

ORIGINAL ARTICLE

Poly(ethylene glycol)-induced acceleration of free radical polymerization of methyl methacrylate: effects of highly viscous solvent and kinetic study

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Poly(ethylene glycol) with a molecular weight of 400 (PEG400) as an environmentally benign and highly viscous polymeric solvent was found to effectively accelerate the free radical polymerization (FRP) of methyl methacrylate and to afford a high-molecular-weight polymer. When the polymerization in PEG400 was performed at a monomer concentration of 3.0 mol l^{-1} and an initiator (2,2'-azobis(isobutyronitrile)) concentration of $0.3 \times 10^{-2} \text{ mol l}^{-1}$, the monomer conversion was completed for 6 h to afford a polymer with a number-average molecular weight (M_n) of 838 000. After polymerization, the PEG400 solvent was readily recovered and reused. The solvent effects of highly viscous PEG400 were kinetically analyzed. The polymerization rate (R_p) was proportional to the monomer concentration and the square root of both the initiator concentration and the viscosity of the polymerization media (η). For the FRP in the mixed solvents of PEG400 and toluene, both R_p and M_n values increased linearly with the square root of the η value. The kinetic study has shown that the highly viscous PEG400 solvent largely suppresses diffusion-controlled bimolecular termination.

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INTRODUCTION

Chemical transformations in an environmentally benign alternative solvent are of growing interest, because volatile organic solvents for synthetic chemistry usually have toxicity and flammability. Although use of nonvolatile organic solvents may cause a separation problem, it can reduce environmental risks. Liquid polymers such as silicone oil, liquid paraffin, poly(ethylene glycol) (PEG) and several oligomers are examples of the most accessible nonvolatile organic solvents, and they can be used to form a highly viscous solution. Among them, PEG with low molecular weight is a versatile nonvolatile solvent for organic reactions because of good solubility of organic substrates in PEG. The PEG solvent offers advantages over conventional organic solvents in terms of low toxicity, low flammability and biodegradability. Recently, PEGs have been used for a variety of organic reactions such as the Suzuki coupling,^{1–6} the Michael addition,⁷ hydrogenation,^{8–11} and so on.^{12–19} Perrier *et al.*²⁰ reported the first use of PEG as a polymerization solvent. They presume that the polarity and metal coordination ability of PEG would promote copper-catalyzed living radical polymerization of methyl methacrylate (MMA) and styrene.

In free radical polymerization (FRP), propagating radicals usually terminate through bimolecular reactions. Such a termination reaction is under diffusion control, so that the termination rate constant (k_t) is

inversely proportional to the viscosity of the polymerization system (η). As such, by substituting $k_{t,0}/\eta$ ($k_{t,0}$ =termination rate constant when $\eta=1$ cP) for k_t in conventional FRP kinetics, the polymerization rate (R_p) can be expressed as Equation (1):^{21,22}

$$R_p = k_p \sqrt{\frac{k_d f}{k_{t,0}}} [M] \sqrt{[I]} \sqrt{\eta} \quad (1)$$

where k_p is the propagation rate constant, k_d and f are the rate constant and the efficiency for decomposition of the initiator, respectively, and $[M]$ and $[I]$ are the concentrations of monomer and initiator, respectively. The number-average degree of polymerization (\bar{P}_n) is generally given by Equation (2) when chain transfer reactions are negligible:^{23,24}

$$\bar{P}_n = \frac{k_p^2 [M]^2}{k_t R_p} \quad (2)$$

Substituting Equation (1) and $k_t=k_{t,0}/\eta$ into Equation (2) gives Equation (3).

$$\bar{P}_n = \frac{k_p [M] \sqrt{\eta}}{\sqrt{k_{t,0} k_d f} \sqrt{[I]}} \quad (3)$$

Equations (1 and 3) show that both R_p and \bar{P}_n are proportional to the square root of η . Thus, highly viscous media is expected to accelerate FRP from the initial stage and to afford a high-molecular-weight polymer. Since the first report of the gel effect,²⁵ the diffusion-controlled termination in radical polymerization has been intensely investigated.^{26–29} It was reported that the FRP of MMA rapidly proceeds in a highly viscous solution of polystyrene.³⁰ Recently, several research groups have investigated the FRPs of methacrylates in ionic liquids as highly viscous nonvolatile solvents and found that polymerizations are accelerated to produce high-molecular-weight polymers.^{31–35} They have proposed several solvent effects such as high viscosity and polarity of ionic liquids,^{31–34} and domain separation.³⁵ Although ionic liquids can be versatile solvents for FRP, the very high cost and the unknown toxicity are their weak points. Thus, we are prompted to develop a new FRP system by using conventional and commercially available nonvolatile solvents.

