Radiochemical studies of free-radical vinyl polymerizations: 7. Polymerization of methyl acrylate

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Termination of poly(methyl acrylate) radicals in benzene solution has been studied by polymerization of the monomer using [^{14}C] azoisobutyronitrile as initiator. When polymerizations were initiated thermally at 60° and 45°C values for the number of initiator fragments per polymer molecule, n, were substantially less than 2 but were dependent upon the rate of initiation, R_i. As R_i was increased n increased, indicating that chain transfer reactions were important. By correcting n for chain transfer it was shown that the polymer radicals most probably terminated by combination. The results at 25°C were more conclusive. With higher rates of photochemical initiation chain transfer reactions became unimportant, values of n were close to 2 and polymer radicals terminated almost exclusively by combination.

INTRODUCTION

Methyl acrylate yields a rather reactive polymer radical and polymerizes much more rapidly than styrene or methyl methacrylate. It has also proved to be a difficult monomer to purify. Consequently there are wide variations in the values of kinetic parameters recorded in the literature[1–9]. The monomer is susceptible to chain transfer reactions and the polymer possesses reactive α-hydrogen atoms which can be abstracted during polymerization to allow formation of branched and probably crosslinked structures[10]. The familiar 'back-biting' reaction, involving abstraction of a hydrogen atom in the δ position with respect to the radical chain end, has also been shown to be likely by its occurrence during thermal degradation of poly(methyl acrylate)[11].

The mode of termination of polymer radicals is also controversial. Consideration of kinetic data led to the conclusion that at 60°C disproportionation was the most prevalent reaction[6]. A similar conclusion was reached by use of the dye interaction technique for determination of carboxyl end groups from the initiator 4,4′-azobis(4-cyano-valeric acid)[12] At 25°C, however, the method of network formation with observation of gel times in a system photoinitiated by manganese carbonyl with poly(vinyl trichloracetate) yielded data consistent with termination by combination of polymer radicals[13].

The present work was undertaken in an attempt to clarify further the mode of termination of polymer radicals. [^{14}C] Azoisobutyronitrile ([^{14}C] AIBN) was used to initiate polymerizations in benzene solutions and polymers were characterized using previously described procedures[14,15].

EXPERIMENTAL

[^{14}C] AIBN, solvents and experimental procedures for thermally initiated polymerizations and for polymer characterization have been described previously[14,16].

Monomer

Methyl acrylate (Fluka, 99.5%) was washed with 2% aqueous ferrous sulphate (x 2), distilled water (x 2), aqueous 2% sodium hydroxide (x 2) and again with distilled water (x 2). The monomer was dried over anhydrous sodium sulphate and distilled at 45°C under reduced nitrogen pressure through an 18 in (457 mm) Vigreux column. The main fraction (70% by volume) was redistilled and a fraction (50%) collected for use. Polymer was formed during the distillations and this was taken as an adequate indication of purity for the first batch of experiments. For most of the experiments, however, the monomer was purified by the following procedure. After the second distillation the monomer was prepolymerized to 6–7% conversion by the action of u.v. light. Pure monomer was then recovered from the mixture under high vacuum and was stored under nitrogen, in the dark, at −15°C.

For calculation of reactant concentrations, the measured monomer densities were 0.952, 0.946, 0.924 and 0.908 g/cm^3 at 20°. 25°, 45° and 60°C, respectively.

Photochemical experiments

The apparatus for photochemical initiation employed a 250 W Mazda ME/D mercury vapour lamp as the u.v. light source. Chance OV1 light filters produced radiation of predominantly 365 nm and this was brought to a parallel beam in the thermostat tank by quartz lenses. The intensity of illumination was adjusted by use of wire gauze and Kodak neutral density filters in the light beams, producing known changes in the rate of initiation.

Dilatometer plots were obtained for all experiments and conversions and rates were calculated from the data of Bengough and Smith[17].

