5582 *Macromolecules* **1998,** *31,* 5582−5587

Living Random Copolymerization of Styrene and Methyl Methacrylate with a Ru(II) Complex and Synthesis of ABC-Type “Block-Random” Copolymers

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Received February 25, 1998; Revised Manuscript Received June 18, 1998

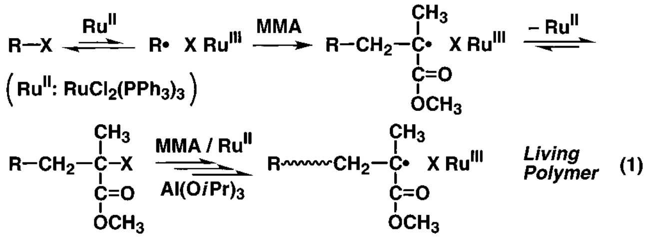
ABSTRACT: The Ru(II)-mediated living radical copolymerization of styrene and methyl methacrylate (MMA) led to novel ABC-type “block-random” copolymers that consist of three segments each of which is a copolymer of the two monomers with a composition differing from each other. Thus, a styrene/MMA mixture (3/1 mole ratio) was polymerized with $CH_3CH(Ph)Br/RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$, and two portions of MMA were sequentially added at varying styrene conversions. The final products are living copolymers with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n \sim 1.5$) where the styrene/MMA sequential compositions from the α- to the ω-ends are about (3/1)−(1/1)−(1/4). Therefore, in the particular example two end segments are rich in either styrene or MMA unit, while the mid segment contains both units at a comparative composition. The basis of this new reaction is that independent of feed composition, both monomers polymerize at nearly the same rates to give virtually “azeotropic” random copolymers that are also living or long-lived and thus possess controlled molecular weights and narrow distributions.

Introduction

A notable feature of free radical polymerization is that a variety of monomers can be copolymerized in a random fashion. The advantage primarily stems from relatively small difference in reactivity even among structurally different monomers, e.g., styrene and methacrylates.[1] The easiness in random copolymerization for a variety of radically polymerizable monomers is in sharp contrast to the situation in ionic counterparts, where monomer reactivity strongly depends on sometimes subtle structural difference, and thereby ionic random copolymerization is possible only for limited pairs of monomers with more or less similar structures.

We have recently reported, and have been pursuing, living radical polymerization of methacrylates,[2] styrenes,[3] and other monomers[4] that are mediated by complexes of such transition metals as ruthenium(II),[2] iron(II),[5] and nickel(II)[6] in combination with halogen-containing initiators R−X (Scheme 1). For example, a combination of an alkyl halide (as an initiator) with $RuCl_2(PPh_3)_3$ ($Ph = C_6H_5$) induces living (or precisely controlled) radical polymerizations of these monomers, sometimes in the presence of another additive such as an aluminum alkoxide; the initiators include haloalkanes (CCl_3Br etc.), haloesters, haloketones ($Cl_2CHCOPh$), and related halogen-containing compounds that are able to generate initiating radicals through the aid of a transition metal complex.[7] Similar examples of the transition metal-mediated living radical polymerizations have been reported by other groups.[8,9]

Scheme 1



These primary reports are for their homopolymerizations, and few deal with corresponding copolymerizations except for papers by Haddleton,[10] where the monomer reactivity ratios are compared in various living/controlled and conventional radical and anionic copolymerizations of methacrylates. Recently, a series of copolymers called gradient copolymers were synthesized by Greszta and Matyjaszewski.[11] In view of the now relatively wide variety of monomers that are applicable to the transition metal-based living radical processes, it is certainly of interest and import to examine copolymerizations of pairs of these monomers. The pertinent questions of immediate significance would include: What are the monomer reactivity ratios under the living radical conditions, in relation to those in the conventional (or nonliving) free radical processes? Given living radical homopolymerizations now possible, are the corresponding copolymerizations with the same or similar initiating systems also living or at least well controlled? These questions are in turn related to the perhaps most important point of inquiry; is the growing species, apparently living and generated by transition metal complexes, in fact a radical that is similar in nature to those in the conventional radical polymerization?

