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NOTES

Synthesis and Polymerization of *N*-[*N'*-(α-Methylbenzyl)aminocarbonylmethyl]citraconimide

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We reported the polymerization of optically active *N*-(substituted)maleimides (RMI) and chiroptical properties of the resulting polymers and copolymers.[1-4] It was suggested that asymmetric induction into the homopolymer and copolymer main chain took place based on chiroptical properties for a model compound of the polymer and for the copolymers. Asymmetric induction was much influenced by optically active *N*-substituents, and its magnitude in the maleimide containing an optically active [(α-methylbenzyl)aminocarbonyl]methy group (MBCM)[5] as a *N*-substituent was greatest reported by the authors so far.[1-5] However, it is not clear how asymmetric induction can be influenced by a substituent located at a carbon of the reacting double bond in the maleimide ring. It can be expected that asymmetric induction into the copolymer main chain caused by a substituent (in this case, methyl group) located at the double bond may be greater than that in the RMI derivatives because of *no symmetric structure* of the citraconimide. This is considered to result from the fact that α-methyl maleimide derivatives (*i.e.*, citraconimide derivatives) contain more *prochiral* carbons.

In this paper, a novel, optically active *N*-[*N'*-(α-methylbenzyl)aminocarbonylmethyl]-citraconimide (MBCC); *i.e.*, the corresponding (α-methyl)maleimide, was prepared from citraconic anhydride, glycine, and (*R*)-(+)-α-methylbenzylamine. MBCC is polymerized and copolymerized with styrene (ST) and methyl methacrylate (MMA) in the presence of radical initiators. The monomer reactivity ratios are determined. From the specific rotation and molecular ellipticity of the copolymers, optical activities for the copolymers contributed to the comonomer unit are discussed, compared with that of MBCM[5] including no α-methyl group in the RMI ring.

EXPERIMENTAL

MBCC Monomer

The MBCC monomer was synthesized from citraconic anhydride, glycine, and (*R*)-(+)-α-methylbenzylamine, as shown in Scheme 1.

N-[(Chlorocarbonyl)methyl]citraconimide (CGCI). A mixture of GCI [mp 128—129°C][6] (27.1 g; 0.16 mol), thionyl chloride (100; 1.04 mol) and *tert*-butylcathecol (0.01 g) was refluxed for 2 h. Unreacted thionyl chloride was

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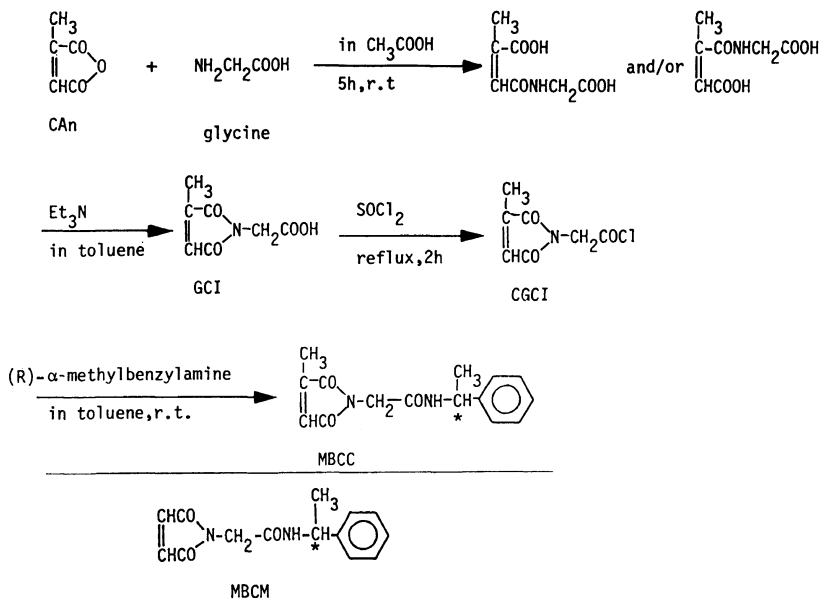

