The initiation activity and kinetic behaviour of the volatile products of plasmas in methyl methacrylate polymerization

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It was found that the volatile products of plasmas of methyl methacrylate, vinyl acetate and methyl isobutyrate can actively initiate the polymerization of methyl methacrylate to produce ultra high molecular weight polymers. The block copolymer can be obtained by programmed feeding of the monomers. The volatile products of the plasmas are living free radicals with a very long lifetime as shown by e.s.r. studies. The reaction kinetics were determined by monitoring the conversion of polymerization with a dilatometer. It is concluded that the polymerization of methyl methacrylate initiated by the volatile products of the plasmas occurs by a quasi-living free radical mechanism with instantaneous initiation and monomer transfer. The results of the conversion curve and the molecular weights calculated by non-steady-state kinetics according to this mechanism are consistent with the experimental results.

(Keywords: plasma; initiation activity; polymerization kinetics; methyl methacrylate)

INTRODUCTION

Plasma initiated polymerization (PIP) discovered by Osada *et al.*[1] at the end of the 1970s has attracted much attention because of its unusual kinetic behaviour. For example, the polymerization can continue for surprisingly long periods, lasting in some cases for weeks[2,3] and even months[4], and a practical aspect is that it produces ultra high molecular weight polymers[3–6] or copolymers[5,7–9]. In general, PIP is carried out by a radio-frequency discharge for a short time in the vapour space above the frozen monomer which is then melted and initiated by the dissolved discharge products. Johnson *et al.*[2] proposed that the non-volatile oil products of the plasma (NVOPP) deposited on the wall of the plasma zone were the initiation species, but the volatile product of the plasma (VPP) could not initiate polymerization. The recent results of Paul *et al.*[10] support Johnson's claim for NVOPP, and showed that NVOPP initiated methyl methacrylate (MMA) polymerization is a classical free radical polymerization, i.e. NVOPP decomposes continuously to produce primary radicals and the chain termination is bi-radical termination. It is, however, open to question that VPP cannot initiate polymerization.

In this work, we collected VPPs of MMA, vinyl acetate (VAc) and methyl isobutyrate (MIB), respectively, and found they are very active in initiating MMA polymerization. The results of kinetic studies and the molecular weight of polymers measured by low angle laser light scattering (LALLS) and the n.m.r. studies of block copolymers show that the mechanism of MMA polymerization initiated by VPP can be described as quasi-living free radical polymerization with instantaneous initiation and monomer transfer.

EXPERIMENTAL

Materials

Commercial MMA and styrene (St) were, respectively, washed three or four times with 5% sodium hydroxide solution and with water, then dried over a 5 Å molecular sieve and fractionated under reduced pressure, and stored at −20°C. Benzene, toluene, MIB and VAc were all analytical grade and were redistilled.

Preparation of VPP initiator. The apparatus to collect VPP initiator is similar to that used by Paul *et al.*[10] for preparing NVOPP. A pair of parallel-plate copper electrodes were placed either side of the glass tube in the plasma zone and connected with a model GP-300-6 high frequency generator. The synthesis conditions of the VPPs of MMA, MIB and VAc were as follows: frequency 13.56 MHz, power 40–60 W, operating pressure 1.3–13 Pa. NVOPP was collected in the flask below the plasma zone, while VPP was collected in another flask which served as the cold trap immersed in liquid nitrogen before the pump. To collect 10 ml of VPP required at least 1–2 days. The VPP collection flask was then removed, purged with nitrogen, and stored below −2°C. The VPPs of MMA and VAc are very light yellow, and the VPP of MIB is colourless. The characteristics of the VPPs have been reported elsewhere[11].

