Initiation of Methyl Methacrylate Polymerization by the Nonvolatile Products of a Methyl Methacrylate Plasma. 1. Polymerization Kinetics

Charles W. Paul,[†] **Alexis T. Bell,*** **and David S. Soong**

Department of Chemical Engineering, University of California, Berkeley, California 94720.

Received December 31, 1984

ABSTRACT: It is concluded that plasma-initiated polymerization of methyl methacrylate occurs by the continuous unimolecular generation of initiating free radicals by a plasma-deposited oil. This conclusion was drawn from the observed dependence of the rate of polymerization on the 0.58 power of the oil concentration and the first power of the monomer concentration. The reaction kinetics were determined by monitoring the conversion of polymerization in sealed ampules with an oblique-line refractometer. The initiating species is not a single compound. Size exclusion chromatography of the oil produced a series of fractions, each of which was effective as an initiator. The activation energy for initiation is ~15 kcal/mol, independent of whether the whole oil or one of its fractions was used.

Introduction

It has been discovered recently that the polymerization of certain vinyl monomers can be initiated by substances formed in the plasma of a low-pressure glow discharge.[1] Typically, the discharge is produced in the vapor space above the partially frozen monomer to be polymerized. The products of this discharge are then dissolved in the thawed monomer and serve as the initiator. With methyl methacrylate (MMA) it has been established that the initiator is present in a nonvolatile oily deposit on the walls of the plasma zone.[2]

Further studies have shown that polymerization following initiation proceeds by a free radical mechanism[2-9] and can continue for surprisingly long periods—in some cases lasting weeks,[2,5] even months.[6] This process, referred to as plasma-initiated or plasma-induced polymerization (PIP) is of practical interest because it produces polymers[5,6,8,10] or copolymers[8,9,11,12] with ultrahigh molecular weights (UHMW). Investigations have already been reported explaining the utility of UHMW polymers produced by PIP as photoresists[13] and enzyme immobilization media.[14] Other applications for UHMW polymers include drag-reducing agents, lubricant additives, or antimisting agents.

The initiation mechanism for PIP has been the subject of considerable speculation.[2,8,9,15-18] Johnson et al.[2] demonstrated that radiation from the plasma is not responsible for MMA polymerization. Simionescu et al.[8,9] have contended that all growing chains are created immediately upon thawing the monomer, by its reaction with plasma-produced radicals. These growing chains are argued to be very long-lived and thus responsible for the longevity of polymerization. Johnson et al.[2] and Kauno[15] have suggested that polymerization is sustained by continuous generation of initiating radicals through reaction of the initiator with monomer[2] or by entropy-driven scission of the high molecular weight polymer chains being produced.[15]

This study was undertaken with the goal of elucidating the nature of the free radical initiation mechanism. Methyl methacrylate was chosen as the starting material for initiator production via the plasma as well as the monomer for subsequent polymerizations. This choice was made because MMA is the most thoroughly characterized initiator-producing compound and its plasma-induced polymerization is known to form ultrahigh molecular weight polymers.[10] The glow discharge was generated with parallel-plate electrodes external to the plasma vessel and operated at high frequency (13.56 MHz). By use of a flow system several grams of plasma-deposited oil could be collected. This oil was then added to glass ampules along with MMA monomer. An oblique-line refractometer was used to monitor the conversion in each sealed ampule. The polymerization kinetics were studied as a function of oil and monomer concentrations and temperature. The oil was fractionated by size exclusion chromatography (SEC), and the fractions were added separately to polymerization ampules in an attempt to identify which fraction contained the active component(s).

Experimental Section

Materials. Methyl methacrylate (Aldrich Chemical Co.) was vacuum-distilled under nitrogen at 38 °C to remove the manufacturer-added inhibitor (65 ppm of hydroquinone monomethyl ether, bp 285 °C). The middle fraction was collected and stored in a freezer at −10 °C. Isopropyl acetate (bp 89.4 °C) was distilled at atmospheric pressure, and the middle fraction was collected and stored in a refrigerator (~0 °C). Benzene (MCB Omni Solv) and carbon tetrachloride (Aldrich Gold Label) were used as received for dissolving the initiator. Chloroform (MCB Omni Solv), used for the same purpose, was first distilled at atmospheric pressure (bp 61 °C). All three solvents were spectrophotometric grade. The carrier liquids for size exclusion chromatography, spectrophotometric-grade carbon tetrachloride and UV-grade tetrahydrofuran (THF), were obtained from Burdick and Jackson.

Preparation of Initiator. The initiator, an oily, nonvolatile substance, was produced with the apparatus shown in Figure 1. Distilled MMA was degassed by the freeze–evacuate–thaw procedure on the vacuum manifold, and then the manifold was shut off from the pump. An ice bath was placed around the flask containing the MMA, and then the flask was opened to the manifold to provide a vapor pressure of ~9.5 torr. A plasma was created in a Pyrex tube attached to the manifold. Power for the discharge was supplied by a 13.56-MHz radio-frequency generator connected to a pair of parallel-plate electrodes through an impedence-matching network. In all cases the power was maintained between 40 and 43 W. MMA was forced to flow through the plasma zone by cracking open a needle valve connecting the system to a vacuum pump. The residence time of the MMA vapor in the plasma (based on the inlet conditions) ranged from 4 to 9 s, depending on the setting of the needle valve. Steady-state operating pressures varied from 8.0 to 9.3 torr. The plasma appeared brightest and broadest at the top of electrodes (the inlet region). A nonvolatile oily deposit was formed on the walls of the plasma zone. As this oil accumulated, it dripped down the walls of the tube into a 25-mL collection flask. Eight to nine hours was required to collect the first drops of the viscous, transparent oil. Its color varied from faint to bright yellow. Oil was collected for 1–3.5 days. The collection flask was then removed, purged

---

[†] Present address: Allied Corp., Morristown, NJ 07960.