We herein report the first use of PEG as a highly viscous, readily available and environmentally benign solvent for FRP of MMA. It was found that the PEG solvent accelerates the FRP to yield a high-molecular-weight poly(methyl methacrylate) (PMMA). To examine the effects of the highly viscous solvent, the FRP system has been kinetically studied; both R_p and M_n are proportional to the square root of η , as presented in Equations (1 and 3).

EXPERIMENTAL PROCEDURE

Materials

MMA (Wako Pure Chemical Industries, Tokyo, Japan, >97%) was washed with an aqueous 5% NaOH solution and then with water, dried over $MgSO_4$ and distilled from CaH_2 under reduced pressure. 2,2'-Azobis(isobutyronitrile) (AIBN) (Kanto Chemical, Tokyo, Japan, 97%) was purified by recrystallization from methanol. PEGs with average molecular weights of 200 (polyethylene glycol 200, Kanto, >90%, molecular weight of 190–210), 400 (polyethylene glycol 400, Kanto, >90%, molecular weight of 380–420), 1000 (polyethylene glycol 1000, Kanto, >90%, molecular weight of 950–1050) and 8000 (polyethylene glycol 6000, Kanto, >90%, molecular weight of 7300–10 200) were used as received. Toluene (Kanto, >99%) was distilled from sodium before use.

Polymerization

In a three-necked flask equipped with a three-way stopcock, PEG400 (30 g, 26.5 ml) was stirred under vacuum to remove dissolved oxygen, and then MMA (3 g, 29.9 mmol) and AIBN (49 mg, 0.298 mmol) were added under nitrogen atmosphere. When using the mixed solvent of PEG400 and toluene, the polymerization system was degassed by three freeze–vacuum–thaw cycles. The mixture was mechanically or magnetically stirred at 60 °C for 6 h under nitrogen atmosphere. Water or methanol (150 ml) was poured into the polymerization solution and the subsequent filtration afforded PMMA (2.85 g) in 95% yield. In cases in which the polymerization rate was estimated, aliquots of the polymerization solution were sampled several times during polymerization and subjected to 1H nuclear magnetic resonance spectroscopy, which informed the monomer conversion by the signal integral ratio between $CH_2=C$ of MMA and $C-CH_3$ of PMMA.

Measurements

Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by size exclusion chromatography in tetrahydrofuran at 40 °C on four tandem polystyrene gel columns (TSKgel G3000H_{XL}, G4000H_{XL}, G5000H_{XL} and G6000H_{XL}, TOSOH, Tokyo, Japan) calibrated against polystyrene standards at a flow rate of 1 ml min⁻¹ with refractive index detection. 1H and ^{13}C nuclear magnetic resonance spectra were recorded on a Bruker Avance-200 (200 MHz for 1H) or a Bruker Avance-600 (600 MHz for 1H) spectrometer (Bruker BioSpin, Kanagawa, Japan) in $CDCl_3$. Tacticities of PMMAs were determined from α -methyl hydrogen signals. Viscosity was measured by sine-wave vibro viscometer SV-10 with two gold-coated transducers and a temperature sensor (A&D Ltd, Tokyo, Japan).

RESULTS AND DISCUSSION

We first carried out the FRP of MMA in PEG to high conversion under a variety of conditions as shown in Table 1 to demonstrate the synthetic utility. We then performed kinetic studies of FRP in the initial stage to understand the solvent effects and mechanistic aspects; the effects of polymerization conditions on the R_p and M_n of the resulting PMMA were investigated.

Polymerization results

To examine the effect of the molecular weights of PEG, the FRPs of MMA with AIBN at 60 °C were conducted in PEGs with molecular

