Polymer Bulletin 16, 277–284 (1986)

Polymer Bulletin

Living radical polymerization in homogeneous system with phenylazotriphenylmethane as a thermal iniferter

Takayuki Otsu and Toshiniri Tazaki

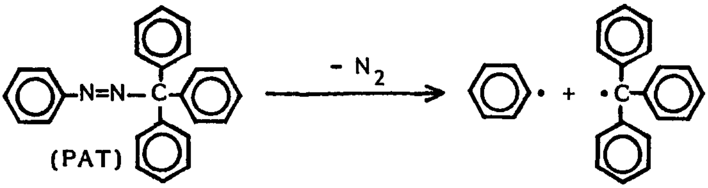
Department of Applied Chemistry, Faculty of Engineering, Osaka City University,
Sugimoto, Sumiyoshi-ku, Osaka, 558 Japan

SUMMARY

Radical polymerization of methyl methacrylate (MMA) with phenylazotriphenylmethane (PAT) was found to give the polymer with a trityl group bonded at its α-chain end which could further dissociate into propagating and trityl radicals. Therefore, it was confirmed that PAT served as a thermal iniferter for polymerization of MMA, which proceeded via a living radical mechanism, i.e. yield and molecular weight of the polymers increased with reaction time. When the polymer thus obtained was used as a polymeric iniferter for the polymerization of styrene (St), the block copolymer was obtained.

INTRODUCTION

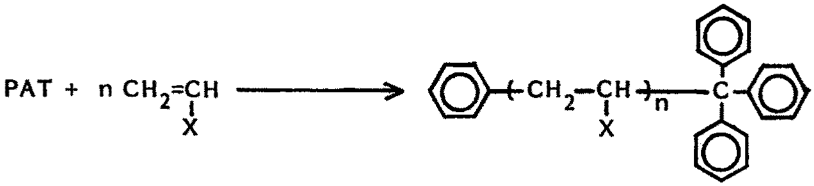
PAT has been known to decompose into a highly reactive phenyl radical and an unreactive trityl radical, according to Eq. 1;



(1)

In 1940s, PAT was examined as an initiator having a modifier function in radical polymerization of butadiene, similar to diazothioethers and diazoaminobenzenes (1). However, the experiment did not give good result, because the activity of PAT as an initiator was low. After that, some studies on the decomposition of PAT and its initiator activity have been performed (2). PAT is now used as a source of phenyl radical in physical organic chemistry.

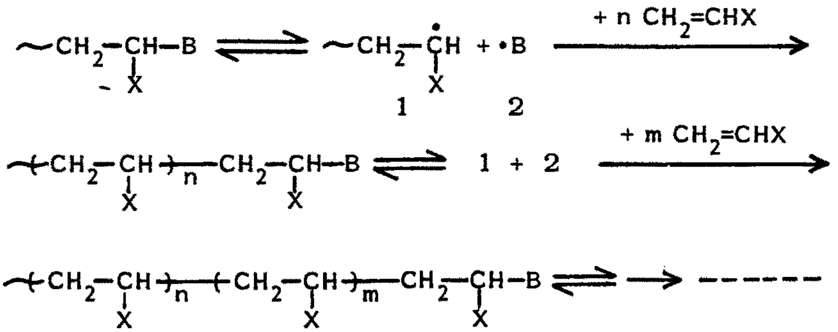
In radical polymerization with PAT, it is expected that phenyl radical in Eq. 1 can easily add to the monomer to initiate polymerization, and trityl radical reacts only with the propagating radical. If the above reactions occur preferentially in radical polymerization of vinyl monomers with PAT, the polymer with phenyl and trityl groups at its ω and α ends, respectively, may be produced as shown in Eq. 2.



(2)

From these viewpoints, we have proposed in 1982 a concept of initiator-transfer agent-terminator (iniferter) to design of the structure of polymer chain end in radical polymerization (3). As reported previously (4,5), the photopolymerizations of St and MMA with some organic sulfur compounds as an iniferter were confirmed to proceed via a mechanism close to this concept, i.e. the resulting polymers have two iniferter fragments bonded at both chain ends.

