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**Donor-Acceptor Complexes in
Copolymerization. XXVII.
Copolymerization of Styrene and
Acrylonitrile in the Presence of
Ethylaluminum Sesquichloride**

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SUMMARY

The copolymerization of styrene (S) and acrylonitrile (AN) in the presence of ethylaluminum sesquichloride (EASC) results in alternating copolymers except when styrene is present in considerable excess in the initial monomer feed. The molecular weight of the copolymer is highest at an equimolar monomer feed. When the concentration of EASC and the S/AN mole ratio are kept constant and the total monomer concentration is increased, the polymerization rate increases and passes through a maximum at a 2:2:1 S/AN/EASC mole ratio but the molecular weight increases and attains a limiting value. The rate of polymerization is proportional to the concentration of EASC. When the concentration of either monomer and the EASC concentration are kept constant and the concentration of the other monomer is varied,

the polymerization rate passes through a maximum at an equimolar ratio, irrespective of which monomer is varied. The molecular weights of the copolymers are unchanged with conversion when the EASC concentration is low but, at a higher EASC concentration, the molecular weight decreases with conversion and attains a limiting value.

INTRODUCTION

The copolymerization of donor and acceptor monomers in the presence of metal halides yields equimolar alternating copolymers, irrespective of the initial monomer charge. The general characteristics of such copolymerizations have been reviewed [1]. The formation of the alternating copolymer is attributed to the homopolymerization of the $[D^+ \cdot A \cdot \cdot MX]$ complex. The polymerization of the complex is influenced by its concentration which is, in turn, dependent on the monomer concentration, the nature of the metal halide and its concentration, the nature and amount of solvent, and the polymerization temperature.

Some of the copolymerization systems which have been studied in detail include styrene-methyl methacrylate [2-4], butadiene-acrylonitrile [5], and butadiene-methyl methacrylate [6] in the presence of metal halides such as $SnCl_4$, $AlCl_3$, $AlEtCl_2$, or $AlEt_{1.5}Cl_{1.5}$, either alone or in conjunction with $VOCl_3$. The copolymerizations are characterized by an initial period during which the molecular weight of the copolymer increases with time and conversion. In the later period, the rate of the polymerization is slower, the molecular weight attains a constant value independent of conversion, and given a long reaction time the polymerization reaches full conversion in which the excess monomer (in the case of a nonequimolar monomer feed) does not participate [7]. The kinetic features of these polymerizations indicate that the course of the polymerization is influenced by several factors including dilution effects and dissociation of the polymerizable complexes.

The copolymerization of styrene (S) and acrylonitrile (AN) in the presence of metal halides has also been reported [8, 9]. The copolymerization of styrene-acrylonitrile in the presence of ethylaluminum sesquichloride (EASC) differs from the copolymerization of styrene-methyl methacrylate (MMA) in several aspects. Thus, whereas the copolymerization of styrene-acrylonitrile is quite

sensitive to temperature [10] and less sensitive to the metal halide content [11] and the presence of solvents such as chloroform [12], the styrene-methyl methacrylate copolymerization behaves in the opposite manner. The energy of activation in the initial stage of the polymerization of the S-AN...EASC complex is also lower than that of the S-MMA-EASC complex.

The present communication describes evidence for the participation of the $[S^+ \cdot AN \cdot \cdot EASC]$ complex and some of the kinetic features of the copolymerization of styrene and acrylonitrile... $Al(C_2H_5)_{1.5}Cl_{1.5}$.

EXPERIMENTAL

The monomers and solvents were purified in the usual manner. Ethylaluminum sesquichloride was received as a 25% solution in toluene from Texas Alkyls Co. and was used as such.

The experiments were carried out either in large test tubes or three-necked flasks. The monomers and solvent toluene were charged into the reaction vessel which was purged with nitrogen. The desired amount of EASC was introduced through a hypodermic syringe and the reaction vessel placed in a thermostated bath. The reaction medium became heterogeneous after several minutes since the alternating copolymer is insoluble in toluene. The reactions were terminated by adding the mixture to a large excess of methanol containing dilute hydrochloric acid. The polymers were purified by solution in acetone and precipitation in methanol and were dried in vacuo at 45°C.