RESULTS

The experimental results are recorded in *Tables 1–5* where

$[M_0]$ is the initial concentration of monomer; $[I_0]$ is the initial concentraton of initiator; P is the extent of polymerization (conversion); R_p is the rate of polymerization; $\bar{M}_n$ is the number-average molecular weight; $\bar{M}_w$ is the weight-average molecular weight; a_p is the ^{14}C specific activity of polymer; R_i is the rate of initiation; k_p is the velocity constant for the propagation reaction; k_t is the velocity constant for the termination reaction; f is the initiator efficiency; and n is the number of initiator fragments per polymer molecule.

The ratios $\bar{M}_n/\bar{M}_w$ recorded in *Table 1* were obtained from gel permeation chromatographs. We are grateful to Mr L. J. Maisey of the Rubber and Plastics Research Association for supplying these data.

The specific activity of the [^{14}C] AIBN was 7.17 x 10^{10} d min^{-1} mol^{-1}.

DISCUSSION

Polymerizations at 60°C

Rates of initiation and initiator efficiencies recorded in *Table 2* show no unusual features and indicate that the initiation reaction was quite normal. However, the values of $k_pk_t^{-1/2}$ are rather variable and this may be due to difficulties associated with the dilatometers not reaching thermal equilibrium until a substantial part of the reaction time had elapsed. For example, at the higher initiator concentration, polymerization was so rapid that reaction times of less than 15 min were required. It was also observed that, at

Table 1 [^{14}C] AIBN-initiated polymerization of methyl acrylate in benzene solution at 60°C ($[M]_0$ = 2.16 mol/l)

Exp. no.	$[I_0]$ (mol/l) X 10^4	P (%)	R_p (mol/l min X 10^3)	$\bar{M}_n$ (X 10^{-6})	$\bar{M}_w/\bar{M}_n$	a_p (d min^{-1} g^{-1}) X 10^{-3}
1	23.68	4.2	8.70	0.53	2.13	58.1
2	13.52	5.9	7.93	0.59	2.26	47.0
3	7.02	6.3	5.66	0.65	–	36.1
4	2.61	4.8	3.06	0.70	–	23.7
5	0.475	7.6	2.04	1.34	–	1.0
6	0.246	7.7	1.44	1.48	–	5.1
7	0.958	7.7	2.89	1.21	–	10.4
8	0.117	7.6	1.01	1.73	–	3.8
9	11.97	12.7	11.90	0.95	–	32.3
10	6.02	7.4	5.29	0.75	–	32.6
11	8.84	14.8	10.95	1.54	3.60	22.4
12	25.48	11.4	14.95	0.83	8.95	41.2
13	14.96	7.8	9.94	0.62	2.15	47.8
14	32.05	5.8	13.1	0.59	–	59.6
15	30.06	4.1	–	–	–	–

Table 2 Calculated values of parameters for methyl acrylate polymerizations at 60°C

Exp. no.	R_i (mol/l min) X 10^7	$k_pk_t^{-1/2}$* ($l^{1/2}$/mol$^{1/2}$ sec$^{1/2}$)	f	n
1	12.12	0.67	0.36	0.85
2	8.93	0.71	0.46	0.77
3	4.90	0.69	0.48	0.65
4	1.74	0.62	0.46	0.46
5	0.342	0.94	0.50	0.27
6	0.176	0.92	0.50	0.21
7	0.718	0.92	0.52	0.35
8	0.092	0.90	0.55	0.18
9	9.22	1.06	0.53	0.85
10	4.13	0.70	0.48	0.67
11	5.89	1.21	0.46	1.40
12	14.80	1.04	0.40	0.95
13	11.40	0.79	0.53	1.03
14	18.74	0.81	0.41	0.98
15	–	0.90	–	–

* $k_pk_t^{-1/2} = R_p(fk_d)^{-1/2}/[M][I]^{1/2}$

Table 3 [^{14}C] AIBN-initiated polymerization of methyl acrylate in benzene solution at 45°C ($[M]_0$ = 2.25 mol/l)