Table 1 Free radical polymerization of MMA with AIBN

| Run | Solvent | [MMA] (mol l ⁻¹) | 10 ² [AIBN] (mol l ⁻¹) | η^a (cP) | Temperature (°C) | 10 ⁵ R_p^b (mol l ⁻¹ s ⁻¹) | Time (h) | Yield (%) | 10 ⁻³ M_n^c | M_w/M_n^d |
|-----|---------|---------------------------------|--|---------------|---------------------|---|-------------|--------------|--------------------------|-------------|
| 1 | PEG200 | 1.0 | 1.0 | 9.62 | 60 | — ^d | 6 | 100 | 101 | 4.68 |
| 2 | PEG400 | 1.0 | 1.0 | 14.5 | 60 | 11.1 | 6 | 95 | 177 | 3.12 |
| 3 | PEG1000 | 1.0 | 1.0 | 37.9 | 60 | 9.62 | 6 | 92 | 132 | 2.33 |
| 4 | PEG8000 | 1.0 | 1.0 | 1680 | 60 | 20.5 | 6 | 99 | 113 | 2.13 |
| 5 | PEG400 | 1.0 | 0.20 | 14.5 | 60 | 5.10 | 6 | 87 | 425 | 1.94 |
| 6 | PEG400 | 1.0 | 1.0 | 14.5 | 60 | 11.1 | 1 | 39 | 278 | 2.74 |
| 7 | PEG400 | 3.0 | 3.0 | 5.27 | 60 | 25.2 | 0.5 | 24 | 186 | 2.33 |
| 8 | PEG400 | 3.0 | 3.0 | 5.27 | 60 | 25.2 | 3 | 99 | 222 | 3.00 |
| 9 | PEG400 | 3.0 | 0.30 | 5.27 | 60 | 10.7 | 6 | 99 | 838 | 1.79 |
| 10 | PEG400 | 1.0 | 1.0 | 13.1 | 70 | 25.6 | 6 | 100 | 74 | 4.14 |
| 11 | PEG400 | 1.0 | 1.0 | 11.1 | 80 | 47.2 | 4 | 98 | 21.1 | 2.74 |
| 12 | Toluene | 1.0 | 1.0 | 0.60 | 60 | 2.33 | 24 | 82 | 8.8 | 2.25 |
| 13 | Toluene | 3.0 | 0.30 | 0.60 | 60 | 3.88 | 26 | 35 | 48.6 | 2.63 |
| 14 | Bulk | 9.4 | 0.94 | 0.63 | 60 | 20.8 | 6 | 92 | 143 | 4.19 |

Abbreviations: AIBN, 2,2'-azobis(isobutyronitrile); MMA, methyl methacrylate; PEG200, poly(ethylene glycol) with molecular weight of 200; PEG400, poly(ethylene glycol) with molecular weight of 400; PEG8000, poly(ethylene glycol) with molecular weight of 8000.

^aInitial viscosity of the polymerization media at the polymerization temperature.

^bPolymerization rate (conversion < 10%).

^cBy size exclusion chromatography in tetrahydrofuran using polystyrene standards.

^dThe polymerization mixture was heterogeneous.

weights of 200 (PEG200), 400 (PEG400), 1000 (PEG1000) and 8000 (PEG8000) (Table 1). For the FRPs in PEG400, PEG1000 and PEG8000, the solutions became cloudy after 30 min and extremely viscous along with the progress of the polymerization without formation of precipitated PMMA. In contrast, the FRP in PEG200 proceeded heterogeneously, precipitating PMMA even at the initial stage. PMMAs were collected by the addition of a large excess of water into the polymerization solution and subsequent filtration. However, the resultant PMMAs were slightly contaminated with the PEG solvent, which was completely excluded by reprecipitation into a large amount of water from tetrahydrofuran. Although the product isolation from a nonvolatile solvent is generally more difficult compared with volatile counterparts, the PMMAs were readily separated from nonvolatile PEG solvent because of large differences in solubility in water between PEG and PMMA. Absence of contamination of the obtained PMMA with PEG also supports the fact that a block copolymer is not formed from them by chain transfer reactions to PEG.

The FRPs in PEG200, PEG400, PEG1000 and PEG8000 for 6 h almost quantitatively produce PMMAs with much higher molecular weights than those in toluene for 24 h (runs 1–4, 12). This particular solvent effect of PEG prompted us to investigate further details, for which the experiments were performed in PEG400 because of the following reasons: the size exclusion chromatography profiles of the PMMAs obtained in PEG400, PEG1000 and PEG8000 are unimodal, whereas the heterogeneous polymerization in PEG200 produces PMMA with a multimodal profile and relatively larger polydispersity (Supplementary Figure S1). Thus, the heterogeneous FRP in PEG200 is not suitable for the mechanistic study. Use of PEG1000 and PEG8000, which are solids at room temperature, is not preferable in terms of handling as the solvent and separation of PMMA from the solvent. The η value of the PEG8000 polymerization system is almost 100 times as large as that of the PEG400 system. If this high viscosity reduces only the bimolecular termination rate, Equation (1) allows us to calculate the estimated R_p value in PEG8000 from the experimental R_p value in PEG400. In fact, the experimental value of $20.5 \times 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}$ (run 4) is much lower than the estimated value of $119 \times 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}$. In addition, the R_p value in PEG1000 is slightly lower than that in PEG400, although the viscosity of the PEG1000 solution is twice higher than that of PEG400. Furthermore, FRP gives a relatively higher molecular weight PMMA in PEG400 than in PEG1000 and PEG8000 (runs 2–4). It is known that in the later stage of bulk polymerization, an extremely viscous system, the propagation rate and the initiator efficiency decrease.^{24,36,37} As the highly viscous polymerization solutions of PEG8000 and PEG1000 are comparable to the later stage of the bulk system, such negative factors would affect FRP results and make them inconsistent with the theoretical kinetics (Equations (1) and (3)). Therefore, we suggest that the viscosities of PEG8000 and PEG1000 are too high to effectively promote FRPs.