The intrinsic viscosities of the polymers were measured at $30 \pm 0.05^\circ C$ in dimethylformamide using an Ubbelohde viscometer.

RESULTS AND DISCUSSION

The formation of an alternating copolymer has been attributed to the homopolymerization of a donor-acceptor complex [1, 13]. In general, the copolymerization yields equimolar copolymers, irrespective of the monomer charge in the feed. Figure 1 and Table 1 present data on the copolymerization of styrene and acrylonitrile in the presence of EASC at different comonomer feeds. There is a maximum in the rate of polymerization at an

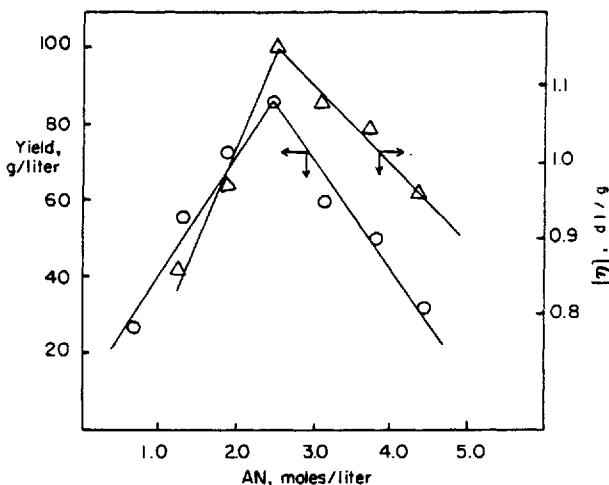


FIG. 1. Dependence of reaction rate (yield in grams/liter after 1 hr) (O) and intrinsic viscosity (DMF, 30°C) (Δ) on acrylonitrile concentration at constant total monomer concentration in toluene at 30°C. $[\text{AlEt}_{1.5}\text{Cl}_{1.5}] = 0.25$ mole/liter; $[\text{S}] + [\text{AN}] = 5.0$ mole/liter.

equimolar comonomer charge. This provides evidence for the participation of an $[\text{S-AN}\dots\text{EASC}]$ complex. Evidence for the formation of the $[\text{S-AN}\dots\text{ZnCl}_2]$ complex has been deduced from the UV spectra [14]. The molecular weight of the copolymer, as determined from the intrinsic viscosity, is also a maximum at a 1:1 S/AN mole ratio in the feed, similar to the results obtained in the alternating copolymerization of butadiene-acrylonitrile and butadiene-methyl methacrylate in the presence of $\text{AlEtCl}_2\text{-VOCl}_3$ [6].

The compositions of the copolymers obtained are presented in Table 1. It is apparent that the copolymers are equimolar in composition except for the copolymer obtained at the high S/AN mole ratio of 7 which analyzed for 40 mole-% acrylonitrile content. It might be argued that this could be due to a low complex concentration because of the presence of styrene in large excess. However, when acrylonitrile was present in large excess ($\text{AN/S} = 7$ in Table 1), the copolymer analyzed as an equimolar composition. Further, when the monomer present in large excess, i.e., styrene, was replaced by an equal or greater volume of toluene, the copolymer had an equimolar composition [12]. The nonequimolar

TABLE 1. Dependence of Reaction Rate on Acrylonitrile Concentration at Constant Total S + AN Concentration^a

[AN] (moles/liter)	S/AN mole ratio	Yield (g/liter)	Composition AN (mole-%)	$[\eta]$ (dl/g)
4.375	0.143	32.2	52	0.96
3.750	0.333	50.8	50	1.05
3.125	0.600	59.5	48	1.08
2.500	1.000	84.5	48	1.15
1.875	1.667	72.5	49	0.97
1.250	3.000	56.2	45	0.86
0.623	7.000	26.8	40	

^a $[S] + [AN] = 5$ moles/liter, $[AlEt_{1.5}Cl_{1.5}] = 0.25$ moles/liter; toluene; total volume, 40 ml; temp, 30°C; time, 1 hr.