0024-9297/85/2218-2312$01.50/0

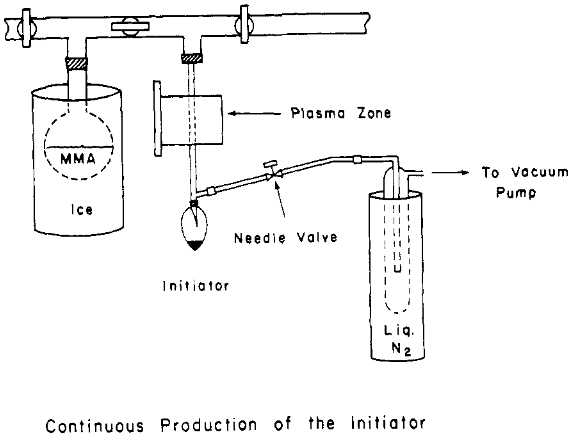


Figure 1. Flow system for initiator production.

with nitrogen, and stored over dry ice (−78.5 °C).

Measurement of Polymerization Kinetics. The polymerization of MMA was initiated by mixing a small amount of the initiator with MMA in a glass ampule with the following procedure. Initiator oil dissolved in carbon tetrachloride or benzene was injected into an ampule with a syringe. The increase in the weight of the ampule was used to determine the exact volume of initiator solution added. The ampule was then connected to the vacuum manifold, and the initiator solution was degassed. Degassed MMA (2 mL) was distilled over into the ampule, and the ampule was then sealed with a torch. The sealed ampule was shaken, wrapped with aluminum foil to exclude light, and placed in a constant-temperature bath.

The conversion of MMA was determined by measuring the change in the index of refraction of the polymerizing mixture with an oblique-line refractometer. This device shines a thin slit of light through the reaction tube at an oblique angle. The image of this light slit is viewed through the reaction tube. The angle of this image is different from the incident angle to a degree that depends on the refractive index of the reaction mixture. It is possible to obtain the complete conversion vs. time history of an ampule with the refractometer. The oblique-line refractometer used in these studies is described in detail in ref 19. Its design is similar to that used by Naylor and Billmeyer[20] and Pulley,[21] who also used it to study the polymerization of MMA.

The variable measured experimentally is the angle of the light slit image. This quantity is then related to the refractive index of the polymerizing mixture by means of a calibration curve. The calibration curve was constructed by using ampules filled with appropriate mixtures of toluene ($n^{25}{}_{\rm D}$ = 1.4900) and octane ($n^{25}{}_{\rm D}$ = 1.3954) and mixtures of toluene and *o*-xylene ($n^{25}{}_{\rm D}$ = 1.5030). These mixtures covered the refractive index range of interest, i.e., from pure MMA at 50 °C to 85% PMMA in MMA at 50 °C—the limiting conversion at this temperature. The refractive index of each standard solution was determined with a Bausch and Lomb Abbe refractometer. Measurements were made at room temperature and then corrected to the temperature of the bath for the oblique-line refractometer by known temperature coefficients.[22,23] For mixtures, volume fraction average coefficients were used.

The extent of monomer conversion, $X_{\rm m}$, was obtained by the following equation:

$$X_{\rm m} = \frac{[n^T{}_{\rm D}(X_{\rm m}) - n^T{}_{\rm D}(0)]}{\rm RII} \tag{1}$$

where $n^T{}_{\rm D}(X_{\rm m})$ is the refractive index of the mixture at conversion $X_{\rm m}$ and temperature T and RII is the refractive index increment. Equation 1 assumes that refractive index and conversion are linearly related. This assumption was found to be valid by Walling and Briggs[24] at 20 °C and MMA conversions up to 40%. Deviations from linearity, if present, should be most pronounced at about 50% conversion, where any excess volume of mixing would be a maximum.

The value of RII was determined from the relation

$$\mathrm{RII} = [n^T{}_{\rm D}(X_{\rm lim}) - n^T{}_{\rm D}(0)]/X_{\rm lim} \tag{2}$$

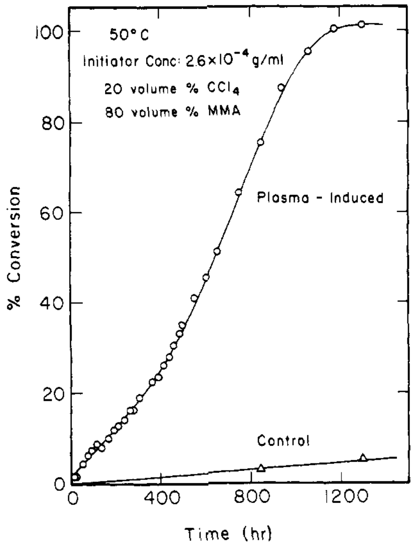


Figure 2. Monomer conversion vs. time.

The refractive index at the limiting conversion, $n^T{}_{\rm D}(X_{\rm lim})$, was determined experimentally. For experiments in which the ampule contained 20% solvent (used to dissolve the initiator), the limiting conversion was 100%. Without any solvent the limiting conversion was taken to be 85% at 50 °C based on results obtained by Martin and Hamielec.[25] The value of RII so computed for the latter case was 9.55×10^{-4} per percent conversion at 50 °C, in good agreement with the valve of 9.4×10^{-4} per percent conversion at 20 °C reported by Walling and Briggs.[24]

For parts of the study, conversion was measured gravimetrically. The ampule contents were dissolved in toluene containing 5×10^{-5} g/mL of 2,2-diphenyl-1-picrylhydrazyl (DPPH) to quench the polymerization. The polymer was then recovered by precipitation in methanol. The ratio of methanol to polymer was at least 6:1.

