Radical polymerization behaviour of macromonomers: 3. Effect of macromonomer concentration

Kiyoharu Tsutsumi and Yoshio Okamoto
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

and Yasuhisa Tsukahara*
Department of Materials Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

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The radical polymerization of a polystyrene macromonomer having a methacryloyl end group (with an M_n of 2700), was investigated at various macromonomer concentrations ([M]), in order to study in detail the effect of [M] on the polymerization behaviour. The polymerization rate (R_p), the degree of polymerization (DP), the concentration of the propagating radical ([M*]), and the initiator efficiency (f) were evaluated by gel permeation chromatography, using an instrument equipped with a laser light scattering detector (l.s.-g.p.c.), and also by electron spin resonance (e.s.r.) spectroscopy. The viscosity of the polymerization solution (η) was also measured, by using an Ubbelohde viscometer. The DP of the formed poly(macromonomer)s changes drastically with [M]. The order of R_p and $R_p/\phi_\eta^{1/2}$, with respect to [M], was 2.2 and 1.3, respectively, where ϕ_η is the ratio of η of the polymerization system to that of the solvent. This indicates that η alone is not responsible for an order of R_p that is larger than unity. Values for the propagation rate constant (k_p) were approximately constant with respect to [M], while those of the termination rate constant (k_t) rapidly decreased with increases in [M]. These results are discussed in terms of [M], η, and the segment density around the propagating radical site.

(Keywords: macromonomer; radical polymerization; segment density)

INTRODUCTION

Since a macromonomer is a monomer which has a large molecular weight, the viscosity of the polymerization solution of a macromonomer is much larger than that of a low-molecular-weight monomer and also depends strongly on the macromonomer feed concentration ([M]). The segment density around the propagating radical site is very different to that of the corresponding linear propagating radical of the corresponding small monomer. Therefore, the characteristics of the polymerization of macromonomers are greatly influenced by [M][1-3].

The dependence of [M] on the polymerization behaviour of a macromonomer has been studied mainly in terms of the kinetic order of the polymerization rate (R_p), with respect to [M]. Asami *et al.* reported the radical polymerization of poly(tetrahydrofuran) macromonomers having a vinylbenzoyloxy or a vinylphenoxy end group, in which they investigated the kinetic order of R_p with respect to both [M] and to the initiator concentration ([I])[4]. Ito *et al.* reported the radical polymerization of poly(ethylene oxide) macromonomers, with vinylbenzyl end groups, in water and benzene. They observed that the kinetic order of R_p with respect to [M] in water was very different to that measured in benzene[5].

We have been investigating the radical polymerization behaviour of polystyrene macromonomers, having methacryloyl and vinylbenzyl end groups, in benzene by g.p.c., using an instrument equipped with a laser light scattering detector, and also by e.s.r. measurements[1-3]. It was found that the R_p and DP of the poly(macromonomer)s greatly depended on the macromonomer concentration[1,3]. We also observed that the propagating radical of the macromonomer had a long enough lifetime to enable the e.s.r. spectrum to be recorded: from this the propagation rate constant (k_p) and the termination rate constant (k_t) were evaluated[2,3].

In this paper, R_p, DP, k_p, k_t and the initiator efficiency f were evaluated as a function of the macromonomer concentration in order to investigate the effect of the macromonomer feed concentration on the radical polymerization behaviour.

EXPERIMENTAL

Materials

A polystyrene macromonomer having a methacryloyl end group (MA-PS) was prepared by the same procedure as described in a previous paper[3]. The number-average molecular weight (M_n) is 2700 and the polydispersity index is 1.07. The end functionality (F) is 0.96, which was estimated by both 500 MHz ^{1}H n.m.r. spectroscopy (using a Varian VXR500 machine) and also from the conversion

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* To whom correspondence should be addressed

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of the macromonomer in its copolymerization with methyl methacrylate (MMA) at 60°C in benzene with azobisisobutyronitrile (AIBN). MMA was distilled under reduced pressure after removal of the stabilizer. The polymerization solvent (benzene) was dried over Na wire, and distilled under nitrogen after removal of the stabilizer. AIBN was used after recrystallization from methanol.

