

Copolymerization of *l*-Menthyl Vinyl Ether with Other Vinyl Ethers and Optical Rotatory Properties of the Copolymers*

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ABSTRACT: The cationic copolymerizations of *l*-menthyl vinyl ether (*l*-MenVE) with methyl vinyl ether (MVE), benzyl vinyl ether (BzVE), and *p*-phenylbenzyl vinyl ether (PhBVE) were carried out in toluene at low temperatures in the presence of $\text{BF}_3 \cdot \text{OEt}_2$. The specific rotation at $589 \text{ m}\mu$ of copoly(*l*-MenVE-MVE) was proportional to the content of *l*-MenVE in the copolymers. In copoly(*l*-MenVE-BzVE) and copoly(*l*-MenVE-PhBVE), however, the absolute values of the specific rotations were higher than those of the corresponding mixtures of the homopolymers. The optical rotatory dispersion curves of these copolymers in cyclohexane showed Cotton effects at π - π^* transition based on the aromatic chromophores. These optical abnormalities of the copolymers may be attributed to some asymmetric conformations induced in the comonomer unit by the steric influence of the asymmetric *l*-MenVE unit.

KEY WORDS Cationic Copolymerization / *l*-Menthyl Vinyl Ether / Methyl Vinyl Ether / Benzyl Vinyl Ether / *p*-Phenylbenzyl Vinyl Ether / $\text{BF}_3 \cdot \text{OEt}_2$ / Optical Activity / Optical Rotatory Dispersion / Asymmetric Conformation /

The evaluation of the optical rotatory properties of the copolymer obtained from the optically active vinyl monomer and the optically inactive vinyl monomer is a useful tool to study the conformational correlation between the monomer units in the copolymer in solution. Recently, Pino and coworkers¹ described how the copolymer of (R)-3,7-dimethyl-1-octene with styrene shows, in the $260\text{-m}\mu$ region, a Cotton effect connected with a formally forbidden π - π^* transition of aromatic chromophore. They also prepared (3S, 9S)-3,9-dimethyl-6-phenylundecane as a low molecular weight model. They concluded that the higher rotational strength of the π - π^* aromatic transition at about $260 \text{ m}\mu$ in the copolymer than that in the low molecular weight model is attributable to the conformational rigidity of the units derived from styrene. Furthermore, they reported that the specific rotations of the copolymers obtained from (S)-4-methyl-1-hexene and 4-methyl-1-pentene in the presence of the $\text{TiCl}_4/\text{Zn}(\text{iso-C}_4\text{H}_9)_2$ catalytic system do not depend

linearly on the content of (S)-4-methyl-1-hexene units.² It is their conclusion that in the copolymer the 4-methyl-1-pentene units can be considered optically active with an overall contribution to the optical rotation.

On the other hand, a linear relationship has been obtained between the optical rotation at $589 \text{ m}\mu$ and the copolymer composition in the copolymers of *d*- and *dl*- α -methylbenzyl methacrylates,³ of *l*- and *dl*-menthyl vinyl ethers,⁴ and of *l*-menthyl acrylate and styrene.⁵

In this paper we describe the results of the cationic copolymerizations of *l*-menthyl vinyl ether (*l*-MenVE) with methyl vinyl ether (MVE), benzyl vinyl ether (BzVE), and *p*-phenylbenzyl vinyl ether (PhBVE), carried out in toluene at low temperatures in the presence of $\text{BF}_3 \cdot \text{OEt}_2$. The optical rotatory power of the copolymer of *l*-MenVE and MVE was proportional to the content of *l*-MenVE in the copolymer. In the copolymers of *l*-MenVE and BzVE and of *l*-MenVE and PhBVE, however, the specific rotations at $589 \text{ m}\mu$ were anomalously dependent on the contents of *l*-MenVE. The optical rotatory dispersion curves of these copolymers showed Cotton effects as-

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sociated with the allowed π - π^* transitions of the aromatic chromophores.

