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Donor-Acceptor Complexes in Copolymerization. VIII. Evidence of Participation of Complexes in Copolymerization of Styrene and Methyl Methacrylate... $Al(C_2H_5)_{1.5}Cl_{1.5}$

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Donor-Acceptor Complexes in Copolymerization. VIII. Evidence of Participation of Complexes in Copolymerization of Styrene and Methyl Methacrylate. . . $\text{Al}(\text{C}_2\text{H}_5)_{1.5}\text{Cl}_{1.5}$

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SUMMARY

The copolymerization of styrene and methyl methacrylate in the presence of ethylaluminum sesquichloride in toluene yields alternating copolymers, independent of initial monomer ratio. The rate of polymerization is not influenced by the presence of an excess of either monomer, the conversion curves following a parallel course at a given total monomer concentration. When the concentration of the $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ and the S/MMA ratio are kept constant and the total monomer concentration is increased, the polymerization rate increases and reaches a limiting value at a S/MMA/Al ratio of 2:2:1. A similar result is obtained when the total monomer and the $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ concentrations are kept constant and the S/MMA ratio is varied. When the concentration of either monomer and the $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ concentration are kept constant and the concentration of the other monomer is varied, the polymerization rate reaches a limiting value at the same mole ratio, irrespective of which monomer is varied. The rate of polymerization is decreased in the presence of a small amount as well

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as a large amount of benzoquinone. However, the rate is higher than in the absence of the quinone when the Al/benzoquinone ratio is 2:1. The conductivity of a toluene solution of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ increases only slightly upon the addition of methyl methacrylate, a further small increase occurring upon the addition of styrene. The results provide evidence for the participation of a comonomer complex in the polymerization, the optimum composition resulting either from the simultaneous interaction of several equilibria or the alignment of the complexes in the form of a matrix.

INTRODUCTION

The formation of alternating copolymers has recently been explained in terms of the homopolymerization of a charge transfer complex between an electron-donor monomer and an electron-acceptor monomer [1-5].

Direct evidence of the participation of a charge-transfer complex in the alternating copolymerization of *p*-dioxene, 1,2-dimethoxyethylene, and 2-chloroethyl vinyl ether with maleic anhydride has been obtained from ultraviolet spectroscopic investigations, and the values of the equilibrium constants of complex formation determined at various temperatures [6].

Kinetic evidence of complex formation in copolymerizations has been found in a study of the terpolymerization of monomer pairs which normally form alternating copolymers, in the presence of a third monomer which had little tendency to copolymerize with either monomer of the pair [7]. Changes in the monomer reactivity ratios in the terpolymerization systems 2-chloroethyl vinyl ether-maleic anhydride-acrylonitrile and *p*-dioxene-maleic anhydride-acrylonitrile as a result of dilution and changes in the nature of the solvent [1] also showed clearly that in these cases a charge-transfer complex between an electron-donor monomer and electron-acceptor monomer enters the growing chain as a single entity. Similarly, kinetic evidence for charge-transfer complex participation has been reported in the spontaneous copolymerization of 1,2-dimethoxyethylene with maleic anhydride and of *p*-dioxene with maleic anhydride [8].

The copolymerization of styrene and methyl methacrylate in the presence of ethylaluminum sesquichloride yields alternating copolymers, irrespective of initial monomer ratio [2, 9, 10]. It has been proposed [4, 10] that the organometal halide bonds with the carbonyl group in the methyl methacrylate, transforming the latter into a stronger electron

acceptor, i.e., increasing e to a more positive value. The methacrylate monomer, having a decreased electron density at the carbon-carbon double bond as a result of the interaction with the metal halide, accepts an electron from the electron-donating styrene monomer and forms a charge transfer complex which undergoes homopolymerization [4].

The copolymerization is characterized by an initial period during which the molecular weight of the copolymer increases with time and conversion. The rate of polymerization then decreases and the molecular weight remains constant at the maximum value attained in the initial stage, independent of conversion [11]. After a sufficiently long reaction period, the polymerization reaches 100% conversion, related to the monomer present in the lowest concentration. The reaction rate, measured as the conversion after 2 hr, as well as the molecular weights of the copolymers, increase with increasing ethylaluminum sesquichloride concentration [11].

The present communication describes additional characteristics of the styrene-methyl methacrylate- $\text{Al}(\text{C}_2\text{H}_5)_{1.5}\text{Cl}_{1.5}$ copolymerization in toluene and clearly indicates the nonradical nature of the reaction as well as the role of the comonomer charge-transfer complex as the active species in the copolymerization.

