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Norman G. Gaylord[a]; Sunit S. Dixit[a]; Sukumar Maiti[a]; Berendra K. Patnaik[a]
[a] Gaylord Research Institute Inc., Newark, New Jersey

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Donor-Acceptor Complexes in Copolymerization. XXXVIII. Photoinduced Polymerization of Comonomer Charge Transfer Complexes of Styrene with Methyl Methacrylate and Acrylonitrile

NORMAN G. GAYLORD, SUNIT S. DIXIT, SUKUMAR MAITI,
and BIRENDRA K. PATNAIK

Gaylord Research Institute Inc.
Newark, New Jersey 07104

ABSTRACT

The copolymerizations of styrene (S) with acrylonitrile (AN) and with methyl methacrylate (MMA) under UV irradiation yield radical copolymers. The copolymerization of S and MMA in the presence of $AlEt_3$ yields MMA-rich copolymer when S/MMA = 1 under UV and equimolar, alternating copolymer when S/MMA $\geqq$ 1 in the dark and S/MMA $>$ 1 under UV. The copolymerization of S and AN in the presence of $AlEt_3$ in the dark and under UV yields equimolar, alternating copolymer when S/AN = 1 and nonequimolar copolymer when S/AN $>$ 1. The copolymerization of S and AN in the presence of $AlEt_{1.5}Cl_{1.5}$ (EASC) under light yields equimolar, alternating copolymer when S/AN = 25/75-75/25. The terpolymerization of S, MMA, and AN (100/50/50) in the presence of EASC at 10-90°C under UV and in the dark in the absence as well as in the presence of benzoyl peroxide yields the same terpolymer containing 50% S and with MMA/AN > 2. The copolymerizations of S and AN and of S and MMA in the presence of ϕ_3P under UV yield radical copolymers. The formation of alternating copolymers is attributed to the excitation of comonomer charge transfer complexes and the homopolymerization of the exciplexes. Nonequimolar copolymers result from dissociation of the propagating chain ends from homopolymerizing exciplexes, followed by radical propagation.

INTRODUCTION

The initiation of the polymerization of vinyl monomers upon exposure to light has generally been induced by the presence of a photoinitiator, e.g., a disulfide or a diketone, which undergoes cleavage to generate radical species, or a photosensitizer, e.g., benzophenone or acetophenone, which becomes excited and then undergoes energy transfer to monomer or reacts with the monomer or solvent to generate the initiating radical species.

In recent years it has been shown that donor-acceptor interaction between a monomer and a nonpolymerizable organic acceptor or donor or an inorganic salt results in photosensitivity and photoinduced polymerization through radical or cationic intermediates. Analogously, charge transfer interaction between polymerizable donor and acceptor monomers permits photoinduced homopolymerization and/or copolymerization through complex, radical and/or cationic mechanisms [1, 2].

The present report describes the photoinduced copolymerizations of styrene with methyl methacrylate and/or acrylonitrile in the absence as well as in the presence of organometallic complexing agents.

RESULTS AND DISCUSSION

In Absence of Complexing Agent

Polymerization does not occur when mixtures of styrene and acrylonitrile (50/50 mole ratio) or styrene and methyl methacrylate (70/30) are kept in the dark at 30°C for 24 hr. However, upon exposure to light of 2537 or 3500 Å wavelength, each of the mixtures undergoes copolymerization to yield a copolymer having the composition expected for a radical propagated copolymerization (Table 1).

TABLE 1. Photoinitiated Copolymerization of S-AN, α-MS-AN, and S-MMA

				Copolymer		
					D/A mole ratio	
Light	D/A mole ratio	Temp. (°C)	Time (hr)	Conversion (%)[a]	Found	Theory
S/AN						
Dark	50/50	30	24.0	0.0		
2537 Å		30	0.5	0.5		
3500 A		30	0.5	0.9		
			6.0	12.2	58/42	59/41
			18.0	31.6		
3500 Å		30	1.0	1.8		
Dark			24.0	2.3		
α-MS/AN						
Dark	80/20	30	24.0	0.0		
3500 Å		30	1.0	0.3	58/42	60/40
S/MMA						
Dark	70/30	30	24.0	0.0		
3500 Å		30	4.0	2.5	65/35	60/40

[a] Based on 1/1 D/A.

The influence of irradiation is demonstrated by the negligible increase in conversion when the light is removed after 1 hr and the comonomer mixture is kept in the dark for 24 hr [3].

The copolymerization of an 80/20 mole ratio mixture of α-methylstyrene and acrylonitrile does not occur in the dark but yields a 58/42 radical copolymer upon exposure to 3500 Å light at 30°C. Fractionation of the copolymer with cyclohexane yields 12% of a cyclohexane-soluble fraction having a 60/40 MS/AN composition and 88% of a cyclohexane-insoluble, acetone-soluble fraction having a 58/42 MS/AN composition.

The homopolymerization of comonomer donor-acceptor charge transfer complexes results in the formation of equimolar, alternating copolymers over a wide range of monomer ratios, irrespective of the nature of the initiator, e.g., heat, peroxides or other free radical precursors, or light [4]. However, when the concentration of complexes is low, free radical propagation results in the formation of copolymers having compositions which are dependent upon the monomer charge in accordance with a free radical mechanism.

Free radical propagation is initiated on the addition of a small amount of maleic anhydride to a mixture of styrene and methyl methacrylate under the conditions where the styrene-maleic anhydride complex undergoes spontaneous polymerization, i.e., at 80°C [5]. Similarly, free radical copolymerization is initiated in a mixture of maleic anhydride, vinylpyrrolidone, and methyl methacrylate under the conditions where the vinylpyrrolidone-maleic anhydride complex undergoes polymerization, i.e., at 30°C under light but not in the dark and at 70°C in air but not in vacuo [6].

