Metal-Containing initiator Systems. XXXVI. Synthesis of Block Copolymer of Methyl Acrylate and α-Methylbenzyl Methacrylate with Binary Initiator System of Cobaltocene and Bis(ethyl acetoacetato)copper(II)

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Metal-Containing Initiator Systems. XXXVI. Synthesis of Block Copolymer of Methyl Acrylate and α-Methylbenzyl Methacrylate with Binary Initiator System of Cobaltocene and Bis(ethyl acetoacetato)copper(II)

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ABSTRACT

Polymerizations of methyl acrylate (MA) and (DL)-α-methyl-benzyl methacrylate (MBMA) with binary initiator system of cobaltocene $[Co(C_5H_5)_2]$ and bis(ethyl acetoacetato)copper(II) $[Cu(eacac)_2]$ were studied in acetonitrile at 25°C. The molecular weight of the polymers obtained by MA was found to increase with time in the early stage of polymerization. Although MBMA was also polymerized by this system, asymmetric selective polymerization was not induced in the presence of (-)-sparteine. The synthesis of the block copolymer of MA and MBMA was attempted by using this initiator system. The block copolymer was obtained in 90% yield in the polymerization of MBMA with a polymer radical which prepared from MA with this system for 1 day. The yield of the block copolymer depended on the prepolymerization time of MA by this system. The resulting block copolymer was characterized by IR, ^{1}H-NMR, and gel-permeation chromatography.

INTRODUCTION

Living radical polymerization has been assumed to occur in the following systems: 1) emulsion polymerization [1, 2], 2) polymerization in matrices [3, 4], 3) coordinated radical polymerization [5, 6], and 4) homogeneous radical polymerization with phenylazotriphenylmethane and tetraethylthiuram disulfide as iniferters [7-11].

In a previous paper [12] we reported that the binary initiator system of cobaltocene $[Co(C_5H_5)_2]$ and bis(ethyl acetoacetato)copper(II) $[Cu(eacac)_2]$ in acetonitrile at $25°C$ could initiate a living-type radical polymerization of methyl methacrylate. This article describes the results of the polymerization and copolymerization of methyl acrylate (MA) and benzyl methacrylate (BzMA) by this system in the presence or absence of (-)-sparteine and of the synthesis of their block copolymers.

EXPERIMENTAL

Materials

$Co(C_5H_5)_2$ and $Cu(eacac)_2$ were prepared according to the methods described in a previous paper [12]. MBMA was prepated by the reaction of methacryloyl chloride with (DL)-α-methylbenzyl alcohol, according to

$$\text{(1)}$$
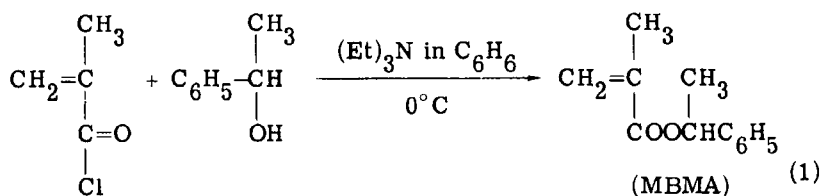
bp, 98-99°C/5 mmHg; n_D^{20} 1.5051 (1.5059) [13]; d_4^{25} 1.0043 g/cm^3.

^{1}H-NMR (in CDCl$_3$): 1.53 (d, 3H, $-CH_3$), 1.88 (s, 3H, $=CH-CH_3$), 5.5, 6.08 (s, 2H, $=CH_2$), 6.0 (q, 1H, $-OCH-$), 7.26 (s, 5H, ph). IR (neat): 1600 (v, C_6H_5), 1640 (m, C=C), 1720 cm^{-1} (s, C=O).

The crude MBMA was purified by repeated distillation under reduced pressure. The MBMA thus obtained was confirmed to be pure by gas chromatography and was used in this study.

Commercial (-)-sparteine was used without further purification. Other monomers, solvents, and reagents were purified by the usual methods.

