Studies of the Mechanism and Kinetics of Plasma-Initiated Polymerization of Methyl Methacrylate

D. R. Johnson,† Y. Osada,‡ A. T. Bell,* and M. Shen§

Department of Chemical Engineering, University of California, Berkeley, California 94720.
Received May 29, 1980

ABSTRACT: The plasma-initiated polymerization of methyl methacrylate was investigated to establish the manner in which the conditions of initiation and subsequent polymerization affect the rate of polymer formation. Experiments were also conducted to identify the nature of the propagation process. The results of these studies suggest that in the presence of a plasma, monomer vapor is converted into a substance which can later serve as an initiator for polymerization of liquid monomer. Polymerization is sustained by a free-radical propagation process which is terminated by disproportionation and chain transfer to the monomer. It is proposed that the growth in polymer molecular weight with increasing monomer conversion and the attainment of molecular ultrahigh molecular weights (e.g., in excess of 10^7 g/mol) can be ascribed to an early onset of the gel effect.

Introduction

In two recent communications Osada et al.[1,2] have reported that a low-pressure plasma produced by an electric discharge can be used to initiate the polymerization of liquid vinyl monomers. This process is referred to as plasma-initiated polymerization. Poly(methyl methacrylate) (PMMA) formed by the plasma technique is linear and can exibit molecular weights in excess of 10^7 g/mol.[1] The tacticity distribution of the polymer suggests that it is formed via a free-radical mechanism.[3] This conclusion is further supported by the monomer–copolymer composition relationship observed when methyl methacrylate and styrene are copolymerized.[2] The present studies were undertaken to elucidate the dependence of polymerization kinetics on the conditions of initiation and subsequent polymerization and to identify more clearly the species responsible for chain growth. The results of these investigations are reported here together with a discussion of a possible mechanism for plasma-initiated polymerization.

Experimental Section

The experimental apparatus and procedure used in the present investigation were essentially identical with those reported by Osada et al.[1,2] Monomeric methyl methacrylate (MMA) (Aldrich Chemical Co.) was purified by vacuum distillation under nitrogen, poured into thin-walled ampules, degassed by repeated freezing and thawing while under a vacuum of 10^{-3}–10^{-4} torr, and finally frozen in liquid nitrogen. The ampule was then inserted between a pair of parallel-plate electrodes connected to an International Plasma Corp. Model 3001 radio-frequency generator which operates at 13.56 MHz and delivers up to 150 W. The ampule was permitted to warm up until droplets of liquid monomer appeared (~−45 °C). A glow discharge was then initiated in the vapor space above the partially frozen monomer. Power levels of 40–80 W and durations of 30–60 s were usually used. Following initiation, the ampule was placed in a constant-temperature bath for prescribed periods of time, after which the polymer was precipitated and analyzed. The viscosity-average molecular weight of the polymer was determined by measuring the intrinsic viscosity of the polymer dissolved in benzene. Values of the constants appearing in the Mark–Houwink relation were taken from ref 4. The procedure described for the polymerization of pure MMA was also used for the polymerization of MMA in dimethyl sulfoxide (Me_2SO) solution and for the copolymerization of MMA and methacrylic acid (MAA).

Results

Kinetics of Polymerization. Figure 1 shows the progress of polymerization for plasma-initiated MMA. For low degrees of conversion, the polymerization rate remains constant at about 4.0×10^{-6} mol/(L·s). At about 10% conversion, the rate increases and then approaches a new constant rate of 7.2×10^{-6} mol/(L·s). The extent of monomer conversion by thermal polymerization, in the absence of plasma initiation, is also shown in Figure 1. The rate of this process is constant at 9.0×10^{-7} mol/(L·s). This value is significantly higher than that reported by other investigators[5-7] and appears to be associated with the presence of very small amounts of peroxides in the monomer. The significance of this observation and the influence of oxygen on the rate of polymerization are discussed more fully below.

The effect of polymerization time on the molecular weights of the polymers formed is shown in Figure 2. The polymer obtained a few minutes after initiation of the monomer already has a molecular weight of 2×10^6 g/mol. With longer periods of postpolymerization the molecular weight of the polymer increases, attaining a value of about 10^7 g/mol after 160 h, or a conversion of 50%. The measurement of polymer molecular weights at monomer conversions in excess of 50% was not possible since the monomer/polymer solution becomes extremely viscous at such high conversions and dissolves very slowly in benzene or toluene. Moreover, it was feared that the continuous stirring required to dissolve the polymer would result in a lowering of its molecular weight.[8,9] Evidence of shear degradation of ultrahigh molecular weight PMMA was, in fact, observed when an attempt was made to measure the molecular weight distribution by gel permeation chromatography.

The effect of radio-frequency power on the initial polymerization rate is shown in Figure 3. It is to be noted that a polymerization rate of 2×10^{-6} mol/(L·s) can be attained by using only a tesla coil to sustain the plasma. As the power increases, the rate increases until a maximum is reached at approximately 40 W. Increasing the power further decreases the polymerization rate, until it asymptotically approaches the thermal rate.

The influence of the duration of plasma initiation on the initial rate of polymerization was also investigated. The results illustrated in Figure 4 show that the polymerization rate increases with increasing duration of initiation, up to a duration of 40 s. Beyond this, no further increase is observed for times up to 100 s. It was found, though, that higher polymerization rates could be achieved by altering the initiation procedure. After an initial initiation for 60 s, the monomer was refrozen and the noncondensable gases were evacuated. The ampule was then disconnected from the vacuum line, the monomer was thawed, and a plasma was again created in the monomer vapor. By repeating this process many times, very long cumulative initiation

† Present address: Chevron Research Co., Richmond, CA 94802.
‡ Present address: Department of Chemistry, Ibaraki University, Mito 310, Japan.
§ Deceased.