Polymerization of the macromonomer

Polymerization of the macromonomer was carried out in benzene at 60°C, using AIBN as the initiator. The mixture of the macromonomer, benzene, and AIBN was divided equally into sixteen parts and placed in glass ampoules. Each ampoule was degassed, sealed under vacuum, and then placed in a thermostated bath (regulated at 60°C), where polymerization was carried out for various times. All of the solutions were homogeneous throughout the polymerization reactions. After polymerization was complete, the ampoules were cooled to −78°C, then the polymerization product was recovered and finally freeze-dried with benzene.

Evaluation of molecular weight and polymerization rate

The weight-average molecular weights of the poly(macromonomer)s (M_ws) and the polymerization rates (R_ps) were determined by using a g.p.c. apparatus which was equipped with a low-angle laser light scattering detector in addition to the conventional refractive index (r.i.) and u.v. detectors (l.s.-g.p.c.)[1]. The apparatus used was a high-speed liquid chromatograph (HLC802A, Tosoh Co. Ltd), equipped with an LS-8 (l.s. detector; He–Ne laser with a detection angle of 5°) and a UV-8 (u.v. detector; 254 nm wavelength, deuterium lamp) detector. This was operated with Tosoh G2000H + G4000H + G6000H columns at 25°C for toluene, or with G3000H + G5000H columns at 30°C for $CHCl_3$. The M_ws of the poly(macromonomer)s were determined from the peak area ratio of the l.s. response to the r.i. response of the polymerization products in the l.s.-g.p.c. scans. The degree of conversion was determined from the ratio of the peak area of the unreacted macromonomer to the total peak area of the polymerization product in the g.p.c. curves, measured with the u.v. detector.

E.s.r. measurements

The mixture of macromonomer, benzene and AIBN was placed in an e.s.r. sample tube (diameter 5 mm, length 180 mm) by using a syringe, where it was degassed and then sealed under vacuum. E.s.r. spectra were taken at 60°C during the polymerization process. Measurements were carried out with a JEOL RE-1X X-band spectrometer with 100 kHz modulation[2,3]. The spectra were recorded with a PC9801RX personal computer (NEC) connected to the spectrometer. The concentrations of the propagating radical ([M*]) were calculated by double integration of the signal and comparison of the signal intensity with that obtained from a standard (i.e. $5.0 \times 10^{-6} - 1.0 \times 10^{-5}$ mol l^{-1} of diphenylpicrylhydrazyl (DPPH) in benzene). The signal of the DPPH was also used as a g-value standard. The magnetic field sweep was calibrated from the splitting constant of Mn^{2+}. The e.s.r. sample tube after measurement at 60°C was cooled to −78°C, where the polymerization product was removed and then freeze-dried with benzene to evaluate M_w and R_p.

The initiator efficiency (f) was measured from the decay rate of the DPPH signal intensity in the e.s.r. spectrum at 60°C.

Viscosity of the polymerization solutions

The viscosities of the polymerization solutions (η) were measured by using an Ubbelohde viscometer at 60.0 ± 0.1°C. η was determined from the flow time ratio of the solution to the solvent (0.4 mN s m^{-2}; 4.00 mP) for benzene at 60°C[6]. The flow time of benzene was 151 s (at 60°C) using this capillary viscometer.

RESULTS AND DISCUSSION

Figure 1 shows the variation of the degree of polymerization of the polymerization product and the conversion of the macromonomer as a function of [M]. All of the polymerization reactions were carried out for 24 h with $[I] = 1.64 \times 10^{-2}$ mol l^{-1}. It is seen that the *DP* of the poly(macromonomer)s varies uniquely as [M] increases, as already reported[1,3]. The conversion of the macromonomer reaches 0.95 at [M] = 0.15–0.20 mol l^{-1}, which is very close to the end group functionality as estimated by ^{1}H n.m.r. spectroscopy. It is also seen that the *DP* of the poly(macromonomer) continues to increase beyond the [M] of the maximum conversion.

