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Solvent Effects on the Heterogeneous Radical Polymerization of Acrylonitrile

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SUMMARY

The heterogeneous radical polymerization of acrylonitrile was carried out in various solvents. The apparent rates and degrees of polymerization decreased in the presence of basic solvents such as alcohols, ethers and amines. The acrylonitrile radical does not readily abstracts an acidic α-hydrogen from solvents such as alkyl nitriles, indicating that the polar effect is more important than resonance stabilization of the resulting radical. Solvation of the electron defficient polyacrylonitrile radical by basic solvents is proposed.

INTRODUCTION

There are many studies on the effects of solvents on the radical polymerization of vinyl monomers. They are concerned with the effects of solvents on the rate of decomposition of initiators, the viscosity effect of solvents, the interactions between monomers and solvents, etc. With respect to the relationships between solvents and propagating radicals, there can be found a great amount of work related to the chain transfer reactions of solvents(1), but relatively little has been mentioned about the solvation of propagating radicals with solvents. It was reported by Russel(2) and Walling(3) that the selectivity for the abstraction of primary and tertiary hydrogens by chlorine atom increases in aromatic solvents, and this effect was explained by the formation of a π-complex between the chlorine atom and the aromatic ring. This idea of π-complex formation was then employed by Litt and Stanett(4) for the slow polymerization of vinyl benzoate, and by Bamford and coworkers (5) for the polymerization of methylmethacrylate in aromatic solvents.More recently Yamamoto et al(6) have studied the kinetics of photo-initiated polymerization of vinyl acetate in various solvents and reported that the rate constant of propagation largely depends on the

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solvents employed. Kamachi et al(7) reported the solvent effects on the radical polymerization of methacrylates and they also suggested the formation of such electron donor-acceptor complex between the propagating radical and the solvents.

Previously we reported the reactivities of chlorophosphines with various vinyl polymer radicals(8)and it was found that the pattern of polymerization of acrylonitrile in the presence of phosphorus trichloride varies depending the solvents employed. In this report the results obtained by the heterogeneous polymerization of acrylonitrile in varying solvents, are described.

EXPERIMENTAL

Acrylonitrile (AN) was purified by the usual method and distilled twice under nitrogen before use. The initiator, 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from methanol. Diphenylpycrylhydrazyl (DPPH) was recrystallized from benzene before use. All the solvents used were reagent grade and they were purified by distillation.

The polymerization was carried out in a Pyrex tube of 1.2 cm diameter and 12 cm length, in which required amounts of reactants were placed and the tube was sealed off after repeated degassing by the freeze and melt process using liquid nitrogen. The apparent rate of polymerization was obtained gravimetrically.

The average degree of polymerization was determined from the intrinsic viscosoty measured at 25°C in dimethyl formamide using an Ubbelohde viscometer and using the following equation(9):

$$[\eta] = 39.2 \times 10^{-3} M_n^{0.75} \qquad \text{in dl/g}$$

The rate constant for the decomposition of AIBN, k_d, was determined from the volume of nitrogen liberated. The initiator efficiency of AIBN was measured from the decrease in absorption of DPPH at 520nm.

A Varian EPR spectrometer Model E line 102 equipped with NMR Magnion gausmeter probe, was used to obtain ESR spectra of the polymerization system.

RESULTS AND DISCUSSION

The rate of decomposition of AIBN does not vary significantly enough to influence the rate of polymerization, as can be seen in Table 1, and also as reported by Olivé(10). The same can be said to the initiator efficiency.

In order to see if there exist any relationship between the rate and degree of polymerization, and the solubility of solvents employed, the amounts of solvents required for precipitation of poly-AN from its dimethyl formamide solution, were determined. However there was no relationship between them.

Table 1. The rate of decomposition of AIBN and the initiator efficiency in some solvents, 50°C.

