Dye-sensitized Photopolymerization of Acrylonitrile-Vinyl Acetate Copolymers

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It has been discovered that vinyl polymerization may be initiated by irradiating with visible light a solution containing certain dyes and a mild reducing agent[1]. Oxygen is necessary for the process. The dye is photoreduced to its leuco form and, on reacting with ambient oxygen free, radicals are produced which initiate the polymerization.

In all the studies carried out with such an initiator, very high molecular weight polymer is obtained. For example, the use of riboflavin (a naturally occurring dye-reducing agent combination) as the photosensitizer results in the polymerization of acrylamide to give a polymer having a molecular weight exceeding ten millions[2]. Copolymers of acrylonitrile and allyl alcohol have been produced by dye-sensitized photopolymerization having molecular weights far in excess of those produced by conventional catalysts[3].

It is the purpose of the present work to study the copolymerization of acrylonitrile and vinyl acetate by dye sensitization under conditions which resemble those carried out using conventional catalysts (e. g., organic peroxides)[4] in order to compare reactivity ratios obtained by the two different methods. A practical consequence of the present work may be to suggest a convenient method of producing these polymers which may be controlled simply by suitably adjusting the light intensity.

Experimental

Materials. — Acrylonitrile (American Cyanamid) and vinyl acetate (Eastman Kodak) having boiling points of 77° and 72°C, respectively, were distilled under helium to remove inhibitor. The dye used was acriflavine (National Aniline) and the reducing agent was allyl thiourea (Eastman Kodak). Dimethylformamide (Matheson) was used as the solvent.

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[1] G. Oster, *Nature*, **173**, 300 (1954).

[2] G. K. Oster, G. Oster and G. Prati, *J. Am. Chem. Soc.*, **79**, 595 (1957).

[3] G. Oster and Y. Mizutani, *J. Polymer Sci.*, **22**, 173 (1956).

[4] C. G. Swain and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 2381 (1946) ; G. M. Burnett and H. W. Melville, *Proc. Roy. Soc.* (London), **A189**, 456 (1947) ; G. Dixon-Lewis, ibid., **A198**, 510 (1949) ; M. S. Matheson, E. E. Auer, E. Bevilacqua and E. J. Hart, *J. Am. Chem. Soc.*, **71** 2610 (1949) ; H. Kwart, H. S. Broadbent and P. D. Bartlett, ibid., **72**, 1060 (1950) ; F. R. Mayo, F. M. Lewis, C. Walling, and W. F. Hulse, ibid., **70**, 1523 (1948).

Table I

Some properties of the comonomer and copolymer systems

Exp. No.	1	2	3	4	5	6	7	8	9	10
Acrylonitrile molar ratio in initial mixture	1.000	0.936	0.867	0.792	0.708	0.618	0.519	0.410	0.289	0.153
Acrylonitrile molar ratio in copolymer	1.000	0.959	0.978	0.954	0.912	0.850	0.816	0.767	0.704	0.618
Relative rate of conversion	8.14	9.78	12.25	14.68	14.78	12.07	5.90	3.48	2.61	1.61
Intrinsic viscosity of copolymer (dl./gm.)	1.239	0.907	0.810	0.690	0.752	0.733	0.879	0.672	0.474	0.364
4.46 μ/5.75 μ infra red absorbance	—	—	1.352	0.865	0.739	0.662	0.602	0.530	0.495	0.467

Procedure and Results.—A total of 10 g. of mixtures in various proportions of acrylonitrile and vinyl acetate was added to 15 ml. of dimethylformamide. To the solution were added the dye and the reducing agent to give a final concentration of 0.00625% and 0.04%, respectively. The final solution was placed in a 50 ml. test tube at a distance 45 cm. from a 500 watt projection lamp. At various times during the irradiation samples were withdrawn and added to a 50—50 mixture of methanol and water. The precipitate was washed with the methanol-water mixture and dried in a vacuum oven at 55°C. The amount of monomer converted as a function of time of irradiation for the various initial mixtures are illustrated in Fig. 1 and the relative rates are given in Table I.