The copolymerizations of styrene and acrylonitrile as well as styrene and methyl methacrylate in the presence of ethylaluminum sesquichloride yield equimolar alternating copolymers unless the concentration of $[\mathrm{D}\overset{+}{\cdot}\overset{-}{\cdot}\mathrm{A}\ldots\mathrm{EASC}]$ complexes is low as a result of increasing the temperature or decreasing the concentration of complexing agent. Thus the styrene-acrylonitrile system yields radical rather than alternating copolymers when the temperature is above 50°C [7, 8] or when the AN/EASC mole ratio is above 50 [8, 9]. Similarly, the styrene-methyl methacrylate system changes from alternating to radical compositions when the temperature is 100°C [8] or when the MAA/EASC mole ratio is above 20 [8].

The concentration of comonomer complexes in the monomer compositions shown in Table 1 would be expected to be extremely low in the absence of a complexing agent. It is therefore proposed that the ground state complexes undergo excitation upon irradiation. The exciplexes begin to polymerize spontaneously but, due to the low concentration of complexes, the terminal unit on a propagating chain undergoes dissociation. The resultant terminal cation radical then initiates radical copolymerization of uncomplexed monomers.

$$\mathrm{S} + \mathrm{AN} \rightleftharpoons [\mathrm{S}{\rightarrow}\mathrm{AN}] \xrightarrow{h\nu} [\mathrm{S}^{\cdot +}\,{}^{\cdot -}\mathrm{AN}] \tag{1}$$

$$[\mathrm{S}^{\cdot +}\,{}^{\cdot -}\mathrm{AN}] \longrightarrow (\mathrm{S\text{-}AN})_x\mathrm{S}^{\cdot +}\,{}^{\cdot -}\mathrm{AN} \longrightarrow (\mathrm{S\text{-}AN})_x\mathrm{S}^{\cdot +} + {}^{\cdot -}\mathrm{AN} \tag{2}$$

$$(\mathrm{S\text{-}AN})_x\mathrm{S}^{\cdot +} + a\mathrm{S} + b\mathrm{AN} \longrightarrow (\mathrm{S\text{-}AN})_x\mathrm{S{-}S}_a{-}\mathrm{AN}_b \tag{3}$$

The photoinitiated copolymerization of isobutyl vinyl ether and acrylonitrile at 50°C proceeds through a radical propagation mechanism, presumably involving photoexcitation of the contact charge transfer complex between the comonomers [10]. Similarly, the copolymerization of butadiene and acrylonitrile under UV irradiation at room temperature yields a copolymer having the composition expected for a radical copolymerization [11].

Reactions similar to those indicated in Eqs. (1)-(3) are presumably involved in the photoinduced isobutyl vinyl ether-acrylonitrile, butadiene-acrylonitrile, styrene-methyl methacrylate, and α-methylstyrene—acrylonitrile copolymerizations.

In Presence of Triethylaluminum

The polymerization of polar vinyl monomers in the presence of trialkyl aluminum compounds has been the subject of a number of investigations [12-20]. However, the mechanism of polymerization is far from clear. Wexler and Manson [18] suggested a coordination mechanism "not clearly free radical nor ionic" in the polymerization of methyl methacrylate by $\mathrm{AlEt_3}$ and the copolymerization of styrene and methyl methacrylate (1:1) by $\mathrm{AlEt_3}$ and $\mathrm{Al(i\text{-}Bu)_3}$. In contrast, Allen and Casey [12, 13] proposed that the polymerization of methyl methacrylate and the copolymerization of styrene and methyl methacrylate by $\mathrm{AlEt_3}$ are photochemically initiated radical reactions. However, while $\mathrm{Al(i\text{-}Bu)_3}$ only initiates methyl methacrylate polymerization at 25°C under light, both homopolymerization and copolymerization of methyl methacrylate and styrene by $\mathrm{Al(i\text{-}Bu)_3}$ occur at 60°C in the dark [14]. An anionic mechanism has been suggested in the polymerization of methyl vinyl ketone and the copolymerization of styrene and methyl vinyl ketone by $AlEt_3$ at 30°C [16].

When an equimolar mixture of styrene and methyl methacrylate containing $AlEt_3$ (S/MMA/Al = 50/50/10) is maintained at 30°C in the dark for 2 hr, a low yield of equimolar copolymer is obtained. NMR analysis indicates the alternating structure of the copolymer (Table 2).

When the equimolar monomer mixture (S/MMA/Al = 50/50/10) is subjected to irradiation under a 500-W tungsten lamp at 50°C, the resultant copolymer contains 63% methyl methacrylate [21]. This is in agreement with the report that irradiation of a similar equimolar monomer mixture under a 100-W tungsten lamp at 0°C yields a copolymer containing about 60% methyl methacrylate [12-14].

In contrast, when the S/MMA mole ratio ranges from 70/30 to 90/10 with MMA/Al = 5-6, irradiation under a 500-W lamp at 5°C yields equimolar, alternating copolymer.

A 70/30 S/MMA monomer mixture (MMA/Al = 6 or 10) yields equimolar alternating copolymer at 30°C in the dark under ambient light as well as under irradiation with light of 2537, 3000 or 3500 Å wavelength. The same copolymer is obtained under ambient light when the reaction temperature is 60°C.

The yield of copolymer is dependent upon the wavelength of the UV light and reaches a maximum under irradiation with 3000 Å light.