Measurement of monomer conversion. The polymerization of MMA was initiated by mixing a small amount of VPP with MMA in a glass dilatometer with a ball volume of 5–10 ml. First, the empty dilatometer and VPP–MMA–benzene solution were degassed, then the solution was rapidly transferred into the dilatometer

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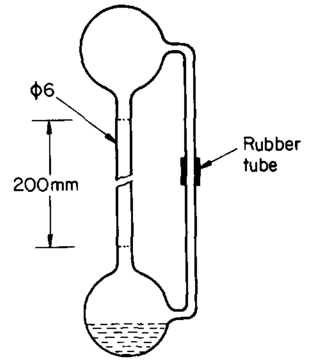

Figure 1 Apparatus for determining the relative viscosity of the polymerization system

under nitrogen, and the dilatometer was then sealed with a torch or with liquid paraffin with a nitrogen bubble on the surface of the solution. The sealed dilatometer was kept in a water bath at a temperature of 60 ± 0.2°C. The results are consistent with those of precipitation from polymerizations in a series of sealed glass ampoules using the same conditions.

E.s.r. spectra of the polymerization process of MMA initiated by VPP were measured using a Bruker ER200D e.s.r. spectrometer with TM110 resonant cavity and 2 mm diameter sample tube[12]. The measurement method and conditions are given in references 12 and 13. The microwave frequency used was 9.78 GHz, the modulation frequency was 0.1 MHz, the modulation amplitude was 4 G and the microwave power was 2.05 mW.

Viscosity of the polymerization system. The relative viscosities of the MMA bulk polymerization system initiated by VPP were measured using the apparatus shown in *Figure 1*. First, VPP–MMA mixture (10 ml) was injected into the apparatus under nitrogen with a syringe, and the apparatus was then inverted to determine the time for the liquid to flow vertically through the capillary t_0. Second, the apparatus was placed in a warm bath to begin the polymerization, and then the apparatus was removed and inverted to determine the time for the liquid to flow through the capillary t. Thus the relative viscosity can be calculated from $\eta_r = t/t_0$. The relative viscosities of PMMA–MMA solutions containing various concentrations of PMMA produced by azobisisobutyronitrile (AIBN) initiated polymerization were also determined using this apparatus.

Measurement of $\langle \mathrm{M}_W \rangle$. The weight-average molecular weights of polymers ($\langle M \rangle_w$) were measured in toluene by the LALLS method using a model KMX-6 low angle scattering photometer, at room temperature. The wavelength of the He–Ne laser source was 6328 Å, the annulus was 6–7°, and the field stop was 0.2 mm. For toluene, the Rayleigh factor[14] $R_\theta = 1.402 \times 10^{-5}$ cm, the refractive index $n = 1.4921 - 5.8 \times 10^{-4}[T(°\mathrm{C}) - 23]$, and the density $\rho = 0.8848 - 8.98 \times 10^{-4}T(°\mathrm{C})$. The specific refractive index increment of our ultra high molecular weight PMMA, $dn/dc = 0.0067$ ml g^{-1}. This result was obtained using a model KMX-16 laser differential refractometer.

Preparation and n.m.r. measurements of MMA–St copolymers. The MMA–St block copolymer was prepared by injecting degassed St monomer (2 ml) into the system after the VPP–MMA–benzene (1:20:100) solution (10 ml) had reacted for 168 h at which time the MMA had been completely converted into poly(methyl methacrylate) (PMMA). The reaction continued for 50 h. Similarly, by adding St to the system which had reacted for 50 h, at which time the MMA monomer conversion had reached 50%, copolymer with a random sequence structure was obtained. Finally, the copolymers were recovered by precipitation in methanol and dried in a vacuum. ^{1}H n.m.r. spectra of copolymer PMMA–polystyrene (PSt) solutions in $DCCl_3$ were measured by using a Varian FT-80 n.m.r. spectrometer with a field intensity of 80 MHz.

RESULTS AND DISCUSSION

Initiation activity of VPP

Johnson *et al.*[2] discharged the vapour of the partially frozen MMA in a closed system. They then thawed the monomer and distilled the volatile fraction over into an ampoule. This ampoule, which was considered to contain the monomer and VPP, was immersed in a warm bath. Since they found no polymer was produced, they concluded that VPP could not initiate MMA polymerization.

