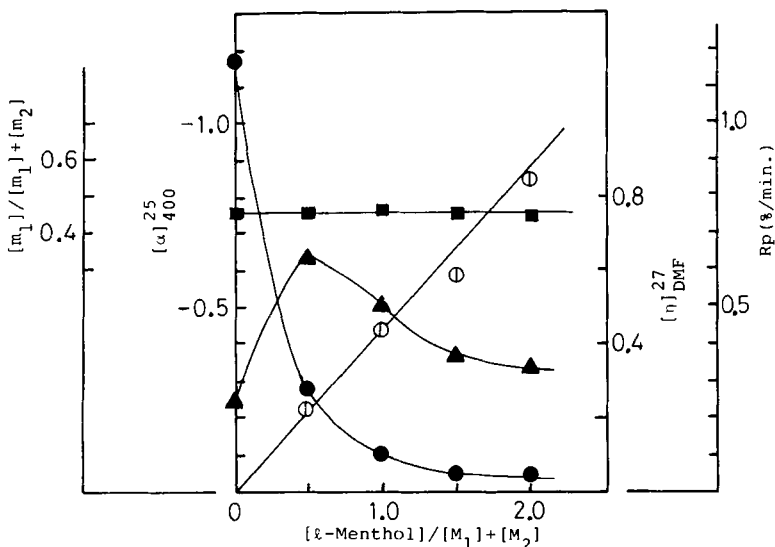


FIG. 1. Relationships between the mole ratio of *l*-menthol vs monomers and R_p (●), $[\eta]$ (▲), $[\alpha]$ (○), and $[m_1]$ mole fraction (■) of the copolymers (Run No. 0-4)

the copolymer composition and the intrinsic viscosity $[\eta]$, and the specific rotation $[\alpha]$ of the copolymers. The copolymers were found to consist of about 1:1 molar composition of IBVE vs MAN, suggesting that the reaction proceeded via the CT complex formed between IBVE and MAN, even in the presence of *l*-menthol. Incidentally, the formation of the CT complex both in the absence and in the presence of *l*-menthol was confirmed via the continuous variation method with UV spectrophotometer (Fig. 2). It is interesting to note that with an increase of the *l*-menthol fraction the values of $[\alpha]$ increased but those of R_p decreased. These observations suggest that an asymmetric induction in the copolymerization might be caused by an interaction between the CT complex and *l*-menthol. There may be other possibilities of yielding an optically active copolymer. One is the possibility of introducing an *l*-menthol unit into the copolymer by esterification of an MAN unit to increase the $[\alpha]$ value of the copolymer. However, it was observed that an optically inactive copolymer was yielded when a copolymer obtained in the absence of *l*-menthol was heated with *l*-menthol in THF at 60°C for 6 h. Alternatively, chain transfer to *l*-menthol might introduce an *l*-menthyl unit to the copolymer. However, ¹H and ¹³C NMR and IR spectral analyses revealed that the copolymer was not contaminated

