

Photopolymerization of Styrene with Azo-Containing Polydimethylsiloxane as Photoinitiator

Te-Chuan CHANG,[†] Hon-Bin CHEN,* and Kuo-Hui WU

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

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

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ABSTRACT: Azo-containing polydimethylsiloxane (PDMS-ACP), prepared by polycondensation reaction of bis(hydroxybutyl) polydimethylsiloxane (PDMS) with 4,4'-azobis-4-cyanopentanoyl chloride (ACPC), was used as the photoinitiator for the polymerization of styrene (St) in bulk. Polymerization of styrene with azobisisobutyronitrile (AIBN) as photoinitiator was conducted for comparison. The propagation and termination rate constants (k_p and k_t), and the fractions β of primary radicals entering into termination were calculated. The values of k_p and k_t in St/PDMS-ACP system were in agreement with that in St/AIBN system. However, 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.

KEY WORDS Macroinitiator / Rate Constant / Photopolymerization / Styrene /

Block copolymers composed of a condensation polymer segments (e.g., polyether, polyester, polyamide, polyurethane, and polysiloxane) with an additional polymer segments (e.g., selected from various types of vinyl polymers) are highly attractive polymers. This type of block copolymers has potential to exhibit a wide variety of new physical and chemical characteristics depending on the combination of the natures of the polymer segments chosen.^{1,2}

Polydimethylsiloxane (PDMS) repeating $-\text{OSi}(\text{CH}_3)_2-$ unit is indeed endowed with unusual properties such as high dynamic flexibility, low entropy of dilution, higher oxidative stability, excellent thermal stability, high lubricity, and low glass transition temperature.³ On the other hand, polystyrene (PSt) has been widely used for many years as a general-purpose thermoplastic in the form of molding, electrical insulation, packaging, etc. Therefore, there has been considerable effort to incorporate PDMS into styrene block polymers by anionic polymerization method,⁴ condensation polymerization,⁵ and free-radical routes.⁶

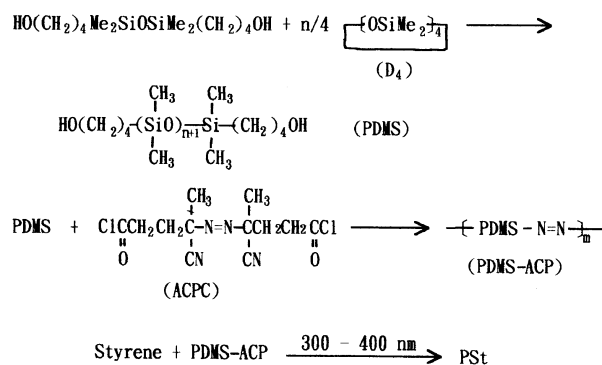
Heitz *et al.* prepared the azo-containing macroinitiators and the copolymers by use of this macroinitiator.⁷ Thereafter, azo-containing macroinitiators for radical polymerization have been studied.⁸ We reported recently the activation energy of thermal decomposition of the azo-containing polydimethylsiloxane (PDMS-ACP) macroinitiator.⁹ Moreover, the apparent activation energy in thermal degradation of the PDMS-*b*-PMMA block copolymers was studied by thermogravimetric analysis.¹⁰ Furthermore, the kinetic parameters of photopolymerization for methyl methacrylate (MMA) with PDMS-ACP as initiator were also evaluated.¹¹ However, the kinetic parameters of photopolymerization for styrene with PDMS-ACP as initiator are not evaluated. The purpose of this work is to evaluate the propagation rate constant k_p and termination rate constant k_t of styrene with PDMS-ACP as photoinitiator

in bulk. The initiator efficiency θ , 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 are also investigated.

EXPERIMENTAL

Materials

4,4'-Azobis-4-cyanopentanoic acid (ACPA; Aldrich), thionyl chloride (Aldrich), triphenylformazan (Tokyo Kasei Co.), and the solvents (reagent grade, Merck) were used without purification. Octamethylcyclotetrasiloxane (D₄; polymerization grade, Hüls-Petrarch) was vacuum distilled over CaH₂ prior to its use. 1,3-Bis(4-hydroxybutyl)tetramethyldisiloxane (polymerization grade, Hüls-Petrarch) was used as received. The monomer styrene (Janssen) was purified by distillation before use. Azobisisobutyronitrile (AIBN; BDH) was recrystallized from ethanol before use. Macroinitiator of the PDMS-ACP was prepared as described previously (Scheme 1).¹¹



Scheme 1.