This paper discusses our first examples of living random copolymerization of methyl methacrylate (MMA) and styrene mediated by the Ru(II)-based initiating systems that are applicable to their living homopolymerizations.[12] We herein report that the random MMA−styrene copolymerization is in fact possible under our conditions and, equally important, that it leads to “living and random” copolymers for which molecular weight and composition can be precisely controlled (Scheme 2). The relative reactivity of MMA and styrene is thus determined under the living conditions. Also discussed is an immediate extension of the living random copolymerization, the synthesis of “block-random” copoly-

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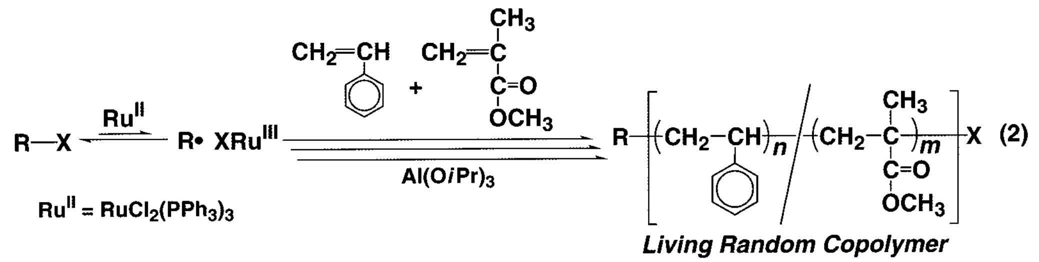
Scheme 2



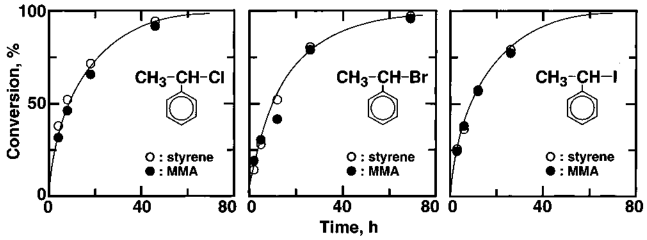


Figure 1. Copolymerization of styrene and MMA with $CH_3CH(Ph)X$ (X = Cl, Br, and I)/$RuCl_2(PPh_3)_3$/$Al(O\textit{i}Pr)_3$ in toluene at 100 °C: $[styrene]_0 = [MMA]_0 = 1.0$ M; $[CH_3CH(Ph)X]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}Pr)_3]_0 = 40$ mM.

mers of an ABC form, which are novel sequence-controlled polymers where each segment consists of a random MMA–styrene copolymer of varying composition.

Results and Discussion

Random Copolymerization of Styrene and MMA. Three 1-phenylethyl halides [$CH_3CH(Ph)X$; (X = Cl, Br, I)] were employed as initiators for the random copolymerization of styrene and MMA (1:1 molar ratio) coupled with $RuCl_2(PPh_3)_3$ in the presence of $Al(O\textit{i}Pr)_3$ in toluene at 100 °C (Figure 1). With each $CH_3CH(Ph)X$, both monomers were consumed almost at the same rates, and their conversions reached over 90% in 50 h.

As shown in Figure 2, the molecular weight distributions (MWDs) of the products from the chloride and the bromide were unimodal and relatively narrow, and the number-average molecular weight ($\bar{M}_n$) increased with conversion; $\bar{M}_n$ was measured by size-exclusion chromatography (SEC). The copolymers with $CH_3CH(Ph)I$ also showed unimodal MWDs that shifted to higher molecular weight with conversion, whereas they became broader during the later stages.

Figure 3 shows the apparent number-average molecular weights ($\bar{M}_n$) and the polydispersity ratios ($\bar{M}_w/\bar{M}_n$) of the copolymers against polymer yield calculated from conversions of both monomers. With the $CH_3CH(Ph)Br$-based initiating system, the $\bar{M}_n$ almost agree with the calculated values based on the assumption that one molecule of the initiator generates one living polymer chain, and the MWDs are relatively narrow. Relative to the bromide, $CH_3CH(Ph)Cl$ gave higher $\bar{M}_n$ and slightly broader MWDs. As we will report shortly,[12] $CH_3CH(Ph)Cl$ is effective for living radical homopolymerization of both styrene and MMA but yields polymers with higher $\bar{M}_n$ due to slow initiation therefrom. In the homopolymerization of styrene with $CH_3CH(Ph)I$, on the other hand, the growing terminal involves an iodide that is rather unstable and thus prone to β-H elimination. Thus, the chloride and iodide initiators were inferior to the bromide as the initiator for living radical copolymerization of MMA and styrene.