Exp. no.	$[I]_0$ (mol/l) X 10^3	P (%)	R_p (mol/l min) X 10^3	$\bar{M}_n$ (X 10^{-6})	a_p (d.min^{-1}g^{-1}) X 10^{-3}
16	3.17	8.51	4.78	2.17	18.9
17	13.0	9.90	11.70	1.71	35.1
18	19.2	6.18	12.62	1.51	39.4
19	1.60	3.65	2.48	13.2	

Table 4 Calculated values of parameters for methyl acrylate polymerization at 45°C

Exp. no.	R_i (mol/l min) X 10^7	$k_pk_t^{-1/2}$ ($l^{1/2}$/mol$^{1/2}$ sec$^{1/2}$)	f	n
16	2.17	0.83	0.57	1.14
17	9.85	0.96	0.63	1.67
18	11.93	0.96	0.51	1.66
19	1.16	0.87	0.50	0.91

Table 5 [^{14}] AIBN-photoinitiated polymerization of methyl acrylate in benzene solution at 25°C ($[I]_0$ = 1.01 X 10^{-2} mol/l)

Exp. no.	$[M]_0$ (mol/l)	P (%)	R_p (mol/l sec) x 10^4	$\bar{M}_n$ (X 10^{-6})	a_p (d.min^{-1} g^{-1}) X 10^{-4}	R_i (relative)	$k_pk_t^{-1/2}$* ($l^{1/2}$/mol$^{1/2}$sec$^{1/2}$	n
20	2.22	7.6	1.74	2.28	2.81	1.14	0.97	1.8
21	2.20	7.6	2.23	1.56	4.29	1.98	0.91	1.9
22	2.21	8.2	1.38	2.76	2.70	0.66	0.95	2.1
23	2.29	7.8	1.81	2.57	2.73	1.00	1.01	2.0
24	4.01	11.2	4.40	–	–	1.00	–	–
25	4.03	9.9	6.05	–	–	3.00	–	–

* Calculated from the relationship:

$$\bar{P}_n^{-1} = \frac{(k_p^2/k_t)zR_p}{[M]^2} + C_M + C_S\frac{[S]}{[M]} + C_I\frac{[I]}{[M]}$$

assuming $C_M = C_S = C_I = 0$ and $z = 1$ (i.e. that polymer radicals terminate solely by combination)

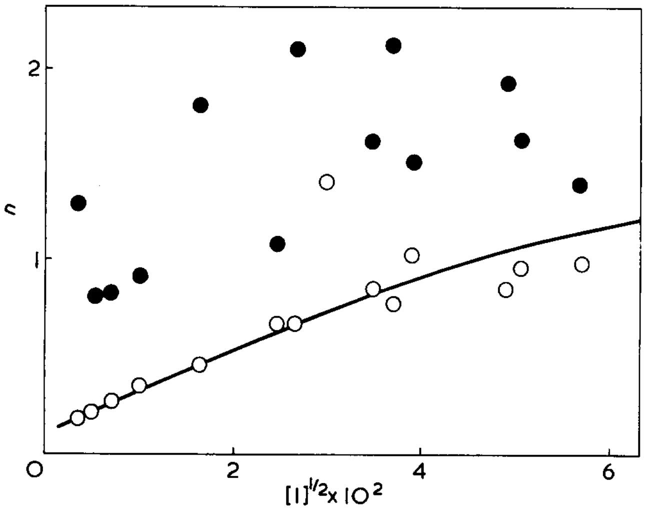

Figure 1 Variation of number of initiator fragments with initiator concentration for polymerization at 60°C: ○, observed values; ●, corrected values

higher monomer concentrations (5.27 mol/l), values of $k_pk_t^{-1/2}$ were higher (~1.7), which indicated that the normal rate equation was not obeyed, in agreement with the work of Burnett and Loan[3]. These experiments could not be pursued at higher monomer concentrations, however, as gel formation occurred even at low (7%) conversions.

Such gel formation is indicative of chain transfer to polymer resulting in branched molecules in which termination by combination causes further crosslinking of the chains. Additional evidence of branching was obtained from gel permeation chromatography of four of the samples recorded in *Table 1*. The ratio $\bar{M}_w/\bar{M}_n$ increased markedly with extent of reaction, indicating the increased formation of branched structures as the polymer concentration increased.