It has been proposed that in the polymerization of acceptor monomers, such as methyl methacrylate and acrylonitrile, in the presence of Lewis acids, the complexation of the monomer with the Lewis acid converts it into a stronger electron acceptor which is now capable of forming a charge transfer complex with uncomplexed monomer [22]. An analogous complex is presumably formed when a donor monomer, such as styrene, and an acceptor monomer are copolymerized in the presence of a Lewis acid [23]. The homopolymerization of the complexes to yield homopolymer and equimolar, alternating copolymer, respectively, may occur spontaneously or may be activated thermally, photochemically, or by the presence of free radical precursors such as peroxide or azo compounds [4].

The complexation of methyl methacrylate with $AlEt_3$ results in the formation of a 1:1 complex when MMA/Al > 1. Complexation of the 1:1 complex with additional monomer results in the formation of a 2:1 MMA–$AlEt_3$ complex which upon irradiation undergoes excitation to form the excited complex.

TABLE 2. Photoinitiated Polymerization of S-MMA...$AlEt_3$[a]

			Copolymer		
				S/MMA mole ratio	
Light	S/MMA/Al mole ratio	Temp. (°C)	Conversion (%)[b]	Found[c]	Theory
Dark	50/50/0	30	0.0[d]		
	70/30/0	30	0.0[d]		
3500 Å	70/30/0	30	2.45[e]	65/35	60/40
Dark	50/50/10	30	0.4	50/50N	50/50
100 W-W	50/50/10	0		40/60[f]	
500 W-W	50/50/10	5	1.74	37/63	
	70/30/5	5	2.79	51/49N	60/40
	80/20/4	5	2.83	51/49	70/30
	85/15/3	5	2.95	51/49	75/25
	90/10/2	5	3.19	50/50	84/16
Dark	70/30/3	30	0.82	51/49	60/40
Ambient	70/30/5	30	0.82	51/49	
		60	0.90	51/49	
2537 Å	70/30/3	30	7.52	47/53N	
3000 Å	70/30/3	30	11.68	47/53	
3500 Å	70/30/3	30	7.80	50/50	
	I/MMA/Al				
500 W-W	50/50/10	5	0.36	50/50N	49/51

[a] [$AlEt_3$] = 10 mmoles.

[b] Based on 1/1 S/MMA; 2 hr.

[c] N = alternating structure confirmed by NMR.

[d] 24 hr.

[e] 4 hr.

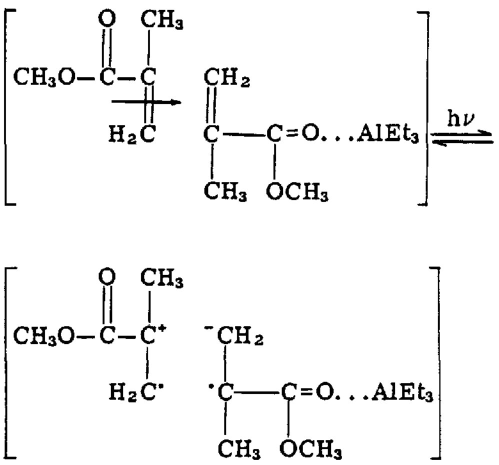
[f] Ref. 12.

$$\mathrm{MMA} + \mathrm{AlEt_3} \longrightarrow \mathrm{MMA}\ldots\mathrm{AlEt_3} \tag{4}$$

$$\mathrm{MMA} + \mathrm{MMA}\ldots\mathrm{AlEt_3} \rightleftharpoons [\mathrm{MMA-MMA}\ldots\mathrm{AlEt_3}] \tag{5}$$

$$\Big\downarrow h\nu$$

$$[\mathrm{MMA}^{+\cdot}\,{}^{\cdot-}\mathrm{MMA}\ldots\mathrm{AlEt_3}] \tag{6}$$



(7)

The excited complex undergoes polymerization to form the homopolymer.

When styrene is present the [S–MMA...AlEt$_3$] complex is formed. The latter may undergo excitation spontaneously due to collision or the presence of adventitious oxygen or upon irradiation.

$$\mathrm{S} + \mathrm{MMA}\ldots\mathrm{AlEt_3} \rightleftharpoons [\mathrm{S-MMA}\ldots\mathrm{AlEt_3}] \rightleftharpoons [\mathrm{S}^{+\cdot}\,{}^{\cdot-}\mathrm{MMA}\ldots\mathrm{AlEt_3}] \tag{8}$$

Since AlEt$_3$ is a weaker Lewis acid than an organoaluminum halide or a metal halide, the concentration of [S-MMA...AlEt$_3$] complexes is undoubtedly low, particularly in an equimolar S/MMA charge.

The formation of equimolar, alternating copolymer from the reactions of 50/50/10 or 70/30/3 S/MMA/Al compositions in the dark (Table 2) is the result of the homopolymerization of the spontaneously excited [S$^{+\cdot}$ $^{\cdot-}$MMA...AlEt$_3$] complexes. The methyl methacrylate-rich copolymer obtained when the 50/50 S/MMA composition is irradiated is indicative of the excitation of the $[\mathrm{MMA}^{\dot{+}}\,{}^{\dot{-}}\mathrm{MMA}\ldots\mathrm{AlEt_3}]$ complex and its copolymerization with the excited $[\mathrm{S}^{\dot{+}}\,{}^{\dot{-}}\mathrm{MMA}\ldots\mathrm{AlEt_3}]$ complex. When styrene is present in excess (S/MMA = 70/30-90/10), the equilibrium in Eq. (8) is shifted to the right, increasing the concentration of the comonomer complex which homopolymerizes to equimolar copolymer. It is noteworthy that no color is observed in the reactions carried out in the dark, while the yellow color which develops on irradiation persists throughout the polymerization period.

