PLASMA-INITIATED POLYMERIZATION OF METHYL METHACRYLATE AND OTHER MONOMERS

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ABSTRACT

A new method, referred to as plasma-initiated polymerization, is described for producing conventional high-molecular weight polymers. Polymerization is initiated by brief exposure of the monomer surface to a low pressure plasma. Propagation of polymer chains then occurs during post-polymerization in the absence of the plasma. Monomers amenable to this technique of polymerization, and the properties of the polymers, will be described.

1. INTRODUCTION

Plasma polymerization generally produces polymers which are highly branched, crosslinked networks whose chemical structure and composition are not simply related to those of the starting monomer. Recently, we have reported (1,2) on a polymerization process whereby a plasma is used to initiate conventional polymerization of liquid methyl methacrylate. The resulting polymer is an uncrosslinked conventional poly (methyl methacrylate) with a very high molecular weight. This process may be called plasma-initiated polymerization. In this work, we shall report on the results of plasma-initiated polymerizations and copolymerizations of a number of vinyl monomers in either bulk liquid state or in solution, in an effort to shed some light on the mechanism of this phenomenon.

2. EXPERIMENTAL

Monomers were purchased from Polysciences, Inc. The liquid monomers (methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, methyl acrylate, n-butyl acrylate, methacrylic acid, acrylic acid, styrene and α-methylstyrene) were purified by vacuum distillation under nitrogen, poured into thin-walled ampules, degassed at 10^{-3} - 10^{-4} torr and subsequently frozen in liquid nitrogen. The partially filled ampules were then inserted between a pair of parallel plate electrodes connected to an International Plasma Corporation Model 3001 Radiofrequency Generator, which operates at 13.46 MHz and delivers up to 150 watts of power. In most of the experiments discussed here, the power was limited to 40 - 80 watts. Prior to initiating polymerization, an ampule was allowed to warm up until droplets of liquids appeared. A glow discharge was then produced in the gas space above the monomer in the ampule. During the discharge, the temperature of the ampule increased slightly. Following the plasma initiation, the ampule was left standing at constant temperature for prescribed periods of time, after which the seal was broken and the contents precipitated and analyzed.

Solid monomers, acrylamide and methacrylamide, were recrystallized twice from methanol. Bulk monomers were polymerized in the manner described above, but in the solid state (no melting). Aqueous solutions of these monomers were handled in the same manner as liquid monomers.

The molecular weights of poly (methyl methacrylate) and poly (methacrylic acid) were determined by intrinsic viscosity measurements at 25°C. Copolymer compositions were determined by high resolution NMR (180 MHz). Copolymers of methyl methacrylate and styrene were dissolved in deuterated chloroform for the analysis. Deuterated pyridine was the solvent for the methyl methacrylate - methacrylic acid copolymers. Elemental analysis was also used in copolymer composition analysis to complement the NMR data.

3. RESULTS AND DISCUSSION

Plasma-Initiated Polymerization of Methyl Methacrylate

The conversion of methyl methacrylate as a function of time is given in Fig. 1. An interesting feature of plasma-initiated polymerization of liquid monomers is that the molecular weight of the resulting polymer is very high despite the correspondingly high rate of polymerization. Figure 1 shows that 10 min after initiation the molecular weight of PMMA has already reached 3 x 10^6 g/mole. The molecular weight continues to increase with increasing degree of conversion, until after 120 hr it has exceeded 10^7 g/mole. By contrast, in comparable cases of polymerizations by γ irradiation, β rays, and high-energy electrons, the molecular weight would be only about 5 x 10^5, 1 x 10^6, and (1.8-3) x 10^6 g/mole, respectively.

The microstructure of PMMA obtained from plasma-initiated polymerization consists of 7% isotactic, 27% heterotactic, and 66% syndiotactic triads. This distribution of tacticity is characteristic of PMMA prepared by conventional radical-initiated polymerization (3). It thus appears that the propagation for plasma-initiated polymerization of methyl methacrylate may also be of free-radical character.

To investigate the effect of temperature on plasma initiated polymerization, the ampule after exposure to the glow discharge was immediately frozen at -78°C in a dry ice-acetone mixture and maintained at this temperature for 65 hours. After this period of time, the ampule was warmed up to 25°C. Post-polymerization of methyl methacrylate was found to proceed in the same manner shown in Fig. 1. Apparently the active species, most probably free radicals, stayed alive for a long time at low temperatures where chain propagation and termination reactions are absent. Post-polymerizations after plasma initiation can proceed over a range of temperatures. The activation energy determined from these data is 9.1 kcal/g-mole, which compares favorably with that (5-6 kcal/g-mole) for free radical polymerizations of methyl methacrylate.