The number of initiator fragments per polymer molecule, *n*, varied with initiator concentration and in general were lower than the value $n = 1$ for termination by disproportionation. These low values almost certainly result from transfer reactions. The very high reactivity of the polymer radicals required low initiator concentrations for reasonable rates of polymerization. Thus, the consequent low concentration of polymer radicals increased the likelihood of transfer events over radical–radical terminations.

As the initiator concentration was increased the effect of transfer on the *n* value was diminished, as can be seen in *Figure 1*. However, it seems likely that even at the highest attainable rates of initiation the value of *n* was lowered because of transfer events.

The data were examined by techniques which seek to negate the effects of chain transfer. In the method of Bailey and Jenkins[18] the gradient of a plot of reciprocal number-average degree of polymerization, $\bar{P}_n^{-1}$, against reciprocal kinetic chain length, ν^{-1}, can be used to indicate the mode of termination. Such a graph is shown in *Figure 2*, where it can be seen that there is a large scatter of points. This scatter is partly due to inaccuracies in the molecular weight measurements. The rapid polymerizations gave rise to polymers of very high molecular weight which in turn gave very small osmotic pressures which were difficult to measure accurately. Nevertheless, it is clear that the data may be divided into two groups. The upper line represents experiments 1–4 while the lower line represents the rest of the data. Both lines have approximately the same gradient of 0.5 which indicates termination predominantly by combination. The intercepts of the lines on the ordinate in *Figure 2* give values for $\bar{P}_0^{-1}$ ($= C_M + C_S\,[S]/[M]$) where C_M and C_S are the chain transfer constants for monomer, M, and solvent, S. A tentative suggestion would be that the monomer used in experiments 1–4 was less pure than that used subsequently and contained a trace of impurity which acted as an efficient transfer agent. In no cases were inhibition or induction periods observed.

Eastmond[19] has suggested that values for $\bar{P}_0^{-1}$ may be used to correct the *n* values for transfer using the relationship:

$$n_{cor} = n\bar{P}_{corr}/\bar{P}_n$$

where:

$$\bar{P}_{corr}^{-1} = \bar{P}_n^{-1} - \bar{P}_0^{-1}$$

Values for n_{corr} are plotted in *Figure 1* and it can be seen that values much closer to 2 are obtained, again indicating that polymer radicals most probably terminate by combination.

Polymerizations at 45°C

Four polymerizations were carried out at 45°C and the results are recorded in *Tables 3* and *4*. Again the calculated values of *n* are affected by transfer (*Figure 3*) though correction for this as described above leads to the conclusion that $n \simeq 2$ and termination is by combination. The plot of $\bar{P}_n^{-1}$ against ν^{-1} (*Figure 4*) has a slope of 0.37. This is outside the range of values predicted for normal termination, though nearer to the value 0.5 at which combination is predicted. The values of $k_pk_t^{-1/2}$ are in reasonable agreement considering the factors mentioned previously.

Polymerizations at 25°C

To reduce still further the effects of chain transfer, the polymerization temperature was reduced to 25°C. At this temperature the thermal dissociation of AIBN is slow, neces-

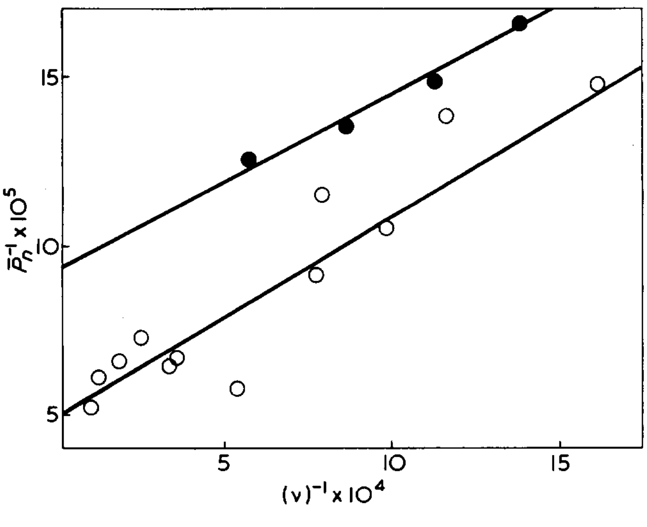

Figure 2 Variation of reciprocal degree of polymerization with reciprocal kinetic chain length at 60°C: ●, experiments 1–4; ○, remaining experiments