Solvent	k_d x 10^{-6} s^{-1}	f
benzene	2.0	0.57
1,2-dichloroethane	2.0	--
acetonitrile	1.5	0.68
isobutyronitrile	1.9	0.57
benzonitrile	1.5	--
ethanol	1.4	--

Figure 1 shows the time-conversion curves for the polymerization of AN in various solvents having secondary hydrogens. As can be seen from the figure the polymerization in propionitrile is rapid and the degree of polymerization is high. The rate and degree of polymerization are low in basic solvents such as ethers, ethanol and triethylamine. It can be said also that almost no chain transfer takes place with propionitrile, although it would give a radical with resonance stabilization due to the -C≡N group, by the loss of α-hydrogen. On the other hand tetrahydrofuran (THF) undergoes chain transfer, thus giving a low molecular weight polymer, despite the fact that the THF radical formed is a nonconjugated one.

Figure 2 shows the polymerization of AN in the presence of various nitriles. It can be seen that the initial rate (within about 30 minutes and 2% conversion) is almost same for all the alkyl nitriles and the degree of polymerization does not differ appreciably with the type of alkyl group. These results show that even the tertiary hydrogen of isobutyronitrile is not easily abstracted by the poly-AN radical.

Figure 3 shows the time-conversion curves for the systems containing triethylamine and its hydrochloride. It can be seen that triethylamine hydrochloride has very little effect on the polymerization, being almost same as that in methanol alone. This suggests that the slow polymerization and the low degree of polymerization of AN in triethylamine, are due to the n-electrons of amine nitrogen, and that the α-hydrogen of ethyl groups is not very susceptible to abstraction. It is likely that the poly-AN radical interacts with with basic solvents which act as donor and thus the electron-defficient poly-AN radical as an acceptor. Furthermore it can be said that the poly-AN radical does not readily abstract α-hydrogen with acidic character, such as those of alkyl nitriles, alkyl chlorides, alkylamine salts, etc. But it can abstract the α-hydrogen of basic solvents such as ethers, alcohols and amines.

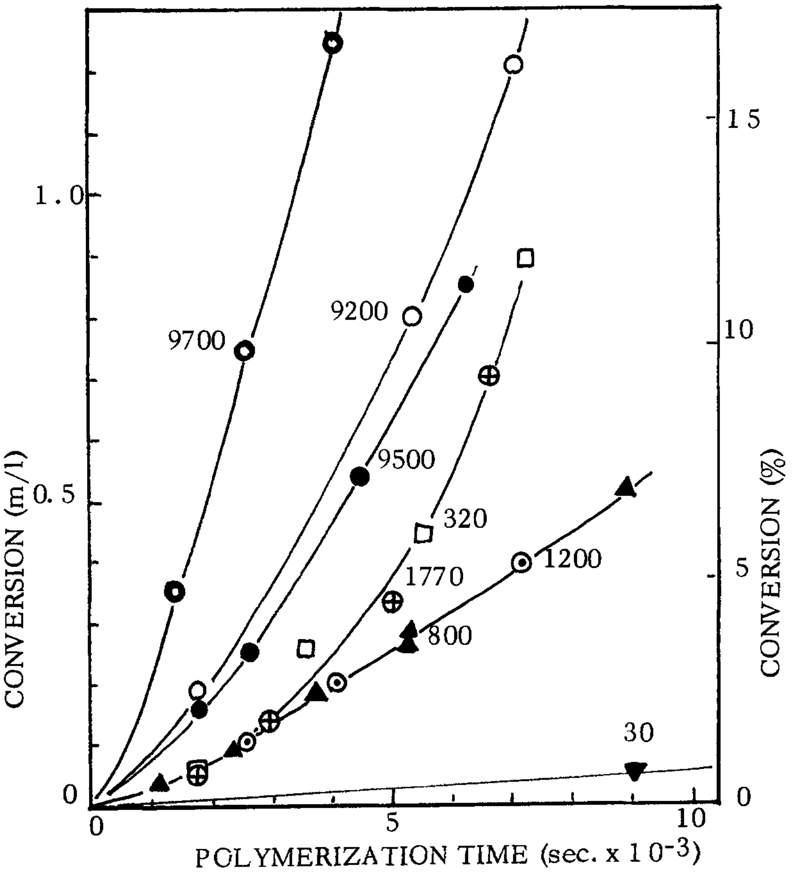

Fig. 1. Polymerization of AN in various solvents at 50°
[AN]= 7.6 m/l.[AIBN]= 0.005 m/l. [AN]/[Solv.] = 1 by volume.
●:benzene, □:THF, ⊕:dioxane, ▲:EtOH, ⊙:diethylether, ▼:triethylamine. The numbers over the points represent average degree of polymerization. ◯:Et-CN, ○:dichloroethane

