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# **Bifunctional Peroxide Initiated Vinyl Polymerisation**

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#### SUMMARY:

The kinetics of polymerisation of methyl methacrylate in bulk have been studied at  $55^{\circ}$ C.,  $60^{\circ}$ C., and  $70^{\circ}$ C. using a bifunctional peroxide, phthaloyl dibenzoyl peroxide as initiator. It is shown that the phthaloyloxy diradicals from the initiator do not contribute measurably to the production of high polymer in the system, and that the mono-radicals are the initiating species. The results conform to the kinetic equations derived for mono-radical initiators. The kinetic constants for the polymerisation reaction and decomposition of the initiator have been evaluated.

### ZUS AMMENFASSUNG:

Die Blockpolymerisation von Methacrylsäuremethylester wird mit einem bifunktionellen Peroxyd, Phthaloyldibenzoylperoxyd, initiiert und die Kinetik der Polymerisation bei 55 °C, 60 °C und 70 °C untersucht. Es wird gezeigt, daß die Phthaloyloxy-Diradikale des Initiators praktisch keine Polymeren erzeugen, sondern daß Monoradikale die Reaktionsketten starten. Die Ergebnisse stimmen mit den für Monoradikal-Initiatoren abgeleiteten kinetischen Gleichungen überein. Die kinetischen Konstanten für die Polymerisationsreaktion und für die Zersetzung des Initiators werden angegeben.

A recent interest is concerned with the possibility of achieving diradical initiation and propagation in polymerisation reactions<sup>1</sup>). The usual free radical initiators in vinyl polymerisations function by producing monoradicals. With initiators yielding diradicals instead, which can propagate polymerisation at both radical ends, high rates can be achieved without sacrificing chain length of the polymers formed. It was originally postulated that pure thermal and photochemical polymerisations proceeded via diradical initiation <sup>1a</sup>). But theoretical calculations for the thermal polymerisation of pure styrene<sup>2,3</sup>) have shown that if diradicals were formed in the initiation process, the highly competitive intramolecular termination reaction would predominate precluding the possibility of growth of many diradicals to long chain polymers. In photopolymerisation the

<sup>1)</sup> W. HAHN and A. FISCHER, Makromolekulare Chem. 21 (1956) 77, 106.

<sup>&</sup>lt;sup>1a</sup>) P. J. FLORY, J. Amer. chem. Soc. 59 (1937) 241.

<sup>&</sup>lt;sup>2</sup>) R. N. HAWARD, Trans. Faraday Soc. 46 (1950) 204.

<sup>&</sup>lt;sup>3</sup>) B. H. ZIMM and J. K. BRAGG, J. Polymer Sci. 9 (1952) 476.

relationship, determined experimentally between the degree of polymerisation of the polymer formed and the overall rate, led to the conclusion that long chain photopolymer resulted from growing monoradicals<sup>4,5</sup>), no evidence has also been found that thermal polymer is produced by diradical propagation.

Efforts have been directed therefore to find a true diradical source and cyclic peroxides<sup>6</sup>), cyclic azo<sup>7</sup>) and disulphide<sup>8</sup>) compounds were tried as initiators but did not yield the desired result of production of high polymers from diradicals. Hence an investigation of the behaviour of a difunctional peroxide as initiator seemed to be pertinent. Phthaloyl dibenzoyl peroxide which would decompose as follows to give a phthaloyloxy diradical and two benzoyloxy monoradicals per molecule has been used in the present study for initiation of polymerisation of methyl methacrylate in bulk at three temperatures, 55 °C., 60 °C., and 70 °C.



The primary decomposition may be followed by some elimination of  $CO_2$ . The results have been compared with those obtained using monoradical initiators, e.g. benzoyl peroxide which has been studied extensively.

#### Experimental

The initiator, phthaloyl dibenzoyl peroxide (PBP) was prepared by shaking together cold chloroform solutions of perbenzoic acid and phthaloyl chloride with ice cold aqueous alkali<sup>9</sup>). The peroxide in the chloroform layer was recovered by evaporation under reduced pressure after drying and recrystallized from benzene-petroleum ether below 50°C. The pure peroxide (m.p. 119°C.) estimated iodometrically using glacial acetic acid as the solvent assayed at better than 98% purity.

