# Donor-Acceptor Complexes in Copolymerization. XXVI. Effect of Solvent, Temperature, and Complexing Agent on the Polymerization of Comonomer Charge Transfer Complexes

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# Donor-Acceptor Complexes in Copolymerization. XXVI. Effect of Solvent, Temperature, and Complexing Agent on the Polymerization of Comonomer Charge Transfer Complexes

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## SUMMARY

The copolymerization of styrene with methyl methacrylate (S/MMA = 4/1) or acrylonitrile (S/AN = 1/1) in the presence of ethylaluminum sesquichloride (EASC) yields 1/1 copolymer in toluene or chlorobenzene. In chloroform the S–MMA–EASC polymerization yields 60/40 copolymer while the S–AN–EASC polymerization yields 1/1 copolymer. In the presence of EASC, styrene–α-chloroacrylonitrile yields 1/1 copolymer (DMF or DMSO), S–AN yields 1/1 copolymer (DMSO) or radical copolymer (DMF), S–MMA yields radical copolymer (DMF or DMSO), α-methylstyrene–AN yields radical copolymer (DMSO) or traces of copolymer (DMF), and α-MS–methacrylonitrile yields traces of copolymer (DMSO) or no copolymer (DMF). When zinc chloride is used as complexing agent in DMF or DMSO, none of the monomer pairs undergoes polymerization. However, radical catalyzed polymerization of isoprene–AN–$ZnCl_2$ in DMF yields 1/1 alternating copolymer. The copolymerization of S/MMA in the presence of EASC yields 1/1 alternating copolymer up to 100°C, while the copolymerization of S/AN deviates from 1/1 alternating copolymer above 50°C. The copolymerization of S/MMA deviates from 1/1 copolymer at MMA/EASC mole ratios above 20 while the copolymerization of S/AN deviates from 1/1 copolymer at MMA/EASC ratios above 50.

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## INTRODUCTION

An alternating copolymer is formed spontaneously or in the presence of a radical catalyst by the homopolymerization of a complex generated by the interaction of a strong donor monomer and a strong acceptor monomer. When the acceptor monomer is not strong enough, activation by metal halide complexation converts a poor acceptor to a relatively stronger one and facilitates the formation of the homopolymerizable $[D^{+\cdot}\bar{\ } A \ldots MX]$ complex. The concentration of the complex is dependent on the monomer and metal halide concentrations, the A/MX ratio, the nature and the concentration of the solvent, and the reaction temperature [1].

$$A + MX \rightleftharpoons A \ldots MX \tag{1}$$

$$D + A \ldots MX \rightleftharpoons [D^{+\cdot}\bar{\ } A \ldots MX] \tag{2}$$

$$n[D^{+\cdot}\bar{\ } A \ldots MX] \longrightarrow \{DA\}_n + nMX \tag{3}$$
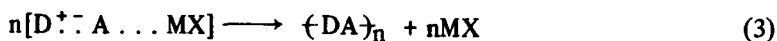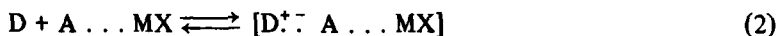
The nature and amount of solvent is known to influence the yield and composition of copolymers in copolymerization involving donor-acceptor complexes. Thus, the azoisobisbutyronitrile-(AIBN) initiated copolymerization of phenanthrene and maleic anhydride yields a 1:2 copolymer in benzene, a 1:1 copolymer in dioxane, and no copolymer in dimethylformamide [2]. The copolymer obtained in benzene has a higher molecular weight than the copolymer obtained in dioxane. The copolymerization of acrylic acid with maleic anhydride in the presence of benzoyl peroxide yields a 1:1 alternating copolymer in the melt and in benzene and a maleic anhydride-rich copolymer in naphthalene [3]. The maleic anhydride content of the copolymer increases with increased concentration of naphthalene.

In the terpolymerizations of acrylonitrile with 2-chloroethyl vinyl ether—maleic anhydride or p-dioxene—maleic anhydride [4], the amount of acrylonitrile incorporated into the terpolymer increases with increasing $\pi$-electron density of the solvent, e.g., xylene $\geqslant$ toluene $\geqslant$ benzene $>$ chlorobenzene $\geqslant$ chloroform, although the maleic anhydride content is equimolar with the vinyl ether content.

The nature of the solvent has an apparent effect in the polymerization of donor monomer-acceptor monomer-metal halide complexes, carried out in the absence or in the presence of radical catalysts. In the copolymerization of styrene and methyl methacrylate in the presence of ethyl aluminum sesquichloride (EASC), the reaction proceeds to complete conversion in

toluene, whereas there is an apparent limiting conversion in a toluene—hexane mixture due to the precipitation of the polymer in the reaction medium [5, 6]. A similar effect is noted in the copolymerization of styrene and acrylonitrile in the presence of EASC in toluene [7].

The metal halide concentration influences the nature of the product in D-A . . . MX polymerizations. In the copolymerization of styrene and acrylonitrile in the presence of zinc chloride, the alternating copolymer is accompanied by an acrylonitrile-rich copolymer if the $ZnCl_2/AN$ mole ratio is high or the reaction is carried out to a high conversion [8], whereas at low $ZnCl_2$ concentration the alternating copolymer is the only product [9]. If the reaction is carried out in benzene, the acrylonitrile-rich copolymer accompanies the alternating S—AN copolymer even when the $ZnCl_2$ concentration is low [10].