We added VPP to MMA monomer and then distilled the mixture. When the distillate was kept at 60°C in a bath for >20 h, the conversion of monomer only was <4%—the same result as in thermopolymerization. When fresh MMA was added to the distillation residue and kept at 60°C for 20 h, 26.2% monomer was converted to ultra high molecular weight PMMA. These results show that VPP is very highly active for initiating MMA polymerization. Because the VPP reacted with the monomer so rapidly to form a polymer, it cannot be distilled out of Johnson's system or from our VPP–MMA mixture. The distillate therefore contains no VPP and therefore cannot cause polymerization. Polymerization by the residue implies that VPP has a very high initiating activity, and this is retained for a very long time.

Kinetic behaviour of polymerization initiated by VPP

The curves of monomer conversion *versus* time of MMA polymerization in benzene initiated by VPP of MMA in *Figure 2* show that the polymerization did not undergo an induction period or autoacceleration. At an earlier stage, the polymerization rate appeared to be independent of reaction time. The polymerization rate is found to decrease exponentially during the whole process. By contrast, a typical free radical polymerization and PIP initiated by NVOPP often starts with an induction period and always undergoes autoacceleration. We can also see from *Figure 2* that the polymerization rate of PIP initiated by VPP is slower than that of common free radicals and much faster than initiated by NVOPP.

A straight line with a slope of 1.09 was obtained from a log–log plot of initial polymerization rate R_p^0 *versus* initial VPP concentration $[\mathrm{VPP}]_0$ as shown in *Figure 3*. This confirms that the rate depends on the first power of the VPP concentration. It can be seen from *Figure 3* that when $[\mathrm{VPP}]_0$ is low, R_p^0 increases rapidly as $[\mathrm{VPP}]_0$ increases; and when $[\mathrm{VPP}]_0$ is sufficiently high, R_p^0 is not responsive to changes in $[\mathrm{VPP}]_0$. This will be further discussed below.

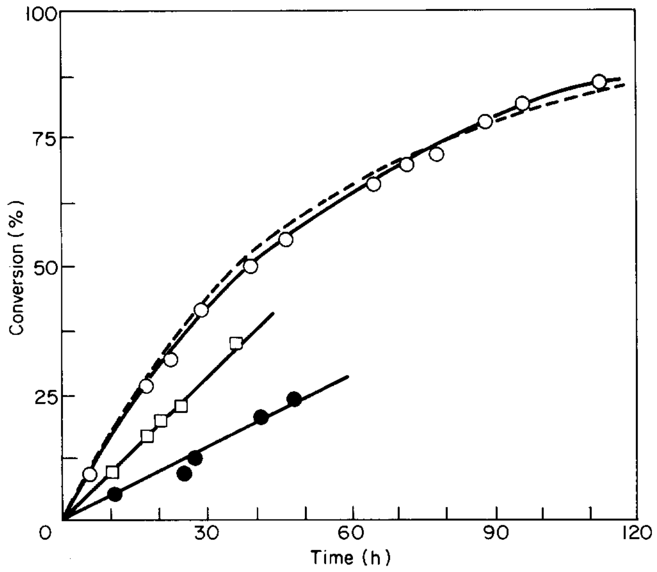

Figure 2 Conversion curves of MMA polymerizations initiated by VPP of MMA. MMA/C_6H_4 = 1 (v/v); temperature 60°C. [VPP] (vol%): (○) 1.5; (□) 1.0; (●) 0.5