Moreover, if the end group of the polymers obtained with such iniferters can further induce radical polymerization as a polymeric iniferter, these radical polymerization may be considered to proceed via a new mechanism, i.e. yield and molecular weight of the polymers increase with reaction time. Therefore, we have also proposed in 1982 an ideal model for living radical polymerization in homogeneous system (6), as shown in Eq. 3;



$$\sim CH_2-\underset{X}{CH}-B \rightleftharpoons \underset{1}{\sim CH_2-\underset{X}{\dot{C}H}} + \underset{2}{\cdot B} \xrightarrow{+\,n\,CH_2=CHX}$$

$$\sim\!\left(CH_2-\underset{X}{CH}\right)_n CH_2-\underset{X}{CH}-B \rightleftharpoons 1 + 2 \xrightarrow{+\,m\,CH_2=CHX}$$

$$\sim\!\left(CH_2-\underset{X}{CH}\right)_n\!\left(CH_2-\underset{X}{CH}\right)_m CH_2-\underset{X}{CH}-B \rightleftharpoons \rightarrow \text{------} \qquad (3)$$

Namely the C-B bond in the propagating chain end dissociates into radicals in which 1 is reactive propagating radical and 2 is an unreactive small radical which does not enter the initiation, but undergoes readily primary radical termination to give the identical C-B bond. Accordingly, if the polymerization proceeds via the repetition of dissociation at the chain end, addition of the monomer to 1, and primary radical termination with 2, such polymerization may proceed via a living radical mechanism according to Eq. 3. As described above (4,5), the polymerizations of St and MMA with sulfur compounds as a photoiniferter were found to be performed by a mechanism close to Eq. 3.

In the previous communication (6), PAT was also described to serve as a thermal iniferter to induce living radical polymerization of MMA. In this paper, the mechanism and characteristics of living radical polymerization of MMA with PAT were investigated in detail. The results obtained are described here.

EXPERIMENTAL

PAT was synthesized by the reaction of triphenylmethyl chloride with phenylhydrazine in dry ether, followed by oxidation with hydrogen peroxide (7). The resulting PAT was then recrystallized from dichloroethane /ethanol: mp 110-112 °C (lit.(8) 111-112 °C). 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. MMA, n-butyl methacrylate (BuMA), benzyl methacrylate (BzMA), and St were distilled under a reduced pressure before use. Solvents and other reagents were used after ordinary purifications.

The polymerization was carried out in a degassed sealed tube without light. After polymerization for a given time, the content of the tubes was poured into an excess amount of methanol to precipitate the polymer which was then purified two or three times by reprecipitating from benzene into methanol. The yield of the polymers was calculated from the weight of the dried polymers.

The block copolymerization was performed in a similar manner. The separation of the polymers obtained from block copolymerization of St into block and non-block polymers was carried out by extracting them with suitable solvents, i.e. acetonitrile, cyclohexane, and benzene were used as extracting solvents for the parent homopoly(MMA), homopoly(St), and block copolymer, respectively.

Intrinsic viscosities, $[\eta]$, were determined in benzene at 30 °C, and the average molecular weights ($\bar{M}$) were calculated from the following equations (9);

$$[\eta] = 6.27 \times 10^{-5}\,\bar{M}^{0.76} \qquad \text{for poly(MMA)}$$
$$[\eta] = 1.03 \times 10^{-5}\,\bar{M}^{0.82} \qquad \text{for poly(BzMA)}$$
$$[\eta] = 4.00 \times 10^{-5}\,\bar{M}^{0.77} \qquad \text{for poly(BuMA)}$$
$$[\eta] = 8.50 \times 10^{-5}\,\bar{M}^{0.75} \qquad \text{for poly(St)}$$

Thermogravimetric analysis (TGA) of the polymers was carried out with a Shimadzu TG-20 thermobalance. About 1.5 mg of the polymer was used and heated in a nitrogen stream at heating rate of 10 °C/min.

Gel permeation chromatography (GPC) was performed in tetrahydrofuran as an eluent at 40 °C with a Toyosoda HLC-802R apparatus.