The report [13] that a mixture of S-MMA-$\mathrm{AlEt_3}$ in 18/2/1 mole ratio at -26°C continues to polymerize long after any free methyl methacrylate would have been consumed, is in accordance with the characteristic of the polymerization of comonomer charge transfer complexes that reaction continues until an equimolar amount of donor and acceptor monomers has been polymerized [4].

The maximum yield under irradiation at 3000 Å is consistent with the reported [12] $\lambda_{\max} = 298 \pm 5$ mμ for a 4:1 MMA-$\mathrm{AlEt_3}$ mixture in toluene. Since styrene also absorbs in this range, it is probable that the $[\mathrm{S}\rightarrow\mathrm{MMA}\ldots\mathrm{AlEt_3}]$ complex also absorbs in the same range. The maximized yield is either the result of the excitation of the ground state comonomer complex or of the $\mathrm{MMA}\ldots\mathrm{AlEt_3}$ complex which then transfers its excitation energy to the comonomer complex. It is also possible that the excited $\mathrm{MMA}\ldots\mathrm{AlEt_3}$ complexes transfer their energy to ground state [S–MMA] complexes which become excited $[\mathrm{S}^{\dot{+}}\,{}^{\dot{-}}\mathrm{MMA}]$ complexes and copolymerize with the $[\mathrm{S}^{\dot{+}}\,{}^{\dot{-}}\mathrm{MMA}\ldots\mathrm{AlEt_3}]$ exciplexes.

The equilibrium concentration of $[\mathrm{D}\rightarrow\mathrm{A}\ldots\mathrm{AlEt_3}]$ complexes is related to the relative donor and acceptor strengths of the monomers. Thus, whereas irradiation of an equimolar S-MMA mixture (S/MMA/$\mathrm{AlEt_3}$ = 50/50/10) at 50°C yields nonequimolar copolymer, a similar isoprene-methyl methacrylate mixture yields equimolar, alternating copolymer (Table 2). The greater donor strength of isoprene as compared with styrene shifts the equilibrium in the interaction with $\mathrm{MMA}\ldots\mathrm{AlEt_3}$ to the right, analogous to the behavior in the presence of excess styrene.

A mixture of styrene, acrylonitrile, and $\mathrm{AlEt_3}$ kept in the dark at 30°C yields an equimolar, alternating copolymer when the S/AN mole ratio is 50/50, but nonequimolar compositions when the S/AN mole ratio is 30/70 or 70/30 (Table 3). Equimolar, alternating copolymers are also formed when the 50/50 S/AN monomer mixture is exposed to ambient light or 2537, 3000, or 3500 Å UV light.

Analogous to the dark reactions, 30/70 and 70/30 S/AN mixtures

TABLE 3. Photoinitiated Polymerization of S-AN...$AlEt_3$[a]

Light	S/AN/Al mole ratio	Copolymer: Conversion (%)[b]	Copolymer: S/AN mole ratio: Found[c]	Copolymer: S/AN mole ratio: Theory
Dark	50/50/0	0.0[d]		
3500 Å	50/50/0	12.2[e]	58/42	59/41
Dark	30/70/6	2.34	57/43	54/46
	50/50/10	3.14	51/49N	59/41
	70/30/6	2.65	59/41	67/33
Ambient	50/50/5	2.50	50/50	59/41
	50/50/10	4.14	52/48	
2537 Å	50/50/5	10.53	52/48N	
3000 Å	50/50/10	12.70	55/45N	
3500 Å	30/70/6	8.81	51/49	54/46
	50/50/6	5.67	51/49N	59/41
	70/30/6	7.12	64/36	67/33
	80/20/6	14.33	63/37	74/26
	90/10/6	27.10	72/28	84/16

[a] $[AlEt_3]$ = 12 mmoles.
[b] Based on 1/1 S/AN; 30°C; 2 hr.
[c] N = alternating structure confirmed by NMR.
[d] 24 hr.
[e] 6 hr.

yield nonalternating copolymers under 3500 Å light. Further, in contrast to the results with S/MMA/$AlEt_3$ mixtures where equimolar copolymers are found from 70/30-90/10 monomer charges, 80/20 and 90/10 S/AN mixtures yield nonequimolar copolymers under 3500 Å light.

Analogous to the results with S/MMA/$AlEt_3$, the highest rate of polymerization in a 50/50 S/AN composition is noted under irradiation with 3000 Å light.

The formation of equimolar, alternating copolymer from an equimolar S-AN mixture in the presence of $AlEt_3$ under irradiation as well as in the dark is due to the greater acceptor strength of acrylonitrile as compared with methyl methacrylate and the higher equilibrium concentration of $[S^{\cdot +}\cdot^{-}AN\ldots AlEt_3]$ complexes. However, nonequimolar or nonalternating copolymers are formed in the dark or under irradiation when the initial S/AN mole ratio deviates from the equimolar composition due to the greater sensitivity of the acrylonitrile compositions to the effect of dilution. Thus the terminal units of the propagating chains derived from the homopolymerization of the excited comonomer complexes dissociate and continue to propagate in accordance with a radical mechanism, resulting in the formation of nonalternating copolymers.

In Presence of Triethylaluminum-Tetrahydrofuran

The polymerization of a 70/30/5 S/MMA/$AlEt_3$ mixture which yields an equimolar, alternating copolymer in the dark as well as under irradiation is unaffected by the presence of tetrahydrofuran until $AlEt_3$/THF = 1. The copolymer produced at this ratio has a radical composition. The course of the dark reaction is not altered by illumination. The addition of carbon tetrachloride to the monomer mixture containing equivalent amounts of $AlEt_3$ and THF increases the yield of radical copolymer (Table 4).