Size Exclusion Chromatography. A portion of the nonvolatile oily product of an MMA glow discharge was fractionated by size exclusion chromatography (SEC). A Waters Associates SEC system with three 100-Å μStyragel columns in series, followed by both a refractive index and an ultraviolet absorption detector, was used. Solutions of up to 30% by volume plasma-produced oil in CCl_4 were injected. These high concentrations were possible with only minor resolution loss because the oil is not very viscous by polymer standards. The flow rate was 0.5 mL/min and the injection volume was 100 μL; higher flow rates or injection volumes reduced the resolution. To estimate the molecular weight of the fractions, a universal calibration curve[26] was constructed with solutions of polystyrene and polyethylene of known molecular weight.[19] This curve yields the product $[\eta]M$ for a given retention volume ($V_{\rm r}$), where $[\eta]$ is the intrinsic viscosity of an eluent and M its molecular weight. To determine M from $[\eta]M$, a Mark–Houwink relationship between $[\eta]$ and M was needed. Since one was lacking for the plasma-produced oil, a relationship established for linear PMMA was adopted.[19] Since the plasma-produced oil is probably highly branched, the above procedure yields molecular weight estimates that can be considered lower bounds.

Results

Polymerization Rate Dependence on Initiator and Monomer Concentrations and Temperature. The rate of polymerization was measured at initiator concentrations of 1×10^{-4} to 43×10^{-4} g/mL. Polymerization reaction mixtures consisted of 20% (volume basis) CCl_4 (the solvent used in making the initiator solutions) and 80% MMA. Conversion vs. time was measured with the oblique-line refractometer. Figure 2 is a typical conversion vs. time plot. The initial rate of polymerization was computed from the slope of a line fitted to the data for conversions of 5–20%. The rate was proportional to the initiator concentration to the 0.58 power, as shown in Figure 3. The ordinate of Figure 3 is a reduced rate of polymerization.

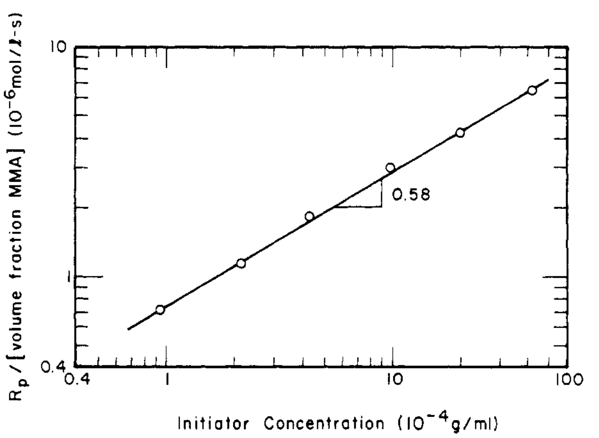


Figure 3. Reduced polymerization rate vs. initiator concentration.

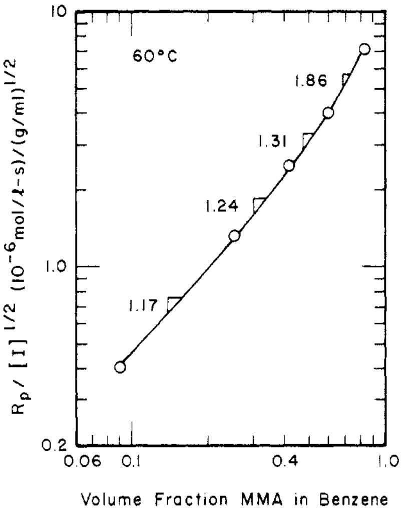


Figure 4. Reduced polymerization rate vs. MMA concentration in benzene.

The measured rate was divided by the monomer concentration (volume fraction) to adjust for the small differences (up to 2.5%) in the monomer concentration in different ampules. This procedure assumes that the rate depends on the first power of the monomer concentration. While the exact power dependence hardly matters for such a small correction, this assumed dependence will shortly be shown to be correct.

The polymerization rate at different monomer concentrations was measured gravimetrically. Solutions of MMA and initiator in benzene were prepared. All polymerizations were conducted for 54.7 h at 60.1 °C. This temperature was chosen so that the viscosity of MMA and benzene would be the same, thus eliminating any changes in polymerization rate constants due to viscosity differences at different monomer concentrations. It has been shown[27] that at 60 °C and low conversions (<4%), the rate constants for MMA polymerization are the same in benzene solution as in pure MMA.

The average rate of polymerization was computed from the amount of polymer produced during the fixed time interval. Conversions reached 20%. The rates are plotted vs. the volume fraction of MMA in Figure 4. This volume fraction is the average of the initial and final values. The ordinate is a reduced polymerization rate. The measured polymerization rate has been divided by the initiator concentration to the 0.5 power to correct for slight variations in the amount of initiator added. The plot curves upward as the volume fraction of MMA increases. This is due to the higher viscosity of the more concentrated solutions (for a fixed monomer conversion), which gives rise to a reduction in termination rate constant and consequently an increase in the polymerization rate. This effect is clearly visible in data taken with the oblique-line refratometer. For an initially 80% MMA solution, Figure 5a, the rate is nearly constant or slightly accelerates up to 20% conversion. On the other hand, in an initially 50% MMA solution, Figure 5b, the rate tapers off with conversion. If radicals are generated continuously at the same rate and the primary rate constants are independent of conversion, the rate of polymerization should decrease linearly with monomer conversion. The contrasting trends observed in Figure 5, parts a and b, are attributed to the presence of a solution viscosity or "gel effect" which accelerates the polymerization rate. This effect subsides, however, as the monomer concentration is reduced. Therefore the true power dependence of the initial polymerization rate on the monomer concentration is given by the slope of Figure 4 in the limit that the monomer concentration approaches zero, because only in this limit are viscosity effects negligible. This limiting slope is close to 1, a value typical of ordinary free radical polymerizations.