EXPERIMENTAL

The polymerization procedure was the same as described previously [11], with reaction components charged by means of hypodermic syringes and the reaction carried out under nitrogen. Intrinsic viscosities were determined in benzene at 30°C in a Ubbelohde viscometer.

RESULTS

As mentioned in the previous communication [11], the polymerization is rather fast at the beginning and its rate decreases with time, finally reaching a stage where the change in rate is negligible. Figure 1 shows conversion curves for the first 4 hr of the copolymerization reaction at two different molar ratios of styrene to methyl methacrylate in the feed. The parallel course of both curves reveals that the reaction rate is not particularly dependent upon whether styrene or methyl methacrylate is present in moderate excess (methyl methacrylate in excess showing a little lower reaction rate at the beginning).

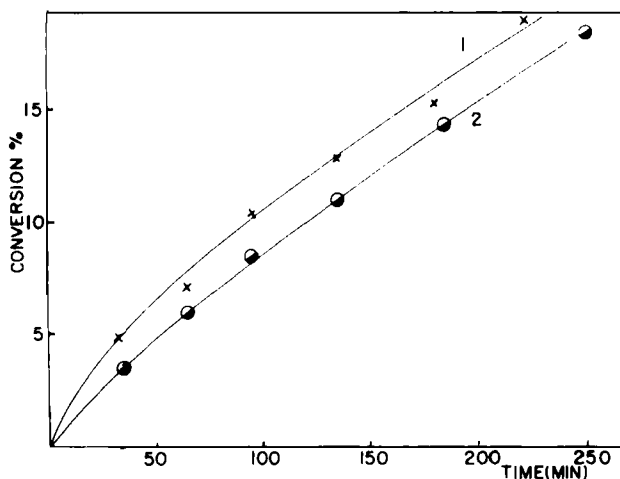


Fig. 1. Dependence of conversion on time for different S/MMA ratios at constant total monomer and ethylaluminum sesquichloride concentrations in toluene at 33°C. $[\text{AlEt}_{1.5}\text{Cl}_{1.5}] = 0.276$ mole/liter. (1) S/MMA = 3/1, $[\text{MMA}] = 0.56$ mole/liter; (2) S/MMA = 1/3, $[\text{MMA}] = 1.68$ mole/liter.

In both cases shown in Fig. 1, there was a twofold excess of the monomer which was present in the lower concentration over the ethylaluminum sesquihalide. When the concentration of the sesquichloride is kept constant and the total monomer concentration is increased (keeping the S/MMA ratio equimolar), the reaction shows an initial rate increase. When the molar ratio of each individual monomer to the aluminum sesquihalide reaches approximately 2:1, i.e., $[\text{MMA}] + [\text{S}] = 4$, the polymerization rate attains a limiting value, independent of further increases in the concentration of monomers (Fig. 2).

When the concentration of either monomer and the concentration of ethylaluminum sesquichloride are kept constant and the concentration of the other monomer is varied, the polymerization rate reaches a limiting value at the same mole ratio, irrespective of which monomer is varied. Thus, the maximum occurs at a concentration of the variable monomer of approximately 1.7 mole/liter when the sesquichloride concentration is 0.28 mole/liter and the fixed concentration of the other monomer is 1.13 mole/liter, i.e., 1.7/1.13/0.28 S/MMA/Al or MMA/S/Al (Fig. 3). Both monomers apparently have the same influence on the reaction rate, as previously shown in Fig. 1. However, there appears to be a decrease in the reaction rate at higher concentrations of methyl methacrylate.

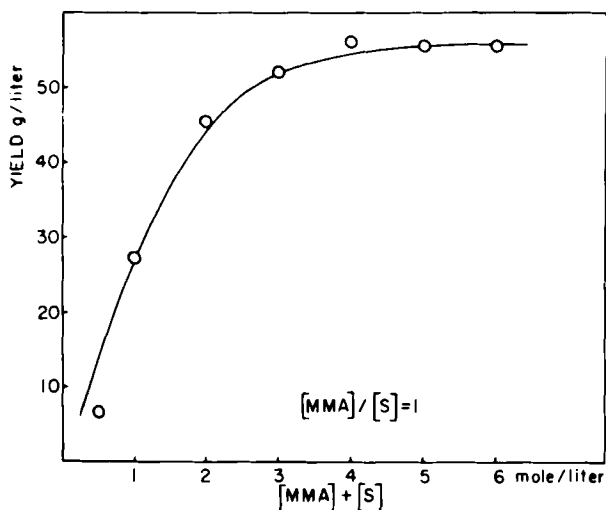


Fig. 2. Dependence of reaction rate (yield in grams/liter after 120 min) on the total monomer concentration at a constant S/MMA ratio in toluene at 33°C. $[AlEt_{1.5}Cl_{1.5}] = 0.613$ mole/liter; S/MMA = 1.