The FRP at 60 °C produced the higher molecular weight PMMA as compared with that at 70 and 80 °C because of the low radical concentration at the relatively low temperature (runs 2, 10 and 11). Thus, the following detailed study was performed at 60 °C.

The time–conversion plots shown in Figure 1 indicate that the FRP proceeded much faster in PEG400 than in toluene. At the monomer concentration of 3.0 mol l^{-1} , the FRP was accelerated in the region over $\sim 30\%$ conversion, and completed in 3 h (run 8, Figure 1a). In contrast, the FRP mixtures in bulk^{36–40} and in ionic liquids^{34,35} are known to solidify without the complete monomer conversion (see also run 14). The value of $\ln([MMA]_0/[MMA])$ versus polymerization

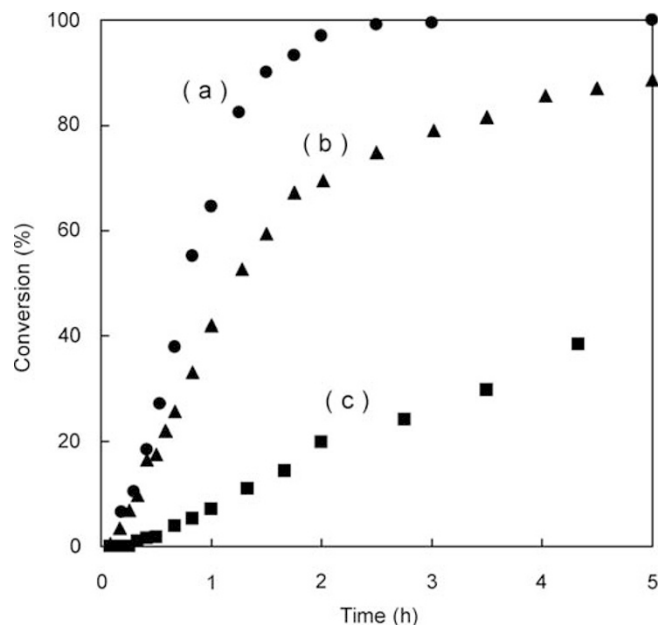


Figure 1 Time versus conversion plots for the polymerization of MMA with AIBN at 60 °C: (a) run 7, 8; (b) run 2, 6; (c) run 12 in Table 1.

time was linearly fitted on the kinetic plots, showing that R_p is proportional to the first order of the monomer concentration (Supplementary Figure S2). Thus, the R_p values under various polymerization conditions were evaluated from these kinetic plots.

The R_p values in PEG400 in the initial stage of polymerization at initial monomer concentrations of 1.0 and 3.0 mol l^{-1} were 4.8 and 2.8 times as large as those in toluene, respectively (runs 2, 9, 12 and 13). Interestingly, these values are almost identical with the square roots of the multiple numbers of η values; the viscosities in PEG400 in these monomer concentrations were 24 and 8.8 times as high as those in toluene, respectively. This is in good agreement with Equation (1).

The molecular weights of the PMMAs obtained in PEG400 were roughly 20 times higher than those obtained in toluene for both monomer concentrations (runs 2, 9, 12 and 13). The M_n value was affected by the initial monomer concentration and monomer conversion (runs 2, 6, 7 and 8). Specifically, it decreased with the progress of the polymerization at an initial monomer concentration of 1.0 mol l^{-1} , but, in contrast, increased gradually in the case of an initial monomer concentration of 3.0 mol l^{-1} (Supplementary Figure S3). This difference is presumably due to the gel effect given by the increased viscosity at the relatively high monomer concentration. Even at a low initiator concentration of $0.3 \times 10^{-2} \text{ mol l}^{-1}$ with a monomer concentration of 3.0 mol l^{-1} , the FRP proceeded rapidly and completed for 6 h, producing the very high-molecular-weight PMMA with M_n of 838 000 and M_w/M_n of 1.79 (run 9). Accordingly, the present synthetic procedure offers a practical advantage for the facile preparation of high-molecular-weight PMMA without chain transfer reactions to PEG400.

These promising results encouraged us to perform further studies, including studies on kinetics. The viscosity of the reaction mixture varies with the progress of polymerization, and the temperature of the polymerization solution may increase at the onset of the gel effect. Thus, the following experiments were conducted at the initial stage of the FRP.