RESULTS AND DISCUSSION

Figs. 1 and 2 show time-conversion and time-molecular weight relations for bulk polymerization of MMA with PAT as a thermal iniferter over temperature range from 60 to 100 °C. The conversion and the molecular weight of the polymers were found to increase linearly from the origin with reaction time, i.e. conversion [see Fig. 4], even though PAT disappeared already by decomposition at the initial stage of polymerization, i.e. 99.9% of PAT decomposed after 6 hr at 60 °C (10).

These observations were in agreement with those reported for polymerization with tetraphenylethanes (11,12), tetraethylthiuram disulfide (3), and diethyldithiocarbamates (4,13). Moreover, the poly(MMA) chain end terminated with trityl radical [see **4** in Eq. 5] was found to be able to redissociate thermally to induce radical polymerization (6). Therefore, the polymerization of MMA with PAT may suggest to proceed via living mono-radical mechanism according to Eq. 3.

To clarify further the observed polymerization behavior, some kinetic parameters were determined according to the conventional treatment. From Fig. 1, the apparent activation energy for overall polymerization of MMA with PAT was calculated to be 62.0 KJ/mol which was lower than that (88 KJ/mol) with AIBN (14), and close to that (72.9 KJ/mol) calculated from the reported rate constants for MMA with PAT (10).

Moreover, the apparent reaction order with respect to the PAT concentration was about 0.25. Although this order was somewhat higher than zero when only the primary radical termination with trityl radical occurred (15), it might be accounted for the fact that the terminated polymer could undergo reinitiation.

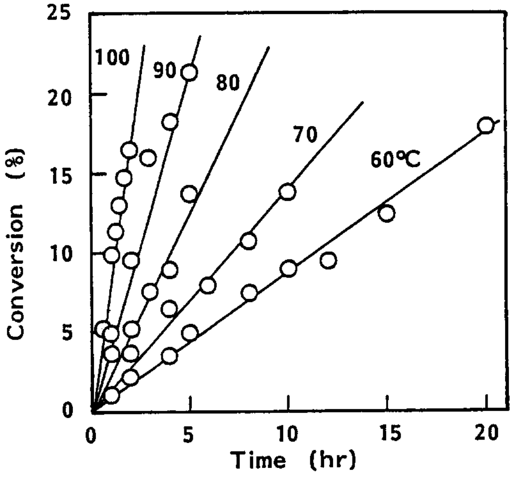


Figure 1 Time-conversion relations in bulk polymerization of MMA with PAT; [PAT] = 1.0 x 10^{-2} mol/l.

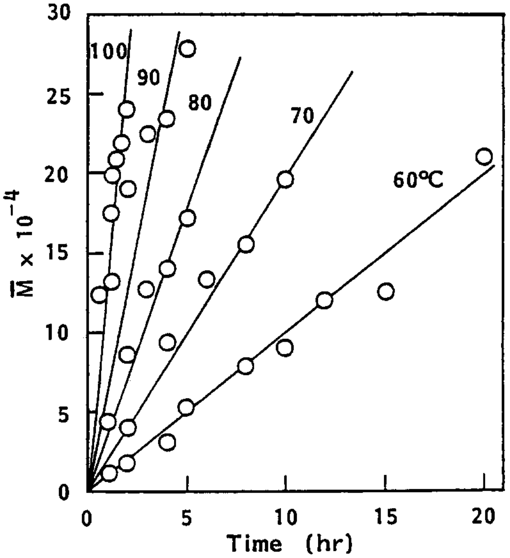


Figure 2 Time-molecular weight relations in bulk polymerization of MMA with PAT; [PAT] = 1.0 x 10^{-2} mol/l.

Fig. 3 shows the results of GPC determination of the polymers isolated at various reaction times in bulk polymerization of MMA with PAT at 60 ℃. The GPC chart of the polymer produced initially (2 hr) showed as an unimordal molecular weight distribution (MWD), but that formed thereafter became a bimordal MWD, i.e. new peak due to higher molecular weight polymer appeared and it shifted to higher molecular weight side with time. In relation to this, the peak of lower molecular weight polymer decreased and that of higher molecular weight polymer increased. These results might be also support that the polymerization of MMA with PAT proceeded via a living radical mechanism even in homogeneous system.

To check whether such polymerization occurs for other methacrylate monomers, the bulk polymerizations of BuMA and BzMA were performed. The observed molecular weight-conversion relations are shown in Fig. 4, in which that for MMA is also indicated as comparison.