0024-9297/81/2214-0118$01.00/0

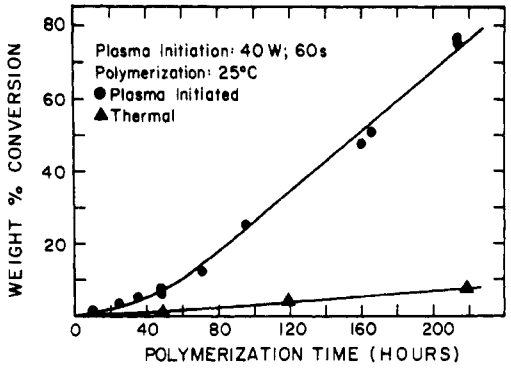


Figure 1. Dependence of monomer conversion on the duration of polymerization.

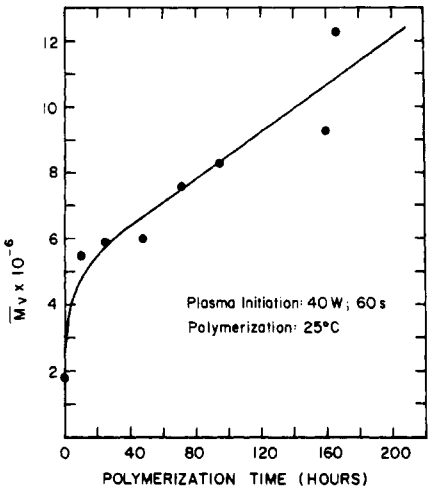


Figure 2. Dependence of polymer molecular weight on the duration of polymerization.

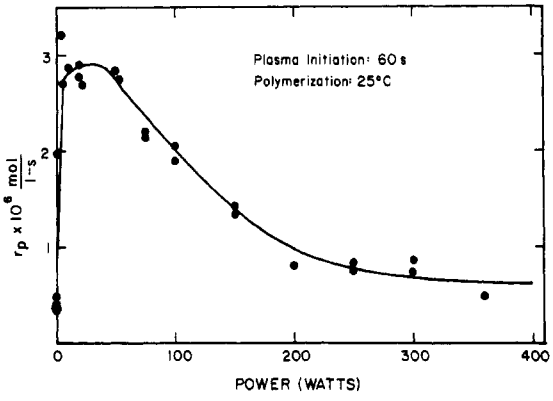


Figure 3. Effect of discharge power on the initial rate of polymerization.

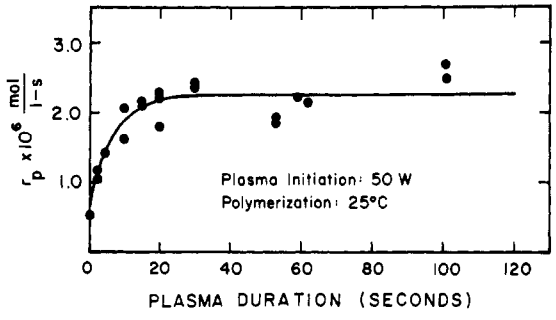


Figure 4. Effect of the duration of plasma initiation on the initial rate of polymerization.

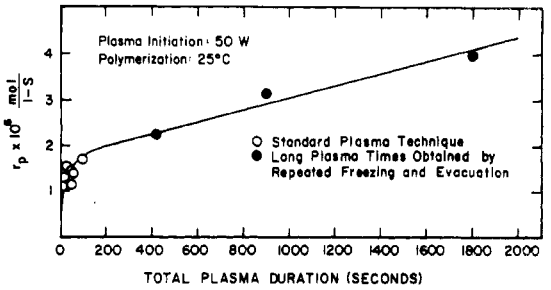


Figure 5. Effect of repeated plasma initiation on the initial rate of polymerization.

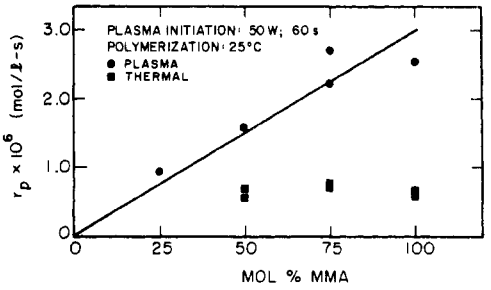


Figure 6. Effect of MMA concentration in Me_2SO solution on the initial rate of polymerization.

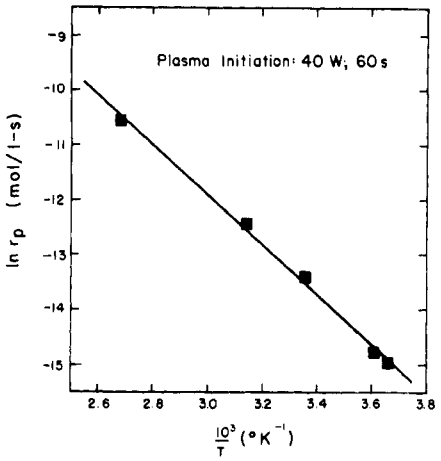


Figure 7. Effect of temperature on the initial rate of polymerization.

durations could be achieved. The results obtained by this procedure are shown in Figure 5. It is apparent that repeated initiation in fresh monomer vapor leads to a continual increase in the polymerization rate.

