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Effect of Solvent on the Radical Copolymerizability of Styrene with Acrylonitrile

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Effect of Solvent on the Radical Copolymerizability of Styrene with Acrylonitrile

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ABSTRACT

Radical copolymerization of styrene (St, M_1) with acrylonitrile (AN, M_2) has been carried out using azobisisobutylonitrile as an initiator in benzene, dimethylsulfoxide, acetonitrile, and ethanol at 60 and 80°C. Good linear correlationships were obtained by plotting the values of log r_1, log r_2, Q_2, and e_2 against those of $\nu C{\equiv}N$ and $\nu C{=}C$ determined in the solvents: the increase in the interaction between AN and the solvent was found to decrease the values of log r_1 and e_2 but to increase those of log r_2 and Q_2. The results are discussed in terms of the solvation both in the ground state and in the transition state.

INTRODUCTION

During the course of our studies on the polymerization of pyridazinones derivatives, we found that solvents strongly affected the copolymerizabilities of these derivatives with styrene (St) and that this was perhaps due to different degrees of solvation of the carbonyl groups by the derivatives both at the ground state and at the transition state [1-3].

Recently, we showed that similar solvent effects were observed in the copolymerization of St with a few vinyl monomers bearing polar groups, i.e., methyl methacrylate [4], N,N-dimethylacrylamide [5], and methyl vinyl sulfoxide [6]. In all these cases, protic solvents such as phenol and carboxylic acid were found to affect the reactivities specifically, apparently due to hydrogen bonding interaction with the polar groups.

More recently, we extended our experiments to an asymmetric inductive copolymerization of St with maleic anhydride in l-menthol to obtain an optically active copolymer [7].

This article deals with the radical copolymerization of St (M_1) with acrylonitrile in a few solvents. The results are discussed in terms of the solvent effect both in the ground state and in the transition state.

EXPERIMENTAL

Styrene (St, M_1), acrylonitrile (AN, M_2), and azobisisobutylonitrile (AIBN) were purified by conventional methods.

Solvents were purified by the ordinary methods.

Measurements of infrared (IR) spectra were taken using a liquid cell or KBr disk with a Yanagimoto LSG-25 IR spectrometer.

Radical copolymerization of St with AN was carried out with AIBN as an initiator in benzene, dimethylsulfoxide (DMSO), acetonitrile (CH_3CN), and ethanol (EtOH) at 60 and 80°C under degassed ampule.

The copolymers were purified by the reprecipitation method from benzene-methanol.

The compositions of the copolymers were determined by elemental analysis.

RESULTS AND DISCUSSION

Free radical copolymerization of St (M_1) with AN has been carried out in a few solvents at 60 and 80°C.

Table 1 summarizes the values of the monomer reactivity ratio (r_1 and r_2), Q_2, and e_2 which varied with the solvents, clearly indicating the occurrence of the solvent effect in the reaction. An

TABLE 1. Copolymerization Parameters of St (M_1) with AN and IR Spectra of AN in Several Solvents

Solvent	°C	r_1	r_2	Q_2	e_2	$\nu C \equiv N$ (cm^{-1})	$\nu C = C$ (cm^{-1})
DMSO	60	0.30	0.17	0.84	0.93	2230.0	1656.4
	80	0.33	0.17	0.78	0.90		
CH_3CN	60	0.33	0.15	0.75	0.93	2235.0	1657.5
	80	0.36	0.17	0.73	0.87		
EtOH	60	0.46	0.07	0.49	1.05	2236.8	1657.6
	80	0.41	0.06	0.52	1.12		
Benzene	60	0.43	0.03	0.44	1.28	2238.0	1658.6
	80	0.55	0.06	0.41	1.05		

unsatisfactory difference in these values with reaction temperature was observed. There was enough difference to estimate such activation parameters as energy and entropy.

The stretching frequencies, $\nu C \equiv N$ and $\nu C = C$, of AN were determined in the solvents and are included in Table 1. Both frequencies were found to be considerably affected by the solvents and to shift to shorter wavelengths in the order benzene, EtOH, CH_3CN, and DMSO. The largest shift of $\nu C \equiv N$ was observed in DMSO. A 8-cm^{-1} shift of $\nu C \equiv N$ to a shorter wavelength is caused by a change from benzene to DMSO. This is perhaps due to the interaction between the $C \equiv N$ group of AN and the $S = O$ group of DMSO as shown in Fig. 1 [8]. It should be noted that the degree of shift in $\nu C \equiv N$ is larger than that in $\nu C = C$. These results appear to indicate that the solvents interact with the $C \equiv N$ group of AN rather than with the $C = C$ group. The possibility of the solvation of the St units may be excluded because there was not any observed shift in the IR spectra of St in these solvents.

It is interesting to note that linear correlations were observed by

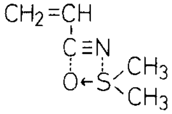

FIG. 1. Four-centered solvation to the C≡N group of AN.

