Effect of Added Solvents on the Radical Polymerization of Acrylonitrile in Liquid Sulfur Dioxide

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Synopsis

Acrylonitrile was polymerized by aa'-azobisisobutyronitrile (AIBN) as an initiator at 50°C in liquid sulfur dioxide mixed with an added solvent. The added solvents were cyclohexane, benzene, toluene, p-xylene, ethylbenzene, isopropylbenzene, p-cymene, chlorobenzene, benzonitrile and ethyl benozate, respectively. In each case, only polyacrylonitrile was obtained and the formation of the polymer was independent on the solvent added. No acrylonitrile polysulfone was found in the reaction mixture. The added solvents showed no appreciable influence on the overall rate of polymerization (Rp) in the range of the experimental condition.

I. Introduction

Olefin in liquid sulfur dioxide usually affords the corresponding polysulfone in the presence of a radical initiator. For example, 1-butene or 2-butene forms copolymer with sulfur dioxide, the molar ratio of which being one to one,[1] and styrene forms styrene polysulfone, the molar ratio of styrene vs. sulfur dioxide being 2 to 1.[1],[2]

On the other hand, no polysuflone was obtained in the radical polymerization of acrylonitrile in liquid sulfur dioxide.[3] In the polymerization of styrene, there is a strong attraction between the vinyl group ($\delta-$charged) and S atom ($\delta+$charged) of sulfur dioxide molecule which might well lead to a complex formation, whereas in the polymerization of acrylonitrile, the vinyl group of which is charged cationic due to the electron attractive property of CN group, thus repelling the sulfur dioxide molecule not to form polysulfone.

Therefore, in the radical polymerization of acrylonitrile, liquid sulfur dioxide plays a role only as a solvent. However, since liquid sulfur dioxide is a polar solvent, there might be expected some interactions with the added solvents. In the present paper, the effect of added solvents on the radical polymerization of acrylonitrile in liquid sulfur dioxide was exmained.

It has been well established by Andrews and Keefer[4] that aromatic hydrocarbons such as benzene, toluene or xylene forms a complex with sulfur dioxide, the

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* Polymerization in Liquid Sulfur Dioxide, Part XII
(1) F.S. Dainton and K.J. Ivin, Proc. Roy. Soc., **A214** (1952), 96.
(2) N. Tokura and M. Matsuda, Kogyo Kagaku Zasshi, **64** (1961), 501.
(3) N. Tokura, M. Matsuda and F. Yazaki, Makromol. Chem. **42** (1960), 108.
(4) L.J. Andrews and R.M. Keefer, J. Am. Chem. Soc., **73** (1951), 4169.

presence of which means a strong interaction between the hydrocarbon and sulfur dioxide. Moreover, many compounds such as phenol, ketone, ether and amine are also knwon to form complexes with sulfur dioxide. In the cationic polymerization of styrene, the addition of aromatic hydrocarbons to sulfur dioxide solution resulted in the depression of both the rate of polymerization and the degree of polymerization. [5]

In the radical polymerization of styrene in liquid sulfure dioxide [6] with added hydrocarbon, Rp (overall rate of polymerization) increases as the content of sulfur dioxide increases in the mixture and addition of cyclohexane depressed Rp more effectively than addition of benzene. Electron accepting compound such as chlorobenzene, benzonitrile and benzaldehyde increased Rp definitely.

The solvent effect in organic chemistry has been summarized in reviews by Walling [7] and, Mayo and Walling [8]. It is generally accepted that the effects of solvent upon the rate of polymerization, copolymerization, and monomer reactivity ratio are little. However, in the recent communications, Russell [9], [10] has shown that chlorine radical attacks aliphatic hydrocarbon in different ways according to the solvents used in the reaction and aromatic hydrocarbon and carbon disulfide have shown special solvent effect upon the course of the reaction which may be attributable to the interaction between radical and the solvent.

The present study of acrylonitrile polymerization in liquid sulfur dioxide with added solvent may be of some importance to elucidate the nature of sulfur dioxide as solvent.

