

ALTERNATING COPOLYMER GRAFT COPOLYMERS—XI. GRAFTING THROUGH MATRIX POLYMERIZATION†

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Abstract—The comonomer complexes generated as a result of the interaction of a donor monomer and an acceptor monomer in the presence of a complexing agent are arrayed in the form of a matrix and undergo radical initiated homopolymerization to yield an alternating copolymer. The array of complexes formed when the copolymerization is carried out in the presence of a polymer which has been precomplexed with a complexing agent undergoes homopolymerization to yield grafted and ungrafted alternating copolymers. Cellulose behaves as a complexing agent per se and, acting as a matrix, promotes the formation of an array of comonomer complexes which homopolymerizes in water to yield grafted and ungrafted alternating copolymers when the water and cellulose contents of the system are maintained within certain limits.

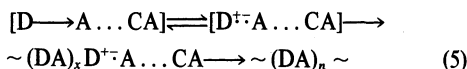
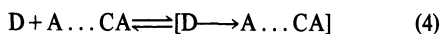
INTRODUCTION

The copolymerization of a strong donor monomer and a strong acceptor monomer, e.g. styrene and maleic anhydride or vinylidene cyanide, yields equimolar, alternating copolymers essentially independent of comonomer feed ratios. The polymerization may occur spontaneously at elevated temperatures, in the presence of a free radical precursor or under ultraviolet irradiation.

The formation of alternating copolymer has been attributed to the homopolymerization of a comonomer donor-acceptor charge transfer complex, whose concentration is dependent upon temperature and dilution, i.e. concentrations of monomers and reaction medium. The polymerizable species is actually the excited complex, generated spontaneously or thermally when the concentration of ground state complexes is sufficiently high. Excitation of ground state complexes also occurs in the presence of a free radical precursor as well as under u.v. irradiation.



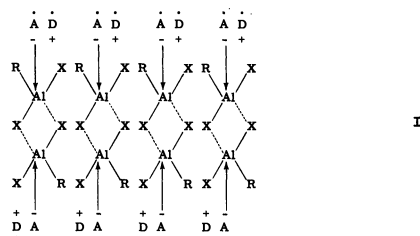
The copolymerization of a strong donor monomer and a weaker electron acceptor, e.g. styrene and acrylonitrile or methyl methacrylate, generally requires the presence of an initiator and yields copolymers whose composition is dependent upon the initial comonomer ratio. However, in the presence of an agent (CA) which is capable of complexing with the acceptor monomer, the latter is converted to a stronger electron acceptor, interacts with the donor monomer to form the ground state comonomer complex and, upon excitation, undergoes homopolymerization to the equimolar, alternating comolymer.



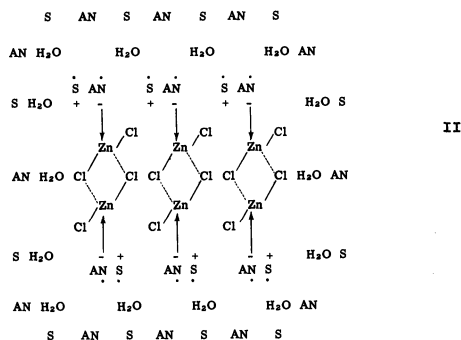
Effective complexing agents include organoaluminum halides as well as metal halides such as zinc chloride. The former promote spontaneous polymerization reactions

although the rate of polymerization is greatly increased in the presence of a radical precursor or under UV irradiation. Copolymerization reactions in the presence of $ZnCl_2$ occur readily at elevated temperatures, e.g. $60^\circ C$ in the absence of a radical catalyst, although the latter is necessary when the reaction is conducted at lower temperatures or in an aqueous medium.

It has been proposed that the comonomer complexes are arrayed in the form of a matrix whose size is determined by the initial complex concentration.^{1,2} The matrix of complexes based on the use of an alkylaluminum dihalide as complexing agent may be represented as in I.



An analogous matrix exists when the comonomer charge transfer complexes are generated in the presence of $ZnCl_2$. When the complexes are formed in an aqueous environment, the uncomplexed monomers and water are excluded from the matrix which may be represented as in II.^{1,3}



In this case, a monomer-soluble initiator generates radicals within the monomer phase and initiates conventional radical copolymerization. A water-soluble initiator can contact the matrix of complexes due to the location of

†Donor-Acceptor Complexes in Copolymerization—LIV.

the aqueous phase at the periphery of the matrix and possibly even within the matrix, due to the presence of the hydrated metal halide, and initiates complex homopolymerization to yield alternating copolymer.