Block Copolymerization and Fractionation of the Polymer

Block copolymerization was performed by the methods described in a previous paper [12]. The block copolymer was separated as follows: The whole polymer obtained was extracted with boiling acetonitrile for 20 h with a Soxhlet apparatus. When the extract was cooled to room temperature, it became white muddy because the low molecular weight homopolymer was contaminated. Therefore, the polymer in the extract was then fractionated into soluble and insoluble polymers by using a mixed solvent, acetonitrile and methanol [0.73:1 (v/v)]. The soluble and insoluble polymers were confirmed to be homopoly(MA) and block copolymer, respectively. Similarly, to separate poly(MBMA), the acetonitrile-insoluble polymer was fractionated with a mixed solvent of benzene and cyclohexane [0.69:1 (v/v)]. The soluble and insoluble polymers were confirmed by IR spectra to be homopolymer of MBMA and its block copolymer with poly(MA), respectively.

Measurements

The compositions of the resulting copolymers were determined by elemental analysis of the carbon content. The ^{1}H-NMR spectrum of each polymer isolated was recorded on a JEOL-LNH-PS-100 (60 MHz) spectrometer in 10% deuterochloroform solution at 30°C using tetramethylsilane as an internal reference. The IR spectra were also measured with a JUSCO IR-G spectrophotometer.

Optical rotation was measured with a JASCO-DIP-140-type apparatus at 20°C. The average molecular weight ($\overline{M}$) of poly(MA) was determined viscometrically in benzene according to the equation [14]: $[\eta] = 4.5 \times 10^{-5} \overline{M}^{0.78}$. The intrinsic viscosity $[\eta]$ of poly(MBMA) was determined in toluene at 25°C. Gel-permeation chromatograms (GPC) were recorded by using a Toyo-Soda HLC-802UR equipped with four columns (G-7000 + G-6000 + G-4000 + G-2000) at 40°C using THF as the eluent.

RESULTS AND DISCUSSION

Polymerization of MA with $Co(C_5H_5)_2/Cu(eacac)_2$

The polymerization of MA with the $Co(C_5H_5)_2/Cu(eacac)_2$ system was carried out in acetonitrile at 25°C. The results obtained are shown in Table 1.

From Table 1 the system used was found to serve as an radical

TABLE 1. Polymerization of MA with the $Co(C_5H_5)_2$/Cu(eacac)2 System in Acetonitrile at $25°C$[a]

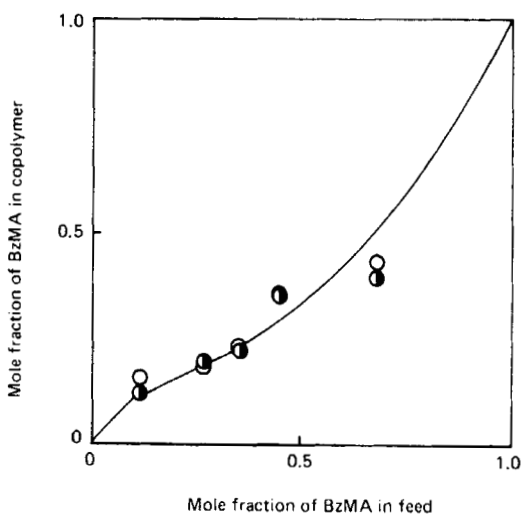| Time (h)	Yield (%)	$\overline{M} \times 10^5$
0.5	13.2	1.58
1.0	20.5	2.39
2.0	27.5	2.63
3.0	24.7	1.93
6.0	36.1	1.77

[a]$[Co(C_5H_5)_2] = [Cu(eacac)_2] = 1.0 \times 10^{-2}$ mol/L, MA 5 mL, CH_3CN 5 mL.

FIG. 1. Copolymer composition curve for the copolymerization of MA with BzMA by $Co(C_5H_5)_2$/Cu(eacac)$_2$ at $25°C$ and by AVN at $40°C$: (○) $Co(C_5H_5)_2$/Cu(eacac)$_2$ system, (●) AVN system.

initiator (see Fig. 1). The average molecular weight of the polymers increased with the polymer yields in the early stage of polymerization, but such an increase was not observed in later stage. This result is somewhat different from that obtained in the polymerization of MMA with this system [12].