II. Experimental

1. *Materials*

Liquid sulfur dioxide was dried by phosphorus pentoxide. Acrylonitrile and azobisiobutyronitrile were purified as was described in the preceding paper [3]. Cyclohexane, benzene, toluene, p-xylene, p-cymene, chlorobenzene and carbon tetrachloride were purified by the general procedures. [6] Ethyl benzene, iso-propylbenzene, benzonitrile and ethyl benzoate of commercial first grade were used after distillation.

2. *General procedure*

Gravimetric method was used. A general survey of the apparatus and the reaction vessel was given in detail in the previous paper. [2] Intrinsic viscosity was measured by a Ubbelohde viscometer in dimethylformamide as a solvent.

(5) N. Tokura, M. Matsuda and Y. Watanabe, J. Polym. Sci., in press.
(6) N. Tokura, M.Matsuda, T. Kawahara and Y. Ogawa, Kogyo Kagaku Zasshi, in press.
(7) C. Walling, *Free Radical in Solution* John Wiley and Sons, New York, (1957), p. 478
(8) F.R. Mayo and C. Walling, Chem. Revs., **46** (1950), 191.
(9) G.A. Russell and H.C. Brown, J. Am. Chem. Soc., **77** (1955). 4031,
(10) C.A. Russell, Tetrahedron **8** (1960), 101.

## III.	Results and discussion

1.	*Polymerization of acrylonitrile in liquid sulfur dioxide with added solvent.*

The initial concentration of acrylonitrile $[M]_0$, and the total volume of the system (sulfur dioxide and added solvent with monomer) were held constant throughout the experiment as 5.03mole/1 and 15 ml, respectively.	Concentrations of liquid sulfur dioxide and the added solvent were in the ranges of 0–13.49 mole/1 and about 7–0 mole/1, respectively.

The concentration of azobisisobutyronitrile was 1.00×10^{-2} mole/1.	The time vs. conversion curves are shown in Figs. 1,2,3 and 4.	The dependence of the rates on temperature is also visualized in these figures.

In each case, Rp decreases as the content of sulfur dixoide increases.	However the Rp's of the respective runs in pure added solvents are differing slightly, i.e., 18×10^{-5}, 12.15×10^{-5}, 15.50×10^{-5} and 19.07×10^{-5} mole $1.^{-1}$ sec.$^{-1}$ for cyclohexane, benzene, p-xylene and chlorobenzene, respectively, in the mixtures of equimolar amount of sulfur dioxide and the added solvent the Rp's, of the runs were almost equal and the solvent effect was not observed as far as the rate of polymerization was concerned.	In each run, autocatalytic effect for the polymerization was seen,
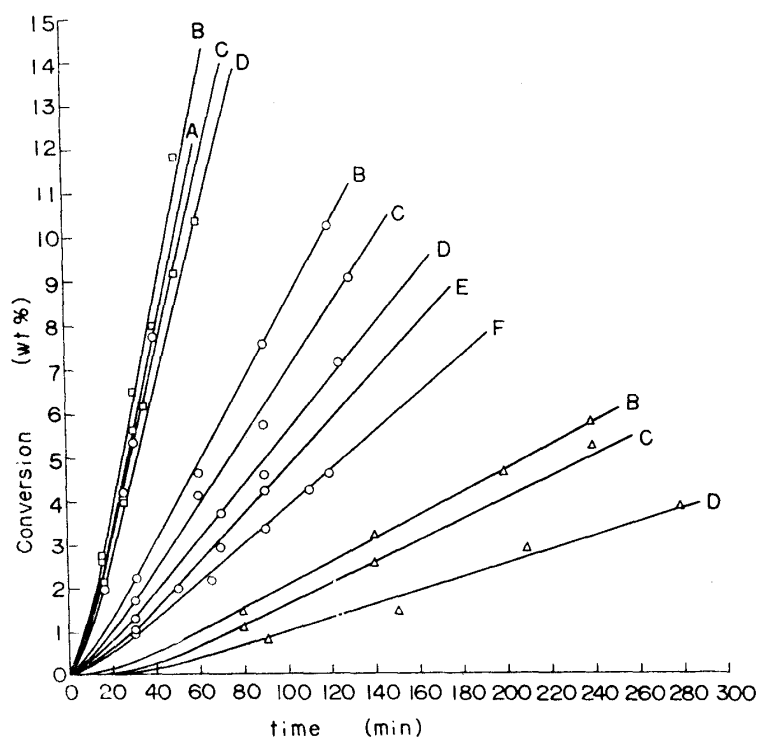