GRAFT COPOLYMERIZATION ONTO PRECOMPLEXED POLYMERS

In the presence of complexing agents

Alternating copolymer graft copolymers may be prepared by carrying out the copolymerization of a donor monomer and an acceptor monomer in the presence of a suitable substrate polymer, under the conditions which are normally used for the preparation of the alternating copolymer in the absence of the polymer. Thus, where a complexing agent such as an organoaluminum halide or $ZnCl_2$ is necessary to promote the formation of the comonomer charge transfer complex, the presence of the complexing agent is necessary in the preparation of the graft copolymer. A free radical catalyst is necessary where it is required in the preparation of the alternating copolymer, e.g. in an aqueous medium, or where it is desired to increase the rate of polymerization and the extent of grafting.⁴

Higher levels of grafting are obtained on polymers containing polar functionality, e.g. ester or nitrile groups, when the latter are complexed with the complexing agent before the addition of the comonomers and radical catalyst.⁵⁻⁷ As a result of precomplexation the matrix of comonomer complexes is arrayed adjacent to the substrate polymer. This apparently promotes grafting due to the proximity of the propagating alternating copolymer chains to the substrate polymer.

The grafting of poly(styrene-alt-acrylonitrile) onto poly(butadiene-co-acrylonitrile) precomplexed with ethylaluminum sesquichloride is summarized in Table 1. Both

Table 3. Graft copolymerization of P(S-alt-AN) onto cellulose... $ZnCl_2$ †

| | | | |
|-----------------------|------|------|------|
| Temperature, °C | 40 | 40 | 50 |
| Time, hr | 3 | 5 | 1 |
| Monomer conversion, % | 22 | 32 | 16 |
| Add-on, % | 221 | 353 | 146 |
| Grafted copolymer | | | |
| % of total | 63.9 | 66.7 | 58.6 |
| AN, mol % | 50.0 | 49.0 | 50.2 |
| $[\eta]$ dl/g‡ | 5.4 | 5.3 | 5.2 |
| Ungrafted copolymer | | | |
| % of total | 36.1 | 33.3 | 41.4 |
| AN, mol % | 50.0 | 50.2 | 52.0 |
| $[\eta]$ dl/g‡ | 5.1 | 4.3 | 3.2 |

† $[S] = [AN] = 1.0$ mol; $[ZnCl_2] = 0.5$ mol; $[K_2S_2O_8] = 0.05$ mol; H_2O , 157 g; wood pulp, 10 g.

‡ $[\eta]$ DMF, 30°C.

the grafted and ungrafted S-AN copolymers have equimolar, alternating structures.

The grafting of P(S-alt-AN) onto a poly(butyl acrylate) latex precomplexed with $ZnCl_2$ is summarized in Table 2. In order to prevent coagulation of the latex on the addition of $ZnCl_2$, the polymer particles are initially swollen with styrene. The use of a water-soluble radical catalyst results in the formation of equimolar, alternating grafted and ungrafted copolymers.

Similar results are obtained in the grafting of P(S-alt-AN) onto cellulose in the presence of $ZnCl_2$ in an aqueous medium using a persulfate catalyst (Table 3).

In absence of complexing agents

Methyl methacrylate undergoes homopolymerization in the presence of an aqueous slurry of various cellulosic

Table 1. Graft copolymerization of P(S-alt-AN) onto precomplexed nitrile rubber... EASC

| Precomplexation | | Polymerization | |
|------------------------|------|---------------------|-----------------|
| P(B-AN) (70:30), g | 4.0 | AN, g (mmol) | 4.1 (77) |
| EASC, mmol | 22 | S, g (mmol) | 8.0 (77) |
| Toluene, ml | 40 | Benzoyl peroxide, g | 0.36 |
| Temp/Time, °C/hr | 40/1 | Temp/Time, °C/hr | 40/5 |
| Monomer conversion 87% | | | |
| Fractionation | | | |
| Solvent | % | BA/S/AN mole ratio | S/AN mole ratio |
| Benzene | 19 | 64/27/9 | 9/0 |
| Acetone | 12 | 0/50/50 | 50/50 |
| Residue | 69 | 40/39/21 | 49/51 |

