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Free Radical Copolymerization of Styrene with N-Substituted Maleimides in Chiral Substances

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ABSTRACT

Optically active copolymers were obtained by radical copolymerization of styrene with N-methyl-, N-cyclohexyl- and N-t-butyl-maleimides in ℓ-menthol or N-p-toluenesulfonyl- and N-carbobenzoyloxy-L-prolines.

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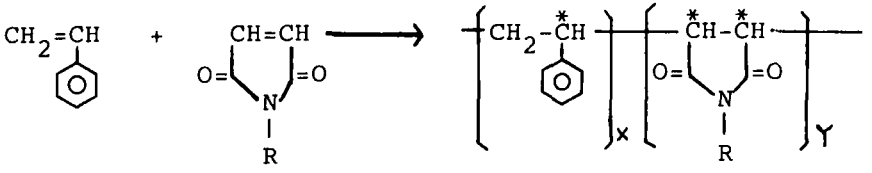
INTRODUCTION

Our preceeding papers showed that optically active copolymers were obtained by free radical copolymerization of maleic anhydride (MAn) with styrene (St) and isobutyl vinyl ether in ℓ-menthol [1-3]. We assumed that this might be caused by hydrogen bonding to the polar carbonyl group of MAn or its propagating radical. The present work deals with the radical copolymerization of St with such N-substituted maleimides as N-methylmaleimide (MMI), N-cyclohexylmaleimide (CMI), N-t-butylmaleimide (BMI), and N-phenylmaleimide (PMI) in several chiral substances.



where R = methyl (MMI), cyclohexyl (CMI), t-butyl (BMI), and phenyl (PMI).

EXPERIMENTAL

Maleimide derivatives were synthesized by the known methods [4, 5] and purified by the usual method.

Styrene (St) was purified by distillation under reduced pressure in a stream of nitrogen.

ℓ-Menthol, $[\alpha]_D^{25}$ -50.1° (concentration = 10, EtOH), was commercially available.

(-)-N-p-Toluenesulfonyl-L-proline(TSP), $[\alpha]_D^{10}$ -92.5° (concentration = 5,MeOH), and (-)-N-carbobenzoyloxy-L-proline(CZP), $[\alpha]_D^{18}$ -38.3° (concentration = 5, EtOH), were prepared by known methods [6].

2,2'Azobisisobutyronitrile (AIBN) and other reagents were purified by ordinary methods.

Copolymerization was carried out in degassed ampules. The prescribed amounts of monomers, initiator, solvent, and chiral substance in a glass tube were flushed three times with nitrogen, sealed in vacuo, and placed in a thermostated incubator. After a definite polymerization time, the ampule was cooled at -60°C to stop the copolymerization. The ampule was broken and the contents were added to a large amount of ether or n-hexane to precipitate the copolymer. All the copolymers were purified by reprecipitation from 1,2-dichloroethane-ether or THF-ether (or n-hexane).

The copolymers were characterized by IR and 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.

RESULTS AND DISCUSSION

Table 1 shows the results of the radical copolymerization of St (M_1) with several substituted maleimides in a few chiral substances. Optically active copolymers were obtained from the MMI, CMI, and BMI systems (Nos. 5-10), but not from the PMI system (No. 3). In the case of the ℓ-menthol systems (Nos. 2 and 5-7), the St-MMI copolymer was found to have the highest $[\alpha]$ value. The St-BMI copolymers obtained in ℓ-menthol (No. 6) and TSP (No. 9) had different α directions, while the MMI systems gave copolymers of the same α direction in ℓ-menthol and TSP (Nos. 5 and 8). This means that the nature of the substituent in maleimide, as well as the combination of monomer and chiral substance, is important in differentiating the enantio faces of the monomers.

Table 2 shows the results of the copolymerization of St (M_1) with MMI and BMI by changing the monomer ratios and concentration of chiral substances. In both cases, common random copolymerization took place; the monomer reactivity ratios were determined to be r_1 = 0.10 and r_2 = 0.04 for the MMI system and r_1 = 0.10 and r_2 = 0.19 for the BMI system. Incidentally, no formation of a CT complex between St and maleimide derivatives was observed by UV spectroscopy either in the absence or the presence of chiral substances. The α value was almost unchanged when the concentration of the chiral substances (Nos. 7-8 and 11-13) or the monomer ratios (Nos. 1-4 and 5-7) were varied.