As is seen from this figure, all of the observed molecular weight-conversion relations were almost linear from the origin. The slope and linearlity of these lines may be a measure of the living nature, i.e. MMA > BuMA > BzMA. It may be assumed that this trend with respect of methacrylate monomers used is accounted for the rate constants of redissociation of the polymer chain end and easiness of primary termination.

The polymers thus obtained at various reaction times are considered to have a dormant living radical species (i.e. iniferter site) at a chain end. Therefore, if these polymers were used as a polymeric iniferter of the polymerization of second monomer, AB type block copolymer must be produced. The results of block copolymerization of St with poly(MMA) obtained by PAT as a polymeric iniferter are summarized in Table 1.

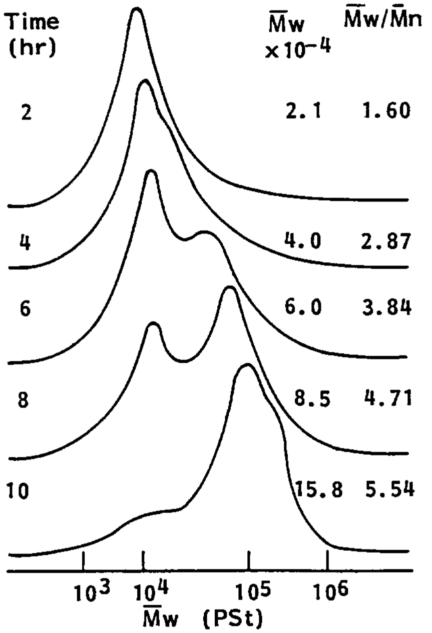


Figure 3 GPC curves of poly(MMA) polymerized in bulk with PAT at 60°C at each time; [PAT] = 1.0×10^{-2}mol/l.

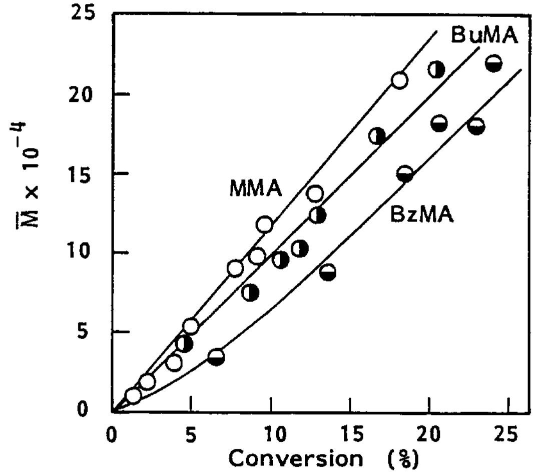
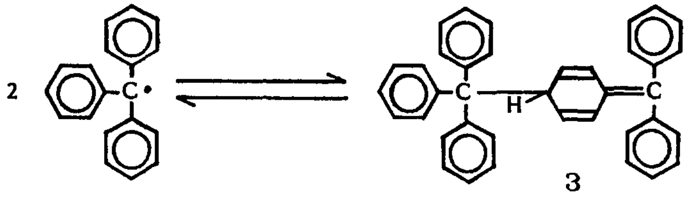


Figure 4 Conversion- molecular weight relations in bulk polymerization of methacrylic esters with PAT at 60°C; [PAT] = 1.0×10^{-2}mol/l.

As seen in this table, the yield of the block copolymers isolated by solvent extraction which were confirmed to be the AB type, was 48-72%, indicating that a considerable amount (28-52%) of unreacted poly(MMA) used as iniferter and homopoly(St) was produced. These observations may be accounted for the fact that the undesirable side reactions leading to the deactivation of the dormant living radical species (i.e. iniferter site) occurred in some extent.

In 1968, Lankamp et.al.(16) reported that the dimer of trityl radicals consisted of the following structure, 1,1-diphenylmethylene-4-trityl-2,5-cyclohexadiene 3 not hexaphenylethane as shown in Eq. 4.



