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Living Radical Polymerization of Alkyl Methacrylates with Ruthenium Complex and Synthesis of Their Block Copolymers[1]

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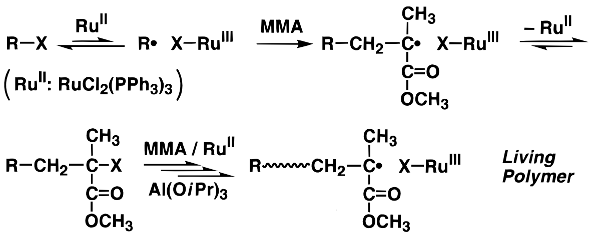
ABSTRACT: Living radical polymerizations of ethyl and *n*-butyl methacrylates (EMA and BMA, respectively) have been achieved with ternary initiating systems that consist of carbon tetrachloride, tris(triphenylphosphine)ruthenium dichloride [$RuCl_2(PPh_3)_3$], and aluminum compounds such as MeAl(ODBP)$_2$ (ODBP, 2,6-di-*tert*-butylphenoxy) and Al(O*i*Pr)$_3$ in toluene at 60−80 °C. The produced polymers had narrow molecular weight distributions (MWDs) ($\bar{M}_w/\bar{M}_n = 1.2-1.5$) and controlled molecular weights that are nearly proportional to monomer conversion. Sequential living polymerizations of these methacrylates from methyl methacrylate (MMA) afforded AB-type block copolymers with narrow MWDs ($\bar{M}_w/\bar{M}_n \sim 1.2$). Further addition of MMA into the living AB block copolymers gave ABA-type triblock copolymers poly(MMA-*b*-BMA-*b*-MMA).

Introduction

Despite such advantages as the wide variety of monomers and simplicity in handling, free-radical polymerization generally gives polymers with uncontrolled molecular weights and often ill-defined structures due to the low selectivity and high reactivity of propagating radical species.[2] Although block copolymers can be prepared by conventional radical polymerizations, for example, by initiation from macroinitiators that contain azo and other radical-generating groups,[2] inevitable side reactions as well as possible low initiation efficiency render the preparation inefficient. Thus, the advent of living radical polymerization has been long waited particularly in the synthesis of well-defined polymers that cannot be obtained by ionic counterparts.

Recently, living or controlled radical polymerizations have been made possible, which have enabled the control of molecular weights of polystyrene, poly(methacrylates), and poly(acrylates).[2−22] The common feature of these controlled radical systems is that they apparently involve reversible and rapid equilibria between activated and dormant species, which are considered crucial for the living and controlled polymerizations by other mechanisms.[1,3,17] The terminal bonds in the dormant species include C−S,[4] C−ON,[8−13] C−Co,[14] C−Cr,[15,16] C−Al,[16] and C−X (X = Cl, Br, I),[5−7,17−22] where these covalent bonds are activated thermally, photochemically, or by transition metal complexes to be converted into growing radical species.

For example, the living radical polymerizations based on the reversible activation of carbon−halogen bonds have been accomplished with transition metal complexes of ruthenium[17−19] and copper.[20,21] They give polymers of very narrow molecular weight distributions (MWDs) and molecular weights predictable from monomer to initiator ratio. As we have recently reported (eq 1), the initiating systems for methyl methacrylate (MMA) may comprise a ruthenium complex [$RuCl_2(PPh_3)_3$], a halide as an initiator (CCl_4,[17] α-haloesters,[18] α-haloketones,[18] sulfonyl chlorides[19]), and an aluminum compound. The polymerization is considered to involve generation of radical species via reversible activation of a terminal carbon−halogen bond assisted by redox reaction of the ruthenium center and addition to monomer in succession.[1,3,17] Such transition metal-catalyzed living polymerizations have also proved effective in the synthesis of end-functionalized polymers.[18−21]



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This study was directed to block copolymerizations of methacrylates (methyl, ethyl, *n*-butyl) with our ruthenium-based initiating systems. In contrast to some results for other living radical and related polymerization systems,[8a,9,10,14,23,24] few solid reports are available for the block polymer synthesis via the transition metal-mediated systems. We herein report on the living polymerizations of alkyl methacrylates [$CH_2{=}C(CH_3)$-CO_2R; R = Et, *n*Bu] with CCl_4 and $RuCl_2(PPh_3)_3$ in the presence of aluminum compounds such as MeAl(ODBP)$_2$ (ODBP, 2,6-di-*tert*-butylphenoxy) and Al(O*i*Pr)$_3$ and then on their block copolymerizations.

