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Birendra K. Patnaik[a]; Norman G. Gaylord[a]
[a] Gaylord Research Institute, Inc., New Jersey

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Donor-Acceptor Complexes in Copolymerization. XLIV. Copolymerization of Styrene and α-Methylstyrene with Acrylic and α-Substituted Acrylic Esters in the Presence of Aluminum Compounds

BIRENDRA K. PATNAIK and NORMAN G. GAYLORD

Gaylord Research Institute, Inc.
New Providence, New Jersey 07974

ABSTRACT

The copolymerization of styrene (S) with methyl acrylate (MA) and with methyl methacrylate (MMA) in the presence of $AlEt_3$ yields equimolar, alternating copolymers while no polymer is formed in α-methylstyrene (MS)-MA and MS-MMA systems. In the presence of $AlEt_{1.5}Cl_{1.5}$ (EASC), S-MA and S-MMA yield alternating copolymers, S-methyl α-chloroacrylate (MCA), MS-MA and MS-MMA yield a mixture of alternating and cationic polymers, and MS-MCA yields cationic polymer only. In the presence of $AlCl_3$, S-MA and MS-MA yield a mixture of alternating and cationic polymers and S-MMA and MS-MMA yield cationic polymer only. The cotacticity distributions of the alternating S-MA and S-MMA copolymers prepared in the presence of $AlEt_3$, EASC, and $AlCl_3$ are the same; the coisotactic, coheterotactic, and cosyndiotactic fractions being approximately in the ratio 1:2:1. The cosyndiotactic fractions of the alternating copolymers prepared in the presence of EASC are in the order MS-MMA > MS-MA > S-MCA > S-MMA = S-MA.

INTRODUCTION

The preparation of alternating copolymers from donor and acceptor monomers has received considerable attention in recent years [1, 2]. The formation of the alternating copolymer has been attributed to the homopolymerization of an excited donor-acceptor (DA) complex. When the donor and acceptor monomers are sufficiently strong, the complexes are readily formed and undergo polymerization spontaneously and/or in the presence of a radical catalyst. When the acceptor monomer is not a sufficiently strong electron acceptor, it may be activated by complexation with a metal halide.

The reactivity in a comonomer composition is controlled by the concentration of the polymerizable DA complex. The complex concentration is dependent upon the nature of the monomers and metal halide, the concentration of the metal halide, the acceptor monomer/metal halide ratio, the nature and amount of solvent, and the reaction temperature [3]. Depending upon these reaction variables, the alternating copolymer may be accompanied or superseded by a conventional radical or cationic polymer [4, 5].

The course of the copolymerization of donor and acceptor monomer pairs is apparently influenced by the nature of the comonomers. Thus, whereas the styrene (S)-acrylonitrile (AN)-ethylaluminum sesquichloride (EASC) system is more sensitive to temperature than the S-methyl methacrylate (MMA)-EASC system, i.e., the alternating copolymer is superseded by the radical copolymer at a lower temperature in the former system, the S-MMA-EASC system is more sensitive to dilution. The alternating copolymer is accompanied by the cationic polymer when the AN in the S-AN-EASC system is replaced by methacrylonitrile or α-chloroacrylonitrile or the S is replaced by α-methylstyrene (MS) [3]. These results indicate that both steric and polar factors determine the course of the reaction.

The nature of the metal halide also influences the rate of alternating copolymer formation, higher reactivity being noted in a system having a higher population of excited species. This explanation has been advanced for the relatively higher efficiency observed with $ZnCl_2$ and $EtAlCl_2$ as compared with $AlCl_3$ in the butadiene-acrylonitrile system [6, 7].

Although the S-MMA system has been investigated in considerable detail [3-10], there is little information available on the effect of substituents in S-acrylic ester systems. The present report describes an investigation of the effect of α-substituents in both donor and acceptor monomers in the S-methyl acrylate (MA) series. The comonomers studied include S-MA, S-MMA, MS-MA, MS-MMA, S-methyl α-chloroacrylate (MCA), and MS-MCA. The halogen content of the metal halide (MX) was varied by the use of $AlEt_3$, $AlEt_{1.5}Cl_{1.5}$ (EASC), and $AlCl_3$. The effect of these variables on the relative triad tacticities of the resultant copolymers was also studied.

EXPERIMENTAL

Materials

The monomers and the solvents were purified in the usual manner. Aluminum triethyl and ethylaluminum sesquichloride were obtained as 25% solutions in toluene (Texas Alkyls Inc.) and were used as received. The transfer and introduction of metal compounds were carried out inside a glove bag under a nitrogen atmosphere.

