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Donor-Acceptor Complexes in Copolymerization. XXVIII. Role of Matrices in Polymerization of Comonomer Charge Transfer Complexes

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Donor-Acceptor Complexes in Copolymerization. XXVIII. Role of Matrices in Polymerization of Comonomer Charge Transfer Complexes*

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ABSTRACT

In a proposed mechanism for the homopolymerization of comonomer charge transfer complexes to alternating copolymers, the dimeric $[D^+ \cdot A \cdot \cdot MX-XM \cdot \cdot A^- \cdot D]$ complexes are arranged in the form of a rigid matrix whose size is determined by the initial complex concentration. After polymerization proceeds through the matrix, uncomplexed monomers diffuse to the complexing agent affixed to the copolymer chain, new complexes are generated, and the new copolymer replicates the molecular weight of the original matrix. The addition of vanadium compound to a $D-A \cdot \cdot R_x AlX_y$ system converts the dimeric to monomeric complexes which form a smaller, flexible matrix and yield lower molecular weight copolymer. Nitriles which coordinate with the Al atom behave similarly to the vanadium compounds.

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INTRODUCTION

The copolymerization of donor and acceptor monomers in the presence of a metal halide such as zinc chloride or aluminum chloride or an organometal halide such as ethylaluminum sesquichloride yields equimolar alternating copolymers independent of initial monomer ratio. The proposed mechanism of copolymerization involves the homopolymerization of a donor-acceptor charge transfer complex [1].

The formation of equimolar copolymers, independent of initial monomer ratio, indicates that the propagating chain end is not a conventional radical or ionic species, since it does not add uncomplexed monomer, i.e., monomer in excess of the equimolar composition, although the monomer may be a normally reactive electron donor such as styrene or butadiene or a normally reactive electron acceptor such as acrylonitrile or methyl methacrylate.

The presence of a radical catalyst results in a rapid radical-initiated homopolymerization of the comonomer charge transfer complex, concurrently with the spontaneous reaction. The radical-initiated reaction also occurs at temperatures where the spontaneous reaction is extremely slow. The formation of alternating copolymers in the presence of the radical initiator, irrespective of monomer charge, indicates that the initiating radical derived from the catalyst preferentially attacks the charge transfer complex, or that the rate of initiation and/or propagation of the complex is far greater than that of conventional radical copolymerization, although the uncomplexed monomers are highly reactive and readily undergo rapid copolymerization in the absence of the complexing agent.

THE STRUCTURE OF THE POLYMERIZABLE SPECIES

The equimolar composition of the charge transfer complex has been suggested by kinetic studies [2-5] and confirmed by cryoscopy [6] and by UV [7] and NMR [6] spectroscopy.

The polymerization of comonomer charge transfer complexes, e.g., styrene-methyl methacrylate-ethylaluminum sesquichloride in toluene [3, 8] or butadiene-acrylonitrile-ethylaluminum dichloride-vanadyl chloride [4], irrespective of initial comonomer ratio, proceeds through an initial stage with a rapid rate of polymerization, followed by a second stage which is slower but proceeds to full conversion

when calculated on the basis of an equimolar copolymer. During the initial stage of the reaction, the molecular weight of the equimolar copolymer increases with conversion and then attains a maximum value which is maintained at a constant level while the polymerization slowly proceeds to full conversion. The maximum molecular weight value increases with an increase in the organoaluminum halide concentration [8].

In the S/MMA/Al system [3], when the concentration of the aluminum compound is kept constant in an equimolar S/MMA mixture, the rate of polymerization increases as the total monomer concentration increases and reaches a maximum value at an S/MMA/Al ratio of 2/2/1. When the total monomer concentration and the aluminum concentration are kept constant and the S/MMA mole ratio is varied, the polymerization rate reaches a maximum at an MMA/Al ratio of 2/1.

Since the equimolar charge transfer complex is the polymerizable species, i.e., the true "monomer," irrespective of the actual composition of the monomer mixture, the maximum polymerization rate at an MMA/Al ratio of 2 indicates that the maximum amount of complex in the monomer mixture is 50% of the total MMA concentration.



$$K = \frac{[\text{S-MMA} \dots \text{Al}]}{[\text{S}] + [\text{MMA} \dots \text{Al}]} \quad (3)$$

Thus, at an equimolar S/MMA ratio, the maximum concentration of complex is 50%. If either the S or MMA...Al concentration is increased, the equilibrium shifts to the right but the maximum complex concentration is still 50% of the MMA. At S/MMA = 1 the complex concentration is therefore actually less than 50% of the MMA and of the total monomer concentration. In the nonequimolar monomer mixture the actual complex concentration is even lower relative to the total monomer concentration. The concentration of the S-MMA-SnCl₄ complex at -78°C has been estimated at 30% at S/MMA = 1 in toluene (S + M = 1.25 mole/liter) [9] and the concentration of the S-AN-ZnCl₂ complex at 30°C has been estimated at 15% at S/AN = 1 in benzene (S + AN = 2.97 mole/liter) [7].