The monomer methyl methacrylate (obtained from Rohm and Haas Co.) was purified by fractionation retaining the middle cut, followed by repeated distillations under reduced pressure in an atmosphere of oxygen free nitrogen. The pure monomer was stored in an amber coloured ground glass stoppered bottle at 5°C.

- <sup>6</sup>) K. E. RUSSEL, J. Amer. chem. Soc. 77 (1955) 4814.
- 7) C. G. OVERBERGER and M. LAPKIN, J. Amer. chem. Soc. 77 (1955) 4651.
- 8) K. E. RUSSEL and A. V. TOBOLSKY, J. Amer. chem. Soc. 76 (1954) 395.
- 9) H. WIELAND and G. RAZUVAJEW, Liebigs Ann. Chem. 480 (1930) 157.

<sup>4)</sup> B. BAYSAL and A. V. TOBOLSKY, J. Polymer Sci. 8 (1952) 529.

<sup>&</sup>lt;sup>5</sup>) D. H. JOHNSON and A. V. TOBOLSKY, J. Amer. chem. Soc. 74 (1952) 938.

Polymerisations were carried out by the sealed ampoule technique. The initiator-monomer systems were taken in pyrex glass ampoules (10 cc. capacity); cooled in a freezing mixture and deaerated with oxygen free nitrogen<sup>10</sup>) before being sealed and thermostated at the required temperatures for suitable reaction times. The tubes were chilled before being opened and the contents quantitatively transferred with acetone as diluent to beakers where the polymer was precipitated with methanol, filtered, washed and dried at 60 °C. to constant weight. The rates were calculated from the weights of the dried polymers. Conversions were always limited to be less than 15%.

The polymer samples were purified by further reprecipitation with methanol from acetone and intrinsic viscosities  $[\eta]$  determined from relative viscosities of the polymer samples in benzene solution measured in an OSTWALD-viscometer at 25°C. Values of  $[\eta]$  were converted to degree of polymerisation using the following relationship<sup>11</sup>).

$$\overline{\mathbf{P}}_{n} = 2.81 \cdot 10^{3} [\eta]^{1.32}$$

## **Results** and Discussion

The dependence of overall rate of polymerisation  $(R_p)$  of methyl methacrylate on the square root of the initiator concentration,  $[I]^{0.5}$  is shown in Fig. 1. It is observed that over a wide range of variation in the latter, a strictly linear relationship is obtained as in the case of simple monoradical initiators. It must be inferred that the initiator efficiency is independent of the concentration of the initiator, since otherwise  $R_p$  would be proportional to a power of [I] other than 0.5.



Fig. 1. Variation of rate with initiator concentration. A: 60°C.; B: 70°C.; C: 55°C.

For the case of monoradical initiated polymerisation in bulk, in the absence of chain transfer to the initiator, the general relation between

<sup>11</sup>) J. H. BAXENDALE, S. BYWATER, and M. G. EVANS, J. Polymer Sci. 1 (1946) 237.

<sup>&</sup>lt;sup>10</sup>) L. F. FIESER, J. Amer. chem. Soc. 46 (1924) 2639.

the number average degree of polymerisation  $\bar{P}_n$  and overall rate of polymerisation  $R_p$  is

$$\frac{1}{\overline{P}_n} = C_m + \frac{A'R_p}{[M]^2}$$
(monoradical line) (1)

where  $C_m$  is the constant for chain transfer to monomer, [M] is the initial monomer concentration and

$$\mathbf{A'} = \frac{2\mathbf{k_{td}} + \mathbf{k_{tc}}}{\mathbf{k_p}^2}$$

 $k_p$ ,  $k_{tc}$  and  $k_{td}$  being the specific reaction rates for propagation, combination and disproportionation respectively. But when initiation occurs by diradicals, neglecting ring formation and in the absence of chain transfer to the initiator the following relationship is obtained for  $1/\bar{P}_n$  and  $R_p^{-5}$ ).

$$\frac{1}{\overline{P}_n} = C_m + \frac{k_{td}}{k_p^2 [M]^2} R_p = C_m + \frac{\varkappa}{1+\varkappa} \frac{A'R_p}{[M]^2}.$$
 (2)

where  $\varkappa = k_{td}/k_{td} + k_{tc}$  varies between 0 and 1 according as  $k_{td} = 0$  or  $k_{tc} = 0$ .

