European Polymer Journal, Vol. 16, pp. 763 to 767
© Pergamon Press Ltd 1980. Printed in Great Britain

0014-3057/80/0801-0763$02.00/0

NON-IDEALITY IN VINYL POLYMERIZATION—VIII

RETARDED POLYMERIZATION OF METHYL METHACRYLATE IN PRESENCE OF *p*-BENZOQUINONE INITIATED BY AZOBISISOBUTYRONITRILE

P. C. Deb* and S. K. Kapoor
Defence Science Laboratory, Metcalfe House, Delhi-110 054, India

(*Received* 2 *October* 1979)

Abstract—Detailed kinetic analysis of AIBN-initiated polymerization of methylmethacrylate in presence of *p*-benzoquinone has been reported. Primary radical transfer, whereby a primary radical transfers its radical reactivity to a transfer agent, has been considered along with macroradical transfer. It is found that the former process is quite appreciable in the system and must be allowed for to arrive at accurate values of transfer constants. Values of transfer constants for both primary radicals and macroradicals towards benzoquinone, and characteristic constants for degradative chain transfer and primary radical transfer have been evaluated applying the mathematical treatment developed previously. The mode of termination of macroradicals by fairly stable microradicals formed as a result of transfer has also been discussed.

INTRODUCTION

In Part VII of the series [1] on non-ideality in vinyl polymerization, we developed detailed mathematical formulations of the kinetics of retarded free-radical vinyl polymerization. Both macro-radical and primary radical transfers were taken into consideration. Primary radicals because of their small size and structure may be much more reactive than a macroradical towards a retarder and this high reactivity may be important in spite of low concentrations in deciding the course of retarded polymerization. Elaborate kinetic treatment of retarded polymerization was first given by Kice [2] and later modified by Atkinson *et al.* [3] Finally Deb [4] derived mathematical relationships which could dispense with both uninhibited rate [2] and trial and error method [3]. However, it was assumed that primary radicals do not enter into transfer reaction with the retarder molecules. Bevington *et al.* [5] have shown that the reactivity of primary radicals may be much higher than that of a macroradical and hence cannot be neglected. Unfortunately no straightforward kinetic relationship was available to afford a reliable value for the constant characterizing primary radical transfer. We report here the results on the retarded polymerization of methyl methacrylate (MMA) initiated by azobisisobutyronitrile (AIBN) in presence of *p*-benzoquinone (BQ). The results have been treated according to the formulations developed in the earlier communication [1].

EXPERIMENTAL

Purifications of MMA and AIBN has already been described; *p*-benzoquinone (BQ) was first recrystallized from *n*-octane, sublimed thrice and stored in the dark.

Polymerization of MMA was followed dilatometrically. Requisite amounts of inhibitor and initiator were dissolved in monomer and filled into a dilatometer having a bulb capacity of about 10 ml and capillary radius of 0.8 mm. The contents were then degassed by repeated freeze/thawing and then sealed. After the contents have melted, the dilatometers were placed in a bath maintained at 50°. The fall of the meniscus was then followed with a cathetometer and the rate of polymerization was calculated.

RESULTS AND DISCUSSION

Dilatometric determinations of rates for all concentrations of AIBN showed no sign of inhibition for the polymerization of MMA in the presence of BQ. Table 1 shows rates of polymerization R_p covering a wide range of concentration of AIBN for three concentrations of BQ. Figures 1–3 show plots of $[I][M]^2/R_p^2$ vs $R_p/[M]^2$ for three concentrations of BQ. The curves are typical of degradative chain transfer. Similar curves were obtained for retarded polymerizations of vinyl chloride [4] and vinyl acetate [7]. Initial slopes and intercepts are shown in Table 2; expressions for these quantities are as follows [1]:

Intercept

$$= \frac{1}{A}\left[1 + 2C_s\,\frac{k_p^2}{k_t}\cdot\frac{k_{rts}}{k_{is}k_p}\cdot\frac{[\mathrm{BQ}]}{[\mathrm{M}]}\right] \qquad (1)$$

Initial slope

$$= \frac{A_1}{A}\left[\frac{k'_{rts}}{k'_{is}k_p}\cdot\frac{2C'_s[\mathrm{BQ}]/[\mathrm{M}]}{(1 + C'_s([\mathrm{BQ}]/[\mathrm{M}])}-\frac{k_{rts}}{k_{is}k_p}\right] \qquad (2)$$

where

$$A = \frac{2f_k k_d k_p^2}{k_t},\quad A_1 = \text{Intercept}\cdot A - 1.$$

---

* Present address: Naval Chemical and Metallurgical Laboratory, Naval Dockyard, Bombay-400 023. India.