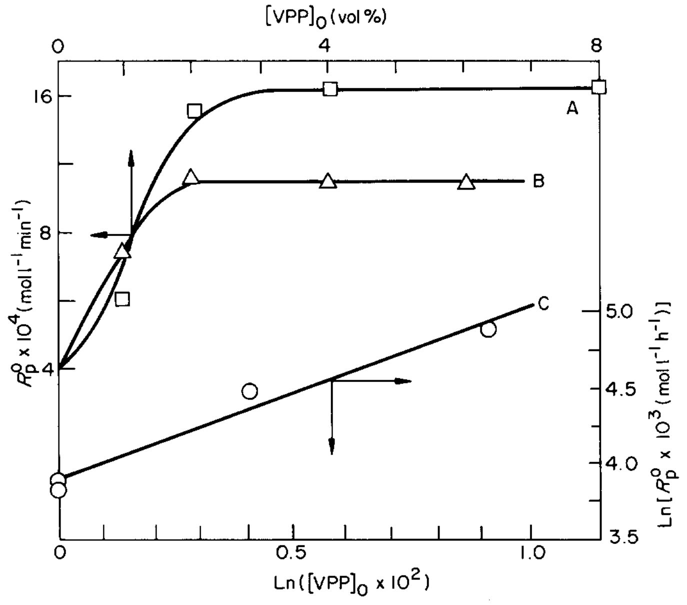

Figure 3 Relationship between the rate of MMA polymerization and VPP concentration: (A) MIB–VPP; (B) VAc–VPP; (C) MMA–VPP

From a log–log plot of R_p^0 *versus* initial monomer concentration $[M]_0$ a straight line plot with a slope of 0.96 was obtained, as shown in *Figure 4*. This indicates that the rate depends on the first power of the monomer concentration.

Thus the following experimental relation can be presented

$$R_p^0 \propto [M]_0^{0.96}[VPP]_0^{1.09} \qquad (1)$$

These results provide evidence that the kinetic behaviour of VPP initiated MMA polymerization is completely different from that of classical free radical polymerization and that of NVOPP initiated polymerization in which the power dependence of R_p^0 on initiator concentration is 0.5, but have some characteristics of living polymerization with instantaneous initiation.

Discussion of the polymerization mechanism

We[11] already know that the very large fraction of VPP collected from the glow discharge is unreacted monomer. The VPPs of MMA and VAc become viscous when kept at room temperature. We found that the e.s.r. spectrum of VPP of MMA is a typical 13-line spectrum of a PMMA free radical (*Figure 5*). This indicated that VPP is a mixture of living free radical and monomer. The living state of the free radicals in VPP is possibly accounted for by the protecting effect of a high concentration of free electrons produced in the plasma process[15,16], or owing to the radicals being of an ionic type[17].

At room temperature, VPP radicals can react directly with monomer in a very fast reaction, so the initiator decomposition process, which is the controlling step of the initiation rate in classical free radical polymerization, does not exist in this system and the initiation is completed instantaneously. In other words, when the frozen VPP of MMA was melted and then was added to the monomer, it became the PMMA oligomer seeds which could propagate with the monomer directly.

One feature of classical free radical polymerization is bi-radical termination. The decrease in termination rate leads to a rapid increase in radical concentration so that autoacceleration occurs. The curve of the e.s.r. peak height of the VPP initiated MMA polymerization system

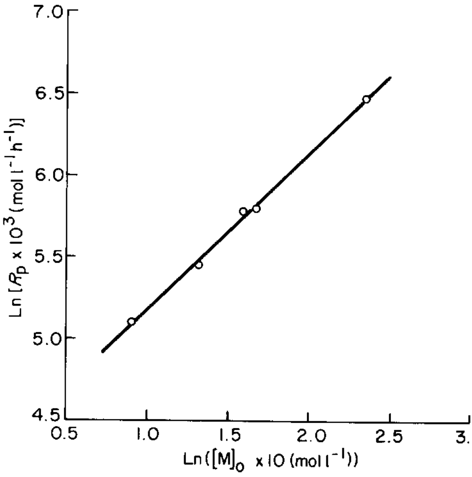

Figure 4 Relationship between the rate of MMA polymerizations and monomer concentration