Polymerization

The copolymerizations were carried out either in 3-necked flasks or large tubes according to procedures described earlier.

The UV irradiated reactions were carried out in a "Rayonet" Srinivasan-Griffith Photochemical Reactor with the tubes suspended in the center 5 in. from sixteen 3000 Å UV lamps.

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.

Spontaneous or "thermal" reactions were carried out under normal room light.

The reactions were terminated by adding the mixture to excess methanol containing hydrochloric acid. The polymers were purified by solution in benzene and precipitation into cyclohexane. Both cyclohexane soluble and insoluble fractions were collected. The polymers were dried at 45°C for 16 hr.

Characterization

The copolymer compositions were determined from elemental and NMR analyses. The NMR spectra of the copolymers were obtained in $CDCl_3$ at 73°C in a 100-MHz JEOL spectrometer using tetramethylsilane as internal standard.

The cotacticities of the copolymers were determined from the absorption of the carbomethoxy protons that appeared as three peaks in the range 6.4-7.2 τ. The peaks in order of increasing field strength were assigned to cosyndiotactic, coheterotactic, and coisotactic triads, respectively. The relative triad fractions were determined by measuring the areas under the peaks with the aid of a planimeter.

RESULTS AND DISCUSSION

Styrene-Methyl Acrylate

The experimental results on the copolymerization of styrene and methyl acrylate in the presence of $AlEt_3$, $AlEt_{1.5}Cl_{1.5}$ (EASC), and $AlCl_3$ are presented in Table 1.

Triethylaluminum is a weak Lewis acid and has been reported to induce the formation of alternating copolymers in the S-MMA system only under photoexcitation and in the presence of excess styrene [11, 12]. The S-MA system in the presence of $AlEt_3$ gave negligible amounts of polymer in the dark at 25° C, while the yields were higher either under ambient or UV illumination or in the presence of a radical catalyst. Under each of these conditions a cyclohexane-soluble fraction was collected. In earlier studies the cyclohexane-soluble fraction has been characterized as essentially polystyrene containing a small amount of the acceptor monomer. The cyclohexane-insoluble fraction, obtained in the experiment carried out in the presence of tBPP, analyzed as a copolymer whose composition was the same as that expected from free radical propagation. When the reaction was carried out under UV irradiation, the copolymer composition was intermediate between that of the equimolar and the radical copolymer. The concentration of [S-MA . . . $AlEt_3$] complexes is probably low due to the poor electron-accepting strength of $AlEt_3$. Under photoexcitation these complexes undergo polymerization to generate equimolar copolymer. However, due to the low concentration of ground state complexes subject to excitation, upon exhaustion of available exciplexes the propagating chain end dissociates and the terminal cation-radical propagates via the radical chain end. The simultaneous formation of cationic polymer suggests that the terminal cation-radical also propagates via the cationic chain end. In contrast, under UV irradiation the S-MMA . . . $AlEt_3$ system yields equimolar copolymer unaccompanied by cationic polymer [11, 12].

In the presence of EASC, alternating copolymers were obtained both spontaneously and in the presence of a peroxide catalyst. The alternating copolymer was not accompanied by any cationic polymer.

In the presence of small amounts of $AlCl_3$ ($MA/AlCl_3 = 20$), the cationic polymer was the only product. In the copolymerization of styrene with ethyl acrylate or MMA in the presence of 2 mole-% $AlCl_3$ the product was identified as polystyrene containing < 10% acceptor monomer [13]. In the presence of larger amounts of $AlCl_3$ ($MA/AlCl_3 = 2$) and a peroxide catalyst, the alternating copolymer was obtained as the major product, accompanied by the cationic polymer.

TABLE 1. Copolymerization of Styrene and Methyl Acrylate

						Copolymer		
							Cyclohexane insoluble	
S (mmoles)	MA (mmoles)	MX (mmoles)	Catalysis	Temp (°C)/ Time (hr)	Conversion (%)	Cyclohexane soluble (wt%)	(wt%)	MA (mole%)
		$AlEt_3$						
70	30	6	Dark	25/7	traces			
70	30	6	UV	25/7	4.9	25	75	37.7
70	30	6	tBPP[a]	25/4	3.7	33	67	27.6[c]
70	30	15	Thermal	30/4	0.53	33	67	
		EASC						
125	125	12.5	Thermal	25/0.5	5.3	0	100	53.4
100	100	50	BP[a]	40/5	80.5	0	100	50.0
		$AlCl_3$						
140	60	3	Thermal	0/0.25	14.9	100	0	
50	50	25	tBPP[a]	-78/0.5	2.6	19.5	80.5	
60	60	30	tBPP[b]	-78/4	20.3	22.5	77.5	51.0

[a] 1 mmole benzoyl peroxide (BP) or t-butyl peroxypivalate (tBPP) added at 0 hr.