Polymerization of MBMA in the Presence of (-)-Sparteine

Recently, Okamoto et al. [15] have found that the highly asymmetric-selective polymerization of (DL)-MBMA occurs with the Grignard reagent-(-)-sparteine catalyst system in toluene at -78°C. In order to check whether the effect of (-)-sparteine is observed for the present initiator system, the polymerization of MBMA with the $Co(C_5H_5)_2/$ $Cu(eacac)_2/(-)$-sparteine system was attempted to acetonitrile at 25°C for 10 h. The results obtained are summarized in Table 2.

From Table 2 the polymer yield was not observed of change with an increase of the concentration of (-)-sparteine. The optical activities of the polymer obtained and unreacted MBMA monomer were barely observed. These results indicate that asymmetric-selective polymeri-

TABLE 2. Polymerization of MBMA with the $Co(C_5H_5)_2/Cu(eacac)_2/$ (-)-sparteine in Acetonitrile at 25°C for 10 h[a]

(-)-sparteine (mL)	Yield (%)	$[\alpha]_D$[b] In polymer obtained	In unreacted monomer
0.02	20.2	+0.25	-
0.05	20.8	+0.52	~0
0.1	22.5	+0.35	~0
0.2	22.2	+0.25	~0
0.4	20.2	+0.27	-
0	12.0	0	0

[a]$[Co(C_5H_5)_2] = [Cu(eacac)_2] = 1.0 \times 10^{-2}$ mol/L, MBMA 5 mL, CH_3CN 5 mL.
[b]Measured in toluene (c = 4 mol/L).

TABLE 3. Polymerization of MBMA with the $Co(C_5H_5)_2/Cu(eacac)_2$ (-)-sparteine System in Acetonitrile at $25°C$[a]

Time (h)	Polymer yield (%)	$[\eta]$ (dL/g)	$[\alpha]_D$ polymer obtained[b]
3	8.2	0.21	+0.36 (c = 3)
6	12.7	-	+0.56 (c = 3)
10	22.5	0.26	+0.35 (c = 4)
15	24.6	-	+0.33 (c = 3)
20	27.6	0.33	+0.23 (c = 4)
81	79.8	0.42	~0 (c = 4)

[a]$[Co(C_5H_5)_2] = [Cu(eacac)_2] = 1.0 \times 10^{-2}$ mol/L, (-)-sparteine 0.1 mL, MBMA 5 mL, CH_3CN 5 mL.

[b]Measured in toluene. Values in parentheses indicate the concentration (mol/L) of the polymers.

zation did not occur with the $Co(C_5H_5)_2/Cu(eacac)_2/$(-)-sparteine system under the present conditions. Next, the effect of reaction on the yield and $[\eta]$ of the polymers in the polymerization of MBMA with the $Co(C_5H_5)_2/Cu(eacac)_2/$(-)-sparteine system was studied.
The results obtained are summarized in Table 3. As shown in this table, both polymer yield and $[\eta]$ increased with polymerization time, but the $[\alpha]_D$ values of the polymers were barely observed, as described above.

Copolymerization of MA with BzMA

In order to reveal the nature of the active center for this polymerization, the copolymerization of MA with BzMA with the $Co(C_5H_5)_2/Cu(eacac)_2$ system was undertaken.
The copolymer composition curve is shown in Fig. 1. The curve obtained for the $Co(C_5H_5)_2/Cu(eacac)_2$ system was in agreement with that obtained by 2,2'-azobis(2,4-dimethylvaleronitrile) (AVN), an ordinary radical initiator. Accordingly, it is clear that the polymerization propagates through a free radical mechanism.

Block Copolymerization of MBMA with Poly(MA) Obtained by $Co(C_5H_5)_2/Cu(eacac)_2$ System

    Table 4 shows the results of the block copolymerization of MBMA with poly(MA) obtained by this initiator system at 25°C in acetonitrile for 1 day.

    From Table 4 the total polymer yield was found to increase with an increase in the concentration of MBMA used, but the yields of both homopoly(MA) and homopoly(MBMA) decreased. When concentrations of MBMA above 3 mL were used, block copolymers were obtained in high yield of about 90%. In the presence of (-)-sparteine as a powerful ligand, however, the yields of both the whole polymer and the block copolymer decreased. The optical activity of homopoly(MBMA) isolated was also not observed, indicating that asymmetric selective polymerization did not occur.