EXPERIMENTAL

Materials

l-Menthyl Vinyl Ether (*l*-MenVE)

l-Menthyl vinyl ether was prepared from *l*-menthol and a large excess of isobutyl vinyl ether by ether interchange reaction catalyzed by a small amount of mercuric acetate. The crude product was purified by fractional distillation under reduced nitrogen pressure, followed by the distillation under high vacuum over lithium aluminum hydride, $[\alpha]_{589}^{15} - 72.7^\circ$ ($c = 2.0$ g/dl, toluene), bp 86.5–87.5°C (15 mm), n_D^{20} 1.4548. The NMR spectrum (neat) showed peaks at ppm 0.70–2.30 (multiplet, 18.40H) assigned to the protons of the menthyl group, 3.48 (peak center, double triplets, 1.11H) assigned to methine (–OCH) proton of the menthyl group, 3.80, 3.86, 4.08, and 4.24 (four doublets, 2.04H) assigned to the β protons of the vinyl group, 6.11–6.33 (quartet, 1.00H) assigned to the α proton of the vinyl group.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.06; H, 12.17. Found: C, 79.13; H, 12.20.

Benzyl Vinyl Ether (*BzVE*)

Benzyl vinyl ether was prepared from benzyl alcohol and acetylene according to Reppe.⁶ It was treated with sodium metal and with calcium hydride, and distilled over lithium aluminum hydride,⁷ bp 59.0°C (5.4 mm), n_D^{20} 1.5162.

p-Phenylbenzyl Vinyl Ether (*PhBVE*)

p-Phenylbenzaldehyde was prepared from biphenyl by the Gattermann–Koch reaction.⁸ Reduction of this aldehyde with lithium aluminum hydride in tetrahydrofuran afforded *p*-phenylbenzyl alcohol in 93% yield. *p*-Phenylbenzyl vinyl ether was obtained in 75% yield by the transesterification reaction of this alcohol and methyl vinyl ether in the presence of molecular sieves, type 4A using mercuric acetate as catalyst.⁹ Purification of the vinyl ether was effected by the distillation under reduced nitrogen pressure, bp 113–115°C (1 mm), mp 51–52°C. The NMR spectrum (CCl_4 , 10 w/v%) showed peaks at ppm 3.94, 4.05, 4.07, and 4.32 (four doublets, 2.04H) assigned to the β protons of the vinyl group, 4.70 (singlet, 2.00H) assigned to the methylene protons of the *p*-phenylbenzyl group, 6.29–6.62 (quartet, 1.00H) assigned to

the α proton of the vinyl group, 7.07–7.52 (multiplet, 8.97H) assigned to the aromatic protons of the *p*-phenylbenzyl group.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.38; H, 6.71.

Methyl Vinyl Ether (*MVE*)

Commercial methyl vinyl ether was purified by the usual method¹⁰ and dried over a mixture of calcium hydride and molecular sieves, type 4A. It was finally transferred under the reduced nitrogen pressure from a flask containing a small amount of lithium aluminum hydride to an ampoule just before use.

Toluene

Toluene was purified as usual¹¹ and then distilled into a reaction vessel attached to a vacuum system using calcium hydride as drying agent.

$BF_3 \cdot OEt_2$

$BF_3 \cdot OEt_2$ was distilled under reduced nitrogen pressure and used as a solution in toluene (0.5 mol/l).

Polymerization

Polymerization was carried out in a glass ampoule under nitrogen atmosphere. Weighed monomers were first placed in the ampoule using syringes except MVE, which was transferred into the ampoule under reduced nitrogen pressure. Then, the solvent was added with a syringe. The solution was immersed in a bath at a constant temperature, and the catalyst solution was added with a syringe. The reaction was terminated by the addition of a trace of ammoniac methanol. Then, the mixture was poured into a large amount of methanol and the precipitated polymer was separated by filtration, washed with methanol, dried, and weighed. In the copolymerization of *l*-MenVE and MVE a methanol soluble polymer was also produced. The mother liquor of the methanol insoluble fraction was evaporated to a small volume. The concentrated solution was poured into a large amount of hot water to precipitate the methanol soluble fraction. It was purified by freeze-drying from benzene solution.

Measurements

Optical rotations were measured on a Yanagimoto OR-10 photoelectric polarimeter using a 0.5-dm cell. The concentration of polymer solution was about 2% in toluene and the precision of the reading was $\pm 0.003^\circ$.

Optical rotatory dispersions between 600 $m\mu$ and 215 $m\mu$ were measured with a Yanagimoto ORD-185 spectropolarimeter on a copolymer solution in cyclohexane at several concentrations. Fused quartz cells of 0.2, 0.05, and 0.01-dm length were used.