Results and Discussion

Homopolymerization. Ethyl methacrylate (EMA) and *n*-butyl methacrylate (BMA) were polymerized with CCl_4 and $RuCl_2(PPh_3)_3$ in conjunction with MeAl(ODBP)$_2$ at 60 °C and Al(O*i*Pr)$_3$ at 80 °C in toluene. For both monomers, polymerizations occurred without an induction period (Figure 1).

The polymerization rate depended on the substituents in the aluminum compounds; MeAl(ODBP)$_2$ led to faster polymerizations than Al(O*i*Pr)$_3$, although the reaction with the former was carried out at a lower temperature (60 °C). This is ascribed to the difference in Lewis acidity between the two aluminum compounds.[25] However, the polymerization with MeAl(ODBP)$_2$ decreased with time probably due to the decomposition of the aluminum compound.

Figures 2 and 3 show the number-average molecular weights ($\bar{M}_n$), the polydispersity ratios ($\bar{M}_w/\bar{M}_n$), and the MWDs of the obtained poly(EMA) and poly(BMA), respectively. Irrespective of the substituents in the

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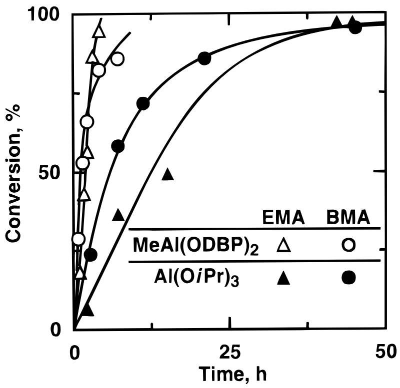

Figure 1. Polymerization of EMA and BMA with $CCl_4/RuCl_2(PPh_3)_3$ in the presence of $MeAl(ODBP)_2$ at 60 °C and Al(O*i*Pr)$_3$ at 80 °C in toluene: $[M]_0 = 2.0$ M; $[CCl_4]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[MeAl(ODBP)_2]_0 = 40$ mM; $[Al(OiPr)_3]_0 =$ 35 (for EMA), 25 (for BMA) mM.

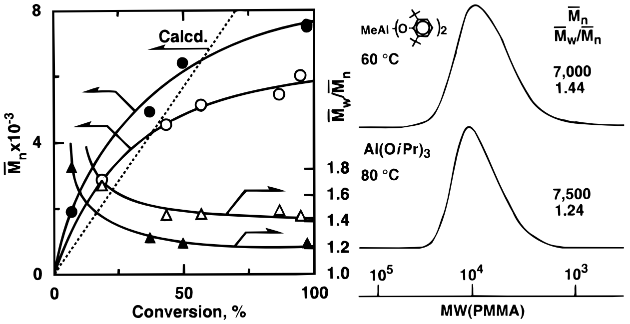

Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(EMA) obtained with $CCl_4/RuCl_2(PPh_3)_3$ in the presence of $MeAl(ODBP)_2$ at 60 °C and Al(O*i*Pr)$_3$ at 80 °C in toluene: $[M]_0 = 2.0$ M; $[CCl_4]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[MeAl(ODBP)_2]_0 = 40$ (○, △) mM; $[Al(OiPr)_3]_0 = 35$ (●, ▲) mM. The diagonal dashed line indicates the calculated $\bar{M}_n$, assuming the formation of one living polymer per CCl_4 molecule. Conversion for MWD curves >95%.

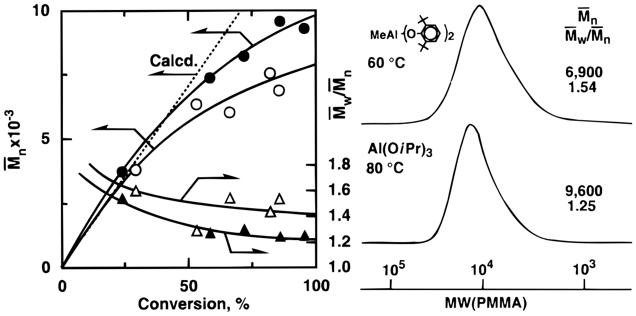

Figure 3. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(BMA) obtained with $CCl_4/RuCl_2(PPh_3)_3$ in the presence of $MeAl(ODBP)_2$ at 60 °C and Al(O*i*Pr)$_3$ at 80 °C in toluene: $[M]_0 = 2.0$ M; $[CCl_4]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[MeAl(ODBP)_2]_0 = 40$ (○, △) mM; $[Al(OiPr)_3]_0 = 25$ (●, ▲) mM. The diagonal dashed line indicates the calculated $\bar{M}_n$, assuming the formation of one living polymer per CCl_4 molecule. Conversion for MWD curves >85%.