Fig. 1.	Liq. SO_2-Cyclohexane

Polym. Temp.		Cyclohexane mole/1	SO_2 mole/1
Δ 40°C	A	6.16	0
o 50°C	B	4.62	3.37
□ 60°C	C	4.23	4.23
	D	3.08	6.74
	E	1.54	10.11
	F	0	13.49
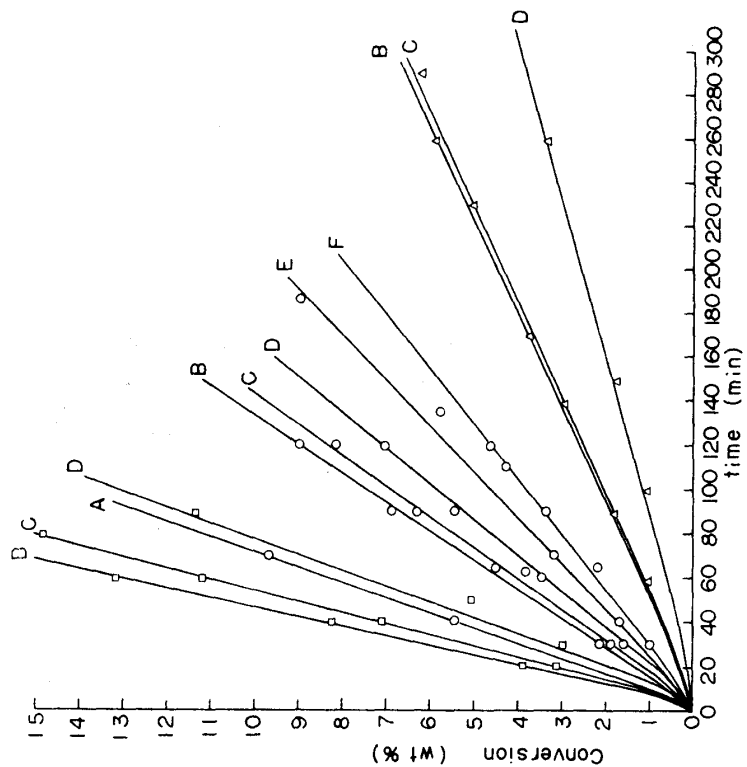
Fig. 2. Liq. SO$_2$-Benzene

Polym. Temp.		Benzene	SO$_2$ mole/l
△ 40°C	A	7.47	0
○ 50°C	B	5.60	3.37
□ 60°C	C	4.83	4.83
	D	3.74	6.74
	E	1.89	10.11
	F	0	13.49