Table 2. Graft copolymerization of P(S-alt-AN) onto precomplexed poly(butyl acrylate)... $ZnCl_2$ latex

| Precomplexation | | Polymerization | |
|--------------------------|--------------|--------------------|-----------------|
| PBA latex (42.5%), g | 18.8 | AN, g (mmol) | 6.6 (125) |
| PBA, g (mmol) | 8.0 (62.5) | $K_2S_2O_8$, g | 0.4 |
| Styrene, g (mmol) | 13.0 (125) | | |
| Temp/Time, °C/hr | 30/24 | Temp/Time, °C/hr | 50/20 |
| $ZnCl_2$, g (mmol) | 4.26 (31.25) | | |
| Temp/Time, °C/hr | 42/5 | | |
| Monomer conversion 88.4% | | | |
| Fractionation | | | |
| Solvent | % | BA/S/AN mole ratio | S/AN mole ratio |
| Hexane | 8.7 | 100/0/0 | |
| Acetone | 7.3 | 1/46.5/52.5 | 47/53 |
| Residue | 84.0 | 25/40/35 | 53/47 |

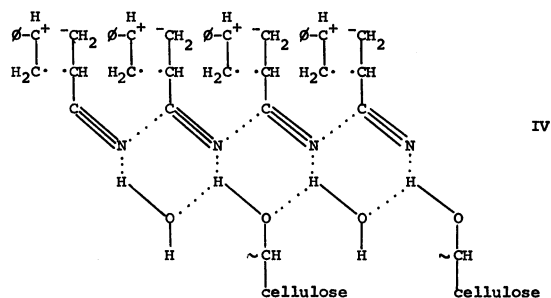
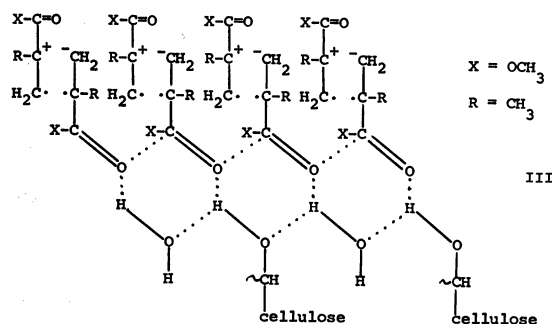
polymers at 85°C in the absence of an added initiator.^{8,9} Both grafted and ungrafted polymers are produced when the reaction is carried out in the presence of cotton, rayon, hemp, paper, wood pulp and starch.

It has been proposed that initiation is due to the presence of peroxides, associated with aldehyde groups, on the cellulose.¹⁰ It has further been proposed¹¹⁻¹³ that cellulose-monomer complexation plays a major role in the reaction, i.e. cellulose acts as a complexing agent for the activation of acceptor monomers, increasing their electron accepting ability and promoting the formation of comonomer charge transfer complexes, in the absence of a metal halide. The cellulose also acts as a matrix for the alignment of comonomer complexes which undergo radical initiated homopolymerization. The matrix in the homopolymerization of methyl methacrylate may be represented as in III. The presence of a polymerization

rylate copolymers are obtained at 16% conversion when a 90/10 molar ratio comonomer mixture is reacted in the presence of wood pulp at 90°C using NaClO₂ as catalyst. However, while the grafted copolymer composition is still equimolar at 60% conversion, the ungrafted copolymer composition approaches that expected in accordance with a conventional radical polymerization.¹⁵

Alternating styrene-acrylonitrile and styrene-methacrylonitrile copolymers are produced both as ungrafted and cellulose graft copolymers when the copolymerizations are carried out in the presence of cellulose using persulfate, persulfate-bisulfite or ceric ammonium nitrate as initiator.¹²

The proposed alignment of comonomer complexes on the cellulose matrix is shown in IV.



initiator such as ceric ammonium nitrate or a persulfate may result in a change in the initiation step but not in the cellulose-monomer complexation which is responsible for the formation of comonomer complexes and their alignment on the cellulosic matrix.

A more convincing demonstration of complexation with cellulose is the formation of equimolar, alternating copolymers from binary monomer mixtures in the absence as well as in the presence of added catalysts. Thus, equimolar poly(butadiene-alt-methyl methacrylate) is grafted onto wood pulp when a comonomer mixture containing 20-50 mol % methyl methacrylate and the wood are heated at 90°C in the absence of a catalyst.¹⁴ Equimolar grafted and ungrafted styrene-methyl methac-

The necessity for the presence of water in the preparation of cellulose graft copolymers, in the absence or presence of a catalyst has been demonstrated and its suggested role is shown in the indicated alignment.

Since the polymerization occurs in a heterogeneous environment wherein both cellulose and the comonomer complexes generated thereon are insoluble in water, the concentration of the latter would not be expected to influence the course of the reaction. However, since the concentration of comonomer complexes is subject to equilibrium considerations, in view of the water solubility of a monomer such as acrylonitrile, at high water contents the complex concentration may be greatly reduced.

