Structural Control of Poly(Methyl Methacrylate)-*g*-poly(Lactic Acid) Graft Copolymers by Atom Transfer Radical Polymerization (ATRP)

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ABSTRACT: Atom transfer radical copolymerization of methyl methacrylate (MMA) and (meth)acrylate-terminated poly(lactic acid) (PLA) macromonomers was investigated. The relative reactivity of methacrylate-terminated macromonomer ($1/r_{MMA} = 1.75$) and acrylate-terminated macromonomer ($1/r_{MMA} = 0.61$) was close to that of 2-hydroxyethyl methacrylate and 2-hydroxyethyl acrylate, respectively. The difference in reactivity in ATRP and conventional radical polymerization is discussed in terms of the diffusion control effect. A mixture of methacrylate-terminated macromonomer and acrylate-terminated macromonomer was copolymerized with MMA by ATRP to give a homogeneously branched PMMA-g-PLA graft copolymer with low polydispersity ($M_w/M_n = 1.15$).

Introduction

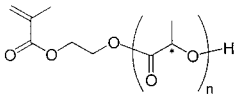
The precise control of polymer architecture or topology is an important issue in polymer science because of the great potential for realizing polymer materials with new properties and/or high performance from inexpensive monomers. In this context, controlled/living radical polymerization systems[1,2] such as atom transfer radical polymerization (ATRP),[3−7] radical polymerization with reversible addition-fragmentation chain transfer (RAFT),[8−11] and the nitroxide-mediated polymerization[12−16] have been extensively studied.

We have improved the structural control of graft copolymers, especially the spacing distribution of branches, by combining the macromonomer method with controlled radical polymerizations.[17,18] This produced almost homogeneously branched poly(methyl methacrylate)-g-poly(dimethylsiloxane) graft copolymers with low polydispersity.

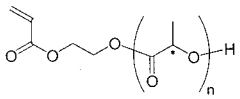
Here we report the structural control of poly(methyl methacrylate)-g-poly(lactic acid) graft copolymers by the ATRP of methyl methacrylate (MMA) and poly(lactic acid) macromonomer. Poly(lactic acid) (PLA) is a biodegradable aliphatic polyester derived from renewable resources.[19,20] It has been investigated as a biomaterial for controlled drug delivery,[21,22] bioabsorbable suture or fiber,[23] and implant for bone fixation.[24] Recently, as the production cost has been dramatically reduced because of technological breakthroughs,[25−27] PLA is proving to be a viable alternative to petrochemical plastics.[28−30] Since graft copolymers have potential as compatibilizers, emulsifiers, thermoplastic elastomers, and impact-resistant plastics, the study on the precise structural control of graft copolymers containing PLA branches will be of significant interest.

In this paper, methacrylate-terminated poly(L-lactic acid) macromonomer (M-PLLA), methacrylate-terminated poly(D,L-lactic acid) macromonomer (M-PDLLA), and acrylate-terminated poly(L-lactic acid) macromonomer (A-PLLA) were prepared (Scheme 1) and copolymerized with MMA using either ATRP or conventional radical polymerization. The difference in reactivity ratios and the copolymer structures between ATRP and conventional radical polymerization will be discussed.

Scheme 1



Methacrylate-terminated PLA macromonomer (M-PLLA, M-PDLLA)



Acrylate-terminated PLLA macromonomer (A-PLLA)

