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**Radiation-Induced Polymerization
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in the Frozen State**

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ABSTRACT

Radiation-induced polymerization of acrylonitrile-urea canal complexes formed in frozen ethylene glycol or tert-butyl alcohol media was investigated. Formation of canal complexes in the frozen state was prolonged. The initial rate of polymerization was enhanced in the frozen state. The degree of polymerization of polymers obtained is found to show no depression at high conversions and is higher in the frozen state, suggesting stabilization of canal complexes by the frozen medium.

INTRODUCTION

The polymerization behavior of monomers can be affected by the physical state of the reaction media. In paraffine oil [1] or in wax [2], monomers were found to be more easily polymerizable than in the solid state. The present paper is concerned with the radiation-induced polymerization of acrylonitrile in a urea canal complex in the frozen state. The effects of the frozen state on the rate and the degree of polymerization were studied. Ethylene glycol (mp -12.6°C) and tert-butyl alcohol (mp 25.5°C) were used as the frozen media.

EXPERIMENTAL

Materials

Acrylonitrile (AN) was washed successively with 5% aqueous solutions of sodium hydroxide, phosphoric acid, and then pure water. After drying over potassium carbonate it was distilled. Urea (U) was purified by twice recrystallizing from methanol solution and dried at 80°C . After 24 hr U was ground and further dried at 80°C for about 50 hr. Ethylene glycol (EG) and tert-butyl alcohol (t-BA) of commercially guaranteed grade were used without further purification.

Polymerizing Procedure

A glass ampule containing a monomer solution consisted of AN, U, and EG (or t-BA) was cooled and stored at -78°C for a week for aging of canal complexes. Unless otherwise mentioned, molar ratios of AN/U/EG and AN/U/t-BA were 1/8.78/118 and 1/8.78/112, respectively. Aged samples were irradiated at -78°C by gamma-radiation from a 7000-Curie ^{60}Co source at the Institute of Scientific and Industrial Research, Osaka University. After irradiation a small amount of methanol containing hydroquinone pre-cooled at -78°C was added into the ampule. Then the content of the ampule was transferred into cold methanol. The precipitated polymers were washed successively with warm water and methanol, and then dried.

Viscosity Measurements

The molecular weights were determined by the viscosity measurement of polymer solutions in dimethylformamide at 25°C with a

dilution-type Ubbelohde viscometer. The relationship used to estimate molecular weight was

$$[\eta] = 2.43 \times 10^{-4} M_v^{0.75}$$

as given by Cleland and Stockmayer [3].

Polymers obtained in canal complexes in the absence of the freezing medium were only soluble in 70% $ZnCl_2$ aqueous solution, and the viscosity numbers, η_{sp}/C , were measured in this solution. Therefore the degree of polymerization of polymers was estimated from the following relationship between η_{sp}/C in 70% $ZnCl_2$ aqueous solution at 60°C and $[\eta]$ in dimethylformamide at 25°C, which was derived by measuring viscosities of polymers soluble in both solvents:

$$[\eta] = 0.59 \times (\eta_{sp}/C)^{0.62}$$

Differential Thermal Analysis

Formation of canal complexes was followed by using differential thermal analysis (DTA). Equipment of the Shimadzu DT-10 type was used. A sample tube of 5 mm bore and 0.25 mm wall-thickness made of Pyrex glass was filled with 0.1 ml of the solution, sealed off, and aged at -78°C. The aged sample was quickly immersed in liquid nitrogen and then transferred to a precooled brass block. In DTA measurement the warming rate was in the range of 0.8 to 2.0°/min. α -Alumina was used as the reference.

RESULTS AND DISCUSSION

Differential Thermal Analysis

The formation and stability of the canal complex were examined by DTA. DTA curves of well-aged frozen samples of AN-U-EG (B) and AN-U-t-BA (C) are shown in Fig. 1. The decomposition peak (-45°C) of the AN-U canal complex formed without the freezing medium is shown in Fig. 1(A). In both B and C the decomposition peak of canal complexes around -45°C and the melting peak of solid AN around -85°C were not observed either. These results suggest that AN-U canal complexes are formed but are enclosed within the frozen media and stabilized up to the melting temperatures of the frozen media (-24 to +22°C).