The polymerization of a 50/50/5 S/AN/$AlEt_3$ mixture which yields an equimolar, alternating copolymer in the dark as well as under irradiation yields radical copolymer when the $AlEt_3$/THF mole ratio <1 in the dark or under illumination (Table 5).

The formation of equimolar copolymers from 70/30/5 S/MMA/$AlEt_3$ in the presence of THF up to $AlEt_3$/THF = 1 is consistent with the ability to form equimolar copolymers up to an MMA/Al mole ratio of 20, although the latter was noted with EASC [8]. The formation of equimolar copolymers from 50/50/5 S/AN/$AlEt_3$ in the presence of even an equimolar amount of THF is also consistent with the lesser sensitivity of the S/AN compositions to metal content, i.e., equimolar copolymers are formed in S/AN/EASC compositions up to an AN/Al mole ratio of 50 [8].

The increased yield of copolymer on the addition of CCl_4 to the S/MMA/$AlEt_3$/THF (70/30/5/5) system is apparently due to the formation of radicals as a result of the reaction of CCl_4 with

TABLE 4. Polymerization of S-MMA...$AlEt_3$ in Presence of THF[a]

Illumination	THF (mmole)	AlR_3/THF mole ratio	Conversion (%)[b]	S/MMA mole ratio[c]
Dark	0		0.80	50/50
	2	5	0.98	50/50
	5	2	0.49	50/50
	10	1	0.98	60/40
Ambient	0		0.82	51/49
	2	5	1.63	47/53
	5	2	0.85	53/47
	10	1	0.74	57/43
	10[d]	1	1.88	60/40

[a] $[AlEt_3]$ = 10 mmole; S/MMA/$AlEt_3$ = 70/30/5; 30°C; 2 hr.
[b] Based on 1/1 S/MMA.
[c] Theory (free radical) S/MMA = 60/40.
[d] 2.5 mmole CCl_4 added.

$AlEt_3$.THF, as reported in the polymerization of vinyl chloride [24]. Radical-initiated polymerization in addition to the spontaneous or photoinduced reactions results in an increased yield as compared to the latter alone.

In Presence of Ethyl Aluminum Sesquichloride

Exposure to UV light greatly increases the rate of polymerization of a 70/30/3 S/MMA/EASC mixture to equimolar, alternating copolymer (Table 6). A similar increase in reaction rate is noted upon irradiation of a 50/50/2.5 S/AN/EASC mixture.

In contrast to the results with the S/AN/$AlEt_3$ system, photoinduced polymerization of S/AN/EASC mixtures yields equimolar

TABLE 5. Polymerization of S-AN...$AlEt_3$ in Presence of THF[a]

Illumination	THF (mmole)	AlR_3/THF mole ratio	Conversion (%)[b]	S/AN mole ratio[c]
Dark	0		2.5	51/49
	5	2	1.21	55/45
	10	1	1.21	55/45
	20	0.5	0.83	58/42
	40	0.25	0.77	58/42
Ambient	0		2.5	50/50
	10	1	1.1	53/47
	20	0.5	1.1	56/44
	40	0.25	0.8	57/43

[a] $[AlEt_3]$ = 10 mmole; S/AN/$AlEt_3$ = 50/50/5; 30°C; 2 hr.
[b] Based on 1/1 S/AN.
[c] Theory (free radical) S/AN = 59/41.

alternating copolymers over a wide range of S/AN ratios, i.e., 25/75-75/25.

The greater electron-accepting ability of EASC as compared with AlR_3 and the resultant higher equilibrium concentration of [S-AN...EASC] complexes as compared with [S-AN...$AlEt_3$] complexes is reflected in the formation of equimolar, alternating copolymers from S/AN mixtures ranging from 25/75-75/25. However, the greater sensitivity to dilution of S/AN compositions as compared with S/MMA compositions is indicated by the formation of nonequimolar copolymers from an 85/15/5 S/AN/EASC charge while 85/15/3 and 90/10/2 S/MMA/$AlEt_3$ charges yield equimolar, alternating copolymers.

Furukawa et al. [25] have reported that in the terpolymerization of butadiene, methyl methacrylate, and acrylonitrile in the presence of EASC or $EtAlCl_2$ (BD/MMA/AN/Al = 120/40/40/4),

TABLE 6. Polymerization of S-MMA and S-AN in Presence of $Et_{1.5}AlCl_{1.5}$

				Copolymer		
					S/A mole ratio	
Light	S/A/Al mole ratio	EASC (mmoles)	Time (hr)	Conversion (%)[a]	Found[b]	Theory
MMA						
Dark	70/30/3	6	1.0	2.62	50/50	60/40
HP Hg	70/30/3	6	0.25	6.46	51/49	
AN						
Dark	50/50/2.5	5	1.0	2.30	54/46	59/41
HP Hg	50/50/2.5	5	0.25	4.91	51/49	
Ambient	12.5/87.5/5	10	1.0	10.7	48/52	45/55
	25/75/5	10	1.0	15.4	50/50N	50/50
	37.5/62.5/5	10	1.0	16.5	52/48	54/46
	50/50/5	10	1.0	21.5	52/48	59/41
	62.5/37.5/5	10	1.0	17.1	51/49	62/38
	75/25/5	10	1.0	12.3	55/45N	69/31
	85/15/5	10	1.0	5.5	60/40	77/23

[a] Based on 1/1 S/A; 30°C.

[b] N = alternating structure by NMR.

the terpolymer always contains 50% butadiene, irrespective of the temperature from 0-50°C. When the reaction is carried out in the dark the MMA/AN mole ratio in the terpolymer varies with the polymerization temperature (Table 7). However, when the reaction is carried out under UV irradiation, the terpolymer composition is constant, independent of temperature. The yield of terpolymer is at a maximum between 330 and 350 mμ radiation, consistent with the UV spectra which indicate the formation of a charge transfer complex with absorption in this region [26].