The plasma-initiated polymerization of MMA dissolved in a solvent was investigated in chloroform, benzene, bromoform, and Me_2SO. Of these solvents only Me_2SO was found to be suitable. No polymer was obtained in either chloroform or benzene solution. Polymerization did proceed in bromoform but the rate of thermal polymerization in this solvent was found to be higher than the rate of plasma-initiated polymerization. The suitability of Me_2SO appears to be due to its very low vapor pressure and inertness. One indication of the latter characteristic is the fact that the rate of thermal polymerization of MMA in Me_2SO solution is identical with that in the pure monomer. A plot of the initial polymerization rate as a function of monomer concentration is shown in Figure 6. These results clearly indicate that the rate is directly proportional to the monomer concentration.

The effect of temperature on the rate of polymerization is shown in Figure 7 for the case of polymerization in pure

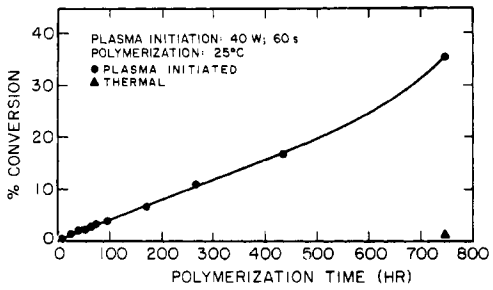


Figure 8. Dependence of monomer conversion on the duration of polymerization following cryogenic purification of the monomer.

monomer. The points shown in this plot were corrected for thermal polymerization by subtracting the rate of thermal polymerization from that observed following plasma initiation. This procedure was justified by noting that the two rates were very nearly additive. From the slope of the Arrhenius line, the global activation energy is estimated to be 9.1 kcal/mol.

Previous investigations[10] have shown that both peroxides and molecular oxygen can significantly influence the rate of MMA polymerization. On the basis of this evidence and the unusually high rate of thermal polymerization observed with doubly distilled MMA, experiments were conducted to investigate the influence of oxygen on the progress of plasma-initiated polymerization of MMA. In an initial experiment, distilled MMA was placed in an ampule and the entire contents was evacuated. A small amount of residue was found in that portion of the ampule originally filled by the monomer. A second experiment was then carried out to see if this residue, presumed to be a peroxide, was responsible for the high rate of thermal polymerization. Two milliliters of distilled MMA was placed in an ampule and degassed by the freeze–thaw technique. A portion of this liquid was then cryogenically distilled under vacuum into a second ampule, which had previously been evacuated. The purified monomer was then plasma initiated and allowed to postpolymerize. Figure 8 illustrates the course of polymerization for this case. The initial polymerization rate is now 1.1×10^{-6} mol/(L·s), a factor of about 4 less than that for the distilled monomer (see Figure 1). It was also observed that the rate of thermal polymerization for the vacuum-purified monomer was very low and consistent with that reported in the literature.[5-7]

Experiments were also carried out to establish the influence of molecular oxygen on the rate of polymerization. In the first series of experiments, ampules containing degassed MMA, which had been plasma initiated, were back-filled with oxygen to specified pressures. The ampules were then sealed and the monomer was allowed to polymerize. After approximately 40 h two phases were observed. The top few milliliters of the monomer/polymer solution was very fluid and contained no polymer. The bottom portion of the fluid was quite viscous and contained all of the polymer. Figure 9 shows how the initial rate of polymerization and the fraction of the total fluid depth occupied by the nonviscous phase change with oxygen pressure. It is apparent that for O_2 pressures below 15 torr, the rate of polymerization increases substantially with O_2 pressure. However, beyond this level there is a continual decrease in the polymerization rate.

The results presented in Figure 9 suggest that the dissolution of small amounts of oxygen in the monomer enhances the rate of polymerization. This conclusion is supported by an experiment in which MMA was not degassed prior to initiation. In this case the initial polymerization rate was 5.2×10^{-6} mol/(L·s). This figure is

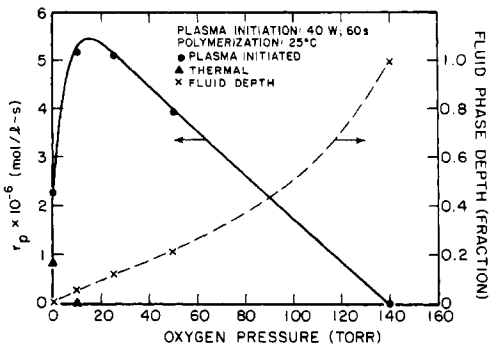


Figure 9. Effect of oxygen partial pressure on the initial rate of polymerization.

Table I
Location of the Initiating Substance Formed in the Plasma

experiment	procedure	$R_p \times 10^6$, mol/(L·s)
1.	(i) 60-s plasma in MMA vapor (ii) evacuation for 5 min to 10^{-3} torr (iii) MMA distilled into ampule (iv) ampule sealed and set aside for polymerization	1.77
2.	(i) MMA distilled into ampule (ii) 60-s plasma in MMA vapor (iii) MMA frozen and ampule evacuated (iv) MMA thawed and distilled into second ampule (v) second ampule sealed and set aside for polymerization	0.47
3.	(i) 60-s plasma in MMA vapor (ii) evacuation for 5 min to 10^{-3} torr (iii) exposure to air for several minutes (iv) ampule reevacuated and filled with MMA (v) ampule sealed and set aside for polymerization	2.03
4.	(i) 60-s plasma in MMA vapor (ii) evacuation for 5 min to 10^{-3} torr (iii) ampule back-filled with 9 torr of O_2 for 5 min (iv) ampule reevacuated and filled with MMA (v) ampule sealed and set aside for polymerization	2.02
5.	standard plasma initiation procedure	1.65

significantly larger than that observed when degassed monomer is used, 2.6×10^{-6} mol/(L·s).