The results obtained in this work for the variation of  $1/\tilde{P}_n$  with  $R_p$  (Fig. 2) exactly fit the monoradical line defined by equation (1) and experimentally determined by TOBOLSKY and BAYSAL<sup>4</sup>) for the poly-



Fig. 2. Dependence of 1/Pn on rate of polymerisation at 60 °C.

merisation of methyl methacrylate using the monoradical initiators azobis-isobutyronitrile and benzoyl peroxide at 60 °C. The limiting lines for diradical initiation and propagation assuming  $k_{tc} = 0$  and  $k_{td} = 0$  are

drawn in Fig. 2 for comparison. The very close agreement of the  $1/P_n$ vs.  $R_p$  relationship with the monoradical line (eq. (1)) clearly indicates the absence of any chain transfer to the initiator and also the absence of diradical propagation of polymerisation to form high polymer to any measurable extent. The phthaloyloxy diradical might have been deactivated by self termination resulting in the formation of rings after addition of a few monomer molecules or by transfer with monomer to form monoradicals which can grow to large polymeric molecules. In methyl methacrylate solution the efficiency of cyclic phthaloyl peroxide in producing long chain polymer has been shown to be very low ( $\approx 0.1 \%$ )<sup>6</sup>). So it is unlikely that chain transfer of the diradicals with monomer occurs appreciably in our system. Intramolecular termination of the diradical ends after addition of a few monomeric units must be the predominant mode of deactivation of the diradicals. Coupling of the diradicals to form small rings may also occur to some extent. Though some recent patents have reported the use of cyclic peroxides like succinoyl and phthaloyl peroxides in polymerisations at high temperatures (100-400 °C.) and pressures (25-500 atms.) no evidence has been furnished that the polymerisation proceeded by diradical initiation and propagation<sup>12</sup>). Using cyclic disulphide<sup>8</sup>) and cyclic azo initiators<sup>7</sup>) it has been demonstrated by other workers that few if any of the diradicals formed grew to long chain polymers.



Fig. 3. Dependence of  $1/P_n$  on rate of polymerisation A: 55 °C.; B: 70 °C.

Since the possibility of diradical propagation can be discounted with the initiator used here, the values of A' have been calculated from the slopes of the  $1/\bar{P}_n$  vs  $R_p$  plots (Figs. 2 and 3) using equation 1. The accu-

<sup>&</sup>lt;sup>12</sup>) H. F. PARK, U.S. Patents 2,620,330 (1952); 2,664,416 (1953); C.A. 47, 4130d; 48, 4252i.

racy of the values depend to a great extent on the accuracy of the determination of the degree of polymerisation. Conversion of intrinsic viscosities to  $\mathbf{\tilde{P}}_n$  has been based on the equation of BAXENDALE et al.<sup>11</sup>), which compares very well with that obtained by BAYSAL and TOBOLSKY<sup>4</sup>) for unfractionated polymethyl methacrylate. The values of A' calculated at the three temperatures 55 °C., 60 °C., 70 °C. fit the equation (Fig. 4)

$$A' = 6.54 \cdot 10^{-5} \exp(9.15 \text{ kcal/RT})$$
(3)

This compares favourably with

 $A' = 5.02 \cdot 10^{-5} \exp(9.35 \text{ kcal/RT})$ 

determined by TOBOLSKY and BAYSAL<sup>13</sup>) for methyl methacrylate and

$$A' = 2.59 \cdot 10^{-5} \exp(9.78 \text{ kcal/RT})$$

obtained from the values of the absolute rate constants determined by MATHESON et al.<sup>14</sup>).



Fig. 4. The Arrhenius plots of  $R_i'/[1]$  and A'

Rates of initiation can be computed from<sup>4</sup>)

$$R_{i} = \frac{2 (k_{tc} + k_{td})}{k_{p}^{2} [M]^{2}} R_{p}^{2} = \frac{2 A' K^{2}[I]}{1 + \chi}$$
(4)

<sup>13</sup>) A. V. TOBOLSKY and B. BAYSAL, J. Polymer Sci. 11 (1953) 471.