monomers and the aluminum compounds, the $\bar{M}_n$ increased with conversion, though smaller than the calculated values assuming that one molecule of CCl_4 generates one living polymer chain. Furthermore, gas chromatographic analysis showed the quantitative depletion of CCl_4 in the very early stage of the polymerizations. These indicate that, as with MMA,[17] CCl_4 serves as an initiator that generates polymer chains. The MWDs were unimodal throughout the reactions and fairly narrow, especially with Al(O*i*Pr)$_3$ ($\bar{M}_w/\bar{M}_n \sim 1.25$).

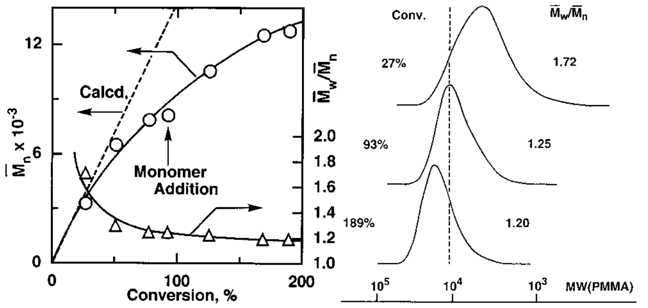

Figure 4. Monomer addition experiments in the polymerization of BMA with $CCl_4/RuCl_2(PPh_3)_3$/Al(O*i*Pr)$_3$ in toluene at 80 °C: $[M]_0 = [M]_{add} = 2.0$ M; $[CCl_4]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(OiPr)_3]_0 = 25$ mM. The diagonal dashed line indicates the calculated $\bar{M}_n$, assuming the formation of one living polymer per CCl_4 molecule.

Such dependence on the aluminum compounds was also observed for the living MMA polymerization.[25] These results suggest the formation of living or long-lived polymers of EMA and BMA with the $CCl_4/RuCl_2(PPh_3)_3$/aluminum compounds.

To examine the living nature of the polymerizations of methacrylates, monomer addition experiments were carried out for the polymerization of BMA; a fresh feed of BMA was added to the reaction mixture when the initial charge had almost been consumed (Figure 4). A smooth second-phase polymerization took place to give quantitative conversion within 40 h. The initial rate was also very similar to that in the first phase, indicating virtually no loss of the active center before and after monomer addition. The $\bar{M}_n$ of the polymers increased almost linearly with conversion even after the monomer addition. The MWD became narrower after the monomer addition ($\bar{M}_w/\bar{M}_n \sim 1.2$) and clearly shifted toward higher molecular weights. These demonstrate that the $CCl_4/RuCl_2(PPh_3)_3$-based initiating system induces living polymerization of alkyl methacrylates other than MMA. Clarification will be needed, however, for the reason for the downward curvature in the $\bar{M}_n$ profiles.

Block Copolymerization. On the basis of the living polymerizations of these methacrylates, sequential block copolymerizations of MMA and BMA were then examined with the ruthenium-based system. For this, MMA was first polymerized with $CCl_4/RuCl_2(PPh_3)_3$ coupled with $MeAl(ODBP)_2$ at 60 °C or Al(O*i*Pr)$_3$ at 80 °C in toluene. After the nearly complete consumption of MMA, a fresh feed of BMA, equimolar to MMA, was added into the living poly(MMA) thus obtained. The second monomer was smoothly polymerized, and as shown in Figure 5B, the MWD shifted to higher molecular weights while keeping a narrow MWD especially with Al(O*i*Pr)$_3$. The MWD of the block copolymers with $MeAl(ODBP)_2$ also shifted to higher molecular weights, but was broader than that with Al(O*i*Pr)$_3$ as with the homopolymers. The products cast from a toluene solution were homogeneous, transparent, and relatively soft, in contrast to the glassy homopoly(MMA) obtained under similar conditions. These suggest the formation of AB-type block copolymers of MMA and BMA with the ternary initiating system (see also the polymer characterization given below).[26]