It should be noted that the melting peak of solid AN was observed

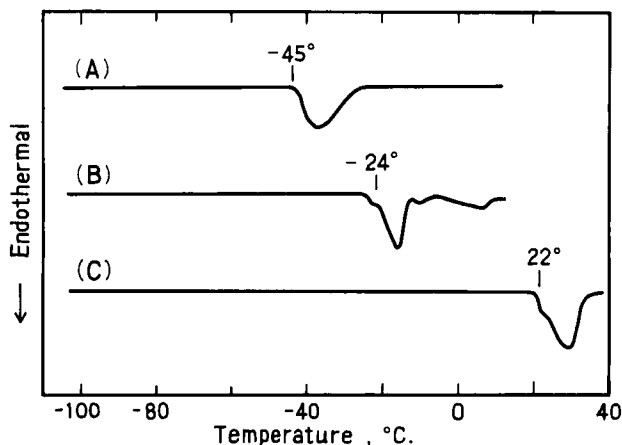


FIG. 1. Differential thermal curves for (A) AN-U (1:8) canal complex, (B) AN-U-EG (1:8.8:118) and (C) AN-U-t-BA (1:4.7:112) frozen solutions, aged at -78°C for 7 days.

for nonaged AN-U-t-BA samples but not observed for nonaged AN-U-EG samples. The nonaged AN-U-t-BA sample seems to be in a crystalline state, but the nonaged AN-U-EG sample at -78°C is in a supercooled liquid state. The thermal behavior of the nonaged AN-U-EG system is further discussed in another paper [5].

Formation of Canal Complex

The time for formation of canal complexes in frozen media was considered by examining the conversion of polymerization. As shown in Fig. 2, the formation seems to be complete after about 100 hr both for EG and t-BA, which can be compared with a time of 20 hr for AN-U canal complex formation without the freezing medium [4].

AN could polymerize only after formation of canal complexes in the U-t-BA medium at -78°C . However, in the supercooled liquid state of the U-AN system (as reported in a later paper), AN could polymerize faster than in canal complexes.

Effect of Urea Concentration on Polymerization

The polymerization rate was changed markedly by urea concentration. At constant AN concentration, conversions were plotted against

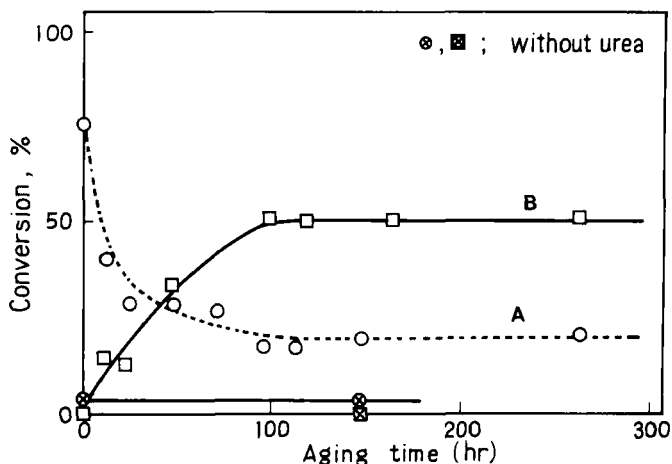


FIG. 2. Conversion vs aging time of acrylonitrile-urea canal complex aged at -78°C in air. (A), AN-U-EG (1:8.8:118); (B), AN-U-t-BA (1:8.8:112). Dose rate, 1.53×10^4 r/hr. Irradiation time, 6.80 hr.

urea concentration (Fig. 3). The conversion increased with the addition of a small amount of urea, even with a 0.01 molar fraction (i.e., AN/U ratio of 1/1.2). In the t-BA system (B) the conversion increased with increasing urea concentration up to a 0.04 molar fraction of urea (AN/U ratio of 1/4.7, and urea became saturated with t-BA at room temperature.).

Course of Polymerization

Conversion curves of AN-U canal complexes are shown in Fig. 4. The acceleration which was observed without the freezing medium was eliminated in the frozen media. In the frozen media the rate of polymerization was approximately proportional to monomer concentration. The initial rate was higher in the frozen media than in the absence of the freezing medium. It is considered that the initial rate may be enhanced by the enclosing effect of the rigid media. The effect is also attributed to the stabilization of canal complexes by the frozen media.

Dose-Rate Dependence

Figure 5 shows the influence of dose rate on the initial reaction rate. The rate of polymerization was found to be proportional to the first