Table 1. Values of rate of polymerization for MMA-BQ-AIBN for systems at 50°

$[I]\ 10^3$ (mol/l)	$10^5 R_p$ mol/l/sec $[BQ] = 4.04 \times 10^{-4}$ (mol/l)	 $[BQ] = 2.02 \times 10^{-4}$ (mol/l)	 $[BQ] = 1.01 \times 10^{-4}$ (mol/l)
9.150	3.863	7.343	8.850
6.100	2.987	4.866	6.432
4.570	2.497	3.865	5.290
3.050	1.617	2.926	3.800
2.440	1.248	2.544	3.390
1.830	0.992	2.075	2.820
1.230	0.650	1.569	2.070
0.915	0.559	1.072	1.600
0.610	0.423	0.850	1.230
0.426	0.345	0.658	0.878
0.183	0.228	0.341	0.425

Table 2. Slopes and intercepts of $[I][M]^2/R_p^2$ vs $R_p/[M]^2$ for MMA-BQ-AIBN system at 50°

[BQ] (mol/l)	Slope	Intercept
4.04×10^{-4}	2.38×10^{16}	385×10^7
2.02×10^{-4}	1.60×10^{16}	195×10^7
1.01×10^{-4}	0.84×10^{16}	105×10^7

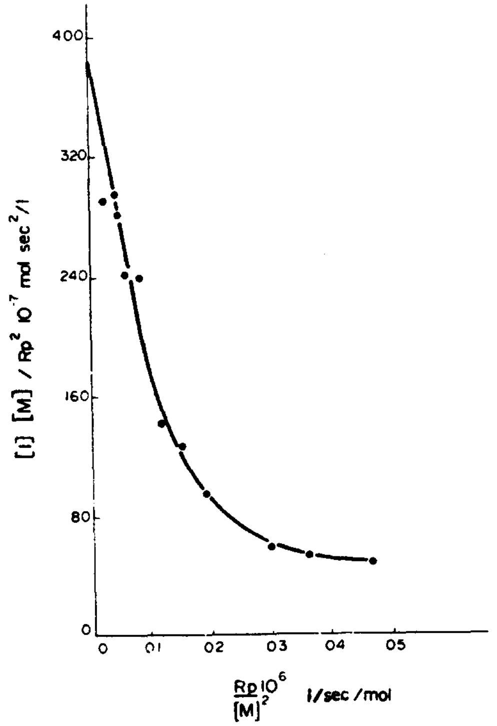


Fig. 1. Plot of $\frac{[I][M]^2}{R_p^2}$ vs $\frac{R_p}{[M]^2}$ for MMA-AIBN-BQ system at 50°[BQ] = 4.04×10^{-4} mol/l.

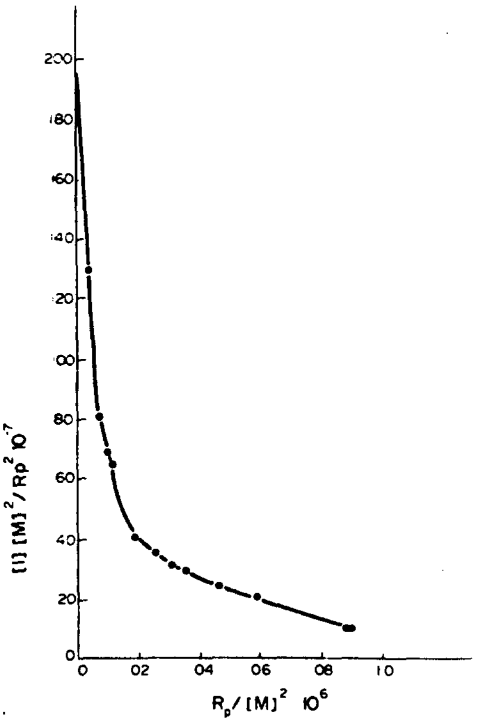


Fig. 2. Plot of $\frac{[I][M]}{R_p^2}$ vs $\frac{R_p}{[M]^2}$ for MMA-AIBN-BQ system at 50°[BQ] = 2.02×10^{-4} mol/l.