<sup>&</sup>lt;sup>14</sup>) M. S. MATHESON, E. E. AUER, E. B. BEVILACQUA, and E. J. HART, J. Amer. chem. Soc. 71 (1949) 497.

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where  $\varkappa$  is as in equation (2) and K is defined by

$$\mathbf{R}_{\mathbf{p}} = \mathbf{K}\mathbf{M}[\mathbf{I}]^{0.5} \tag{5}$$

and obtained from the slopes of the plots of  $R_p$  against  $[I]^{0.5}$  in Fig. 1. Values of  $R_i/[I] = R_i (1 + \varkappa)/[I]$  were thus calculated for the three temperatures and  $-\log R_i'/[I]$  plotted against 1/T in Fig. 4. Good linearity is obtained fitting the equation

$$R_i'/[I] = 1.075 \cdot 10^{15} \exp(-30.07 \text{ kcal/RT})$$
 (6)

By the use of radioactive azo-bis-isobutyronitrile as initiator for methyl methacrylate polymerisation ARNETT<sup>15</sup>) has shown by direct experiment that x is close to zero and that termination by combination is predominant. Further an initiator efficiency close to unity and independent of temperature has been indicated for benzoyl peroxide<sup>16</sup>). The results reported in this paper justify the reasonable conclusion that in the present system the diradicals did not measurably contribute to the initiation of polymer chains and that polymerisation with the initiator (PBP) resulted from the two benzoyloxy monoradicals produced for each molecule of the initiator decomposed. Therefore  $R_i'/[I]$  can be equated approximately to 2 k<sub>d</sub>, k<sub>d</sub> being the specific rate of spontaneous decomposition of the peroxide used (PBP). So from equation (6), for (PBP)

$$k_d = 5.375 \cdot 10^{14} \exp(-30.07 \text{ kcal/RT})$$
 (7)

The value of  $k_d$  calculated thus involves an uncertainty factor of two since evidence has not been conclusive for termination by combination alone. There is a wide divergence of opinion with regard to the mechanism of termination predominant with methyl methacrylate. As an example one may quote the disparate results obtained using radioactive initiators by BEVINGTON et al.<sup>17</sup>) who conclude that disproportionation occurs to a much greater extent than combination between polymethyl methacrylate radicals.

The activation energy for the spontaneous decomposition of (PBP) viz. 30.07 kcals. is seen to be of the same order as for benzoyl peroxide ( $\approx$  30.0 kcals.).

<sup>&</sup>lt;sup>15</sup>) L. M. ARNETT and J. H. PETERSON, J. Amer. chem. Soc. 74 (1952) 2031.

<sup>&</sup>lt;sup>16</sup>) A. V. TOBOLSKY and R. B. MESROBIAN, Organic Peroxides, Interscience Publ. Co. New York 1954, p. 156.

<sup>&</sup>lt;sup>17</sup>) J. C. BEVINGTON, H. W. MELVILLE, and R. P. TAYLOR, J. Polymer Sci. 12 (1954) 449; 14 (1954) 463.

The kinetic constants have been summarised in Table 1.

| Temp. °C. | A'    | R <sub>i</sub> '/[I]  | К                     |
|-----------|-------|-----------------------|-----------------------|
| 55        | 81    | 0.891 · 10-5          | $2.345 \cdot 10^{-4}$ |
| 60        | 66.31 | $1.957 \cdot 10^{-5}$ | 3.841 · 10-4          |
| 70        | 44.38 | 7.335 • 10-5          | 9.09 · 10-4           |

Table 1. Kinetic constants for bulk polymerisation of methyl methacrylate initiated by PBP

 $A' = 6.54 \cdot 10^{-5} \exp(9.15 \text{ kcal/RT})$ 

 $R_i'/[I] = 1.075 \cdot 10^{15} exp(-30.07 kcal/RT)$ 

 $K = 6.99 \cdot 10^9 \exp(-20.21 \text{ kcal/RT})$ 

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