Experimental Section

Materials. Tetrahydrofuran (THF) was distilled from purple sodium benzophenone ketyl solutions. Methyl methacrylate (MMA) (99%, Acros) was washed 3 times with 5% aqueous sodium hydroxide and once with water. After drying with magnesium sulfate, MMA was distilled from calcium chloride. 2-Hydroxyethyl methacrylate (HEMA) (97%, Aldrich) and 2-hydroxyethyl acrylate (HEA) (96%, Aldrich) were both dried over molecular sieves and distilled. MMA and *p*-xylene (99%, Acros) were deoxygenated by bubbling nitrogen gas through them for more than 1 h just before the polymerization. High purity L-lactide (L-LTD) (>99.9%) and D-lactide (D-LTD) (>99.9%) were supplied by Mitsui Chemicals and purified by recrystallization from toluene and dried in a vacuum (<3 mmHg) overnight at room temperature.[31] Copper chloride (CuCl) (98%, Aldrich) was stirred in glacial acetic acid overnight, filtered, and washed with absolute ethanol and ethyl ether under nitrogen. The solid was dried under vacuum at room-temperature overnight. 4,4′-Di-*n*-nonyl-2,2′-bipyridine (dnNbpy) was synthesized by a modified literature procedure.[32] Ethyl 2-bromoisobutyrate (EBiB) (98% Aldrich), benzoyl peroxide (BPO) (Fisher, 75%), stannous octoate (SnOct) (Alfa Aesar, technical grade), and all other reagents were used as received.

Measurements. Gel permeation chromatography (GPC) measurements in THF were conducted using a Waters 515 liquid chromatograph pump (1 mL/min, 30 °C) equipped with four columns (guard, 10^5 Å, 10^3 Å, 100 Å; Polymer Standards Service) in series with a Waters 2410 differential refractometer with diphenyl ether as an internal standard. The molecular weights of the copolymers were determined on the basis of low polydispersity poly(methyl methacrylate) (PMMA) standards. The conversion of MMA was measured on a Shimadzu GC-14A gas chromatograph (GC) equipped with a FID detector using a widebore capillary column (30 m, DB-Wax, J&W Sci.). The injector and detector temperature was 250 °C; the column temperature was kept at 40 °C for 2 min, followed by an

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increase to 160 °C at the rate of 40 °C/min and held for 2 min. ^{1}H NMR spectra in deuterated chloroform ($CDCl_3$) were measured with a 300 MHz Bruker spectrometer using Tecmag data acquisition software.

Syntheses. PLA macromonomers were prepared by a ring-opening polymerization of lactide using 2-hydroxyethyl methacrylate or 2-hydroxymethyl acrylate as the initiator.[33,34] Lactide is often contaminated with a small amount of protic compounds such as lactic acid, lactic acid dimer, and water.[31] It is extremely important to use highly purified lactide for the macromonomer preparation because these impurities can act as undesirable initiators in the lactide polymerization and produce nonfunctionalized PLA and decrease its functionality.

Methacrylate-Terminated Poly(L-Lactic Acid) Macromonomer (M-PLLA). L-LTD (20.0 g, 0.14 mol) was placed into a 100 mL round-bottom flask equipped with a stir bar. After a toluene solution of SnOct (16 mg/mL-toluene) was added, the flask was capped with a rubber septa and evacuated (1 mmHg) through a needle for more than 3 h. The flask was filled with nitrogen gas, and HEMA (0.9 g, 5 mol %/LTD) was added via a syringe. The reaction flask was immersed in an oil bath at 120 °C, and L-LTD was melted with stirring. Although the reaction mixture solidified in about 1 h, the reaction was continued for 3 h. After cooling, the reaction mixture was dissolved in chloroform (40 mL) and poured into 2-propanol (800 mL). The precipitated polymer was recovered by filtration and washed with cold methanol and dried in a vacuum at room temperature. Yield = 18.6 g (89%). The functionality (F = 1.0 ± 0.03) was calculated from the NMR peak intensities at δ = 1.9 ppm (s, 3H, methyl) for the methacrylate end-group and at δ = 4.4 ppm (q, 1H, methine) for the 2-hydroxypropionate end-group.[33,35] The number average molecular weight (M_n = 2800) was estimated from the peak intensities at δ = 5.2 ppm for the ester methine protons in the polyester chain and at δ = 4.4 ppm (q, 1H, methine) for the 2-hydroxypropionate end-group. M_w/M_n = 1.16 (by GPC).