Figure 4 shows ^{1}H NMR spectra of the polystyrene, the poly(MMA), and the random copolymers of styrene and MMA obtained with the $CH_3CH(Ph)Br$/$RuCl_2(PPh_3)_3$/$Al(O\textit{i}Pr)_3$ system. In the copolymer spectra, signals of the main chain and the pendant groups are broad and completely different from those for the homopolymers, demonstrating the formation of neither block copoly-

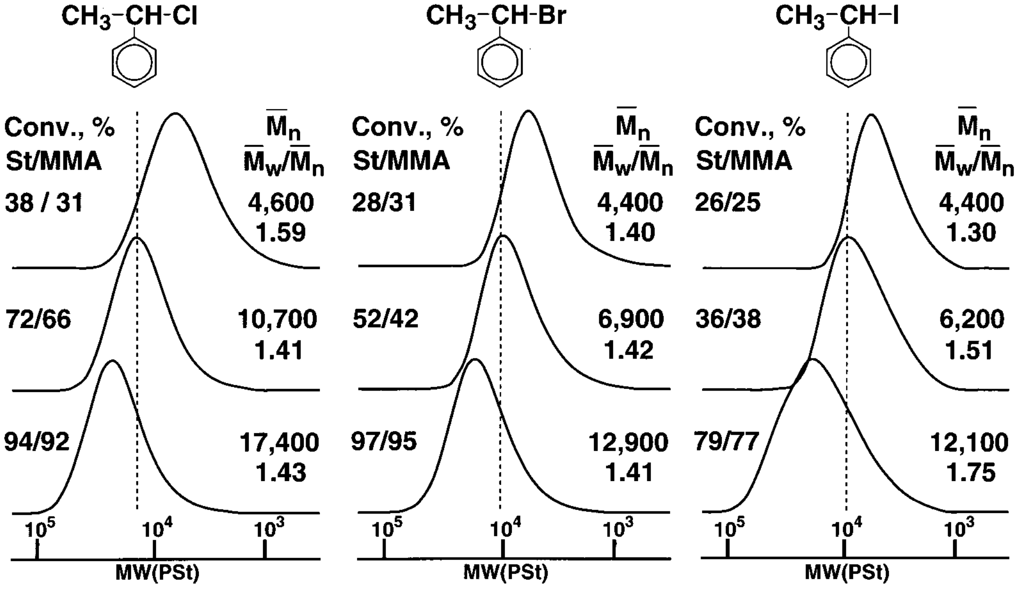


Figure 2. SEC curves of random copolymers of styrene and MMA obtained with $CH_3CH(Ph)X$ (X = Cl, Br, and I)/$RuCl_2(PPh_3)_3$/$Al(O\textit{i}Pr)_3$ in toluene at 100 °C: $[styrene]_0 = [MMA]_0 = 1.0$ M; $[CH_3CH(Ph)X]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}Pr)_3]_0 = 40$ mM.

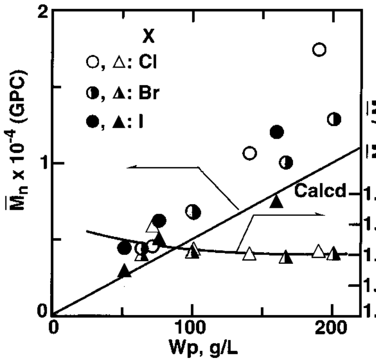


Figure 3. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of random copolymers of styrene and MMA obtained with $CH_3CH(Ph)X$ [X = Cl (○, △), Br (◑, ▲), and I (●, ▲)]/$RuCl_2(PPh_3)_3$/$Al(O\textit{i}Pr)_3$ in toluene at 100 °C: $[styrene]_0 = [MMA]_0 = 1.0$ M; $[CH_3CH(Ph)X]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}Pr)_3]_0 = 40$ mM. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per $CH_3CH(Ph)X$ molecule.

mers nor homopolymer blends but random copolymers. The unit ratio of styrene to MMA (copolymer composition) was obtained from the peak intensity ratio of the aromatic protons (6.5–7.5 ppm) for the styrene unit to the aliphatic protons (0.3–3.7 ppm) for the both units. The observed ratio, styrene/MMA = 28/30, was in good agreement with the calculated value (28/31) from the initial monomer feed ratio and the gas-chromatographic conversions, which indicates that once consumed, both monomers were built into the copolymers.