composition could be attributed to the dissociation of the propagating chain end as observed in S-AN copolymerization at higher temperatures or high AN/EASC mole ratios [10, 11]. However, the reaction temperature is only 30°C and the EASC concentration is not low. Nevertheless, the higher-than-equimolar styrene content in the copolymer produced at high styrene monomer charge indicates either that dissociation of the propagating chain end may also result from dilution, as noted in the copolymerization of styrene and sulfur dioxide in the presence of a large amount of solvent [15], or heterogeneity, as noted in the heterogeneous copolymerization of styrene and maleic anhydride in benzene [16]. Alternatively, the nonequimolar composition may be attributed to the presence of the $[S^+ \cdot S-AN \dots EASC]$ complex, as proposed in the styrene-sulfur dioxide copolymerization [17]. A further possibility is the grafting of the chains arising from the polymerization of the $[S^+ \cdot AN \dots EASC]$ complex on polystyrene produced by cationic polymerization initiated by EASC-AN [18].

When the concentration of EASC is kept constant and the total

monomer concentration is increased, at an equimolar S/AN ratio, the reaction rate shows an initial increase, attains a maximum when the mole ratio of each of the individual monomers to the EASC reaches 2:1, i.e., S:AN:EASC = 2:2:1, and then decreases (Fig. 2). In the copolymerization of S-MMA in the presence of EASC, the rate increases and then levels off with increasing total monomer concentration [2]. The molecular weight of the S-AN copolymer initially increases with increasing total monomer concentration and then levels off with further increases in the monomer concentration.

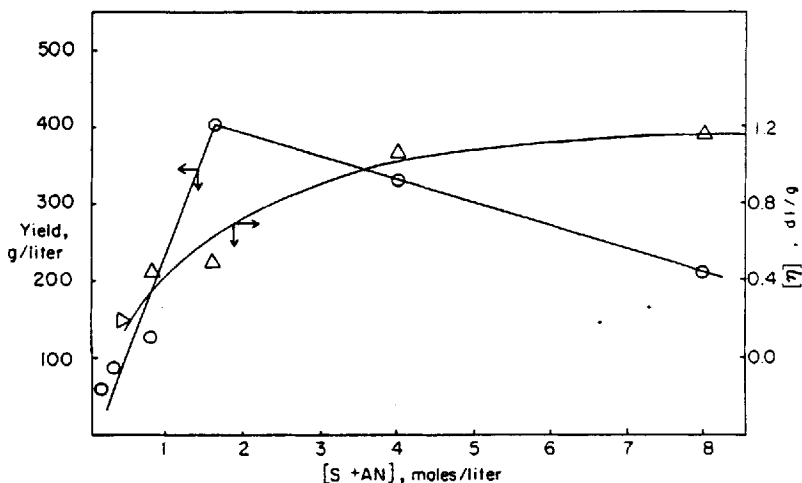


FIG. 2. Dependence of reaction rate (yield in grams/liter after 1 hr) (O) and intrinsic viscosity (DMF, 30°C) (Δ) on total monomer concentration at a constant S/AN ratio in toluene at 30°C. $[AlEt_{1.5}Cl_{1.5}] = 0.40$ mole/liter; S/AN = 1.

Table 2 presents the experimental data on the effect of EASC concentration on the rate of copolymerization. The rate of copolymerization increases with increasing concentration of EASC. Figure 3 shows the effect of $[AlEt_{1.5}Cl_{1.5}]$ on the rate of polymerization (data from Table 2). Since the slope of the line is unity,

$$R_p \propto [AlEt_{1.5}Cl_{1.5}] \quad (1)$$

TABLE 2. Effect of EASC Concentration on S-AN Copolymerization^a

[EASC] (moles/liter)	Time (hr)	Yield (g/liter)	Composition AN (mole-%)	$[\eta]$ (dl/g)
0.125	0.5	18.3	50	0.70
	1.0	35.0		0.81
	4.0	49.3		0.83
	7.0	71.3	54	0.77
	21.0	89.7		0.70
	72.0	301.7	54	
0.250	0.25	16.4	50	0.86
	0.5	21.2		0.92
	1.0	49.0	52	0.96
	2.0	60.6		0.96
	4.0	64.7		0.98
	7.0	147.7	50	1.04
	24.0	278.9		1.02
	48.0	294.5		1.09
	72.0	354.6		1.08
	96.0	453.8	53	1.09
0.375	0.25	48.7		1.20
	0.5	59.2	54	1.13
	1.0	71.4		1.30
	3.0	95.7	52	1.17
	7.0	111.1		1.25
	21.0	168.1	56	1.18

^a[S] = 1.5 moles/liter, [AN] = 3.5 moles/liter; toluene; temp, 30°C.