Methacrylate-Terminated Poly(D,L-Lactic Acid) Macromonomer (M-PDLLA). An amorphous M-PDLLA was prepared by the same procedure as M-PLLA but using a mixture of L-LTD (10 g, 0.07 mol) and D-LTD (10 g, 0.07 mol) as the monomer. The polymerization was performed at 130 °C for 2.5 h. Yield = 18.7 g (89%). F = 0.99 ± 0.03 (by ^{1}H NMR). M_n = 3350 (by ^{1}H NMR). M_w/M_n = 1.20 (by GPC).

Acrylate-Terminated Poly(L-Lactic Acid) Macromonomer (A-PLLA). A-PLLA was prepared by replacing HEMA with HEA in the method for M-PLLA synthesis. The polymerization was performed at 120 °C for 2.5 h. Yield = 19.9 g (96%). F = 0.98 ± 0.03 (by ^{1}H NMR). M_n = 2690 (by ^{1}H NMR). M_w/M_n = 1.22 (by GPC).

Copolymerizations. *Atom Transfer Radical Polymerization.* In a typical copolymerization, a 25 mL Schlenk flask equipped with a stir bar containing M-PLLA (M_n = 2800, 1.40 g, 0.50 mmol) and diphenyl ether (2.37 g) was deoxygenated by degassing and back-filling with nitrogen. CuCl (4.7 mg, 0.047 mmol) and dnNbpy (38.9 mg, 0.095 mmol) were placed in a 25 mL round-bottom flask equipped with a stir bar. This flask was capped with a rubber septum, purged with nitrogen gas for half an hour, and then charged with deoxygenated MMA (1.38 g, 13.8 mmol) via a syringe. The mixture was stirred at room temperature under nitrogen for about half an hour until a homogeneous maroon-colored solution formed. Xylene (1.6 mL) was added via a syringe to the Schlenk flask, and the PLLA/solvent mixture was heated (100−120 °C) and stirred to dissolve the PLLA macromonomer. The Schlenk flask was placed in a 90 °C oil bath under nitrogen. After an addition of 9.3 mg of ethyl 2-bromoisobutyrate (EBiB) to the catalyst/monomer solution in the round-bottom flask, this solution was cannula-transferred to the Schlenk flask under a nitrogen flow. Periodically, 0.2 mL of the reaction mixture was removed for kinetic and molecular weight analysis.

Conventional Radical Copolymerization Initiated by BPO. The same procedure as that for the ATRP described above was applied, except using 11.5 mg (0.047 mmol) of BPO instead of CuCl, dnNbpy, and EBiB.

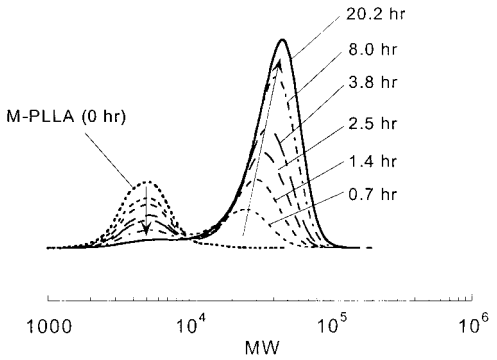


Figure 1. GPC traces for the ATRP of MMA and M-PLLA (M_n = 2800, M_w/M_n = 1.16, F = 1.0). Conditions: $[MMA]_0/[M\text{-}PLLA]_0/[EBiB]_0/[CuCl]_0/[dnNbpy]_0$ = 289.5/10.5/1/1/2, xylene = 21 wt %, diphenyl ether = 36 wt %, 90 °C, under N_2.

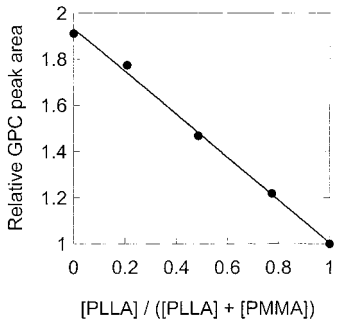


Figure 2. Dependence of GPC peak intensity of the PLLA/PMMA mixture solution on the composition. The sample solutions were injected at the same concentration (10 mg/mL).