The formation of terpolymers with compositions which vary with temperature in the dark polymerizations is related to the relative concentrations of [BD$^{\dot{+}\dot{-}}$A...Al≡] and [BD$^{\dot{+}\dot{-}}$MMA...Al≡] excited complexes as a function of temperature. The formation of terpolymers with constant composition in the polymerizations under irradiation, independent of temperature, suggests that the relative concentrations of [BD→AN...Al≡] and [BD→MMA...Al≡] ground state complexes are independent of temperature and under irradiation are converted to the same relative concentrations of exciplexes.

The terpolymerization of 100/50/50/10 S/MMA/AN/EASC mixture in the dark over the temperature range 10-90°C yields terpolymers in which the donor monomer styrene comprises 50 mole % of the composition, i.e., the terpolymer results from the copolymerization of [S$^{\dot{+}\dot{-}}$MMA...EASC] and [S$^{\dot{+}\dot{-}}$AN...EASC] exciplexes. However, the most noteworthy aspects of the terpolymer compositions are the MMA/AN mole ratio which is >2 despite the equimolar initial charge and the relative constancy of the terpolymer composition independent of temperature from 10-90°C (Table 8).

The polymerization rate is greatly increased under UV irradiation but the terpolymer composition is essentially the same as that obtained in the dark reaction, independent of temperature.

When the dark reaction is carried out in the presence of benzoyl peroxide, the terpolymer composition is again unchanged, irrespective of temperature, although the rate of polymerization, particularly when the reaction is carried out at 50-90°C, is higher than in the dark or photoinduced polymerizations.

The S-MMA-AN...EASC system obviously differs from the BD-MMA-AN...EASC system in that polymerizations carried out in the dark, either spontaneously or in the presence of benzoyl peroxide, as well as under irradiation, yield essentially the same copolymer independent of temperature. This suggests that the relative amounts of [S→AN...Al≡] and [S→MMA...Al≡] ground state complexes are independent of temperature. However, in

TABLE 7. Terpolymerization of BD/MMA/AN in Presence of $EtAlCl_2$ (BD/MMA/AN/Al = 120/40/40/4 Mole Ratio)

Dark					UV light				
Temp. (°C)	Copolymer, mole ratio				Temp. (°C)	Copolymer, mole ratio			
	BD	MMA	AN	MMA/AN		BD	MMA	AN	MMA/AN
0	50	41	9	4.55	2	50	34	16	2.12
19	52	26	23	1.13	21.5	50	33	17	1.94
30	56	20	24	0.83	30	49	33	18	1.83
40	47	18	35	0.51	40	50	33	17	1.94
50	47	17	36	0.47	50	52	32	16	2.02
									1.97 ± 0.08

this case the same relative amounts of the ground state complexes are converted to exciplexes with change in temperature. UV irradiation and benzoyl peroxide increase the concentration of exciplexes and/or initiate their polymerization without influencing their relative concentrations.

The most surprising data in Table 8 relate to the results obtained at 70 and 90°C. Although it has been demonstrated that the S-AN...EASC system yields radical copolymer rather than equimolar, alternating copolymer at temperatures above 50°C [8], the terpolymer composition indicates the absence of a temperature effect.

This suggests that the presence of the S-MMA-EASC complexes, either in the ground or in the excited state, prevents the conversion of S-AN...EASC complexes to uncomplexed monomers. The absence of the temperature effect and the formation of terpolymers with a constant composition, independent of temperature, irradiation, or the presence of a radical catalyst suggest that the S-AN-EASC and S-MMA-EASC complexes are aligned in the same array or matrix of complexes.

The terpolymerization of a 220/40/60/10 S/MMA/AN/EASC mixture in the dark at temperatures of 10-50°C yields terpolymers containing 50 mole % styrene and an MMA/AN mole ratio ≥ 2, although the initial MMA/AN mole ratio is 0.67. The styrene content of the terpolymer increases when the terpolymerization is carried out at 70 or 90°C (Table 9).

The polymerization rate is greatly increased under UV irradiation but, in contrast to the dark reaction, the terpolymer composition is essentially unchanged over the temperature range 10-90°C.

The rate of polymerization is even more greatly increased when the dark reaction is carried out in the presence of benzoyl peroxide and, analogous to the dark reaction in the absence of the peroxide, the terpolymer composition changes at elevated temperatures.

The composition change which occurs at 70 and 90°C in the dark is apparently the result of the previously noted sensitivity of S-AN systems to monomer concentration. However, the effect appears to be related to the relative concentrations of the two comonomer exciplexes since the composition is constant under irradiation. It is also notable that the terpolymer compositions are approximately the same as those produced in the presence of a far smaller concentration of styrene and that the terpolymer is richer in methyl methacrylate although the initial MMA/AN mole ratio is 40/60.