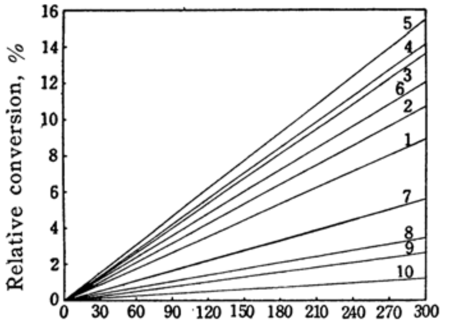

Fig. 1. Conversion as a function of time of irradiation for various initial monomer mixtures.

Curve No.	1	2	3	4	5
acrylonitrile molar ratio	1.000	0.936	0.867	0.792	0.708
Curve No.	**6**	**7**	**8**	**9**	**10**
acrylonitrile molar ratio	0.618	0.519	0.410	0.289	0.153

When the molar ratio of acrylonitrile in the original mixture exceeds 0.792, the system becomes turbid during irradiation. In such cases the suspensions were agitated prior to the withdrawal of samples.

For other studies (see below) the samples were purified by first dissolution in dimethylformamide, precipitation and repeated washing with the alcohol-water mixture.

Nitrogen analyses were carried out by the Kjeldahl method and the results obtained were corrected according to the procedure of Nozaki5). The nitrile content of the polymer, as determined from the nitrogen analyses, are given in Fig. 2 as a function of acrylonitrile concentration in the starting mixture.

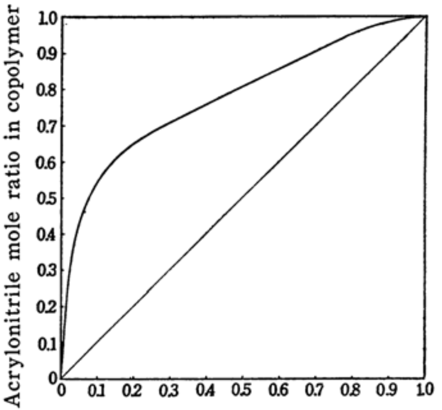

Fig. 2. Copolymerization curve. The straight line represents that expected for an "ideal" copolymerization system.

All the copolymers studied were soluble in dimethylformamide. The copolymers, obtained when the initial molar ratio was 0.519 or greater in acrylonitrile, exhibited only slight swelling in acetone. On the other hand, for a ratio of 0.410, the copolymer was swollen by acetone and for a ratio of 0.289, the copolymer was completely soluble in acetone. The viscosities of solutions of the copolymers in dimethylformamide at 30°C. were determined at 30°C. were determined in a Ubbelohde viscometer with a flow time of 300 sec. The intrinsic viscosities, calculated in the usual manner, are given in Table I.

Samples of the polymers were prepared for infrared analysis by mixing 5 mg. of the polymers with 500 mg. of dried potassium bromide and made into a disc tablet by means of a hydraulic press. In Fig. 3 are illustrated the infrared spectra as obtained on a Perkin-Elmer Model 21 Infra Red spectrometer.

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5) K. Nozaki, *J. Polymer Sci.*, **1**, 455 (1946).