Bamford et al(11) attempted to explain the high chain transfer constant of triethylamine by proposing an electron transfer from the amine to the poly-AN radical and by the stabilization of triethylamine radical. However, there is no evidence for such an electron transfer.

The electron spin resonance spectra of the polymerization systems in benzene and in the presence of triethylamine were taken. The g values changed appreciably indicating that an interaction of poly-AN radical with triethylamine, takes place, as shown in Table 2. The present authors wish to propose, tentatively, a simple solvation of poly-AN radical by the n-electrons

Table 2. ESR spectra data for the polymerization of AN. (Spectra were taken at - 100°C)

	(G Hz)	g
in benzene	9,1293	2,0025 ± 0.0005
in triethylamine	9,1239	2,0003 ± 0.0005

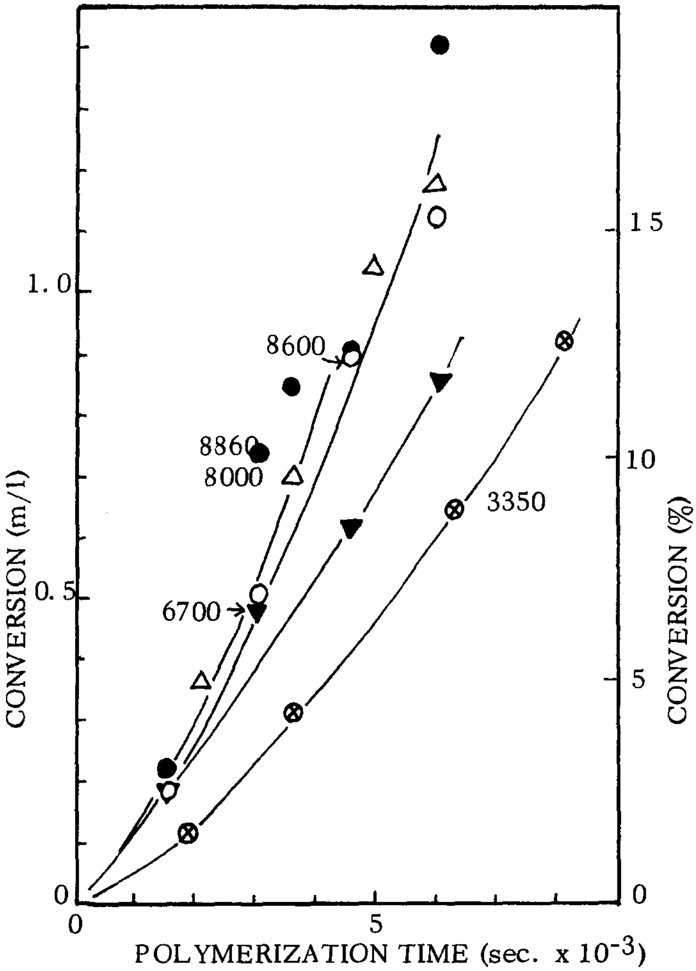

Fig. 2. Polymerization of AN in various nitriles at 50°. [AN]=7.6 m/l. [AIBN]=0.005 m/l. AN=5 ml. RCN=1 ml. Benzene=4 ml. ●:CH_3CN, △:C_2H_5CN, ▼:n-C_3H_7CN, ○:i-C_3H_7CN, ⊗:C_6H_5CN

The numbers over the points represent average degree of polymerization.