The influence of oxygen during the initiation of polymerization was also examined. If 1 torr of O_2 was added to an ampule containing degassed and frozen MMA and the monomer was subsequently initiated, the polymerization rate was found to be 2.8×10^{-6} mol/(L·s). Raising the O_2 pressure to 9 torr increased the rate to 4.6×10^{-6} mol/(L·s). These results clearly indicate that the presence of small amounts of oxygen during initiation have no effect on the rate of polymerization.

Identification of Active Species. A variety of experiments were conducted to investigate the nature and origin of the active species responsible for polymerization. In the first series, efforts were made to identify the role of a viscous oil which deposited on the ampule wall during plasma initiation. The results of this series are summarized in Table I. In the first experiment, a small amount of purified MMA was cryogenically distilled into an ampule and then plasma initiated in the usual fashion. Next, the ampule was evacuated to less than 10^{-3} torr for 5 min.

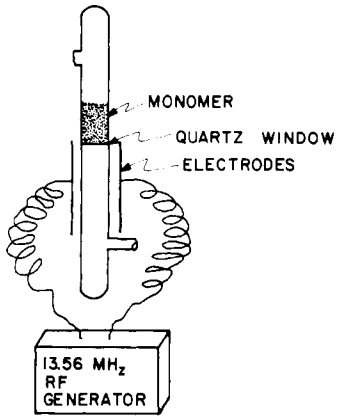


Figure 10. Apparatus used to investigate the role of UV radiation on the initiation of polymerization.

During this time all of the liquid monomer was removed from the ampule, but the viscous oil did not evaporate. Two milliliters of fresh MMA was now distilled into the ampule, and the ampule was sealed. The ampule was then shaken to dissolve the oil in the MMA and put into a constant-temperature bath. The resulting rate of polymerization was the same as for an ampule of monomer which had been initiated in the usual manner.

The initial procedure for the second experiment was the same as the first. However, following initiation, the monomer in the ampule was distilled over into a second ampule. This ampule was now sealed and set aside for polymerization. The rate of polymerization in this case was about one-quarter of that observed normally.

The third and fourth experiments of the series were identical with the first except that the viscous oil was exposed to air or oxygen for several minutes before being dissolved in the fresh MMA. Table I shows that this step enhances the rate of polymerization over that normally observed and that no differences are detected between exposure to air or 9 torr of pure O_2.

The extent to which photons produced in the plasma contribute to the initiation of polymerization was investigated next. A specially designed ampule, shown in Figure 10, was used for part of these experiments. Liquid monomer was transferred into the upper portion of the ampule and vapor was introduced into the lower portion of the ampule. A plasma was now initiated in the lower portion of the ampule. Photons with wavelengths above 200 nm, generated in the plasma, could pass into the liquid monomer by transmission through the fused-quartz window separating the halves of the ampule but contact of the liquid monomer with charged or free-radical species present in the plasma was excluded. Monomer initiated in this fashion did not polymerize at a rate in excess of that associated with thermal polymerization.

In a second set of experiments benzoin was added to MMA and the mixture was then plasma initiated in the normal fashion. The results given in Table II show that benzoin addition suppressed, rather than enhanced, the rate of polymer formation. These observations, taken together with those of the preceding experiment strongly suggest that photochemical processes do not contribute significantly to the formation of the species which initiate polymerization.

To test whether propagation occurs via a free-radical or an ionic mechanism, we copolymerized MMA and methacrylic acid (MAA). The composition of the polymer for each monomer composition was obtained by means of ^1H NMR. Figure 11 illustrates the polymer composition as a function of monomer composition. The data points are

Table II
Effect of Benzoin Addition to MMA

benzoin concn, mol/L	polymer yield,[a] %
0	2.13
6×10^{-3}	1.5
6×10^{-2}	1.0
6×10^{-1}	1.0

[a] Determined after polymerization at 25 °C for 24 h.

seen to be very close to the curve based upon conventional free-radical copolymerization of MMA and MAA (r_{MMA} = 0.55, r_{MAA} = 1.55).[4] Furthermore, NMR spectra of the copolymer show a splitting of the methoxy group line at δ = 4.3 due to shielding by the neighboring carboxylic group on the chain, a feature which is characteristic of random copolymers formed via free-radical polymerization.

Yet further evidence for free-radical chain growth was obtained from experiments in which either water or diphenylpicrylhydrazine (DPPH) was added to the monomer. The addition of 0.2 mL of water to 2 mL of MMA followed by plasma initiation in the usual manner resulted in the same polymerization as in the absence of water. If polymerization had occurred by an anionic mechanism, the addition of water would have instantaneously terminated the reaction. When a small crystal of DPPH was added to the monomer and the monomer subsequently plasma-initiated, no polymer could be produced. Since DPPH is a known radical scavenger, this result suggests that plasma-initiated polymerization proceeds via a free-radical chain-growth mechanism.

