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Photopolymerization of Methyl Acrylate in Dimethyl Sulfoxide

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SUMMARY

Methyl acrylate in dimethyl sulfoxide was polymerized by 2537 Å ultraviolet light. The photo reaction exhibited zero-order kinetics for a given initial concentration and produced short chain polymers ($\bar{M}_W \sim 20{,}000$). Low sulfur values of isolated polymers indicated no appreciable solvent incorporation during the polymerization.

INTRODUCTION

Grafting styrene to gluten protein [1] showed the feasibility of photo graft polymerization reactions in dimethyl sulfoxide (DMSO); however, large amounts of styrene were necessary to effectively compete with solvent incorporation. In order to gain more information on the photoaddition of this solvent to polymers, we explored the usefulness of DMSO as a solvent for the homopolymerization of methyl acrylate initiated by 2537 Å UV light.

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EXPERIMENTAL

Reagents

Methyl acrylate (Eastman practical) was distilled under vacuum before use. DMSO (Baker analyzed grade) was used as received.

Polymerization Procedure

Solutions of freshly distilled methyl acrylate in DMSO (0.138, 0.276, 0.522 M) were photolyzed up to 1 hr in quartz test tubes (20 X 175 mm). The tubes were rotated inside a Rayonet photochemical reactor at a distance of 6 cm from the light sources (16 RPR-2537 Å). After photolysis, the solutions were quenched with hydroquinone and the remaining concentration of monomer was determined by gas chromatography. The solutions were then dialyzed against 70% ethanol to remove the remaining monomer and DMSO. After dialysis the solutions were lyophilized, and the resulting solid was purified by precipitation from a 2-butanone solution with cold methanol.

Molecular Weight Determinations

To determine molecular weights of the purified polymers we measured their intrinsic viscosity $[\eta]$, which was then related to weight-average molecular weight, $\bar{M}_W$, from equations in the literature. The equation, $[\eta]_{25°} = 1.41 \times 10^{-4}\ \bar{M}_W{}^{0.67}$, obtained by Kotera et al. [2] from measurements on fractions within a M_W range of $(1.7\text{-}6.8) \times 10^5$, agrees well with the equation, $[\eta]_{20} = 3.5 \times 10^{-5}\ \bar{M}_W{}^{0.81}$, obtained by Soboleva et al. [3] from measurements on fractions within a $\bar{M}_W$ range of $(0.6\text{-}24) \times 10^5$. Since our viscosity measurements were made at 25°C, we used Kotera's equation to calculate $\bar{M}_W$ values. Because the validity of the above equation is unknown at the low $[\eta]$ values encountered in our work and because our samples were not fractionated, the $\bar{M}_W$ values given in Table 1 should be considered as qualitative.

RESULTS

The decrease in monomer concentration with respect to time is shown in Fig. 1 for three initial concentrations of methyl acrylate. Each reaction, for a given initial monomer concentration, follows zero-order

Table 1. Intrinsic Viscosities and Molecular Weights of Polymethyl Acrylate

Sample			
Molarity	Photolysis time (min)	$[\eta]_{25°}$	$\bar{M}_W$
0.552	20	0.104 ± 0.002	1.9×10^4
0.552	40	0.118 ± 0.002	2.3×10^4
0.552	60	0.118 ± 0.002	2.3×10^4
0.276	40	0.110 ± 0.002	2.1×10^4
0.276	60	0.100 ± 0.01	1.8×10^4
0.138	60	~0.077	1.2×10^4

kinetics. The rate depends, however, on the initial concentration of monomer in a nonlinear fashion (Fig. 2). Intrinsic viscosities were measured on samples after 20, 40, 60 min of photolysis time for each of the three initial monomer concentrations, and then $\bar{M}_W$ was calculated (Table 1). Amounts of material lost by dialysis ($\bar{M}_W < 10{,}000$) are indicated by the difference between the weight of product isolated after dialysis and weight of product calculated from gas chromatography of unconsumed monomer (Table 2).

DISCUSSION

The photopolymerization of methyl acrylate in DMSO proceeded at a constant rate for a given initial monomer concentration and produced low-molecular weight polymers whose average molecular weight did not exceed 22,000. A high percentage of the polymer formed (20-60%) was of sufficiently low molecular weight to be lost by dialysis and, therefore, was not characterized or represented in $\bar{M}_W$ determinations.