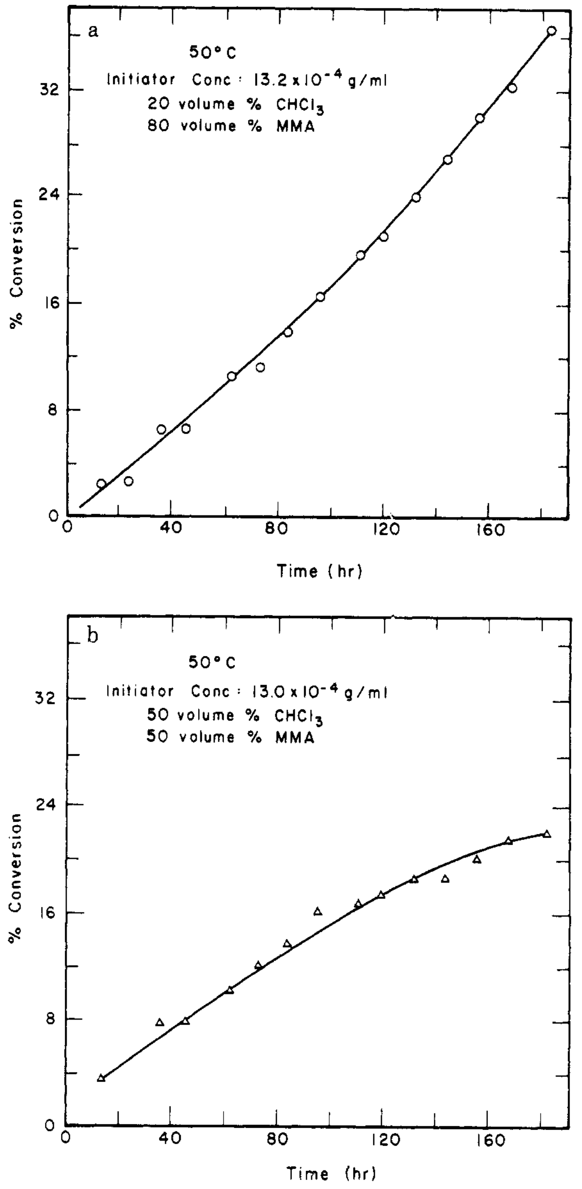


Figure 5. (a) Monomer conversion vs. time for 80 vol % MMA in $CHCl_3$. (b) Monomer conversion vs. time for 50 vol % MMA in $CHCl_3$.

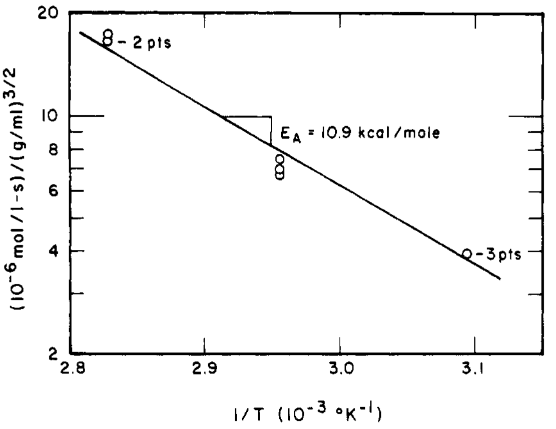


Figure 6. Reduced polymerization rate vs. $1/T$.

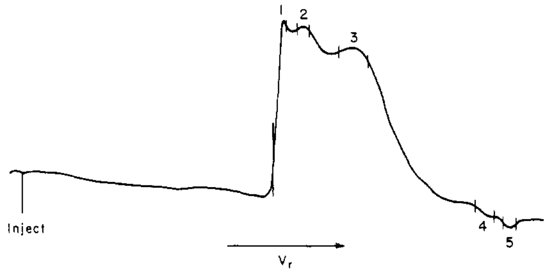


Figure 7. SEC elution chromatogram of the initiator obtained with refractive index detection. Fractions were collected between the vertical marks.

The rate of polymerization was also measured at different temperatures. Polymerizations above 50 °C were conducted in an oil bath. However, conversion was measured by removing the ampules from the oil bath and inserting them momentarily in the oblique-line refractometer (at 50 °C). Three polymerization temperatures were used, 50, 65, and 80 °C, and three ampules were run at each temperature. The reduced polymerization rate is plotted against $1/T$ in Figure 6. From the slope of this plot an overall activation energy, E_A, of 10.9 kcal/mol was determined. This value is close to the value of 9.1 kcal/mol obtained by Johnson et al.[2] If polymerization occurs by a free radical mechanism, then an apparent activation energy for the initiation process, E_i, can be computed from[28]

$$E_A = E_p + 0.5(E_i - E_t) \qquad (3)$$

with an activation energy for propagation, E_p, of ~4.7 kcal/mol and an activation energy for termination, E_t, of ~2.3 kcal/mol,[29] the value computed for E_i is 14.7 kcal/mol.

Polymerizations Using Initiator Fractions. Fractionation of the plasma-produced oil by SEC resulted in the elution chromatogram shown in Figure 7. The primary features are three broad, overlapping peaks for which the refractive index is greater than that of the carrier ($n^{20}{}_D(\mathrm{CCl})_4 = 1.4601$). Two broad minor peaks of lower molecular weight and refractive index less than the carrier also appear. Central cuts of each peak (shown in Figure 7) were collected as they eluted. After many injections, the accumulated fractions were stored in a −10 °C freezer.

The activity of the oil fractions for initiating the polymerization of MMA was investigated with the following procedure. A 0.11–0.5-mL aliquot of a fraction was added to an ampule and mixed with spectrophotometric-grade CCl_4 so that the ampule contained 0.5 mL of CCl_4. The ampule was attached to the vacuum manifold and degassed. Two milliliters of degassed MMA was then added to the ampule. Polymerization rates were determined at 50, 65, and 80 °C. There was an insufficient volume of fractions 1, 5, and 6 to supply three polymerization ampules each. Consequently polymerizations using fractions 1 and 6 were only conducted at 50 and 80 °C, while fraction 5 was only used at 50 °C.

