Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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T. C. Chang[a]; H. B. Chen[b]; S. Y. Ho[b]; Y. S. Chiu[c]
[a] Department of Applied Chemistry, Chung Cheng Institute of Technology Taoyuan, Taiwan, Republic of China [b] Department of Chemistry, National Tsing Hua University Hsinchu, Taiwan, Republic of China [c] Chemical Systems Research Division Chung Shan Institute of Science and Technology Taoyuan, Taiwan, Republic of China

To cite this Article Chang, T. C. , Chen, H. B. , Ho, S. Y. and Chiu, Y. S.(1996) 'Photopolymerization of Methyl Methacrylate with Azo-Containing Polydimethylsiloxane as Photoinitiator', Journal of Macromolecular Science, Part A, 33: 9, 1263 — 1272

To link to this Article: DOI: 10.1080/10601329608010920

URL: http://dx.doi.org/10.1080/10601329608010920

J.M.S.—PURE APPL. CHEM., A33(9), pp. 1263–1272 (1996)

PHOTOPOLYMERIZATION OF METHYL METHACRYLATE WITH AZO-CONTAINING POLYDIMETHYLSILOXANE AS PHOTOINITIATOR

T. C. CHANG*

Department of Applied Chemistry
Chung Cheng Institute of Technology
Taoyuan, Taiwan 33509, Republic of China

H. B. CHEN and S. Y. HO

Department of Chemistry
National Tsing Hua University
Hsinchu, Taiwan 30043, Republic of China

Y. S. CHIU

Chemical Systems Research Division
Chung Shan Institute of Science and Technology
Taoyuan, Taiwan 32526, Republic of China

ABSTRACT

Azo-containing polydimethylsiloxane (PDMS-ACP), prepared by the polycondensation reaction of hydroxybutyl-terminated polydimethylsiloxane (PDMS) with 4,4′-azobis-4-cyanopentanoyl chloride (ACPC), was used as the photoinitiator for the polymerization of methyl methacrylate (MMA) in bulk. Polymerization of MMA with azobisisobutyronitrile (AIBN) as the photoinitiator was conducted for comparison. The propagation and termination rate constants (k_p and k_t), and the fraction β of primary radicals entering into termination were evaluated. The termination rate constant 4.5×10^7 mol·L^{-1}·s^{-1} in the MMA/PDMS-ACP system was smaller than 9.1×10^7 mol·L^{-1}·s^{-1} in the MMA/

AIBN system. The photoinitiator efficiency Φ of PDMS-ACP was found to be smaller than that of AIBN. The ratio $\sigma k_t/k_i$ of the rate constants for chain termination and chain initiation by primary radicals were determined to be 7.9×10^7 and 5.8×10^7 for PDMS-ACP and AIBN, respectively.

INTRODUCTION

Block copolymers composed of a condensation polymer segment with an additional polymer segment are highly attractive materials. The macro initiator may offer advantages over the monomeric initiator, such as zero migration and greater reactivity [1, 2]. Thus, macro initiators have become unique key materials for producing various block copolymers via radical polymerization by providing high-performance or high-functional materials with a variety of molecular-pair designs never attained before [3, 4].

The macroazoinitiator (MAI), a polymer containing azo groups as parts of its backbone chain, can be prepared by condensing small molecular weight azo compounds with a functionalized polymer. The earliest report on the synthesis of a block copolymer via MAI was published in 1967 [5]. Since then, MAI has provided a useful means of preparing block copolymers via radical polymerization [6–12].

Polydimethylsiloxane (PDMS) with repeating $-OSiMe_2-$ units is endowed with such unusual properties as high dynamic flexibility, low entropy of dilution, high oxidative stability, excellent thermal stability, and low glass transition temperature [13]. Therefore, there has been considerable effort to incorporate the functionalized polymer PDMS into vinyl block polymers [10, 14–19]. These block copolymers are of interest in such fields of adhesion, coating, and printing.

Recently, we reported the activation energy, activation enthalpy, activation entropy, and activation free energy of the thermodecomposition of PDMS-ACP in toluene. Moreover, the polydimethyl-siloxane-poly(methyl methacrylate) block copolymers (PDMS-*block*-PMMA) were prepared with PDMS-ACP MAI at 80°C, and their microstructure revealed phase modification [20]. However, information on the absolute kinetic parameters of polymerization for MMA initiated with MAI has been limited [7]. The purpose of this work is to evaluate k_p and k_t of MMA with PDMS-ACP photoinitiator in bulk. The initiator efficiency Φ, the fraction β of primary radicals entering into termination, and the ratio $\sigma k_t/k_i$ of the rate constants for chain termination and chain initiation by primary radicals were also investigated.