Discussion

The results of the present investigation, taken together with those obtained earlier by Osada et al.,[1,2] clearly indicate that chain propagation during polymerization proceeds via a free-radical mechanism. Four observations lead to this conclusion. First, the microstructure of PMMA obtained by plasma-initiated polymerization is found to consist of 7% isotactic, 27% heterotactic, and 66% syndiotactic triads,[1] in good agreement with the tacticity distribution for radical-initiated polymerization.[3] Second, the copolymerization of MMA with MAA and styrene[2] produces monomer/copolymer composition relations identical with those for free-radical copolymerization.[7] Third, the inhibition of plasma-initiated MMA by DPPH indicates suppression of chain propagation by free-radical trapping. Fourth, the lack of inhibition of MMA polymerization by water indicates that chain propagation does not proceed by an ionic mechanism and, hence, by inference does proceed by a free-radical mechanism.

The sustained polymerization of MMA following plasma initiation, illustrated in Figure 1, is similar in a number of respects to that observed following initiation with UV radiation[11-17] or high-energy electrons.[18] Several attempts have been made to explain this phenomenon. Melville[11] in his original work suggested that the double bond of the monomer is activated during irradiation and that these activated species then initiate free-radical polymerization during the dark period. A different and more satisfying interpretation was given by Bamford and Dewar.[13,14] They proposed that an initiator or catalyst is formed during the period of irradiation, which then produces free radicals either by its own decomposition or by reaction with the monomer. A similar interpretation was subsequently supported by the work of MacKay and Melville.[12] While neither set of authors was able to establish the identity of the initiator, Bamford and Dewar[13,14] proposed that the initiator might be a derivative of dimethylenecyclo-

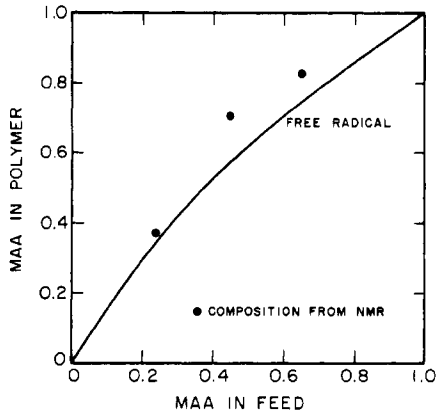
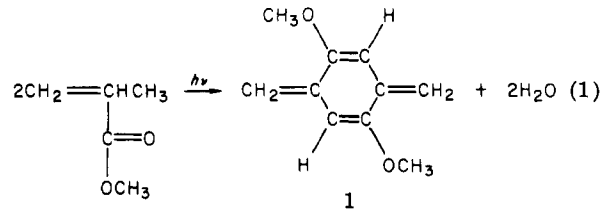


Figure 11. Polymer/monomer composition relation for the copolymerization of MMA and MAA.

hexadiene, formed by the photochemical condensation shown in (1). This hypothesis is supported by the work



1

of Szwarc,[19,20] which demonstrated that structures such as 1 can form biradicals and hence act as effective initiators.

The possibility that an initiator might be formed when a plasma is sustained in MMA vapor is also plausible. While the plasma-chemical synthesis of structure 1 has not been reported, many other intra- and intermolecular organic reactions are known to occur under mild plasma conditions.[21] The fact that plasma initiation is most effective when conducted at relatively low discharge powers (see Figure 3) is also consistent with the hypothesis that an initiator is formed from the monomer. Presumably, sufficient power must be supplied for the plasma to facilitate the condensation of monomer units, but not so much that extensive molecular fragmentation occurs. The results presented in Table I suggest further that the initiator is retained in the viscous oil deposited on the portions of the ampule wall in contact with the plasma. Since the wall of the ampule is cold at the time of initiation, this may help to stabilize the formation of a product such as structure 1 and prevent its rapid reaction to form a polymer.[19]

A mechanism for the progress of polymerization following initiation can now be envisioned in terms of reactions 2–5. The species I represents the initiator formed

$$I \rightarrow R\cdot \tag{2}$$

$$R\cdot + M \rightarrow R'\cdot \tag{3}$$

$$2R\cdot \rightarrow P^{=} + P^{-} \tag{4}$$

$$R\cdot + M \rightarrow P^{-} + R''\cdot \tag{5}$$

in the plasma. The decomposition of this species (reaction 2) initiates polymerization, which then propagates via further monomer addition (reaction 3). Termination of chain growth (reaction 4) is taken to occur by disproportionation,[22] and chain transfer (reaction 5) is assumed to occur primarily to the monomer.

The proposed scheme leads to an expression for the rate of polymerization given by

$$R_p = k_p(k_c/k_t)^{1/2}[I]^{1/2}[M] \tag{6}$$

where k_c, k_p, and k_t are the rate coefficients for conversion of initiator to free radicals, chain propagation, and chain termination, respectively. The form of eq 6 predicts that the rate of polymerization should be proportional to the monomer concentration. Such a dependence was in fact observed (see Figure 6) when MMA was polymerized in Me_2SO solution. The dependence on catalyst or initiator concentration is harder to confirm, but some supportive evidence can be developed. If it is assumed that the amount of initiator formed is proportional to the duration of plasma initiation, then the rate of polymerization should be proportional to the square root of the duration of initiation. The data presented in Figure 5 have been replotted on full logarithmic coordinates in Figure 12. It is apparent that while the least-squares line (A) fitted through the points has a slope of 0.4, a line with slope 0.5 (B) could also be drawn through the points. These observations further suggest that the form of eq 6 is correct.