Results and Discussion

Relative Reactivity of Macromonomers. The atom transfer radical copolymerization of MMA and methacrylate-terminated poly(L-lactic acid) macromonomer (M-PLLA) (M_n = 2800, M_w/M_n = 1.16, F = 1.0) was performed in solution at 90 °C (molar ratio $[MMA]_0/[M\text{-}PLLA]_0$ = 96.5/3.5, weight ratio = 50/50). Although M-PLLA was insoluble in the solvent (mixture of xylene and diphenyl ether) at room temperature, the reaction mixture became homogeneous when it was heated to 90 °C and kept as a maroon-colored solution throughout the reaction. The GPC traces of the samples taken from the reaction mixture showed a continuous increase in the concentration and molecular weight of the copolymer, along with a continuous decrease in the concentration of the macromonomer (Figure 1).

To measure the conversion of PLA macromonomer, the relationship between the polymer concentration and its relative intensity in the GPC traces was studied. A linear correlation between the concentration of the PLA in the sample and the RI intensity in GPC was confirmed by measuring the peak areas of sample solutions at various concentrations of PLA. The RI response of the peak intensities of different compositions of PMMA/PLA mixtures added linearly (Figure 2). The ratio of response factors of PMMA to PLLA at the same concentration (I_R) was 1.91. The conversion of PLA macromonomer (x) for the kinetic sample were calculated by using eq 1

$$A_R = (1 - x)/(x + w_R y I_R) \quad (1)$$

where, A_R is the area ratio of residual macromonomer peak to copolymer peak in the GPC, y is the conversion

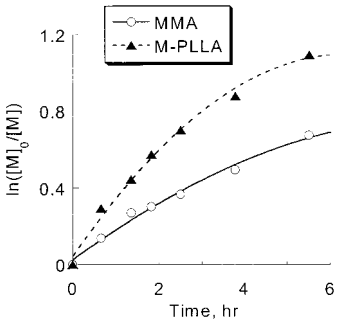


Figure 3. Kinetic plot for the ATRP of MMA and M-PLLA (M_n = 2800, M_w/M_n = 1.16, F = 1.0). Conditions: [MMA]$_0$/[M-PLLA]$_0$/[EBiB]$_0$/[CuCl]$_0$/[dnNbpy]$_0$ = 289.5/10.5/1/1/2, xylene = 21 wt %, diphenyl ether = 36 wt %, 90 °C, under N_2.

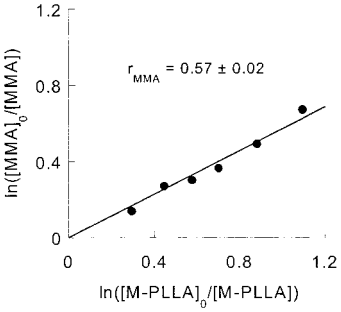


Figure 4. Jaacks plot for the ATRP of MMA and M-PLLA (M_n = 2800, M_w/M_n = 1.16, F = 1.0). Conditions: [MMA]$_0$/[M-PLLA]$_0$/[EBiB]$_0$/[CuCl]$_0$/[dnNbpy]$_0$ = 289.5/10.5/1/1/2, xylene = 21 wt %, diphenyl ether = 36 wt %, 90 °C, under N_2.

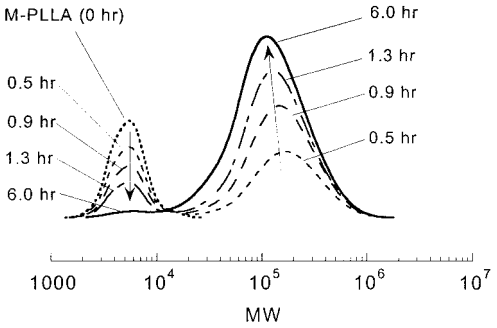


Figure 5. GPC traces for the conventional radical polymerization of MMA and M-PLLA (M_n = 2800, M_w/M_n = 1.16, F = 1.0). Conditions: [MMA]$_0$/[M-PLLA]$_0$/[BPO]$_0$ = 289.5/10.5/1, xylene = 21 wt %, diphenyl ether = 36 wt %, 90 °C, under N_2.