Monomer Reactivity Ratio (*r*). The random copolymerizations of styrene and MMA with $CH_3CH(Ph)Br/RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$ were also performed at varying feed monomer compositions. At any feed composition, both monomers were consumed almost at the same rates. The more MMA in the initial monomer feed, the faster the polymerization (Figure 5). This might result from the difference of polymerizability between styrene and MMA; in the homopolymerization with the same initiating system, MMA can be polymerized much faster than styrene.

Figure 6 shows $\bar{M}_n$ against polymer yield calculated from the SEC traces and conversions of both monomers. Irrespective of the monomer composition, the $\bar{M}_n$ increased with the polymer yields, and the MWDs of the copolymers were narrow. These results indicate that living radical copolymerizations proceeded irrespective of the monomer feed ratio. In addition, the unit ratios of all copolymers by ^{1}H NMR were in good agreement with the calculated values based on the monomer composition in feed and the gas-chromatographic conversions.

The copolymerization composition curve shown in Figure 7 was also obtained from the series of copolymerizations described above. The copolymer compositions were determined from the initial polymerization rates of styrene and MMA.[13] The solid curve was for the living radical copolymerization, and the dashed one for a conventional free radical copolymerization with AIBN.[14] The solid curve is closer to the diagonal line than one for free radical polymerization, and thus the Ru(II)-mediated system yields not only "living" but also virtually "azeotropic" random copolymers independent of feed composition.

The monomer reactivity ratio was obtained by the Fineman–Ross method for the living random copolymerization with the Ru(II)-based initiating system: $r_1 = 0.63$, $r_2 = 0.60$ (M_1 = MMA) or $r_1 = 0.70$, $r_2 = 0.72$ (M_1 = styrene). Although those r_1 and r_2 values by a differential method should be treated with caution, they apparently indicate that the unit distributions along the copolymers are rather "ideal random" than "alternating" as for free radical copolymerization. The most interesting point is, therefore, that the composition of copolymer can easily be determined by monomer feed composition, and we can thus synthesize random copolymers of styrene and MMA with controlled composition and molecular weights, on the bases of the living *and* azeotropic nature of the copolymerization.

Synthesis of "Block-Random" Copolymers. Noting the nearly azeotropic and living copolymerization described above, we synthesized novel "block-random"