When the total monomer concentration and the S/MMA mole ratio are kept constant and the aluminum concentration is varied, the intrinsic viscosity reaches a maximum value at an S/MMA/Al ratio of 2/2/1 but the polymerization rate reaches a maximum value at a 2/2/2 ratio (Fig. 1) [8]. Since the molecular weight is dependent upon the complex concentration, this is consistent with the maximum at a 2/2/1 concentration. However, the maximum rate at 1/1/1 when the complex concentration is maximum at 2/2/1 indicates that the excess aluminum is involved in the initiation step.

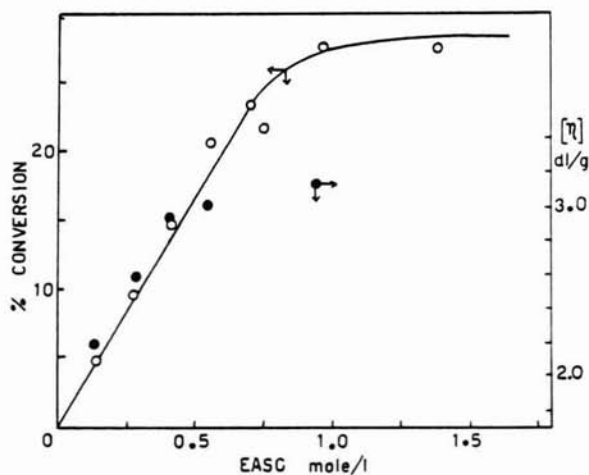
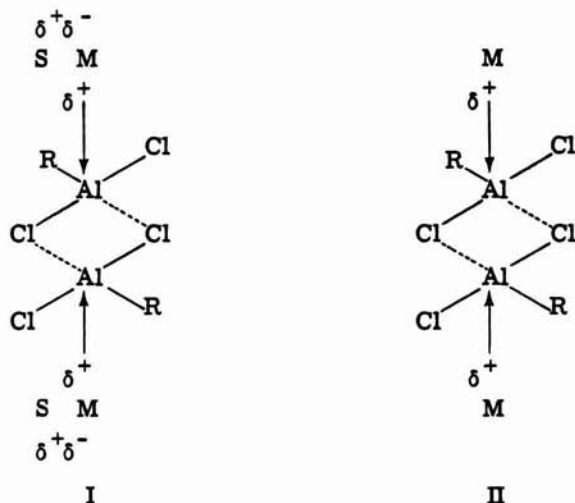


FIG. 1. Dependence of (O) conversion after 2 hr reaction period and (●) intrinsic viscosity (benzene, 30°C) of copolymer on concentration of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$. $[\text{S}] = [\text{MMA}] = 1.12$ mole/l, toluene, 30°C, room light.

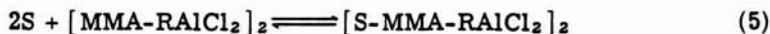
Although the polymerizable complex has an equimolar composition D:A:MX = 1:1:1, it apparently exists in dimeric form. Thus the MMA-ZnCl₂ [10], S-MMA-ZnCl₂ [7], MMA-RAlCl₂ [6], MAN-RAlCl₂ [6], and AN-RAlCl₂ [6] complexes have been shown to exist in dimeric form. Since benzene and styrene both displace AN from an (AN)₂ZnCl₂ complex and MMA from an (MMA)₂ZnCl₂ complex [7] and benzene is coordinated indirectly to RAlCl₂ through MMA [6], this suggests that the S-MMA-RAlCl₂ (or R_{1.5}AlCl_{1.5}) as well as the analogous complexes containing butadiene or styrene as donor

monomer, methyl methacrylate or acrylonitrile as acceptor monomer and R_xAlCl_y or $ZnCl_2$ as complexing agent exist in dimeric form.

The $[S-MMA-RAI Cl_2]_2$ and the $[MMA-RAI Cl_2]_2$ complexes may be represented as



If we assume that all of the aluminum is complexed, irrespective of monomer ratio when $M/Al \geq 1$, the $[S-MMA-RAI Cl_2]_2$ complex is the polymerizable species since the copolymer is equimolar.



The $[MMA-RAI Cl_2]_2$ complex apparently plays a role in the initiation step either by shifting the equilibrium to the right or as the initiating species.