Scheme 1.

removed by evaporation, and the residual product was distilled under reduced pressure to obtain pure CGCI; yield 76%, bp 70°C/ 4.4×10^{-2} mmHg. IR (KBr disk) (cm^{-1}): 1795 (COCl); 1780 and 1710 (CONCO); 1644 (C=C); 1355 (CH_3); 860 (CH); 690 (*cis* H–C=C–). ^1H NMR (δ, ppm from TMS in $CDCl_3$): 6.50—6.41 (m, 1H, H–C=C–); 4.61 (s, 2H, N–CH_2); 2.11 (d, J=4 Hz, 3H, CH_3–C=C).

N-[N'-((R)-α-Methylbenzyl)aminocarbonylmethyl]citraconimide (MBCC). A benzene (250 ml) solution of CGCI (9.0 g, 0.10 mol) was added dropwise to a solution of (*R*)-α-methylbenzylamine (6.1 g, 0.05 mol) and triethylamine (4.65 g, 0.05 mol) in benzene (250 ml) at 0—5°C, and the mixture was stirred at room temperature for 2 h. The precipitated product was filtered, washed with water, dried, and recrystallized twice from methanol–water (1 : 3) to obtain pure MBCC; 8.8 g, yield 64.6%, mp 154—155°C, $[\alpha]_D^{25}$ =115.2° (c=1 g dl^{-1}, l=10 cm, THF). IR (KBr disk) (cm^{-1}): 3248 (NH): 1708 and 1718 (C=O), 1644 (CONH); 1620 (C=C), 1545 and 1490 (CONH); 1380 (CH_3); 860 (CH); 690 (*cis* H–C=C–H). ^1H NMR (δ, ppm from TMS in $CDCl_3$): 7.31—7.01 (m, 5H in phenyl group); 6.63 (d, J=10.1 Hz, 1H, CONH): 6.36—6.16 (m, 1H, CH=C); 5.21—4.71 (m, 1H, N–CH); 4.01 (s, 2H, N–CH_2); 2.01 (d, J=4Hz, 3H, CH_3–C=C); 1.45 (d, J=8.1 Hz, 3H, N–C–CH_3). *Elemental analysis* (%). Found: C, 65.51%; H, 5.90%; N, 10.08%. Calcd for $C_{15}H_{16}O_3N_2$: C, 66.17%; H, 5.92%; N, 10.29%.

N-Glycinyl-(RS)-α-methylsuccinimide (GMSI). A mixture of glycine (13.5 g) and (*RS*)-α-methylsuccinic anhydride (20.6 g) in acetic acid (300 ml) was stirred at r.t. for 7 h. After the reaction was completed, acetic acid was evaporated. The redidual oil was stirred for 0.5 h at about 200°C and was distilled under reduced pressure to obtain crude GMSI. The distillate (mp 99—105°C) was recrystallized from chloroform to give pure GMSI: yield 70%, mp 105—106°C, IR (KBr disk) (cm^{-1}): 3450 (OH); 2950 (CH, CH_2, CH_3); 1750 and 1700 (CONCO); 1430—1320 (CH, CH_2, CH_3); ^1H NMR (δ, ppm from TMS in $CDCl_3$): 10.0 (s, 1H, COOH); 4.24 (s, 1H, N–CH_2);

3.20—2.01 (m, 3H, CO–CH–CH_2–CO); 1.34 (d, J=8.1 Hz, 3H, CH_3–C).

N-[(Chlorocarbonyl)methyl]-(RS)-α-methylsuccinimide (CGMSI). CGMSI was prepared from GMSI, thionyl chloride and *tert*-butylcathecol, according to a method similar to that for CGCI: yield 75%, bp 110°C/1.2×10^{-1} mmHg. IR (KBr disk) (cm^{-1}): 2970—2860 (CH, CH_2, CH_3); 1800 (COCl); 1780 and 1710 (CONCO); 1410—1300 (CH, CH_2, CH_3). ^{1}H NMR (δ, ppm from TMS in $CDCl_3$): 4.59 (s, 2H, N–CH_2); 3.30—2.15 (m, 3H, COCH–CH_2CO); 1.37 (d, J=8.1 Hz, 3H, CH_3–C).

