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# 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 $5 \times 10^{-5}$ g/mL of 2,2-diphenyl-1-picrylhydrazyl (DPPH) in toluene such that the final polymer concentration was less than $5 \times 10^{-3}$ 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

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

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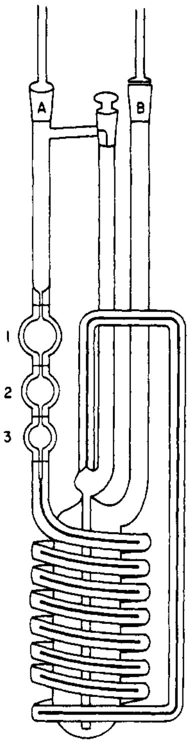

**Figure 1.** Low-shear, multiple-bulb, capillary viscometer.

precipitation in methanol. The ratio of methanol to polymer solution was at least 6:1. The precipitate was recovered by filtration and dried to constant weight at 60 °C in a vacuum oven.

**Molecular Weight Determination.** The molecular weights of the polymers produced by plasma-induced polymerization were determined from intrinsic viscosity measurements. To eliminate the effects of shear stress, a low-shear, multiple-bulb, capillary viscometer was used (see Figure 1). Shear was reduced below that in an ordinary capillary viscometer by the use of a very thin (0.115-cm i.d.), long (1.1 m) capillary and a small hydrostatic head. The shear stress at the capillary wall, based on the hydrostatic head, was 1.240 dyn/cm$^2$ at bulb 1, 0.815 dyn/cm$^2$ at bulb 2, and 0.342 dyn/cm$^2$ at bulb 3. However, even at these low shear stresses, the intrinsic viscosity, $[\eta]$, was found to be a function of shear stress. From a plot of $[\eta]$ vs. $\tau_w$ it was possible by extrapolation to determine the value of $[\eta]$ at zero shear stress.

The procedure for molecular weight determination was as follows. A measured quantity of polymer was placed in an aluminum-foil-wrapped flask along with methyl ethyl ketone (MEK). The flask was agitated on a shaker table for 1–2 days to dissolve the polymer. The resulting solution was filtered through a coarse glass frit and then pipetted into the viscometer. The viscometer was placed in a water bath maintained at 25 ± 0.1 °C.

Values of the intrinsic viscosity, $[\eta]$, were obtained for each bulb and for all three bulbs together. From these values, a plot of $[\eta]$ vs. the wall shear stress was constructed. The intercept on this plot was taken as the zero-stress intrinsic viscosity, $[\eta]_{\tau_w=0}$. Values of $M_v$ were calculated by the Mark–Houwink equation for PMMA in MEK at 25 °C[15]

$$[\eta]_{\tau_w=0} = (0.0071\ \mathrm{cm^3/g})M_w^{0.72}$$

This equation has been verified by light scattering measurements on PMMA samples with molecular weights of up to $3 \times 10^7$ produced by PIP.[5]

## Results and Discussion

The results shown in Figure 2 demonstrate that the viscosity-average molecular weight, $M_v$, increases with monomer conversion. Even at low conversions $M_v$ exceeds $10^7$. It is noted, though, that the polymers formed by PIP were lower in molecular weight than the control sample.

The central question of interest is whether the molecular weights of the polymers produced by PIP are higher than those that might be expected by free radical polymerization. To answer this question, the experimental results will be compared with molecular weight predictions based on a theoretical model of the kinetics of free radical polymerization.

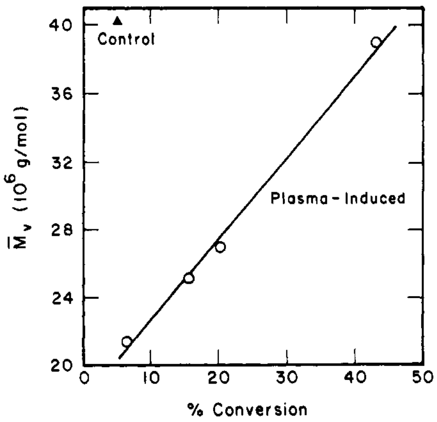

**Figure 2.** Viscosity-average molecular weight as a function of MMA conversion.

The number-average degree of polymerization, $\bar{x}_n$, is given by the ratio of the rate of polymerization to the rate of production of chain ends divided by two. Chain ends are produced by the following processes:

Primary Initiation

$$\mathrm{I} \xrightarrow{k_i} 2\mathrm{R}\cdot \tag{I}$$

Termination by Disproportionation

$$\mathrm{M}_n\cdot + \mathrm{M}_m\cdot \xrightarrow{k_{td}} \mathrm{P}_n + \mathrm{P}_m{}^{=} \tag{II}$$

Chain Transfer

monomer
$$\mathrm{M}_n\cdot + \mathrm{M} \xrightarrow{k_{tr,M}} \mathrm{M}_1\cdot + \mathrm{P}_n \tag{III}$$

polymer
$$\mathrm{M}_n\cdot + \mathrm{P} \xrightarrow{k_{tr,P}} \mathrm{P}\cdot + \mathrm{P}_n \tag{IV}$$

initiator
$$\mathrm{M}_n\cdot + \mathrm{I} \xrightarrow{k_{tr,I}} \mathrm{I}\cdot + \mathrm{P}_n \tag{V}$$

Reaction IV, chain transfer to polymer, does not affect the number-average molecular weight. While this reaction ends the growth of one chain, it permits further growth of another. If the primary initiation step, reaction I, produces a pair of radicals on different sites of the same molecule, then initiation produces no chain ends. For now, it will be assumed that initiating radical sites are on different molecules, but this contribution to the rate of chain end production will be kept track of by placing it in braces, so that its effect on molecular weight prediction can be assessed later. Thus

$$\bar{x}_n^{-1} = (\{2k_i[\mathrm{I}]\} + 2k_{td}[\mathrm{M}\cdot]^2 + 2k_{tr,M}[\mathrm{M}\cdot][\mathrm{M}] + 2k_{tr,I}[\mathrm{M}\cdot][\mathrm{I}])/2R_p \tag{1}$$

where $[\mathrm{M}\cdot] \equiv \sum[\mathrm{M}_n\cdot]$. At high degrees of polymerization $R_p$ can be represented by

$$R_p = k_p[\mathrm{M}\cdot][\mathrm{M}] \tag{2}$$

Dividing the last two terms of the numerator on the right-hand side of eq 1 by eq 2 yields

$$\bar{x}_n^{-1} = \left\{\frac{k_i[\mathrm{I}]}{R_p}\right\} + \frac{k_{td}[\mathrm{M}\cdot]^2}{R} + C_M + C_I\frac{[\mathrm{I}]}{[\mathrm{M}]} \tag{3}$$

where $C_i \equiv k_{tr,i}/k_p$ is the chain-transfer constant for species

$i$. Paul et al.[12] have recently shown that the rate of plasma-induced polymerization is well represented by the expression

$$R_p = k_p(k_i/k_t)^{1/2}[I]^{1/2}[M] \tag{4}$$

Equations 2–4 can now be combined to obtain

$$\bar{x}_n = \left[\left(\frac{R_p}{k_p^2[M]^2}\right)(\{k_t\} + k_{td}) + C_M + C_I\frac{[I]}{[M]}\right]^{-1} \tag{5}$$

Using the definition $k_t \equiv k_{tc} + k_{td}$ and the data of Bevington et al.,[16] which show that at 25 °C $k_{td} \simeq 3k_{tc}$, we obtain

$$\bar{x}_n = \left[\left(\frac{R_p}{k_p^2[M]^2}\right)(\{1\} + 0.75)k_t + C_M + C_I\frac{[I]}{[M]}\right]^{-1} \tag{6}$$

The following parameters were used to evaluate eq 6. Values of $k_p = 4.1 \times 10^2$ L mol$^{-1}$ s$^{-1}$ and $k_t = 4.3 \times 10^7$ L mol$^{-1}$ s$^{-1}$ were taken from ref 17. A value of $C_M = 5.11 \times 10^{-6}$ was obtained from the recent data of Stickler and Meyerhoff.[18] Since $C_I$ is unlikely to be very different from $C_M$ (based on its structure[19]) and the ratio $[I]/[M] \simeq 10^{-4}$, the term involving $C_I$ in eq 6 was neglected.