The global activation energy for postpolymerization, E_a, was found to be 9.1 kcal/mol. If the polymerization kinetics are described by eq 6, then E_a can be expressed as

$$E_a = E_p - \tfrac{1}{2}E_t + \tfrac{1}{2}E_c \tag{7}$$

where E_p, E_t, and E_c are the activation energies for propagation, termination, and initiator decomposition, respectively. Reported values for E_p lie between 4.4 and 6.3 kcal/mol and those for E_t between 0 and 0.5 kcal/mol.[4] These values can be used to estimate that E_c should be between 7.4 and 11.7 kcal/mol. Such values are a factor of 3–4 smaller than the activation energies associated with traditional peroxide and azo initiators but may not be unreasonable for formation of free radicals from a dimethylenecyclohexadiene-type initiator (e.g., structure 1).

The proposed mechanism of polymerization also explains why the molecular weight of the polymer formed is very high and increases with the conversion of the monomer. If chain transfer to the polymer is neglected, the extent of polymerization, ν, can be expressed as

$$\frac{1}{\nu} = \frac{k_{tr,M}}{k_p} + \frac{k_t[R\cdot]}{k_p[M]} \tag{8}$$

The extent of polymerization at the onset of polymerization can be evaluated by using eq 9 to determine the

$$[R\cdot] = R_p/k_p[M] \tag{9}$$

concentration of free radicals. Introduction of $R_p = 4 \times 10^{-6}$ mol/(L·s), determined from Figure 1, and the values of $k_p = 200$ L/(mol·s), $k_t = 15 \times 10^6$ L/(mol·s), and $k_{tr,M}/k_p = 0.12 \times 10^{-4}$, determined for the photopolymerization of MMA at 25 °C,[4] leads to a value of $\nu = 3.6 \times 10^4$. The corresponding value of the weight-average molecular weight, 7.2×10^6 g/mol, calculated on the assumption of a dispersity index of 2, is in reasonable agreement with that measured experimentally at the beginning of polymerization (e.g., 2×10^6 to 5×10^6 g/mol).

The rise in molecular weight of PMMA with increasing duration of polymerization can be ascribed to a reduction in the magnitude of k_t as the viscosity of the polymer/monomer solution rises to a point where the recombination of free radicals becomes diffusion limited. This is known as the gel or Tromsdorf effect.[22] In view of the high molecular weight of the polymer produced as soon as polymerization begins, the viscosity of the reacting medium becomes very high for monomer conversions of even a few percent. As a result it seems possible that the onset of the gel effect could occur already at low conversion. The ab-

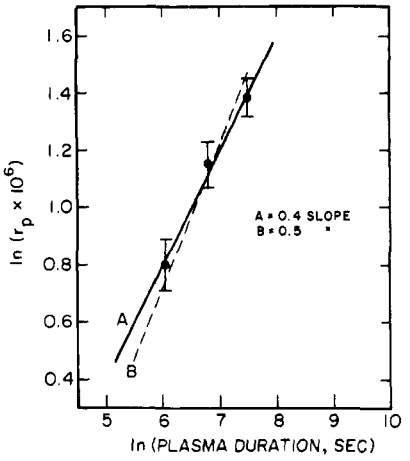


Figure 12. Dependence of the initial rate of polymerization on the duration of plasma initiation.

sence of a sudden rise in the rate of polymerization as the molecular weight increases might be explained by the fact that, contrary to the case of photopolymerization, the concentration of initiator is not constant but, instead, declines exponentially with time. The low apparent activation energy associated with formation of free radicals from the initiator, reaction 2, supports the hypothesis.

With a decrease in the rate of radical recombination, chain transfer to the monomer eventually becomes the controlling factor governing the extent of polymerization. Under these circumstances ν is given by $\nu = k_p/k_{tr,M}$. With the value of $k_p/k_{tr,M}$ given previously, an upper limit of $\nu = 8.8 \times 10^4$ or a weight-average molecular weight of 1.7×10^7 g/mol would be anticipated. A somewhat higher value of 2×10^7 g/mol is obtained if account is taken of the increase in k_p with extent of polymerization, reported by Kornienko et al.[15,16] In both cases, it is noted that the maximum molecular weight anticipated is in reasonable agreement with that observed in Figure 2 (e.g., 9×10^6 to 1.2×10^7 g/mol).

Finally, we note that the effects of oxygen on the rate of postpolymerization found in this work are similar to those reported by Barnes.[10] His work showed that if a radical polymerization was carried out in the presence of a limited amount of oxygen, an induction period occurred during which no polymer was formed. This period was followed by polymerization at a rate exceeding that occurring in the absence of oxygen. When polymerization was carried out in an atmosphere containing oxygen, two phases were apparent, a fluid upper phase and a viscous lower phase which contained almost all of the polymer.

Barnes[10] explained these observations in the following manner. In the presence of oxygen, the free radicals generated by decomposition of the initiator are rapidly trapped to form peroxide radicals. Since the latter species are relatively unreactive, propagation is suppressed. Once the available oxygen has been consumed, free radicals are produced via decomposition of the initiator as well as the peroxide free radicals, stored up during the induction period. The existence of a second source of free radicals explains why an abnormally high polymerization rate is observed after the induction period.