Figure 2 shows log–log plots of R_p *versus* [M], where it is seen that log R_p increases almost linearly with log [M]. The apparent kinetic order of R_p with respect to [M] is 2.2. This high order of R_p is mainly ascribed to the [M]-dependent gel effect. The variations in the R_p and *DP* values with [M] are summarized in *Table 1*.

In order to estimate the dependence of the gel effect on [M], the viscosity of the polymerization solution (η) was

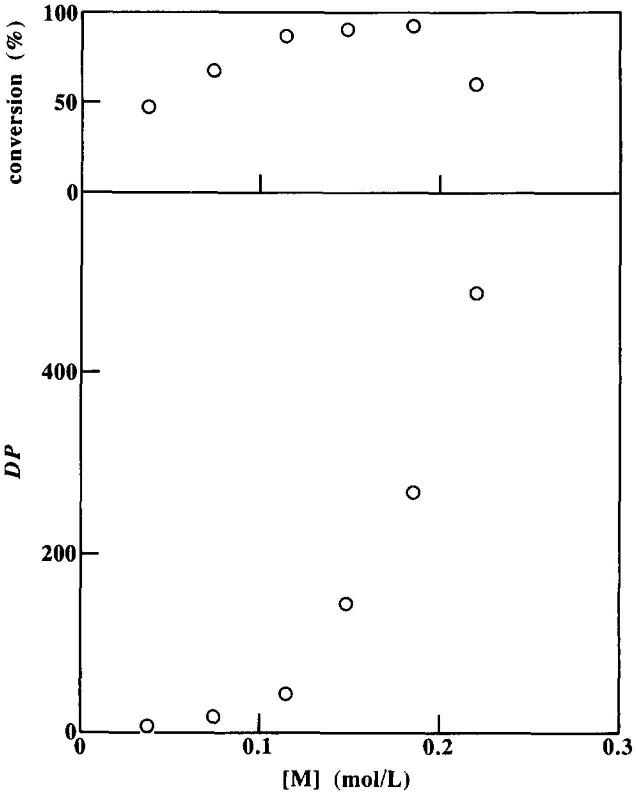

Figure 1 Conversion of macromonomer (top) and *DP* of poly(macromonomer) (bottom) *versus* [M] plots for the polymerization of MA-PS2700, carried out in benzene with AIBN at 60°C for 24 h

Table 1 Values obtained for the propagation rate constant (k_p) and the termination rate constant (k_t) for the polymerization of MA-PS2700[a]

[M][b] (mol l^{-1})	$R_p \times 10^6$ (mol l^{-1} s^{-1})	DP[c]	[M*] $\times 10^6$ (mol l^{-1})	k_p[d] (l mol^{-1} s^{-1})	k_t[e] (l mol^{-1} s^{-1})	$k_p/k_t^{1/2}$
0.220	25	490	4.2	28	1 500	0.72
0.185	17	270	2.6	35	4 700	0.47
0.148	7.4	140	1.7	29	8 500	0.31
0.114	3.8	43	1.3	25	25 000	0.16
0.0741	1.5	17	0.76	26	74 000	0.095
0.0370	0.54	6	0.49	30	190 000	0.068

[a] Polymerization was carried out at 60°C using AIBN as the initiator: $[I] = 1.64 \times 10^{-2}$ mol l^{-1}