The concentration of the metal halide influences the equilibrium in the complex formation. Thus at low metal halide concentrations, the equilibria in Eqs. (1) and (2) are shifted to the left, resulting in increased amounts of uncomplexed monomers which, under suitable activation, e.g., thermal or radical initiation, result in nonequimolar random copolymers. This has been observed in the copolymerization of styrene and acrylonitrile in the presence of EASC where a free radical propagated S—AN copolymer was obtained at an AN/EASC mole ratio of 100 and an alternating copolymer at an AN/EASC mole ratio of 5-50 [11].

The effect of temperature in the polymerization of the donor-acceptor complexes in the presence of metal halides is quite pronounced. At a lower temperature the equilibrium in Eq. (2) shifts to the right. Increasing the temperature shifts the equilibria to the left in Eqs. (1) and (2), resulting in increased concentrations of uncomplexed monomers. Such reversal of the equilibrium and the formation of nonequimolar random copolymers at a ceiling temperature of about $60°C$ has been observed in the copolymerization of styrene and acrylonitrile in the presence of EASC [12].

The present communication describes the effect of the nature and concentration of various solvents, the temperature, and the concentration of complexing agent on the copolymerization of several donor-acceptor comonomer pairs in the presence of EASC and zinc chloride.

## RESULTS AND DISCUSSION

### Effect of Solvents

As reported earlier, the spontaneous copolymerization of styrene with

**Table 1.** Copolymerization of S–MMA and S–AN in Presence of
$AlEt_{1.5}Cl_{1.5}$ in Various Solvents at 40°C

| Solvent (ml) | S/MMA[a] | | S/AN[b] | |
|---|---|---|---|---|
| | Conversion (%)[c] | S/MMA mole ratio | Conversion (%) | S/AN mole ratio |
| Toluene | | | | |
| 20 | 33.7 | 52/48 | 18.7 | 52/48 |
| 50 | 29.4 | 52/48 | 17.3 | 53/47 |
| 100 | 30.1 | 55/45 | 7.1 | 51/49 |
| 200 | 29.8 | 52/48 | 5.4 | 50/50 |
| 400 | 16.9 | 54/46 | 3.2 | 50/50 |
| Chlorobenzene | | | | |
| 20 | 43.1 | 54/46 | 18.8 | 54/46 |
| 50 | 32.6 | 55/45 | 16.7 | 53/47 |
| 100 | 31.9 | 54/46 | 14.6 | 53/47 |
| 200 | 27.7 | 54/46 | 14.9 | 52/48 |
| 400 | 21.8 | 55/45 | 7.7 | 53/47 |
| Chloroform | | | | |
| 20 | 51.4 | 56/44 | 9.7 | 53/47 |
| 50 | 33.8 | 58/42 | 4.7 | 53/47 |
| 100 | 22.3 | 59/41 | 5.8 | 53/47 |
| 200 | 11.0 | 95/5 [d] | 0.6 | 56/44 |
| 400 | 0 | | 0 | |

[a] [S] = 0.16 mole; [MMA] = 0.04 mole; [EASC] = 0.02 mole; 1 hr.
[b] [S] = 0.1 mole; [AN] = 0.1 mole; [EASC] = 0.02 mole; 1 hr.
[c] Calculated on the basis of 1:1 S-MMA complex.
[d] Extraction with cyclohexane yields soluble polystyrene fraction (63%)
and insoluble 58:42 S/MMA copolymer fraction (37%).

methyl methacrylate or acrylonitrile in the presence of $AlEt_{1.5}Cl_{1.5}$ results
in an equimolar, alternating copolymer. Table 1 shows the effect of the
nature and the amount of solvent on the copolymerization of S–MMA
(S/MMA/Al = 8/2/1) and S–AN (S/AN/Al = 5/5/1). Free radical copolym-
erization of an 80/20 S/MMA charge should yield a 70/30 copolymer
while a 50/50 S/AN charge should yield a 60/40 copolymer.

When the reaction is carried out in toluene or chlorobenzene, the

copolymer composition is essentially equimolar in both the S—MMA. . . Al and S—AN . . . Al polymerizations when the solvent concentration is varied over a twentyfold range. The low conversion at high solvent concentrations, i.e., at low monomer concentrations, is due to the low complex concentration, although the copolymer composition is not affected.

When the S—MMA . . . Al polymerization is carried out in chloroform, the conversion is lower at a given high solvent concentration than when the polymerization is carried out in toluene or chlorobenzene. The decrease in conversion is accompanied by a change in copolymer composition. When the reaction mixture contains 200 ml chloroform the product analyzes as a 95:5 S/MMA composition. However, extraction with cyclohexane fractionates the product into polystyrene containing a trace of comonomer (63%) and a 58:42 S/MA copolymer (37%). The latter composition is also obtained when 50 and 100 ml chloroform are used.