(4)

Therefore, the isolation of a considerable amount of unreacted homopoly(MMA) as seen in Table 1 might suggest that the following deactivation reaction [Eq. 5] occurred competitively in the polymerization of MMA with PAT. Where 7 is formed by an intermolecular hydrogen transfer (i.e. a homolytic substitution to the benzene nucleus) and does not redissociate into reactive radical. The possibility of such reaction may be also supported from the result that the reaction of radical with 1,1-diphenyl-2-picrylhydrazyl (DPPH) gave mainly

Table 1 Results of Block Copolymerization of St with poly(MMA) (4)$^{a)}$

Poly(MMA) 4$^{b)}$ (g)	Time (hr)	Yield (g)	Fractions extracted (%)$^{c)}$ Homo-poly(MMA)	Homo-poly(St)	Block copolymer
0.36	5	0.55	22.7 (6.9)	9.2 (55.7)	63.1 (62.5)$^{d)}$
0.38	5	0.62	36.3 (12.5)	8.4 (49.9)	55.7 (63.8)$^{d)}$
0.40	5	0.57	45.5	6.7	47.8
0.30	10	0.97	23.7	13.3	63.0
0.30	15	1.10	19.5	23.7	69.1
0.30	20	1.60	17.9	9.3	72.3
0.30$^{e)}$	20	1.80	14.9	72.9	12.2

a) Polymerization conditions: St 10 ml, in bulk at 80 °C.

b) Prepared by bulk polymerization with PAT at 60 °C; [PAT] = 1.0×10^{-2} mol/l.

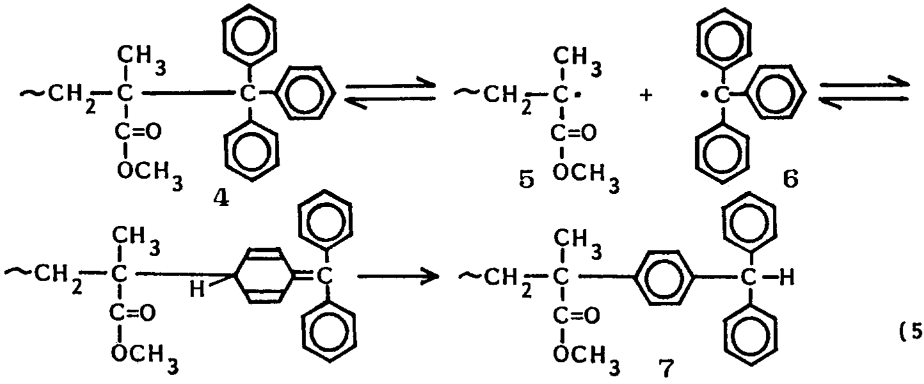
c) Values in parenthesis indicated the viscosity-average molecular weight($\bar{M}$); $\bar{M} \times 10^{-4}$.

d) The viscosity-average molecular weight of block copolymers were calculated from the following equation (17-19).

$$[\eta]_B^{2/3} = x\,[\eta]_{M_1}^{2/3} + (1-x)\,[\eta]_{M_2}^{2/3}$$

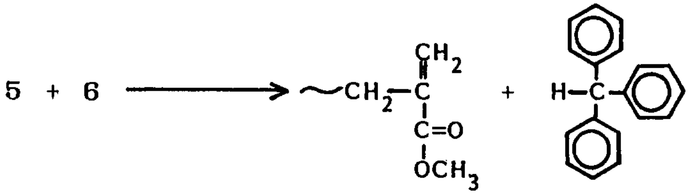
where $[\eta]_B$ is the intrinsic viscosity of the block copolymer, $[\eta]_{M_1}$ and $[\eta]_{M_2}$ are those of polymers of M_1(MMA) and M_2 (St), respectively. X is the weight fraction of M_1 unit. These values were in agreement with those calculated for AB type.

e) Polymerized with AIBN ; [AIBN] = 1.0×10^{-2} mol/l.



(5)

a radical substituted product to the benzene nucleus in DPPH (20,21). The other deactivation reactions may be as follows: (i) ordinary bimolecular terminations of the poly(MMA) radicals, (ii) dimerization of the trityl radicals, followed by hydrogen transfer like Eq. 5, and (iii) a disproportionation between poly(MMA) and trityl radicals as shown in Eq. 6.



(6)

Similar deactivation reactions may also be expected to occur in the block copolymerization of St, because the homopoly(St) was formed.