The clean formation of the AB-type diblock copolymer prompted us to synthesize ABA-type triblock copolymer of methacrylates. Because of the combination of hard PMMA and soft PBMA segments (T_g = 105 and 20 °C, respectively), the MMA−BMA−MMA triblock copolymer is of interest as they would be thermoplastic

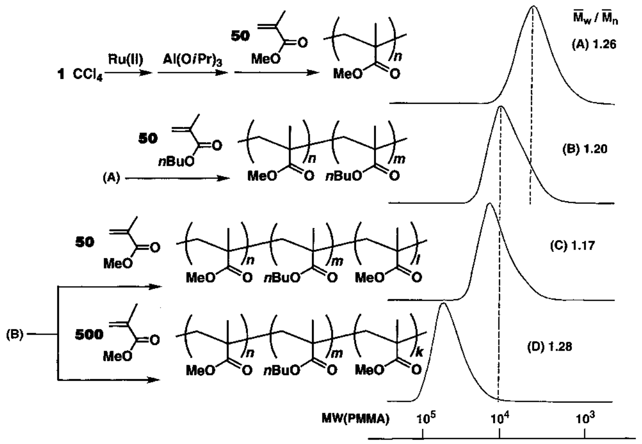

Figure 5. MWD curves of poly(MMA) (A), MMA–BMA block (B), and MMA–BMA–MMA block (C, D) copolymers obtained with $CCl_4/RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$ in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[CCl_4]_0 = 40$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}Pr)_3]_0 = 40$ mM. The molar ratio of the monomers to CCl_4: MMA = 50 (A); MMA/BMA = 50/50 (B); MMA/BMA/MMA = 50/50/50 (C), 50/50/500 (D).

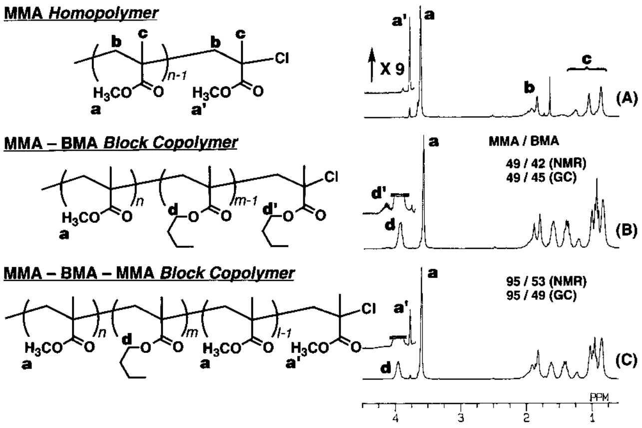

Figure 6. ^{1}H NMR spectra of poly(MMA) (A), MMA–BMA block (B), and MMA–BMA–MMA block (C) copolymers obtained with $CCl_4/RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$ in toluene at 80 °C. The ^{1}H NMR spectra denoted as A, B, and C were of the polymers A, B, and C in Figure 5, respectively.

elastomers above room temperature.[27] Thus, MMA was added into the living MMA–BMA diblock copolymer (Figure 5B). The added MMA feed was smoothly consumed, and the MWD shifted clearly to higher molecular weights while keeping narrow MWDs ($\bar{M}_w/\bar{M}_n = 1.17$) (Figure 5C). When the amount of the second addition of MMA was 10 times the first MMA feed, the MWD curve remarkably shifted without any trace of the remaining MMA homopolymer and the AB block precursors (Figure 5D). These results further show that each step of the sequential polymerization is living or virtually free from chain transfer and termination to give homopolymers.

Figure 6 shows ^{1}H NMR spectra of the poly(MMA) (A) and the block copolymers of MMA and BMA (B, C) obtained therefrom with $CCl_4/RuCl_2(PPh_3)_3$ in the presence of $Al(O\textit{i}Pr)_3$. In Figure 6B, the signals of the BMA repeat units are seen, in addition to the MMA units. The unit ratio of MMA to BMA was obtained from the peak intensity ratio of the ester methyl protons (a) in the MMA unit to the ester methylene protons (d) adjacent to the oxygen atom in the BMA unit. The observed ratio, 49/42 (MMA/BMA), was in good agreement with the calculated value (49/45) from the monomer feed ratio and the gas chromatographic conversions. The overall segmental composition of the triblock copolymers (Figure 6C) was also in agreement with the calculated value (MMA/BMA = 95/53 vs 95/49). Thus, the ruthenium-based living radical polymerization is effective in the synthesis of block copolymers of methacrylates.