^{1}H- and ^{13}C-NMR and IR apectral analyses revealed that optically active copolymers were not contaminated with chiral substance units incorporated by side reactions such as chain transfer to chiral substances and esterification of the maleimide monomers or the copolymers. It was also observed that the St-MMI copolymer obtained in the absence of chiral substance when heated with an excess of ℓ-menthol in THF at 60°C for 13 h yielded an optically inactive copolymer. A meaningful explanation of this novel asymmetric induction is not available, but one possibility is hydrogen bonding interaction between the maleimide and protic chiral substance as in the case of St and isobutyl vinyl ether-maleic anhydride systems [1-3]. However, no asymmetric induction occurred in the radical copolymerization of St with methyl methacrylate (MMA) and methacrylic acid (MA), of indene with acrylic acid, or of MMA with MA and methyl acrylate in chiral substances [2]. The five-membered maleimide has a far lower degree of freedom than the above common vinyl monomers. Thus, a protic

TABLE 1. Radical Copolymerization of St (M_1) with N-Substituted Maleimides (M_2) in Chiral Substances at 60°C[a]

Run	M_2 (mmol)	Chiral substance[b]	Time (min)	Yield (%)	$\frac{d[m_2]}{d([m_1] + [m_2])}$	$[\alpha]_{400}^{25}$ (solvent, concentration)
1[c]	PMI (8.7)	None	42	66.8	0.50	0.00 (DCE,[h] 2.5)
2	PMI (8.7)	Ment	10	32.3	-	0.00 (DCE, 2.5)
3	PMI (8.7)	Ment[d]	20	14.6	-	0.00 (DCE, 2.5)
4	PMI (8.7)	Camp	43	19.8	-	0.00 (DCE, 2.5)
5	MMI (17.0)	Ment	8	11.6	0.49	+1.20 (DCE, 3.0)
6	BMI (17.0)	Ment	30	41.9	0.52	+0.36 (THF, 1.6)
7	CMI (17.0)	Ment	23	22.7	0.50	+0.22 (THF, 2.0)
8[e]	MMI (17.0)	TSP	56	92.4	-	+0.43 (THF, 2.5)
9[c,f]	BMI (17.0)	TSP	70	24.0	-	-1.08 (THF, 2.3)
10[f,g]	BMI (8.5)	CZP	10	64.4	-	-1.39 (THF, 2.1)

[a] [AIBN] = 0.1 wt%, $[M_1] = [M_2]$ = [chiral substance].
[b] Ment: (-)-ℓ-menthol; Camp: (+)-D-campholic acid; TSP: (-)-N-p-toluenesulfonyl-L-proline; CZP: (-)-N-carbobenzoyloxy-L-proline.
[c] THF (10 mL) was used as the solvent.
[d] [ℓ-Menthol] = 61.11 mmol.
[e] THF (15 mL) was used as the solvent.
[f] AIBN = 0.2 wt%.
[g] At 70°C.
[h] DCE: 1,2-dichloroethane.

TABLE 2. Copolymerization of St (M_1) with MMI and BMI[a]

Run	M_2[b] (mmol)	Chiral substance (mmol)	Temperature (°C)	Time (min)	Yield (%)	$\frac{d[m_2]}{d([m_1] + [m_2])}$	$[\alpha]_{400}^{25}$ (solvent, concentration)
1	MMI (3.5)	Ment (8.7)	50	15	3.2	0.42	+1.10 (DCE, 2.0)
2	MMI (8.7)	Ment (8.7)	50	16	9.8	0.49	+1.15 (DCE, 2.0)
3	MMI (10.0)	Ment (8.7)	50	16	2.8	0.50	+0.80 (DCE, 2.0)
4	MMI (14.0)	Ment (8.7)	50	46	3.1	0.52	+0.90 (DCE, 2.0)
5	BMI (6.8)	Ment (17.0)	60	157	41.1	0.43	+0.17 (THF, 2.0)
6	BMI (13.6)	Ment (17.0)	60	55	54.4	0.49	+0.18 (THF, 2.0)
7	BMI (17.0)	Ment (17.0)	60	30	41.9	0.52	+0.36 (THF, 1.6)
8	BMI (17.0)	Ment (85.0)	60	157	97.7	-	+0.35 (THF, 2.0)
9	BMI (20.4)	Ment (17.0)	60	52	66.9	0.55	-
10	BMI (27.2)	Ment (17.0)	60	133	47.1	0.64	-
11	BMI (8.5)	CZP (8.5)	70	10	64.4	-	-1.39 (THF, 2.1)
12	BMI (8.5)	CZP (25.5)	70	13	51.0	-	-1.54 (THF, 2.1)
13	BMI (8.5)	CZP (55.0)	70	34	45.0	-	-1.56 (THF, 2.1)

[a] [AIBN] = 0.1 wt% for Nox. 1-10, 0.2 wt% for Nos. 11-13.
[b] $[M_1] + [M_2]$ = 17 mmol for Nos. 1-4 and Nos. 11-13, 34 mmol for Nos. 5-10.

chiral substance might rather effectively fix the geometry of the maleimide monomer or its radical via hydrogen bonding to induce an asymmetric center in the product.

On this assumption, we have preliminarily carried out the radical homopolymerization of N-isopropylmaleimide (14 mmol) in CZP (14 mmol) using 5 wt% AIBN at 70°C for 90 min to get 20.5% of optically active polymer ($[\alpha]_{400}^{25}$ +1.30° in THF). No contamination of CZP in the polymer was spectroscopically confirmed. Further investigations on this line are now being conducted in our laboratory. The results will be reported in the future.

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