STUDIES IN PHOTOPOLYMERIZATION
IV: PHOTOPOLYMERIZATION OF METHYL METHACRYLATE
USING PEROXYDIPHOSPHATE AS A PHOTOINITIATOR

SUBASINI LENKA and PADMA L. NAYAK

Laboratory of Polymers and Fibers, Department of Chemistry, Ravenshaw College, Cuttack 753003 (India)

(Received March 14, 1986)

Summary

Photopolymerization of methyl methacrylate was carried out using peroxydiphosphate as a photoinitiator. The rate R_p of polymerization increases as the initiator mole fraction is increased. The initiator exponent was computed to be 0.5. The rate of polymerization increases with increasing monomer concentration and the monomer exponent was calculated to be 1.5. The reaction was carried out at three different temperatures and the overall activation energy was computed to be 4.7 kcal mol^{-1}. The kinetic data and other evidence indicate that the overall polymerization takes place by a radical mechanism, and rate expressions have been derived. A suitable mechanism has been suggested.

1. Introduction

Peroxydiphosphate ion (PP, $P_2O_8^{4-}$) is used as a photo-oxidant [1] and a thermal initiator [2 - 4] of vinyl polymerization, and a number of peroxides [5 - 12] are used as photoinitiators of this process. Battaglia [13], in a survey of the UV spectra of peroxides, has shown that the spectra of peroxydiphosphate and its protonated forms are very similar to those of other peroxides. The similarity between the spectra led several researchers to predict that PP would be activated to radical reaction comparable with those observed with hydrogen peroxide [14] and peroxydisulphate [15].

We have reported the thermal, vinyl [2 - 4] and graft copolymerization [16 - 19] of a number of vinyl monomers using PP as an initiator. This paper presents the results of a study of the photopolymerization of methyl methacrylate (MMA) with PP as the photoinitiator.

2. Experimental details

The $K_4P_2O_8$ was obtained from FMC Corporation, U.S.A., as a gift sample and was 98.5% pure after recrystallization. The monomer MMA

was purified according to standard procedures [16 - 19]. All the chemicals used in the preparation of solutions were BDH AnalaR reagents.

The polymerization was carried out in an aqueous medium; after addition of the required amount of monomer containing known amounts of initiator and other additives, the solution was flushed with purified nitrogen gas, stoppered and placed in a thermostat at a chosen temperature. The reaction vessel was illuminated by monochromatic light of wavelength 440 nm by placing a Corning filter in front of a 125 W high pressure mercury lamp (Philips India Ltd.). The cell that was used as the reaction vessel had a path length of 4.5 cm in the direction of the beam, a diameter of 5 cm and a capacity of about 70 ml, and was fused at both ends with flat Pyrex plates fitted with two outlet tubes with standard B_{12} cones on the top.

To stop further polymerization taking place after the light sources were cut off, 10 ml 1 wt.% hydroquinone solution were added to the reaction mixture. The precipitated polymer was filtered, washed repeatedly with water and dried in vacuum to constant weight at 60 °C. The rate of polymerization was calculated from the weight of polymer obtained.

The intrinsic viscosities $[\eta]$ of the polymers were measured in benzene solution at 30 ± 0.05 °C using an Ubbelohde viscometer. The results were expressed in decilitres per gram. The molecular weight of the poly(methyl methacrylate) was calculated from the viscosity data by using the equation [20]

$$[\eta] = 8.69 \times 10^{-5} \, M_{n}^{-0.76}$$

3. Results and discussion

MMA was photopolymerized in aqueous solutions in the presence of PP as the initiator. A typical set of time–conversion curves at 35 °C is shown in Fig. 1.
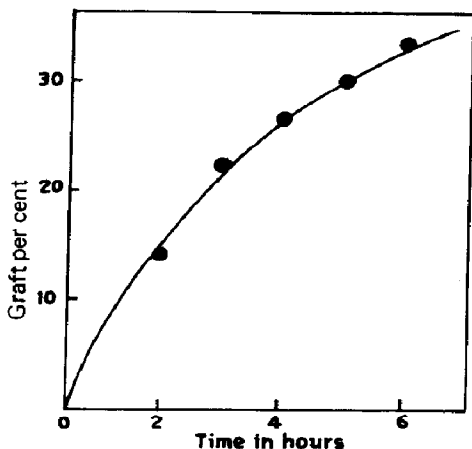

Fig. 1. Conversion–time curve ($[PP] = 1.0 \times 10^{-2}$ M; $[H^{+}] = 1.5 \times 10^{-1}$ M; $[MMA] = 14.08 \times 10^{-2}$ M; temperature, 35 °C).