In the copolymerization of styrene with methyl methacrylate in the presence of EASC, the reaction order of $[\text{AlEt}_{1.5}\text{Cl}_{1.5}]$ is between 1 and 2 [3]. In the copolymerizations of butadiene with acrylonitrile [5] or methyl methacrylate [6] in the presence of AlEtCl_2 and VOCl_3 , although the rate of polymerization was found to be proportional to $[\text{AlEtCl}_2]^{1.5}$, the complexed monomer was found to be proportional to $[\text{AlEtCl}_2]$, indicating that the complexed monomer involves 1 mole of the aluminum component. Since EASC is used alone in the present investigation, without combination with any other component such as VOCl_3 , the rate of polymerization which

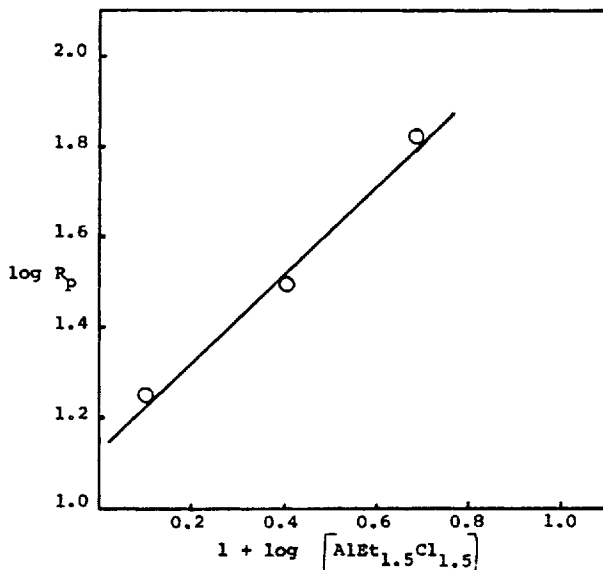


FIG. 3. Effect of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ concentration on the rate of polymerization (from the initial slope of the reactions carried out up to 4 hr—data from Table 2) of the $[\text{S-AN} \dots \text{AlEt}_{1.5}\text{Cl}_{1.5}]$ complex.

depends on the concentration of the complex is proportional to the concentration of EASC.

However, evidence of the complexity of the dependence of the reaction rate on $[\text{AlEt}_{1.5}\text{Cl}_{1.5}]$ is presented in Table 3 and Fig. 4, where the reactions are carried out at constant S/AN/Al mole ratio. Figure 4 shows the dependence of $\log R_p$ on $\log [\text{AlEt}_{1.5}\text{Cl}_{1.5}]$ where R_p represents the yield after a 2-hr reaction period and $[\text{AlEt}_{1.5}\text{Cl}_{1.5}]$ represents the concentration at constant S/AN/Al ratio. At lower concentrations the slope of the curve appears to be 1.5 whereas at higher concentrations the yield appears to be independent of the EASC concentration.

From the data in Table 2 it would appear that the rate of polymerization continuously decreases with time, irrespective of the EASC concentration, and that the molecular weights of the copolymers are fairly unchanged during the course of the reaction.

TABLE 3. Dependence of Reaction Rate on EASC Concentration at Constant S:AN:EASC Ratio^a

[S] (mmole)	[AN] (mmole)	[EASC] (mmole)	Yield (g/liter)	Composition AN (mole-%)
10	10	1.0	11.0	
15	15	1.5	26.3	
20	20	2.0	41.5	50
50	50	5.0	45.4	
100	100	10.0	44.9	50
150	150	15.0	44.5	
200	200	20.0	45.8	53

^aToluene; total volume, 45.0 ml.; temp, 30°C.; time, 2 hr.