A free radical copolymerization, e.g., initiated by the ion-radical from a dissociated complex

$$[D^{+\overline{\cdot}} A \ldots MX] \rightleftharpoons D^{+\cdot} + {}^{\overline{\cdot}}A \ldots MX \tag{4}$$
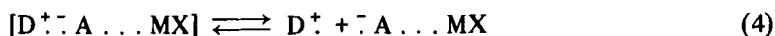
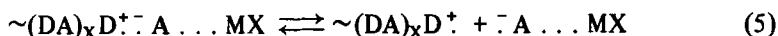should have yielded a 70:30 S/MMA composition. It has been proposed [11-14] that the formation of nonequimolar copolymer is due to the dissociation of the propagating chain end as a result of dilution

$$\sim(DA)_x D^{+\overline{\cdot}} A \ldots MX \rightleftharpoons \sim(DA)_x D^{+\cdot} + {}^{\overline{\cdot}}A \ldots MX \tag{5}$$

The formation of a 58:42 S/MMA copolymer over a wide range of chloroform contents indicates that an interaction with the solvent is probably more important than the dilution effect.

Although equimolar copolymers are generally formed in the copolymerization of strong donor monomers and strong acceptor monomers, a 2:1 styrene—sulfur dioxide copolymer is formed in an excess of the electron-accepting sulfur dioxide [15] while a 1:2 phenanthrene—maleic anhydride copolymer is formed in the electron-donating benzene [2]. It has been proposed [16] that the 1:1 styrene—sulfur dioxide complex is a sufficiently strong electron-accepting species in sulfur dioxide to complex with an additional styrene molecule

$$S + [\cdot S^{+\overline{\cdot}}SO_2 \cdot](SO_2) \rightleftharpoons [\cdot S^{+\overline{\cdot}}S\text{-}SO_2 \cdot](SO_2) \tag{6}$$
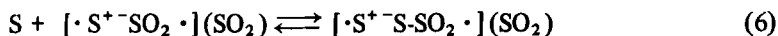
Although phenanthrene is a strong electron acceptor, it is not sufficiently

strong to displace dimethylformamide from a DMF—maleic anhydride complex. However, it is strong enough to form a 1:1 phenanthrene—maleic anhydride complex in dioxane despite the presence of the dioxane—maleic anhydride complex. The 1:1 phenanthrene—maleic anhydride complex is a sufficiently strong electron acceptor to complex with an additional maleic anhydride molecule in benzene but not in dioxane

$$Ph + [DMF-MAnh] \rightleftharpoons [\cdot Ph^{+ -}MAnh\cdot] + [DMF\cdot MAnh] + DMF \quad (7)$$

$$[\cdot Ph^{+-}MAnh\cdot] + [\phi H\cdot MAnh] \rightleftharpoons [\cdot Ph^{+-}MAnh-MAnh\cdot] + \phi H \quad (8)$$
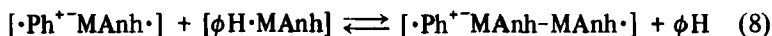
The spontaneous bulk copolymerization of the 1:1 and 2:1 MMA–ZnCl$_2$ complexes with styrene at 30°C yields a S/MMA copolymer with a 1:1 composition at high S/MMA monomer ratios and a composition approaching 1:2 at low S/MMA ratios [17]. The electroinitiated bulk copolymerization of a 3/5/1 S/MMA/ZnCl$_2$ charge at 0°C similarly yields a copolymer with a composition approaching 1:2 S/MMA [18].

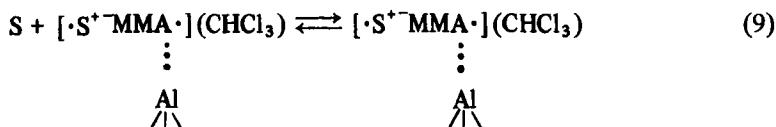The essentially 60:40 S/MMA composition formed from the S—MMA. . . Al polymerization in chloroform may be a mixture of 1:1 and 1:2 copolymers or may be the result of the copolymerization of 1:1 and 2:1 S—MMA . . . Al⋚ complexes which are present in chloroform at the monomer charge used

$$S + [\cdot S^{+-}MMA\cdot](CHCl_3) \rightleftharpoons [\cdot S^{+-}MMA\cdot](CHCl_3) \quad (9)$$
$$\vdots \qquad\qquad\qquad\qquad\quad \vdots$$
$$\underset{/|\backslash}{Al} \qquad\qquad\qquad\qquad \underset{/|\backslash}{Al}$$

In contrast to the S—MMA . . . Al⋚ polymerization, the S—AN . . . Al⋚ polymerization in chloroform yields essentially equimolar copolymer independent of the chloroform concentration, although the conversions are low. This suggests that the 2:1 S—AN . . . Al⋚ complex is not formed and/or that the propagating chain end in the [S$^{+-}$ AN . . . Al⋚] homopolymerization is not readily dissociated in chloroform due to solvation of the chain end.

The copolymerization of styrene with α-chloroacrylonitrile and methacrylonitrile in the presence of EASC or zinc chloride, in the absence as well as in the presence of a peroxide catalyst, yields a mixture of equimolar, alternating copolymer and styrene-rich copolymer [14]. The copolymerization of α-methylstyrene with acrylonitrile and methacrylonitrile under the same conditions yields a mixture of equimolar, alternating copolymer and poly-

(α-methylstyrene) [13, 14]. The formation of the nonequimolar copolymer and poly(α-methylstyrene) is attributed to cationic polymerization initiated by the cation-radical resulting from the dissociation of the propagating chain end at high dilutions, e.g., low metal halide and low complex concentrations, as shown in Eq. (5). The formation of nonequimolar copolymer in the copolymerization of styrene with α-chloroacrylonitrile has been attributed to radical coupling of the terminal cation-radicals to form a polymeric dication. In the case of α-methylstyrene copolymerization, a one-electron transfer from monomeric α-methylstyrene to the terminal cation-radical results in the formation of a monomer cation radical which subsequently couples to give a dication.