Model Compound of Poly(MBCC): N-[N'-((R)-α-Methylbenzyl)aminocarbonylmethyl]-(RS)-α'-methylsuccinimide (MBCSI). MBCSI was synthesized from CGMSI and (*R*)-α-methylbenzylamine, according to a method similar to that for MBCC. MBCSI was purified by recrystallization from benzene: yield 65%, mp 123—124°C, $[\alpha]_D$ 121.3° (c=1.0 g dl^{-1} l=5 cm, THF), IR (KBr disk) (cm^{-1}): 3250 (NH); 3060—2860 (CH, CH_2, CH_3); 1770 and 1705 (O=C–N–C=O), 1650 (CONH); 1550 and 1490 (CONH); 1420, 1400, and 1330 (CH, CH_2, CH_3). ^{1}H NMR (δ, ppm from TMS in $CDCl_3$): 7.35—7.11 (m, 5H in phenyl group); 6.68—6.25 (m, 1H, CONH); 5.30—4.81 (m, 1H, N–CH); 4.06 (s, 2H, N–CH_2); 3.21—2.11 (m, 3H, CH–CH_2); 1.45 (d, J=8.1 Hz, 3H, N–C–CH_3); 1.28 (d, J=7.5 Hz, 3H, CH_3–C).

Other Material

ST, MMA, and solvents, tetrahydrofuran (THF), chlorobenzene (CB), *o*-xylene (*o*-X), toluene (TOL), dioxane (DOX), and methanol, were purified by the usual methods. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol and other commercial available initiators were used without further purification.

Homopolymerization and Copolymerization

Radical solution homopolymerization and copolymerization were carried out in sealed tube at constant temperature (50—160°C). After copolymerization, the copolymer solution was poured into a large amount of methanol. To remove unreacted optically active monomer, reprecipitation was repeated twice from acetone–methanol. The compositions of the copolymer obtained were determined by nitrogen analysis.

Measurements.

D-Line specific rotations, circular dichroism (CD), IR, and NMR spectra were obtained using the same instruments reported previously.[4,7] Molecular weights of the polymers were measured by gel permeation chromatographic (GPC) analysis using the same technique reported previously.[8]

RESULTS AND DISCUSSION

Radical Homopolymerization of MBCC

Radical solution polymerazations of MBCC were performed with AIBN, di-*tert*-butyl peroxide and 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hex-3-yne at 50—110°C under several conditions. However, no appreciable polymers could be obtained. Bulk polymerization at 160°C and photopolymerization at 30°C gave some oligomers whose amounts were detected in the GPC chart. $\bar{M}_w$s of the oligomers were presumed about 860 but could not be separated from the monomer. That MBCC contains little homopolymerizability may be contributed to steric hindrance by α-methyl group located at the double bond in the maleimide ring and the long *N*-substituent, *i.e.*, *N*-(α-methylbenzyl)-aminocarbonylmethyl group. This is because *N*-(α-methylbenzyl)citraconimide could be polymerized in bulk conditions.[6]

Radical Copolymerizations of MBCC with ST and MMA

The results of radical copolymerizations of MBCC (M_1) with ST (M_2) and MMA (M_2) in dioxane (DOX; 6 ml) at 60°C in the presence of AIBN (1.0×10^{-2} mol l^{-1}) are summarized

Table I. Radical Copolymerization of MBCC (M_1) with ST (M_2) or MMA (M_2) in DOX (6 ml) at 60°C[a]