Photopolymerization

The reaction mixture of styrene and the initiator (PDMS-ACP or AIBN) was placed into a dilatometer (25 mL) which was degassed by the typical freeze-thaw

[†] To whom correspondence should be addressed.

technique and sealed under vacuum (10^{-4} mmHg). The Pyrex dilatometer was kept at $30 \pm 0.05^\circ\text{C}$ in a water bath. The light source was a high-pressure mercury lamp (Osram 200 W) equipped with a filter to pass 300–400 nm.

Rate of polymerization R_p was determined by measuring the variation of the solution meniscus in the capillary tube of the dilatometer as a function of duration of reaction. The rate of initiation R_i was determined according to the inhibition method, and the scavenger 1,3,5-triphenylverdazyl (TPV) was prepared from triphenylformazan (Tokyo Kasei Co.).¹² The average lifetime of radicals (τ) was determined with a rotting sector as described before.^{11,13}

Characterization

The number-average molar molecular weight ($\bar{M}_n = 3000$) of the PDMS was calculated from the absorption of the butyl group for PDMS relative to 2.0 ppm (internal standard; CH_3CN) in $^1\text{H NMR}$ spectrum; the molecular weight dispersity of the PDMS ($D = 2.0$) was calculated based on polystyrene standards from gel permeation chromatography (GPC; Waters).

The azo group content in PDMS-ACP was $2.9 \times 10^{-4} \text{ mol g}^{-1}$ as determined from the intensity in the UV spectrum at 348 nm based on AIBN ($\epsilon_{348} = 14.7 \text{ K mol}^{-1} \text{ cm}^{-1}$).⁹ GPC (THF): (\bar{M}_n) = 7300, $D = 1.8$.

The precipitated polymer was filtered and washed with methanol, and purified by three successive precipitation from chloroform solutions by adding methanol. Number-average molecular weight (\bar{M}_n) and molecular weight dispersity (D) of polymers were measured by GPC, with columns (Shodex KF 801 + 802 + 803 + 804), and tetrahydrofuran as eluent (1 mL min^{-1}).

RESULTS AND DISCUSSION

The photolysis of PDMS-ACP may initiate the polymerization of styrene. The rate of polymerization R_p of styrene with PDMS-ACP as initiator is in agreement with that with AIBN as initiator (Table I). Moreover, the number-average molecular weights of polymers prepared with the PDMS-ACP as initiator is found to be similar with those obtained from AIBN as initiator

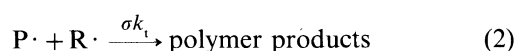
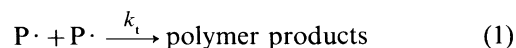
Table I. The rates of photopolymerization (R_p), initiator efficiency (Φ), the fraction of primary radical terminating the chain (β), the number-average molar mass (\bar{M}_n) of the polymers, and the molecular weight distribution (D) obtained for the photopolymerization of styrene in bulk with PDMS-ACP and AIBN as initiator

Initiator	$[\text{I}]^a (\times 10^2)$ mol L^{-1}	$R_p (\times 10^5)$ $\text{L mol}^{-1} \text{ s}^{-1}$	Φ	β	$\bar{M}_n (D)$ $(\times 10^3 \text{ g})$
PDMS-ACP	0.2	2.6	0.61	0.18	106.8 (1.7)
	0.5	3.4	0.43	0.21	76.8 (1.8)
	1.0	4.4	0.37	0.24	42.1 (1.7)
	1.5	4.9	0.32	0.25	34.2 (1.9)
AIBN	0.2	2.0	0.85	0.06	100.3 (1.8)
	0.5	3.3	0.91	0.09	56.9 (1.8)
	1.0	4.2	0.73	0.11	37.1 (2.0)
	1.5	4.9	0.67	0.13	30.1 (2.1)

^a Concentration of azo groups.

(Table I).

The value of R_p increases in bulk polymerization with an increase in the concentration of initiators. Plots of $\log R_p$ vs. $\log [\text{I}]$ give straight lines with slopes of 0.27 for St/PDMS-ACP system and 0.44 for St/AIBN system, respectively. $[\text{I}]$ is the mean concentration of azo groups that is also equal to the mean concentration of the monofunctional group initiator (AIBN) in the system. The reaction order 0.27 with respect to initiator PDMS-ACP was found to be much less than 0.5. This result may be due to decrease in initiator efficiency Φ . Alternatively, the termination process may alter from the normal bimolecular termination between two chain radicals ($\text{P}\cdot$) to termination by reaction of a chain radical with a primary radical ($\text{R}\cdot$),¹⁴ particularly in St/PDMS-ACP system.