[b] Values not corrected with the end functionality

[c] Determined by g.p.c. using a light scattering detector

[d] $k_p = R_p/([M][M^*])$

[e] $k_t = R_p/(2DP[M^*]^2)$

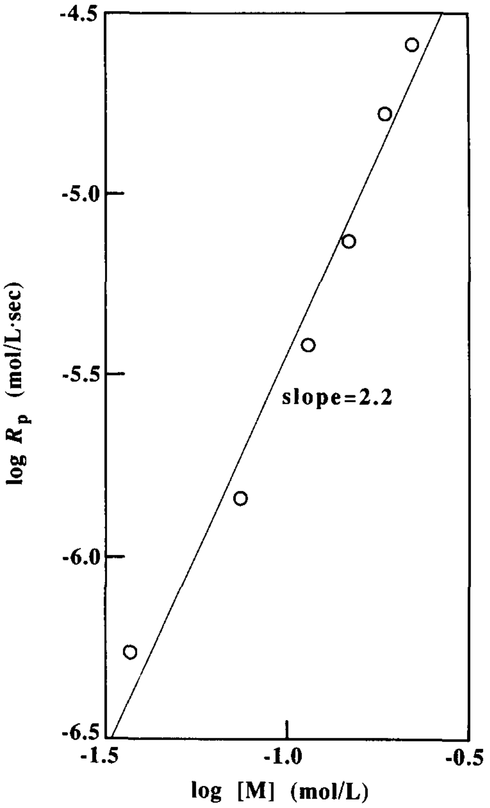

Figure 2 Log–log plots of R_p *versus* [M] for the polymerization of MA-PS2700, with $[I] = 1.64 \times 10^{-2}$ mol l^{-1}

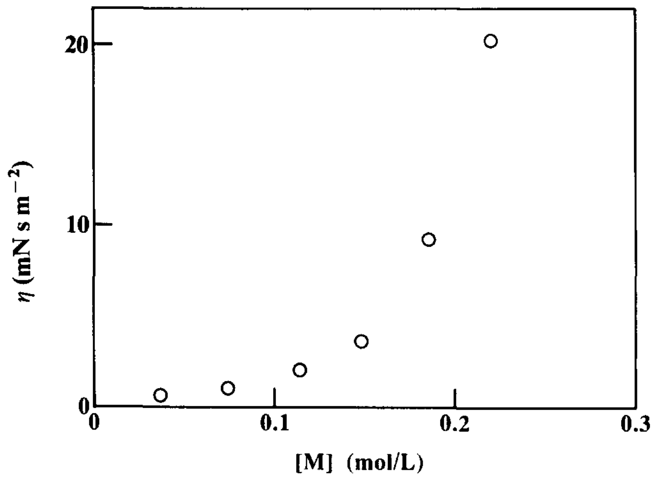

Figure 3 Dependence of the viscosity of the solution of MA-PS2700 at 60°C on [M]

measured by an Ubbelohde viscometer. The dependence of η on [M] is shown in *Figure 3*, in which η rapidly increases with an increase in [M], as seen for *DP* in *Figure 1*.

For a diffusion controlled reaction such as the bimolecular termination of radical polymerization, the observed rate constant of the bimolecular reaction (k_{obs}) between A and B is proportional to the diffusion constant (D), according to the Smoluchowski equation[7]:

$$k_{obs} = 4\pi l_{AB} D_{AB} \qquad (1)$$

where l_{AB} is the distance between molecules A and B, and D_{AB} is the sum of the diffusion constants (i.e. $D_A + D_B$). D_i (i = A or B) is expressed by the Stokes–Einstein relationship:

$$D_i = kT/6\pi\eta r_i \qquad (2)$$

where η, r_i, k and T are the solution viscosity, the molecular radius, the Boltzmann constant and the absolute temperature, respectively. Thus, the rate constant in the diffusion controlled reaction is inversely proportional to the solution viscosity. This gives R_p from the following equation[8,9]:

$$R_p = (k_d f/k_{t0})^{1/2} k_p [I]^{1/2} [M] \phi_\eta^{1/2} \qquad (3)$$

where k_d and k_p are the rate constants for the decomposition of the initiator and the propagation reactions, respectively; k_{t0} is defined by $k_{t0} = k_t \phi_\eta$, where k_t is evaluated from the e.s.r. spectrum and $\phi_\eta = \eta/\eta_0$, i.e. the ratio of η to the solvent viscosity (η_0). When η_0 is defined as 1 mN s m^{-2} (1 cP), $k_{t0}/\phi_\eta = k_{t0}/\eta^9$.

Figure 4 shows log–log plots of $R_p/\phi_\eta^{1/2}$ *versus* [M]. The apparent kinetic order of R_p with respect to [M] decreases from 2.2 to 1.3. However, the order is still larger than unity, which might be due to another reason, possibly the specific multi-branched structure of the propagating radical of the macromonomer.