Solution viscosities were determined using an Ostwald viscometer on a 0.5% solution of copolymer in benzene at 30°C.

NMR spectra were obtained at 50°C with a JNM-4H-100 spectrometer (JEOL) at 100MHz by using 10w/v% polymer solution in carbon tetrachloride containing a few percent of tetramethylsilane as an internal standard. An NMR spectrum of *l*-MenVE (neat) was also obtained at room temperature with the same spectrometer. The precision of chemical shift measurements was ± 0.05 Hz. An NMR spectrum of PhBVE (CCl₄, 10w/v%) was obtained at room temperature with a JNM-MH-60 spectrometer (JEOL) at 60MHz using tetramethylsilane as an external standard. The precision of chemical shift measurements was ± 0.35 Hz.

Ultraviolet spectra were determined with a Hitachi 124 spectrophotometer.

RESULTS

The copolymerizations of *l*-menthyl vinyl ether with methyl vinyl ether and with benzyl vinyl ether were carried out with BF₃·OEt₂ in toluene at -78°C. The results are shown in Tables I and II. The polymerization reactions were per-

formed for a sufficient time to reach high yields of the polymers. In the copolymerization of *l*-MenVE and MVE, methanol soluble polymers were obtained by increasing the content of MVE in the monomers charged. The compositions of these copolymers were determined by elementary analysis and NMR spectroscopy. The carbon content was employed for the composition analysis of the copolymers of *l*-MenVE and MVE [copoly(*l*-MenVE-MVE)] (Table I), and the hydrogen content for the copolymers of *l*-MenVE and BzVE [copoly(*l*-MenVE-BzVE)] (Table II). In the NMR analysis, the composition of copoly(*l*-MenVE-MVE) was calculated from the intensity ratio of the methoxy proton signal to the remainder, and that of copoly(*l*-MenVE-BzVE) was determined from the intensity ratio of the phenyl proton signal to the remainder. As shown in Tables I and II, the copolymer compositions by elementary analysis were in good agreement with those calculated from NMR spectroscopy.

The optical rotations of the copolymers and those of the binary mixtures of the corresponding homopolymers were measured on 2% solution in toluene and plotted against the compositions. A linear relationship between the specific rotation and the composition was obtained in copoly(*l*-MenVE-MVE) as well as in the mixtures of poly(*l*-menthyl vinyl ether) (*P-l*-MenVE) and poly(methyl vinyl ether) (PMVE) (Figure 1). On the other hand, in the case of *l*-MenVE and BzVE, the optical rotation of the homopolymer mixture

Table I. Copolymerization of *l*-MenVE(M₁) and MVE(M₂)^a

M ₁ /(M ₁ +M ₂) (wt %)	Yield (%)	m ₁ /(m ₁ +m ₂)(wt %)		η_{sp}/C (dl/g)	[α] ¹⁵ ₅₈₉ (deg)
		from C%	from NMR		
100	93	100	100	0.60	-227.2
92.2	95	96.1	94.9	0.36	-217.7
80.5	82	95.7	95.1	0.34	-215.2
73.9	78	91.8	94.0	0.29	-210.4
68.1	70	90.1	91.8	0.29	-207.9
39.6	42	67.6	68.4	0.48	-162.2
	13 ^b	41.4	41.0	0.42	-97.2
24.9	47 ^b	49.5	51.8	0.42	-107.1
11.2	99 ^b	13.7	14.4	1.33	-37.9
0	85 ^b	0	0	1.45	0

^a Polymerization condition: Total monomer, 10 mmol; Solvent, Toluene 20 ml; Initiator, BF₃·OEt₂ 0.1 mmol; Temp., -78°C; Time, 22 hr.

^b Methanol soluble polymer.