Monomers Polymerized by Plasma Initiation

Polymerization data for all of the vinyl monomers utilized in this study are summarized in Table 1. Methacrylic acid (MAA) and acrylic acid (AA) are polymerized immediately upon exposure to the plasma. Because the resulting polymers are insoluble in their monomers, the products are precipitated out and conversion is low despite prolonged post-polymerization. However, if water is now added as solvent, polymerization becomes homogeneous and high conversions can be readily achieved with post-polymerization. For example, after a 15 second plasma initiation period more than 80% yield was obtained for a 75% aqueous solution of MAA. The molecular weight, determined by intrinsic viscosity measurements, was found to be 4.5×10^6 g/mole.

When solid monomers of acrylamide (AM) and methacrylamide (MAM) were subjected to plasma initiation, only trace amounts of insoluble polymers were obtained. However, when aqueous solutions of AM and MAM were used in the plasma-initiated polymerization high conversions were again achieved upon post-polymerization. Polyacrylamide was found to be completely soluble, whereas polymethacrylamide forms a gel. It is of interest to note that no polymer was formed during the post-polymerization period if the monomer solution was not previously exposed to the plasma.

Monomers Not Polymerized by Plasma Initiation

When styrene and α-methylstyrene were subjected to plasma treatment, the monomers became yellowish and only trace amounts of insoluble films were formed. The discoloration was intensified and extensive formation of dark films were observed if carbon tetrachloride was added as the solvent. No post-polymerization was detectable for these monomers. Generally, styrene and α-methylstyrene readily undergo thermal polymerization. However, no thermal polymerization was possible for these monomers after having been subjected to plasma treatment for one minute or less. It has been demonstrated from the emission spectra of glow discharge plasma of benzene (4) and its derivatives (5) that most of the reaction intermediates are phenyl or benzyl radicals which subsequently form a variety of compounds such as acetylene, methylacetylene, allene, fulvene, biphenyl, poly(p-phenylenes), etc. It is possible that styrene and α-methylstyrene behave similarly, so that species from the monomer plasma are poor initiators for polymerization.

Although methacrylate polymerized readily upon plasma initiation, ethyl methacrylate (EMA) and n-butyl methacrylate (BMA) gave only low yields (1-2%) of polymer regardless of the length of post-polymerization period. Apparently the small amount of polymer was formed during the plasma initiation period (up to 60 seconds), and no further polymerization took place when plasma was turned off. Parallel experiments of dark polymerization (no plasma initiation) under the same conditions also resulted in no polymer formation. On the other hand, methyl acrylate (MA) and n-butyl acrylate (BA) did not polymerize at all upon plasma treatment.

The observation holds true even when the initiation period was increased to 15 minutes (see Table 1), despite the fact that the propagation constants from photopolymerization studies (6), indicate that its value is higher for MA (k_p = 720 ℓ/mole-sec) than for MMA (k_p = 143 ℓ/mole-sec) at 30°C.

Copolymerizations of Methyl Methacrylate

Copolymerizations of methyl methacrylate with styrene (STY) were carried out by subjecting the monomer mixtures to a plasma for 20-30 seconds, followed by post-polymerization at 5°C for 120 hours. Parallel dark polymerizations (no plasma initiation) experiments were also conducted under similar conditions. The results are given in Table 2. The presence of styrene monomer appears to exert a strong inhibiting effect on the reactions, as seen in the precipitous decreases in yield with increasing styrene concentration. When styrene exceeded 40% in the monomer mixture, discoloration and insoluble homopolymerization. To analyze the chemical composition of the copolymers, insolubles were filtered off and the dissolved polymers were precipitated in methanol. The resulting products were dried. Copolymer composition data are shown in Figure 2. The results from NMR and elemental analyses are seen to be in satisfactory agreement. Those for copolymers obtained from dark reactions (not shown) were found to be similar. These data are compared with the curve calculated from the copolymer composition equation, using r(MMA) = 0.46 and r(STY) = 0.52 reported for free radical copolymerizations (7). The typical sigmoidal curve is followed by our plasma-initiated copolymerization data, suggesting a free radical nature of these reactions. The NMR spectra show a splitting at 3.5 ppm, which is attributed to the screening effect of the neighboring phenyl groups. The implication is that each monomer unit in the copolymer is distributed randomly which is typical of STY/MMA copolymers obtained via free radical polymerization.