EXPERIMENTAL

Materials

4,4′-Azobis-4-cyanopentanoic acid (Aldrich) and thinyl chloride (Aldrich), triphenylformazan (Tokyo Kasei Co.) were used without purification. Octamethylcyclotetrasiloxane (D_4; polymerization grade, Hüls-Petrach) was vacuum distilled over CaH_2 prior to use. 1,3-Bis(4-hydroxybutyl)tetramethyldisiloxane (M_2; polymerization grade, Hüls-Petrach) was used as received. The monomer methyl methacrylate (Janssen) was purified by distillation before use. Azoisobutyronitrile (BDH) was recrystallized from ethanol just before use. The inhibitor 1,3,5-triphenylverdazyl (TPV) was prepared from triphenylformazan (Tokyo Kasei Co.) [21].

PDMS

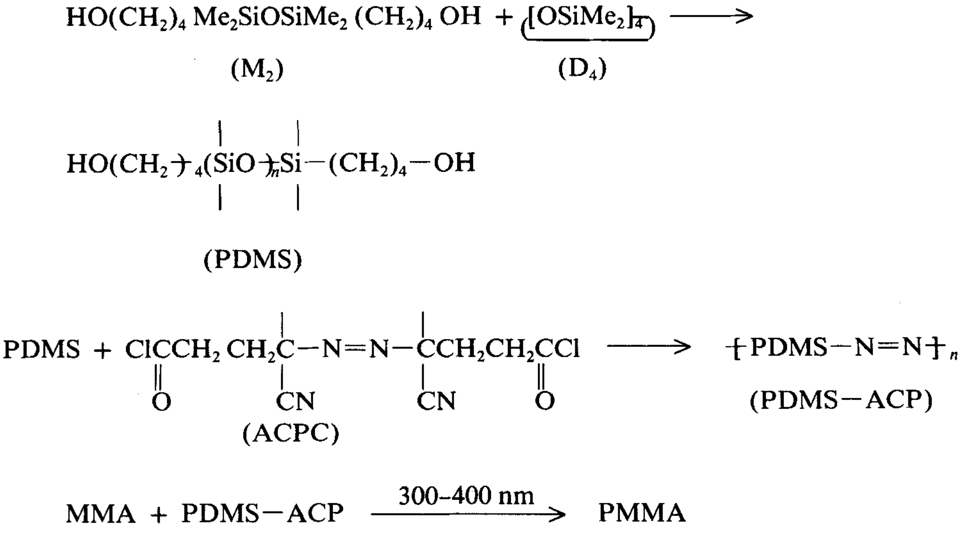
Colorless PDMS, where the molar ratio (D_4/M_2) was 9.95, was prepared by the Yilgor method [22]. IR (KBr): 1060, 1111 (ν SiOSi), 1261, 800, 702 (ν $SiCH_3$) cm^{-1}. ^1H NMR ($CDCl_3$): 3.58 (t, 2H, $-CH_2O-$), 1.58 (m, 2H, $-CH_2-$), 1.37 (m, H, $-CH_2-$), 0.48 (t, 2H, $-CH_2-Si$), 0.10 (s, *n*H, $-SiCH_3$) ppm. The number-average molecular weight ($\overline{M}_n = 3000$) was calculated from the absorption of the butyl group for PDMS relative to 2.0 ppm (internal standard; CH_3CN) in ^1H-NMR spectrum. In addition, the molecular weight dispersity ($D = 2.0$) was obtained from GPC.

ACPC

ACPC was prepared by the procedure of Ueda [23]. UV (toluene): 234 (C=O, n,π*), 350 (N=N, π, π*) nm. IR (KBr): 1789 (ν C=O) cm^{-1}. ^1H NMR ($CDCl_3$): 2.90-3.22 (m, 2H, $-CH_2-$), 2.38-2.64 (m, 2H, $-CH_2-$), 1.73 (s, 3H, $-CH_3$), 1.68 (s, 3H, $-CH_3$) ppm.