[b] 1 mmole tBPP added at 0 and 2 hr.

[c] Composition expected for radical copolymer.

TABLE 2. Copolymerization of α-Methylstyrene and Methyl Acrylate

					Copolymer			
							Cyclohexane insoluble	
MS (mmoles)	MA (mmoles)	MX (mmoles)	Catalysis	Temp (°C)/ Time (Hr)	Conversion (%)	Cyclohexane soluble (wt%)	(wt%)	MA (mole %)
		$AlEt_3$						
70	30	15	Thermal	30/1	0			
70	30	6	UV	25/7	Traces			
70	30	6	tBPP[a]	25/4	Traces			
		EASC						
140	60	10	Thermal	30/0.5	3.7	5	95	48.6
		$AlCl_3$						
140	60	3	Thermal	0/0.05	12.8	100	0	
50	50	25	tBPP[a]	-78/0.5	2.1	30.5	69.5	48.6
60	60	30	tBPP[b]	-78/4	2.3	34	66	

[a] 1 mmole tBPP added at 0 hr.

[b] 1 mmole tBPP added at 0 and 2 hr.

α-Methylstyrene—Methyl Acrylate

Table 2 summarizes the results in the copolymerization of α-methylstyrene and methyl acrylate in the presence of the various aluminum compounds.

No polymer was obtained spontaneously at 30°C in the presence of $AlEt_3$. Traces of polymer were obtained under UV irradiation and in the presence of the peroxide. In contrast, the S-MA . . . $AlEt_3$ system, under similar conditions, gave a mixture of nonequimolar and cationic polymers. The reaction medium became yellow in the MS-MA . . . $AlEt_3$ system, indicating the formation of the MA . . . $AlEt_3$ complex. However, the absence of polymerization, to other than a very limited extent even under irradiation, suggests that the ground state [MS-MA . . . $AlEt_3$] complex is formed in very low concentration, if any. This may be attributed to a steric factor as well as the weak Lewis acid character of $AlEt_3$.

The alternating copolymer was the predominant product, accompanied by 5% of the cationic polymer, when the MS-MA copolymerization was conducted in the presence of EASC.

The cationic polymer was the only product from the copolymerization in the presence of a small amount of $AlCl_3$ ($MA/AlCl_3$ = 20). However, when the $MA/AlCl_3$ ratio was reduced to 2 and the reaction was initiated by a peroxide, the alternating copolymer accompanied the cationic polymer. The higher yield of the latter in the MS-MA . . . $AlCl_3$ system as compared to the S-MA . . . $AlCl_3$ system may be due to the direct polymerization of MS as a result of electron transfer to $AlCl_3$ [13].

Styrene-Methyl Methacrylate

The results in the copolymerization of styrene and methyl methacrylate are summarized in Table 3. Copolymerization in the presence of $AlEt_3$ gave equimolar, alternating copolymer in the dark when $S/MMA \geq 1$ and under UV when $S/MMA > 1$ [12]. The alternating copolymer was the only product in the presence of EASC. The addition of AIBN or a peroxide to the S-MMA . . . EASC system increased the yield of alternating copolymer.

The cationic polymer was the only product obtained in the presence of $AlCl_3$, irrespective of the amount of metal halide or the presence of a peroxide. In contrast, alternating copolymer accompanied the cationic polymer in the S-MA . . . $AlCl_3$ and MS-MA . . . $AlCl_3$ systems when $MA/AlCl_3$ = 2 in the presence of the peroxide. The failure to obtain alternating copolymer in the S-MMA . . . $AlCl_3$ system is related to the lower concentration of ground state and/or excited complexes resulting from the weaker electron accepting characteristics of MMA as compared to MA. However, alternating copolymer has been prepared when the S-MMA . . . $AlCl_3$ system has been subjected to UV radiation [14].