Run	M_2	M_1 in monomer	Polym. time	Conversion	N-Analysis	M_1 in copolymer	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	$[\alpha]_D^{25}$[c]
		mol%	h	%	%	mol%	$\times 10^{-4}$		deg
1	ST	10.0	12	13.2	3.62	17.2	1.76	1.18	42.9
2	ST	30.0	12	17.2	6.46	39.2	2.72	1.32	74.9
3	ST	50.0	12	20.7	7.18	46.9	2.94	1.56	81.4
4	ST	70.2	12	17.4	7.25	47.7	2.27	1.23	80.6
5	ST	89.8	48	2.4	7.20	47.1	1.55	1.66	75.1
6	MMA	10.0	48	23.0	1.11	4.25	2.47	1.41	13.1
7	MMA	29.2	48	15.8	2.56	10.9	2.61	1.31	31.2
8	MMA	50.0	48	11.8	4.33	21.1	1.98	1.26	47.6
9	MMA	70.0	96	3.5	4.69	23.6	1.28	1.11	62.8
10	MMA	90.0	96	trace	—	—	—	—	—

[a] $[AIBN]=1.0\times10^{-2}$ mol l^{-1}; $M_1+M_2=1.0$ g.
[b] By GPC.
[c] $c=1.0$ g dl^{-1}; THF, $l=10$ cm.

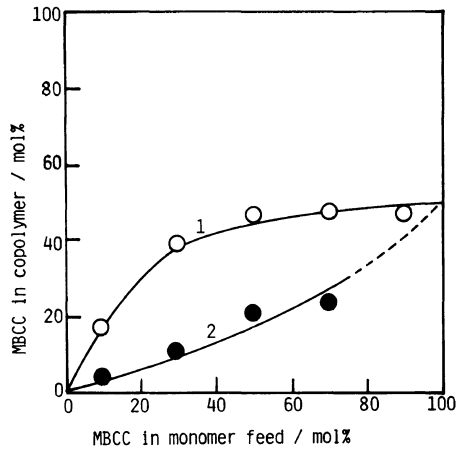

Figure 1. Copolymer composition curves for the (1) MBCC/ST and (2) MBCC/MMA systems.

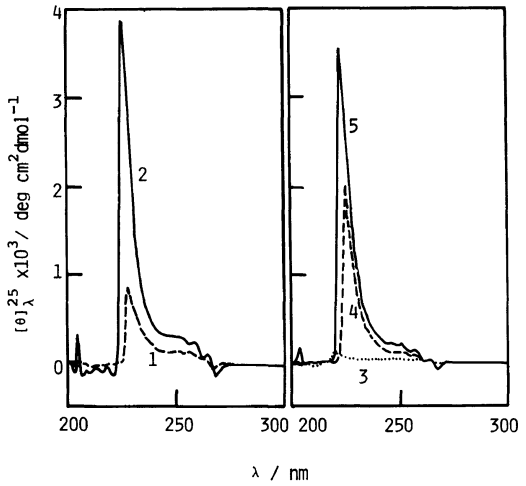

Figure 2. CD spectra for (1) poly(MBCC-*co*-ST) [run 1], (2) poly(MBCC-*co*-ST) [run 5], (3) poly(MBCC-*co*-MMA) [run 6], (4) poly(MBCC-*co*-MMA) [run 8], and (5) poly(MBCC-*co*-MMA) [run 9].

in Table I. Copolymerization proceeded homogeneously throughout. When the concentration of MBCC in the feed increased, the yield of the copolymer extremely decreased in both systems. As can be seen from Table I, the yield of poly(MBCC-*co*-MMA) was almost zero at 90 mo% of MBCC feed. The resulting copolymers were colorless powders and optically active.

Copolymer composition curves in the polymerizations of MBCC with ST and MMA are shown in Figure 1. Monomer reactivity ratios, r_1 and r_2 were determined as $r_1=0.00$ and $r_2=0.27$ in the MBCC/ST system and $r_1=0.00$ and $r_2=3.57$ in MBCC/MMA system, according to the high-conversion method reported by Tüdös and co-workers.[9] These

copolymerization parameters were compatible with MBCC having no homopolymerizability.