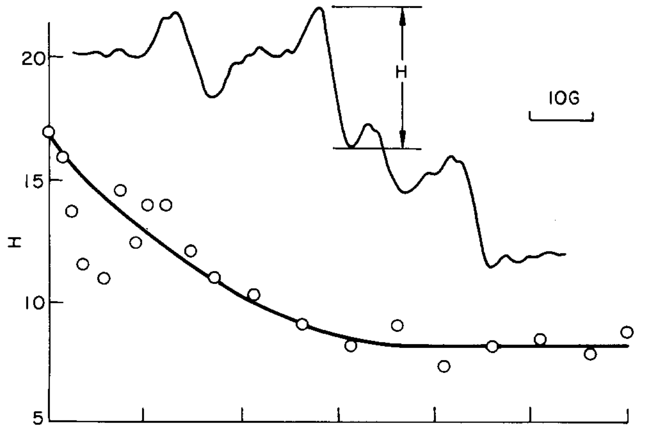

Figure 5 E.s.r. spectrum and its intensity change for the VPP of MMA

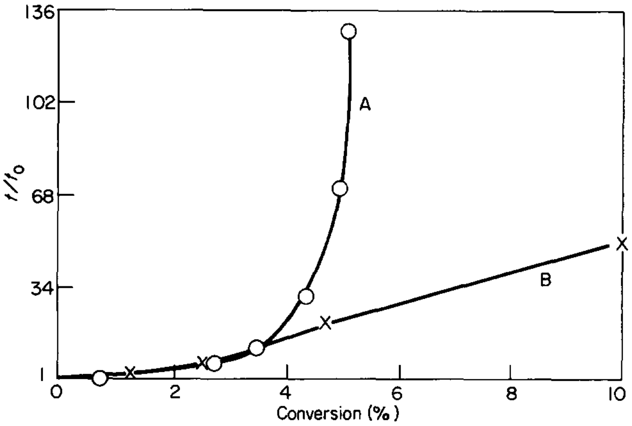

Figure 6 Relative viscosities t/t_0 *versus* conversion in MMA polymerization initiated by (A) VPP and (B) AIBN

versus reaction time in *Figure 5* shows that the radical concentration was highest at the very beginning and then dropped in a short time (~1 h, which is very short for a polymerization which lasts >100 h) and then remained unchanged until the reaction ended. These results show that radical termination existed only at the beginning, so the whole reaction process acts as a living polymerization and there is no autocorrelation. This situation results, firstly, from the very low concentration of radicals. In common radical polymerization the radical concentration lies between 10^{-8} mol l^{-1} and 10^{-6} mol l^{-1}. However, in VPP initiated polymerization the radical concentration is 10^{-9} mol l^{-1} or lower, so that the bi-radical termination rate is two to six orders of magnitude slower than that in common radical polymerizations. Secondly, because the termination is a diffusion controlled process and the viscosity increases in VPP initiated MMA polymerization systems much faster than in common systems such as AIBN initiated MMA polymerization (*Figure 6*), the termination rate is reduced even further so that termination cannot occur.

Note that to obtain a large enough signal intensity, the e.s.r. peak height in *Figure 5* is measured using the bulk of VPP of MMA, i.e. VPP concentration [VPP] = 100%. If [VPP] is much lower, such as [VPP] < 5% as in an actual polymerization system, termination cannot occur even at the beginning of the polymerization. The curves of R_p^0 *versus* $[VPP]_0$ in VPPs of VAc and MIB initiated MMA polymerizations (*Figure 3*) show that when $[VPP]_0$ is lower, termination did not contribute to the polymerization, and R_p^0 increased as $[VPP]_0$ increases. When $[VPP]_0$ is larger than a certain value, although it cannot be neglected, termination leads the radical concentration to level rapidly to this value and finally the contribution of termination tends to zero and R_p^0 is independent of $[VPP]_0$. Thus, VPP initiated MMA polymerization appears always as a living polymerization macroscopically.