THE POLYMERIZATION PROCESS

During the initial, rapid stage of polymerization the molecular weight of the copolymer increases with conversion. During the

second, slower stage of polymerization the molecular weight remains at the maximum level attained in the initial stage. The rate of polymerization during the first stage, the maximum molecular weight, and the conversion at which the former decreases and the latter becomes constant are dependent upon the initial concentration of complexing agent [2, 3, 8].

The polymerization does not attain steady-state conditions and the rate of polymerization continually decreases. The highest concentration of polymerizable complexes exists at the very beginning of the reaction period.

The increase of molecular weight with conversion during the initial stage is indicative of a nonsteady state reaction and suggests that little or no termination occurs during this stage. Since the concentration of comonomer complexes is highest during this stage, it is apparent that termination involving these complexes does not occur to any appreciable extent. The increase in molecular weight with conversion, irrespective of the monomer/complexing agent ratio and initial monomer feed ratio indicates the absence of termination involving the monomers.

The decrease in the copolymer molecular weight when the solvent concentration is increased is indicative of a decreased complex concentration rather than termination involving solvent since the growing chain does not undergo conventional chain transfer to solvents.

These observations lead to the conclusion that the polymerization reaction is nonterminating. However, the attainment of a constant molecular weight in the second stage rather than a steady increase until all of the polymerizable monomer is consumed indicates that "living" polymerization is not involved. This is confirmed by the addition of an equimolar monomer mixture to a polymerizing composition after or during the second stage. Thus, when an amount of an equimolar mixture of styrene and methyl methacrylate even greater than the amount originally present is added to an S/MMA/ $\text{Et}_{1.5}\text{AlCl}_{1.5}$ system at full conversion or at any conversion after the molecular weight has become constant, the added monomer yields a copolymer which has the same molecular weight as the initial copolymer at all conversions during the polymerization of the new monomers (Table 1) [11].

It is therefore apparent that the copolymer formed during the first stage of polymerization directs the subsequent polymerization. Since full conversion is achieved independent of the initial MMA/Al ratio, new complexes are formed continually until monomer is deleted. Nevertheless, the new complexes have no influence on

TABLE I. Multistage Polymerization of S-MMA-Et_{1.5}AlCl_{1.5} at 30°C

No.	Charge			Time (days)		Conversion (%)	[η] ^a (dl/g)
	S (moles)	MMA (moles)	Al (moles)	Toluene (ml)	Interval		
1	0.02	0.02	0.01	24.5	4	4	2.22
2	0.04	0.04	-	24.5	2	6	2.24
					5	11	2.20
3	0.06	0.06	-	24.5	7	18	2.22
					7	25	2.24

^aToluene, 30°C.

the molecular weight. Since the limiting or peak molecular weight and the conversion during the first stage are determined by the initial S/MMA/Al ratio, the concentration of complexes at the onset of polymerization is the dominant factor in both the first and second stages.

The actual concentration of complexes is influenced by the initial monomer ratio in that, whereas large excesses of donor monomer do not influence the rate of polymerization, large excesses of acceptor monomer decrease the rate, apparently by changing the dielectric constant of the reaction medium and dissociating the complexes [2] or the propagating chain end [12].

The interaction of the donor monomer (D) and the activated acceptor monomer (A...MX) is considered to involve a change in the electron densities of the respective reactants.



The contribution of the dative, ionic structure to the complex composition increases with the electron accepting strength of the complexing agent and/or the complexed acceptor monomer and the electron donating strength of the donor monomer.

The nonionic form of the complex may be considered as the ground state of the comonomer charge transfer complex and the ionic form as the excited, polymerizable stage. Excitation may occur through the collision of complexes or as a result of the transfer of energy from the excited species which result from the decomposition of free radical precursors. When the complex concentration is low, little or no polymerization occurs due to the infrequency of collisions.

Energy transfer from excited species has been proposed in the radical-catalyzed copolymerization of conjugated dienes and maleic anhydride to alternating copolymers [13]. The excitation of a charge transfer complex has been proposed in the copolymerization of butadiene and acrylonitrile to alternating copolymers in the presence of metal halides under UV irradiation [14].

The excitation of the polymerizable comonomer complex may actually occur through energy transfer from the complexed acceptor monomer which is initially excited. In addition, the excited complexed acceptor monomer may be responsible for the initiation of

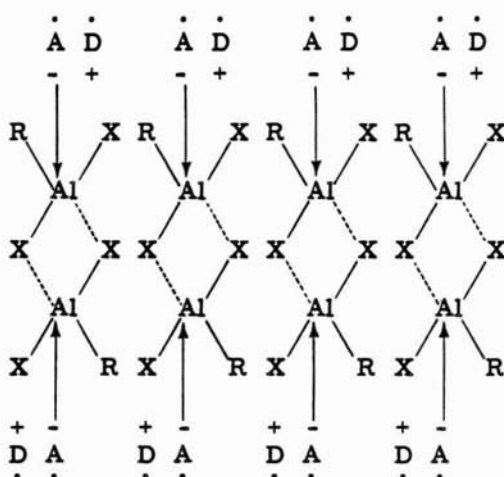
polymerization, e.g. through hydrogen abstraction from the comonomer complex.