It is also important problem to obtain the poly(MMA) with the thermally-stable chain end through these polymerization. In fact, the polymer obtained by PAT was less stable than that by AIBN, as is seen from TGA curve [Fig. 5]. Since the deactivation reaction was found to occur according to Eq. 5, the polymer obtained by PAT was heated in benzene at 80 °C for 5 hr. The TGA curve of the resulting polymer was in quite agreement with that obtained with AIBN, indicating that the polymer obtained by PAT was stabilized by such treatment.

REFERENCES

1. "Synthetic Rubbers," ed. by G. S. Whitby, John Wiley & Sons, Inc., New York (1954).
2. G. V. Schulz, Z. Elektrochem., 47, 265 (1941).
3. T. Otsu and M. Yoshida, Makromol. Chem., Rapid Commun., 3, 127 (1982).
4. T. Otsu and A. Kuriyama, Polym. Bull., 7, 45 (1982).
5. A. Kuriyama and T. Otsu, Polym. J., 16, 511 (1984).
6. T. Otsu, M. Yoshida, and T. Tazaki, Makromol. Chem., Rapid Commun., 3, 133 (1982).
7. R. G. Kryger, J. P. Lorand, and N. R. Herron, J. Am. Chem. Soc., 99, 7589 (1977).

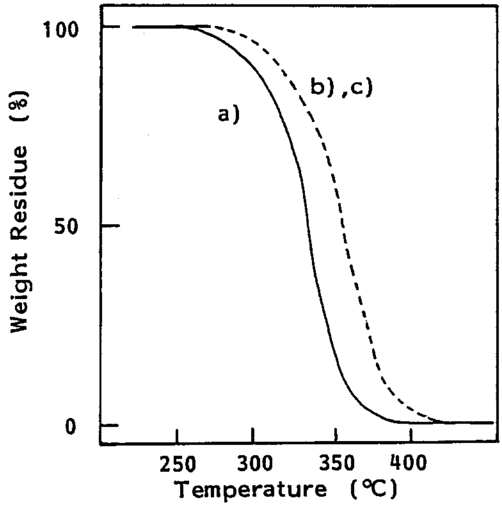


Figure 5 TGA curves of poly(MMA)s:
a) prepared with PAT in bulk at 60°C; [PAT] = 1.0×10^{-2} mol/l.
b) prepared with AIBN in bulk at 60°C; [AIBN] = 1.0×10^{-2} mol/l.
c) heated the poly(a) in benzene at 80°C.

8. R. F. Bridger and G. A. Russel, J. Am. Chem. Soc., 85, 3574 (1963).
9. M. Kurata, Y. Tsunashima, M. Iwata, and K. Kamada, in "Polymer Handbook," ed. by J. Brandcup and E. H. Immergut, John Wiley & Sons Inc., New York, Chap. 4, (1975).
10. M. G. Alder and J. E. Leffler, J. Am. Chem. Soc., 76, 1425 (1954).
11. E. Borsig, M. Lazár, and M. Čapla, Makromol. Chem., 105, 212 (1967).
12. A. Bledzki, H. Balard, and D. Braun, Makromol. Chem., 182, 3195 (1981).
13. T. Otsu and M. Yoshida, Polym. Bull., 7, 197 (1982).
14. T. Otsu, "Radical Polymerization (I), Elementary Reaction Mechanism," Kagaku-Dojin, Kyoto, (1971).
15. G. S. Misra, A. Hafeez, and K. S. Sharma, Makromol. Chem., 51, 123 (1962).
16. H. Lankamp, W. Th. Nauta, and C. Maclean, Tetrahadron Lett., 1968, 249.
17. T. Kotaka, T. Uda, T. Tanaka, and H. Inagaki, Makromol. Chem., 176, 1273 (1975).
18. H. Ohmura, T. Kotaka, and H. Inagaki, Polymer, 10, 501 (1969).
19. T. Kotaka, H. Ohmura, and H. Inagaki, Polymer, 10, 517 (1969).
20. A. Henglein, Makromol. Chem., 15, 188 (1955).
21. R. H. Poirier, E. J. Kahler, and F. Benington, J. Org. Chem., 17, 1437 (1952).

Accepted August 14, 1986