3.1. Effect of initiator

The rate of photopolymerization was investigated by varying the PP concentration over the range 0.001 - 0.0075 M at different concentrations of MMA ((14.08 - 32.85) $\times 10^{-2}$ M at 35 °C). The rate of polymerization increases with increasing [PP]. The plots of R_p vs. $[PP]^{1/2}$ (Fig. 2) are linear, indicating that the order of the dependence on [PP] is 0.5. This is also evident from the linear plots of log R_p vs. $\log[PP]^{1/2}$ (Fig. 3) which have a slope of 0.5.
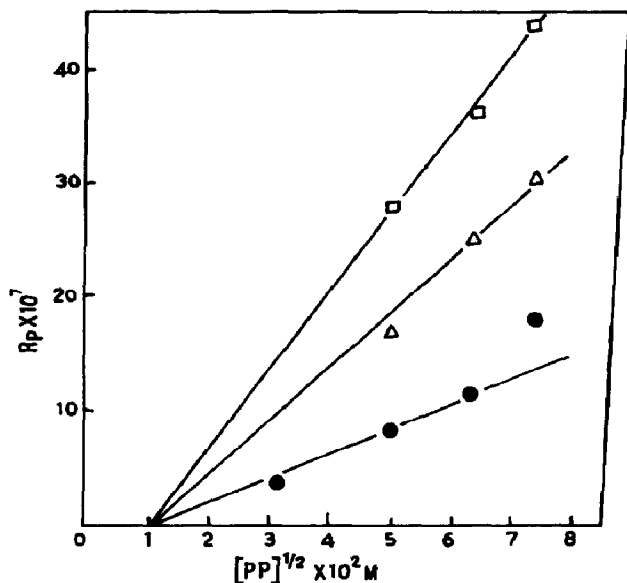

Fig. 2. Plot of R_p vs. $[PP]^{1/2}$ ($[H^+]$ = 1.5 × 10^{-1} M; time, 5 h; temperature, 35 °C): ●, [MMA] = 14.08 × 10^{-2} M; △, [MMA] = 23.47 × 10^{-2} M; □, [MMA] = 32.85 × 10^{-2} M.
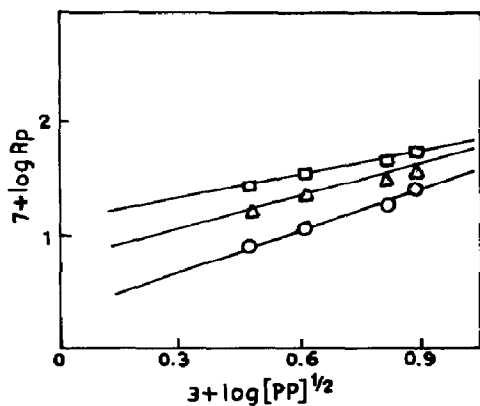

Fig. 3. Plot of log R_p vs. $\log[PP]^{1/2}$ ($[H^+]$ = 1.5 × 10^{-1} M; time, 5 h; temperature, 35 °C): ○, [MMA] = 14.08 × 10^{-2} M; △, [MMA] = 23.47 × 10^{-2} M; □, [MMA] = 32.85 × 10^{-2} M.

3.2. Effect of monomer

The rate R_p of polymerization increases on increasing the monomer concentration over the range 0.0469 - 0.4694 M at different PP concentrations ($(0.5 - 1.5) \times 10^{-2}$ M). The plots of R_p vs. $[MMA]^{3/2}$ are linear, indicating that the order of the dependence on monomer concentration (Fig. 4) is 1.5.