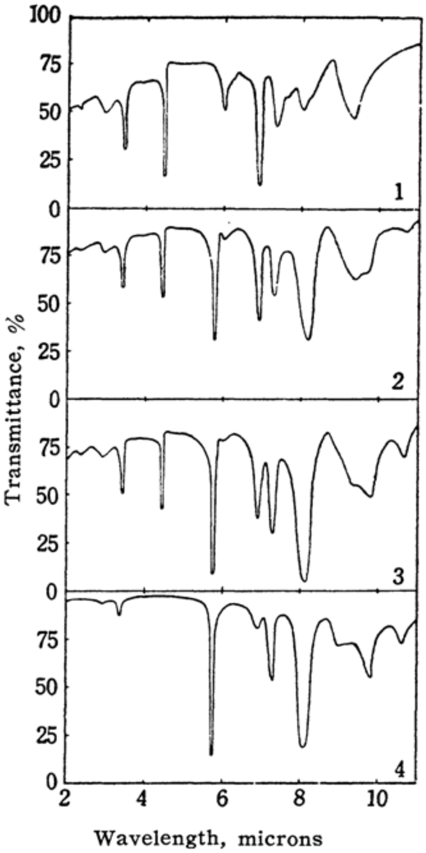

Fig. 3. Infra red spectra of the polymers having the molar ratios of acrylonitrile in the polymers of (1) 1.000, (2) 0.954, (3) 0.767, and (4) 0, respectively.

Discussion

It is instructive to represent the data of Fig. 1 in terms of conversion as a function of acrylonitrile content in the initial mixture (Fig. 4). A maximum rate is obtained when the molar ratio of acrylonitrile is about 0.70. If the intrinsic viscosity-molecular weight relation is the same for all the polymers, (which it probably is not) then the molecular weight is the greatest for the pure acrylonitrile system. In any case, the molecular weights probably do not exceed 20,000. On the other hand, dye sensitized photopolymerization of acrylonitrile in saturated zinc chloride solutions yields polymer with molecular weights exceeding one million⁶⁾.

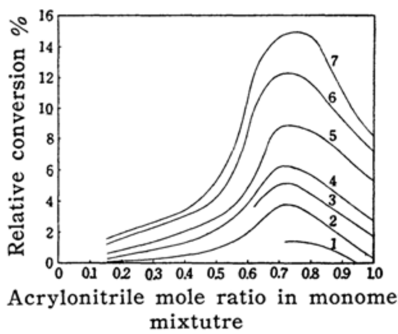

Fig. 4. Conversion of monomer as a function of acrylonitrile in original mixture.

Curve No.	1	2	3	4	5	6	7
Time of irradiation (min.)	30	60	90	120	180	240	300

The infra red spectra of the polymers shown in Fig. 3 are consistent with the nitrogen analysis. With decreasing nitrile content in the copolymer, the absorption band characteristic of that group at 4.46 μ is suppressed as the absorption band characteristic of the carbonyl group of acetate at 5.75 μ increases. Hence the ratio of these two absorption peaks decreases as the nitrogen content decreases (see Table I). Other significant changes in the infra red spectra take place in the 9—10 μ region.

From the data in Fig. 2 we calculate the reactivity ratios r_1 and r_2 (for acrylonitrile and vinyl acetate, respectively) using the well known expression⁷⁾,

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

where F_1 is the acrylonitrile molar ratio in the copolymer, and f_1 and f_2 are the molar ratios of acrylonitrile and vinyl acetate, respectively, in the original mixture. By curve fitting methods, we obtain the values $r_1=3.88$ and $r_2=0.009$. These results differ somewhat from those of Mayo et al.⁴⁾ who obtain values of $r_1=4.05$ and $r_2=0.016$ for bulk polymerization of acrylonitrile-vinyl acetate mixtures using peroxide catalysts.

The copolymer having a molar ratio of acrylonitrile of 0.704 (initial mixture ratio of 0.289) is soluble in acetone and hence could be dry spun from this inexpensive solvent. It is interesting that although this polymer is rich in nitrile groups it is, nevertheless, soluble in acetone. Apparently the polymer has random alternation of nitrile and acetate groups since the product $r_1 r_2$ is small.

Summary

Copolymers of acrylonitrile and vinyl acetate have been produced using a dye-

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6) G. Oster and H. Lieberman, to be published.

7) I. Skeist, *J. Am. Chem. Soc.*, **68**, 1781 (1946).

reducing agent combination as the photosensitizer. Visible light was employed as the radiation source. Nitrogen analyses and infra red analyses were performed on the polymers obtained. The copolymerization ratios were 3.88 and 0.009 for acrylonitrile and vinyl acetate, respectively. Below an initial monomer molar ratio of acrylonitrile of 0.3, the resultant copolymer dissolves in acetone.

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