Furthermore, Figure 6A contains a small absorption (a′) near the large peak of the main-chain methyl ester proton (a). This is ascribed to the terminal methyl ester proton adjacent to the chlorine atom at ω-end, $-CH_2CMeCl(CO_2C\textit{H}_3)$. It disappeared in the spectrum of the diblock copolymer, while another small absorption (d′) appeared near the large peak (d) of the methylene protons of the BMA unit, and peak d′ was due to the terminal BMA unit at ω-end. These spectral changes indicate that the growing poly(MMA) terminal unit was virtually converted into the poly(BMA) terminal after the addition of BMA into the living poly(MMA), and that living block copolymerizations indeed occurred efficiently. On further addition of MMA into the diblock copolymers, absorption d′ (BMA end) disappeared and a′ appeared (MMA end) again. This also indicates the formation of the ABA-type block copolymers.

In conclusion, the $CCl_4/RuCl_2(PPh_3)_3$/aluminum compound initiating systems are effective in living radical polymerizations of methacrylates including methyl (MMA), ethyl (EMA), and *n*-butyl (BMA) derivatives. AB-type and ABA-type block copolymers of the methacrylates can be obtained by the ternary initiating systems.

Experimental Section

Materials. MMA, BMA (both Tokyo Kasei; purity >99%), and EMA (Wako Chemicals; purity >99%) were dried overnight over calcium chloride and distilled twice over calcium hydride under reduced pressure before use. CCl_4 (Wako Chemicals; purity >99%) was dried overnight over calcium chloride and doubly distilled over phosphorus pentoxide and then over calcium hydride before use. $MeAl(ODBP)_2$ was prepared by adding a solution of 2.0 M Me_3Al solution (in *n*-hexane, 5 mL) into 2,6-di-*tert*-butylphenol (577 mM in toluene, 35 mL) stirring the mixture for 1 h at 25 °C. $RuCl_2(PPh_3)_3$ (Merck; purity >99%), $Al(O\textit{i}Pr)_3$ (Aldrich; purity >99.99%), Me_3Al (Aldrich; 2.0 M solution in *n*-hexane), and 2,6-di-*tert*-butylphenol (Aldrich; purity >99%) were used as received. Toluene (solvent), *n*-octane, *n*-heptane, and tetralin (internal standards for gas chromatographic analysis of MMA, EMA, and BMA, respectively) were dried overnight over calcium chloride, distilled twice over calcium hydride, and bubbled with dry nitrogen for more than 15 min immediately before use.

Polymerization Procedures. Polymerization was carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for BMA polymerization is given below. The polymerization was initiated by adding solutions of $Al(O\textit{i}Pr)_3$ (0.5 mL) and $RuCl_2(PPh_3)_3$ (1.0 mL) in toluene, sequentially in this order, into a mixture (1.0 mL) of BMA (0.795 mL), tetralin (0.20 mL), and CCl_4 (0.0048 mL) in toluene at room temperature. The total volume of the reaction mixture was thus 2.5 mL. Immediately after mixing, the solution was terminated by cooling the reaction mixtures to −78 °C and adding methanol (1.0 mL). Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with tetralin as an internal standard. The quenched reaction solutions were diluted with toluene (~20 mL) and rigorously shaken with an absorbent [Kyowaad-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical] (~5 g) to remove the metal-containing residues. After the absorbent was separated by filtration (Whatman No. 113V), the filtrate was washed with water and evaporated to dryness to give the products, which were subsequently dried overnight.

Measurements. The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ ratios of the polymers were measured by size-exclusion chromatography (SEC) in chloroform at room temperature on three polystyrene gel columns (Shodex K-802 + K-803 + K-804) that were connected to a Jasco Trirotar-V precision pump and a Jasco 830-RI refractive index detector. The columns were calibrated against 11 standard poly(MMA) samples (Polymer Laboratories; $\bar{M}_n = 630-220\,000$; $\bar{M}_w/\bar{M}_n = 1.06-1.22$) as well as monomer. ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-GSX270 spectrometer, operating at 270.7 MHz. Polymers for ^{1}H NMR analysis were fractionated by preparative SEC (column, Shodex K-2002).

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