The cationic nature of the propagation has been confirmed by carrying out the reactions in electron donating solvents such as dimethylformamide, dimethylsulfoxide, and hexamethylphosphoramide. The results in the copolymerization of styrene and α-chloroacrylonitrile in these basic solvents are summarized in Table 2. When the reaction is carried out in bulk or in toluene using EASC or zinc chloride as the metal halide, a styrene-rich copolymer accompanies the equimolar copolymer. When the reaction is carried out in DMF using EASC as the metal halide, the equimolar copolymer is the only product. The copolymer yield, however, is much lower than that obtained in the reaction carried out in bulk. The copolymer yield is not affected by the order of addition of the reactants, i.e., when EASC is added to the monomer mixture in the solvent or the monomer mixture is added to the EASC in the solvent, or by the DMF concentration at DMF/EASC mole ratios of 1 and 7. The decreased yield is expected not only due to the dilution effect but also due to a decreased concentration of complexes because of the complexation of the solvent with the EASC.

Similar results are obtained when dimethylsulfoxide is used as the solvent while hexamethylphosphoramide (HMP) prevents copolymerization. This is attributed to the total complexation of the EASC by the HMP. The absence of copolymerization has been noted in the reaction of butadiene and acrylonitrile in the presence of $AlEtCl_2$ when the reaction is carried out in basic solvents such as DMF, tetrahydrofuran, and pyridine [19].

No copolymer is obtained when zinc chloride is used as the complexing agent with styrene–α-chloroacrylonitrile in electron-donating solvents. The failure may be attributed to the weaker electron-accepting strength of zinc chloride as compared to that of EASC and the total complexation of the metal halide by the solvent.

The equimolar copolymer obtained in the reactions carried out in DMF or DMSO generally has a higher molecular weight than the copolymer

Table 2. Copolymerization of S–α-ClAN ... MX in Electron-Donating Solvents

| S/ClAN (moles) | MX (mole) | Solvent, ml | Method[a] | Temp (°C)/ time (hr) | Yield (%)[b] | Cyclohexane extraction | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Soluble | | Insoluble | | |
| | | | | | | Wt-% | ClAN (Mole-%) | Wt-% | ClAN (Mole-%) | $[\eta]^c$ (dl/g) |
| | | | | EASC | | | | | | |
| 0.1/0.1 | 0.02 | None | A | 25/1 | 43.5 | 41 | 4 | 59 | 44 | 0.28 |
| 0.1/0.1 | 0.02 | DMF, 1.55 | A | 25/1 | 2.7 | 0 | | 100 | 49 | 0.45 |
| 0.1/0.1 | 0.02 | DMF, 10 | A | 25/1 | 2.4 | 0 | | 100 | 52 | 0.39 |
| 0.1/0.1 | 0.02 | DMF, 1.55 | B | 25/1 | 2.4 | 0 | | 100 | 48 | 0.37 |
| 0.1/0.1 | 0.02 | DMF, 10 | B | 25/1 | 2.2 | 0 | | 100 | 49 | 0.22 |
| 0.1/0.1 | 0.02 | DMSO, 10 | A | 30/2 | 7.3 | 0 | | 100 | 52 | 0.35 |
| 0.1/0.1 | 0.02 | DMSO, 10 | B | 30/2 | 3.5 | 0 | | 100 | 50 | 0.83 |
| 0.16/0.04 | 0.02 | DMSO, 10 | A | 30/3 | 5.8 | 0 | | 100 | 48 | 0.30 |
| 0.1/0.1 | 0.02 | HMP, 10 | A | 30/2 | 0 | 0 | | | | |
| | | | | $ZnCl_2$ | | | | | | |
| 0.1/0.1 | 0.02 | None | A | 40/1 | 53.6 | 93.5 | 6 | 6.5 | 48 | 0.43 |
| 0.1/0.1 | 0.02 | DMF, 10 | A | 40/3 | 0 | | | | | |
| 0.16/0.04 | 0.02 | DMSO, 10 | A | 60/3 | 0 | | | | | |

[a] A = MX added to mixture of S, α-ClAN, and solvent; B = mixture of S and α-ClAN added after 15 min to mixture of MX and solvent.

[b] Based on 1:1 S–α-ClAN complex.

[c] MEK, 30°C.

obtained in the reaction carried out in bulk. This suggests that in these solvents the propagating chain end does not dissociate as readily as in their absence, i.e., DMF apparently solvates the terminal complex and prevents dissociation. This also accounts for the absence of the cationic polymer.