More cogent evidence of living radical polymerization was given by two kinds of MMA–St copolymers prepared by VPP initiated copolymerizations with a programmed feeding of MMA and St monomer. Sample A was prepared by injecting St monomer into the system after MMA initiated by VPP had reacted for 168 h, after which the MMA had been completely converted into PMMA, and then the reaction was allowed to continue for 50 h. Sample B was prepared by adding St to the system which had reacted for 50 h when the monomer conversion had reached 50%. The ^{1}H n.m.r. spectra of the two samples are shown in *Figure 7*. Both spectra show α-methyl proton peaks at around $\delta = 1$ ppm, the methoxyl proton peak at $\delta = 3.4$ ppm and the benzene ring proton peaks of the PSt component at $\delta = 7.14$ and 7.3 ppm. These results show that the two samples are actually MMA–St copolymers. There are two important differences between the spectra of samples A and B: the weak peaks at 0.6 and 2.8 ppm in the spectrum of sample B have disappeared in that of sample A. This shows that sample A is different from sample B in the sequence structure. Bovey[18] demonstrated that the signal of methoxyl protons which appears at 3.4 ppm in PMMA is shifted to higher field and split into several peaks in St–MMA random copolymers, and the α-methyl peak is also shifted to higher field in the random copolymer. Overberger and Yamamoto[19] also found these peaks are not shifted in the St–MMA block copolymer. These results were attributed to the shielding effect of adjacent phenyl groups. It is obvious that sample B contains some random sequence structure and sample A is a pure block copolymer which has no random sequence of St and MMA. These results suggest that a block copolymer can be formed only if all of the MMA monomers were consumed prior to addition of the St monomers as in the mechanism of VPP initiated PIP in which the chain radicals can keep propagating indefinitely.

Theoretical calculation

Assume the VPP initiated MMA polymerization process has the following mechanism:

$$R_n + M \xrightarrow{k_p} R_{n+1} \qquad n = 0, 1, 2, \ldots \qquad (2)$$

where R_n and M are the *n*-mer radical and monomer, respectively, and k_p is the propagation rate constant. The polymerization rate can be written as in equation (1):

$$R_p = k_p[M][VPP] \qquad (3)$$

where [M] is the monomer concentration and [VPP]

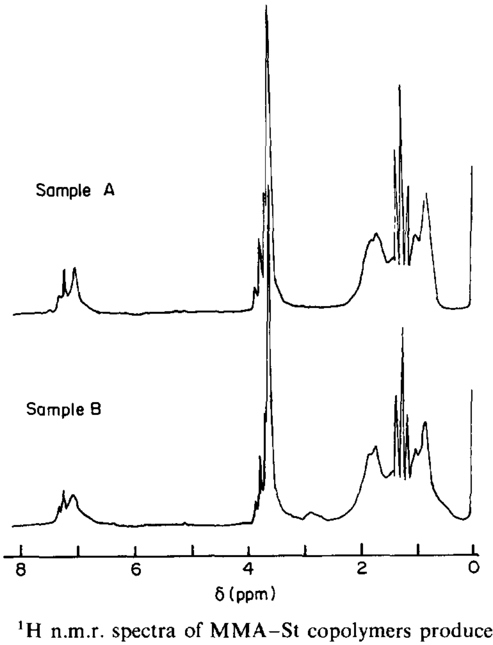

Figure 7 ^{1}H n.m.r. spectra of MMA–St copolymers produced from St polymerization after MMA polymerization initiated by VPP

Table 1 Weight average molecular weight of PMMA produced by VPP initiated polymerization

	$\langle M \rangle_W$ ($\times 10^{-7}$)	
Y_W (%)	Experimental[a]	Theoretical[b]
10.9	1.814	1.997
15.6	1.799	1.998
21.9	1.987	1.999