Copolymerization of *l*-Menthyl Vinyl Ether**Table II.** Copolymerization of *l*-MenVE(M₁) and BzVE(M₃)^a

M ₁ /(M ₁ +M ₃) (wt %)	Yield (%)	m ₁ /(m ₁ +m ₃) (wt %)		η_{sp}/C (dl/g)	[α] ¹⁵ ₅₈₉ (deg)
		from H%	from NMR		
100	93	100	100	0.60	-227.2
79.5	76	84.0	84.5	0.89	-198.8
61.7	96	64.1	67.9	1.32	-164.2
53.1	97	51.6	51.3	1.69	-149.2
49.1	89	50.0	49.6	1.55	-146.5
39.5	94	34.1	34.8	1.69	-118.0
29.2	99	26.3	25.5	1.80	-92.1
25.0	98	24.9	25.1	1.89	-82.4
0	98	0	0	—	0

^a Polymerization condition: Total monomer, 10 mmol; Solvent, Toluene 20 ml; Initiator, BF₃·OEt₂ 0.1 mmol; Temp., -78°C; Time, 5 hr.

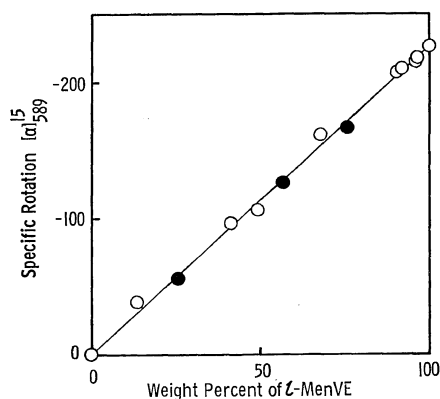


Figure 1. The relationship between specific rotation and *l*-MenVE content in copoly(*l*-MenVE-MVE).

- : Copoly(*l*-MenVE-MVE).
●: Mixtures of P-*l*-MenVE and PMVE.

was proportional to the content of P-*l*-MenVE, but the optical rotations of the copolymers were deviated from the straight line and their absolute values were larger than those of the corresponding mixtures of the homopolymers (Figure 2).

The optical rotatory dispersions were measured on P-*l*-MenVE and some of the copolymers obtained. The dispersion curves of P-*l*-MenVE and the copolymer of *l*-MenVE and BzVE (51.6:48.4) in cyclohexane are shown in Figure 3. The dispersion of P-*l*-MenVE fitted simple Drude plots. The copolymer of *l*-MenVE and MVE (67.6:32.4) gave a similar dispersion curve to that of P-*l*-MenVE, and its optical rotations per *l*-MenVE unit agreed exactly with those of the P-*l*-MenVE over the whole wave length measured.

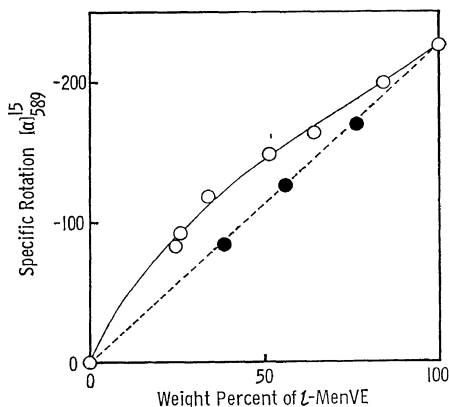


Figure 2. The relationship between specific rotation and *l*-MenVE content in copoly(*l*-MenVE-BzVE).

- : Copoly(*l*-MenVE-BzVE).
●: Mixtures of P-*l*-MenVE and Poly-BzVE.

On the other hand, the dispersion of the copoly(*l*-MenVE-BzVE) showed a Cotton effect with a trough at 221 m μ . This is associated with the allowed π - π^* transition of phenyl chromophore because the ultraviolet spectrum of the copolymer shows a large absorption band at 220 m μ . There is no Cotton effect connected with the formally forbidden π - π^* transition of the aromatic chromophore in the 260-m μ region.

In copoly(*l*-MenVE-BzVE), the Cotton effect was observed as described above, but was not distinct because the measurement was done near the limit of the region which could be investigated with our spectropolarimeter. Therefore, in order to obtain a more definite observation on the Cotton effect, *p*-phenylbenzyl vinyl ether (PhBVE) was

Table III. Copolymerization of *l*-MenVE(M_1) and *p*-PhBVE(M_4)^a

$M_1/(M_1+M_4)$ (wt %)	Yield (%)	$m_1/(m_1+m_4)$ (wt %)			$[\alpha]_{589}^{20}$ (deg)
		from C%	from NMR	from UV	
100	98	100	100	100	-212.9
80.3	94	81.8	78.9	76.1	-176.1
60.4	89	61.5	58.3	56.1	-146.6
50.1	92	50.8	49.3	47.7	-134.2
41.8	91	37.6	40.2	37.1	-117.3
25.8	90	25.5	24.2	23.9	-89.1
0	72	0	0	0	0

^a Polymerization condition: Total monomer, 6 mmol; Solvent, Toluene 30 ml; Initiator, $\text{BF}_3 \cdot \text{OEt}_2$ 0.13 mmol; Temp., -30°C ; Time, 26 hr.