As shown in Fig. 1, in the copolymerization of equimolar amounts of styrene and acrylonitrile in the presence of cellulose [(S + AN)/cellulose = 15.7 wt ratio], using K₂S₂O₈ as radical initiator at 40°C, the conversion is

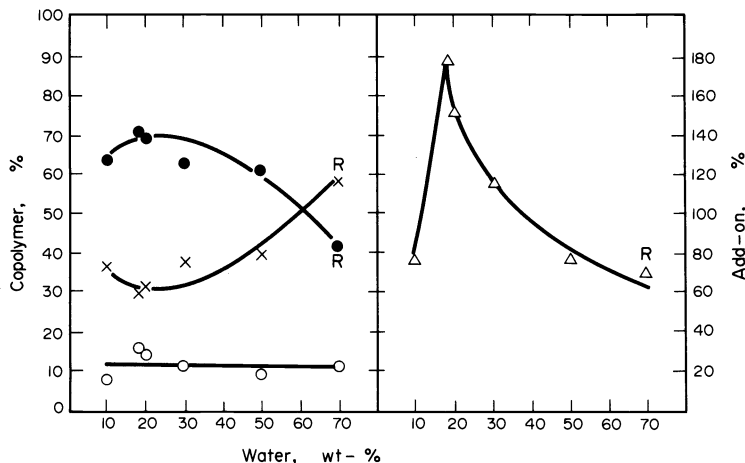


Fig. 1. Effect of water content in S-AN copolymerization in the presence of cellulose. [S] = 52.0 g (0.5 mol); [AN] = 26.5 g (0.5 mol); [K₂S₂O₈] = 2.7 g (10 mmol); [cellulose] = 5.0 g; [H₂O] = 10-70 wt %; 40°C; 3 hr. R = radical copolymer; O, Conversion, %; x, Ungrafted polymer, % of total copolymer; ●, Grafted copolymer, % of total copolymer; Δ, Add-on, %.

essentially independent of water content over the range of 10–70 wt % of the total reaction mixture. The lowest yield of grafted copolymer is obtained at 70% water while the maximum yield is obtained at 18–20% water. Further, both grafted and ungrafted copolymers obtained at 70% water content are the free radical copolymer, i.e. S/AN mole ratio = 60/40, while the grafted and ungrafted copolymers obtained at lower water contents are equimolar, alternating copolymers, as determined by elemental analyses and/or NMR analyses. The lowest add-on is also obtained at 70% water while the maximum add-on is obtained at 18% water.

The formation of grafted and ungrafted alternating copolymers indicates that both originate as a result of interaction, i.e. complexation, of the comonomers with cellulose. When the copolymerization of styrene and acrylonitrile is carried out in the absence of cellulose at 40 and 60°C, as shown in Table 4, the conversion is lower, the copolymer does not have an alternating structure and its molecular weight is quite low.

As shown in Fig. 2, the copolymerization in the presence of cellulose with 50 wt % water, using a redox catalyst system at 40°C, proceeds rapidly to essentially quantitative conversion, yielding equimolar, alternating grafted and ungrafted copolymers at all conversions. The

Table 4. Effect of temperature and presence of cellulose on S-AN copolymerization†

| Cellulose, g | 5.0 | 0 | 5.0 | 0 |
|---------------------|-------|------|--------|--------|
| Temp/time, °C/hr | 40/3 | 40/3 | 60/0.5 | 60/0.5 |
| Conversion, % | 13.9 | 7.4 | 18.6 | 8.2 |
| Ungrafted copolymer | | | | |
| % of total | 31 | 100 | 52 | 100 |
| AN, mol % | 45.7‡ | 33.7 | 46.8‡ | 35.1 |
| [η], dl/g | 3.8 | 0.9 | 2.0 | 0.7 |
| Grafted copolymer | | | | |
| % of total | 69 | | 48 | |
| AN, mol % | 46.9‡ | | 45.4‡ | |
| [η], dl/g | 2.6 | | 1.8 | |
| Add-on, % | 151 | | 141 | |

†[S] = 52.0 g (0.5 mol); [AN] = 26.5 g (0.5 mol); [H_2O] = 20.9 g (20 wt %); [$\text{K}_2\text{S}_2\text{O}_8$] = 2.7 g (10 mmol).