Linearity of plots for each of the three lines suggests that once the reaction has started, the rate follows zero-order kinetics for each. Because slopes of the three lines differ however, the rate must be influenced by the initial concentration of monomer (Fig. 2). Dependence of the kinetics

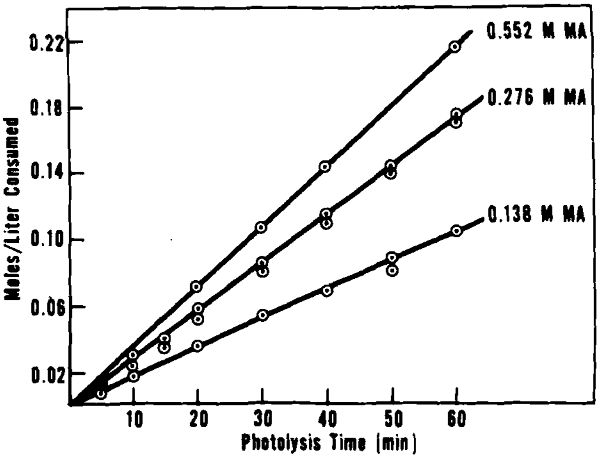

Fig. 1. Amount of monomer consumption for three initial concentrations as a function of photolysis time.

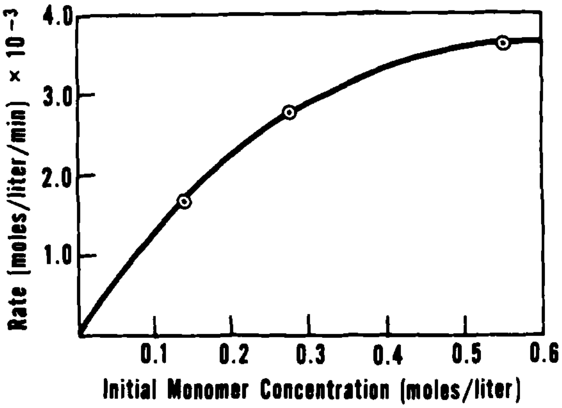

Fig. 2. Rate of photopolymerization as a function of initial monomer concentration.

on the initial monomer concentration may be due either to assistance by the monomer in the termination step or to hindrance by the monomer in the initiation step.

Sulfur analysis of the recovered polymer gave values of 0.3-0.4% and indicated a low level of solvent participation in the polymerization. The lack of solvent reactivity can be contrasted with the photolysis of protein

Table 2. Amounts of Polymethyl Acrylate

Sample		Product calculated (g)	Product found (g)
Molarity	Photolysis time (min)		
0.552	20	0.25	0.13
0.552	40	0.49	0.31
0.552	60	0.74	0.60
0.276	20	0.19	0.08
0.276	40	0.39	0.20
0.276	60	0.59	0.34
0.138	40	0.24	0.15
0.138	60	0.36	0.21

in DMSO [4] where high percentages of sulfur were incorporated. It can also be contrasted with the photolysis of protein in DMSO-styrene mixtures, were large amounts of styrene [10-15% (v/v)] were necessary to compete effectively with DMSO for the reactive site on the protein during the photo graft polymerization of styrene to gluten [1]. Apparently, DMSO is primarily a photo reactive solvent in the presence of protein functional groups, but it is not incorporated during the photo homopolymerization of methyl acrylate in dilute solution.

The mention of firm names or trade products does not constitute an endorsement by the U.S. Department of Agriculture over other products or firm names not mentioned.

REFERENCES

[1] K. Eskins and M. Friedman, *Polym. Preprints, Amer. Chem. Soc., Div. Polym. Chem.*, **10**(1), 351 (1969).

[2] A. Kotera, T. Saito, Y. Watanabe, and M. Ohma, *Makromol. Chem.*, **87**, 195 (1965).

[3] I. G. Soboleva, N. V. Makletsova, and S. S. Medvedev, *Dokl. Akad. Nauk SSSR*, **94**, 289 (1954), quoted by S. Krause, in *Dilute Solution*

Properties of Acrylic and Methacrylic Polymers, Part I, Revision 1, Rohm & Haas Co., Philadelphia, Pa., Feb. 7, 1961.

[4] K. Eskins and M. Friedman, *Polym. Preprints, Amer. Chem. Soc., Div. Polym. Chem.*, 9(1), 461 (1968).

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