Conversion (wt %)   time (min)
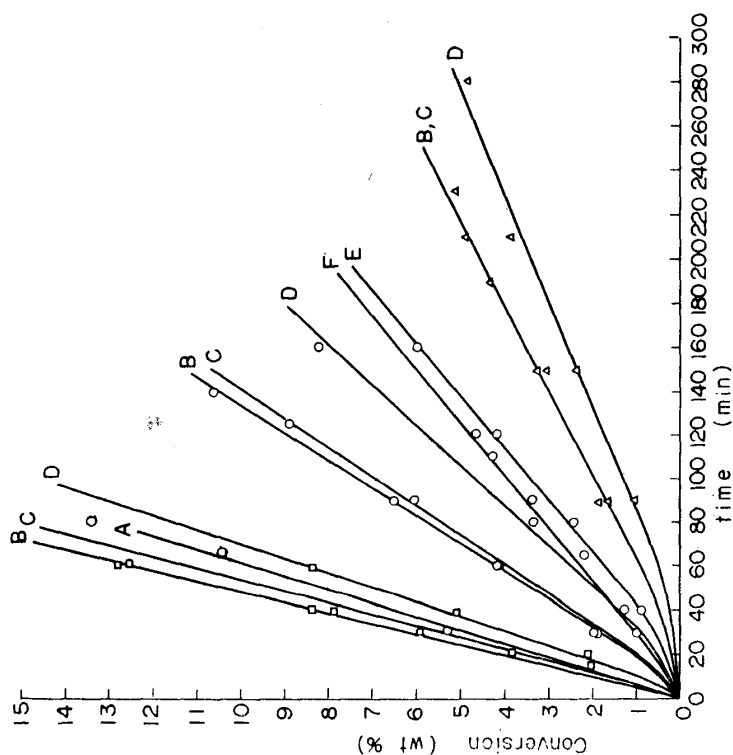
Fig. 3. Liq. SO$_2$-p-Xylene

Polym. Temp.		p-Xylene	SO$_2$ mole/l
△ 40°C	A	5.38	0
○ 50°C	B	4.04	3.37
□ 60°C	C	3.84	3.84
	D	2.96	6.74
	E	1.35	10.11
	F	0	13.49

Conversion (wt %)   time (min)
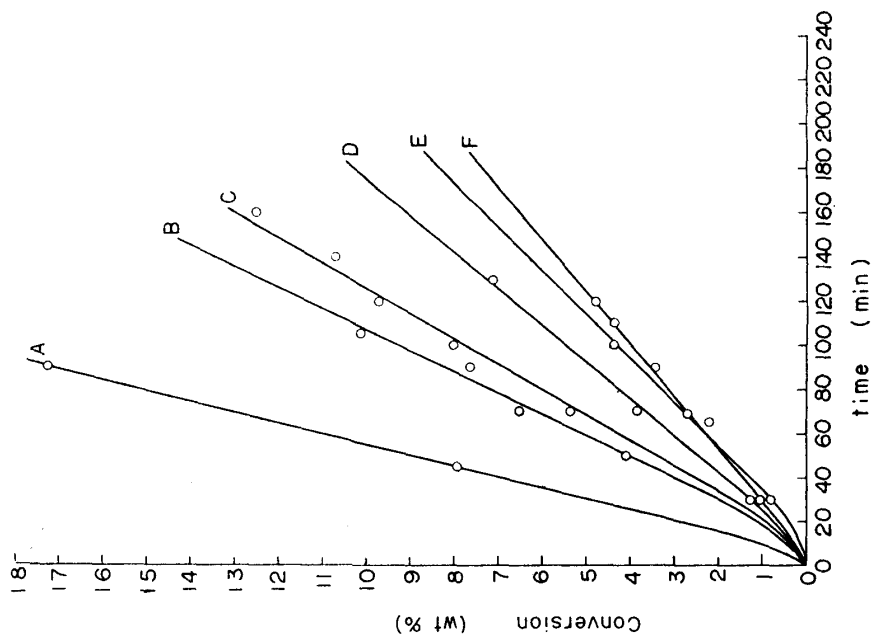
Fig. 4. Liq. SO$_2$-Chlorobenzene
Polym. Temp. 50°C

Chlorobenzene		SO$_2$ mole/l	
A	6.52		0
B	4.89		3.37
C	4.40		4.40
D	3.26		6.70
E	1.63		10.11
F	0		13.49