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

The relationship between R_p , $[\text{M}]$ and $[\text{I}]$ is given by¹⁵:

$$[\text{M}]/R_p = \frac{\lambda}{[\text{I}]^{0.5}} + \frac{\mu}{[\text{M}]} \quad (3)$$

where λ is the value of $(k_t/2k_d)^{0.5}/k_p$, μ is the value of $\sigma k_t/k_i k_p$, and $[\text{M}]$ is the monomer concentration. A plot of $[\text{M}]/R_p$ vs. $1/[\text{I}]^{0.5}$ at constant monomer concentration gives straight lines (Figure 1) for PDMS-ACP and AIBN, as predicted by eq 3. Accordingly, it is considered that initiators also act as terminators in the photopolymerization of styrene. The values of λ and μ are obtained from the slopes and the intercepts of the straight lines, respectively. The resulting values are listed in

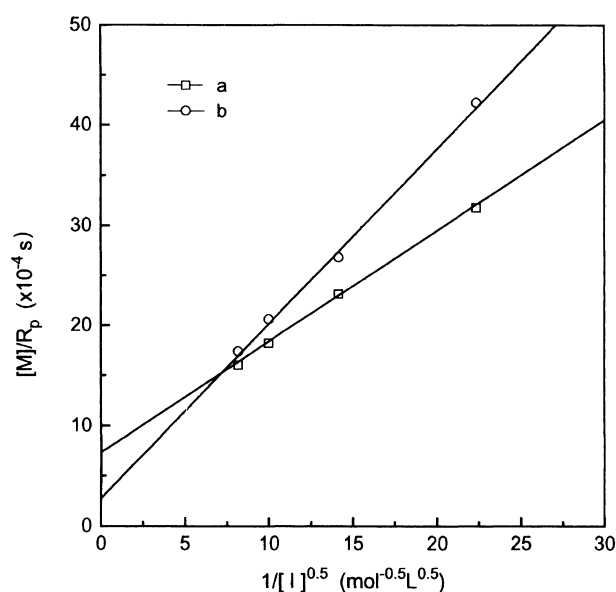


Figure 1. Plots of equation (3) showing the dependence of the rate of polymerization on initiator concentration: (a) PDMS-ACP; (b) AIBN.

Table II. Kinetic parameters of photopolymerization of styrene in bulk

Parameters	Initiator ^a	
	PDMS-ACP	AIBN
$R_p/\times 10^{-5} \text{ M s}^{-1}$	4.4	4.2
$R_i/\times 10^{-8} \text{ M s}^{-1}$	9.2	7.9
τ/s	1.0	1.2
$k_p/\text{M}^{-1} \text{ s}^{-1}$	55.6	53.4
$k_t/\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	1.1	0.9
$\lambda/\times 10^3 \text{ M}^{0.5} \text{ s}$	11.0	17.4
$\mu/\times 10^5 \text{ M s}$	5.8	2.3
$k_d/\times 10^{-6} \text{ s}^{-1}$	12.4	5.4
$\sigma k_i k_t^{-1}/\times 10^7$	3.2	1.2

^a Concentration of azo group = 0.01 mol L⁻¹.

Table II. It is found that the value of μ in st/PDMS-ACP system is larger than that in St/AIBN system. The result implies that fraction β of primary radical termination in macroinitiator PDMS-ACP is larger than that in AIBN initiator.

The fraction β of primary radicals entering into termination was calculated by¹⁵:

$$\beta = \sigma R_i / R_d = \frac{\Phi^{0.5}}{1 + (\lambda[M]/\mu[I]^{0.5})} \quad (4)$$

where σR_i 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 equation¹⁵:

$$\Phi^{0.5} = \lambda R_p / [I]^{0.5} [M] \quad (5)$$

The values of Φ and β are listed in Table I for polymerization of styrene. The data indicate that the values of Φ in both polymerizations decrease with increase in concentration of initiator, whereas the values of β increase. Moreover, the value of Φ for the polymerization of styrene with PDMS-ACP as initiator is smaller than that with AIBN as initiator, whereas the value of β in the St/PDMS-ACP system is larger than that in the St/AIBN system.