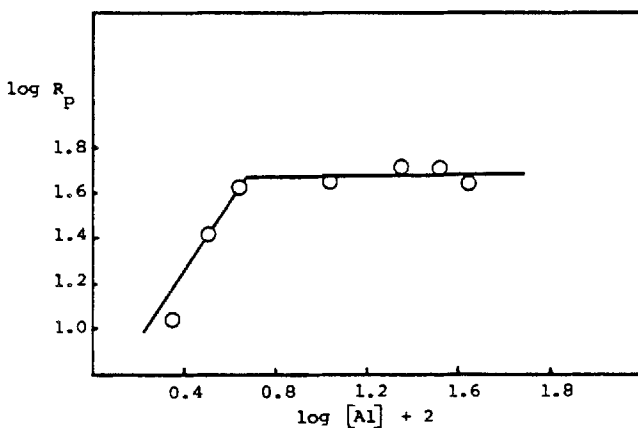


FIG. 4. Dependence of reaction rate (yield in grams/liter after 2 hr) on $AlEt_{1.5}Cl_{1.5}$ concentration at constant S/AN/Al ratio of 10/10/1 in toluene at 30°C.

Table 4 and Fig. 5 present data on the dependence of the reaction rate on the concentration of either of the monomers when the concentrations of one of the other monomers and EASC are kept constant.

TABLE 4. Dependence of Reaction Rate on Monomer Concentration at Constant Concentrations of One Monomer and EASC^a

[S] (moles/liter)	[AN] (moles/liter)	Yield (g/liter)	Composition AN (mole-%)
1.67	0.354	7.87	48
1.67	0.835	10.19	47
1.67	1.670	12.05	53
1.67	2.505	11.37	53
1.67	3.340	9.44	50
1.67	6.680	9.39	55
0.354	1.67	7.97	51
0.835	1.67	10.40	50
1.670	1.67	11.80	46
2.505	1.67	8.40	53
3.340	1.67	8.04	48
6.680	1.67	5.34	41

^a [AlEt_{1.5}Cl_{1.5}] = 0.167 moles/liter; toluene; total volume, 30 ml; temp, 30°C.; time, 90 min.

It is evident that the polymerization rate reaches a maximum value at an equimolar ratio of the monomers, irrespective of which monomer is varied. In the copolymerization of styrene and methyl methacrylate in the presence of EASC, a limiting value is observed at higher styrene concentrations and a decreased rate at higher concentrations of methyl methacrylate [2].

Furukawa et al. [6] have reported that the rate of copolymerization in the butadiene-acrylonitrile system is proportional to the concentration of butadiene and inversely proportional to the square of the acrylonitrile concentration, i.e.,

$$R_p \propto [BD][AN]^{-2} \quad (2)$$

However, these reactions were studied in the range where the acrylonitrile concentration was always much higher than the butadiene concentration (AN/BD = 2.30-5.73). It is, thus, apparent that