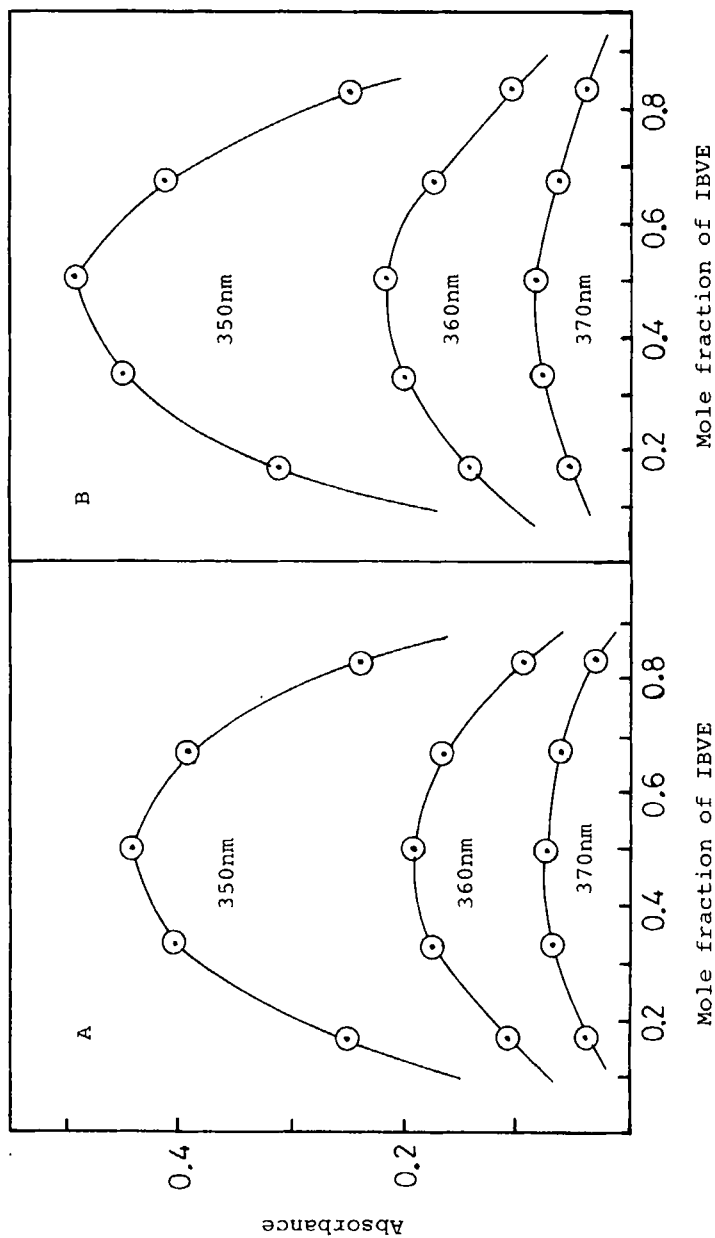


FIG. 2. Continuous variation method for the CT complex of IBVE with MAn in THF solution at 25°C. A: In the absence of *l*-menthol, $[IBVE] = 1.23 \text{ mol/L}$, $[MAn] = 1.23 \text{ mol/L}$. B: In the presence of *l*-menthol, $[IBVE] = 1.23 \text{ mol/L}$, $[MAn] = [l\text{-menthol}] = 1.23 \text{ mol/L}$.

TABLE 2. Influence of Temperature on the Copolymerization of IBVE (M_1) with MAN (M_2) in the Presence of ℓ -Menthhol^a

Run	Temperature (°C)	ℓ -Menthhol (mol/L)	Time (min)	Yield (%)	$R_p \times 10^5$ (mol/L·s)	$\frac{[m_1]}{[m_1] + [m_2]}$	$[\eta]_{DMF}^{27}$	$[\alpha]_{400}^{25}$ (THF)
T6-0	60	0.0	20	16.72	29.28	0.47	0.17	0.00
T6-1	60	2.14	50	13.65	9.57	0.47	0.23	-0.10
T5-0	50	0.0	60	17.88	10.45	0.48	0.20	0.00
T5-1	50	2.14	130	12.61	3.58	0.48	0.26	-0.14
T4-0	40	0.0	120	12.24	3.57	0.48	0.25	0.00
T4-1	40	2.14	250	7.75	1.09	0.49	0.33	-0.16

^a $[M_1] = [M_2] = 1.05$ mol/L; $[AIBN] = 1.16 \times 10^{-2}$ mol/L; solvent, THF; total volume 22 mL.