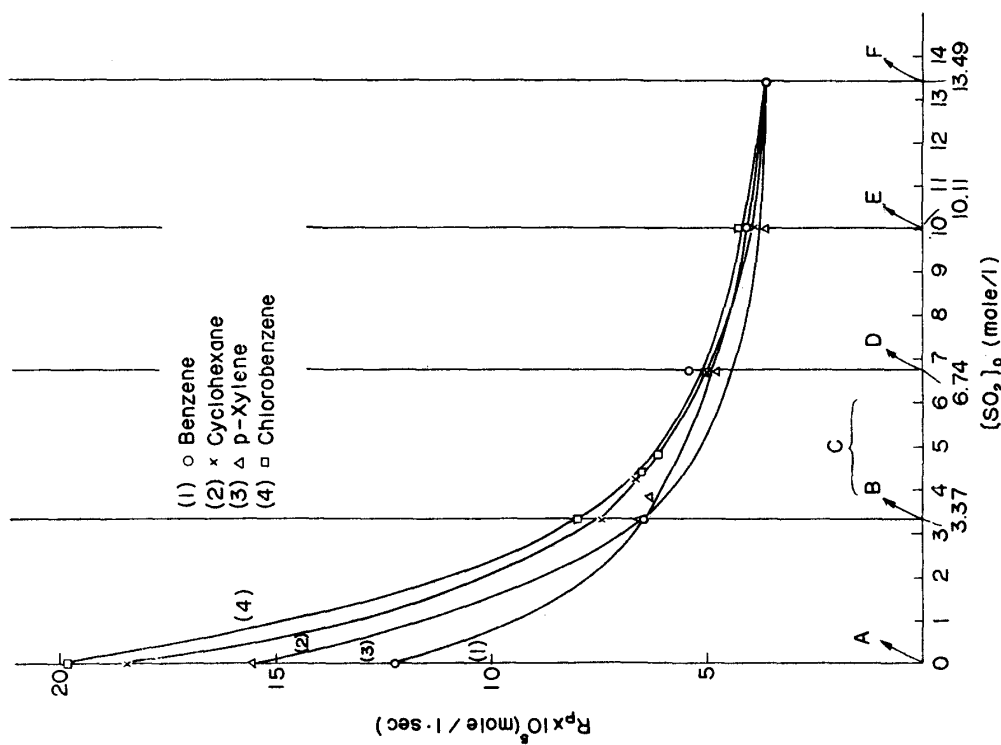(1) ○ Benzene
(2) × Cyclohexane
(3) △ p-Xylene
(4) □ Chlorobenzene

Fig. 5.

however this phenomenon is not peculiar for acrylonitrile polymerization.

The degree of polymerization, Pn was calculated by the R.C. Houtz's equation[11],

$$[\eta] = 1.75 \times 10^{-3} \ [M_w]^{0.66} \ (25°C).$$

A similar relation exists between benzene and cyclohexane. In case of chlorobenzene, the Pn curve has a maximum at point B. However, no decisive conclusion is available from these results. The activation energies obtained in the conditions as shown in Figs. 1, 2 and 3 were all in the range of about 25 kcal/mole. Since it seemed likely to be inconvenient to compare the effect of added solvent, a system consisting of carbon tetrachloride- SO_2 added solvent was used as the following.

