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Radiation-Induced Polymerization of Urea Canal Complex. Part 4. Radiation-Induced Polymerization of Acrylonitrile in Urea-Ethylene Glycol Supercooled Liquid System

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ABSTRACT

The radiation-induced polymerization of acrylonitrile in a frozen urea-ethylene glycol solution at -78°C was investigated. The thermal behavior of the system was also analyzed by using differential thermal analysis.
The presence of urea enhanced the polymerization in a supercooled liquid state. In the IR spectra of polymers obtained in the supercooled liquid state, the absorption band at 2030 cm^{-1} due to the keteneimine structure was observed.

INTRODUCTION

In a previous paper [1] concerning radiation-induced polymerization of acrylonitrile in urea canal complex in the presence of a frozen ethylene glycol medium, polymerization was found to be faster

in the nonaged frozen medium than in the well-aged canal complex.

In the present report the polymerization of acrylonitrile in the nonaged state is investigated in connection with the thermal behavior of the frozen system.

EXPERIMENTAL

Materials

Acrylonitrile (AN), urea (U), and ethylene glycol (EG) were purified and used as in the previous paper [1].

Polymerization and Analysis of Polymers

The required amounts of AN and U were dissolved in EG (molar ratio of AN/U/EG was 1/8.78/118 unless otherwise specially mentioned) in glass ampules, and those ampules were quickly cooled to -78 C. In the case of the aged samples, the ampules were stored at -78°C for various periods. The ampules were irradiated at -78°C by using the ^{60}Co irradiation facility of the Research Reactor Institute, Kyoto University. After irradiation, cold methanol containing hydroquinone was added to the ampules and processed as in the previous report [1].

The degree of polymerization ($\overline{DP}$) of the polymer was calculated as indicated in the previous report.

Differential Thermal Analysis

The thermal behavior of the frozen AN-U-EG system was analyzed by the differential thermal analysis (DTA) method. Equipment of the Shimazu DT-10 type was used, and the measurements were as in the previous report [1].

RESULTS AND DISCUSSION

Polymerization Rate at Various Aging Times of the AN-U Canal Complex

The percentage conversions of AN to polymer after 6.8 hr of irradiation were determined for various aging times of the AN-U canal complex, varying from zero to 265 hr at a fixed molar ratio

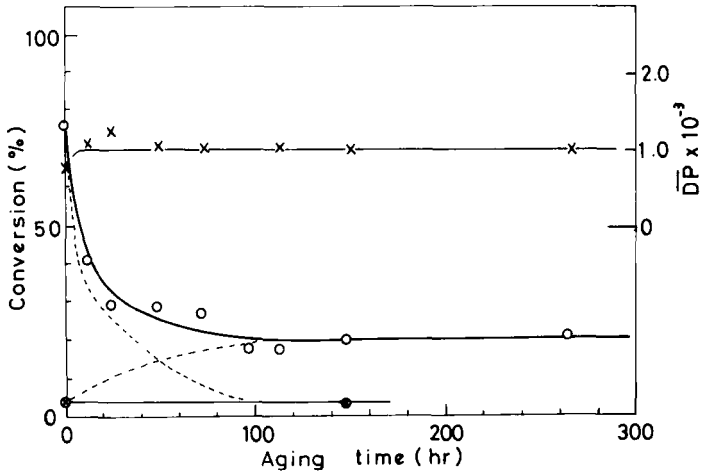

FIG. 1. The rate and the degree of polymerization plotted as a function of aging time of acrylonitrile-urea canal complex stored at -78°C in ethylene glycol in air. AN:U:EG = 1:8.8:118; dose-rate, 1.53×10^4 r/hr, irradiation time, 6.8 hr. Without urea; ⊗.