TABLE 8. Terpolymerization of S-MMA-AN in Presence of EASC (S/MMA/AN/Al = 100/50/50/10 mmoles)[a]

Temperature, °C	10	30	50	70	90
			Dark		
Time, hr	2.0	2.0	1.0	0.5	0.25
Conversion, %	3.00	5.00	4.72	6.00	5.83
S/MMA/AN mole ratio	53/34/13	53/39/8	54/37/9	55/34/11	52/33/15
MMA/AN mole ratio	2.62	4.88	4.12	3.09	2.20
av			3.38 ± 0.89		
			UV Irradiation (HP Hg)		
Time, hr	2.0	2.0	1.0	0.5	0.25
Conversion, %	13.57	25.20	18.00	15.51	9.64
S/MMA/AN mole ratio	50/40/10	52/38/10	52/37/11	52/37/11	52/36/12
MMA/AN mole ratio	4.00	3.80	3.36	3.36	3.30
av			3.56 ± 0.27		
			Benzoyl Peroxide in Dark		
Time, hr	1.0	0.75	0.5	0.25	0.25
Conversion, %	3.38	15.84	26.26	33.96	31.57
S/MMA/AN mole ratio	51/41/8	49/42/9	53/37/10	50/36/14	53/35/12
MMA/AN mole ratio	5.12	4.67	3.70	2.57	2.92
av			3.80 ± 0.88		

[a] Total volume 40 ml with toluene.

TABLE 9. Terpolymerization of S-MMA-AN in Presence of EASC (S/MMA/AN/Al = 220/40/60/10 mmoles)[a]

Temperature, °C	10	30	50	70	90
			Dark		
Time, hr	2.0	2.0	1.0	0.5	0.25
Conversion, %	3.88	7.96	5.97	8.82	10.23
S/MMA/AN mole ratio	52/32/16	53/33/14	54/33/13	56/29/15	59/23/18
MMA/AN mole ratio	2.00	2.36	2.54	1.93	1.28
av			2.02 ± 0.34		
			UV Irradiation (HP Hg)		
Time, hr	2.0	2.0	1.0	0.5	0.25
Conversion, %	15.0	28.80	14.20	14.42	12.23
S/MMA/AN mole ratio	54/35/11	53/34/13	55/33/12	54/32/14	54/31/15
MMA/AN mole ratio	3.18	2.62	2.75	2.29	2.07
av			2.58 ± 0.32		
			Benzoyl Peroxide in Dark		
Time, hr	1.0	0.75	0.5	0.25	0.25
Conversion, %	6.14	17.06	43.34	33.22	37.71
S/MMA/AN mole ratio	53/38/9	52/36/12	53/32/15	55/31/14	64/30/6
MMA/AN mole ratio	4.22	3.00	2.14	2.21	5.00
av			3.31 ± 1.04		

[a] Total volume 40 ml with toluene.

It has been reported [8] that styrene-rich products are formed when the copolymerizations of S-MMA-EASC and S-AN-EASC are carried out in the presence of chloroform. The same effect is noted when the S-MMA-AN-EASC terpolymerization is conducted in the presence of chloroform (Table 10). However, the change in composition is more apparent in the 100/50/50/10 S/MMA/AN/Al system which is less influenced by light and generally yields a constant composition in the dark or light. The styrene-rich 220/40/60/10 monomer charge which is more affected by light gave the terpolymer with the lower styrene content.

TABLE 10. Terpolymerization of S-MMA-AN-EASC in $CHCl_3$[a]

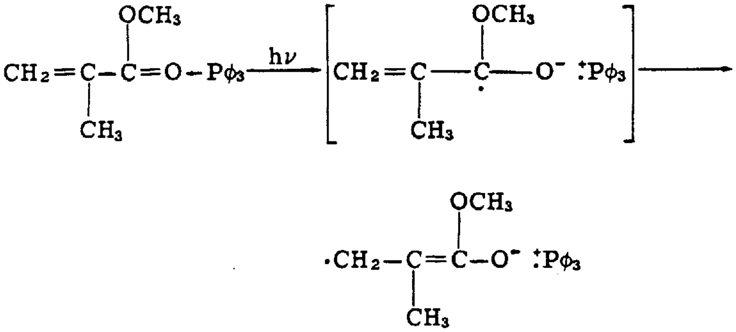
Charge		
S/MMA/AN/Al, mmoles	100/50/50/10	220/40/60/10
Terpolymer		
Conversion, %	0.66	5.00
S/MMA/AN mole ratio	83/10/7	56/26/18

[a] Ambient illumination; 50 ml $CHCl_3$; 40°C; 3 hr.

In Presence of Triphenylphosphine

The photoinitiated polymerization of acrylic monomers in the presence of triphenylphosphine has been attributed to the formation of a complex between ϕ_3P and the monomer (λ_{max} = 292 mμ) [27]. It has been proposed that the complex involves the phosphorus atom and the carbonyl oxygen of the monomer. Upon irradiation phosphorus donates one unpaired electron to the oxygen, generating a charge transfer complex. A rearrangement of electrons produces a monomer radical which then propagates according to a conventional radical mechanism.

The formation of an equimolar copolymer from the photoinduced copolymerization of equimolar amounts of styrene and methyl methacrylate in the presence of ϕ_3P has been considered evidence for a free radical methanism.



$$CH_2{=}\underset{CH_3}{C}-\overset{OCH_3}{C}{=}O-P\phi_3 \xrightarrow{h\nu} \left[CH_2{=}\underset{CH_3}{C}-\overset{OCH_3}{\underset{\bullet}{C}}-O^- \;\overset{+}{\cdot}P\phi_3\right] \longrightarrow \cdot CH_2-\underset{CH_3}{C}{=}\overset{OCH_3}{C}-O^- \;\overset{+}{\cdot}P\phi_3$$

(9)

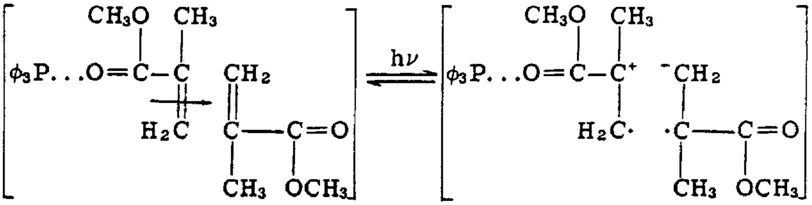
The photochemical nature of the copolymerization reaction is evident from the lack of reaction in the dark even when the acceptor monomer/ϕ_3P mole ratio = 5 or 10 (Table 11). Irradiation of S/MMA (70/30) and S/AN (50/50) mixtures in the presence of ϕ_3P at 3000 Å yields copolymers having the compositions expected from a free radical propagated polymerization.