‡Alternating copolymer by NMR analysis.

relative amounts of grafted and ungrafted copolymers are relatively constant up to about 65% conversion, while at higher conversions the amount of alternating ungrafted copolymer increases. The intrinsic viscosity of the ungrafted copolymer remains relatively constant at all conversions. However, the intrinsic viscosity of the grafted copolymer increases with conversion. This suggests that at higher conversions, the number of grafting sites either decreases or are less accessible or that grafting occurs onto already grafted copolymer rather than onto cellulose.

When the styrene-acrylonitrile copolymerization is carried out with 50 wt % water, using a redox catalyst system at 40°C, the conversion after 1 hr increases as the cellulose content is increased from 0.5–5 g, i.e. from 0.6–6% based on monomer concentration (Fig. 3). However, while the relative amount of graft copolymer increases as the cellulose content is increased from 0.5 to 3.5 g, there is no further increase at 5.0 g cellulose. Consistent with the higher conversion at the latter level of cellulose, the add-on is increased. Most significantly, both

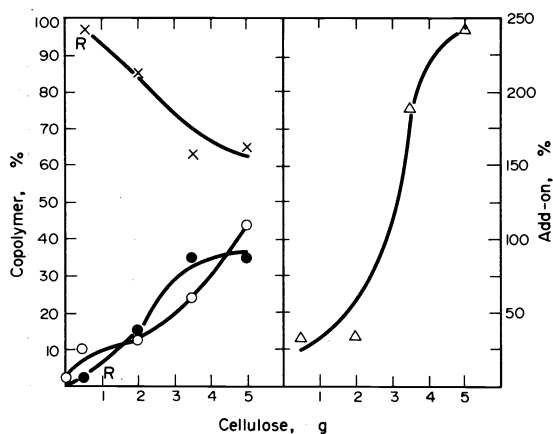


Fig. 3. Effect of cellulose content in S-AN copolymerization in the presence of cellulose. [S] = 52.0 g (0.5 mol); [AN] = 26.5 g (0.5 mol); [H_2O] = 78.5–83.5 g (50 wt %); [cellulose] = 0–5 g; [$\text{K}_2\text{S}_2\text{O}_8$] = 0.27 g (1 mmol); [$\text{Na}_2\text{S}_2\text{O}_5$] = 0.19 g (1 mmol); 40°C; 1 hr; R = radical copolymer; O, Conversion, %; X, Ungrafted copolymer, % of total copolymer; ●, Grafted copolymer, % of total copolymer; Δ, Add-on, %.

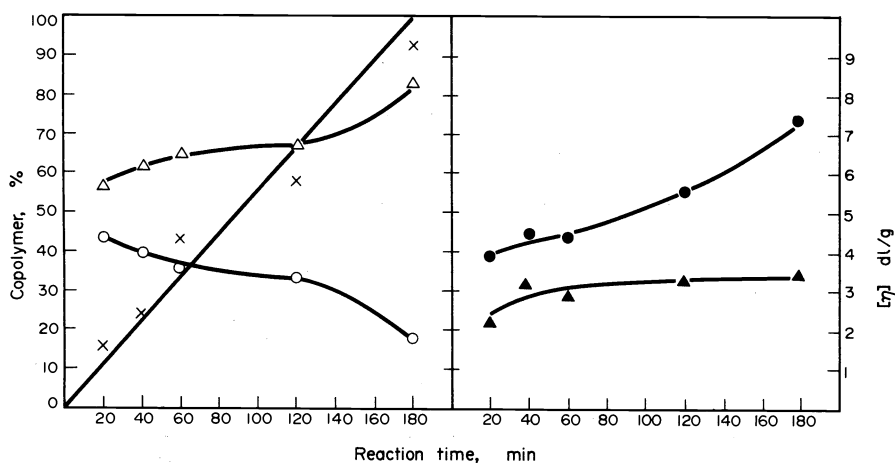


Fig. 2. S-AN copolymerization in the presence of cellulose. [S] = 52.0 g (0.5 mol); [AN] = 26.5 g (0.5 mol); [H_2O] = 83.5 g (50 wt %); [cellulose] = 5.0 g; [$\text{K}_2\text{S}_2\text{O}_8$] = 0.27 g (1 mmol); [$\text{Na}_2\text{S}_2\text{O}_5$] = 0.19 g (1 mmol); 40°C; X Conversion, %; Δ, Ungrafted copolymer, % of total copolymer; ●, Grafted copolymer, % of total copolymer.

grafted and ungrafted S-AN copolymer have a free radical composition when prepared in the presence of 0.5 g cellulose and equimolar compositions at higher cellulose concentrations.