Table I
Characteristics of the Initiator Fractions

	fraction					
	1	2	3	5	6	control[d]
mol wt[a]	1300	1000[b]	450	100	<100[c]	
proportion of initiator, wt %	3.3	11.3	84.4	1.0	0[e]	
R_p[f]	4.4	3.7	1	0.9	3.3	0.11[g]
% IC[h]	10	30	60	0.6	0	
E_A, kcal/mol	11.8	10.3	12.3		11.3	17

[a] These molecular weight estimates are probably lower bounds.[19] [b] The SEC system used to estimate molecular weights did not resolve fractions 1 and 2, so their molecular weights should be very similar. [c] The universal calibration curve for the SEC system did not extend to the elution volume at which this peak appeared. [d] The control sample was composed of 0.5 mL of the CCl_4 effluent from the SEC columns (collected after all initiator fractions eluted) and 2 mL of MMA. The control using eluted CCl_4 polymerized about as fast (within the experimental accuracy) as a control using CCl_4 that had not passed through the SEC system (used directly from the bottle). [e] Fraction 6 is believed to be an impurity and not a component of the plasma-produced oil. [f] Polymerization rate relative to a given mass. [g] Polymerization rate of the control relative to that of fraction 3 at 80.4 °C. [h] The percentage of the initiating capacity of the plasma-produced oil which resides in each fraction. These percentages were computed from the weight percent of the initiator contained in each fraction and the relative polymerization rate for a given mass of initiator component added.

The results of polymerization initiated by individual oil fractions are summarized in Table I. The weight percent of the initiator oil in each fraction was estimated from the relative quantity of each fraction, as determined by the SEC chromatogram, and the relative concentration of plasma-produced material each fraction contained, as estimated from their ^1H NMR spectra.[19] About 99 wt % of the initiator is contained in the first three fractions. The concentration of plasma-produced material in each fraction was also used to determine the relative polymerization rate for a given mass of initiator component added.[19] From these values and the weight percent of the initiator contained in each fraction, the percentage of the initiating capacity of the plasma-produced oil due to each fraction was computed. More than 99% of the initiating capacity of the plasma-produced oil resides in the first three fractions. The relative effectiveness (per unit mass) of the first five fractions, as initiators, is in the same sequence as their molecular weights: 1 > 2 > 3 > 5. There was a yellow tint to these fractions, which was also in the order 1 > 2 > 3. (Fraction 6 was clear and none of fraction 5 was available at the time of the comparison.) Interestingly, the lowest molecular weight initiator-containing fraction (5) was almost as effective as the third fraction, which contained 60% of the initiating capacity. The impurity (fraction 6) was more effective than fraction 3. On a volume basis, however, both fractions 5 and 6 were significantly less effective than fraction 3. Finally, it should be noted that all fractions initiated polymerization at a rate above that in the control sample.

For fractions 1–3 and 6 an overall activation energy for the polymerization rate was evaluated. Values obtained were similar for each of these fractions (see Table I) and close to that of the unfractionated initiator (10.9 kcal/mol). The activation energy for the control sample was 17 kcal/mol and corresponds to an activation energy for in-

Table II
Rate of MMA Polymerization Using Different Plasma-Produced Initiators and Plasma Powers

power, W	$10^6 R_p$,[a,b] mol L^{-1} s^{-1}	
	i-PrAc plasma products	MMA plasma products
40	3.1	6.5
100	1.2	
200	0.59	

[a] The polymerization temperature was 50 °C. The plasma duration was 8 min, the initial plasma pressure was 8 torr, and 2 mL of MMA was added to each ampule after plasma exposure. [b] Control sample polymerization rate 0.1 × 10^{-6} mol L^{-1} s^{-1}.

itiation of 26.9 kcal/mol, as calculated from eq 3. This value is in good agreement with the value of 25.9 kcal/mol obtained by Stickler and Meyerhoff[30] for the thermal polymerization of MMA.

Polymerization Initiators from the Plasma of a Non-vinyl Compound. Ampules were filled with isopropyl acetate vapor, and a glow discharge was created. The plasma was ignited at a pressure of 8 torr with a Tesla coil, but the pressure rose ~0.5 torr during the 8 min that the plasma was on. After the discharge was shut off, the ampules were filled with 2 mL of liquid MMA and sealed under vacuum. No plasma deposit was visible at powers of 40 or 100 W. At 200 W an intensely bright blue plasma created a yellow film on the walls of the plasma zone. When MMA was added, the film flaked off as long slender needles that slowly settled to the bottom of the ampule. After the ampule was sealed, conversion was monitored with the oblique-line refractometer. As before, the initial slope of a conversion vs. time plot was used to determine the polymerization rate. As shown in Table II, the rate decreased with power. While the initiator produced in the isopropyl acetate plasma was twofold less effective in initiating MMA polymerization than that produced from MMA, the measured rates were well above the background rate at all plasma powers.

Discussion

There is convincing evidence[2-9,31] that plasma-induced polymerization occurs by a free radical mechanism. A key issue that remains unresolved, though, is the mechanism of initiation. Some insights into this question can be gained by considering the dependence of the polymerization rate on the initiator and monomer concentrations. The reaction sequence for free radical polymerization is

Initiation

$$a\mathrm{I} + b\mathrm{M} \xrightarrow{k_{i1}} c\mathrm{R}\cdot \qquad \text{(I)}$$

$$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_{i2}} \mathrm{M}_1\cdot \qquad \text{(II)}$$

Propagation

$$\mathrm{M}_n\cdot + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_{n+1}\cdot \qquad \text{(III)}$$

Termination

$$\mathrm{M}_n\cdot + \mathrm{M}_m\cdot \xrightarrow{k_{tc}} \mathrm{P}_{n+m} \qquad \text{(IV)}$$

$$\mathrm{M}_n\cdot + \mathrm{M}_m\cdot \xrightarrow{k_{td}} \mathrm{P}_n + \mathrm{P}_m^{=} \qquad \text{(V)}$$

where I is the initiator (which could be a radical), M is the monomer (MMA), R· is an initiating radical, M· is a growing chain, P is a dead polymer, and $\mathrm{P}^{=}$ represents a polymer chain with an unsaturated end group. The initiation process is formally divided into two steps. The primary initiation step, reaction I, is unknown and therefore written with unspecified stoichiometry; however, it is assumed that neither polymer nor solvent participates in this step. Primary initiation is defined as a reaction (or sequence of reactions) that produces "reactive" initiating radicals, R·. By "reactive", it is meant that their average lifetime is much less than that of growing chains (less than a few minutes at the growing-chain concentrations in this study). Since the average degree of polymerization is ~10^5, R· need only be ~10^{-3} as reactive as growing chains toward monomer in order to satisfy this very weak definition of reactive.