The dominant role of the comonomer complexes present at the onset of polymerization in the first stage of polymerization indicates that the formation of new complexes by the transfer of complexing agent from the copolymer to uncomplexed acceptor monomer does not influence the maximum molecular weight. Decreasing the initial complex concentration by diluting the monomer solution at a fixed S/MMA/Al ratio or by decreasing the concentration of complexing agent at a fixed S/MMA ratio and total monomer concentration decreases the length of the first stage and the maximum molecular weight [8]. The number of complexes which may be formed ultimately at a fixed S/MMA/Al ratio should not be influenced by the presence of solvent or excess of monomer. If there is no termination, then the final molecular weight in the first stage should be independent of the concentration of solvent or excess monomer. Since these factors do influence the final molecular weight, the complexes present initially must behave in a different manner than those formed subsequently.

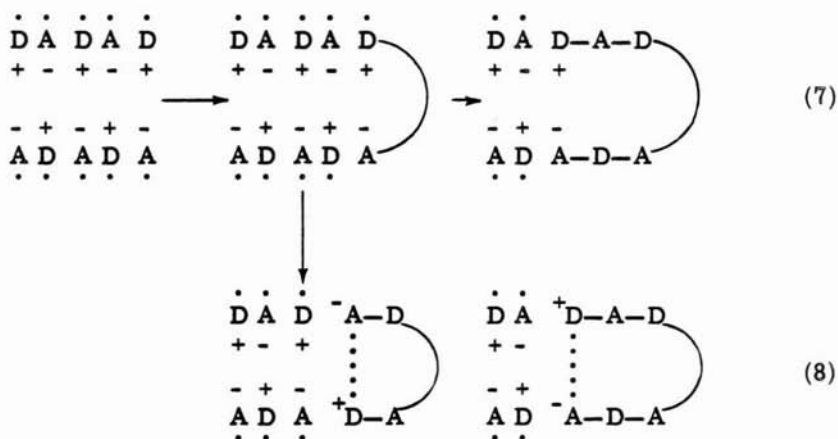
The formation of a matrix or ordered array of those comonomer complexes initially present provides a different environment from that available for the complexes formed later. The size of the matrix is determined by the initial complex concentration and is therefore influenced by dilution and temperature. The formation of aggregates or a matrix has been suggested in the free-radical-initiated polymerization of methyl methacrylate in the presence of $ZnCl_2$ [10, 15] and $SnCl_4$ [10], and allyl alcohol and allyl acetate in the presence of $ZnCl_2$ [16], the γ -ray-initiated polymerization of methyl methacrylate in the presence of $ZnCl_2$ and $SnCl_4$ [10], and the photoinitiated polymerization of methyl methacrylate in the presence of $AlBr_3$ [17].

The matrix of dimeric complexes may be represented as in III. The matrix may exist as a closed loop or a circular band. Polymerization may involve either a donor and an acceptor monomer associated with a given Al atom or a donor monomer associated with one Al atom of a dimer and an acceptor monomer associated with the other Al atom.

It has earlier been suggested [18] that the charge transfer complex may behave as a diradical or as a dipole. Initiation by radical coupling would yield a dipolar structure which could propagate in two directions by addition of complexes to each end or by insertion into a macrocycle.



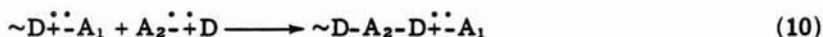
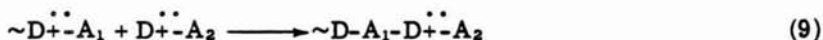
III



An analogous situation would exist if initiation involves ionic coupling and the complex adds to the chain to generate radical species.

Although propagation within a matrix of complexes may be sufficient to explain the exclusion of uncomplexed monomer molecules from the growing chain as well as the absence of the characteristic

behavior of either radical or ionic polymerization, it has been proposed [1] that only one end of the growing chain is involved in the propagation step. In this case initiation occurs within the matrix by hydrogen transfer or abstraction and the growing chain end is a complex. Propagation involves the addition of a complex to the chain end and may be an addition or an insertion reaction.



The initiation of radical [12] and cationic [19] polymerization under conditions of high dilution, e.g., low concentration of complexing agent or elevated temperature, is consistent with the dissociation of the terminal end group in Eqs. (9) and (10).