    Table 5 also summarizes the results of the block copolymerization of MBMA with poly(MA) obtained by the $Co(C_5H_5)_2/Cu(eacac)_2$ system in acetonitrile at 25°C for 2 days. The total yield also showed a tendency to decrease with an increase in the concentration of MBMA, but the block copolymers were obtained in yields of about 50%. In a previous paper [12] we reported that the yield of block copolymer was found to increase with prepolymerization time in order to obtain poly-(MMA) with the $Co(C_5H_5)_2/Cu(eacac)_2$ system. The results obtained above were different from that of the block copolymerization of St with poly(MMA).

    Figure 2 shows the IR spectra of each fraction (Run 3) shown in Table 4. Fraction A, which was soluble in acetonitrile/methanol [0.73/1 (v/v)], showed an absorption band at 1720 cm^{-1} due to the carbonyl group of the MA unit, and this agreed with the IR spectrum of poly(MA). Fraction B, which was soluble in benzene/cyclohexane [0.69/1 (v/v)], showed characteristic absorptions at 1720 and 1600 cm^{-1} due to carbonyl and aromatic groups of the MBMA unit, respectively. However, the IR spectrum of Fraction B was quite similar to that part of Fraction C insoluble in benzene/cyclohexane [0.69/1 (v/v)].

    The ^{1}H-NMR spectra of these fractions (Run 3) in Table 4 are shown in Fig. 3. Fraction A had absorption bands at 1.7, 2.2, and 3.65 ppm, which are assigned to the protons of methylene and methine, respectively. Fraction B also showed absorptions at 5.5 and 7.2 ppm due to the protons of α-methine and phenyl, respectively. The absorbance due to protons of both poly(MA) and poly(MBMA) was observed in Fraction C, indicating that Fraction C is the block copolymer.

    Figure 4 shows the separate GPC curve of these fractions. The molecular weights ($\overline{M}_{GPC}$) of these fractions were estimated from

TABLE 4. Block Copolymerization of MBMA with Poly(MA) Obtained by $Co(C_5H_5)_2/Cu(eacac)_2$

Run	MBMA (mL)	Time (h)	Total yield (%)	Yield of fractionated polymers		
				Homopoly(MA) (%)	Homopoly(MBMA) (%)	Block copolymer (%)
1	-	-	30.7	-	-	-
2	1	24	20.6	71.5	23.7	4.8
3	2	24	46.6	25.9	6.1	68.0
4	3	24	46.4	1.7	6.1	92.2
5	4	24	55.1	0.7	5.3	94.0
6	5	24	56.0	0.7	5.3	94.0
7	2	24	38.7	25.3	49.8	24.9

[a]Block copolymerization were carried out at 25°C. Poly(MA) preparation conditions: $[Co(C_5H_5)_2 = [Cu(eacac)_2] = 1.0 \times 10^{-2}$ mol/L, MA 2 mL, CH_3CN 2 mL at 25°C for 1 day.

[b]Indicates the result in the presence of (–)-sparteine (0.1 mL).

TABLE 5. Block Copolymerization of MBMA with Poly(MA) Obtained by $Co(C_5H_5)_2/Cu(eacac)_2$

Run	MBMA (mL)	Time (h)	Total yield (%)	Yield of fractionated polymers		
				Homopoly(MA) (%)	Homopoly(MBMA) (%)	Block copolymer (%)
8	-	-	53.4	-	-	-
9	2	24	47.6	48.3	2.0	49.7
10	3	24	44.8	39.5	1.8	58.7
11	4	24	34.9	45.4	2.4	52.2
12	5	24	21.9	10.0	5.7	40.4