If it is assumed that propagation occurs far more frequently than initiation, then the rate of polymerization can be approximated by

$$R_p = \mathrm{d[M]}/\mathrm{d}t \simeq k_p[\mathrm{M}\cdot][\mathrm{M}] \qquad [\mathrm{M}\cdot] \equiv \sum_n [\mathrm{M}_n\cdot] \qquad (4)$$

The concentration of growing chains can be eliminated from this expression by assuming the initiating radical and growing-chain concentrations are at steady state and that the steady-state concentration of initiating radicals is much less than that of growing chains. The latter assumption is valid simply by the definition of R·. Thus

$$\mathrm{d}[\mathrm{R}\cdot]/\mathrm{d}t \simeq 0 = ck_{i1}[\mathrm{I}]^a[\mathrm{M}]^b - k_{i2}[\mathrm{R}\cdot][\mathrm{M}] \qquad (5)$$

$$\mathrm{d}[\mathrm{M}\cdot]/\mathrm{d}t \simeq 0 = k_{i2}[\mathrm{R}\cdot][\mathrm{M}] - 2[\mathrm{M}\cdot]^2(k_{tc} + k_{td}) \qquad (6)$$

Adding eq 5 and 6 and defining $k_t \equiv k_{tc} + k_{td}$ yield

$$ck_{i1}[\mathrm{I}]^a[\mathrm{M}]^b = 2[\mathrm{M}\cdot]^2 k_t \qquad (7)$$

$$[\mathrm{M}\cdot] = (ck_{i1}/2k_t)^{1/2}[\mathrm{I}]^{a/2}[\mathrm{I}]^{a/2}[\mathrm{M}]^{b/2} \qquad (8)$$

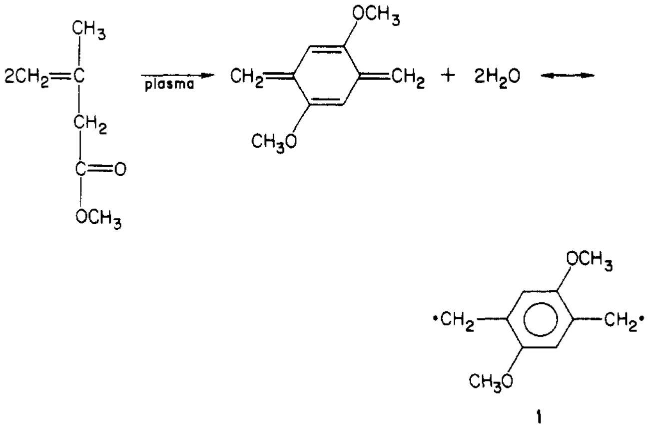
Substituting this expression for $[\mathrm{M}_n\cdot]$ into eq 4 gives

$$R_p = k_p(ck_{i1}/2k_t)^{1/2}[\mathrm{I}]^{a/2}[\mathrm{M}]^{1+b/2} \qquad (9)$$

The observed nearly half-order dependence of the rate of polymerization on the initiator concentration implies $a = 1$, while the almost first-order dependence on the monomer concentration requires $b = 0$ in the equation above. Furthermore, since radical sites are always generated in pairs, $c = 2$. Thus the primary initiation step, reaction I, involves the unimolecular creation of radical pairs from the initiator compound. With $a = 1$, $b = 0$, and $c = 2$, eq 5 becomes

$$R_p = k_p(k_{i1}/k_t)^{1/2}[\mathrm{I}]^{1/2}[\mathrm{M}] \qquad (10)$$

Johnson et al.[2] proposed that the biradical 1 may be formed in an MMA plasma and be responsible for the plasma-induced polymerization of MMA.



1

The authors argued that 1 could initiate polymerization continuously, provided its reaction with monomer was sufficiently slow. Thus the primary step was assumed to be of the form

$$\mathrm{I} + \mathrm{M} \xrightarrow{k_{i1}} \mathrm{R}\cdot \qquad \text{(VI)}$$

This implies that the coefficient b in reaction I is 1. The observation that b is not 1, but 0, rules out this mechanism and any others like it, which assume that the initiator reacts with monomer to form reactive initiating radicals.

Other investigators[8,9,16,17] have proposed that plasma-produced radicals are responsible for initiation. These cannot be stable radicals that continuously initiate polymerization by reaction with monomer, for the reasons just mentioned. However, if the plasma-produced radicals are of ordinary reactivity toward an olefin, they should then form growing chains via reaction I within a very short time, t, after contacting the monomer. The magnitude of t can be estimated from

$$t \simeq 1/k_p[\mathrm{M}] = 1/(400\ \mathrm{L\ mol^{-1}\ s^{-1}})(10\ \mathrm{mol/L}) = 2.5 \times 10^{-4}\ \mathrm{s} \qquad (11)$$

t was evaluated by using the value of k_p at 25 °C cited in ref 32. This calculation indicates that polymerization would begin quite promptly. The next question is whether polymerization still proceeds for hundreds of hours as observed (see Figure 2) without further initiation. The number of growing chains at 50 °C can be computed from the initial rate of polymerization as follows:

$$[\mathrm{M}\cdot] = R_p/k_p[\mathrm{M}] = (6.5 \times 10^{-6}\ \mathrm{mol\ L^{-1}\ s^{-1}})/(823\ \mathrm{mol\ L^{-1}\ s^{-1}})(10\ \mathrm{mol/L}) = 8.3 \times 10^{-10}\ \mathrm{mol/L} \qquad (12)$$

As termination occurs, the population of growing chains falls according to eq 6

$$\mathrm{d}[\mathrm{M}\cdot]/\mathrm{d}t = -2k_t[\mathrm{M}\cdot]^2 \qquad (13)$$

Integrating eq 13 from $t = 0$ to t gives

$$1/[\mathrm{M}\cdot] - 1/[\mathrm{M}\cdot]_{t=0} = 2k_t t \qquad (14)$$

With a value of 4.6×10^7 mol L^{-1} s^{-1} for k_t at 50 °C,[32] the time required for 90% of the chains initially present to terminate is 2 min. Consequently, it would appear impossible for a polymerization reaction that proceeds for hundreds of hours to have been initiated only at the start of the reaction.