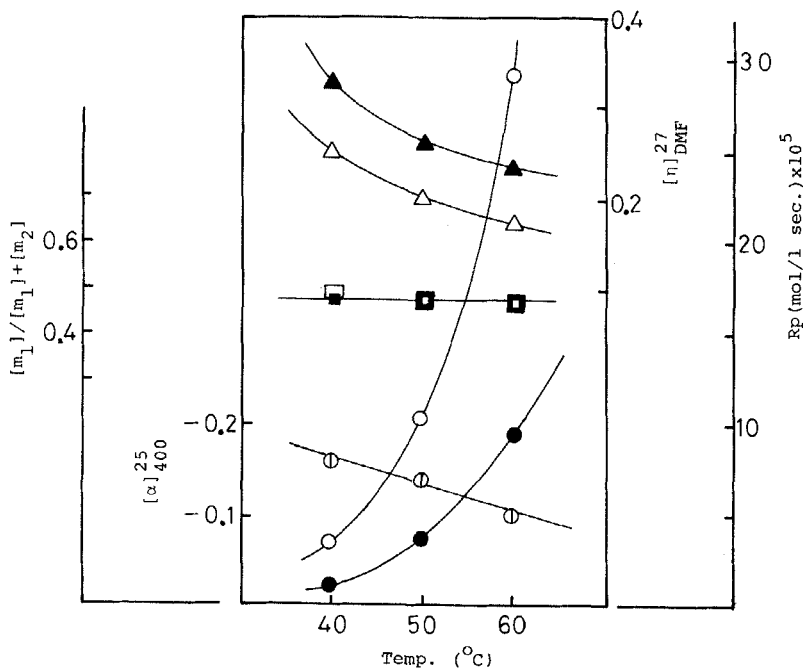


FIG. 3. Influence of temperature on R_p (\bullet , \circ), $[\eta]$ (\blacktriangle , \triangle), $[\alpha]$ (\blacklozenge , \lozenge), and the $[m_1]$ mole fraction (\blacksquare , \square) of the copolymers. (\bullet , \blacktriangle , \blacksquare): In the presence of ℓ -menthol. (\circ , \triangle , \square): In the absence of ℓ -menthol. $[M_1] = [M_2] = 1.05$ mol/L, $[\ell\text{-menthol}] = 2.14$ mol/L, $[AIBN] = 1.16 \times 10^{-2}$ mol/L, solvent THF, total volume 22 mL.

with an ℓ -menthyl unit. This is also suggested to be less possible in light of the facts that no optically active copolymer was obtained in the radical copolymerizations of styrene with maleic acid and methyl methacrylate in the presence of camphoric acid or sparteine, of indene with acrylic acid in the presence of oleic cholesterol, and of methyl methacrylate with maleic acid and methyl acrylate in the presence of camphoric acid or sparteine [12].

Table 2 and Fig. 3 show the results of copolymerization of IBVE (M_1) with MAN (M_2) both in the absence and in the presence of ℓ -menthol at 40, 50, and 60°C. The overall activation energies for the copolymerizations were calculated by Arrhenius plots of R_p values to be 22.0 kcal/mol in the absence of ℓ -menthol and 22.8 kcal/mol in its presence. Alternate copolymers were obtained for all the systems, and the increase of the reaction temperature decreased

TABLE 3. Influence of Monomer Ratio on the Copolymerization of IBVE (M_1) with MAN (M_2) in ℓ -Menthol at 60°C^a

Run	M_1 mole ratio	Time (min)	Yield (%)	R_p (%/min)	$\frac{[m_1]}{[m_1] + [m_2]}$	$[\eta]_{DMF}^{27}$	$[\alpha]_{400}^{25}$ (THF)
0 ^b	0.50	18	20.39	1.13	0.50	0.26	0.00
1	0.13	2880	0.0	-	-	-	-
2	0.25	1440	Trace	-	-	-	-
3	0.33	285	1.65	0.01	0.45	0.39	-1.75
4	0.50	57	5.85	0.10	0.48	0.48	-0.46
5	0.67	20	10.35	0.52	0.48	0.76	-0.13
6	0.75	32	16.80	0.53	0.47	0.79	-0.10
7	0.83	9	5.32	0.59	0.49	0.83	-0.08

^a $[M_1] + [M_2] = 46.1$ mmol, [ℓ -menthol] = 46.5 mmol, [AIBN] = 2.43×10^{-4} mol.