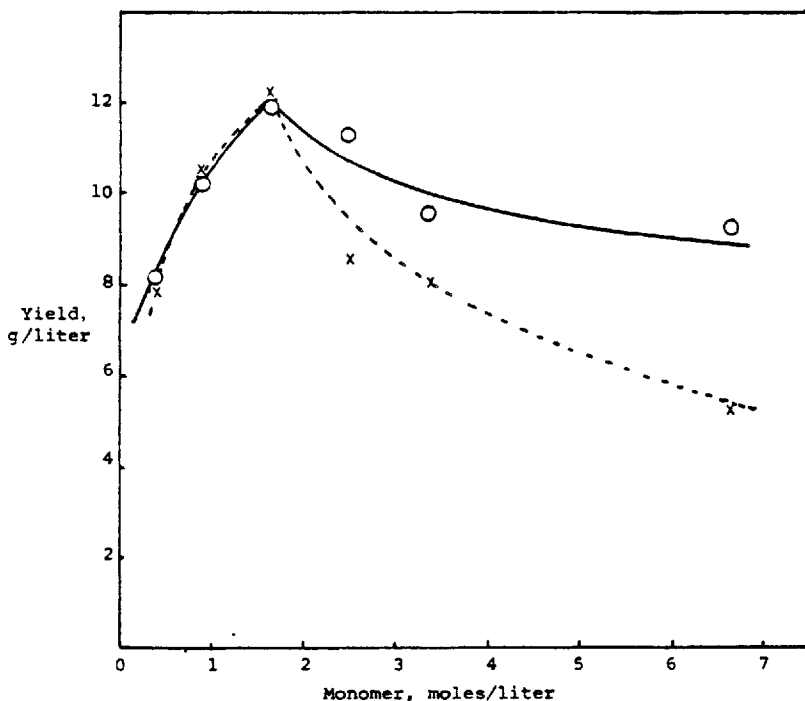


FIG. 5. Dependence of reaction rate (yield in grams/liter after 90 min) on the concentration of one monomer at constant concentrations of the other monomer and $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ in toluene at 30°C . $[\text{AlEt}_{1.5}\text{Cl}_{1.5}] = 0.167$ mole/liter; (O) $[\text{S}] = 1.67$ mole/liter, $[\text{AN}] = \text{varied}$; (X) $[\text{AN}] = 1.67$ mole/liter, $[\text{S}] = \text{varied}$.

the behavior of the styrene-acrylonitrile polymerization in this range of monomer concentrations is similar. However, the validity of Eq. (2) over the entire range of acrylonitrile concentrations, i.e., including AN/BD mole ratios of less than unity, is questionable. It is probable that at increased butadiene concentrations the rate would attain a maximum value at an equimolar ratio of the monomers.

The rate of copolymerization of butadiene and methyl methacrylate in the presence of $\text{AlEtCl}_2\text{-VOCl}_3$ is reported [6] to be constant, irrespective of the initial concentration of either of the monomers and the polymerization time, i.e.,

$$R_p \propto [\text{BD}]^0 [\text{MMA}]^0 \quad (3)$$

In contrast, the copolymerizations of styrene with acrylonitrile and with methyl methacrylate in the presence of EASC are characterized by a continuous decrease in the reaction rate with time.

It is also apparent (Fig. 5) that, beyond the equimolar composition, the rate of polymerization decreases with increased concentration of either of the monomers but the decrease is more pronounced when styrene is present in excess. This might be due to the fact that the molecular weight of styrene is twice that of acrylonitrile and the rates have been expressed as grams/liter. It is also possible that the [S-AN...EASC] complex is more stable in a medium richer in acrylonitrile than in styrene. This is reflected in the composition of the copolymer obtained in the reaction carried out at a higher S/AN mole ratio (Table 4). Since the AN/EASC mole ratio is 10, a ratio where dissociation of the propagating chain end is not observed [11], the composition may be attributed to the participation of the [S⁺-S-AN...EASC] complex. Similar results have also been obtained in the experiments summarized in Table 1.

The copolymerization of donor and acceptor monomers in the presence of organoaluminum halides is characterized by the absence of steady-state conditions in the initial stage. Thus the molecular weights of the copolymers increase with conversion in the initial stage. In the copolymerizations of butadiene with acrylonitrile or methyl methacrylate the molecular weights increase several times over a short range of conversions [6]. In the copolymerization of styrene with methyl methacrylate in the presence of EASC the molecular weight increases with conversion and in some cases passes through a maximum, particularly at low concentrations of the reaction components [3]. The non-terminating nature of the initial stage of the polymerization has been attributed to the existence of an ordered array of complexes whose size is determined by the initial complex concentration [7]. It has been suggested that, in the later, slow propagating stage, the uncomplexed monomer diffuses to the complexing agent affixed to the copolymer chain, resulting in the generation of new complexes in the immediate vicinity of the copolymer chain, and that the latter acts as a template for the new complexes and thereby replicates the molecular weight. Evidence for this postulate has been obtained by adding monomer mixture in several stages to the reaction medium [19].