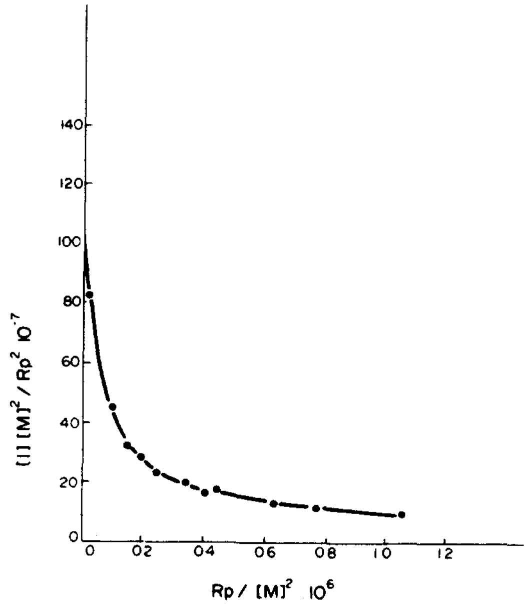


Fig. 3. Plot of $\frac{[I][M]^2}{R_p^2}$ vs $\frac{R_p}{[M]^2}$ for MMA–AIBN–BQ system at 50°[BQ] = 1.01×10^{-4} mol/l.

C_s and C'_s are the transfer constants of BQ with respect to macroradical and primary radical respectively, being k_{trs}/k_p and k'_{trs}/k_i according to the following reactions

$$I \xrightarrow{k_d} 2R^{\cdot}$$

$$\begin{tikzcd} & & P_1^{\cdot} \\ R^{\cdot} + BQ \arrow[r, "k'_{trs}"] & RBQ^{\cdot} \arrow[ur, "k'_{is}", "+M"'] \arrow[dr, "k'_{rts}", "+P^{\cdot}"'] & \\ & & \text{Dead polymer} \end{tikzcd}$$

$$R^{\cdot} + M \xrightarrow{k_i} P_1^{\cdot}$$

$$P_1^{\cdot} + M \xrightarrow{k_p} P_2^{\cdot}$$

$$P_2^{\cdot} + M \xrightarrow{k_p} P_3^{\cdot}$$

$$\begin{tikzcd} & & P_1^{\cdot} \\ P^{\cdot} + BQ \arrow[r, "k_{trs}"] & PBQ^{\cdot} \arrow[ur, "k_{is}", "+M"'] \arrow[dr, "k_{rts}", "+P^{\cdot}"'] & \\ & & \text{Dead polymer} \end{tikzcd}$$

$k_{rts}/k_{is}k_p$ and $k'_{rts}/k'_{is}k_p$ represent the characteristic constants of degradative transfer of macroradical and primary radical respectively. RBQ$^{\cdot}$ and PBQ$^{\cdot}$ are not necessarily addition products and may represent mixture of a neutral molecule and a quinone radical. In the case of a mixture, they would represent quinone radical.

Assuming that primary radical transfer is absent and retardation is only due to macroradical transfer, the intercept and slope are given by

Intercept

$$= \frac{1}{A}\left[1 + 2C_s \frac{k_p^2}{k_t} \cdot \frac{[BQ]}{[M]} \cdot \frac{k_{rts}}{k_{is}k_p}\right]$$

Slope

$$= \frac{1}{A} \cdot 2C_s \frac{k_p^2}{k_t} \frac{[BQ]}{[M]} \cdot \frac{k_{rts}^2}{k_{is}^2 k_p^2}$$

So that, $\frac{k_{rts}}{k_{is}k_p} = \frac{\text{Slope}}{\text{Intercept} - (1/A)}$.

The average values of constants so obtained are:

$$\frac{2f_k k_d k_p^2}{k_t} = 2.2 \times 10^{-8}\ \text{l/mol/sec}^2,$$

$$\frac{k_{rts}}{k_{is}k_p} = 7 \times 10^6\ \text{mol/sec/l and } C_s = 20 \text{ at } 50°.$$

Primary radical transfer would alter the expression for the slope only and hence the values of $2 f_k k_d k_p^2/k_t$ and $C_s . k_{rts}/k_{is}k_p$ would be correct. Individual values of C_s and of $k_{rts}/k_{is}k_p$ would be in error if obtained as above when primary radical transfer occurs. Using the literature value [8] of $k_p^2/k_t = 7.020 \times 10^{-3}$ l/mol/sec, $k_d = 2.10 \times 10^{-6}$/sec and $f_k = 0.70$ [9], we obtain $2f_k k_d k_p^2/k_t = 2.16 \times 10^{-8}$ l/mol/sec^2; in excellent agreement with the value obtained in the present study.

Utilising the intercepts and initial slopes for the three ratios of [BQ]/[M], we have found the values of various constants using relationships (1) and (2) (see Table 3).