The formation of nonequimolar copolymer and/or cationic polymer has also been noted in radical catalyzed styrene—$SO_2$ and p-substituted styrene—$SO_2$ copolymerizations. Thus styrene-rich copolymers are obtained in the copolymerization of styrene and sulfur dioxide in solvents such as dichlorobenzene, cyclohexane, sulfolane, nitrobenzene, and pyridine [20], and in bulk copolymerization with a high styrene content in the monomer feed [21]. In the radical-catalyzed copolymerization of p-methylstyrene [22] and p-isopropylstyrene [23] with sulfur dioxide, a cationic homopolymer accompanies the 2:1 copolymer. In the presence of DMF, the radical-catalyzed reactions yield the copolymer and the cationic polymerization is completely inhibited. Attempts to prepare the $\alpha$-methylstyrene—$SO_2$ copolymer in the presence of a radical catalyst yields poly-$\alpha$-methylstyrene but no copolymer. In the presence of DMF no product is obtained [22].

The formation of styrene-rich copolymers may be attributed to the dissociation of the propagating chain end under conditions of high dilution and the subsequent addition of styrene to the terminal cation-radical, probably through radical propagation. The cationic polymer generated in the copolymerizations of sulfur dioxide with p-methylstyrene, p-isopropylstyrene, and $\alpha$-methylstyrene is attributable to the dissociation of the propagating chain end followed by a one electron transfer from the monomer to generate a monomer cation-radical which couples and propagates cationically.

In view of the observation that DMF inhibits the formation of styrene-rich copolymer in the S—$\alpha$-ClAN . . . Al reactions but yields higher molecular weight equimolar copolymer, the AIBN-catalyzed copolymerization of styrene and sulfur dioxide was carried out in the presence of DMF (Table 3). It is evident from the table that although 2:1 S—$SO_2$ copolymers are obtained in comparable yields in the absence as well as in the presence of DMF, the copolymer obtained in the latter case has a much higher molecular weight than the copolymer obtained in bulk. This confirms the ability of DMF to solvate the terminal complex on the propagating chain and delay dissociation and/or termination.

When the copolymerization of other monomer pairs such as styrene—acrylonitrile, styrene—methyl methacrylate, $\alpha$-methylstyrene—acrylonitrile, and $\alpha$-methylstyrene—methacrylonitrile, in the presence of EASC or zinc

**Table 3.** Copolymerization of Styrene and $SO_2$[a]

| Solvent, ml | Yield (%) | Cyclohexane | | | |
| | | Soluble | Insoluble | | |
| | | Wt-% | Wt-% | $SO_2$ (Mole-%) | $[\eta]$[b] (dl/g) |
|---|---|---|---|---|---|
| Bulk | 13.9 | 0 | 100 | 32 | 0.37 |
| DMF, 10 | 14.3 | 0 | 100 | 32 | 0.73 |

[a][S] = 0.2 mole; [$SO_2$] = 0.1 mole; [AIBN] = 2.5 mmole; 25°C; 18 hr.
[b]DMF, 30°C.

chloride, is carried out in electron-donating solvents, the yields are either greatly reduced or no copolymer is obtained (Table 4).

In the styrene—acrylonitrile . . . EASC polymerization in DMF, the yield is decreased and the copolymer composition approaches that expected from free radical propagation. When DMSO is used as the solvent, the copolymer composition is somewhat closer to equimolar. This may be due to the decreased complexation of the metal halide with DMSO as compared to DMF. It is known that although DMSO has a high electron-donating power, it also has electron-accepting power [24]. When zinc chloride is used as the metal halide in DMF or DMSO, no polymer is obtained. The free radical composition from S—AN . . . EASC polymerization in DMF is attributed to the decreased availability of the metal halide for complexation with acrylonitrile because of its depletion by complexation with the electron-donating solvent, a result similar to that observed in the S—AN . . . EASC copolymerization in toluene at low EASC concentrations [11]. The increased activity of EASC as compared to zinc chloride is due to its stronger electron-accepting ability.

In the copolymerization of α-methylstyrene with acrylonitrile in the presence of EASC, only traces of polymer are formed in DMF, whereas when DMSO is used as the solvent and the reaction is catalyzed by benzoyl peroxide, the product which is obtained in extremely low yield contains 41 mole-% acrylonitrile, a composition expected from the free radical propagation of the monomer feed. The use of zinc chloride as the metal halide fails to yield polymer in either DMF or DMSO.

The polymerization of styrene—methyl methacrylate . . . EASC in either DMF or DMSO yields radical copolymer while the attempted polymerization

of α-methylstyrene—methacrylonitrile . . . EASC in either DMF or DMSO fails to yield copolymer.

Thus using EASC as the complexing agent, S—α-ClAN yields an equimolar copolymer (DMF or DMSO), S—AN yields an equimolar copolymer (DMSO) or a radical copolymer (DMF), S—MMA yields a radical copolymer (DMF or DMSO), α-MS—AN yields a radical copolymer (DMSO) or no copolymer (DMF), while α-MS-MAN yields no copolymer (DMF). When zinc chloride is used as complexing agent in DMF or DMSO, none of the monomer pairs undergoes polymerization. The results obtained with EASC are consistent with the relative electron-accepting strengths of the acceptor monomers while the results obtained with zinc chloride, the weaker Lewis acid, indicate the inability of either the donor or acceptor monomers to compete as electron donors with DMF to permit the generation of sufficient $[D^{+\overline{\cdot}} A \ldots ZnCl_2]$ complexes to undergo spontaneous polymerization.