Chiroptical Properties of Copolymers

The CD spectra for poly(MBCC-*co*-ST)s and poly(MBCC-*co*-MMA)s are shown in Figure 2. In the CD spectra for poly(MBCC-*co*-ST)s, the negative Cotton effect around 270 nm was observed, and ascribed to the $\pi \rightarrow \pi^*$ transition of phenyl groups of ST and MBCC monomer units. The positive Cotton effect was observed at about 225 nm, and attributed to the $n \rightarrow \pi^*$ transition of the carbonyl groups. In the CD spectra of the poly(MBCC-*co*-MMA)s, similar patterns were observed.

The relationship between the specific rotation of the copolymers and measurement temperature gave linearity, and the slopes were very small (temperature coefficient: $\Delta[\alpha]_D/\Delta T = -0.13$ to -0.06). This suggests that the main chain of the copolymer scarcely contains a helical structure and/or that there are no competing conformational states contributing to the optical activity.

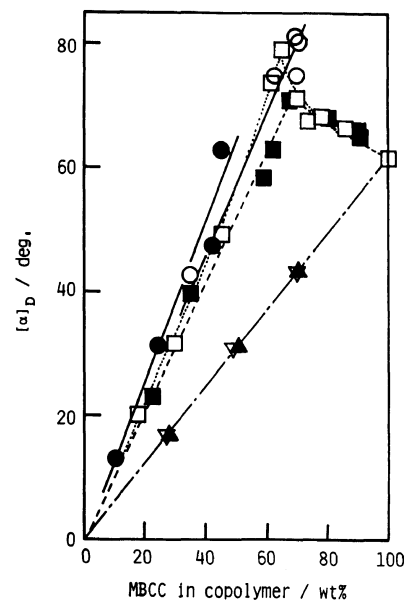

Figure 3. Dependence of specific rotations $[\alpha]_D^{25}$ on the composition (wt%) of (○) poly(MBCC-*co*-ST)s, (●) poly(MBCC-*co*-MMA)s, (□) poly(MBCM-*co*-ST)s, (■) poly(MBCM-*co*-MMA)s, (▽) mixtures of poly(MBCM) and poly(ST), and (▲) mixtures of poly(MBCM) and poly(MMA).

Figur 3 shows the dependence of specific rotations $[\alpha]_D^{25}$ on the composition (mol%) of poly(MBCC-*co*-ST)s and poly(MBCC-*co*-MMA)s. These plots were in fair agreement with those in the MBCM/ST and MBCM/MMA systems reported previously.[5]

In the previous paper,[5] absolute specific rotations and molecular ellipticities of poly(MBCM-*co*-ST)s indicated the curves having maximum. That is, considerable deviation from linearity was observed. Absolute specific rotations of a mixture of poly(MBCM) and poly(ST) gave a good linear relationship, as shown in Figure 3. In the poly(MBCM-*co*-MMA)s, the same tendency could be observed. This suggests that optical activity is influenced by the comonomer, ST or MMA.

In this MBCC, neither MBCC homopolymers nor MBCC *rich* copolymers could be obtained. Accordingly, specific rotations of the MBCC homopolymer and MBCC rich copolymers could not be measured. The specific rotation of a model compound of poly(MBCC); *i.e.*, MBCSI was almost equal to that of a model compound of poly(MBCM); *i.e.*, *N*-[*N'*-((*R*)-α-methylbenzyl)-aminocarbonylmethyl]succinimide.[5] The results of the MBCC systems agreed with those of the MBCM systems.[5] However, no homopolymers of MBCC could be obtained under several conditions (polymerization temperature: 100—200°C; radical initiators: di-*t*-butylperoxide; 2,5-dimethyl-2,5-di(*t*-butylperoxy)heyne-3; 1,1-bis(*t*-butylperoxy)3,3,5-trimethylcyclohexane). Consequently, asymmetric induction copolymerization cannot be disscussed in detail at present.

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