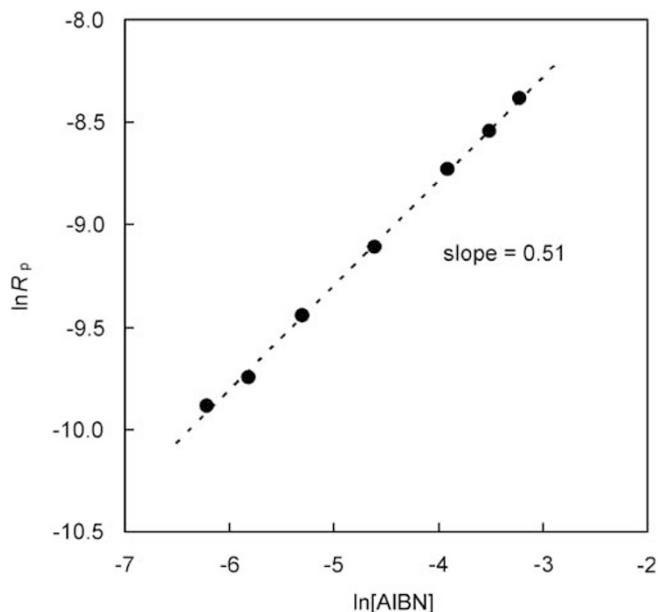


Figure 2 Plots of $\ln R_p$ versus $\ln[\text{AIBN}]$ for the polymerization of MMA with AIBN at 60 °C: $[\text{MMA}] = 1.0 \text{ mol l}^{-1}$.

Effects of initiator concentration

Values of R_p were measured at various initiator concentrations ranging from 0.2×10^{-2} to $4 \times 10^{-2} \text{ mol l}^{-1}$ to examine the termination mechanism. A linear relationship between $\ln[\text{AIBN}]$ and $\ln R_p$ was observed with a slope value of 0.51, indicating that the R_p is proportional to the square root of the initiator concentration (Figure 2). This relationship, in common with the usual solution FRP of MMA, suggests that bimolecular terminations are dominantly involved. By contrast, it is known that single-molecular terminations take place in extremely viscous media, such as a later stage of bulk polymerization,⁴¹ and in a methanol/water system for dispersion polymerization.⁴² These termination processes are attributed to the lack of mobility of polymer radicals and precipitation of the produced polymer, respectively. The R_p values in these cases are proportional to the 0.6–0.8th order of the initiator concentration. On the other hand, the diffusion of polymer chains in PEG400 is not completely suppressed, and polymer radicals have enough mobility to allow bimolecular collisions.

The molecular weights of PMMAs obtained at monomer conversions of $< 10\%$ were examined by varying the initiator concentration. As shown in Figure 3a, when the initiator concentration is decreased, the M_n value increases and reaches 258 000 at the very low initiator concentration of $0.3 \times 10^{-2} \text{ mol l}^{-1}$ with almost constant M_w/M_n values. Expectedly, there is a linear relationship between the M_n value and the reciprocal square root of the initiator concentration as shown in Figure 3c, which is in good agreement with Equation (3). Thus, the molecular weight of the resulting PMMA can be controlled by the initiator concentration at least in the range between 0.3×10^{-2} and $18 \times 10^{-2} \text{ mol l}^{-1}$.

Effects of monomer concentration

The FRPs were carried out at various monomer concentrations ranging from 0.3 to 9.4 mol l^{-1} . The resultant relationships of R_p and η to the monomer concentration are plotted in Figure 4. The R_p value increases linearly with increasing the monomer concentration

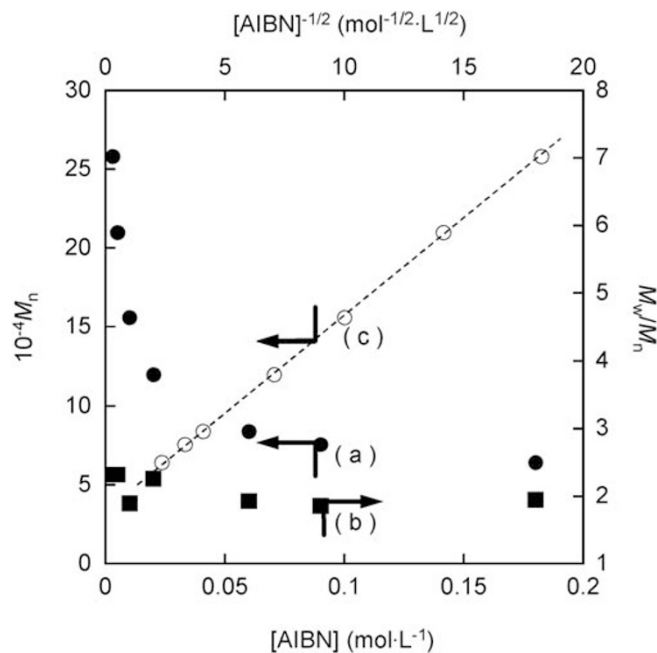


Figure 3 The M_n and M_w/M_n values of PMMA obtained by polymerization in PEG400 with AIBN at 60 °C: $[\text{MMA}] = 1.0 \text{ mol l}^{-1}$; (a) $10^{-4} M_n$ versus $[\text{AIBN}]$; (b) M_w/M_n versus $[\text{AIBN}]$; (c) $10^{-4} M_n$ versus $[\text{AIBN}]^{-1/2}$.