PDMS-MAI

The hydroxyl-terminated PDMS (10 mmol) was dissolved in a solution of triethylamine (20 mmol) and $CHCl_3$ (100 mL) contained in a predried flask under nitrogen. A solution of ACPC (10 mmol) in $CHCl_3$ (50 mL) was added slowly (30 minutes) with vigorous stirring at 5°C under dry nitrogen. After addition, the solution was held for 24 hours at 30°C. $CHCl_3$ (150 mL) was then added to the reaction mixture washed with water (3 × 150 mL), and dried with Na_2SO_4 (overnight). After the chloroform was evaporated, PDMS-ACP was obtained, (Scheme 1). The azo group content in PDMS-ACP was 2.9×10^{-4} $mol \cdot g^{-1}$ as determined from the intensity in the UV spectrum at 348 nm based on AIBN ($\epsilon_{348} = 14.7$ $L \cdot mol^{-1} \cdot cm^{-1}$) [24]. GPC (THF): $\overline{M}_n = 7100$, $D = 1.8$.



$$\underset{(M_2)}{HO(CH_2)_4Me_2SiOSiMe_2(CH_2)_4OH} + \underset{(D_4)}{[OSiMe_2]_4} \longrightarrow$$

$$\underset{(PDMS)}{HO(CH_2)_4(SiO)_nSi-(CH_2)_4-OH}$$

$$PDMS + \underset{(ACPC)}{ClC(=O)CH_2CH_2C(CN)-N=N-C(CN)CH_2CH_2C(=O)Cl} \longrightarrow \underset{(PDMS-ACP)}{[PDMS-N=N]_n}$$

$$MMA + PDMS-ACP \xrightarrow{300\text{-}400\ nm} PMMA$$

SCHEME 1.

Photopolymerization

Methyl methacrylate in bulk and the initiator (PDMS-MAI or AIBN) were placed into a dilatometer (25 mL) which was degassed by the typical freeze-thaw technique and sealed under vacuum (10^{-4} mmHg). The Pyrex dilatometer was kept at 30 ± 0.05°C in a water bath at constant temperature. The light source was a high-pressure mercury lamp (Osram 200 W) equipped with a filter to pass 300–400 nm. The intensity of the light at the sample was 30 $\mathrm{mW \cdot cm^{-2}}$. The precipitated polymer was filtered and washed with methanol and purified by three successive reprecipitations from chloroform solutions by adding methanol.

The rate of polymerization (R_p) was determined by measuring the variation of the condition of the solution in the capillary tube of the dilatometer as a function of the duration of the reaction. The rate of initiation (R_i) was determined according to the inhibition method, and the average lifetime of radicals (τ) was determined with a rotating sector as described previously [25, 26].

Characterization

^{1}H (Varian EM-390), IR (Bomen DA 3.002) and UV (Shimadzu UV-2100) spectrometers were used as required. Number-average molecular weight ($\overline{M}_n$) and molecular weight dispersity (D) of the polymers were measured by GPC (Waters), with columns (Shodex KF 801 + 802 + 803 + 804), and with toluene (or tetrahydrofuran) as the eluent (1 $\mathrm{mL \cdot min^{-1}}$) for PDMS (or PMMA).

RESULTS AND DISCUSSION

The synthesis of PDMS-ACP and its thermal polymerization of MMA were reported previously [20]. Our recent studies reveal that the photolysis of PDMS-ACP may initiate the polymerization of MMA. The rate of polymerization R_p of MMA with the initiator PDMS-ACP is higher than that with AIBN (Table 1). Moreover, the number-average molecular weights of polymers prepared with the initiator PDMS-ACP are found to be higher than those of polymers obtained from AIBN (Table 1).

Effect of Initiator Concentrations

The value of R_p increases in bulk polymerization with an increase in the concentration of initiator. Plots of log R_p vs log[I] give straight lines with slopes of 0.34 for PDMS-ACP and 0.44 for AIBN, as shown in Fig. 1. [I] is the mean concentration of azo groups, which is also equal to the mean concentration of the monofunctional group initiator (AIBN) in the system. The reaction order of 0.34 with respect to initiator PDMS-ACP is much less than 0.5, which may be due to a decrease of initiator efficiency Φ [27] with increasing initiator concentration (Table 1). Alternatively, the termination process may alter from the normal bimolecular termination between two chain radicals (P•) to termination by reaction of a chain radical with a primary radical (R•) [28], particularly in the MMA/PDMS-ACP system.