The oxygen-inhibition mechanism proposed by Barnes[10] also explains why a fluid layer is formed above the polymer/monomer mixture. The upper layer acts as an oxygen barrier to the lower layer. Oxygen diffuses down from the upper layer and reacts with all radicals there. Beyond a certain depth, oxygen is not present and polymerization proceeds uninhibited. Some of the peroxides formed in the upper layer diffuse to the lower layer and initiate polymerization, giving rise to a greater local rate compared to an oxygen-free system.

Conclusions

The results of the present investigation have shown that the polymerization of liquid MMA can be initiated by a viscous oil formed by brief sustainment of a low-pressure plasma in MMA vapor. While the structure of the initiating component has not been identified, it is proposed that this substance may be a derivative of dimethylenecyclohexadiene. The available evidence suggests that the initiator is produced by direct action of electron–molecule reactions, occurring in the plasma, and not by photochemical processes.

The kinetics of postpolymerization, the monomer/copolymer composition relationship for the copolymerization of MMA with MAA and styrene, the tacticity distribution of PMMA produced by plasma-initiated polymerization, and the effects of water, DPPH, and oxygen lead to the conclusion that chain propagation during polymerization occurs via a free-radical mechanism. At the onset of polymerization, chain termination appears to take place by both disproportionation and chain transfer to the monomer. Because the concentration of propagating chains is low, polymers with molecular weights above 10^6 g/mol are produced immediately and the viscosity of the polymer/monomer solution rises rapidly. This leads to an early inception of the gel effect and a consequent rise in polymer molecular weight as polymerization proceeds. Once 50% of the monomer has been converted, the polymer molecular weight exceeds 10^7 g/mol, a level consistent with termination dominated by chain transfer to the monomer.

In the course of the present work it has also been shown that the rate of polymerization can be enhanced by small amounts of oxygen dissolved in the monomer. The accelerating effects of oxygen are ascribed to the formation of peroxides during the early stages of postpolymerization. Once the available oxygen has been consumed, the peroxides decompose, thereby contributing an additional source of free radicals from which chain growth can begin.

References and Notes

(1) Osada, Y.; Bell, A. T.; Shen, M. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 309.
(2) Osada, Y.; Shen, M.; Bell, A. T. *ACS Symp. Ser.* **1979**, *No. 108*.
(3) Bovey, F. A. "Polymer Conformation and Configuration"; Academic Press: New York, 1969.
(4) Brandrup, J.; Immergut, E. H., Eds. "Polymer Handbook", 2nd ed.; Wiley-Interscience: New York, 1975.
(5) Burnett, G. M.; Ducon, G. L. *Makromol. Chem.* **1962**, *51*, 154.
(6) Mackay, M. W.; Melville, M. W. *Trans. Faraday Soc.* **1949**, *45*, 323.
(7) Walling, C.; Briggs, E. R. *J. Am. Chem. Soc.* **1946**, *68*, 1141.
(8) McIntyre, D.; Fetters, L. J.; Slagowski, E. *Science* **1972**, *176*, 1041.
(9) Slagowski, E.; Fetters, L. J.; McIntyre, D. *Macromolecules* **1974**, *7*, 394.
(10) Barnes, C. E. *J. Am. Chem. Soc.* **1945**, *67*, 217. *Ibid.* **1950**, *72*, 210.
(11) Melville, H. W. *Proc. R. Soc. London, Sect. A* **1937**, *163*, 511.
(12) MacKay, M. W.; Melville, H. W. *Trans. Faraday Soc.* **1950**, *46*, 63.
(13) Bamford, C. H.; Dewar, M. J. S., *Discuss. Faraday Soc.* **1947**, *2*, 310.
(14) Bamford, C. H.; Dewar, M. J. S. *Proc. R. Soc. London, Sect. A* **1949**, *197*, 356.
(15) Kornienko, G. I.; Chevenka, A.; Bel'govskii, I. M.; Yenikolopyan, N. S. *Polym. Sci. USSR (Engl. Transl.)* **1969**, *11*, 3072.
(16) Kornienko, G. I.; Bel'govskii, I. M.; Yenikolopyan, N. S. *Polym. Sci. USSR (Engl. Transl.)* **1972**, *14*, 1793.
(17) Garina, E. S.; Olenin, A. V.; Zubov, V. P.; Kuchanov, S. I.; Povolotskaya, E. S.; Kabanov, V. A. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2199.

(18) Majury, T. G. J. Polym. Sci. 1955, 15, 297.
(19) Szwarc, M. Discuss. Faraday Soc. 1947, 2, 46.
(20) Szwarc, M. J. Polym. Sci. 1951, 6, 319.
(21) Suhr, H. In "Techniques and Applications of Plasma Chemistry"; Hollahan, J., Bell, A. T., Eds.; Wiley: New York, 1974.
(22) Burnett, G. M. "Mechanism of Polymer Reactions"; Interscience: New York, 1954.

Role of Solvent in Polymer "Catalysis". Polyelectrolyte Catalysis in the Aquation of Tris(oxalato)cobaltate in Binary Mixtures of Water with Dimethylformamide or Dimethyl Sulfoxide

Mutsuyuki Sugimura, Tsuneo Okubo, and Norio Ise*

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.
Received July 11, 1980

ABSTRACT: The catalytic influence of poly(ethylenimine propionate) (PEI·PA) and other polyelectrolytes on the reaction tris(oxalato)cobaltate, $Co(C_2O_4)_3^{3-}$ (I) → $Co(C_2O_4)_2(H_2O)_2^-$ (II) (step A) → products (Co^{2+}, $H_2C_2O_4$, H_2O, and CO_2) (step B) was studied in binary mixtures of dimethylformamide or dimethyl sulfoxide with water. The first-order rates of the reactions I → products and II → products dramatically increased with decreasing water content. Furthermore, the rate-determining step of the aquation shifted from step A to step B by the addition of the organic solvents. These results supported a significant "dehydration" effect of the activated complex ions and hydronium cations in the two reactions. The enhanced reactions were retarded by PEI·PA addition, which clearly demonstrated the role of the "hydration" (selective water absorption) by the polymer. These "dehydration" and "hydration" effects were also supported by fluorescence, NMR, and light scattering measurements. In pure water, reaction of I was sharply accelerated by PEI·PA, whereas cationic polymers such as poly(4-vinyl-*N*-ethylpyridinium bromide) decelerated the reaction. The latter observation was explained by the so-called "primary salt effect" of the macroions.