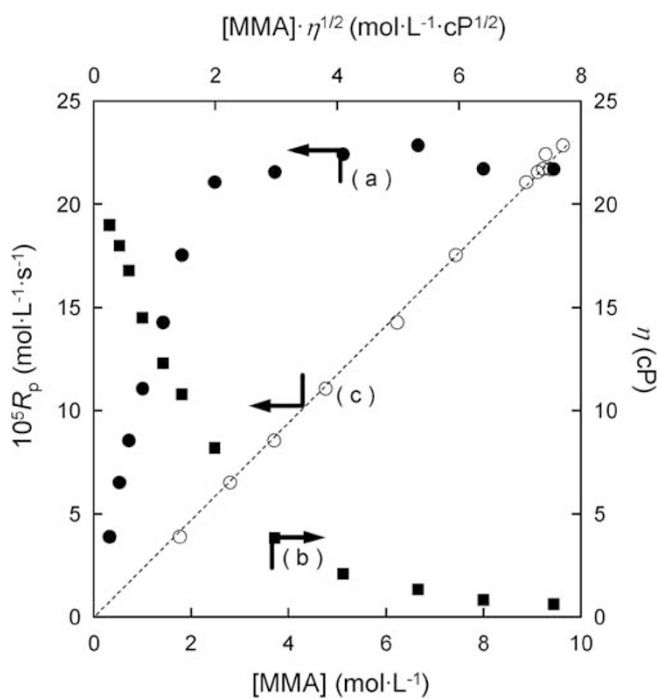


Figure 4 R_p and η values in the polymerization of MMA in PEG400 with AIBN at 60 °C: $[\text{AIBN}] = 1.0 \times 10^{-2} \text{ mol l}^{-1}$; (a) R_p versus $[\text{MMA}]$, (b) η versus $[\text{MMA}]$, (c) R_p versus $[\text{MMA}]\eta^{1/2}$.

in the range of $< 2.5 \text{ mol l}^{-1}$ and then becomes almost constant (Figure 4a). It is obvious that the η value decreases when the monomer concentration is increased because of the much lower viscosity of MMA than PEG400 (Figure 4b). Thus, the variable η

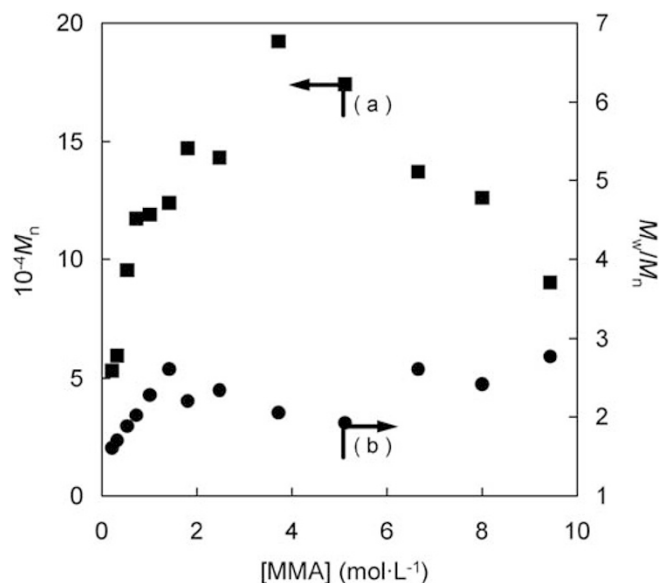


Figure 5 The M_n and M_w/M_n values of PMMA obtained by the polymerization in PEG400 with AIBN at 60 °C: [AIBN]= 1.0×10^{-2} mol l $^{-1}$; (a) $10^{-4}M_n$ versus [MMA]; (b) M_w/M_n versus [MMA].

values should be considered for this kinetic study. When we plot R_p against $[MMA]\eta^{1/2}$ as shown in Figure 4c, the data points fall on a straight line that passes through the origin. This relationship clearly proves Equation (1). Furthermore, this is also supported by the linear plots of $R_p/[MMA]$ against $\eta^{1/2}$ and of $R_p/\eta^{1/2}$ against [MMA] (Supplementary Figure S4).