The role of the donor monomer is clearly demonstrated by the copolymerization of isoprene and acrylonitrile in the presence of zinc chloride in DMF (Table 5). When DMF is present the AN—$ZnCl_2$ system probably contains DMF—AN . . . $ZnCl_2$ complexes rather than AN—AN . . . $ZnCl_2$ complexes. Although styrene and α-methylstyrene can displace AN in AN—AN . . . $ZnCl_2$ to form the S—AN . . . $ZnCl_2$ and MS—AN . . . $ZnCl_2$ complexes, respectively, they apparently cannot displace DMF in the DMF—AN . . . $ZnCl_2$ complex. However, the stronger donor monomer isoprene generates the $[I^{+\overline{\cdot}} AN \ldots ZnCl_2]$ complex even in DMF and equimolar, alternating copolymer is formed in the presence of a radical catalyst.

The polymerization proceeds in a homogeneous medium. The lower conversions in the presence of ammonium persulfate may be due to its low solubility in DMF and the higher DMF concentration. The failure to obtain polymer in 15 min at 40°C with t-butyl peroxypivalate in the absence of zinc chloride is probably due to the slow propagation rate of conventional radical species. The formation of radical copolymer in an I—AN . . . $ZnCl_2$ polymerization when an organic peroxide is used in an aqueous medium [25] and equimolar copolymer when it is used in DMF is due to the heterogeneity of the former system, i.e., the complexes which apparently are aligned in an ordered array or matrix are insoluble in the aqueous phase and in the monomer phase. The organic peroxide enters the monomer phase and initiates radical copolymerization. A water-soluble catalyst such as ammonium persulfate enters the aqueous phase which penetrates as well as surrounds the matrix of complexes and initiates homopolymerization of the complexes to yield alternating copolymer.

**Table 4.** Copolymerization of Donor (D) and Acceptor (A) Monomers in Presence of Metal Halides (MX) in Electron-Donating Solvents[a]

| D/A (mole) | MX, mole | Solvent, ml | Temp (°C)/ time (hr) | Yield (%)[b] | Cyclohexane | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Soluble | | Insoluble | |
| | | | | | Wt-% | A (Mole-%) | Wt-% | A (Mole-%) |
| | | *Styrene–Acrylonitrile* | | | | | | |
| 0.1/0.1 | EASC, 0.02 | Toluene 8.8 | 30/1 | 15.3 | 0 | | 100 | 47 |
| | | DMF, 10 | 30/3 | 8.7 | 0 | | 100 | 43 |
| | | DMSO, 10 | 30/3 | 5.1 | 0 | | 100 | 46 |
| | ZnCl₂, 0.02 | DMF, 10 | 40/3 | 0 | | | | |
| | | DMSO, 10 | 60/3 | Trace | | | | |
| | | *Styrene–Methyl Methacrylate* | | | | | | |
| 0.4/0.1 | EASC, 0.02 | Toluene 8.8 | 40/1 | 38.6 | 0 | | 100 | 48 |
| | | DMF, 10 | 30/3 | 2.1 | 100 | 29 | 0 | |
| | | DMSO, 10 | 30/3 | 3.3 | 100 | 26 | 0 | |
| | ZnCl₂, 0.02 | DMF, 10 | 40/3 | 0 | | | | |
| | | | 60/3 | 0 | | | | |

**α-Methylstyrene—Acrylonitrile**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 0.16/0.04 | EASC, 0.02 | Toluene 8.8 | 20/1 | 18.8 | 45 | 0 | 55 | 45 |
| | | DMF, 10 | 20/1 | Trace | | | | |
| | | DMF, 10[c] | 20/1 | Trace | | | | |
| | | DMSO, 10 | 30/5 | 1.7 | 0 | | 100 | 42 |
| | | DMSO, 10[c] | 30/5 | 1.2 | 0 | | 100 | 41 |
| | | HMP, 10[c] | 30/5 | 0 | | | | |
| | $ZnCl_2$, 0.02 | None | 40/1 | 13.5 | 2 | | 98 | 46 |
| | | DMF, 10 | 40/3 | 0 | | | | |
| | | DMSO, 10 | 60/3 | 0 | | | | |

**α-Methylstyrene—Methacrylonitrile**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 0.125/0.125 | EASC, 0.0125 | None | 0/3 | 0.8 | 45 | 0 | 55 | 50 |
| | | DMF, 10 | 0/3 | 0 | | | | |
| | | DMSO, 10 | 0/3 | Trace | | | | |

[a]MX added to mixture of D, A, and solvent.
[b]Based on 1:1 D-A complex.
[c]0.5 mmole benzoyl peroxide added.

**Table 5.** Copolymerization of Isoprene–Acrylonitrile . . . $ZnCl_2$ in Dimethylformamide at 40°C[a]

|  |  |  |  |  | Copolymer | |
| --- | --- | --- | --- | --- | --- | --- |
| I/AN (mole) | $ZnCl_2$ (mole) | DMF (ml) | Catalyst, g. | Time (hr) | Yield (%)[b] | AN (mole-%) |
| 0.35/0.15 | 0 | 11.7 | TBPP, 3.6 | 0.25 | 0 | |
| 0.35/0.15 | 0.15 | 11.7 | TBPP, 3.6 | 0.25 | 12.8 | 51 |
| 0.35/0.15 | 0.15 | 34.8 | APS, 3.4 | 0.5 | 1.1 | 47 |
| 0.15/0.35 | 0.15 | 34.8 | APS, 3.4 | 2.0 | 1.4 | 55 |

[a]Mixture of I and AN added to mixture of dry $ZnCl_2$ and DMF.
[b]Based on 1:1 I–AN complex.