1,3,5-Triphenylverdazyl (TPV) was used as the scavenger, which traps a primary radical in the polymerization system [eq 6], to determine the rate of initiation (R_i). The inhibiting effect of TPV on photopolymerization in the St/PDMS-ACP system is shown in Figure 2. Generally, inhibition mechanism should be same regardless of concentration TPV, giving same slopes. However, the slope at high concentration of TPV is different from that at low concentration in St/PDMS-ACP system. The result is also observed at St/AIBN system. It is revealed that the products of TPV inhibition with primary radicals show the secondary inhibiting action.¹⁶ The correlation between the concentration of scavenger [TPV] and the duration of inhibition in the St/PDMS-ACP system is shown in Figure 3. The rate of initiation R_i was calculated from the slope of Figure 3 according to eq 7. R_i of styrene with PDMS-ACP as initiator ($9.2 \times 10^{-8} \text{ mol L}^{-1} \text{ s}^{-1}$) is in agreement with that with AIBN as initiator ($7.9 \times 10^{-8} \text{ mol L}^{-1} \text{ s}^{-1}$). Moreover, the value of k_p^2/k_t is derived from eq 8.

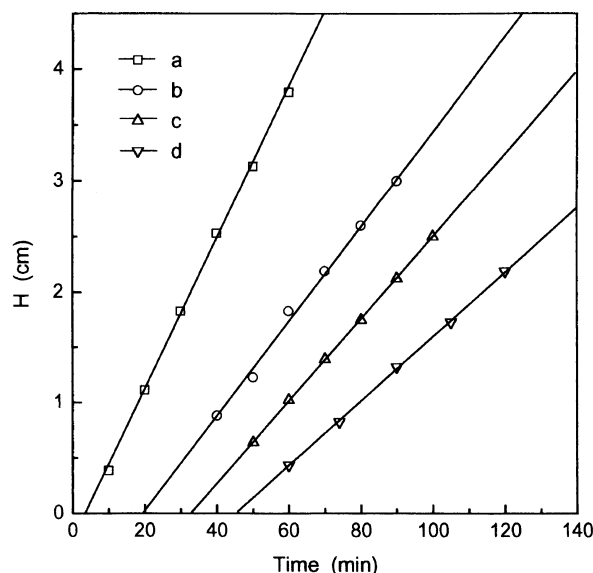


Figure 2. The TPV inhibition effect on the photopolymerization of styrene in bulk initiated by PDMS-ACP (concentration of azo group = 0.01 mol L⁻¹); [TPV] (in mmol L⁻¹): (a) 0; (b) 13; (c) 19; (d) 26.

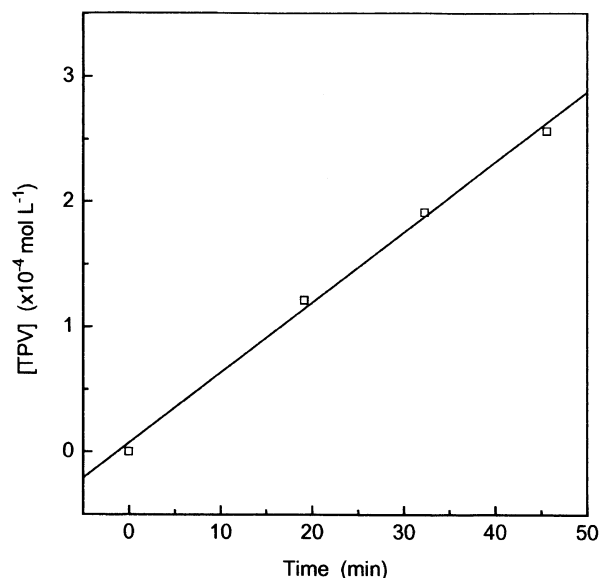
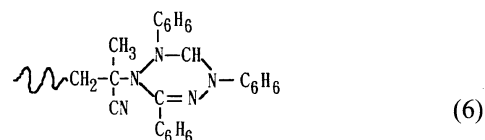
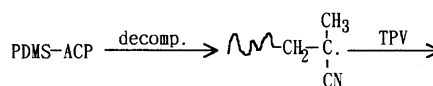


Figure 3. Plots of [TPV] vs. induction time in polymerization of styrene in bulk with PDMS-ACP (concentration of azo group = 0.01 mol L⁻¹).



$$R_i = \frac{[\text{TPV}]_0}{\Delta t} = \frac{\text{Initial concentration of scavenger}}{\text{Time of inhibition period}} \quad (7)$$

$$\frac{k_p^2}{k_t} = \frac{R_p^2}{R_i[M]^2} \quad (8)$$

The average lifetime τ of the chain radicals can be determined by the rotating sector method. The data are listed in Table II. The value of τ in St/PDMS-ACP system (1.0 s) is close to St/AIBN system (1.2 s). In addition, the value of k_p/k_t is derived from eq 9.