The product $C_s . k_{trs}/k_{is}k_p$ which equals 138×10^6 mol/sec/l agrees excellently with the value of 140×10^6 obtained from the intercepts alone. However, individual values differ slightly and the value of C_s obtained assuming only macroradical transfer is higher by about 25%. This can be explained the fact that, when primary radical transfer is not considered, the total retardation is considered in terms only of macroradical transfer and hence given a higher weighting. The value of C'_s (ratio of rate constant of primary radical transfer k'_{trs} to k_i, the rate constant of initiation) is about 3×10^3 times higher than the transfer constant of BQ towards the macroradical. A value of about 3500 for C'_s was reported for styrene–BQ–AIBN system at 60° by Bevington *et al.* [5]. Thus it seems that the reaction between primary radicals and BQ molecules cannot be neglected, particularly if the monomer is comparatively unreactive. A higher value for MMA than for styrene can be explained because of lower reactivity of MMA and higher reactivity of PMMA radical. Comparing the relative rates

Table 3. Values of various characteristic constants in the retarded polymerization of MMA–AIBN with BQ

$\frac{k_{rts}}{k_{is}k_p}$	$\frac{k'_{rts}}{k'_{is}k_p}$	C_s	C'_s
8.4×10^6	4.3×10^6	16.4	5×10^4

$\frac{k_{rts}}{k_{is}k_p}$ represents the characteristic constant of degradative chain transfer.

$\frac{k'_{rts}}{k'_{is}k_p}$ represents the characteristic constant of retardation due to primary radical transfer.

C_s and C'_s represent transfer constants of BQ with PMMA radicals and primary radicals respectively.

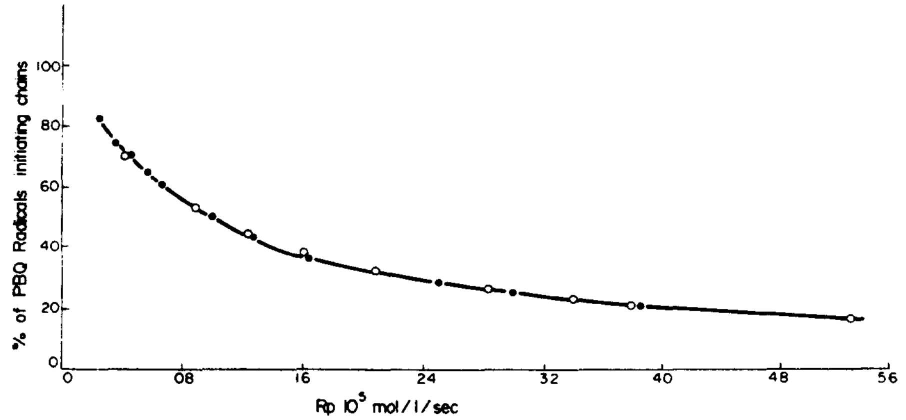


Fig. 4. Variation of the extent of PBQ radicals initiating chains with rate of polymerization for MMA–BQ–AIBN system at 50°. ——for [BQ] = 2.02 × 10^{-4} mol/l; (●) for 4.04 × 10^{-4} mol/l and (○) for 1.01 × 10^{-4} mol/l of BQ.

of initiation (R_i) and transfer (R_{tr}) by primary radicals, we find for 2.02 × 10^{-4} mol/l of BQ,

$$\frac{R_{tr}}{R_i} = \frac{k'_{trs}}{k_i}\frac{[\mathrm{R}^{\cdot}][\mathrm{BQ}]}{[\mathrm{R}^{\cdot}][\mathrm{M}]} = C'_s\frac{[\mathrm{BQ}]}{[\mathrm{M}]} = 1.09$$

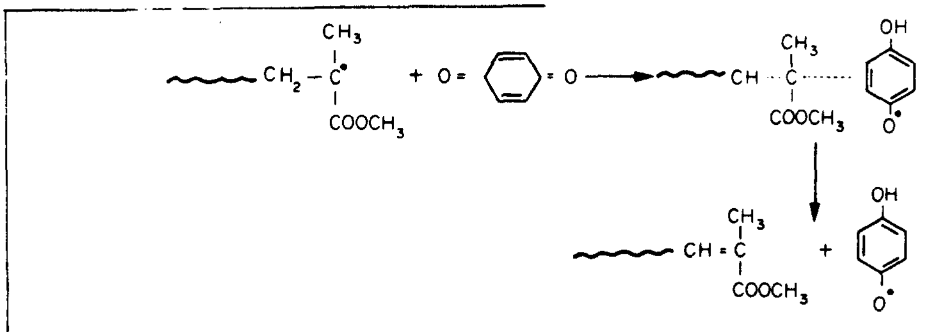
This shows that, at this concentration of BQ, rate of consumption of primary radicals by retarder molecules equals that by monomer. Thus it is evident that primary radical transfer in BQ-retarded polymerisation of MMA cannot be neglected because this process contributes appreciably towards the total retardation of the overall rate of polymerization. It is evident therefore that, if the total efficiency of the initiator is 0.70, the efficiency of initiation (f_i) is reduced to about 0.35 because of primary radical transfer.