At low conversions, the rate of polymerization, $R_P$, was $1.6 \times 10^{-6}$ mol L$^{-1}$ s$^{-1}$. For this rate, eq 6 predicts that $M_n$ should be $7.6 \times 10^6$ if pairs of initiating radicals are not part of the same molecule (case I) and $11.7 \times 10^6$ if they are (term in braces in eq 6 neglected, case II). The predictions of $M_n$ can be converted into approximate values of $M_v$ by noting that $M_v$ is much closer to $M_w$ than $M_n$ and that $M_w/M_n \simeq 2$ at low conversions.[20] Therefore, in this regime, $M_v \simeq 2M_n$. Thus, the above predictions for $M_n$ correspond to values of $M_v = 15.2 \times 10^6$ (case I) or $23.4 \times 10^6$ (case II). The data in Figure 2 extrapolate to $M_v = 18.0 \times 10^6$ at 0% conversion, in good agreement with both predicted values.

To compare predictions with experiment at the highest conversion shown in Figure 2, 40%, the dependence of $R_p$ and $k_t$ on conversion must be taken into account. At 40% conversion, the rate of polymerization was twice its initial value. The termination rate constant, however, has been estimated[20] to be reduced by a factor of 100 on going from pure monomer to 40% polymer. The net result is that the term involving the product of $R_p$ and $k_t$ in eq 6 becomes almost insignificant at this conversion. The molecular weight distribution also broadens at high conversions and a good estimate at 40% conversion of $M_w/M_n$ is 3.[20] The value of $M_v$ at 40% conversion is therefore predicted to be $54.0 \times 10^6$ (case I) or $56.7 \times 10^6$ (case II). These are instantaneous values, while the measured value corresponds to the accumulated polymer produced at all times. Consequently, the measured value of $M_v$ should be somewhere between the 0% and 40% conversion predictions, or about $35 \times 10^6$ (case I) or $40 \times 10^6$ (case II). Both values are very close to the value of $39 \times 10^6$ obtained experimentally.

The polymer formed in the control sample had about twice the molecular weight of the plasma-induced polymer at the same conversion. This finding is to be expected from eq 6 and is due to the much slower rate at which the control polymerizes. The predicted value of $M_v$ for the control is $35 \times 10^6$ (case I) or $37 \times 10^6$ (case II), while experimentally $M_v = 40 \times 10^6$. It is significant to note that the molecular weight of the control sample in the present study is higher than that reported in other recent studies of PIP. For example, in their work on MMA polymerization, Johnson et al.[8] reported that the molecular weight of the control sample was lower than that of the polymers produced by PIP. Simionescu et al.[1] reported a similar finding in their work on styrene.

The data in Figure 2 extend only up to 40% conversion. For conversions of this level and less, the polymer is totally soluble. At higher monomer conversions a fraction of the polymer becomes insoluble due to the occurrence of cross-linking. Thus, for example, at 61% monomer conversion, only 0.5% of the polymer is soluble. A sample at 80% conversion (the limiting conversion at 25 °C) swelled to 50 times its initial volume when placed in a flask of toluene. Standard swelling theory[21] and published interaction parameters[22,23] yield an estimated $1.4 \times 10^6$ molecular weight between cross-links for this sample.[12]

Two reactions can contribute to cross-linking: (1) addition of growing chains to the unsaturated end groups of dead chains produced by chain transfer to monomer and termination by disproportionation, and (2) addition of growing chains to dead polymer through the end containing the initiator, since the initiator has been found[19] to contain ~6% olefinic carbon atoms. For total cross-linking of the sample to occur entirely by the first of these processes, chain ends must be formed more frequently by chain transfer to monomer and termination by disproportionation than by initiation and every unsatured end group must eventually react with a growing chain. Only under these conditions could the number of cross-linking sites equal the number of molecules and the formation of an infinite network be possible. While calculations show that the first of these two conditions is satisfied for monomer conversions >40%, the second condition cannot be satisfied until nearly 100% conversion. Consequently, we conclude that the second cross-linking process must contribute significantly at conversions between 40% and 80%. The relative rate at which growing chains react with the unsaturated groups of initiator and monomer molecules should be nearly independent of conversion. However, the probability that reaction with an initiator molecule results in cross-linking (i.e., that a given initiator molecule is already attached to other polymer molecules when a growing chain reacts with it) should increase with conversion. By this mechanism cross-linking should become more frequent (relative to polymerization) at higher conversions, as was observed.

## Conclusions

The molecular weight of PMMA produced by plasma-induced polymerization of MMA exceeds $10^7$ and increases with monomer conversion. Analysis of the polymerization process assuming conventional free radical polymerization kinetics reveals that the ultrahigh molecular weights are the result of the very slow rate of polymerization. Polymer cross-linking becomes increasingly important at monomer conversion above 40%, due to the reaction of growing chains with unsaturated groups at the ends of other dead polymer chains. These unsaturated end groups arise by chain transfer to monomer, termination by disproportionation, and unsaturation in the initiating species.