When the total monomer concentration and the ethylaluminum sesquichloride concentration are kept constant and the S/MMA mole ratio is varied, the polymerization rate reaches a maximum at an MMA/Al mole ratio of approximately 2/1. Figure 4 shows the maximum at approximately $[MMA] = 0.8$ mole/liter when $[Al] = 0.4$ mole/liter although the MMA/S mole ratio is 0.36 at this point. The lower rate when methyl methacrylate is present in excess is clearly shown.

It was previously reported [11] that when the total monomer concentration and S/MMA mole ratio are kept constant and the ethylaluminum sesquichloride concentration is varied, the polymerization rate reaches a limiting value at an S/MMA/Al mole ratio of 1/1/1 although the intrinsic viscosity reaches a maximum value at S/MMA/Al mole ratios of 2/2/1–1/1/1.

The unconventional nature of the copolymerization of styrene and methyl methacrylate to alternating copolymers is clearly demonstrated by the effect of p-benzoquinone on the polymerization rate (Fig. 5). At a low benzoquinone concentration the rate is decreased. However, as the amount of benzoquinone is increased the rate of polymerization increases above the rate attained in the absence of the quinone, goes through a maximum, and then decreases. There is no obvious relationship between the

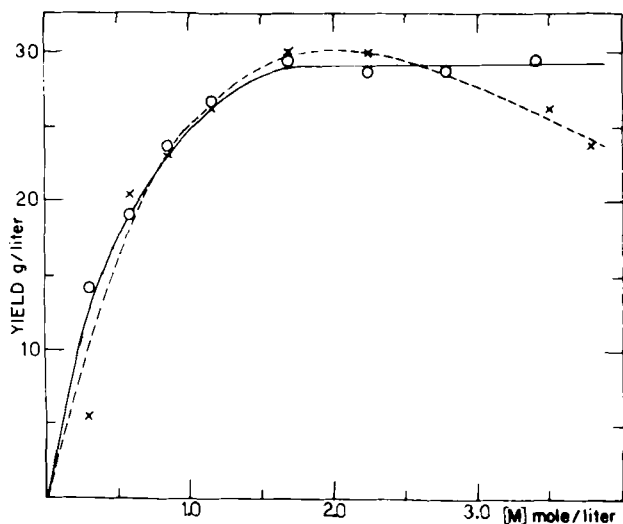


Fig. 3. Dependence of reaction rate (yield in grams/liter after 120 min) on the concentration of one monomer at constant concentrations of the other monomer and ethylaluminum sesquichloride in toluene at 33°C. $[\text{AlEt}_{1.5}\text{Cl}_{1.5}] = 0.277$ mole/liter (O) $[\text{S}] = 1.13$ mole/liter, $[\text{MMA}] =$ varied; (X) $[\text{MMA}] = 1.13$ mole/liter, $[\text{S}] =$ varied.

quinone concentration at the point of maximum rate and either the total monomer concentration (0.05) or the concentration of either monomer (0.1). However, there is a significant relationship with the ethylaluminum sesquichloride content, i.e., the maximum occurs at a quinone/Al molar ratio of 0.5, which corresponds to an equimolar carbonyl/Al ratio.

Figure 6 shows the results of conductivity measurements in the styrene-methyl methacrylate-ethylaluminum sesquichloride system in toluene at 20°C. The specific conductivity of the $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ increases only slightly upon the addition of methyl methacrylate. A further increase occurs upon the addition of styrene. Although these data do not provide any information on the concentration of the $[\text{S}^+\text{MMA} \dots \text{Al}]$ complex, they show unambiguously the direct interaction of styrene with the complexed methyl methacrylate. They also indicate that the ionic dissociation of the complex is not much different from that of the aluminum sesquichloride alone and that the dissociation relationships remain unchanged during at least 2 hr of the polymerization under the indicated conditions. The values of κ show that the absolute concentration of ions must be very low. It is interesting