Substitution of a portion of the cellulose by ZnCl_2 results in a decrease in the conversion and, at higher ZnCl_2 contents, in the amount of grafted equimolar copolymer (Fig. 4). However, the ZnCl_2 results in a slight increase in the conversion and amount of grafted copolymer as compared with the results in the absence of ZnCl_2 . The combination of 0.5 g cellulose and 4.5 g ZnCl_2 yields equimolar, alternating grafted and ungrafted copolymers although radical copolymers are obtained in the absence of ZnCl_2 . The AN/ ZnCl_2 molar ratio is 15/1 at this composition, a ratio which yields non-equimolar S-AN copolymer in the absence of cellulose. Thus, equimolar alternating grafted and ungrafted S-AN copolymers are obtained in the presence of amounts of cellulose and ZnCl_2 which individually promote the formation of non-equimolar copolymers.

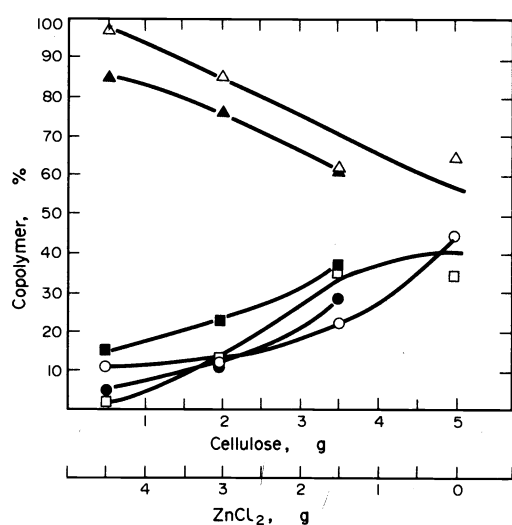


Fig. 4. Effect of ZnCl_2 in S-AN copolymerization in the presence of cellulose. $[\text{S}] = 52.0$ g (0.5 mol); $[\text{AN}] = 26.5$ g (0.5 mol); $[\text{H}_2\text{O}] = 79.0\text{--}83.5$ g (50 wt %); $[\text{cellulose} + \text{ZnCl}_2] = 5.0$ g; $[\text{K}_2\text{S}_2\text{O}_8] = 0.27$ g (1 mmol); $[\text{Na}_2\text{S}_2\text{O}_5] = 0.19$ g (1 mmol); 40°C ; 1 hr.

| ZnCl_2 | | |
|-----------------|---------|------------------------|
| absent | present | |
| ○ | ● | Conversion, % |
| △ | ▲ | Ungrafted copolymer, % |
| □ | ■ | Grafted copolymer, % |

The formation of an alignment of S-AN comonomer complexes on the cellulosic matrix results in the generation of high molecular weight alternating copolymer. A reduction in the molecular weight is noted when various additives are present during the copolymerization reaction (Table 5). Unfortunately, the rate of polymerization is reduced in the presence of these additives. This suggests that the molecular weight reduction results either from a complexation of the additives with the cellulose, reducing the concentration of homopolymerizable comonomer complexes or that the additive competes with one of the monomers due to the donor or acceptor character of the additive. The increase in the amount of ungrafted copolymer in the case of dimethylaniline and benzaldehyde may also be attributed to the termination of propagating chains by these additives or to the initiation of polymerization by their reaction with the catalyst. The effect of methanol may be to change the distribution of monomer, i.e. monomer adsorbed onto cellulose or desorbed into the water-solvent system.

The copolymerization of an equimolar mixture of styrene and acrylonitrile under u.v. irradiation in an aqueous medium yields a radical copolymer. When the photoinduced copolymerization is carried out in the presence of cellulose, the conversion is higher and both grafted and ungrafted copolymers have an alternating structure (Table 6). The compositions and structures of both copolymers are obviously the result of interaction with the cellulose, i.e. the formation of comonomer complexes, and independent of the nature of the initiator.