Intensive studies on the rate enhancement and retardation effects of polyelectrolytes have been carried out hitherto.[1-6] Recently, we reported a pronounced role of solvent in polyelectrolyte catalysis in cyanoethylation of amino acids in dimethyl sulfoxide (Me_2SO) + H_2O systems and in esterolysis in hexanol + H_2O systems.[7] The role of solvent in polyelectrolyte-catalyzed interionic reaction was clearly demonstrated by our recent work on the influence of high pressure on rate constants.[8] In this report, the solvation effect of polyelectrolytes on the aquations of tris(oxalato)cobaltate and its reaction intermediate in dimethylformamide (DMF) + H_2O and Me_2SO + H_2O mixtures is further studied.

Experimental Section

Materials. The tris(oxalato)cobalt complex $K_3Co(C_2O_4)_3$ was synthesized by the method of Bunton et al.[9] The stable reaction intermediate of $K_3Co(C_2O_4)_3$, $Co(C_2O_4)_2(H_2O)_2^-$, was obtained from $K_2C_2O_4$, CoC_2O_4, and H_2O_2.[10] Poly(ethylenimine) (PEI) was kindly donated by Nippon Shokubai Co., Tokyo (degree of polymerization 100). Purification was carried out by ion exchange through columns of Amberlite IRA-400 and IR-120B. The propionate of PEI (PEI·PA) was obtained from PEI and an equivalent amount of propionic acid. Polybrene (3,6-Ionene polymer, 1,5-dimethyl-1,5-diazaundecamethylene polymethobromide) was purchased from Aldrich Chemical Co. This polymer was purified by repeated precipitation, using a H_2O + acetone mixture. The details of the preparation of poly(4-vinyl-*N*-ethylpyridinium bromide) (C2PVP) were described in a preceding paper.[11] Brij 35, $C_{12}H_{25}(OCH_2CH_2)_{23}OH$, and cetyltrimethylammonium bromide (CTABr) were commercially available and used without further purification. 8-Anilino-1-naphthalenesulfonic acid (ANS) was commercially available and used after repeated recrystallization from water. DMF and Me_2SO were of spectral grade. Water was deionized and distilled for solution preparation.

Kinetic Measurements. The reactions of $Co(C_2O_4)_3^{3-}$ (I) and $Co(C_2O_4)_2(H_2O)_2^-$ (II) were followed by the absorption decrease at 425 nm, using a high-sensitivity spectrophotometer (SM-401, Union Engineering Co., Osaka-fu) and a stopped-flow spectrophotometer (RA-1100, Union Engineering). The molar extinction coefficients of I and II were 209 and 168 M^{-1} cm^{-1}, respectively, at 425 nm.

Fluorescence Measurements. A fluorescence spectrophotometer (FS-401, Union Engineering) was used for the fluorescence measurements of ANS.

Nuclear Magnetic Resonance Measurements. Chemical shifts of protons of water molecules in DMF + H_2O and Me_2SO + H_2O mixtures were determined by using an NMR spectrometer (JNM-PMX60, JEOL Ltd., Tokyo).

Results and Discussion

A. Reactions of I and II in Water, DMF + H_2O, and Me_2SO + H_2O. The aquation reaction of $Co(C_2O_4)_3^{3-}$ (I) in both aqueous and organic media is believed to proceed via an intermediate, $Co(C_2O_4)_2(H_2O)_2^-$ (II), as given in eq 1.[9,10,12] The absorption spectra I and II in water gave two

$$Co(C_2O_4)_3^{3-} \xrightarrow[\text{step A}]{H_3O^+ + 2H_2O} HC_2O_4^- + H_2O$$

I

$$Co(C_2O_4)_2(H_2O)_2^- \xrightarrow[\text{step B}]{3H_3O^+} CO^{2+} + 1.5H_2C_2O_4 + 5H_2O + CO_2 \quad (1)$$

II

clear peaks at 425 and 605 nm and at 420 and 600 nm, respectively. The molecular extinction coefficients of the peaks (10^2 order) coincided with the literature values.[10] New absorption peaks appeared around 500 nm when PEI·PA was added to solutions containing I or II, due to the production of complexes of Co^{2+} with PEI. A typical example of the time dependence of the absorption spectra of a solution of I in the presence of PEI·PA is seen in Figure 1. The absorption spectra of I and II in DMF or Me_2SO in the presence of a small amount of water were quite similar to those in water. However, the peaks were slightly red-shifted (2–5 nm) in the organic solvents. The rate constants of I → products and II → products in the presence of the polymer were obtained from the absorption decrease at 425 or 600 nm. For several cases, the rate constants thus obtained were compared with those ob-

0024-9297/81/2214-0124$01.00/0