It is well-known that MMA polymerization initiated by one pulse of UV light,[33] γ-rays,[34] or electrons[33] continues for hundreds of hours, but at a slowly decaying rate. Polymerization is believed to be due to the production of a thermally unstable compound during irradiation (such as a peroxide),[35] which through its decomposition continuously generates initiating radicals that sustain the polymerization. However, it is possible that the long duration of these polymerizations is not due to the continuous generation of initiating radicals but rather to a reduction in the chain termination rate constant due to the fact that all growing chains are very long in such a slowly polymerizing system. Theoretical calculations[36] predict a decrease in k_t with chain length even in very dilute polymer solutions. This decrease in k_t would proportionately increase the average lifetime of the radicals (see eq 11). If long-lived radicals are responsible for the extended polymerization of MMA after irradiation (the "aftereffect"), it is still unlikely that they are responsible for plasma-induced polymerization for the following reasons. First, it has been observed that the rate of polymerization slowly decays with time during the aftereffect, even at low conversions. By contrast, in plasma-induced polymerization the rate slightly accelerates (see Figure 2). Second, by such a mechanism, the number of long-lived growing chains, and therefore the rate of polymerization (see eq 4), should be directly proportional to the first power of the amount of initiator added. The observed half-order dependence of the rate on the initiator concentration is evidence against a long-lived-radical mechanism.

The above discussion indicates that our polymerization data are inconsistent with any scheme in which stable plasma-produced radicals initiate polymerization continuously or one where reactive plasma-produced radicals initiate polymerization rapidly once contacted with monomer. Thus, plasma-produced radicals of any type are not responsible for polymerization. This conclusion is further supported by electron spin resonance data[37] (which show that the initiator contains very few radicals but decomposes slowly to produce radicals with time).

The mechanism by which the initiator generates free radicals is unknown. Apparently, it is not due to the decomposition of any specific compound produced by the plasma, as all fractions of the initiator are effective, although to different degrees (see Table I). The overall activation energy for polymerization was similar when each of the first three fractions was used as the initiator. This result implies that the primary initiation reaction is probably similar for each fraction. The very low value of the effective activation energy for primary initiation (~15 kcal/mol) implies that if this reaction involves a bond-breaking process, this bond must be either very unstable or bond breaking must occur simultaneously with some other highly exothermic reaction. Moreover, it seems unlikely that the primary initiation process should require the presence of any specific functional groups since plasma-induced polymerization has been achieved with a variety of compounds.[1,7,8,17] Although most of the earlier work was conducted with compounds containing a vinyl group, the experiments with isopropyl acetate (summarized in Table II) and those of Kuzuya et al.[17] using methyl isobutyrate demonstrate that compounds without vinyl groups can also form polymerization initiators in a plasma.

Conclusions

The polymerization of MMA can be initiated by a nonvolatile, oily compound produced in a plasma sustained in MMA vapor. The kinetics of polymerization are characterized by a 0.58-order dependence on oil concentration, a first-order dependence on monomer concentration, and an apparent activation energy of 10.9 kcal/mol. The initiating species is not a single compound but, rather, consists of a spectrum of compounds ranging in molecular weight from 100 to 1300. All molecular weight fractions are capable of initiating polymerization, albeit with different efficiencies. It is concluded that the polymerization of MMA is initiated by the continuous unimolecular decomposition of species present in the plasma-produced oil.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund administered by the American Chemical Society.

Registry No. MMA, 80-62-6.

References and Notes

(1) Osada, Y.; Bell, A. T.; Shen, M. In "Plasma Polymerization"; Shen, M., Bell, A. T., Eds.; American Chemical Society: Washington, DC, 1979; ACS Symp. Ser. No. 108.
(2) Johnson, D. R.; Osada, Y.; Bell, A. T.; Shen, M. *Macromolecules* **1981**, *14*, 118.
(3) Simionescu, B. C.; Natansohn, A.; Simionescu, C. I. *Polym. Bull. (Berlin)* **1980**, *2*, 809.
(4) Simionescu, B. C.; Natansohn, A.; Leanca, M.; Ananiescu, C.; Simionescu, C. I. *Polym. Bull. (Berlin)* **1980**, *3*, 247.