The initiation of polymerization within the matrix of complexes occurs spontaneously as a result of thermal excitation. When the initial complex concentration is low because of the relatively poor electron accepting and donating strengths of the monomers, the complexing agent nature or concentration or the temperature, the matrix is small. Due to insufficient excitation within the matrix of complexes, spontaneous initiation does not occur. However, the addition of a radical catalyst results in the excitation of the complexes and polymerization is initiated.

The molecular weight of the copolymer formed in the first stage of the polymerization of comonomer charge transfer complexes is determined by the size of the matrix, i.e., the complex concentration. The diffusion of the unpolymerized monomers to the complexing agent affixed to the copolymer chain results in the generation of new complexes on or in the immediate vicinity of the copolymer. The latter acts as a template and the slow rate of polymerization is a function of the time necessary for the formation of a void-free array of complexes. The new polymer replicates the molecular weight of the original matrix. This process is repeated until full conversion is attained.

Although the copolymerization of donor and acceptor monomers in the presence of complexing agents such as $ZnCl_2$, $AlBr_3$, and $R_{1.5}AlCl_{1.5}$ is generally carried out in an anhydrous medium, copolymerization can be carried out in an aqueous medium using complexing agents which are inert or form hydrates under the polymerization conditions, e.g., $ZnCl_2$, $MgCl_2$, or $NiCl_2$ [20] (Table 2).

TABLE 2. Polymerization of S/AN/MX and I/AN/MX in Aqueous Medium

MX	D/AN/MX mole ratio	Catalyst	Temp/Time (°C)/(hr)	Yield (%)	Copolymer		$[\eta]$ (dl/g) DMF, 30°C
					AN (mole-%)	AN (mole-%)	
			S/AN/MX ^a				
ZnCl ₂	2/2/1	KPS	40/5	12.2	50.8	1.65	
ZnCl ₂	2/2/1	KPS/SMB ^d	30/0.5	40.0	50.1	2.27	
ZnCl ₂	2/2/1	APS	40/3	22.6	47.7		
MgCl ₂	2/2/1	APS	40/3	4.2	51.1		
NiCl ₂	2/2/1	APS	40/3	3.5	48.6		
			I/AN/MX				
ZnCl ₂	7/3/7 ^b	KPS	38/1	8.8	51.3	0.3	
ZnCl ₂	7/3/3 ^c	APS	40/0.25	27.6	51.0		

^aS/AN/MX, 0.2/0.2/0.1 moles; water, 31.4 ml; catalyst, 10 mmoles.

^bI/AN/ZnCl₂, 0.44/0.19/0.44 moles; water, 26 ml; catalyst, 0.56 mmole.

^cI/AN/ZnCl₂, 0.35/0.15/0.15 moles; water, 8 ml; catalyst, 14.9 mmoles.

^dKPS/SMB, 0.01/0.005 moles.

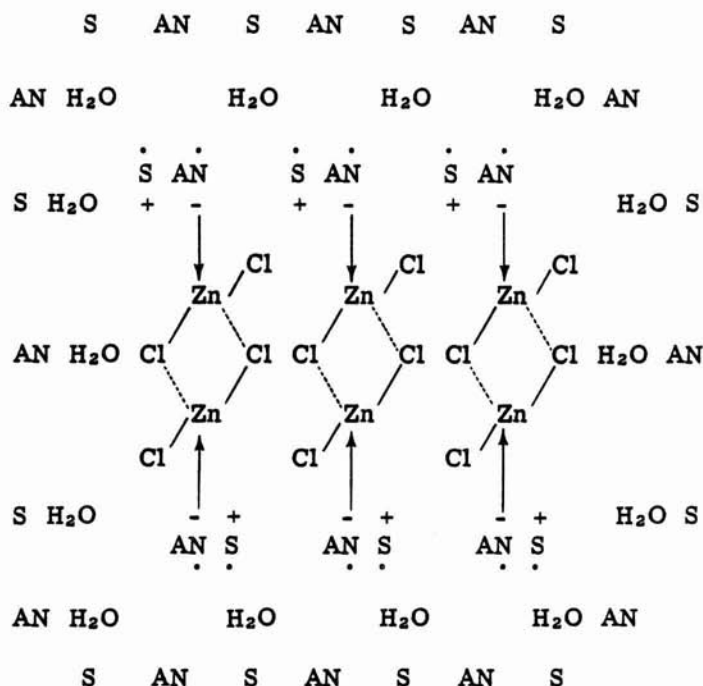
The polymerization is carried out in the absence of an emulsifier. The comonomer complex and the copolymer are insoluble in water and therefore the reaction takes place in a heterogeneous environment. Although water is an inert ingredient in the polymerization, the reaction is carried out with as little water as is practical for effective stirring. A dilution effect is noted in the presence of excess water, resulting in a shift in copolymer composition to yield nonequimolar copolymers.