Measurement of the radical concentration [M*], as a function of [M], by e.s.r. spectroscopy enables us to evaluate the dependence of the propagation rate constant, k_p, and the termination rate constant, k_t, on [M], by the use of equations (4) and (5):

$$k_p = R_p/[M][M^*] \qquad (4)$$

$$k_t = R_p/2v_p[M^*]^2 \qquad (5)$$

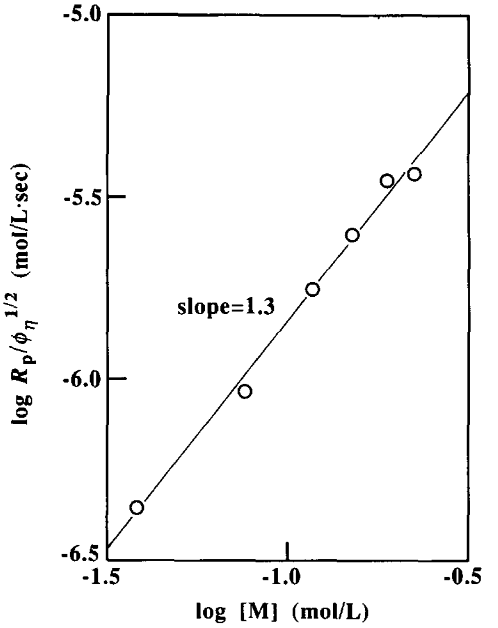

Figure 4 Log–log plots of R_p/ϕ_η *versus* [M] for the polymerization of MA-PS2700, with $[I] = 1.64 \times 10^{-2}$ mol l^{-1}

where v_p is the kinetic chain length. The values of k_p, k_t and $k_p/(k_t^{1/2})$ evaluated from equations (4) and (5) are summarized in *Table 1*, together with R_p, *DP* and [M*]. The k_t values given in *Tables 1* and *4* (see later) were calculated with $v_p = DP$, assuming that the bimolecular termination takes place by a disproportionation reaction[3]. The k_p and k_t values are plotted against [M] in *Figure 5*, where it can be seen that k_p is around 25–35 l mol^{-1} s^{-1} and is approximately constant with respect to [M]. On the other hand, k_t depends strongly on [M] and rapidly decreases from 19 000 to 1500 l mol^{-1} s^{-1} with an increase of [M] from 0.0370 to 0.2200 mol l^{-1}. Therefore, the observed increase in [M*] with [M] in *Table 1* might be a reflection of a decrease in k_t.

Table 2 summarizes the viscosity effect on k_t by comparing values of the latter with those of η, ϕ_η and the product of k_t and ϕ_η ($k_t\phi_\eta$). It is seen that this product gradually decreases with increases in the value of [M]. This might again indicate that an increase in the segment density around the radical site as [M] increases also has an influence on the polymerization reaction.

The initiator efficiency (f) is influenced by the viscosity through the 'cage' effect: f can be expressed by equation (6), i.e.

$$f = R_i/(2k_d[I]) \qquad (6)$$

where R_i is the initiation rate. The efficiency can be estimated by the decay rate of the e.s.r. signal intensity of DPPH when added to the polymerization solution, by using the k_d value taken from the literature. It can also be estimated from kinetic data by using the following equation:

$$f = (R_p/k_p[M])^2 k_t/(k_d[I]) \qquad (7)$$

Values of f obtained by using equations (6) and (7) are summarized in *Table 3*. A good agreement is seen between the two sets of values, which gradually decrease with an increase in the value of [M]. The variation of f with [M] in *Table 3* might be the result of a balance in the change of the viscosity of the polymerization solution and the ratio of monomer to initiator concentration with [M].