(5) Simionescu, B. C.; Leanca, M.; Ananiescu, C.; Simionescu, C. I. *Polym. Bull. (Berlin)* **1980**, *3*, 437.
(6) Simionescu, B. C.; Leanca, M.; Ioan, S.; Simionescu, C. I. *Polym. Bull. (Berlin)* **1981**, *4*, 415.
(7) Simionescu, B. C.; Natansohn, A.; Leanca, M.; Ananiescu, C. *Polym. Bull. (Berlin)* **1981**, *4*, 569.
(8) Simionescu, C. I.; Simionescu, B.; Leanca, M.; Ananiescu, C. *Polym. Bull. (Berlin)* **1981**, *5*, 61.
(9) Simionescu, B. C.; Popa, M.; Ioan, S.; Simionescu, C. I. *Polym. Bull. (Berlin)* **1982**, *6*, 415.
(10) Kashiwagi, Y.; Einaga, H.; Fujita, H. *Polym. J. (Tokyo)* **1980**, *12* (4), 271.
(11) Simionescu, B. C.; Ioan, S.; Simionescu, C. I. *Polym. Bull. (Berlin)* **1982**, *6*, 409.
(12) Ioan, S.; Simionescu, B. C.; Simionescu, C. I. *Polym. Bull. (Berlin)* **1982**, *6*, 421.
(13) Gavens, L. M.; Wu, B. J.; Hess, D. W.; Bell, A. T.; Soong, D. S. *J. Vac. Sci. Technol., B* **1983**, *1*, 481.
(14) Osada, Y.; Iino, Y.; Iriyama, Y. *Chem. Lett.* **1982**, 171.
(15) Kauno, S.; *J. Phys. Soc. Jpn.* **1979**, *47*, 947.
(16) Kuzuya, M.; Kamya, K.; Kawaguchi, T.; Okuda, T. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 509.
(17) Kuzuya, M.; Kawaguchi, T.; Daikyo, T.; Okuda, T. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 515.
(18) Johnson, D. R. M.S. Thesis, University of California, Berkeley, CA, 1979.
(19) Paul, C. W. Ph.D. Thesis, University of California, Berkeley, CA, 1984.
(20) Naylor, M. A.; Billmeyer, F. W., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 2181.
(21) Pulley, J. M.S. Thesis, Rensselaer Polytechnic Institute, Troy, NY, 1969.
(22) *Beilstein, 4th ed.* 1972.
(23) "International Critical Tables"; McGraw-Hill: New York, 1930; Vol. VII.
(24) Walling, C.; Briggs, E. R. *J. Am. Chem. Soc.* **1946**, *68*, 1141.
(25) Martin, F. L.; Hamielec, A. E. In "Polymerization Reactors and Processes"; Henderson, J. N., Bouton, T. C., Eds.; American Chemical Society: Washington, DC, 1979; ACS Symp. Ser. No. 104.
(26) Ouano, A. C. *J. Macromol. Sci.* **1973**, *C9* (1), 123.
(27) Otsu, T.; Nozaki, T. *Mem. Fac. Eng., Osaka City Univ.* **1971**, *12*, 123.
(28) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953.
(29) Ross, R. T.; Lawrence, R. L. *AIChE Symp. Ser.* **1976**, *160* (72), 74.
(30) Stickler, M.; Meyerhoff, G. *Makromol. Chem.* **1978**, *179*, 2729.
(31) Akovali, G.; Demirel, G.; Ozkar, S. *J. Macromol. Sci., Chem.* **1983**, *A20* (8), 887.
(32) Brandrup, J., Immergut, E. H., Eds. "Polymer Handbook"; Wiley: New York, 1975.
(33) Majury, T. J. *J. Polym. Sci.* **1955**, *15*, 297.
(34) Okamura, S.; Hayashi, K. *Isotopes Radiat.* **1958**, *1*, 102.
(35) Chapiro, A. "Radiation Chemistry of Polymeric Systems"; Wiley: New York, 1962.
(36) Olaj, O. F.; Zifferer, G. *Proc. IUPAC 28th Macromol. Symp.* 1982, 511.
(37) Paul, C. W.; Bell, A. T.; Soong, D. S., *Macromolecules*, following paper in this issue.

Initiation of Methyl Methacrylate Polymerization by the Nonvolatile Products of a Methyl Methacrylate Plasma. 2. Molecular Weight Measurements

Charles W. Paul,† Alexis T. Bell,* and David S. Soong

Department of Chemical Engineering, University of California, Berkeley, California 94720.
Received December 31, 1984

ABSTRACT: Plasma-induced polymerization of MMA produces PMMA with a molecular weight exceeding 10^7. The polymer molecular weight increases with monomer conversion, nearly doubling in going from 7% to 40% conversion. At conversions above 40%, PMMA samples were very lightly cross-linked and insoluble. Unsaturation of the initiator fragments contributes to cross-linking. The absolute value of the molecular weight and its dependence on conversion are interpreted in terms of a free radical polymerization mechanism.

Introduction

Previous studies[1–7] have demonstrated that ultrahigh molecular weight (UHMW) polymers can be produced by the process termed plasma-induced (initiated) polymerization (PIP). Recent investigations of PIP indicate that it proceeds via a free radical chain-growth process.[1–4,8–11] This has raised the question of whether the observed very high molecular weights might not also be explained by the same mechanism. In the present paper, we report measurements of the molecular weights of poly(methyl methacrylate) (PMMA) produced by PIP as a function of monomer conversion. These data are discussed in the light of a free radical mechanism of chain growth. Evidence for cross-linking at monomer conversions above 40% is also presented, and possible mechanisms for causing cross-linking are examined.

Experimental Section

Polymer Synthesis. The plasma-induced polymerization of MMA was carried out in a manner similar to that described in ref 8. Degassed MMA was transferred cryogenically into a glass ampule and frozen. Polymerization was initiated by igniting a low-pressure plasma in the vapor space above the frozen monomer. The plasma was maintained by a set of parallel-plate electrodes placed around the ampule and connected to a radio-frequency generator. After 60 s, the plasma was extinguished and the monomer refrozen. The vapor space was then evacuated, and the ampule was sealed with a torch at some point above the electrode region. The ampule was then allowed to thaw, after which it was shaken for several minutes to dissolve any nonvolatile plasma products deposited on the ampule walls. [These nonvolatile products are known[8,12] to contain the initiator species.] A set of ampules prepared in a similar manner was placed in a water bath maintained at 25 °C and covered to exclude light. The extent of polymerization in each ampule was determined periodically with an oblique-line refractometer.[12–14]

When the extent of polymerization in a given ampule had reached a desired level, the ampule was broken open and the contents transferred to an Erlenmeyer flask. To each flask was added a sufficient quantity of a solution of 5×10^{-5} g/mL of 2,2-diphenyl-1-picrylhydrazyl (DPPH) in toluene such that the final polymer concentration was less than 5×10^{-3} g/mL. The radical scavenger DPPH ensured that no further polymerization occurred. The flasks were wrapped in aluminum foil to prevent photodegradation of the polymer. They were then gently agitated by placing them on a shaker table until dissolution was complete (up to several days). The dissolved polymer was recovered by

---

† Present address: Allied Corp., Morristown, NJ 07960.

0024-9297/85/2218-2318$01.50/0