TABLE 3. Copolymerization of Styrene and Methyl Methacrylate

					Copolymer			
							Cyclohexane insoluble	
S (mmoles)	MMA (mmoles)	MX (mmoles)	Catalysis	Temp (°C)/ Time (hr)	Conversion (%)	Cyclohexane soluble (wt%)	(wt%)	MMA (mole %)
		$AlEt_3$						
140	60	12	Thermal	30/2	0.48	0	100	49.0
70	30	6	UV	25/7	13.1	0	100	51.2
140	60	12	500-W light	5/2	2.8	0	100	49.0
		EASC						
100	100	20	Thermal	25/1	2.0	0	100	48.7
12	12	2	AIBN	30/2	9.4	0	100	51.3
100	100	20	BP[a]	25/1	10.3	0	100	49.2
		$AlCl_3$						
140	60	3	Thermal	0/0.25	14.7	100	0	
50	50	25	tBPP[a]	-78/0.5	20.0	100	0	
50	50	25	tBPP[b]	-78/4	28.6	100	0	

[a] 1 mmole peroxide added at 0 hr.

[b] 1 mmole tBPP added at 0 and 2 hr.

α-Methylstyrene—Methyl Methacrylate

Table 4 summarizes the results in the copolymerization of α-methylstyrene and methyl methacrylate. Little or no polymer was obtained in the presence of $AlEt_3$, irrespective of the reaction conditions. The alternating copolymer was accompanied by the cationic polymer in the copolymerizations carried out in the presence of EASC, in the absence or presence of a peroxide. The cationic polymer was the sole product obtained in the presence of $AlCl_3$ even when a peroxide was present, analogous to the behavior in the S-MMA... $AlCl_3$ system.

Styrene— and α-Methylstyrene—Methyl α-Chloroacrylate

Table 5 presents the results in the copolymerization of methyl α-chloroacrylate (MCA) with styrene and α-methylstyrene in the presence of EASC. In the S-MCA copolymerization the alternating copolymer was the major product, accompanied by the cationic polymer, in contrast to the S-MA and S-MMA copolymerizations in the presence of EASC where the alternating copolymer was the only product. In this respect MCA behaves in a manner similar to α-chloroacrylonitrile in copolymerization with styrene in the presence of EASC [5].

Under the same conditions the MS-MCA... EASC system yielded the cationic polymer accompanied by 1% of cyclohexane-insoluble, presumably alternating, copolymer. This amount of cationic polymer is far greater than that obtained in the copolymerizations of MS with the other acrylic esters in the presence of EASC. This is attributable to the low concentration of homopolymerizable complexes, resulting from both polar and steric factors and the resultant early dissociation of the complex at the propagating chain end.

Recapitulation of Copolymerization Behavior

The course of the copolymerization of styrene and α-methylstyrene with acrylic and α-substituted acrylic esters is dependent upon the nature of the aluminum compound and the specific comonomer pair. In the presence of $AlEt_3$ under UV light, S-MA and S-MMA yield equimolar, alternating copolymers while MS-MA and MS-MMA yield little or no polymer. In the presence of EASC, S-MA and S-MMA yield alternating copolymers; S-MCA, MS-MA, and MS-MMA yield a mixture of alternating copolymer and cationic polymer; and MS-MCA yields cationic polymer only. In the presence of $AlCl_3$, S-MA and MS-MA yield both alternating and cationic polymers, and S-MMA and MS-MMA yield cationic polymer only.

TABLE 4. Copolymerization of α-Methylstyrene and Methyl Methacrylate

						Copolymer		
							Cyclohexane insoluble	
MS (mmoles)	MMA (mmoles)	MX (mmoles)	Catalysis	Temp (°C)/ Time (hr)	Conversion (%)	Cyclohexane soluble (wt%)	(wt%)	MMA (mole %)
		$AlEt_3$						
70	30	15	Thermal	30/60	0			
70	30	6	UV	25/7	0			
140	60	12	500-W light	5/1.5	0			
70	30	6	tBPP[a]	25/4	Traces			
		EASC						
125	125	12.5	Thermal	30/2.5	2.7	34	66	49.4
125	125	12.5	BP[a]	30/2	6.8	28	72	51.3
		$AlCl_3$						
140	60	3	Thermal	0/0.5	73.4	100	0	
50	50	25	tBPP[a]	-78/0.5	34.6	100	0	
65	65	32	tBPP[b]	-78/4	43.4	100	0	

[a] 1 mmole peroxide added at 0 hr.

[b] 1 mmole tBPP added at 0 and 2 hr.