(AN/U/EG = 1/8.78/118), dose rate (1.53×10^4 r/hr) and temperature (-78°C). Figure 1 shows that the polymerization rate decreases rapidly with aging time, approaching the ultimate rate value for the canal complex. It is considered that at an early stage of the aging process two types of polymerizations (in the supercooled liquid state and in the canal complex) coexist. The contribution of the faster polymerization in the supercooled liquid state seems to decrease as canal complex formation proceeds. At the same time the phase change in the U-EG medium may take place from a supercooled liquid to a crystalline state.

Discussion on polymerization in the well-aged stage was presented in the previous paper [1], and the present studies are concerned with fast polymerization at zero-aging time.

Effect of Urea Concentration on Polymerization

The polymerization rate of AN in the frozen EG-U medium (at the fixed AN/EG ratio) was plotted against urea concentration. The presence of urea is essential for fast polymerization, as shown in Fig. 2. More than 0.05 molar fraction of urea in EG is required for effective polymerization rates, and the ultimate rate is reached at about 0.08 molar fraction of urea.

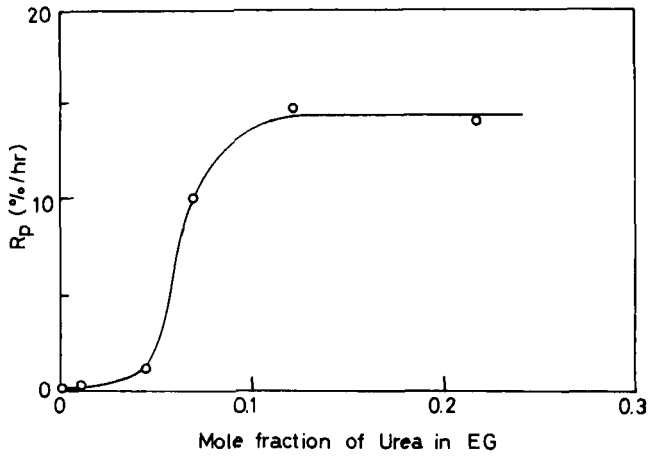

FIG. 2. The rate of polymerization of acrylonitrile vs urea concentration in ethylene glycol solution at -78°C at the fixed AN/EG molar ratio, 8.47×10^{-3}. Dose-rate, 1.53×10^{4} r/hr.

Effect of Dose Rate on Polymerization Rate

The relationship between the polymerization rate and the dose rate was plotted in which the dose-rate exponent was estimated to be 1.0 as shown in Fig. 3. This suggests unimolecular termination owing to immobilized growing polymer radicals.

Differential Thermal Analysis

The DTA method was applied to the monomer system in order to clarify the thermal behavior of the frozen solutions under the polymerization conditions. Figure 4(3) shows that the frozen monomer solution with the same composition as the polymerized samples has a glass transition temperature (T_g) of -115°C, a crystallization temperature (T_c) of -70°C, and a melting temperature (T_m) of -24°C. In the temperature range of T_g to T_c, the system is in a supercooled liquid state. Since the polymerization temperature (-78°C) lies in this range, this polymerization is considered to proceed in the supercooled liquid state.

T_g and T_c increase with increasing urea concentration at a fixed

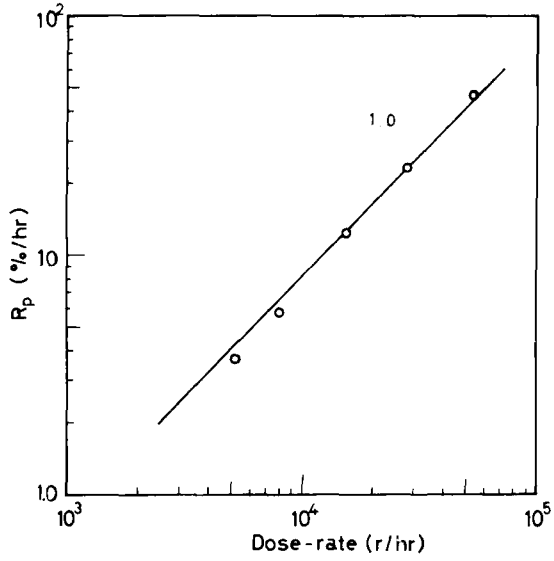

FIG. 3. Dose-rate dependence of the rate of polymerization of acrylonitrile in frozen urea-ethylene glycol solution at -78° C in air. AN:U:EG = 1:8.8:118.