Alternating grafted and ungrafted styrene-acrylonitrile

Table 6. Photocopolymerization of S-AN in presence of cellulose†

| Cellulose, g | 0 | 5.0 | 5.0 |
|---------------------------------------|------|-------|-------|
| Temp/time, $^\circ\text{C}/\text{hr}$ | 40/6 | 37/6 | 60/1 |
| Conversion % | 5.3 | 14.9 | 8.1 |
| Ungrafted copolymer | | | |
| % of total | 100 | 34 | 50 |
| AN, mol % | 42.9 | 46.6‡ | 46.7‡ |
| $[\eta]$, dl/g | 2.1 | 2.4 | 2.5 |
| Grafted copolymer | | | |
| % of total | | 66 | 50 |
| AN, mol % | | 47.8‡ | 47.0‡ |
| $[\eta]$, dl/g | | 3.8 | 5.3 |
| Add-on, % | | 154 | 63 |

† $[\text{S}] = 52.0$ g (0.5 mol); $[\text{AN}] = 26.5$ g (0.5 mol); $[\text{H}_2\text{O}] = 20.9$ g (20 wt %); 500 W high pressure Hg lamp.
‡Alternating copolymer by NMR analysis.

Table 5. Effect of additives on S-AN copolymerization in presence of cellulose†

| Additive | Reaction time, min | Yield, % | Copolymer‡ | | | |
|-----------------|--------------------|----------|-------------|---------------|-----------|---------------|
| | | | Ungrafted % | $[\eta]$ dl/g | Grafted % | $[\eta]$ dl/g |
| None | 20 | 15.5 | 56 | 2.2 | 44 | 4.0 |
| Dimethylaniline | 20 | 5.3 | 70 | 1.9 | 30 | 3.1 |
| Benzaldehyde | 40 | 12.3 | 77 | 1.6 | 23 | 2.3 |
| Methanol | 40 | 16.2 | 53 | 1.2 | 47 | 2.3 |

† $[\text{S}] = 52.0$ g (0.5 mol); $[\text{AN}] = 26.5$ g (0.5 mol); $[\text{H}_2\text{O}] = 78.5$ g (50 wt %); $[\text{K}_2\text{S}_2\text{O}_8] = 0.27$ g (1 mmol); $[\text{Na}_2\text{S}_2\text{O}_5] = 0.19$ g (1 mmol); $[\text{cellulose}] = 5.0$ g; $[\text{additive}] = 5$ ml; 40°C .

‡Alternating copolymer by elemental and NMR analyses.

copolymers are also formed as a result of redox initiated copolymerization in the presence of starch, casein and collagen (Table 7). Thus, the amide groups in the latter substrates are apparently capable of promoting the formation of comonomer complexes.

The generation of complexes in the presence of soluble as well as insoluble starch, as indicated by the formation of alternating copolymers, suggests that homogeneous as well as heterogeneous environments provide effective matrices. This is consistent with the formation of alternating copolymers when various donor and acceptor monomers are copolymerized in the presence of organoaluminum halides and other complexing agents in both homogeneous and heterogeneous environments.

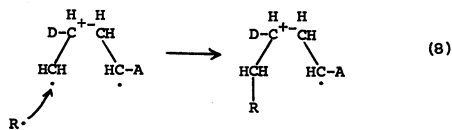
MECHANISM OF ALTERNATING COPOLYMER GRAFT COPOLYMERIZATION

Although the presence of a radical precursor increases the rate of polymerization and yield of alternating copolymer, in the absence as well as in the presence of complexing agents, the presence of little or no catalyst moieties in the copolymer in many cases, indicates that while the radical species may play a role in the polymerization, they may not be incorporated to a significant extent into the polymer chain. It has been proposed that the radicals derived from the catalyst act to convert the ground state to the excited charge transfer complex¹⁶ and/or abstract a hydrogen atom from the excited complex to initiate polymerization.

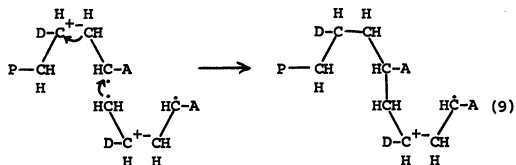
The absence of chain transfer reactions and the failure to incorporate chlorine-containing moieties in alternating copolymers prepared in chloroform or carbon tetrachloride in the presence of radical catalysts, further indicates the non-conventional nature of the initiation as well as the propagation steps in the homopolymerization of comonomer charge transfer complexes.

A recently proposed¹⁷ revised mechanism for the polymerization of comonomer complexes suggests that in those cases where catalyst residues are absent from the copolymer, despite the use of a radical precursor, or due to thermal activation in the absence of a catalyst, initiation occurs as a result of hydrogen abstraction. Thus, in the presence of a radical precursor, radical species initiate polymerization by reaction with a comonomer complex without becoming incorporated into the copolymer chain.