TABLE 1. The Rates of Photopolymerization (R_p), Initiator Efficiency (Φ), the Fraction of Primary Radicals Terminating the Chain (β), the Number-Average Molar Mass ($\overline{M}_n$) of the Polymers, and the Molecular Weight Dispersity (D) Obtained for the Photopolymerization of MMA in Bulk with PDMS-ACP and AIBN

	$[\mathrm{I}]^a$, 10^{-2} mol·L^{-1}	R_p, 10^{-5} L·mol^{-1}·s^{-1}	Φ	β	$\overline{M}_n$, 10^3 g	D
PDMS-ACP	0.2	13.4	0.53	0.19	252	1.4
	0.5	17.6	0.37	0.22	181	1.6
	1.0	22.6	0.30	0.25	147	1.6
	1.5	25.3	0.25	0.25	113	1.8
AIBN	0.2	6.8	0.86	0.10	174	1.6
	0.5	10.3	0.74	0.14	132	1.6
	1.0	13.4	0.62	0.17	106	1.6
	1.5	15.6	0.56	0.19	98	1.8

[a] Concentration of azo groups.

$$\mathrm{P}\bullet + \mathrm{P}\bullet \xrightarrow{k_t} \text{polymer products} \tag{1}$$

$$\mathrm{P}\bullet + \mathrm{R}\bullet \xrightarrow{\sigma k_t} \text{polymer products} \tag{2}$$

where k_t and σk_t are the rate constants for two chain radicals termination and with a primary radical termination, respectively. Here σ is a constant.

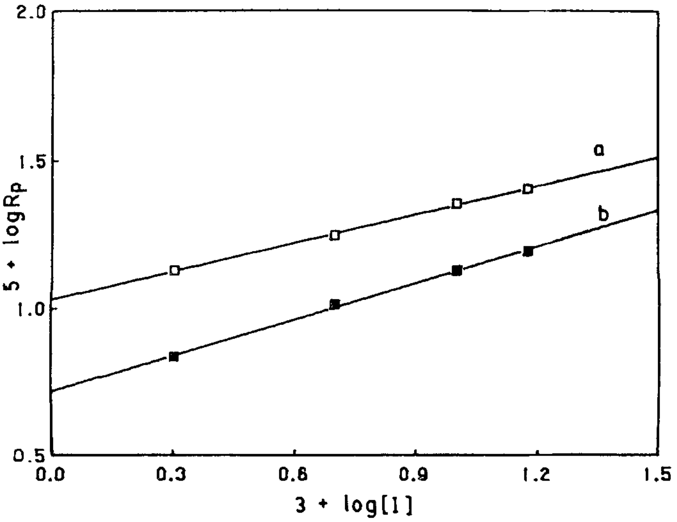


FIG. 1. Effect of concentrations of initiator on the rate of photopolymerization (R_p) of MMA in bulk: (a) PDMS-ACP and (b) AIBN.

Calculation of k_p and k_t

1,3,5-Triphenylverdazyl (TPV) was used as the inhibitor to determine the rate of initiation (R_i). The inhibiting effect of TPV on photopolymerization in the MMA/PDMS-ACP system is shown in Fig. 2. The correlation between the concentration of inhibitor [TPV] and the duration of inhibition in the MMA/PDMS-ACP system is shown in Fig. 3. The initiation rate R_i was calculated from the slope of Fig. 3 according to Eq. (3). The rates of initiation of polymerization of MMA are listed in Table 2. The data indicate that the rate of initiation of PDMS-ACP (13.2×10^{-8} mol·L^{-1}·s^{-1}) is greater than that of AIBN (9.5×10^{-8} mol·L^{-1}·s^{-1}) in the MMA system. The result may be due to a high local concentration of the initiating radicals in the PDMS-ACP initiator [29]. The value of k_p^2/k_t is derived from Eq. (4).

$$R_i = \frac{[\mathrm{TPV}]_0}{\Delta t} = \frac{\text{Initial concentration of inhibitor}}{\text{Inhibition period}} \tag{3}$$

$$\frac{k_p^2}{k_t} = \frac{R_p^2}{R_i[\mathrm{M}]^2} \tag{4}$$

The average lifetime τ of the chain radicals, determined by the rotating sector method, are listed in Table 2. The value of k_p/k_t is derived from Eq. (5).