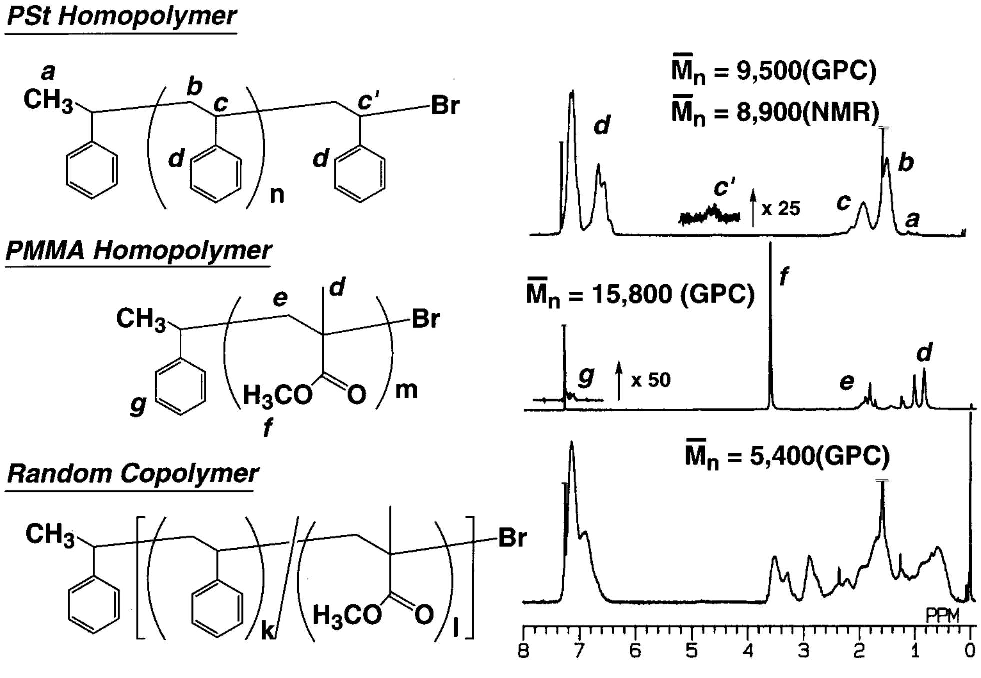


Figure 4. ^{1}H NMR spectra of the polystyrene, the poly(MMA), and the random copolymer of styrene and MMA obtained with $CH_3CH(Ph)Br/RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$ in toluene at 100 °C.

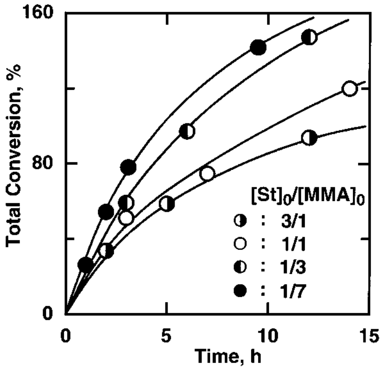


Figure 5. Random copolymerization of styrene and MMA with $CH_3CH(Ph)Br/RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$ in toluene at 100 °C: $[\text{total monomer}]_0 = 2.0$ M ($[\text{styrene}]_0/[\text{MMA}]_0 = 3/1$ (◑); 1/1 (○); 1/3 (◐); 1/7 (●)); $[CH_3CH(Ph)Br]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}Pr)_3]_0 = 40$ mM.

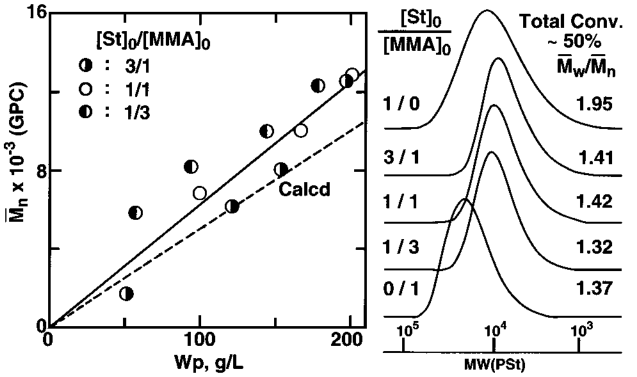


Figure 6. $\bar{M}_n$ and SEC curves of random copolymers of styrene and MMA obtained with $CH_3CH(Ph)Br/RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$ in toluene at 100 °C: $[\text{total monomer}]_0 = 2.0$ M ($[\text{styrene}]_0/[\text{MMA}]_0 = 3/1$ (◑); 1/1 (○); 1/3 (◐)); $[CH_3CH(Ph)Br]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}Pr)_3]_0 = 40$ mM. Total conversion of SEC curves ~50%.

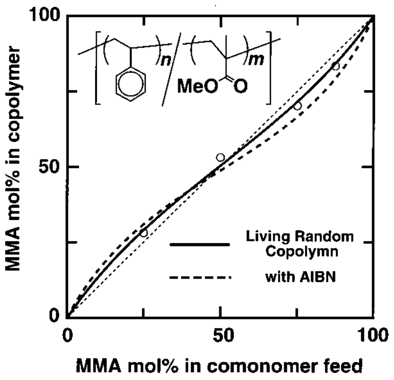


Figure 7. Copolymer composition curves obtained from random copolymerization of styrene and MMA. The solid curve was obtained with $CH_3CH(Ph)Br/RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$ in toluene at 100 °C and the dashed one from conventional free radical polymerization with AIBN.

copolymers that consist of three segments each of which is a styrene–MMA random copolymer of a specified composition different from each other, as illustrated in Scheme 3. Thus, a styrene-rich monomer mixture (styrene/MMA = 75/25 equiv, or 3/1 mole ratio; hereafter, "equiv" means mole equivalent to the initiator) was copolymerized with the $CH_3CH(Ph)Br/RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$ system in toluene at 80 °C, and two feeds of fresh MMA (25 equiv each) were sequentially added to the reaction mixtures at 52 and 89% styrene conversions.