[a] Block copolymerization were carried out at 25°C. Poly(MA) preparation conditions: $[Co(C_5H_5)_2]$ = $[Cu(eacac)_2]$ = 1.0×10^{-2} mol/L, MA 2 mL, CH_3CN 2 mL at 25°C for 2 days.
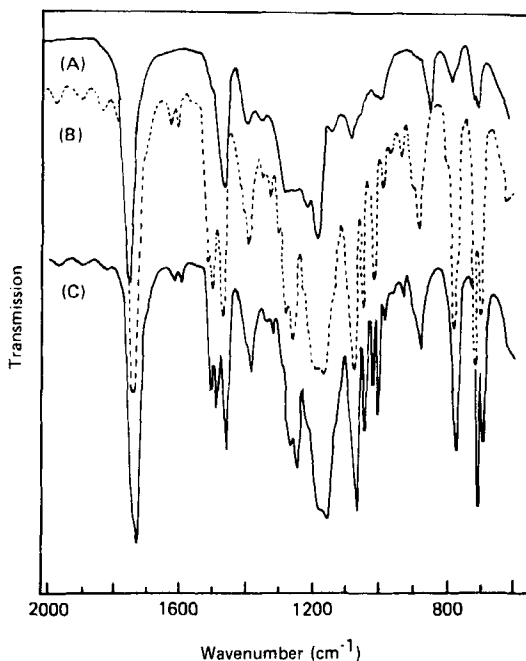
FIG. 2. IR spectra of homopoly(MA) (A), homopoly(MBMA) (B), and block copolymer (C) thus isolated.

the peaks of the GPC chromatogram to be 190,000, 999,000, and 1,580,000 for Fractions A, B, and C, respectively. This result also suggests that Fraction C is the block copolymer. Fraction A showed a very weak response to UV of 254 nm, in agreement with the fact that this part consists of homopoly(MA).

On the other hand, Fractions B and C, containing MBMA units, gave large peaks due to absorbance of UV.
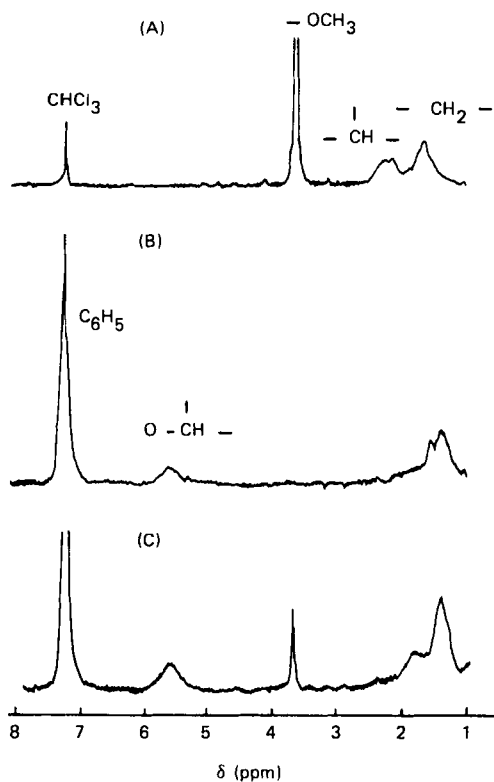
FIG. 3. ^{1}H-NMR spectra of homopoly(MA) (A), homopoly(MBMA) (B), and block copolymer (C) isolated.
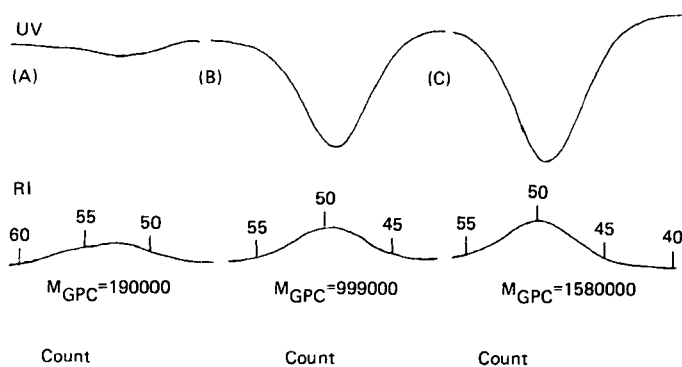
FIG. 4. GPC curves of homopoly(MA) (A), homopoly(MBMA) (B), and block copolymer (C).

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