^bIn the absence of ℓ -menthol but in THF (10 mL).

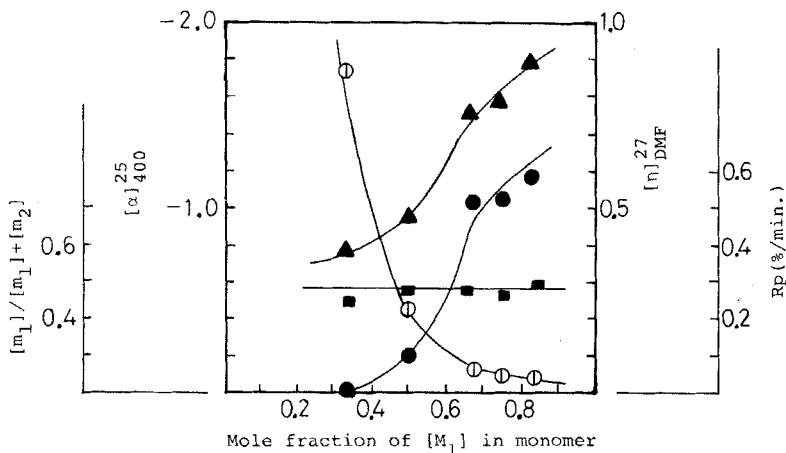


FIG. 4. Influence of monomer ratio of R_p (●), $[\eta]$ (▲), $[\alpha]$ (○), and $[m_1]$ mole fraction (■) of the copolymers. $[M_1] + [M_2] = 46.1$ mmol, $[\ell\text{-menthol}] = 46.5$ mmol, $[AIBN] = 2.43 \times 10^{-4}$ mol at 60°C .

the values of $[\eta]$ and $[\alpha]$. It is noted that the values of R_p in the presence of ℓ -menthol were smaller than those in the absence of ℓ -menthol while larger $[\eta]$ values were obtained in the former case, indicating that ℓ -menthol might affect the polymerizability.

The influence of monomer composition in the copolymerization was examined (Table 3 and Fig. 4). Alternate copolymers were found to be formed, regardless of monomer composition in the feed, suggesting that the polymerization proceeds via the CT complex even in the presence of ℓ -menthol. However, it should be noted that the polymerization phenomena characteristic of the CT complex were not observed; namely, the maximum values in R_p and $[\eta]$ were not observed at a 1:1 molar ratio of IBVE and MAN in the monomer feed, and these values decreased with an increase of MAN in the feed, while the $[\alpha]$ value increased with an increase of the MAN fraction. Several possibilities might be responsible for this anomalous behavior. A possibility of collapse of the CT complex via hydrogen bonding interaction with ℓ -menthol can be ruled out because alternate copolymers were obtained for every system. On the other hand, the poor solubility of the resulting copolymer might be responsible for this behavior since the polymerization proceeded heterogeneously in ℓ -menthol. However, a homogeneous system using THF as solvent showed similar tendencies (Table 4 and Fig. 5).

Here we wish to postulate the assumption that an equilibrium would be formed by an interaction between ℓ -menthol and the CT

TABLE 4. Influence of Monomer Ratio on the Copolymerization of IBVE (M_1) with MAn (M_2) in the Presence of ℓ -Menthol at 60°C^a