Copolymerization data for methyl methacrylate and methacrylic acid are shown in Table 3. In this system, post-polymerization proceeded more rapidly and with better yields than the MMA/STY system. Monomer mixtures with high molar ratios of MAA became cloudy with increasing conversion because of the poor solubility of the copolymer in the monomer. Dark reaction proceeded slowly, and it was necessary to heat the reacting mixture to 80°C for a few hours to start the polymerization. Mole fractions of MMA units in the copolymer were determined by NMR spectra. The methoxy peak at 4.5 ppm was used to monitor the MMA concentration. However, with decreasing MMA content the peak becomes too broad to permit accurate analysis. Nevertheless, the estimated copolymer composition data appear to be in rough agreement with those obtained from free radical copolymerizations (6). It is of interest to note that the methoxy peak did show splitting with increasing MMA content as a result of the screening effect of the neighboring carboxylic groups. This observation is indicative of random sequence distribution in the copolymer, which is characteristic of radical initiated copolymerization of MMA and MAA.

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Table 1. Plasma Initiated Polymerization Data of Vinyl Monomers

Monomer	Polym. Medium	Plasma Duration (Sec)	Post-Polym. Condition	Yield (%)
Methyl Methacrylate	Bulk Liq.	60	100 hr., 25°C	40
Methacrylic Acid	Bulk Liq.	30	168 hr., 5°C	3
	75% Aq. Soln.	15	90 hr., 5°C	80
Acrylic Acid	Bulk Liq.	30	168 hr., 5°C	3
	75% Aq. Soln.	15	90 hr., 5°C	50
Methacrylamide	Bulk Solid	120	45 hr., 20°C	Trace
	30% Aq. Soln.	12	45 hr., 20°C	80
Acrylamide	Bulk Solid	40	45 hr., 20°C	Trace
	50% Aq. Soln.	15	45 hr., 20°C	60
Ethyl Methacrylate	Bulk Liq.	60	168 hr., 5°C	1
n-Butyl Methacrylate	Bulk Liq.	30	168 hr., 5°C	1-2
Methyl Acrylate	Bulk Liq.	180	200 hr., 20°C	0
	Bulk Liq.	900	168 hr., 5°C	0
n-Butyl Acrylate	Bulk Liq.	20	168 hr., 5°C	0
	Bulk Liq.	60	168 hr., 5°C	0
	94% CCl_4 Soln.	60	66 hr., -15°C	0
	50% CCl_4 Soln.	15	66 hr., -15°C	0
α-methylstyrene	Bulk Liq.	30	168 hr., 5°C	0

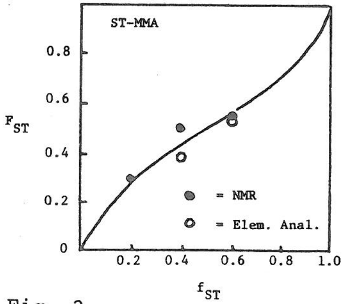

Fig. 2

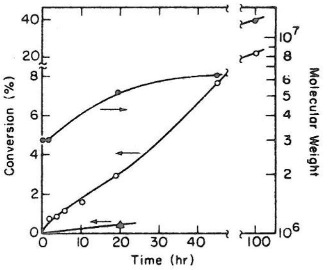

Fig. I

Table 2. Plasma-Initiated Copolymerization of Methyl Methacrylate and Styrene*

Monomer Molar Ratio (MMA/STY)	% Conversion Plasma Initiated	Dark**
10/0	16.7	1.8
8/2	0.4	0.3
6/4	0.5	0.2
4/6	0.2	0.3
2/8	trace	0.15
0/10	none	0.14

* Polymerization Conditions: Power 50W; plasma duration 20-30 sec; post-polymerization at 5°C for 120 hr.

** Dark polymerization was carried out in the same condition but without plasma-exposure.

Table 3. Plasma-Initiated Copolymerization MMA with MAA

Monomer Molar Ratio (MMA/MAA)	% Conversion Plasma*	Dark**
76/24	1.7	4.9
55/45	2.2	3.2
35/65	4.6	1.25
17/83	4.5	2.2

* Polymerization Conditions: Power 50W; plasma duration 30-60 sec; post-polymerization at 5°C for 48 hr.

** Dark polymerization was carried out at 80°C for 2-3 hr. without plasma-exposure.