$$\frac{k_p}{k_t} = \frac{R_p \tau}{[M]} \quad (9)$$

The values of the rate constant of polymerization k_p and of termination k_t are then calculated from eq 8 and 9. The rate constants k_p and k_t are 55.6 and 1.1×10^7 $\text{L mol}^{-1} \text{s}^{-1}$ in the St/PDMS-ACP system, and 53.4 and 9.0×10^6 $\text{L mol}^{-1} \text{s}^{-1}$ in the St/AIBN system, respectively. These values of k_p and k_t agree with the literature values.¹⁷ On the other hand, the number-average molecular weight (\bar{M}_n) of the polymers prepared with PDMS-ACP as initiator are found to be similar with those with AIBN as initiator (Table I). This observation suggests that the propagation radicals are less effective by the PDMS segments in the St/PDMS-ACP system.

The decomposition rate constant k_d for initiator can be calculated by:

$$\begin{aligned} \lambda &= (k_t/2k_d)^{0.5}/k_p \\ k_d &= k_t/2(\lambda k_p)^2 \end{aligned} \quad (10)$$

The value of k_d for PDMS-ACP ($12.4 \times 10^{-6} \text{s}^{-1}$) is notably greater than that for AIBN ($5.4 \times 10^{-6} \text{s}^{-1}$). Moreover, the value of k_d for PDMS-ACP initiator in styrene is in agreement with that in methyl methacrylate ($15.5 \times 10^{-6} \text{s}^{-1}$).¹¹ On the other hand, 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 according to the following equation:

$$\begin{aligned} \mu &= \sigma k_t/k_i k_p \\ \sigma k_t/k_i &= \mu k_p \end{aligned} \quad (11)$$

The values of $\sigma k_t/k_i$ are 3.2×10^7 and 1.2×10^7 for PDMS-ACP and AIBN, respectively. The results reveal that the rate of primary radical termination in PDMS-ACP macroazoinitiator is greater than that in AIBN.

Taking into account that PDMS-ACP macroinitiator gives a small initiator efficiency Φ , and a greater fraction β of primary radicals termination, it may be concluded that the increased size of the primary radicals reduces their diffusion apart, thus increases the chance of recombination.¹⁸

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REFERENCES

1. R. P. Kambour, H. J. Klopfer, and S. A. Smith, *J. Appl. Polym. Sci.*, **26**, 847 (1986).
2. A. Ueda and S. Nagai, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 405 (1986).
3. S. J. Clarson and J. A. Semlyen, "Siloxane Polymers," Ellis Horwood-PTR, Prentice Hall, New York, N.Y., 1993, p. 72.
4. S. J. Clarson, J. O. Stuart, C. E. Selby, A. Sabata, S. D. Smith, and A. Ashraf, *Macromolecules*, **28**, 674 (1995).
5. P. Chaumont, G. Beinert, J. Herz, and P. Rempp, *Eur. Polym. J.*, **15**, 459 (1979).
6. H. Inoue, A. Matsumoto, K. Matsukawa, A. Ueda, and S. Nagai, *J. Appl. Polym. Sci.*, **40**, 1917 (1990).
7. R. Walz, B. Bomer, and W. Heitz, *Makromol. Chem.*, **178**, 2527 (1977).
8. H. Kinoshita, N. Tanaka, and T. Araki, *Makromol. Chem.*, **194**, 2335 (1993).
9. T. C. Chang, H. B. Chen, Y. C. Chen, and S. Y. Ho, *J. Polym. Sci., Polym. Chem. Ed.*, **34**, 2613 (1996).
10. T. C. Chang, Y. C. Chen, Y. S. Chiu, and S. Y. Ho, *Polymer*, **37**, 2963 (1996).
11. T. C. Chang, H. B. Chen, S. Y. Ho, and Y. S. Chiu, *J. Macromol. Sci. Pure Appl. Chem.*, **A33**, 1263 (1996).
12. R. Kuhn and H. Trisch, *Monatsh. Chem.*, **95**, 457 (1964).
13. H. B. Chen, T. C. Chang, Y. S. Chiu, and S. Y. Ho, *J. Polym. Sci. Polym. Chem. Ed.*, **33**, 679 (1995).
14. K. Ito, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 701 (1980).
15. M. Niwa, T. Matsumoto, and H. Izumi, *J. Macromol. Sci. Pure Appl. Chem.*, **A24**, 567 (1987).
16. T. Milczarska and J. Szafer, *Makromol. Chem.*, **218**, 171 (1994).
17. M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc.*, **73**, 1700 (1951).
18. A. Onen, S. Denizligil, and Y. Yagci, *Makromol. Chem.*, **217**, 79 (1994).