molar ratio of AN to EG as shown in Fig. 4(2)-(4). It is considered that the presence of urea may stabilize the supercooled liquid state by forming hydrogen bonding with EG molecules.

The rapid enhancement of the polymerization rate at 0.05 molar fraction of urea, which corresponds to a AN/U/EG molar ratio of 1/6.2/118 (Fig. 2), might be correlated with the fact that T_c at this molar ratio could be raised to higher than -78° C, bringing the frozen system to the supercooled liquid state.

Although the AN solution with a AN/EG molar ratio of 1/118 did not have T_g or T_c, the AN solution with a higher monomer concentration (a ratio of 4/118) showed only a T_m of solidified AN at -85° C, except for the T_m of EG as shown in Fig. 4(1). This T_m of solidified AN was never found in the frozen solutions where urea existed.

The T_g and T_c of pure EG were found to be at -121 to -119° C and -88° C, respectively. The observed T_g is in good agreement with the reported value of -119° C [2].

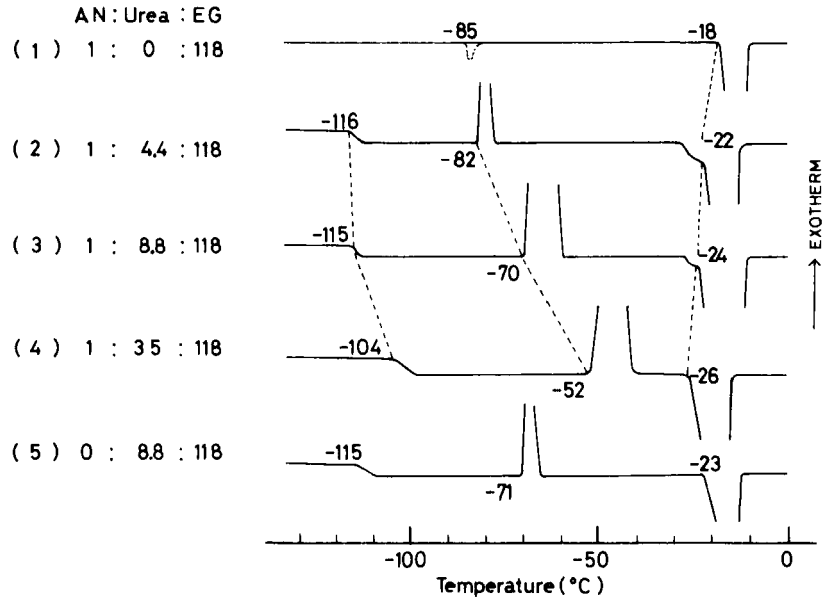

FIG. 4. DTA curves of the frozen acrylonitrile-urea-ethylene glycol system.

Infrared Spectra of Polymers

The IR spectra of polyacrylonitrile obtained in the polymerization of the AN-U-EG system at various states are shown in Fig. 5. The spectra of polymers obtained in the liquid state at both -20 and +20°C and in the supercooled liquid state at -78°C showed the characteristic absorption band at 2030 cm^{-1} due to the keteneimine structure, while the spectrum of the polymer obtained from polymerization in the crystalline state at -35°C showed little absorption at 2030 cm^{-1}. The keteneimine structure is considered to mainly arise from the termination reaction of the radical $\rangle C{=}C{=}N\cdot$ isomerized from the growing polymer radical [3]. It seems easier for this type of radical to be isomerized in the supercooled liquid state.