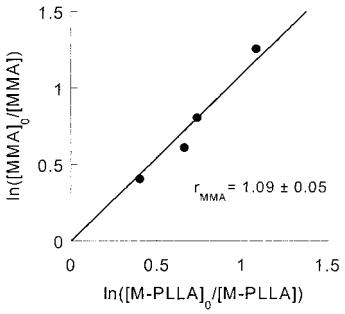


Figure 6. Jaacks plot for the conventional radical polymerization of MMA and M-PLLA (M_n = 2800, M_w/M_n = 1.16, F = 1.0). Conditions: [MMA]$_0$/[M-PLLA]$_0$/[BPO]$_0$ = 289.5/10.5/1, xylene = 21 wt %, diphenyl ether = 36 wt %, 90 °C, under N_2.

of MMA (estimated from GC), and w_R is the weight ratio of MMA to PLA macromonomer in the feed.

The kinetic plot indicated that M-PLLA was consumed faster than MMA (Figure 3). Since the macromonomer feed composition was low (3.5 mol %), the reactivity ratio of MMA (r_{MMA}) was estimated using the simplified method (eq 2) suggested by Jaacks.[36] By plotting kinetic data of MMA against those of M-PLLA, $r_{MMA} = 0.57 \pm 0.02$ was obtained from the slope (Figure 4):

$$r_{MMA} = \ln([MMA]_0/[MMA])/\ln([\text{macromonomer}]_0/[\text{macromonomer}]) \quad (2)$$

The relative reactivity of the macromonomers was evaluated by $1/r_{MMA} = 1.75$. This value means that the rate constant for the reaction of the methacrylate radical at the growing chain with M-PLLA is 1.75 times higher than that with MMA.

An amorphous poly(D,L-lactic acid) macromonomer containing a methacrylate end group (M-PDLLA) (M_n = 3350, M_w/M_n = 1.20, F = 1.0) was also copolymerized with MMA using ATRP under the same conditions. Unlike M-PLLA, M-PDLLA was soluble in the reaction solvent even at room temperature. The GPC traces of the kinetic samples were similar to those in Figure 1, and the conversion of the macromonomer was calculated in the same way (the intensity ratio of PMMA to PDLLA at the same concentration was $I_R = 1.91$). The reactivity ratio r_{MMA} was 0.68 ± 0.01, and therefore, $1/r_{MMA} = 1.47$. This indicates that the compatibility of the PLA macromonomer does not significantly affect the copolymerization reactivity as long as the reaction mixture is homogeneous.

Eguiburu et al.[37] reported $r_{MMA} = 1.01 \pm 0.17$ for the conventional radical copolymerization of MMA and methacrylate-terminated PLLA macromonomer (M_n = 4500) in dioxane at 60 °C. They concluded that the PLLA chain did not noticeably modify the kinetic parameters of the copolymerization because they found $r_{MMA} = 0.85 \pm 0.01$ for copolymerization of MMA with the model compound (2-acetoxyethyl methacrylate) under the same conditions.

To discuss the difference between ATRP and conventional radical polymerization, a conventional radical polymerization of MMA and M-PLLA using BPO as the initiator under the same conditions (feed composition, temperature, solvent, concentration) as the ATRP systems was carried out, as described above. The reaction mixture was clear and homogeneous throughout the reaction. The GPC traces of the kinetic samples showed that the concentration of copolymer increased continuously and the molecular weight distribution broadened toward the lower side (Figure 5). The kinetic study revealed that both MMA and M-PLLA were consumed almost simultaneously. The reactivity ratio $r_{MMA} = 1.09 \pm 0.05$ calculated from the Jaacks plot (Figure 6) was close to the value reported by Eguiburu ($r_{MMA} = 1.01 \pm 0.17$).