TABLE 11. Photoinitiated Polymerization of S/MMA and S/AN in Presence of Triphenylphosphine

				Copolymer		
					S/A mole ratio	
Light	S/A (mmoles)	ϕ_3P (mmoles)	Time (hr)	Conversion (%)[a]	Found	Theory
S/MMA						
Dark	70/30	6.0	3	0.0		
3000 Å		0.001	1.5	0.52	64/36	60/40
		6.0	3	4.84	65/35	
S/AN						
Dark	100/100	10.0	3	0.0		
3000 Å		2.0	1.5	1.35	56/44	59/41
		10.0	3	11.04	56/44	

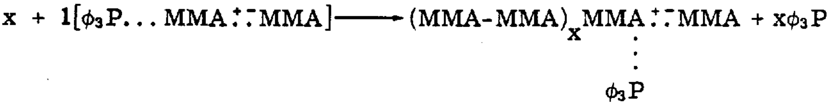
[a] Based on 1/1 S/A; 30°C.

Complexation of ϕ_3P with the acrylic monomer would be expected to decrease its electron accepting ability, i.e., the complexed monomer becomes a donor relative to the uncomplexed acceptor monomer and a donor-acceptor charge transfer complex may be formed [3].

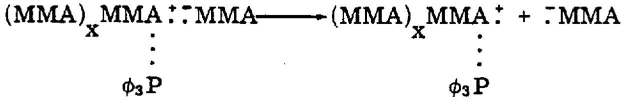


(10)

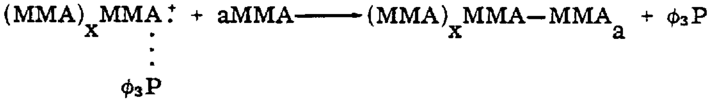
Homopolymerization of the complex may proceed in the same manner as with the complexes containing AlR_3 and EASC. However, if the concentration of complexes is low, the propagating chain end may dissociate and propagate as a conventional free radical species. When styrene is present, the product is the radical copolymer of styrene and methyl methacrylate.



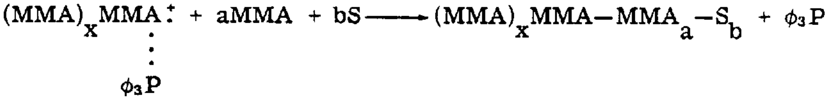
$$x + 1[\phi_3P\ldots\mathrm{MMA}^{\cdot+}\,{}^{\cdot-}\mathrm{MMA}] \longrightarrow (\mathrm{MMA\text{-}MMA})_x\underset{\underset{\phi_3P}{\vdots}}{\mathrm{MMA}^{\cdot+}}\,{}^{\cdot-}\mathrm{MMA} + x\phi_3P \tag{11}$$



$$(\mathrm{MMA})_x\underset{\underset{\phi_3P}{\vdots}}{\mathrm{MMA}^{\cdot+}}\,{}^{\cdot-}\mathrm{MMA} \longrightarrow (\mathrm{MMA})_x\underset{\underset{\phi_3P}{\vdots}}{\mathrm{MMA}^{\cdot+}} + {}^{\cdot-}\mathrm{MMA} \tag{12}$$



$$(\mathrm{MMA})_x\underset{\underset{\phi_3P}{\vdots}}{\mathrm{MMA}^{\cdot+}} + a\mathrm{MMA} \longrightarrow (\mathrm{MMA})_x\mathrm{MMA{-}MMA}_a + \phi_3P \tag{13}$$



$$(\mathrm{MMA})_x\underset{\underset{\phi_3P}{\vdots}}{\mathrm{MMA}^{\cdot+}} + a\mathrm{MMA} + b\mathrm{S} \longrightarrow (\mathrm{MMA})_x\mathrm{MMA{-}MMA}_a{-}\mathrm{S}_b + \phi_3P \tag{14}$$

EXPERIMENTAL

The monomers and solvents were purified in the usual manner. Triethylaluminum and ethyl aluminum sesquichloride were used as 25% solutions in toluene (Texas Alkyls Co.).

The polymerization reactions were carried out in large test tubes stoppered with serum caps. The tubes were purged with nitrogen and the monomers were charged. The monomers were further purged with nitrogen by bubbling nitrogen for 5 min. The toluene solution of complexing agent was introduced through a hypodermic syringe and the tubes were placed in a thermostated bath for the desired reaction time.

In the reactions carried out in the dark, the tubes were wrapped with aluminum foil.

The UV irradiated reactions were carried out in a "Rayonet" Srinivasan-Griffith Photochemical reactor with the tubes suspended in the center 5 in. from 16 UV bulbs. The reaction tubes were either Pyrex (3500 Å) or quartz (2537 and 3000 Å).

In the reactions carried out under illumination from a 500-W bulb source, the reaction tube was placed in a thermostated water bath 6 in. from the source.

The reactions were terminated by adding the mixture to excess methanol containing dilute hydrochloric acid. The polymers were purified by solution in benzene or acetone and precipitation in methanol and were dried in vacuo at 45°C for 16 hr.

The copolymer compositions were determined from elemental analyses and the structure from NMR analyses in $CDCl_3$ at 100 MHz at 73°C using tetramethylsilane as internal standard.

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