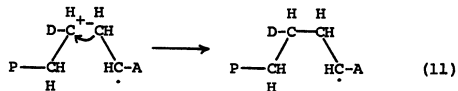
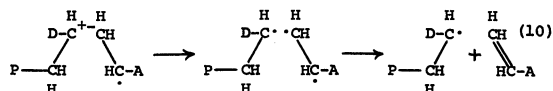
where catalyst residues are found in the copolymer, initiation proceeds through radical coupling.



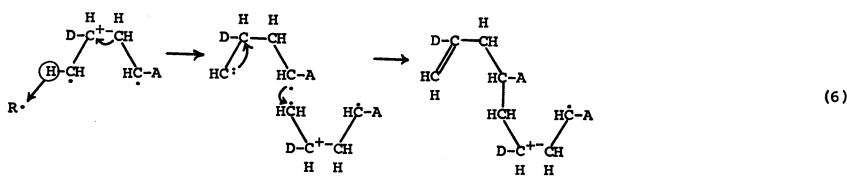
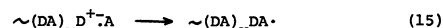
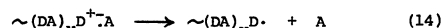
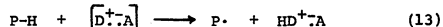
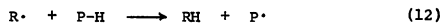
Irrespective of the mode of initiation, the propagation step involves the addition of a comonomer complex to the ion pair chain end.



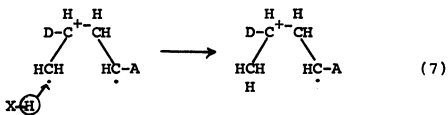
Termination occurs through the generation of radical species through reverse electron transfer or intramolecular coupling, followed by radical coupling or disproportionation.



Consistent with the proposed mechanism, grafting of alternating copolymer chains onto a suitable substrate polymer may be attributed to coupling of the terminal radical shown in eqns (10) and (11) with a radical generated on the substrate polymer as a result of hydrogen abstraction by a catalyst radical or the excited complex.

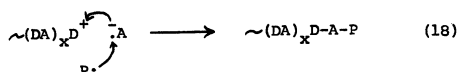


In the absence of a radical catalyst, initiation occurs as a result of hydrogen abstraction by an excited complex from solvent, monomer or polymer, if any or all of these are present in the system, or through intercomplex hydrogen transfer.



In those cases of radical catalyzed polymerization,

Grafting may also occur through a concerted reaction.



Graft copolymerization in accordance with the indicated mechanism occurs as a result of a termination reaction, in contrast to conventional grafting reactions wherein propagation of grafting chains is initiated by active species on the substrate polymer. Grafting by initiation may occur to a certain extent in the preparation of alternating copolymer graft copolymers, particularly in

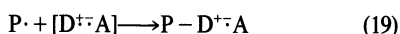
Table 7. S-AN copolymerization in presence of various substrate polymers†

| Substrate | Starch | | | |
|----------------------|---------|-----------|--------|----------|
| | Soluble | Insoluble | Casein | Collagen |
| Time, min | 60 | 60 | 60 | 30 |
| Conversion, % | 85.2 | 52.9 | 17.7 | 10.8 |
| Ungrafted copolymer‡ | | | | |
| % of total | 86 | 64 | 40 | 25 |
| [η], dl/g | 2.2 | 2.9 | 3.5 | 5.3 |
| Grafted copolymer‡ | | | | |
| % of total | 14 | 36 | 60 | 75 |
| [η], dl/g | 3.9 | 3.4 | 3.5 | 6.0 |

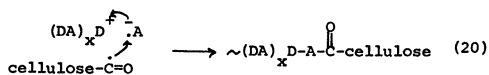
†[S] = 52.0 g (0.5 mol); [AN] = 26.5 g (0.5 mol); [H₂O] = 83.5 g (50 wt %); [K₂S₂O₈] = 0.54 g (2 mmol); [Na₂S₂O₅] = 0.38 g (2 mmol); [substrate] = 5.0 g; 40°C.

‡Alternating copolymer by NMR analysis.

those cases where catalyst residues have been found in the copolymers prepared in the absence of a substrate polymer.



In the case of graft copolymerization on cellulose, although radicals generated on the cellulose backbone through catalyst attack may initiate graft polymerization, as shown in eqn (19), it is presumed that the predominant grafting reaction is termination of propagating chains by coupling with terminal radicals on the cellulose chains, as shown in eqns (16–18). The latter result from hydrogen abstraction, by catalyst radicals or excited complexes, from the terminal aldehyde on the cellulose chain. Alternatively, grafting may occur through a concerted reaction. The ungrafted alternating copolymer is initiated



either by the radical from the catalyst or by hydrogen abstraction from cellulose and terminates without interaction with the cellulose.

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