Run	M_1 mole ratio	Time (min)	Yield (%)	R_p (%/min)	$\frac{[m_1]}{[m_1] + [m_2]}$	$[\eta]^{27}_{DMF}$	$[\alpha]^{25}_{400}$ (THF)
1	0.17	1030	0.98	-	0.44	-	-
2	0.33	199	12.04	0.06	0.49	0.16	-0.49
3 ^b	0.33	28	20.31	0.73	0.50	0.22	0.00
4	0.50	51	13.62	0.27	0.50	0.25	-0.10
5 ^b	0.50	19	19.93	1.05	0.50	0.29	0.00
6	0.67	24	11.62	0.48	0.49	0.32	-0.08
7	0.83	24	14.11	0.59	0.49	0.38	-0.05
8 ^b	0.83	20	20.60	1.03	0.50	0.40	0.00

^a $[M_1] + [M_2] = 46.1$ mmol; $[\ell\text{-menthol}] = 46.6$ mmol; $[AIBN] = 2.6 \times 10^{-4}$ mol; solvent, THF (10 mL).

^bAbsence of ℓ -menthol.

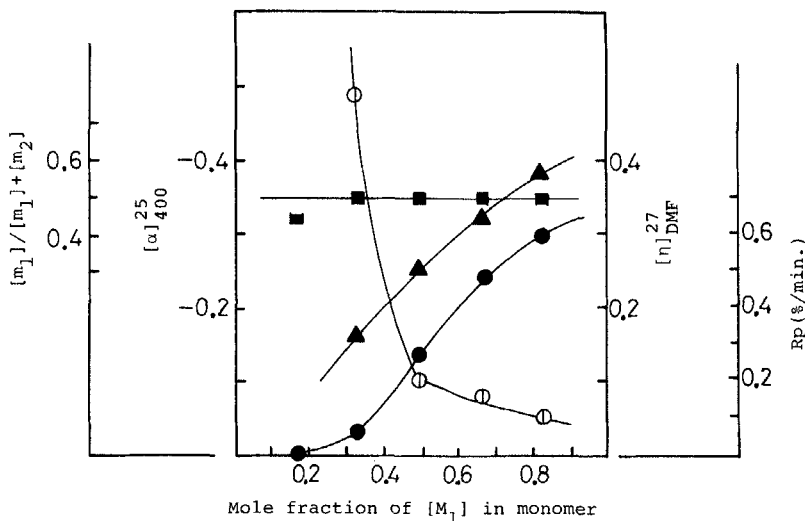
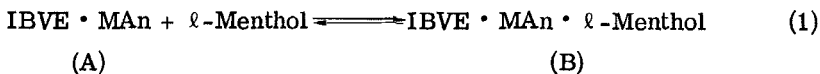


FIG. 5. Influence of monomer ratio on R_p (●), $[\eta]$ (▲), $[\alpha]$ (○), and $[m_1]$ mole fraction (■) of the copolymers. $[M_1] + [M_2] = 46.1$ mmol, $[\ell\text{-menthol}] = 46.6$ mmol, $[AIBN] = 2.6 \times 10^{-4}$ mol, solvent THF (10 mL) at 60°C .

complex, possibly via a hydrogen bonding, and that the polymerization proceed from both Complexes A and B



This will result in the formation of an alternate copolymer. The increase in $[\alpha]$ of the copolymer with an increase of both the ℓ -menthol fraction in Fig. 1, and the MAN fraction in Fig. 4 could be explained by assuming this equilibrium. The decrease in R_p values with the addition of ℓ -menthol, as shown in Figs. 1 and 3, might be explained by assuming that the polymerization velocity from B is smaller than that from A, perhaps by a steric effect in the growing radical of Complex B. A similar explanation could be applied to the decrease of R_p in Figs. 4 and 5.

A more meaningful explanation of this novel asymmetric induction is not available, but it should be emphasized that asymmetric induction occurred only in the MAN-IBVE and MAN-styrene systems. No optically active copolymer was obtained for other systems as

described in a previous paper [12]. In any event, we believe that a protic chiral solvent may interact with the CT complex formed between MAn and styrene or IBVE via hydrogen bonding to form a three-dimensional complex that might play an important role in asymmetric induction.

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