Table 5 presents data on the molecular weights of the copolymers with increasing conversion in the copolymerization of styrene and

TABLE 5. Dependence of Molecular Weight on Conversion in S-AN Copolymerization in Presence of EASC at a Constant Total Concentration of Monomers^a

Time (hr)	70:30 S-AN		50:50 S-AN		30:70 S-AN	
	Conversion (%) ^b	$[\eta]$ (dl/g)	Conversion (%)	$[\eta]$ (dl/g)	Conversion (%) ^b	$[\eta]$ (dl/g)
0.25	7.02	0.90	4.6	1.14	5.65	0.86
0.50	8.59	0.85	5.4	1.15	7.30	0.92
1.0	9.32	0.86	6.5	1.27	8.45	0.96
4.0	11.8	0.88	9.4	1.28	11.2	0.98
6.0	13.2	0.80	9.2	1.08		
7.0					25.5	1.09
24.0	18.1	0.75	15.4	1.16	38.1	1.02
72.0	36.0	0.72	29.5	1.10	61.1	1.08

^a $[S] + [AN] = 5.0$ mole/liter; $[A]Et_{1.5}Cl_{1.5}] = 0.25$ moles/liter; toluene; temp, 30°C.

^bBased on 1:1 S-AN complex.

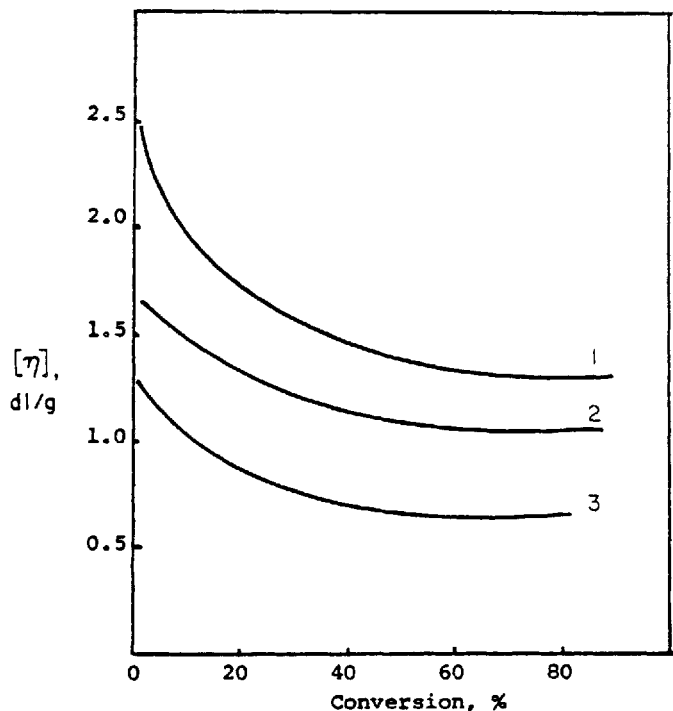


FIG. 6. Dependence of intrinsic viscosity (DMF, 30°C) of S-AN copolymers on the conversion in S-AN...AlEt_{1.5}Cl_{1.5} polymerization in toluene at different temperatures. [S] = [AN] = 4.4 mole/liter; [AlEt_{1.5}Cl_{1.5}] = 0.44 mole/liter. (1) 15°C; (2) 30°C; (3) 45°C.

acrylonitrile in which the initial mole fraction of the reactants is varied. It is apparent that the intrinsic viscosities either remain constant or increase slightly. This is in contrast to the styrene-methyl methacrylate system where a significant increase in molecular weight is observed in the initial stages of the polymerization. The results in the S-AN system may be explained by the rapid attainment of the equilibrium and the instantaneous formation of the matrix followed by a rapid polymerization within the matrix. This is consistent with the fact that acrylonitrile is a stronger acceptor than methyl methacrylate and that the equilibrium constant for complexation of AlEtCl₂ with acrylonitrile at 5°C is

reported to be larger than that for methyl methacrylate [20]. The constancy of the molecular weight can be attributed to the replication of the molecular weight in the second stage of the reaction.

However, when the reactions are carried out at a higher EASC concentration, although the S/AN/Al ratio is unchanged, the molecular weight decreases initially with conversion and then attains a constant value (Fig. 6). This may be attributed to the fact that the copolymerization of styrene and acrylonitrile in the presence of EASC is extremely exothermic and some of the heat generated locally may promote the breaking of the original matrix into one of smaller dimensions.

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