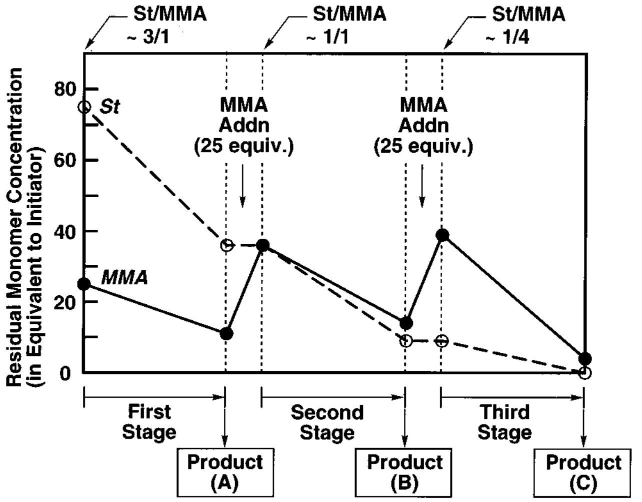
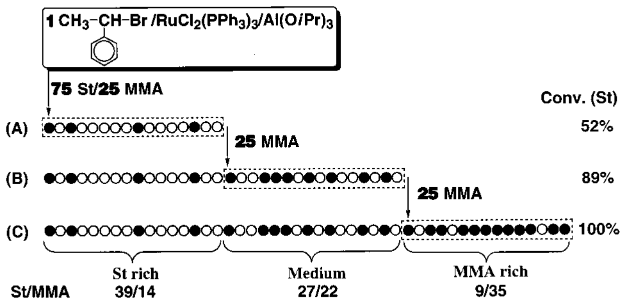


Figure 8. Changes in monomer concentrations (in equiv. to the initiator) in the course of the three-stage consecutive random copolymerization of styrene (○) and MMA (●) with the $CH_3CH(Ph)Br/RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$: the scale of the abscissa is arbitrary; the monomer concentration data are based on gas-chromatographic analysis. See Figure 9 and Scheme 3 for products A–C.

Scheme 3



Monomer Composition* (styrene/MMA)	Reaction Stage		
	First	Second	Third
Initial	75/25	36/36	9/39
		+25 eq MMA	+25 eq MMA
Final	36/11	9/14	0/4
Copolymer Composition* (styrene/MMA)	(A) 39/14	(B) 66/36	(C) 75/71

(*) Equivalent to the initiator.

Figure 8 schematically shows changes in monomer concentrations (in equiv) in the course of this three-stage consecutive random and living copolymerization, and Figure 9 presents the SEC traces and ^1H NMR spectra for a series of the products (A–C) obtained at the end of each stage.

In the first stage from the 75/25 equiv styrene/MMA mixture, a nearly azeotropic copolymerization proceeded to reach 52% styrene and 56% MMA conversions in 19 h, giving product (A) that is a random copolymer of styrene/MMA = 39/14 units on the number-average basis (by ^1H NMR). At this point, therefore, the remaining monomer mixture consists of styrene/MMA = 36/11 equiv. As already shown in the preceding section, the copolymerization is living, or involving long-lived random copolymers.

To this monomer mixture with the living copolymer (A), a fresh MMA feed (25 equiv, neat) was added to