A value of C_s of 16.4 is substantially higher than reported by Bagdasar'ian and Sinitsina [10]. These authors determined their values from molecular weight measurements and this is not a reliable method as pointed by Eastmond *et al* [3], particularly when rate data are not available at sufficiently low rates of initiation.

We now proceed to analyse the termination processes by the radical formed as a result of transfer by macroradicals. The fraction F of PBQ$^{\cdot}$ or BQ$^{\cdot}$ radicals which engage in re-initiation is given by

$$F = \frac{k_{is}[\mathrm{PBQ}^{\cdot}][\mathrm{M}]}{k_{is}[\mathrm{PBQ}^{\cdot}] + k_{rts}[\mathrm{PBQ}^{\cdot}][\mathrm{P}^{\cdot}]} = \frac{1}{1 + (k_{rts}/k_{is}k_p)\cdot R_p/[\mathrm{M}]^2}. \quad (3)$$

Figure 4 shows the variation of F, in%, with R_p calculated utilizing the value of $k_{rts}/k_{is}k_p$ derived earlier. The solid line represents the curve for 2.02 × 10^{-4} mol/l of BQ. The agreement of data for 4.04 × 10^{-4} mol/l and 1.01 × 10^{-4} mol/l of benzoquinone with those for 2.02 × 10^{-4} mol/l is excellent and shows the applicability of the method and the reliability of rate data. The extent of re-initiation increases with decrease in the rate of polymerization because the concentration of macroradicals at low rates of polymerisation is low and the quinone radical survives for an appreciable time and thus is able to enter into re-initiation. Using a value of 460 for k_p, we obtain $k_{rts}/k_{is} = 3.86 \times 10^9$ or $k_{is} = 2.59 \times 10^{-9} k_{trs}$. Assuming that k_{rts} lies in the range 10^6–10^{10}, the two extremes corresponding to macro-macro and micro-macro radical deactivation, k_{is} lies in the range 10^{-4}–10^{-1}. A value in the vicinity of 10^{-1} seems to be reasonable in view of the extent of re-initiation just described. The likely value for k_{rts} can then be taken as 10^9–10^{10} which corresponds to micro-micro or micro-macro radical reactions. This implies that the result of transfer is a separate micro-radical rather than a macro-radical having a quinone unit at the end. This may be achieved through disproportionation as follows:



In primary radical transfer a similar treatment cannot be applied as the radical produced by transfer is also a small radical irrespective of combination or disproportionation. The more likely radical produced in primary radical transfer would be an addition product because of the absence of methylene group in the primary radical.

Thus it is seen that, provided mathematical formulations of detailed kinetic analysis of retarded polymerization are available, it is possible to obtain reliable values of all the characteristic constants including that of primary radical transfer. Tracer studies and molecular weight measurements may substantiate the conclusions of kinetic analysis but simple rate measurements are sufficient to elucidate all aspects of retarded polymerization of vinyl monomers.

Acknowledgements—The authors thank Dr S. R. Chatterjee, Principal Scientific Officer for valuable criticism and Dr A. K. Sreedhar, Director, Defence Science Laboratory, for permission to publish this paper.

REFERENCES

1. P. C. Deb, *Eur. Polym. J.* **16**, 759 (1980).
2. J. L. Kice, *J. Am. chem. Soc.* **76**, 6274 (1954).
3. W. H. Atkinson, C. H. Bamford and G. C. Eastmond, *Trans. Faraday Soc.* **66**, 1446 (1970).
4. P. C. Deb, *Eur. Polym. J.* **11**, 31 (1975).
5. J. C. Bevington, N. A. Ghanem and H. W. Melville. *J. chem. Soc.* 2822 (1955).
6. P. C. Deb and S. K. Kapoor, *Eur. Polym. J.* **15**, 477 (1979).
7. P. C. Deb and S. Ray, *Eur. Polym. J.* **14**, 607 (1978).
8. I. Bandrup and E. H. Immergut. *Polymer Handbook*. Interscience, New York (1966).
9. P. C. Deb and G. Meyerhoff, *Eur. Polym. J.* **10**, 709 (1974).
10. Kh. S. Bagdasar'ian and Z. A. Sinitsina. *J. Polym. Sci.* **52**, 31 (1961).