**Table 6.** Copolymerization of S–MMA and S–AN in presence of $AlEt_{1.5}Cl_{1.5}$ at Different Temperatures

|  | S/MMA[a] | | | S/AN[b] | | |
| --- | --- | --- | --- | --- | --- | --- |
| Temp (°C) | Time (min) | Conversion, (%)[c] | MMA (mole-%) | Time (min) | Conversion (%) | AN (mole-%) |
| 40 | 60 | 38.6 | 48 | 15 | 7.0 | 52 |
| 50 |  |  |  | 15 | 8.3 | 53 |
| 60 |  |  |  | 60 | 19.8 | 43 |
| 70 | 60 | 26.1 | 46 | 60 | 18.6 | 41 |
| 80 | 45 | 25.9 | 46 |  |  |  |
| 90 | 30 | 24.6 | 46 |  |  |  |
| 100 | 15 | 21.1 | 44 |  |  |  |

[a] [S] = 0.16 mole; [MMA] = 0.04 mole; [EASC] = 0.008 mole. Free radical copolymer 69:31 S/MMA.

[b] [S] = [AN] = 0.1 mole; [EASC] = 0.02 mole. Free radical copolymer 60:40 S/AN.

[c]Based on 1:1 S–MMA complex.

In the homogeneous DMF system both organic and water-soluble catalysts initiate complex polymerization.

### Effect of Temperature

The reaction temperature is known to play a significant role in the polymerization of donor-acceptor complexes. An effective temperature range for the polymerization of several comonomer complexes in the presence of metal halides has been reported. Thus in the copolymerization of styrene and acrylonitrile in the presence of EASC, a shift from the equimolar composition is observed above $50°C$, and at $70°C$ the copolymer has the composition expected from a free radical polymerization. Similarly, a shift in composition is observed in $\alpha$-methylstyrene−acrylonitrile . . . EASC polymerization at $70°C$ [12]. Room temperature was found to be the optimum temperature in the copolymerization of cyclopentene with acrylonitrile or methyl acrylate in the presence of EASC [26].

The results in the copolymerization of styrene and methyl methacrylate in the presence of EASC at various temperatures and a comparison of the results from styrene−acrylonitrile polymerization are presented in Table 6. It is evident that even at $90°C$ the S–MMA copolymer has a composition close to equimolar and a shift is noticed at $100°C$. In the latter case the composition is still closer to an equimolar composition than that expected from free radical propagation.

It is therefore apparent that the $[S^{+\cdot} MMA . . . Al^{\leqslant}]$ complex is much more stable to temperature as compared to the $[S^{+\cdot} AN . . . Al^{\leqslant}]$ complex. The sensitivity in the acrylonitrile system may be due to the high dielectric constant of acrylonitrile (38.0 at 33.5 MHz). It is known that the ionizing power of the medium facilitates the formation of ionic species from a neutral donor-acceptor complex [27]. The dissociation of the complex because of the increased temperature results in free uncomplexed monomers which are subject to random copolymerization yielding nonequimolar copolymers.

The composition of the nonequimolar copolymer suggests a free radical propagation of the uncomplexed monomers. Further evidence for such radical propagation is presented in Table 7 which indicates the results when styrene and acrylonitrile in 30:70 mole ratio are copolymerized in the presence of EASC at different temperatures. From the monomer reactivity ratios ($r_S$ = 0.4, $r_{AN}$ = 0.04), it is expected that a radical propagation from this monomer feed would result in the initial formation of an equimolar but nonalternating S−AN copolymer. Thus, the copolymers obtained at $15\text{-}80°C$

**Table 7.** Effect of Temperature in Copolymerization of 30:70 S—AN in Presence of $AlEt_{1.5}Cl_{1.5}$ [a]

| Temp ($^\circ$C) | Conversion, (%) [b] | Copolymer AN (mole-%) |
|---|---|---|
| 15 | 2.1 | 49 |
| 30 | 4.1 | 52 |
| 45 | 5.3 | 50 |
| 60 | 5.9 | 48 |
| 70 | 5.1 | 47 |
| 80 | 10.6 | 48 |

[a] [S] = 0.06 mole; [AN] = 0.14 mole; [EASC] = 3 mmoles; toluene as added with EASC; 0.5 hr.

[b] Based on 1:1 S—AN complex.

**Table 8.** Effect of $AlEt_{1.5}Cl_{1.5}$ Concentration on Copolymerization of S—MMA and S—AN

| S/MMA [a] | | | S/AN [b] | | |
|---|---|---|---|---|---|
| MMA/Al mole ratio | Conversion (%) [c] | MMA (mole-%) | AN/Al mole ratio | Conversion (%) | AN (mole-%) |
| | | | 5 | 15.3 | 47 |
| 10 | 20.0 | 46 | 10 | 9.4 | 48 |
| 20 | 14.2 | 42 | 20 | 7.3 | 46 |
| 50 | 11.5 | 39 | 50 | 4.8 | 47 |
| 100 | 6.5 | 31 | 100 | 3.7 | 39 |

[a] [S] = 0.16 mole; [MMA] = 0.04 mole; toluene added to maintain total volume of 24.5 ml; $50^\circ$C; 2 hr. Free radical copolymer 69:31 S/MMA.