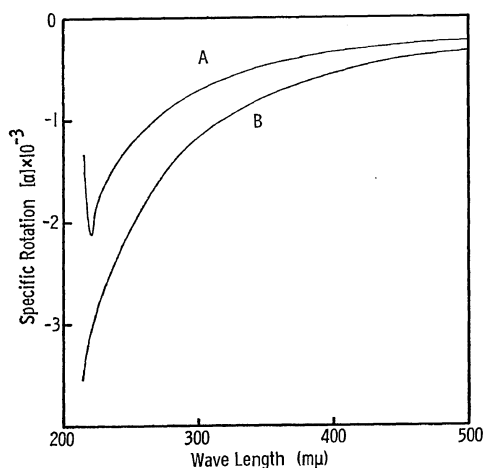


Figure 3. Optical rotatory dispersion curves
(A): Copoly(*l*-MenVE-*Bz*VE) (51.6:48.4).
(B): *P-l*-MenVE.

employed to be copolymerized with *l*-MenVE, because a PhBVE unit has an absorption deeper than that of a BzVE unit. The results of the copolymerization are shown in Table III. In this case, the copolymer composition was also determined by measuring the UV absorption^{1,5} in tetrahydrofuran using the band at 253 $m\mu$ and the molar extinction coefficient of the homopolymer of PhBVE ($\epsilon = 19800$). As shown in Figure 4, a similar relationship was observed between the specific rotation and the copolymer composition to that obtained with copoly(*l*-MenVE-*Bz*VE). Figure 5 shows the optical rotatory dispersion curve of the copolymer of *l*-MenVE and PhBVE (81.8:18.2) in cyclohexane. It has a clear π - π^* Cotton effect with a trough at 266 $m\mu$ and a peak at 250 $m\mu$ corresponding to the π - π^* transition at

253 $m\mu$ in the UV spectrum of the copolymer in tetrahydrofuran.

DISCUSSION

It was already known that the polymerization of vinyl ether gives a highly isotactic polymer in hydrocarbon solvent with cationic initiator at low temperature.^{7,12-15} The homopolymer of *l*-MenVE prepared under the same conditions as employed in the copolymerization described above was crystalline in X-ray diffraction pattern, and showed so high a melting point (210–235°C) that the homopolymer is expected to have fairly high isotacticity. From NMR study it has been also found that the homopolymer of BzVE was able to take a very high isotacticity of more than 90% in dyad.⁷ The reactivities of *l*-MenVE and BzVE are similar to each other in the cationic copoly-

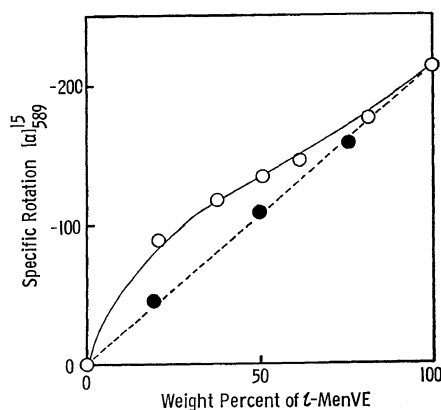


Figure 4. The relationship between specific rotation and *l*-MenVE content in copoly(*l*-MenVE-PhBVE).

○: Copoly(*l*-MenVE-PhBVE).
●: Mixtures of *P-l*-MenVE and Poly-PhBVE.

merizations with *n*-butyl vinyl ether,¹⁶ and so these two monomers are expected to copolymerize randomly, forming a highly coisotactic copolymer. It is reasonable to say that PhBVE may also form a highly isotactic homopolymer and copolymer with *l*-MenVE because the lateral chain of the PhBVE unit in the polymer is analogous to that of BzVE unit.