Although the copolymerization in bulk or in a hydrocarbon solvent can occur spontaneously as well as in the presence of an organic peroxide or other organic free radical precursor, the polymerization in an aqueous medium requires a water-soluble peroxygen compound, such as a persulfate, or a redox system, such as persulfate-bisulfite. Monomer-soluble catalysts such as benzoyl peroxide, tert-butyl peroxyvalate, and azobisisobutyronitrile do not initiate the formation of alternating copolymers from styrene-acrylonitrile- $ZnCl_2$ or isoprene-acrylonitrile- $ZnCl_2$ in an aqueous medium, but instead form radical copolymers.

The water-soluble catalysts are generally effective at temperatures below those at which they are effective in emulsion or aqueous solution polymerization. Thus, whereas ammonium persulfate per se is used in emulsion polymerization at temperatures above $50^\circ C$, it is effective in the complex polymerization at $30^\circ C$. The use of a redox system such as potassium persulfate-sodium metabisulfite permits the reaction to be carried out either at a lower temperature or with lower initiator concentrations.

The formation of alternating copolymers in the presence of water-soluble catalysts and not monomer-soluble catalysts is consistent with the arrangement of the polymerizable complexes in a matrix from which uncomplexed monomers are excluded (IV). The water-soluble initiator can contact the matrix of complexes due to the location of the aqueous phase at the periphery of the matrix and possibly even within the matrix due to the presence of the hydrated metal halide. A monomer-soluble initiator generates radicals within the monomer phase and initiates conventional radical copolymerization.

Cellulose appears to behave as a polymeric complexing agent and a matrix upon which comonomer charge transfer complexes can be arrayed [28]. Equimolar grafted copolymers on cellulose are formed when either butadiene and methyl methacrylate (monomer charge 20-50 mole-% methyl methacrylate) in the absence of a catalyst or styrene and methyl methacrylate (90/10 mole ratio) in the presence of $NaClO_2$ are copolymerized at $90^\circ C$ in an aqueous suspension of wood pulp.



IV

Similarly, equimolar grafted copolymers are formed at 30°C upon γ -irradiation of viscose rayon immersed in a methanol solution containing either butadiene and acrylonitrile (monomer charge 30-90 mole-% acrylonitrile) or styrene and acrylonitrile (monomer charge 25-75 mole-% acrylonitrile). Similar results are obtained in the radiation-induced graft copolymerization of butadiene-acrylonitrile and styrene-acrylonitrile onto polyvinyl alcohol fibers.

Extremely high molecular weight equimolar alternating grafted and ungrafted copolymers are obtained when styrene and acrylonitrile are copolymerized in the presence of zinc chloride at 40-50°C in the presence of an aqueous suspension of wood pulp containing potassium persulfate or a persulfate-bisulfite redox system.

It is apparent that, in the absence of a metal halide, cellulose and presumably also polyvinyl alcohol, act as complexing agents and promote the generation of comonomer complexes which are arrayed

on the polymeric matrix. The presence of the metal halide results in an even greater number of complexes which are also arrayed on the substrate polymer.

THE EFFECT OF MODIFIERS

The copolymerization of butadiene and acrylonitrile in the presence of a metal halide or organometal halide yields an alternating copolymer in the absence as well as in the presence of a free radical catalyst, irrespective of monomer charge [1, 21]. The addition of a vanadium compound [4, 5, 21, 22] to a BD-AN- R_xAlCl_y as well as a BD-MMA- R_xAlCl_y system results in increased rates of polymerization. Titanium [21, 23] and chromium [23] compounds are also effective in the BD-AN copolymerization.

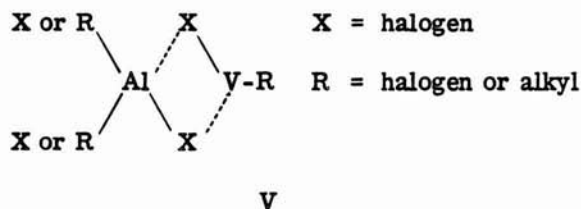
Analogous to the S-MMA- R_xAlCl_y system, the polymerizations of BD-AN and BD-MMA with the $EtAlCl_2-VOCl_3$ combination are characterized by an increase in the molecular weight of the alternating copolymer with increasing conversion [4, 5]. With both acrylic monomers, at a fixed BD/A/Al ratio the rate of polymerization increases with increasing $VOCl_3$ concentration. Similarly at a fixed BD/A/V ratio the rate of polymerization increases with increasing $EtAlCl_2$ concentration. The molecular weights of the copolymers are lower than those obtained in the absence of the vanadium compound and decrease with increasing vanadium concentration.