$$\frac{k_p}{k_t} = \frac{R_p\tau}{[\mathrm{M}]} \tag{5}$$

Thus, the values of the rate constant of polymerization k_p and of termination k_t are calculated from Eqs. (4) and (5). The rates of constants k_p and k_t are 495 and 4.5×10^7 L·mol^{-1}·s^{-1} in the MMA/PDMS-ACP system and 446 and 9.1×10^7

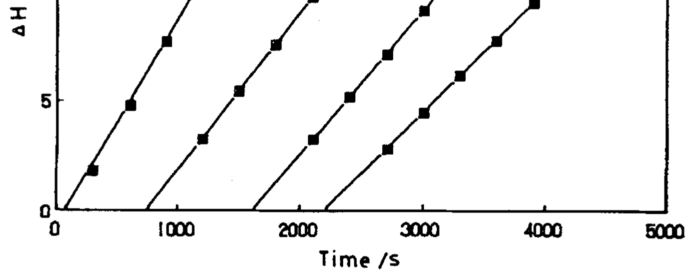


FIG. 2. The TPV inhibition effect on the photopolymerization of MMA in bulk initiated by PDMS-ACP (concentration of azo group = 0.01 mol·L^{-1}); [TPV] (in mmol·L^{-1}): (a) 0, (b) 9.7, (c) 15.7, and (d) 46.8.

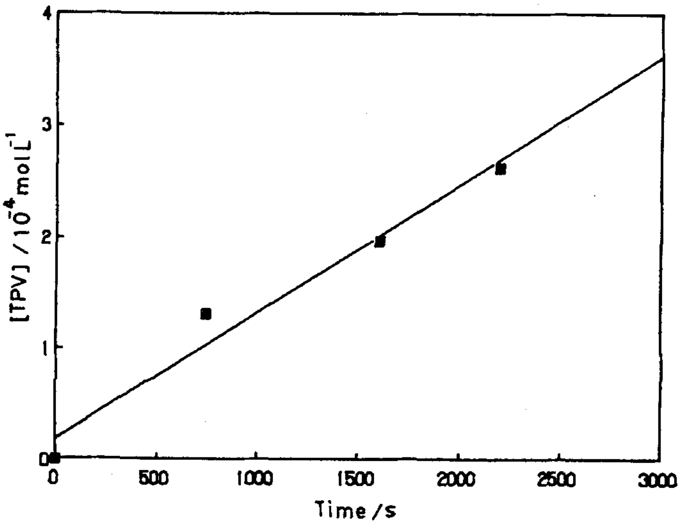


FIG. 3. Plot of [TPV] vs induction time in the polymerization of MMA in bulk with PDMS-ACP (concentration azo group = 0.01 mol·L^{-1}).

L·mol^{-1}·s^{-1} in the MMA/AIBN system, respectively. These values (k_p and k_t) agree with the literature values [30–32]. These results indicate that the termination reaction is a fast reaction between two radicals and is easily diffusion-controlled; thus, it is sensitive to viscosity. On the other hand, the number-average molecular weight ($\bar{M}_n$) of polymers (Table 1) prepared using PDMS-ACP are found to be higher than those of polymers obtained from AIBN. This observation suggests that the higher viscosity could be the cause of a lower k_t in the PDMS-ACP-initiated system.

TABLE 2. Kinetic Parameters of Photopolymerization[a] of MMA

	Initiator	
Parameters	PDMS-ACP	AIBN
R_p, 10^{-5} mol·L^{-1}·s^{-1}	17.2	13.4
R_i, 10^{-8} mol·L^{-1}·s^{-1}	13.2	9.5
τ, seconds	0.4	0.3
k_p, L·mol^{-1}·s^{-1}	495.2	445.8
k_t, 10^7 L·mol^{-1}·s^{-1}	4.5	9.1
λ, 10^3 $mol^{0.5}$·$L^{-0.5}$	2.2	5.3
μ, 10^5 mol·s·L^{-1}	1.6	1.3
$\sigma k_t k_i^{-1}$, 10^7	7.9	5.8

[a]Polymerization in bulk at 30°C; concentration of azo group = 0.01 mol·L^{-1}.