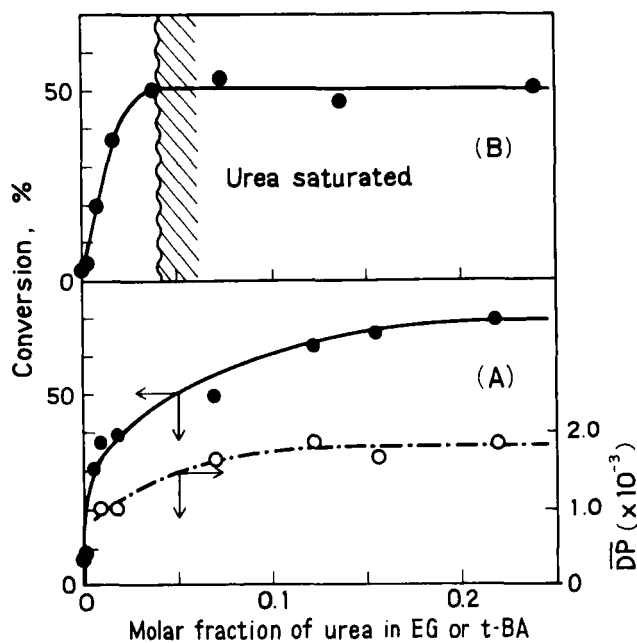


FIG. 3. Conversion and degree of polymerization as a function molar ratio of urea in (A) ethylene glycol and (B) *t*-butyl alcohol solutions, aged at -78°C for 7 days. $\text{AN/EG} = 8.47 \times 10^{-3}$, $\text{AN/t-BA} = 8.93 \times 10^{-3}$. Dose rate, 1.53×10^4 r/hr. Irradiation time, 16.9 hr for (A) and 7.10 hr for (B).

power of dose rate in both the EG and *t*-BA frozen systems. This suggests unimolecular termination in the frozen state.

Degree of Polymerization

The degrees of polymerization of polymers obtained in canal complexes are plotted as a function of conversion in Fig. 6. A notable feature of polymers obtained in the frozen media is that the degree of polymerization does not show any depression at higher conversions. In contrast, a tremendous decrease in the degree of polymerization was observed [4] in the absence of the frozen medium. The degree of polymerization is also higher in the *t*-BA frozen medium than

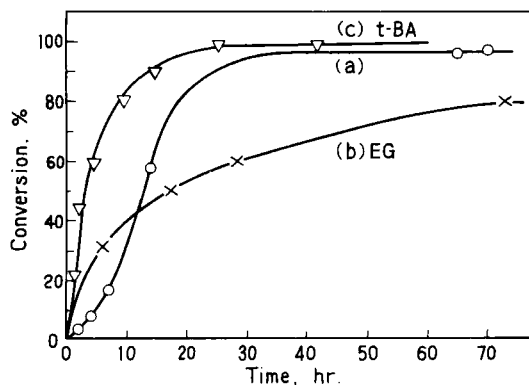


FIG. 4. The course of the polymerization of acrylonitrile-urea canal complex in (a) AN-U (1:8.78) without freezing medium, (b) AN-U-EG (1:8.78:118), and (c) AN-U-t-BA (1:8.78:112) frozen solutions, aged at -78°C for 7 days. Dose-rate, 1.45×10^4 r/hr for (a) and 1.53×10^4 r/hr for (b, c).

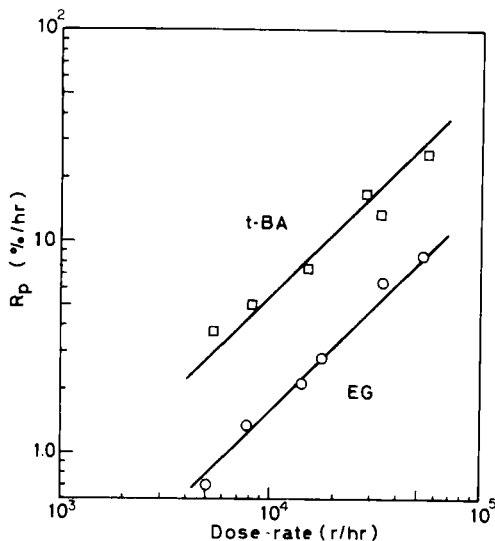


FIG. 5. Dose-rate dependence of rate of polymerization of acrylonitrile-urea canal complex at frozen states at -78°C in air. (\circ) AN-U-EG (1:8.78:118). (\square) AN-U-t-BA (1:8.78:112).

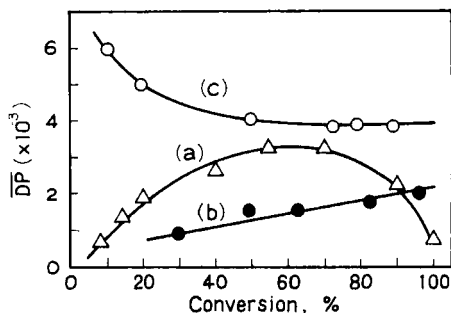


FIG. 6. Degrees of polymerization plotted against conversion. Polyacrylonitriles prepared from urea canal complex in (a) AN-U without freezing medium, (b) AN-U-EG, and (c) AN-U-t-BA frozen solutions.

in the EG system. These results seem to indicate that the more rigid the frozen systems are, the more stabilized are the canal complexes, and the more enhanced are the rate and the degree of polymerization.

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