The dependence of the rate of polymerization on the Al and V concentrations is the same in the BD/AN and BD/MMA systems and the concentration of active species is a function of $[EtAlCl_2]^{0.5}[VOCl_3]^{0.5}$. The active initiating species is presumed to arise from the dissociation of an $EtAlCl_2-VOCl_3$ complex through a redox mechanism. However, the acrylic monomer appears to participate in the initiation because no initiation takes place in its absence [4].

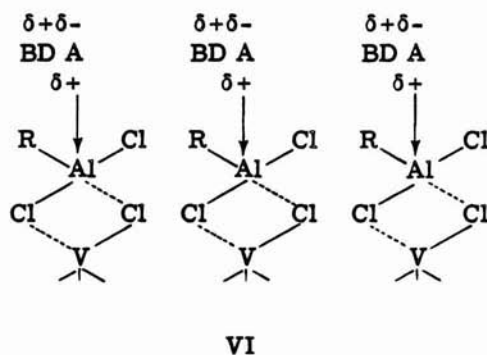
In view of the considerable increase in polymerization rate in the presence of a small amount of the vanadium compound, it has been proposed [4] that the latter acts not only as a generator of the initiating species but also functions to regenerate or recycle the aluminum compound. The acrylic monomer is also presumed to participate in the regeneration or catalyst-transfer reaction.

The effect of the vanadium compound can be readily interpreted on consideration of the matrix of dimeric complexes discussed in the previous section.

The interaction of a vanadium halide and an aluminum halide or alkyl has been shown to form a complex for which a monomeric rather than a dimeric structure is proposed [24].



The addition of a vanadium compound to a BD/A/AlCl₂ system should convert the dimeric complex to monomeric complex. In contrast to the rigid matrix resulting from the interaction of the dimeric complexes, the monomeric complexes should form a flexible matrix (VI).



At low vanadium concentrations the dimeric matrix coexists with the monomeric matrix. The rate of propagation in the latter far exceeds that in the former. The higher the vanadium concentration the greater the number of monomeric complexes and the higher the rate of polymerization. As a result of its flexibility, the dimensions of the matrix, which may be closed as proposed earlier, may be smaller, resulting in the formation of lower molecular weight copolymer.

It has been suggested [5, 6] that the BD/AN/Al system contains a relatively high concentration of the $\text{EtAlCl}_2 \cdot (\text{AN})_2$ complex. The interaction of the latter with the polymer-containing matrix may result in the transfer of the vanadium from the matrix to the complex, followed by displacement of one AN molecule by BD. If the transfer occurs on or near the matrix, the new polymer may replicate the original polymer.

The active or initiating species may be the V-Al-AN complex which functions to abstract hydrogen from the BD-AN-Al-V complex [1] or may be in an excited state and transfers its excitation energy to the comonomer complex.

Organic modifiers also influence the rate of polymerization and the molecular weight of the copolymers. It has been noted that free radical catalysts such as benzoyl peroxide and azobisisobutyronitrile are effective initiators in the polymerization of comonomer charge transfer complexes, in many cases at temperatures far below those at which they are normally used [1].

The rate of polymerization in the S/MMA/AlEt_{1.5}Cl_{1.5} (1/1/0.18) system at 10°C increases with increasing concentration of azobisisobutyronitrile [3]. However, there is no detectable evolution of nitrogen at this temperature. Similarly, there is no detectable decomposition of the azo compound in the presence of the aluminum compound in the absence of the monomers at 10°C [25].

The rate of nitrogen evolution at 60°C in the dark of an equimolar AIBN/AlEt_{1.5}Cl_{1.5} composition in toluene is extremely rapid. However, the rate is reduced by 70% in the presence of the monomer mixture (S/MMA/Al/AIBN = 1/1/0.1/0.1). In the absence of the aluminum compound, the rate of decomposition of AIBN in the monomer mixture is reduced by more than 90% [26]. Similar behavior is noted at 30°C although the rate of decomposition of the azo compound is greatly reduced in all cases.

When the S/MMA/Al ratio is constant at 1/1/0.16 and the total volume is constant, the rate of polymerization at 30°C in the dark in toluene increases and the molecular weight decreases as the AIBN/Al mole ratio increases. The rate increases with increasing AIBN concentration, reaches a maximum at an AIBN/Al mole ratio of 1-1.25, and then decreases (Fig. 2). The reaction in ordinary room light behaves similarly. In the absence of the aluminum compound, the rate of copolymerization (random) is much slower but increases continually with increasing AIBN concentration [25].