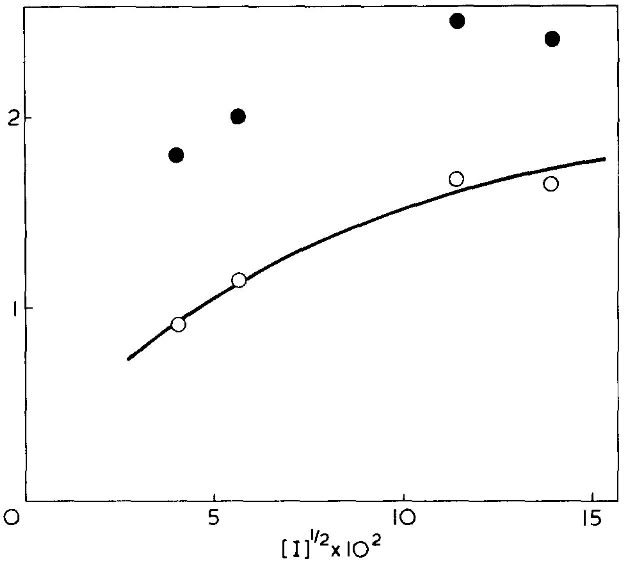

Figure 3 Variation of number of initiator fragments with initiator concentration for polymerization at 60°C; ○, observed values; ●, corrected values

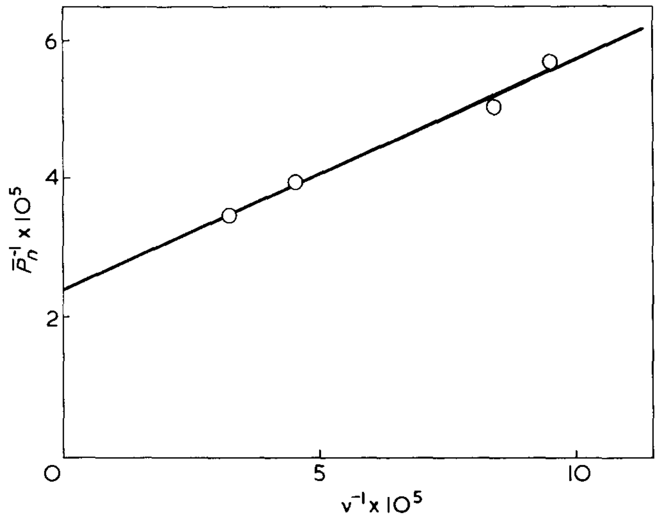

Figure 4 Variation of reciprocal degree of polymerization with reciprocal kinetic chain length at 45°C

sitating the use of photochemical decomposition. The results are recorded in *Table 5*.

To obtain the lowest possible molecular weights, very high rates of initiation were employed. There should have been no problems of equilibration of reaction temperature; however, the high rates and consequent heats of polymerization led to a slight increase in temperature of about 0.8°C. Another problem due to the high initiator concentrations was that thermal decomposition of the AIBN became significant at 25°C. For these reasons the accuracy of the kinetic data is limited. However, a plot of R_p against relative [M] $[R_i]^{1/2}$ (*Figure 5*) was linear and indicated that the termination reaction was normal. The values of k_pk_t are in reasonable agreement and are consistent with termination by combination. A plot of $\bar{P}_n^{-1}$ against R_p (*Figure 6*) is linear and passes through the origin, indicating that chain transfer reactions are unimportant under the conditions used, and the values of n are close to 2 showing that polymer radicals terminate exclusively by combination.