Figure 5 shows the dependency of the polymer molecular weight on the monomer concentration at the initial stage of the FRP with an initiator concentration of 1.0×10^{-2} mol l $^{-1}$. The M_n value increases with increasing monomer concentration in the range of <4 mol l $^{-1}$ and then decreases gradually. The PEG400 solvent system is more efficient to produce high-molecular-weight PMMA than the bulk polymerization ([MMA]=9.44 mol l $^{-1}$), and the monomer concentrations of 2–5 mol l $^{-1}$ are appropriate for such a purpose. Equation (3) suggested to us to plot M_n against $[MMA]\eta^{1/2}$, but a linear relationship was not clearly observed. The chain transfer reaction rate to MMA and PEG400 would be different. Thus, the deviation from a linear relationship is probably because the monomer concentration affected the frequency of chain transfer reactions.

Effects of viscosity

To gain additional insights into this kinetic study, FRPs were carried out in a variety of PEG400-toluene mixed solvents that can control the η values ranging from 0.60 to 14.5 cP without changing the monomer and initiator concentrations. All FRPs in the mixed solvents homogeneously proceeded with the first order with respect to the monomer concentration (Supplementary Figure S5). Increasing the proportion of PEG400 in the mixed solvent causes the η and R_p values to increase (Supplementary Figure S6). The plot of $\ln R_p$ versus $\ln \eta$ was found to show a linear relationship with a slope value of 0.49 (Figure 6), and therefore the plot of R_p versus $\eta^{1/2}$ is a good fit for the straight line that passed through the origin (Supplementary Figure S7). These data also clearly support Equation (1).

The M_n of the PMMAs obtained at monomer conversions $<10\%$ also increased from 16 000 to 119 000 with increase in the η value, and the M_w/M_n values were within 1.7–2.3 (Figure 7). The slope value of

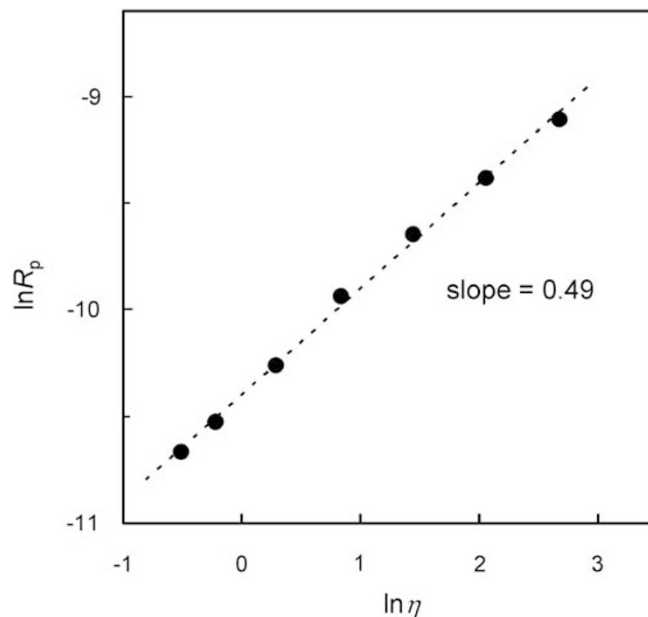


Figure 6 Plots of $\ln R_p$ versus $\ln \eta$ for the polymerization of MMA with AIBN at 60 °C in the mixed solvents of PEG400 and toluene at various ratios: [MMA]=1.0 mol l $^{-1}$; [AIBN]= 1.0×10^{-2} mol l $^{-1}$.

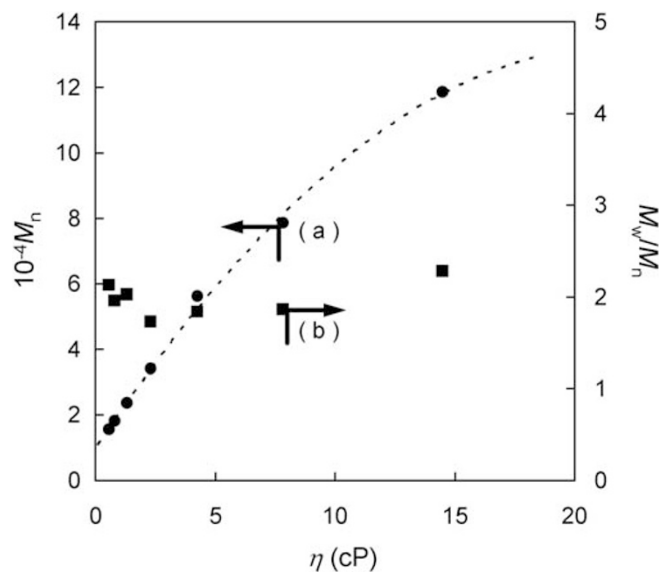


Figure 7 The M_n and M_w/M_n values of PMMA obtained by polymerization with AIBN at 60 °C in the mixed solvents of PEG400 and toluene at various ratios: [MMA]=1.0 mol l $^{-1}$; [AIBN]= 1.0×10^{-2} mol l $^{-1}$; (a) $10^{-4}M_n$ versus η ; (b) M_w/M_n versus η .

the linear plots of $\ln M_n$ versus $\ln \eta$ is 0.65 (Figure 8). Although this value is slightly deviated from the theoretical value of 0.50, the M_n value increases almost linearly with the square root of η (Supplementary Figure S8). This result is also in good agreement with Equation (3).