2. *Polymerization in carbon tetrachloride-sulfur dioxide added solvent system.*

The polymerization was carried out at 50°C. Carbon tetrachloride was used
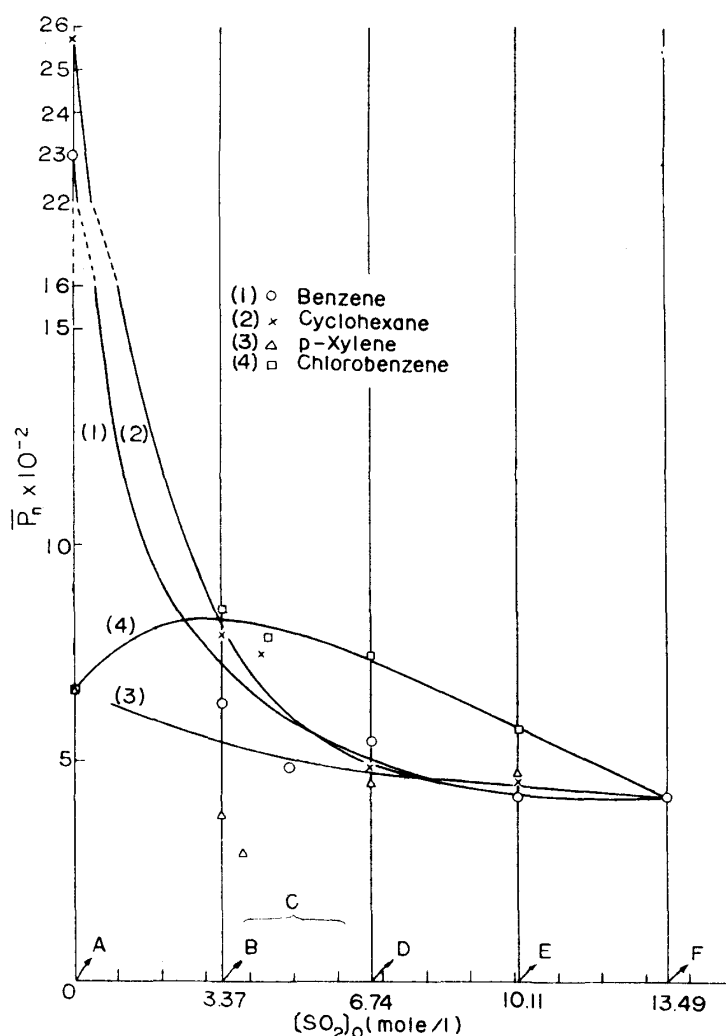

(1) ○ Benzene
(2) × Cyclohexane
(3) △ p-Xylene
(4) □ Chlorobenzene

Fig. 6.

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(11)   R.C. Houtz, Textile Research J., **20** (1950), 786.

as the diluent of the system since it was found by Das et al. [12] that the solvent chain transfer constant of CCl_4 was the least (0.85×10^{-4}) as compared to that of benzene (2.46×10^{-4}) and toluene (5.83×10^{-4}) in the polymerization of acrylonitrile at 60°C.

The effect of equimolar amount of the added solvent and sulfur dioxide on the rate of polymerization is seen in Fig. 7. Since aromatic hydrocarbons form 1: 1
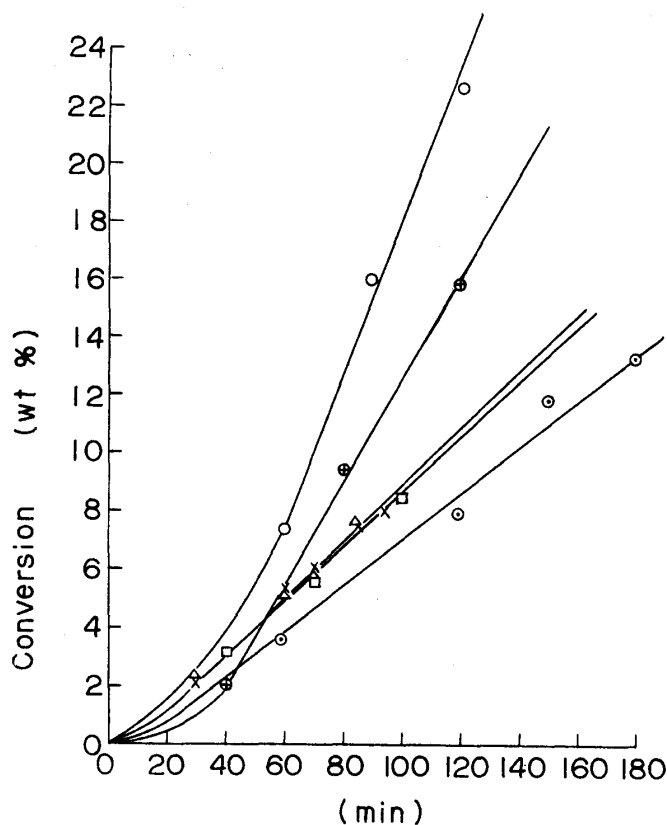

Fig. 7.