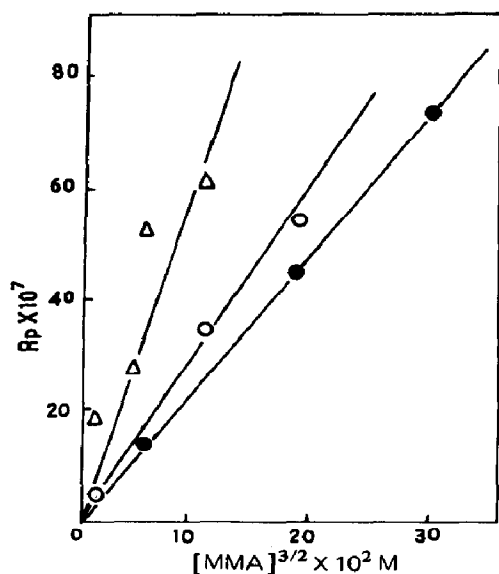Fig. 4. Plot of R_p vs. $[MMA]^{3/2}$ ($[H^+] = 1.5 \times 10^{-1}$ M; time, 5 h; temperature, 35 °C): ●, $[PP] = 0.5 \times 10^{-2}$ M; ○, $[PP] = 1.0 \times 10^{-2}$ M; △, $[PP] = 1.5 \times 10^{-2}$ M.

3.3. Effect of temperature

The rate of polymerization was measured at three different temperatures at fixed monomer and initiator concentrations. The rate of polymerization increases with increasing temperature. From the slope of the Arrhenius plot of $\log R_p$ vs. $1/T$ (Fig. 5), the overall activation energy was computed to be 4.7 kcal mol^{-1}.
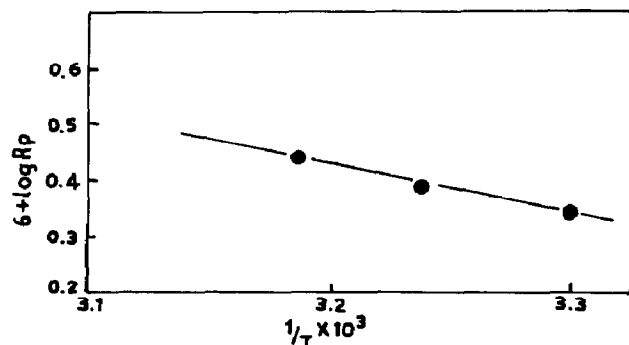

Fig. 5. Arrhenius plot of $\log R_p$ vs. $1/T$.

3.4. Effect of solvents

The photopolymerization of MMA using PP as the initiator was investigated in different polar, dipolar aprotic and non-polar solvents such as ethanol, dioxan and n-hexane.

The chain transfer constants Cs for these solvents at 35 °C were computed by plotting the reciprocal degree of polymerization $1/\bar{p}_n$ $vs.$ [S]/[M] for different solvents (Fig. 6). The observed Cs values for hexane, dioxan and ethanol were 0.33×10^{-3}, 0.38×10^{-3} and 0.43×10^{-3} respectively. It has been reported that the rates of polymerization in certain solvents have values different from those that would be expected if the solvent acted as an inert diluent. Tobolsky and Matlak [21] reported an enhancement of the rate of polymerization of MMA initiated by cumene hydroperoxide in the presence of a number of polar solvents. Burnett and coworkers [22, 23] observed a similar enhancement of the rate by polar solvents in the polymerization of MMA by azobis(isobutyronitrile), but the addition of non-polar solvents had no effect on the rate of polymerization for either of the systems. Tobolsky and Matlak [21] explained the rate-enhancing effect by considering the increased production of free radicals in the presence of these solvents. Burnett and coworkers [22, 23] suggested that the rate enhancement might be due to the increased initiator efficiency in the presence of a solvent which increases the rate of polymerization. Henrici-Olive and Olive [24], while studying the effect of solvent in free-radical polymerization, explained the effect by considering the formation of a charge transfer complex between polymer radicals and monomer and solvent molecules. Bamford and Brumby [25], while investigating the effect of solvent in the polymerization of MMA, suggested that the dependence of the rate of polymerization on the nature of the solvent arises partly from the solvent dependence of the propagation rate constant, and that the rate of initiation is not influenced by the properties of the solvent.
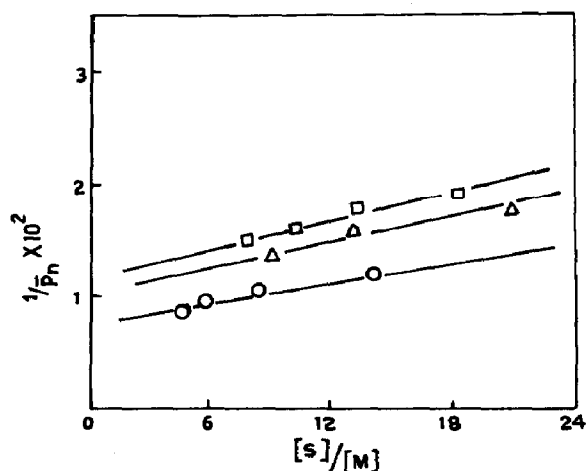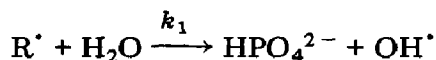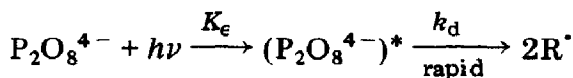