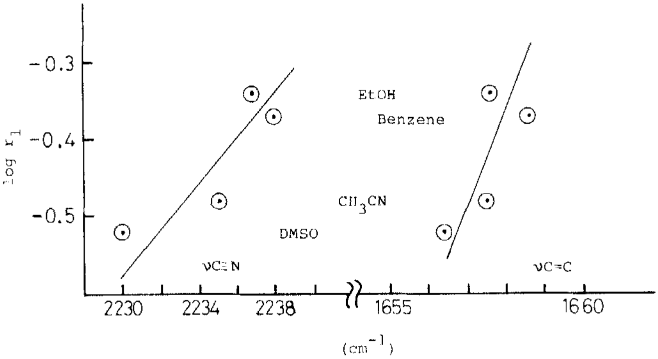

FIG. 2. Dependence of log r_1 at 60°C on the νC≡N and νC=C of AN in several solvents.

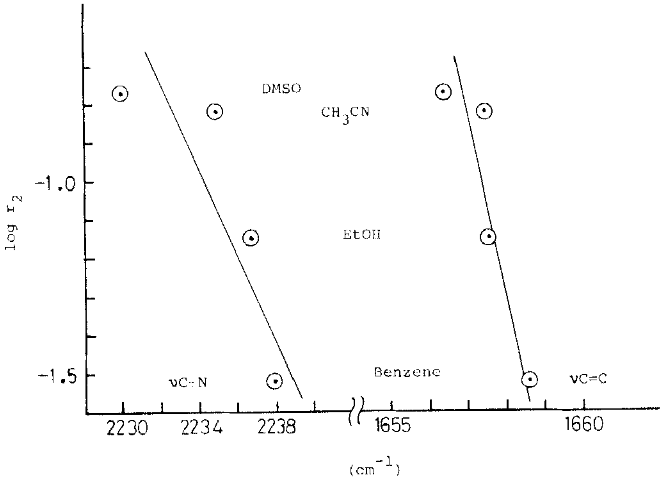

FIG. 3. Dependence of log r_2 at 60°C on the νC≡N and νC=C of AN in several solvents.

plotting the values of log r_1 and log r_2 against those of νC≡N and νC=C (Figs. 2 and 3).

In the case of r_1, the increase in the interaction between AN and the solvent is deduced to enhance copolymerizability, while the same increment in the interaction increased the r_2 values, i.e., the drop in the copolymerizability. Although it is rather difficult to evaluate the reason for this observation, the above finding seems to imply that the

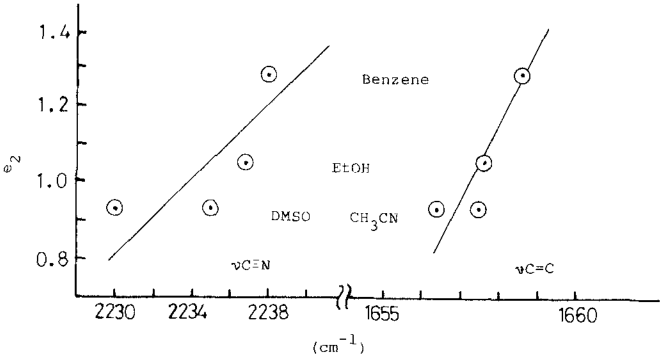

FIG. 4. Dependence of e_2 value at 60°C on the νC≡N and νC=C of AN in several solvents.

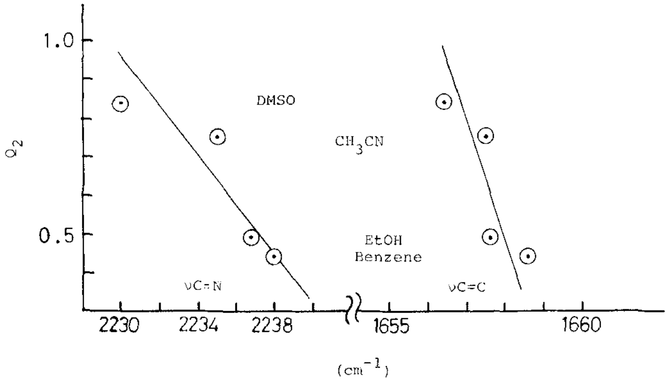

FIG. 5. Dependence of Q_2 value at 60°C on the νC≡N and νC=C of AN in several solvents.

reactivity is influenced by the different degree of solvation of AN at the ground state. This may be partly supported by the fact that linear relationships were obtained for plots of e_2 values against νC≡N and νC=C (Fig. 4). That is, the e_2 values linearly decrease with an increase of the interaction between AN and the solvents. Such a reduction in the e_2 values with the solvent-AN interaction may be rationalized by the so-called four-centered solvation of the C≡N group of AN as depicted in Fig. 1.

On the other hand, it is quite interesting to note that straight lines were obtained by plots of Q_2 values with the values of νC≡N and νC=C (Fig. 5). In this case the Q_2 values increased with an increase of the solvent-solute interaction. One possible explanation for this is that the solvation to the C≡N group enhances the stabilization of the growing AN radical by spreading it over a solvated molecule, perhaps the four-centered type of species. If this is valid, it will be a solvation effect in the transition state.

In summary, the copolymerizability of St with AN is affected by the different degree of solvation to the C≡N group of AN both in the ground state and in the transition state.

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