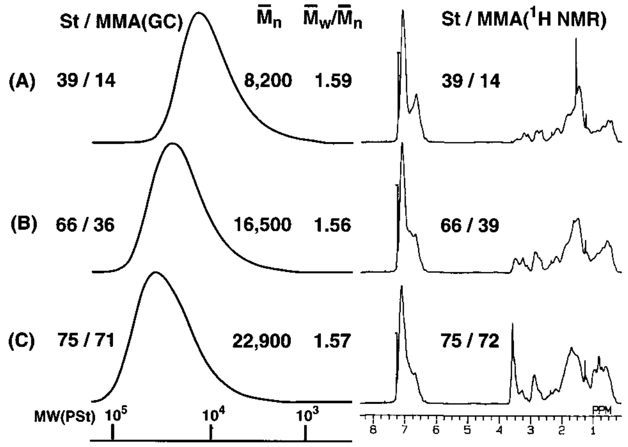


Figure 9. SEC curves and ^{1}H NMR spectra of "random-block" copolymer synthesized as illustrated in Scheme 3. The SEC curves and ^{1}H NMR spectra donated as (A)–(C) were of copolymers obtained at first, second, and third stage, respectively.

form a new starting monomer mixture of styrene/MMA = 36/36 [36/(11 + 25) equiv]. A second-stage azeotropic and living copolymerization ensued from the 1/1 mixture to reach 89% styrene conversion in an additional 27 h, giving product B, which is an AB-block polymer where a newly formed 27/22 (~1/1) styrene/MMA random copolymer segment is attached to the initial 39/14 (~3/1) styrene/MMA copolymer segment (A). At the end of the second stage, the remaining monomer mixture thus consisted of styrene/MMA = 9/14 equiv.

To this mixture was added a second feed of fresh MMA (again 25 equiv, neat) to form a new monomer solution with styrene/MMA = 9/39 [9/(14 + 25)] equiv with which the third-stage copolymerization started from the living end of the product (B). Within 69 h the third stage was practically completed to reach ca. 100% styrene and MMA conversions (4 equiv of MMA remaining unreacted). Thus, the third stage produced a third copolymer segment of styrene/MMA = 9/35 [9/(39 − 4)] units, attached to the second-stage AB block copolymer, to give product C, which is an ABC-type block copolymer with three random copolymer segments of different compositions, i.e., styrene/MMA ratios in DP$_n$ from the α-end to the ω-end: (39/14)–(27/22)–(9/35) or nearly (3/1)–(1/1)–(1/4).

These results indicate that all chains of the copolymers have nearly the same composition as that of the comonomer feed. The composition is essentially the same along the backbone as shown in Scheme 3; i.e., the comonomer composition is the same within one segment and does not change until a new feed of monomers is added. Thus, the "block-random" copolymers are different from the "gradient" copolymers[11] where the comonomer composition *gradually* changes as a function of copolymer chain length.

As seen from Figure 9, the overall styrene/MMA compositions of the copolymers, determined by NMR, are excellently close to the values expected from the gas-chromatographic (GC) conversions of the two monomers: styrene/MMA (GC vs NMR), (A) 39/14 vs 39/14; (B) 66/36 vs 66/39; (C) 75/71 vs 75/72. Judged from the SEC/MWD traces, in addition, the long lifetime of the growing ends is apparently retained throughout the consecutive reactions, allowing the overall molecular weights to increase with increasing monomer conversions. The broadened complex NMR absorptions in the 0–3 ppm range further show the randomness in copolymer sequences.

Thus, living nature, nearly azeotropic characters, and randomness of the Ru(II)-mediated copolymerization of styrene and MMA have opened a new method to synthesize ABC-type "block-random" copolymers with controlled compositions and molecular weights. Obviously, these polymers, with three random copolymer segments covalently connected in series, different from usual block copolymers (with two or more "homopolymer" segments), "tapered" or "gradient" copolymers (where repeat unit sequences change gradually along the main chain from α- to ω-ends),[11] and related copolymers.[15]