Fig. 6. Plot of $1/\bar{p}_n$ $vs.$ [S]/[M]: ○, hexane; △, dioxan; □, ethanol.
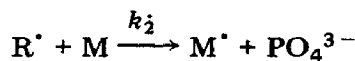
3.5. Mechanism

The chemistry of peroxide compounds has been reviewed in a number of monographs and reviews [5 - 12]. Peroxides contain two adjacent oxygen atoms with overlapping lone-pair orbitals. The average bonding energy is about 34 kcal mol^{-1}. On excitation by the 313 and 254 nm spectral lines of the mercury arc, excess energy of as much as 56 kcal mol^{-1} and 78 kcal mol^{-1} respectively is carried away by the primary radicals.

The first step on absorption of incident light involves the excitation of the PP molecules, which decompose to yield the phosphate ion radical. This phosphate ion radical may then interact with a water molecule to produce the $OH^{\cdot}$ radical ($R^{\cdot} \equiv PO_4^{2-\cdot}$):
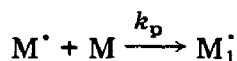
$$P_2O_8^{4-} + h\nu \xrightarrow{K_\epsilon} (P_2O_8^{4-})^* \xrightarrow[\text{rapid}]{k_d} 2R^{\cdot}$$

$$R^{\cdot} + H_2O \xrightarrow{k_1} HPO_4^{2-} + OH^{\cdot}$$

From the above reaction mechanism it is evident that the $R^{\cdot}$ or $OH^{\cdot}$ radicals and/or both the radicals might initiate polymerization, but from the dye partition technique developed by Saha et al. [26] it was observed that the poly(methyl methacrylate) does not contain an OH group. Hence the initiation is due to phosphate ion radical, as elaborated in the following mechanism.
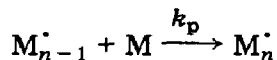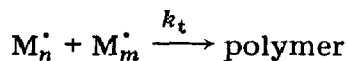
Initiation

$$R^{\cdot} + M \xrightarrow{k_2} M^{\cdot} + PO_4^{3-}$$

Propagation

$$M^{\cdot} + M \xrightarrow{k_p} M_1^{\cdot}$$

and so on until

$$M_{n-1}^{\cdot} + M \xrightarrow{k_p} M_n^{\cdot}$$

Mutual termination

$$M_n^{\cdot} + M_m^{\cdot} \xrightarrow{k_t} \text{polymer}$$

Termination by primary radical

$$M_n^{\cdot} + R^{\cdot} \xrightarrow{k_t'} \text{polymer}$$

On making the usual assumption that stationary state conditions hold for free radicals or radical chains and that the rate constants for propagation and termination are independent of chain length, the following rate expressions have been derived. For example, for mutual termination

$$\frac{d[R^{\cdot}]}{dt} = 0 \qquad \frac{d[M_n^{\cdot}]}{dt} = 0$$

$$\frac{d[R^{\cdot}]}{dt} = K_{\epsilon}k_d[P_2O_8{}^{4-\cdot}]h\nu - k_1[R^{\cdot}] = 0$$

or

$$[R^{\cdot}] = \frac{K_{\epsilon}k_d[P_2O_8{}^{4-}]h\nu}{k_1}$$

$$\frac{d[M_n^{\cdot}]}{dt} = k_{\dot2}[R^{\cdot}][M] - k_t[RM_n^{\cdot}]^2 = 0$$

or

$$[RM_n^{\cdot}] = \left(\frac{k_{\dot2}}{k_t}[R^{\cdot}][M]\right)^{1/2}$$

$$R_p = k_p\left(\frac{K_{\epsilon}k_d k_{\dot2}h\nu}{k_1 k_t}\right)^{1/2}[P_2O_8{}^{4-}]^{1/2}[M]^{3/2}$$