The maximum rate of polymerization at an equimolar AIBN/Al ratio, which represents a 2/1 nitrile/Al ratio, indicates an interaction between these reactants. The rate of decomposition of AIBN is insufficient to explain the results. If the nitrile groups

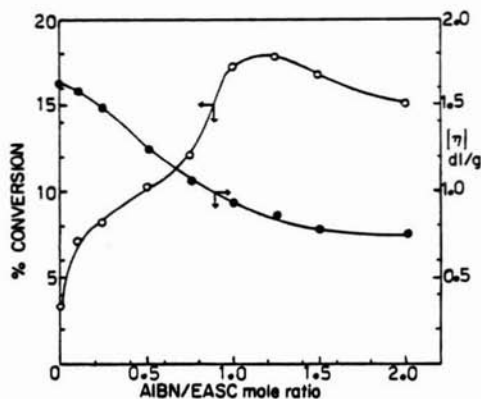


FIG. 2. Dependence of (O) conversion after 2 hr reaction period and (●) intrinsic viscosity (toluene, 30°C) of copolymer on AIBN/EASC mole ratio. $[S] = [MMA] = 0.48$ mole/l, $[EASC] = 0.08$ mole/l, toluene, 30°C, dark.

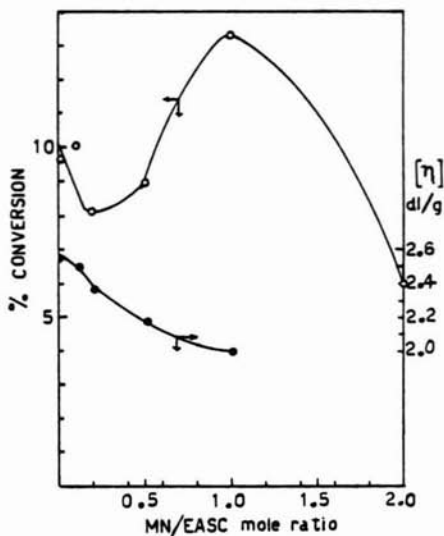
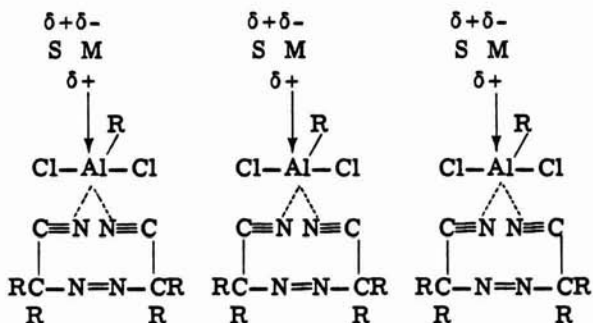


FIG. 3. Dependence of (O) conversion after 2 hr reaction and (●) intrinsic viscosity (toluene, 30°C) of copolymer on malononitrile (MN)/EASC mole ratio. $[S] = [MMA] = 0.5$ mole/l, $[EASC] = 0.2$ mole/l, toluene, 30°C, room light.

of AIBN compete with MMA in complexation with the aluminum compound, the concentration of polymerizable comonomer complexes should decrease with a corresponding decrease in the polymerization rate. This is actually noted when the AIBN/Al ratio is further increased.

The participation of two nitrile groups per aluminum atom suggests the formation of a ring structure, i.e., the azo compound acting as a dinitrile converts the dimeric comonomer complex to a monomeric complex which then forms the flexible matrix previously proposed in the case of the $\text{RAlCl}_2\text{-VOCl}_3$ system. The formation of 2:1 complexes has been reported in the reaction of propionitrile, benzonitrile, and other simple nitriles with ZnCl_2 , BF_3 , and TiCl_4 [27].



VII

The disubstitution on the carbons alpha to the nitrile groups undoubtedly contributes to the formation of a 9-membered ring (VII).

The apparent influence of ring formation and ring size is demonstrated when saturated dinitriles (DN) are substituted for AIBN in the $\text{S/MMA/Et}_{1.5}\text{AlCl}_{1.5}(1/1/0.4)$ system. At $\text{DN/Al} = 1$, malononitrile (6-member ring) increases the rate of polymerization and decreases the molecular weight, succinonitrile (7-member ring) and glutaronitrile (8-member ring) have little or no effect while adiponitrile, pimelonitrile, and suberonitrile decrease the rate but have little effect on the molecular weight.

The effect of the malononitrile/Al ratio is shown in Fig. 3. The rate of polymerization decreases at low malononitrile concentrations, then increases, and reaches a maximum at 1/1 before decreasing at ratios > 1 .

The significance of the 2/1 CN/Al ratio is clearly shown when propionitrile is used as the modifier. The general shape of the curve is similar to that obtained with malononitrile. However, the maximum is reached at a 2:1 propionitrile/Al ratio [25].

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