On the other hand, an acrylate-terminated PLLA macromonomer (A-PLLA) was copolymerized with MMA using ATRP under the same conditions as those of the MMA/M-PLLA system. The kinetic data showed that MMA was consumed faster than the A-PLLA macromonomer, $r_{MMA} = 1.63 \pm 0.10$.

Copolymerizations of MMA with 2-hydroxyethyl methacrylate (HEMA) or 2-hydroxyethyl acrylate (HEA) using ATRP under similar conditions ([MMA]$_0$/[HEMA]$_0$ = [MMA]$_0$/[HEA]$_0$ = 96.5/3.5) was also studied. By the Jaacks method, the r_{MMA} for MMA/HEMA system was estimated to be 0.67 ± 0.02 and was close to that for the ATRP of MMA/M-PLLA or MMA/M-PDLLA. The

Table 1. Reactivity Ratios for the Copolymerization of MMA (M_1) with Comonomers (M_2)

M_2	polymerization system	solvent[h]	$[M_1]_0$, mol/L	temp., °C	r_1[i]	$1/r_1$	ref
M-PLLA[a]	ATRP	DPE/xylene	2	90	0.57 ± 0.02	1.75	this work
M-PDLLA[b]	ATRP	DPE/xylene	2	90	0.68 ± 0.17	1.47	this work
HEMA[c]	ATRP	xylene	4	90	0.67 ± 0.02	1.49	this work
HEMA[c]	conventional (AIBN)	(bulk)	9	80	0.75	1.33	38
AEM[d]	conventional (AIBN)	dioxane	1	60	0.85 ± 0.01	1.18	37
M-PLLA[e]	conventional (AIBN)	dioxane	1	60	1.01 ± 0.17	0.99	37
M-PLLA[a]	conventional (BPO)	DPE/xylene	2	90	1.09 ± 0.05	0.91	this work
A-PLLA[f]	ATRP	DPE/xylene	2	90	1.63 ± 0.10	0.61	this work
HEA[g]	ATRP	xylene	2	90	1.57 ± 0.07	0.64	this work

[a] Methacrylate-terminated poly(L-lactic acid) macromonomer, $M_n = 2800$. [b] Methacrylate-termnated poly(D,L-lactic acid) macromonomer, $M_n = 3350$. [c] 2-Hydroxyethyl methacrylated. [d] 2-Acetoxyethyl methacrylate. [e] Methacrylate-terminated poly(L-lactic acid) macromonomer, $M_n = 4500$. [f] Acrylate-terminated poly(L-lactic acid) macromonomer, $M_n = 2690$. [g] 2-Hydroxyethyl acrylate. [h] DPE: diphenyl ether. [i] Determined by Jaacks method.

r_{MMA} for MMA/HEA system was estimated to be 1.57 ± 0.07 and was close to that for the ATRP of MMA/A-PLLA.

The reactivity ratios obtained in this study are summarized in Table 1 and compared to literature values. Since we cannot directly compare the reactivity ratios among the polymerization systems performed under different conditions (temperature, solvent, concentration), the data should be used only for relative comparison. The reactivity ratio of MMA for ATR copolymerization of MMA and HEMA was comparable to the value ($r_{MMA} = 0.75$) reported by Fink for the conventional radical copolymerization of these two monomers in bulk at 80 °C.[38] In fact, the copolymerization reactivity ratios in ATRP are consistent with those in conventional radical polymerizations.[39−41]

The copolymerization reactivity of the macromonomer is often lower than the inherent reactivity of the macromonomer based on the chemical structure of the terminal group.[42] One of the two major factors that reduce the reactivity is the diffusion control or kinetic excluded volume associated with the large size of the macromonomer.[43,44] The other is the potential incompatibility of macromonomer and propagating comonomer chain due to thermodynamic repulsive interaction.[45]

Eguiburu confirmed that PMMA and PLA are miscible through a differential scanning calorimetry study.[37] They found only one T_g for blends of PMMA and PDLLA, regardless of their blend composition. Therefore, the incompatibility effect can be ignored in the copolymerization of PLA macromonomer and MMA.