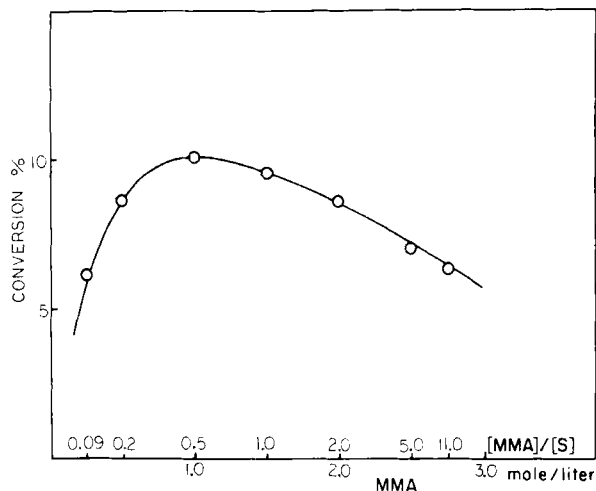


Fig. 4. Dependence of reaction rate (yield in grams/liter after 120 min) on S/MMA mole ratio at constant total monomer concentration in toluene at 33°C. $[\text{AlEt}_{1.5}\text{Cl}_{1.5}] = 0.368$ mole/liter; $[\text{S}] + [\text{MMA}] = 3.0$ mole/liter.

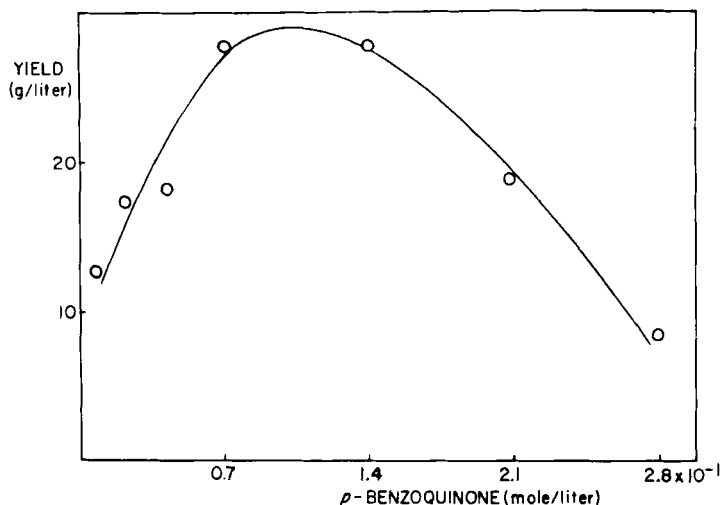


Fig. 5. Dependence of reaction rate (yield in grams/liter after 120 min) on the amount of p-benzoquinone added to the reaction mixture in toluene at 33°C. $[\text{AlEt}_{1.5}\text{Cl}_{1.5}] = 0.277$ mole/liter; $[\text{S}] = [\text{MMA}] = 1.13$ mole/liter.

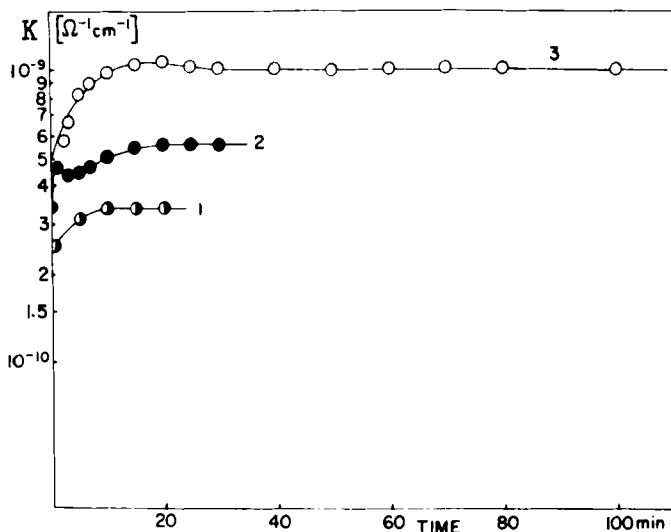


Fig. 6. Dependence of the specific conductivity of 50 ml toluene at 20°C on time, upon the addition of (1) 2 mmoles of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$, followed by the addition of (2) 4 mmoles of methyl methacrylate, followed by the addition of (3) 4 mmoles of styrene.

to note that the structure of the cations formed by the dissociation must be such that they cannot induce a cationic polymerization of styrene. Otherwise this should have caused much higher changes in the conductivity, as is the case in the purely cationic polymerization of styrene.