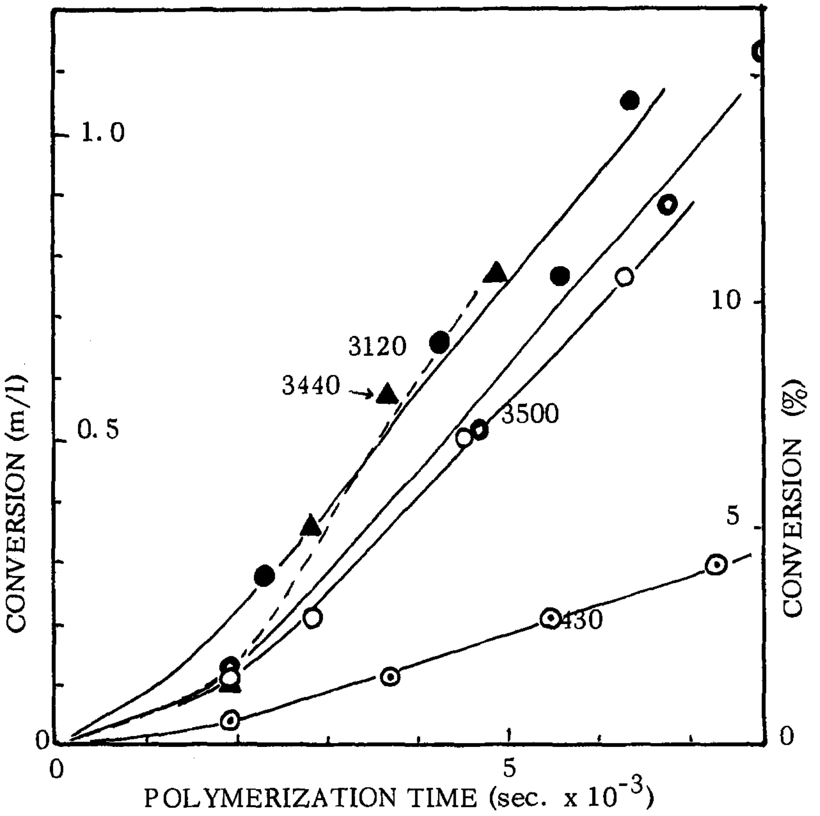

Fig. 3. Polymerization of AN in the presence of triethylamine and its hydrochloride at 50°C in methanol

[AN]=7.6 m/l. [AIBN]=0.005 m/l. Solvent:methanol.
▲ :methanol, ⊙:0.267 m/l of triethylamine, ●:0.067 m/l of hydrochloride, ●:0.267 m/l of hydrochloride, ○:0.538 m/l of hydrochloride.

of the basic solvents. The α-hydrogen of the basic solvents may stabilize the transition state. In order that the chain transfer takes place, it may be necessary to have solvation so that the α-hydrogen to be abstracted, gets close to the poly-AN radical, forming a favourable transition state, as shown in Figure 4 for example with triethylamine.

The reason why the rate and degree of polymerization are higher in alkyl nitriles than in other solvents, is not known at moment. When the polymerization was carried out with varying ratios of propionitrile to methanol, the rate and degree of polymerization decreased with decrease in the ratio of propionitrile to methanol.

More detailed studies are being carried out at the present, and it is hoped that the problems will be clarified in future.

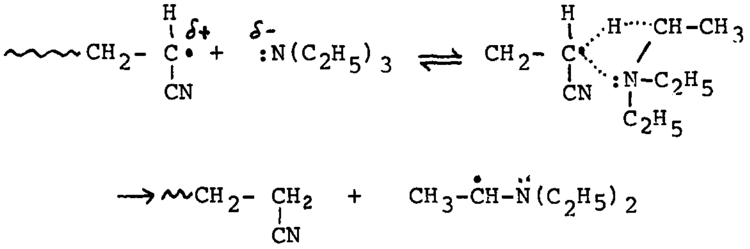

Fig. 4. A stabilization of poly-AN radical with basic solvents and the chain transfer

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