[b] [S] = 0.1 mole; [AN] = 0.1 mole; toluene added to maintain total volume of 26.9 ml; $30^\circ$C; 1 hr. Free radical copolymer 60:40 S/AN [11].
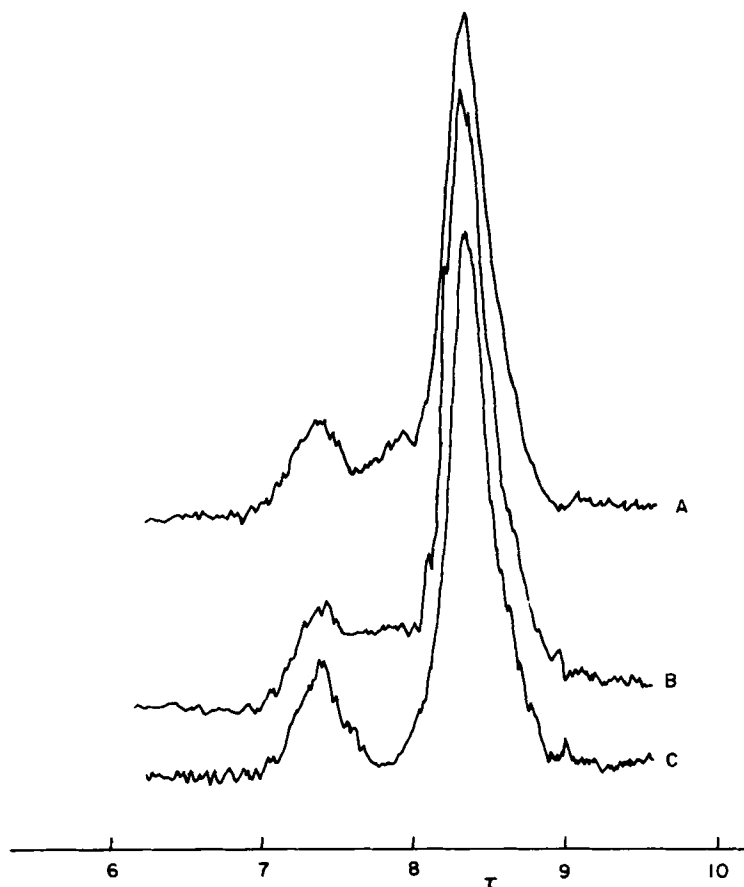
[c] Based on 1:1 S—MMA complex.

**Fig. 1.** NMR spectra of aliphatic protons in styrene-acrylonitrile copolymers. (A) Prepared in presence of EASC at 70°C, AN = 47 mole-%. (B) Prepared in presence of benzoyl peroxide at 60°C, AN = 49.5 mole-%. (C) Alternating copolymer prepared in presence of $ZnCl_2$ at 60°C, AN = 49.5 mole-%.

are found to be equimolar in composition. The nonalternating nature of the copolymers prepared at 70 and 80°C is confirmed from their NMR spectra which are presented in Fig. 1. The NMR spectra of these copolymers are different from that of the alternating copolymer and are identical to that of the equimolar random copolymer in which the absorptions of various sequences of acrylonitrile centered triads are observed. The increased yield at 80°C compared to that at 70°C in Table 7 can be explained by the normal energy of activation in free radical copolymerization.

**Effect of AlEt$_{1.5}$Cl$_{1.5}$ Concentration**

The copolymerization of styrene–acrylonitrile in the presence of EASC yields the equimolar S–AN copolymer at initial AN/EASC mole ratios of 5-50. However, when the AN/EASC ratio is increased to 100, the copolymer has the composition expected from free radical propagation [12].

The effect of EASC concentration in the copolymerization of styrene–methyl methacrylate and a comparison with the styrene–acrylonitrile data are presented in Table 8. It is evident that at an MMA/EASC mole ratio of 20 the copolymer composition has already deviated considerably from the equimolar composition. The deviation progressively increases as the MMA/AlEt$_{1.5}$Cl$_{1.5}$ mole ratio increases, and at MMA/EASC = 100 the copolymer composition is essentially that expected from the free radical polymerization of the 4:1 S/MMA feed. Thus the polymerization of S–MMA is more sensitive than that of S–AN to the EASC concentration. The difference may be due to the higher concentration of polymerizable complexes in the S–AN–Al$\leqslant$ system. The equilibrium constant for complexation of EtAlCl$_2$ with acrylonitrile at 5°C is reported to be larger than that for methyl methacrylate [28].

## EXPERIMENTAL

The reactions were carried out either in tubes or 3-necked flasks. Unless indicated otherwise, the desired amount of EASC in toluene was added dropwise to the mixture of donor and acceptor monomers and solvent. The reactions were terminated by adding the reaction mixture to excess methanol containing dilute hydrochloric acid. The polymers were purified by solution in acetone or benzene and precipitation in methanol.

The NMR spectra of the samples were run in CDCl$_3$ at 100 MHz at 73°C using tetramethylsilane as the internal standard.

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