If the termination were due to primary radical $R^{\cdot}$ then the rate expression for R_p would be

$$R_p = \left(\frac{k_p k_{\dot2}}{k_t'}\right)[M]^2$$

which indicates that the plots of R_p vs. $[M]^2$ should be linear. But the plots of R_p vs. $[MMA]^{3/2}$ (Fig. 4) and R_p vs. $[PP]^{1/2}$ (Fig. 2) based on our experimental observations are linear, indicating the termination to be mutual.

Acknowledgment

References

1 R. J. Lussier, W. M. Risen, Jr., and J. O. Edwards, *J. Phys. Chem.*, 74 (1970) 4039.
2 P. L. Nayak, S. Lenka and M. K. Mishra, *J. Polym. Sci.*, 19 (3) (1981) 839.
3 S. Lenka, P. L. Nayak and A. K. Dhal, *J. Polym. Sci.*, 10 (1981) 211.
4 P. L. Nayak, S. Lenka and A. K. Dhal, *J. Makromol. Chem.*, 1 (1980) 313.
5 A. G. Davies, *Organic Peroxides*, Butterworth, London, 1961.
6 J. O. Edwards (ed.), *Peroxide Reaction Mechanisms*, Wiley-Interscience, New York, 1962.
7 E. G. E. Hawkins, *Quart. Rev. (London)*, 4 (1950) 251.
8 E. G. E. Hawkins, *Organic Peroxides*, Van Nostrand, Princeton, NJ, 1961.
9 J. E. Leffler, *Chem. Rev.*, 45 (1949) 385.

10 W. Machu, *Wasserstoffperoxyd*, Springer, Vienna, 1951, 2nd edn.

11 N. A. Miles, in R. E. Kirk and D. Othmer (eds.), *Encyclopedia of Chemical Technology*, Vol. 10, Wiley-Interscience, New York, 1953, p. 58.

12 G. A. Sofer, A. G. H. Dietz and E. A. Hauser, *Ind. Eng. Chem.*, 45 (1953) 2743.

13 C. J. Battaglia, *Ph.D. Thesis*, Brown University, U.S.A., 1962.

14 M. C. R. Symons, in J. C. Edwards (ed.), *Peroxide Reaction Mechanisms*, Wiley-Interscience, New York, 1962.

15 A. Haim and W. K. Wilmarth, in J. O. Edwards (ed.), *Peroxide Reaction Mechanisms*, Wiley-Interscience, New York, 1962, p. 176 ff.

16 P. L. Nayak, S. Lenka and M. K. Mishra, *J. Appl. Polym. Sci.*, 25 (1980) 63.

17 P. L. Nayak, S. Lenka and M. K. Mishra, *Angew. Makromol. Chem.*, 84 (1980) 183.

18 P. L. Nayak, S. Lenka and M. K. Mishra, *J. Polym. Sci.*, 18 (1980) 2247.

19 P. L. Nayak, S. Lenka and M. K. Mishra, *J. Appl. Polym. Sci.*, 26 (1981) 733.

20 T. G. Fox, J. B. Kinsinger, H. F. Mason and I. M. Schuele, *Polymer*, 3 (1962) 71.

21 A. V. Tobolsky and L. R. Matlak, *J. Polym. Sci.*, 55 (1961) 49.

22 G. M. Burnett, W. S. Dailey and J. M. Pearson, *Trans. Faraday Soc.*, 61 (1965) 1216.

23 D. B. Anderson, G. M. Burnett and A. C. Gowan, *J. Polym. Sci. A*, 1 (1963) 1465.

24 G. Henrici-Olive and S. Olive, *Makromol. Chem.*, 96 (1966) 221.

25 C. H. Bamford and S. Brumby, *Makromol. Chem.*, 105 (1967) 122.

26 M. K. Saha, P. Ghosh and S. R. Palit, *J. Polym. Sci. A*, 2 (1964) 1366.