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# Reversible Singlet Energy Transfer in 1,3-Di(2-naphthyl)propyl Acetate

**J. Vandendriessche, P. Collart, and F. C. De Schryver***

*Department of Chemistry, University of Leuven, Celestijnenlaan 200 F, B-3030 Heverlee, Belgium*

**Q. F. Zhou and H. J. Xu**

*Institute of Photographic Chemistry, Academia Sinica, Bei Sha Tan, Beijing, The People's Republic of China.*

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ABSTRACT: The photophysical properties of 1,3-di(2-naphthyl)propyl acetate at low temperatures (253–213 K) in isooctane were investigated. Fluorescence lifetime measurements revealed the existence of two excimers and reversible singlet energy transfer. The rate constant of singlet energy transfer from the methylene-substituted naphthalene to the naphthalene next to the acetate group equals $1.3 \times 10^9$ ($\pm 7 \times 10^8$) $s^{-1}$. The rate of the reverse process equals $2.7 \times 10^9$ ($\pm 1.5 \times 10^9$) $s^{-1}$.

## Introduction

Intramolecular excimer formation in molecules containing two or more naphthalene chromophores has been the subject of active research since the first observations by Vala et al.[1] and has been reviewed recently.[2] Although previously only one excimer fluorescence peak and decay were observed for R–CHX–Z–CHY–R, where R = 1-naphthyl or 2-naphthyl, X, Y = H or methyl, and Z = $CH_2$,[3] recent results based on fluorescence decay measurements indicate more complex kinetics.[4,5] The analysis of the decay parameters measured in the excimer region as well for 1,3-di(1-naphthyl)propane in methylene chloride, for 1,3-di(2-naphthyl)propane in tetrahydrofuran and methylene chloride,[4] for *meso*-bis[1-(2-naphthyl)ethyl] ether in isooctane, and for bis(1-naphthylmethyl) ether[5] confirms the presence of more than one excimer species. The photophysical properties of poly(1-vinylnaphthalene) and poly(2-vinylnaphthalene) were shown to be complex.[5,6] Whether electronic energy migration between the chromophores of the polymer in solution occurs is still a point of discussion.[2]

To gain some insight into this problem the photophysical properties of 1,3-di(2-naphthyl)propyl acetate (DNPA) (R = 2-naphthyl, X = H, Y = $OCOCH_3$, Z = $CH_2$) were investigated. The introduction of an acetate group influences the radiative and nonradiative decay processes of the naphthalene chromophore next to the acetate group. The process of reversible singlet energy transfer becomes thus detectable with a fluorescence lifetime apparatus.

## Experimental Section

Fluorescence spectra and quantum yields were obtained with a computerized Spex Fluorolog 1902 using double monochromators in both excitation and emission. Quantum yields were determined by using quinine sulfate in 0.1 N $H_2SO_4$ ($\Phi_f = 0.545$)[7] as standard. Correction for the refractive index of the solvents was applied. The optical densities were measured with a Perkin-Elmer Lamba 5 UV–vis spectrophotometer. The absorbances at the excitation wavelength were less than 0.1. Fluorescence decays were measured with a Spectra Physics frequency-doubled cavity-dumped mode-locked synchronously pumped R6G dye-laser system with time-correlated single-photon-counting detection. The fluorescence lifetime apparatus, the associated optical and electronic components, and data analysis are described in detail elsewhere.[8]

1,3-Di(2-naphthyl)propyl acetate (DNPA), (2-naphthyl)methyl acetate (NMA), and 2-methylnaphthalene (MN) are the same as used before and of HPLC controlled purity.[9] Isooctane (Merck for fluorimetry) was purified over a column with silica gel and carbon black. No fluorescence could be detected from the purified solvent under the excitation conditions used in this work. The solutions were deareated by the freeze–pump–thaw method (typically 4 cycles). The temperature of the sample was kept constant by circulating nitrogen through the cell holder. The temperature stability was better than 1 K.

## Results

**Absorption Spectra.** The positions of the absorption maxima in the absorption spectrum of NMA and in the absorption spectrum of MN are identical in the 240–300-nm region ($^1L_a$) but different in the 300–450-nm region ($^1L_b$) (Figure 1). The experimentally determined molar

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