[a] By LALLS
[b] Using equation (10)

the radical concentration at time t, respectively. The monomer conversion formula is derived as

$$Y = 1 - \exp\left(-k_p \sum_n R_n t\right) \tag{4}$$

The corresponding weight conversion is

$$Y_W = \left[1 - \exp\left(-k_p \sum_n R_n t\right)\right] \Bigg/ \left[1 + a\varepsilon \exp\left(-k_p \sum_n R_n t\right)\right] \tag{5}$$

The weight average degree of polymerization of the polymer can be given as[20]:

$$\langle X \rangle_W = 1 + \alpha + \alpha/(1 + \alpha) \tag{6}$$

$$\alpha = [M_0]Y \Big/ \sum_n R_n \tag{7}$$

where $\sum R_n$ is the total radical concentration and a and ε are the volume fraction and expansion coefficient of the monomer, respectively. For the system with $[M_0] = 5\ \mathrm{mol\,l^{-1}}$ and $\sum R_n = 6.9 \times 10^{-9}\ \mathrm{mol\,l^{-1}}$, $k_p = 700\ \mathrm{l\,mol^{-1}\,s^{-1}}$ (ref. 9) and $\varepsilon = -0.2212$ (ref. 21) at 60°C, the conversion curve (dotted curve in *Figure 2*) calculated from equation (5) is consistent with the experimental results. However, $\langle M \rangle_W$ calculated from equation (6) is $\sim 10^{11}\ \mathrm{g\,mol^{-1}}$ which is much larger than the experimental value of $10^7\ \mathrm{g\,mol^{-1}}$ (*Table 1*). This indicated that the mechanism for living polymerization with instantaneous initiation is in essence reasonable, but the process of chain transfer which caused the decrease in the degree of polymerization must be taken into account.

Although the chain radical concentration is very low and the chain transfer constant for the monomer is very small, the chain transfer to monomer cannot be neglected for this polymerization which took >100 h and for a kinetic chain length of 10^5 or more. The chain transfer probability for monomer can be evaluated by:

$$p_{tr} = 1 - (1 - C_m)^{\alpha} \tag{8}$$

where $C_m = k_{tr}/k_p$ is the transfer constant for monomer and α is the kinetic chain length. When $\alpha = 10^5$, p_{tr} is close to unity. So the mechanism of VPP initiated MMA polymerization may be considered as

$$\begin{aligned} R_n + M &\xrightarrow{k_p} R_{n+1} \\ R_n + M &\xrightarrow{k_{tr}} P_n + R_1 \end{aligned} \tag{9}$$

where P_n is dead n-mer. The conversion formula is given by equations (4) and (5), and the constant k_p in equation (3) should be replaced by $(k_p + k_{tr})$. The weight average degree of polymerization becomes[22]:

$$\langle X \rangle_W = \frac{1 + (C_m + 3 + 2/C_m)\alpha - 2[1 - \exp(-C_m\alpha)]/C_m^2}{1 + (1 + C_m)\alpha} \tag{10}$$

Using $C_m = 10^{-5}$ from reference 18, the $\langle M \rangle_W$ calculated from equation (10) agree very well with the experiments as shown in *Table 1*. This result showed that the mechanism quoted in reaction (9) is reasonable for a VPP initiated MMA polymerization.

The above discussion on the mechanism of VPP initiated MMA polymerization is based on the comparison of the macroscopic phenomena with the accepted theory of polymerization kinetics. Accepting that some very low terminations exist in the system, we concluded that the mechanism of VPP initiated polymerization is a quasi-living process.

Many phenomena, however, have not been clarified. In particular, the living nature of VPP radicals and chain radicals could not be explained by classical radical theory. To confirm the mechanisms of VPP initiated polymerization outlined above, we have to clarify the composition and the structure of VPP and study the influence of every component on the polymerization. This will be our aim in further investigations.

ACKNOWLEDGEMENT

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