○ Ethyl Benzoate   ⊕ Benzonitrile   × p-Xylene   △ Benzene
□ Chlorobenzene   ⊙ p-Cymene

molar complex with sulfur dioxide [4] and the strength of the complex formation should be dependent on the electron donative capacity of the hydrocarbon, the curves in Fig. 7 reveal some interesting results. The condition of the polymerization was, $[M]_0 = 2.66$ mole/1, $[SO_2]_0 = 3.96$ mole/1, [added solvent]$_0 = 3.96$ mole/1, $[AIBN]_0 = 2.15 \times 10^{-1}$ mole/1, total volume 17 ml (diluted with CCl_4). The order of the rate was,

ethyl benzoate > benzonitrile > p-xylene ≒ benzene ≒ chlorobenzene > p-cymene

the aromatic compounds with electron-donating group indicating the lesser rates. The elemental analyses of the polymers obtained are listed in Table 1, which indicates the polymers obtained were all of polyacrylonitrile as reported in the previous paper. [3]

The lesser content of nitrogen in the polymers may be perhaps due to the loss of

(12) S.K. Das, S.R. Chatterjee and S.R. Palit, Proc. Roy. Soc., A227 (1955), 252.

Table 1.   Elemental analyses of the polymers

Added Solvent	C%	H%	N%
Benzene	66.18	5.11	23.78
Chlorobenzene	67.19	5.25	25.40
p-Cymene	68.04	5.40	24.50
Benzonitrile	68.64	5.22	24.71
Ethyl benzoate	67.17	5.43	23.89
Calcd. for polyacrylonitrile	67.92	5.66	26.42

-CN group during the polymerization.[13]

3.   Order of solvent participation

The overall rate of polymerization with respect to the added solvent may be written as

$$Rp = k[Solvent]^n$$

where Rp is the overall rate of polymerization, k is the rate constant, [solvent] is the concentration of the solvent added and n is the order of the solvent participation.

The Rp's for the respective solvents added were calculated from the respective time-conversion lines as the usual procedures in a condition ($[M]_0 = 3.02$mole/1, $[AIBN]_0 = 1.22 \times 10^{-2}$ mole/1, $[SO_2]_0 = 6.74$ mole/1, diluted with CCl_4 to total volume of 15 ml., at 50°C). The values of k and n are obtained from the intercepts and the slopes of the respective log Rp vs. log [Solvent] plots, and listed in Table 2.

Generally speaking, the effects of these added solvents are of minor importance as compared to the case of cationic polymerization.[5] No significant influence was observed except in the case of p-xylene, to whom the present authors have no pertinent explanation at present.

Bamford and Jenkins[15] examined the effect of lithium chloride on the polymerization of acrylonitrile in dimethylformamide. According to their opinion, Rp was increased by the interaction of chloride anion with nitrile group of acrylonitrile. However, no decisive evidence of such an interaction was indicated. The study on the effects of salts on the acrylonitrile polymerization in liquid sulfur dioxide may be of any help to elucidate above solvent effect and is now

Table 2.   The rate constants, k and the order of solvent
participation, [14] n for   Rp=k [Solvent]

Solvent	$k \times 10^5$	n
Bezene	1.96	0.092
Toluene	1.88	−0.013
p-Xylene	1.99	0.346
Isopropylbenzene	1.01	0.018
Ethylbenzene	1.55	0.107
Chlorobenzene	3.48	−0.156

(13)   K. Nakatsuka, Kobunshi Kagaku, **15** (1958), 43.
(14)   H.E. Zaugg, J. Am. Chem. Soc., **83** (1961), 837.
(15)   C.H. Bamford and A.P. Jenkins, Proc. Roy. Soc., **A241** (1957) 364.

in progress in this laboratory.   The results may be published in the near future.

Acknowledgment