DISCUSSION

Taking into account that benzoquinone, when present in a suitable concentration, not only does not retard the copolymerization, but on the contrary actually exhibits an accelerating effect, and also that there is a certain concentration of free cations, as indicated by the conductivity measurements, but that these cations fail to induce the cationic polymerization of styrene, it is reasonable to conclude that the active species in the polymerization are neither free radicals nor cations. The experimental results, however, can be readily explained by the assumption, already made in early communications [4, 10, 11], that none of the reaction components

enter the polymerization as a single particle and that all of them form a complex which behaves like a monomer molecule. From this point of view, it is logical that there is only a certain ratio of reaction partners at which the concentration of the complexes reaches a limiting or maximal value (which makes itself evident by a limiting reaction rate). This is the case observed in the dependence of the reaction rate (yield after a 2-hr reaction period) on the concentration of both monomers (Figs. 2 and 3) at a constant concentration of the organoaluminum compound as well as in the dependence of the rate on the organoaluminum halide concentration [11]. Neither an excess of either monomer nor of the aluminum compound results in an increase in the yield and therefore these excesses do not play any role in the polymerization reaction.

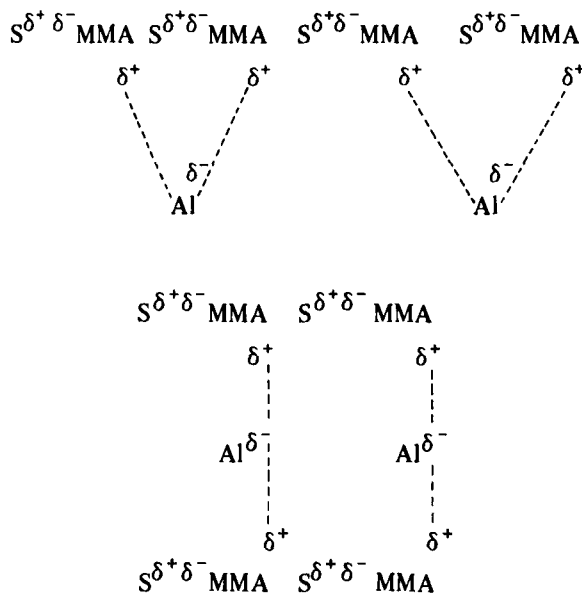
Although it has been proposed that the formation of alternating copolymers results from the homopolymerization of a complex in which the donor and acceptor monomers are present in equimolar proportions, and it has been presumed that the activator, i.e., the metal halide or organometal halide, forms an equimolar complex with the acceptor monomer, the optimum 2:1 relationship between the concentration of either monomer and the concentration of the activator may be explained in either of two ways.

The aluminum-complexed monomers probably exist in equilibrium with free monomer molecules, the equilibrium being shifted to the right so that the equilibrium constant is high. If all of the aluminum is bound to the complex at a twofold excess of both monomers, a further increase in the concentration of either or both monomers would result in only a small increase in the complex concentration, and consequently a negligible increase in the rate of polymerization.

The negative effect of the excess of methyl methacrylate on the reaction rate, as shown in Figs. 3 and 4, can be due either to the competition of excess MMA with styrene in the formation of the active complex or to the dissociation of the complex as a consequence of a higher dielectric constant of the medium containing a greater amount of methyl methacrylate.

An alternative explanation for the 2/2/1 S/MMA/Al stoichiometry for optimum activity lies in the arrangement of the complexes in a matrix, as previously proposed [11]. The maximum activity would result when the position of a complex is fixed by its neighbors, in a linear and/or a parallel alignment. The size, e.g., length, of the matrix is determined by the concentration of complexes. The latter is dependent upon the concentration of activator, the temperature, and the dilution which influence the equilibria.

The increase in molecular weight with conversion is indicative of the progress of the propagating chain end along the matrix. The lower the



activator concentration, the lower the complex concentration and the smaller the matrix. The latter is then responsible for a lower maximum molecular weight.

The absence of copolymerization with an excess of either monomer is due initially to the exclusion of free monomer from the matrix and later, when the end of the matrix is reached, the inability of the propagating chain end, which is neither a conventional radical nor an ion, to add to a monomer double bond.

The retardation which is noted in the presence of a small amount of benzoquinone would be due to the competition of the quinone carbonyl groups with the methyl methacrylate carbonyl groups in complexation with the aluminum activator or, in its capacity as a strong electron acceptor, in complexation with the styrene donor monomer. The resultant lower concentration of comonomer complexes would yield a decreased rate of polymerization. The increase rate of polymerization when the aluminum:benzoquinone ratio is 2:1, i.e., when the $Al/C=O$ ratio is 1, may indicate the participation of the latter in the matrix, e.g., matrix extension or widening. When the benzoquinone is present in even greater quantities, it again competes with methyl methacrylate in complexation with styrene,

reducing the concentration of comonomer complexes and the polymerization rate.

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