CONCLUSIONS

In methyl acrylate polymerizations in benzene solution at 60° and 45°C the observed numbers of AIBN initiator fragments per polymer molecule were significantly reduced by the occurrence of chain transfer reactions. Corrections to allow for transfer events were applied to the data and gave results supporting the conclusion that termination of poly (methyl acrylate) radicals occurred predominantly by combination.

In the case of photoinitiated polymerizations at 25°C, the values of n were close to 2 as would be expected for polymer radical combination. In these experiments chain-transfer reactions were unimportant.

The relative tendency of polymer radicals to terminate by a particular mode is generally governed by three factors: (i) the number of hydrogens available for disproportionation; (ii) the reactivity of the polymer radical; (iii) the bulkiness of substituents on the radical carbon atom. These factors for poly(methyl acrylate) radicals can be considered by

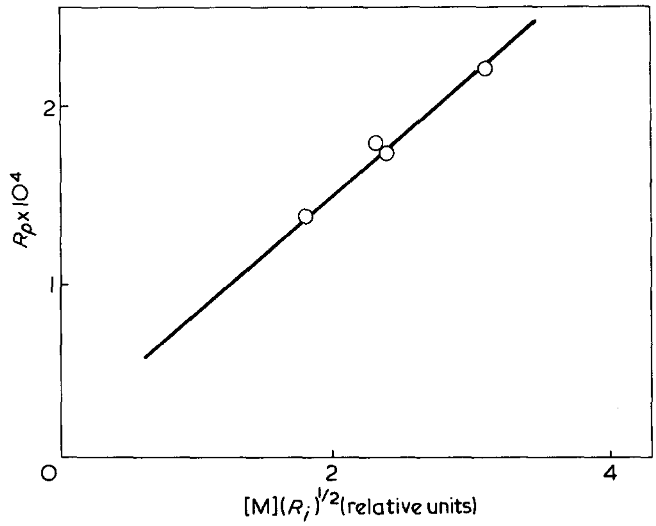

Figure 5 Variation of rate of polymerization with relative [M] $(R_i)^{1/2}$ for photopolymerization at 25°C

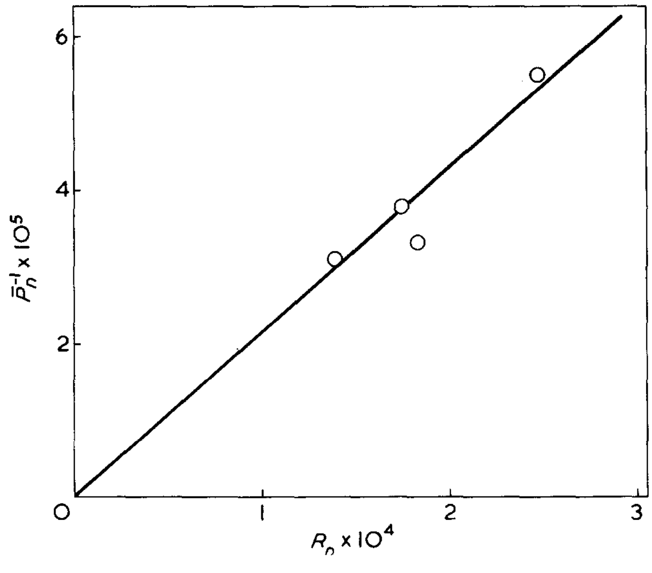

Figure 6 Variation of reciprocal degree of polymerization with rate of photopolymerization 25°C

comparison with poly(methyl methacrylate) radicals which have previously been shown to undergo termination predominantly by disproportionation.

The availability of hydrogen atoms gives a ratio of 5:2 in favour of disproportionation for methyl methacrylate. On the other hand the higher reactivity of poly(methyl acrylate) radicals for hydrogen abstraction in chain transfer reactions favours disproportionation for methyl acrylate. The steric hindrance shown in the combination reaction of two poly (methyl methacrylate) radicals will be much greater than in the combination of two poly(methyl acrylate) radicals because of the absence of the two α-methyl groups in the latter case. This factor favours combination for methyl acrylate.

From the results reported above it appears that the availability of hydrogen atoms and steric effects are more important than the reactivity of the terminating polymer radicals.

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