Russell *et al.* reported the variation of f in the bulk polymerization of MMA. When the weight fraction of polymer (w_p) was less than 0.75, f gradually decreased with an increase in w_p: when w_p exceeded 0.75, f fell drastically with w_p[10]. In this study, the maximum macromonomer concentration [M] is 2.20×10^{-1} mol l^{-1},

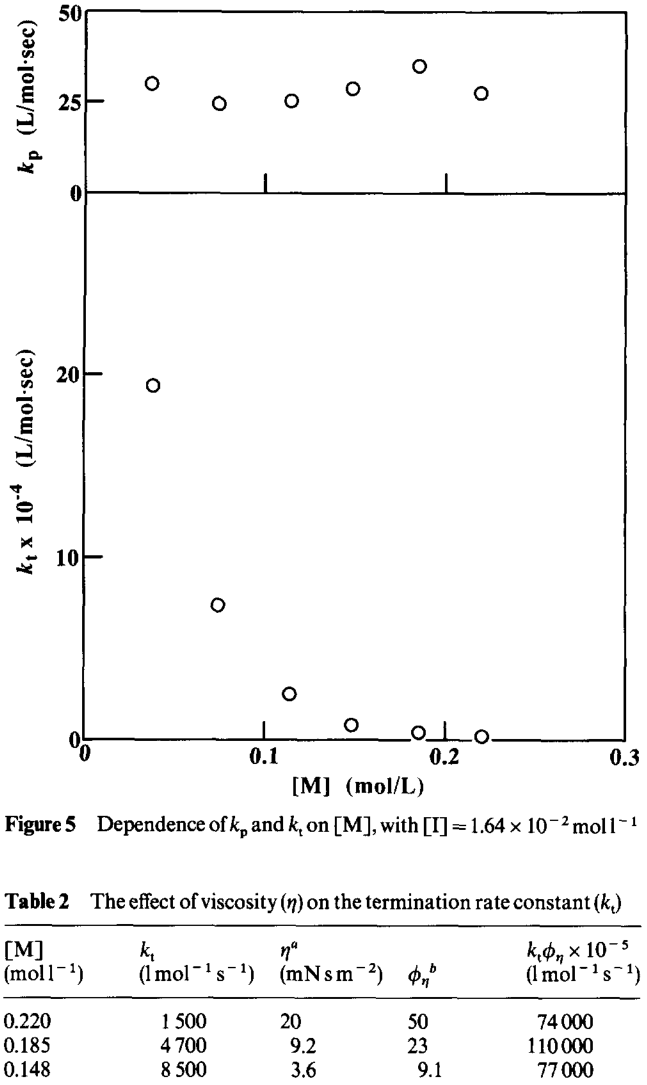

Figure 5 Dependence of k_p and k_t on [M], with $[I] = 1.64 \times 10^{-2}$ mol l^{-1}

Table 2 The effect of viscosity (η) on the termination rate constant (k_t)

[M] (mol l^{-1})	k_t (l mol^{-1} s^{-1})	η^a (mN s m^{-2})	$\phi_\eta{}^b$	$k_t\phi_\eta \times 10^{-5}$ (l mol^{-1} s^{-1})
0.220	1 500	20	50	74 000
0.185	4 700	9.2	23	110 000
0.148	8 500	3.6	9.1	77 000
0.114	25 000	2.0	4.9	120 000
0.0741	74 000	1.0	2.5	190 000
0.0370	190 000	0.61	1.5	300 000

[a] Measured by Ubbelohde viscometer
[b] $\phi_\eta = \eta/\eta_0$, where $\eta_0 = 0.4$ mN s m^{-2} (400 mP) for benzene at 60°C[6]

Table 3 Comparison of observed and calculated values of the initiator efficiency as a function of [M]

[*M*] (mol l^{-1})	$R_i \times 10^{8a}$ (mol l^{-1} s^{-1})	f Observed^b	f Calculated^c
0.220	3.6	0.11	0.16
0.185	5.4	0.16	0.19
0.148	6.6	0.20	0.16
0.114	7.5	0.23	0.27
0.0741	8.9	0.27	0.25
0.0370	11.0	0.32	0.27

[a] Calculated from the decay rate of the e.s.r. spectrum of DPPH (for details, see text)
[b] Using equation (6)
[c] Calculated using equation (7), with $k_d = 1.01 \times 10^{-5}$ s^{-1} for AIBN in benzene at 60°C

Table 4 Comparison between the radical polymerization behaviour of MA-PS2700 and MMA