Experimental Section

Materials. MMA (Tokyo Kasei; purity >99%), styrene (Wako Chemicals; purity >99%), 1-bromoethylbenzene (Tokyo Kasei; purity >95%), and 1-chloroethylbenzene (Tokyo Kasei; purity >97%) were dried overnight over calcium chloride and distilled twice over calcium hydride under reduced pressure before use. 1-Iodoethylbenzene was prepared by adding solution of 1.04 M anhydrous hydrogen iodide solution (in *n*-hexane, 0.5 mL) into styrene (250 mM in toluene, 1.58 mL) at −20 °C. $RuCl_2(PPh_3)_3$ (Merck; purity >99%) and $Al(O\textit{i}Pr)_3$ (Aldrich; purity >99.99%) were used as received. Toluene (solvent), *n*-hexane (solvent for hydrogen iodide solution), *n*-octane, and tetralin (internal standards for gas-chromatographic analysis of styrene and MMA, 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 sealed glass tubes. A typical example for copolymerization of styrene and MMA with $CH_3CH(Ph)Br/RuCl_2(PPh_3)_3/Al(O\textit{i}Pr)_3$ is given below: The polymerization was initiated by adding solutions of $Al(O\textit{i}Pr)_3$ (0.48 mL) and $CH_3CH(Ph)Br$ (0.122 mL) in toluene, sequentially in this order, into a mixture (1.0 mL) of styrene (0.17 mL), MMA (0.16 mL), *n*-octane (0.063 mL), and tetralin (0.063 mL) in toluene at room temperature. The total volume of the reaction mixture was thus 1.5 mL. Immediately after mixing, the solution was placed in a oil bath at 100 °C. The polymerization was terminated by cooling the reaction mixtures to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with *n*-octane and tetralin as internal standards for MMA and styrene, respectively. 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 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 40 °C on three polystyrene gel columns (Shodex K-805L x 3) that were connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index detector. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemical Co.; $\bar{M}_n$ = 580–1547000; $\bar{M}_w/\bar{M}_n \leq 1.1$) 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 (Shodex K-2002 column).

Acknowledgment. With appreciation M.S. acknowledges the support from the New Energy and Industrial Technology Development Organization (NEDO) under the Ministry of International Trade and Industry (MITI), Japan, through the grant for “Precision Catalytic Polymerization” in the Project “Technology for Novel High-Functional Material” (fiscal 1996-2000). Y.K. is grateful to the Japan Society for the Promotion of Sciences for Young Scientists and the partial support of this work by the Grant-in-Aid for Scientific Research (No. 3370) from the Ministry of Education, Science, Culture, and Sports, Japan.

References and Notes

(1) Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Pergamon: Oxford, 1995.

(2) (a) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721. (b) Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 1070. (c) Matsuyama, M.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A, Polym. Chem.* **1996**, *34*, 3585. (d) Kotani, Y.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 6979. (e) Nishikawa, T.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 2244.

(3) Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1996**, *45*, 113, 1143; *Polym. Prepr. Jpn.* **1997**, *46*, 148.

(4) (a) Watanabe, K.; Nishikawa, T.; Matsuyama, M.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1997**, *46*, 148. (b) Senoo, M.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1997**, *46*, 1534.

(5) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 4507.

(6) Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 2249.

(7) Ando, T.; Kamigaito, M.; Sawamoto, M. *Tetrahedron* **1997**, 53, 15445.

(8) For recent reviews on living/controlled radical polymerizations, see: (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66. (b) Davis, T. P.; Kukulj, D.; Haddleton, D. M.; Maloney, D. R. *Trends Polym. Sci.* **1995**, *3*, 365. (c) Hawker, C. J. *Trends Polym. Sci.* **1996**, *4*, 183. (d) Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *4*, 371. (e) Sawamoto, M.; Kamigaito, M. In *Polymer Synthesis (Materials Science and Technology Series)*; Schlüter, A.-D., Ed.; VCH: Weinheim, Germany, in press.

(9) (a) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614. (b) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970. (c) Granel, C.; Dubois, P.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1996**, *29*, 8576.

(10) (a) Suddaby, K. G.; Hunt, K. H.; Haddleton, D. M. *Macromolecules* **1996**, *29*, 8642. (b) Haddleton, D. M.; Crossman, M. C.; Hunt, K. H.; Topping, C.; Waterson, C.; Suddaby, K. G. *Macromolecules* **1997**, *30*, 3992.

(11) Greszta, D.; Matyjaszewski, K. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1996**, *37* (1), 569.

(12) Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1997**, *46*, 1536.

(13) Initial polymerization rates of styrene and MMA were obtained from the first-order plots of each monomer based on the gas-chromatographic conversions.

(14) Ito, T.; Otsu, T. *J. Macromol. Sci.-Chem.* **1969**, *A3*, 197.

(15) Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y.; Miyamoto, T.; Shimizu, Y. *Macromolecules* **1996**, *29*, 3050.

MA980294X