Nevertheless, we still need to consider the diffusion control effect. Radke and Müller[44] clearly demonstrated evidence for the diffusion control effect by performing a conventional radical copolymerization of methacrylate-terminated PMMA macromonomer with MMA. The relative reactivity of the macromonomer decreased unless the copolymerization was conducted with a sufficiently low molar ratio of macromonomer or with a low macromonomer concentration.

In the controlled radical copolymerization systems, since the time interval of monomer addition to a polymer chain is much larger (seconds or minutes) than that in conventional radical system (milliseconds), the diffusion control effect becomes less important.[17,18,46] We have reported that the overall reactivity of the macromonomer is close to the inherent reactivity of the terminal group in ATRP[17] and RAFT[18] copolymerizations of methacrylate-terminated poly(dimethylsiloxane) macromonomer with MMA.

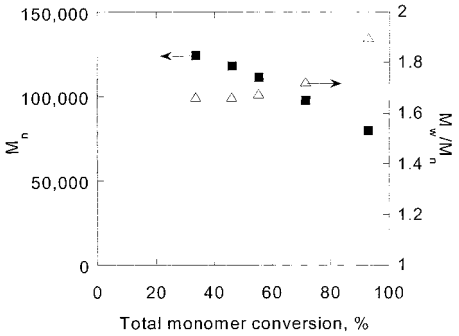


Figure 7. Dependence of molecular weight and polydispersity on conversion for the conventional radical polymerization of MMA and M-PLLA ($M_n = 2800$, $M_w/M_n = 1.16$, $F = 1.0$). Conditions: $[MMA]_0/[M\text{-}PLLA]_0/[BPO]_0 = 289.5/10.5/1$, xylene = 21 wt %, diphenyl ether = 36 wt %, 90 °C, under N_2.

Considering, however, negligibile diffusion control effect, we can conclude that the reactivity of methacrylate-terminated PLA macromonomer ($1/r_{MMA}$) in the ATRP system reflects the inherent reactivity of terminal 2-oxyethyl methacrylate group ($1/r_{MMA} > 1$). On the other hand, the reactivity of M-PLLA in the conventional radical system is reduced by the diffusion control effect and coincides with that of MMA ($1/r_{MMA} \approx 1$).

Copolymer Structures. Since the copolymerization reactivity of M-PLLA in the conventional radical polymerization with MMA is close to that of MMA, the graft copolymer obtained in this system should have homogeneously distributed branches. However, it obviously has a high polydispersity (Figure 7). The copolymer structure can be drawn as polymer A in Scheme 2. From the $1/r_{MMA}$ values, the ATRP of M-PLLA and MMA may give a copolymer structure such as polymer B, and the ATRP of A-PLLA and MMA may give a structure such as polymer C. Both polymer B and polymer C have low polydispersity ($M_w/M_n < 1.2$).

To confirm the good structural control of graft copolymers, we copolymerized an equivalent mixture of M-PLLA and A-PDLLA (1/1 by weight) with MMA using ATRP under the same conditions described above. The kinetics revealed that MMA and the PLA macromonomer were converted almost simultaneously and the average reactivity ratio of MMA (r_{MMA}) obtained by the Jaacks method was 1.07 ± 0.04 (Figure 8). It seems reasonable to assume that half of the PLA macromono-