Monomer	[M] (mol l^{-1})	k_p (l mol^{-1} s^{-1})	$k_t \times 10^{-3}$ (l mol^{-1} s^{-1})	f_{obs}	$R_p \times 10^6$ (mol l^{-1} s^{-1})		DP	
					Calculated[c]	Observed	Calculated[d]	Observed
MMA	0.220	515[a]	26 000[a]	0.5[b]	6.4	–	39	–
	0.148	515[a]	26 000[a]	0.5[b]	3.3	–	20	–
	0.0370	515[a]	26 000[a]	0.5[b]	1.1	–	7	–
MA-PS2700	0.220	28	1.5	0.11	21	25	590	490
	0.114	25	25	0.23	3.5	3.8	47	43
	0.0370	30	190	0.32	0.58	0.54	5	6

[a] Data from refs. 11 and 12
[b] Data from ref. 13
[c] Using equation (8)
[d] Calculated using equation (9) with $[I] = 1.64 \times 10^{-2}$ mol l^{-1}, and $k_d = 1.01 \times 10^{-5}$ s^{-1}, for AIBN in benzene at 60°C

which corresponds to a weight fraction of macromonomer of 0.62. Thus, w_p is less than the critical value for this large reduction in f.

It is interesting and important to compare the k_p, l_t, R_p and DP values of MA-PS2700 with those of the corresponding MMA monomer. *Table 4* shows a comparison of the values of k_p and k_t of the macromonomer with those of MMA, with the latter obtained from the literature[11,12]. The k_p values of the macromonomer are smaller than those of MMA by about one order of magnitude. Since the activation controlled step can be considered to be predominant in the propagation reaction, the small k_p values for the macromonomer might be ascribed to the steric hindrance associated with the local specific multi-branched structure at the vicinity of the propagating active site. This might decrease the steric factor in the frequency term in the Arrhenius-type formulation. In addition, a diffusion control effect on k_p can be involved, because the propagation reaction of the macromonomer is a repetition of the reaction between a multi-branched polymer radical and the polymerizable functional group at a polymer chain end. However, further study is necessary to clarify this point.

The k_t values of the macromonomer shown in *Table 4* are smaller than those of MMA by two to four orders of magnitude, as shown previously[2,3]. This is the result of the diffusion control effect associated with the [M]-dependent viscosity of the polymerization media. The specific multi-branched structure is also responsible for the diffusion control effect, as a result of the effect of the excluded volume, which prevents the approach of the macromonomer molecules to the propagating active site against the large segment density gradient. Recently, Hatada *et al.* estimated the k_t of syndiotactic poly(methyl methacrylate) macromonomers which had a vinylbenzyl end group from the decay rate of the e.s.r. spectra of the propagating radical in benzene at 30°C[14]. These estimated k_t values were much smaller than those of the corresponding styrene monomer.

R_p and DP can be expressed, in terms of the kinetic data, as follows:

$$R_p = (fk_d[I]/k_t)^{1/2}k_p[M] \qquad (8)$$

$$DP = k_p[M]/2(fk_dk_t[I])^{1/2} \qquad (9)$$

Table 4 shows a comparison of R_p and DP of the macromonomer with those calculated for MMA with $f = 0.5$[13]. There are several different values of k_p depending on the experimental method used[11]. The initiator efficiency of MMA also depends on both the MMA concentration and the temperature. Thus, the calculated values of R_p and DP for MMA shown in *Table 4* are just rough estimates. However, certain features can be observed in this table. First, the R_p and DP values of the macromonomer are smaller than those of MMA when $[M] = 3.70 \times 10^{-2}$ mol l^{-1}. This is because the diffusion control effect is not strong enough to reduce the termination rate at this low concentration. Secondly, and in contrast, the R_p and DP values of the macromonomer are larger than those of MMA when $[M] = 2.20 \times 10^{-1}$ and 1.14×10^{-1} mol l^{-1}. This is because the extent of the decrease in k_t is much larger than that in k_p. It has been considered that the polymerizability of the macromonomers is very low in comparison to the corresponding low-molecular-weight monomers because of the high segment density associated with the specific multi-branched structure of the propagating radical. However, *Table 4* indicates that the polymerizability of the macromonomer is not necessarily low, but R_p and DP for the macromonomer can be larger than the corresponding small monomer (MMA) under the same polymerization conditions.

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