On the other hand, in the spectrum of the polymer prepared from well-aged samples, an absorption band around 1675 cm^{-1} was observed

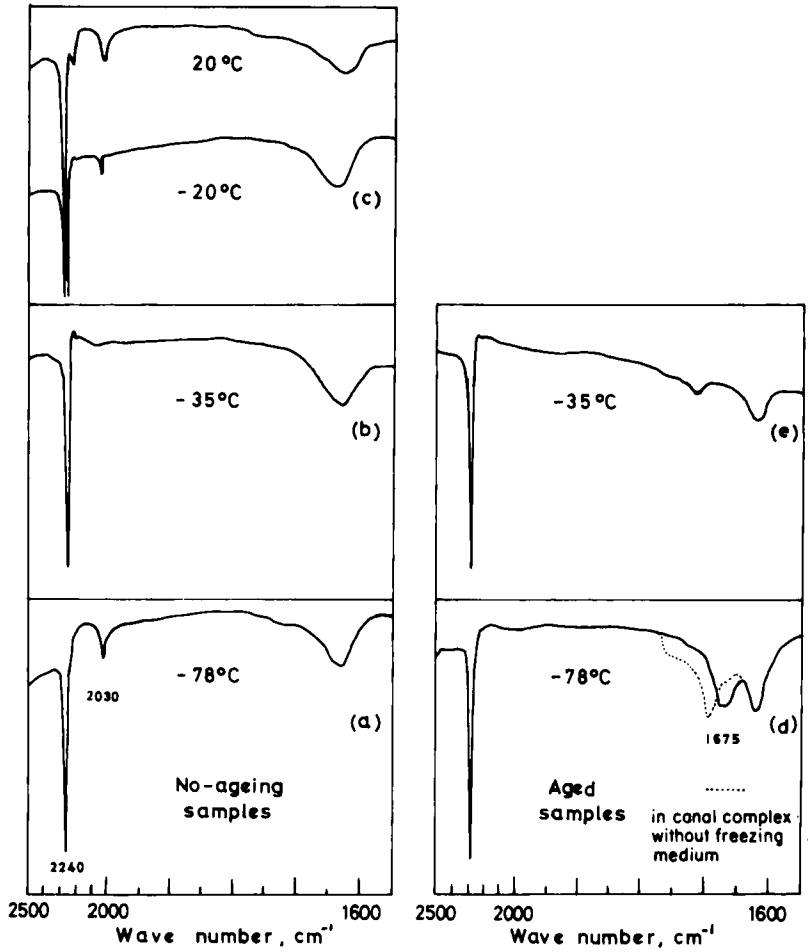

FIG. 5. Infrared spectra of polyacrylonitrile obtained in the acrylonitrile (1)-urea (8.78)-ethylene glycol(118) system. (a-c) Non-aged samples; (d, e) aged samples.

which was similar to the characteristic band seen in the spectrum of polymers prepared from the canal complex without a freezing medium [4] (Fig. 5(d,e)). These results show that the random arrangement of monomers in the supercooled liquid medium is transferred through the aging period to an orderly arrangement in the canal complex.

In conclusion, the fast polymerization in a nonaged system is thought to proceed at the supercooled liquid state at -78°C, and on raising the temperature between T_c and T_m the polymerization proceeds in the crystalline state. After an appropriate aging period, slow polymerization occurs in the canal complex formed in the crystallized medium.

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REFERENCES

[1] T. Maekawa, S. Okamura, and K. Hayashi, J. Macromol. Sci.—Chem., A9, 257 (1975).
[2] D. H. Rasmussen and A. P. MacKenzie, J. Phys. Chem., 75, 967 (1971).
[3] C. Schneider, Makromol. Chem., 56, 228 (1962).
[4] M. Kawasaki, T. Maekawa, K. Hayashi, and S. Okamura, J. Macromol. Chem., 1, 489 (1966).

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