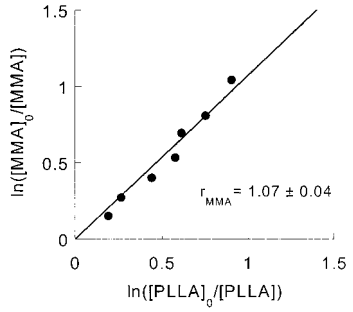


Figure 8. Jaacks plot for the ATRP of MMA and M-PLLA ($M_n = 2800$, $M_w/M_n = 1.16$, $F = 1.0$) and A-PLLA ($M_n = 2690$, $M_w/M_n = 1.22$, $F = 1.0$). Conditions: $[MMA]_0/[M\text{-}PLLA]_0/[A\text{-}PLLA]_0/[EBiB]_0/[CuCl]_0/[dnNbpy]_0 = 289.5/5.3/5.3/1/1/2$, xylene = 21 wt %, diphenyl ether = 36 wt %, 90 °C, under N_2.

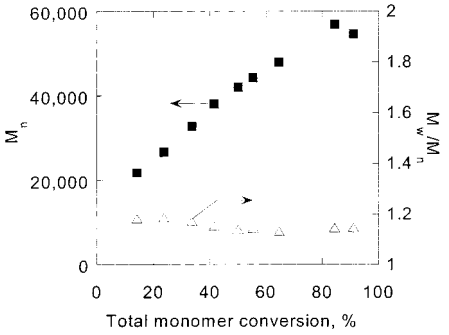
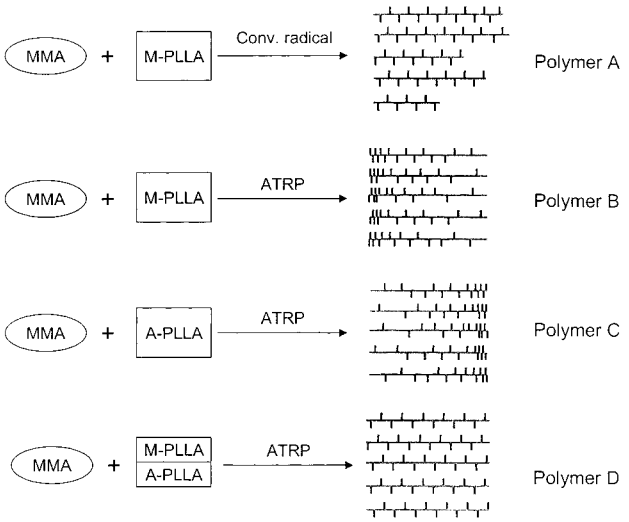


Figure 9. Dependence of molecular weight and polydispersity on conversion for the ATRP of MMA and M-PLLA ($M_n = 2800$, $M_w/M_n = 1.16$, $F = 1.0$) and A-PLLA ($M_n = 3350$, $M_w/M_n = 1.20$, $F = 1.0$). Conditions: $[MMA]_0/[M\text{-}PLLA]_0/[A\text{-}PLLA]_0/[EBiB]_0/[CuCl]_0/[dnNbpy]_0 = 289.5/5.3/5.3/1/1/2$, xylene = 21 wt %, diphenyl ether = 36 wt %, 90 °C, under N_2.

Scheme 2



mer (M-PLLA) having higher reactivity ($1/r_{MMA} = 1.75$) was incorporated into copolymer primarily at the early stage, with the other half (A-PLLA) having lower reactivity ($1/r_{MMA} = 0.61$) incorporated mainly at the later stage of the reaction. The molecular weight increased proportionally to the monomer conversion, and the polydispersity was low ($M_w/M_n = 1.15$) even at high monomer conversion (>90%) (Figure 9). The copolymer structure should have homogeneously distributed side chains and can be expressed as polymer D in Scheme 2.

Conclusions

The reactivities of (meth)acrylate-terminated PLA macromonomers in copolymerizations with MMA using ATRP were close to the inherent reactivity of the terminal 2-oxyethyl (meth)acrylate group because both the incompatibility effect and the diffusion control effect were insignificant. Copolymerization of methacrylate-terminated macromonomer and acrylate-terminated macromonomer with MMA therefore produced homogeneously branched PMMA-g-PLLA graft copolymer with quite low polydispersity.

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