As described in the preceding section, the optical rotations of the homopolymer mixtures containing P-*l*-MenVE as one component were proportional to the amount of P-*l*-MenVE, showing that the optical activity of P-*l*-MenVE is not affected by the presence of the other poly-(vinyl ether). On the other hand, in the copoly-(*l*-MenVE-BzVE) and copoly(*l*-MenVE-PhBVE), the optical rotations were not proportional to the content of *l*-MenVE; their absolute values exceeded those of the corresponding homopolymer mixtures (Figures 2 and 4). Furthermore, the optical rotatory dispersion curves were anomalous in the regions where the absorption bands of the allowed π - π^* transitions of aromatic chromophores appear (Figures 4 and 5), while the dispersion of P-*l*-MenVE fitted simple Drude plots in the range measured.

As a cause of the enhancement of the optical activity in the copolymer it might be probable that the optical rotation of P-*l*-MenVE would depend on the degree of polymerization, and the optical rotatory power of the *l*-MenVE unit in

its short sequence, corresponding to its oligomer, might be larger than that in the longer sequence or high polymer. However, this is not likely because of the linearity of the optical rotation vs. *l*-MenVE content in copoly(*l*-MenVE-MVE), although the copolymer seems to be a block one as stated below. Furthermore, the Cotton effects observed in the copolymers suggest that the optical rotations were contributed by the monomer units containing aromatic groups, which have inherently no true asymmetric center.

The P-*l*-MenVE obtained here exhibited a rotatory power about three times higher than that of the starting monomer or of the low molecular weight model reported by Liquori and coworkers.¹⁷ Such enhancement of the optical activity of isotactic polymer has been reported on poly-(α -olefin)s^{1,18-22} and poly(vinyl ether)s^{17,23,24} and explained by the prevalence of helical conformation of the polymer in solution. It may be assumed that both the copoly(*l*-MenVE-BzVE) and copoly(*l*-MenVE-PhBVE) were coisotactic, and the *l*-MenVE unit has the same asymmetric conformations in these copolymers as that in the homopolymer. Under these assumptions, it may be probable that the optical abnormalities of the copolymers described above are caused by some asymmetric conformations of BzVE and PhBVE units induced by the adjacent *l*-MenVE units. When the BzVE or PhBVE unit takes an asymmetric conformation, the aromatic chromophore in the lateral chain is coincidentally perturbed by dissymmetric surroundings, and so the Cotton effect appears at the absorption band of the aromatic group. A similar phenomenon was observed by Pino and his coworkers on the copolymer of (R)-3,7-dimethyl-1-octene and styrene.¹

The enhancement of the optical rotation in the copolymer was still recognized on the copolymers in which *l*-MenVE contents are small. This phenomenon suggests that even a short sequence of *l*-MenVE units may have the same asymmetric conformations and similar effect on the adjacent BzVE or PhBVE unit as those of the longer sequences.

On the other hand, in the case of the copolymers of *l*-MenVE and MVE no abnormal optical properties were observed. Two reasons may be

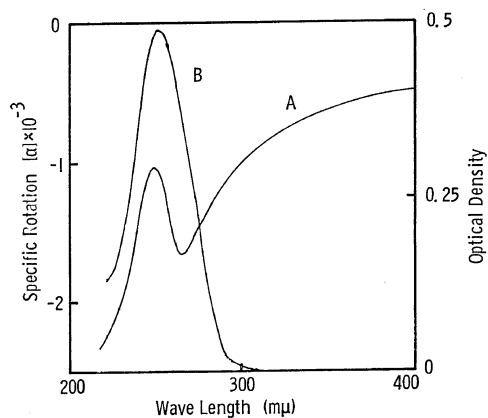


Figure 5. Optical rotatory dispersion curve (A) and UV absorption curve (B) of copoly(*l*-MenVE-PhBVE) (81.8:18.2). (B): $c = 2.2 \times 10^{-4}$ g/l.

given explaining this fact: (a) The methoxy group in MVE was so small that the MVE units were not sterically influenced by the asymmetric conformations of *l*-MenVE units. (b) The polymers produced were rather block copolymers because the polymerization reactivity of MVE is considerably smaller than that of *l*-MenVE.¹⁶ In the latter case, the optical properties will be similar to those of the mixtures of both homopolymers.

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