Calculation of Φ and β

The relationship between R_p, [M], and [I] is given by [29, 33]

$$\frac{[M]}{R_p} = \frac{\lambda}{[I]^{0.5}} + \frac{\mu}{[M]} \tag{6}$$

where $\lambda = (k_t/k_d)^{0.5}/k_p$ and $\mu = \sigma k_t/k_i k_p$. A plot of $[M]/R_p$ vs $1/[I]^{0.5}$ at constant monomer concentration gives straight lines (Fig. 4) for PDMS-ACP and AIBN, as predicted by Eq. (6). Accordingly, it is considered that initiators also act as terminators in the photopolymerization of MMA. The values of λ and μ are obtained from the slopes and the intercepts of the straight lines, respectively, and are listed in Table 2. It is found that the value of λ for PDMS-ACP is smaller than that for AIBN. However, the values of μ for PDMS-ACP and AIBN are nearly the same. The results may be due to the small k_t and higher fraction of primary radical termination of PDMS-ACP.

The fraction β of primary radicals entering into termination was calculated by [29, 33]

$$\beta = \frac{\sigma R_t}{R_d} = \frac{\Phi^{0.5}}{1 + (\lambda[M]/\mu[I]^{0.5})} \tag{7}$$

where σR_t and R_d are the rate of termination by primary radicals and the rate of initiator decomposition, respectively. The value of initiator efficiency Φ can be obtained from the known values of λ, R_p, $[I]^{0.5}$, and [M] according to the following equation [29, 33]:

$$\Phi^{0.5} = \lambda R_p/[I]^{0.5}[M] \tag{8}$$

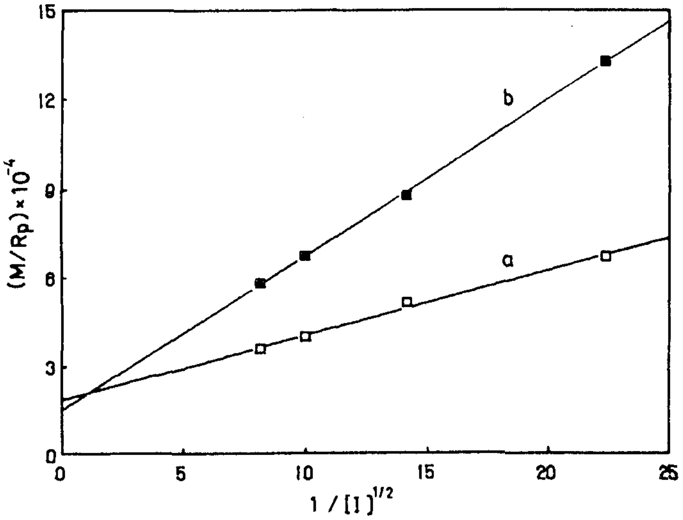


FIG. 4. Plot of Eq. (8) showing the dependence of the rate of polymerization on initiator concentration: (a) PDMS-ACP and (b) AIBN.

The values of Φ and β are listed in Table 1 for the polymerization of MMA. The data indicate that the values of Φ in both polymerizations decrease with an increase in the concentration of initiator, whereas the values of β increase. Moreover, the values of Φ for the polymerization of MMA with PDMS-ACP are smaller than with AIBN, whereas the values of β in the MMA/PDMS-ACP system are larger than that in the MMA/AIBN system. Furthermore, the ratio of the rate constants of termination and initiation by primary radicals $\sigma k_t/k_i$ can be obtained from the known values of μ and k_p. The ratio $\sigma k_t/k_i$ is 7.9×10^7 and 5.8×10^7 for PDMS-ACP and AIBN, respectively. The results reveal that the rate of primary radical termination in polymeric azo initiator is higher than that in AIBN. As expected, the increased size of the primary radicals reduces their diffusion, thus increasing the chance of recombination [34].

CONCLUSION

The photopolymerization kinetics of MMA were carried out with PDMS-ACP as an initiator in bulk. Because PDMS-ACP initiator itself is a polymer, the kinetic data for the polymerization of MMA with polymeric initiator (PDMS-ACP) are different from that with structural model (AIBN). As compared with AIBN, the initiator PDMS-ACP gave higher R_p, smaller k_t, smaller initiator efficiency Φ, and higher fraction β of primary radicals termination. The lower k_t could be the reason for the greater viscosity in the polymerization of MMA with PDMS-ACP as an initiator. On the other hand, the larger deviation of PDMS-ACP concentration on R_p than of AIBN (on R_p) from the simple kinetic equation may be due to high primary radical termination. The increased size of the primary radicals reduces their diffusion, thus increasing the chance of recombination.

ACKNOWLEDGMENT

We thank the National Science Council of the Republic of China for financial support (NSC 85-2113-M-014-004).

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Received July 18, 1995
Revision received December 30, 1995