The 0.5th-order dependence of both R_p and M_n on η can be derived from the fact that the bimolecular termination rate is inversely proportional to η .

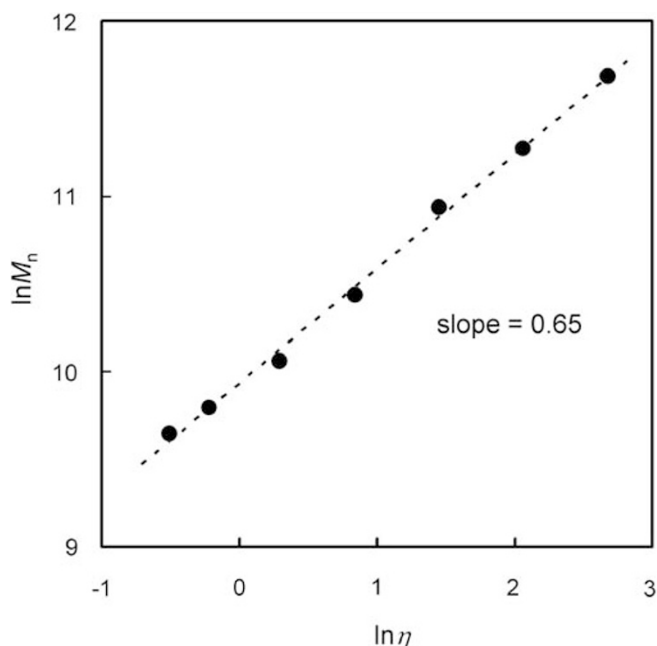


Figure 8 Plots of $\ln M_n$ versus $\ln \eta$ for the polymerization of MMA with AIBN at 60 °C in the mixed solvents of PEG400 and toluene at various ratios: $[MMA]=1.0 \text{ mol l}^{-1}$; $[AIBN]=1.0 \times 10^{-2} \text{ mol l}^{-1}$.

Other aspects

Because of the low coordination ability of PEG, it is highly unlikely that the ethylene glycol unit and the terminal alcohol of PEG can activate MMA like the Lewis acid, which is known to accelerate the FRP of MMA.^{43–45} The tacticity of PMMAs is not affected by the volume ratio of PEG400 to toluene in the mixed solvent and molecular weight of the PEG used; the triad syndiotacticity (rr) was constantly within 60.1–62.9%. This also suggests that there is hardly such an interaction of PEG400 with the monomer and/or the polymer terminal.

Highly viscous media have been reported to reduce initiator efficiency by impeding the diffusion of primary radicals out of cage.^{24,37,46,47} However, it would be negligible in the PEG400 solvent because, as mentioned above, R_p has a linear relationship with the square root of the η value. This clear relationship also suggests that the termination reaction would be hardly affected by the polymer chain length.

Recovery and reuse

Polymerization was carried out under the conditions of run 2 in Table 1. By the addition of ethanol into the polymerization mixture, PMMA was precipitated and filtered, and subsequently PEG400 was recovered by concentrating the filtrate. PEG400 was degassed *in vacuo* and reused for polymerization. This cycle was repeated three times, and PEG400 was finally recovered in 92%. The PMMAs with M_n values of 130 000–140 000 were reproducibly obtained in >90% yield. The PEG400 solvent can be recovered readily and reused without any loss of efficiency.

Conclusion

We have shown that the PEG solvent accelerates the FRP of MMA to quantitatively produce high-molecular-weight PMMA. This solvent system for FRP offers 'green', efficient and practical advantages. The kinetic results of the FRP in PEG400 demonstrate that both the R_p

and M_n of the resulting PMMA are proportional to the square root of η . Therefore, it is reasonable that the highly viscous PEG400 solvent impedes translational diffusion of propagating radicals and consequently reduces the bimolecular termination rate. The diffusion of MMA, in contrast, is hardly suppressed. As a result, the diffusion-controlled process increases the polymerization rate to produce high-molecular-weight PMMA. We suggest that the diffusion-controlled termination in PEG400 can be extended to other radical polymerizations; vinyl monomers with low polymerizability are now under examination. In addition, such a kinetic study as mentioned above is expected to be effective also for mechanistic elucidation of FRPs in newly emerging solvents such as ionic liquids and supercritical fluids.

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