TABLE 5. Copolymerization of Methyl α-Chloroacrylate with Styrene (S) and α-Methylstyrene (MS)

				Copolymer			
						Cyclohexane insoluble	
Donor (mmoles)	MCA (mmoles)	EASC (mmoles)	Temp (°C)/ Time (hr)	Conversion (%)	Cyclohexane soluble (wt%)	(wt%)	MCA (mole %)
S, 50	50	8	10/3	16.0	20	80	51.0
MS, 50	50	8	10/3	11.9	99	1	

Tacticities of Copolymers

The stereochemistry of the polymers resulting from the polymerization of various acrylic and methacrylic esters with different initiator systems has been intensively investigated [15]. The nature of the α-substituent as well as the ester alkyl group have a significant effect on the product of radical polymerization. Thus, whereas the syndiotacticity of poly(methyl methacrylate) [16] and poly(methyl α-chloroacrylate) [17] increased with decreased polymerization temperature, the stereoregularity of poly(methyl acrylate) [18] showed no such temperature dependence. In the radical polymerization of a series of methacrylic esters, the increased bulkiness of the alkyl group resulted in the formation of a less syndiotactic polymer and significant deviations from Bernouilian statistics [15]. The microstructure of a number of copolymers derived from styrenes and acrylic esters have been reported from high resolution NMR studies [19]. Excellent agreement has been obtained between the observed and calculated triad and pentad sequence distributions [20, 21].

The homopolymerization of metal halide complexed methyl methacrylate and the tacticities of the resulting polymers have been investigated in some detail [22, 23]. In general, the tacticities of the polymers from the complexes were different from those obtained by radical polymerization of the uncomplexed monomer. The tacticity was fairly independent of the polymerization temperature and depended on the nature of the metal halide and the composition of the complex. Attempts to correlate the tacticities with the bulkiness and the stability of the complex and the viscosity of the medium have not been successful.

The cotactic sequence distributions in the alternating S-MMA copolymers prepared from MMA complexed with various metal halides have been reported [9, 10, 14, 24]. In most cases the distribution was random and the I, H, and S fractions were approximately in the ratio 1:2:1. However, under certain conditions the copolymers had preferred cotactic distributions. Thus the use of $SnCl_4$ [14] or $ZnCl_2$ at MMA/$ZnCl_2$ ratios of 3-10 [10] resulted in copolymers having a significantly smaller coisotactic fraction. Similarly, the copolymerization of a 1:1 MMA. . . $ZnCl_2$ complex with styrene resulted in a copolymer richer in coisotacticity than that obtained with a 2:1 MMA. . . $ZnCl_2$ complex. Such differences in behavior have been attributed to the structure of the MMA. . . $ZnCl_2$ complex.

Table 6 summarizes the cotactic distributions of the S-MA, S-MMA, MS-MA, MS-MMA and S-MCA alternating copolymers prepared in the presence of different metal halides. The NMR spectra of S-MA, S-MMA, MS-MA, and MS-MMA alternating copolymers prepared in the presence of EASC are shown in Fig. 1.

The cotacticities of the alternating S-MA copolymers prepared in the presence of EASC and $AlCl_3$ are the same, indicating that there is no

TABLE 6. Relative Tacticities of Alternating Copolymers

Copolymer	MX	Reaction conditions	Cotacticity S	H	I	Ref.
S-MA	EASC	25°C	22	51	27	
	$AlCl_3$	-78°C, tBPP	25	50	25	
S-MMA	$AlEt_3$	5°C, 500 W	23	39	38	
		25°C, UV	24	34	42	
	EASC	25°C	22	44	34	
		25°C, BP	24	46	30	
		30°C, AIBN	25	47	28	
	$AlCl_3$	-75°C, UV	20	44	36	14
	$ZnCl_2$	30°C	28	44	28	9
		30°C	24	46	30	24
		30°C, BP	23	47	30	24
	$SnCl_4$	-78°C, UV	39	54	7	24
		-75°C, UV	34	57	9	14
	BF_3	-75°C, UV	26	40	34	14
MS-MA	EASC	30°C	33	42	25	
	$AlCl_3$	-78°C, tBPP	39	34	27	
MS-MMA	EASC	30°C	53	39	8	
S-MCA	EASC	10°C	30	53	17	

effect of the degree of chlorine substitution in the aluminum compound. In the S-MMA series, the cotacticities of the polymers prepared in the presence of the various aluminum compounds are more or less the same except that the copolymer prepared in the presence of $AlEt_3$ has a slightly higher coisotactic triad fraction. It also appears that the presence of radical catalysts such as AIBN or benzoyl peroxide does not influence the cotactic distribution.

The metal halides BF_3, $AlCl_3$, and $ZnCl_2$ behave in a similar manner. However, when $SnCl_4$ is used as the metal halide, the copolymer has a significantly lower coisotactic fraction suggesting a preference for cosyndiotactic propagation. Spectroscopic studies of the formation of the S-MMA. . . $SnCl_4$ complex indicate that MMA is

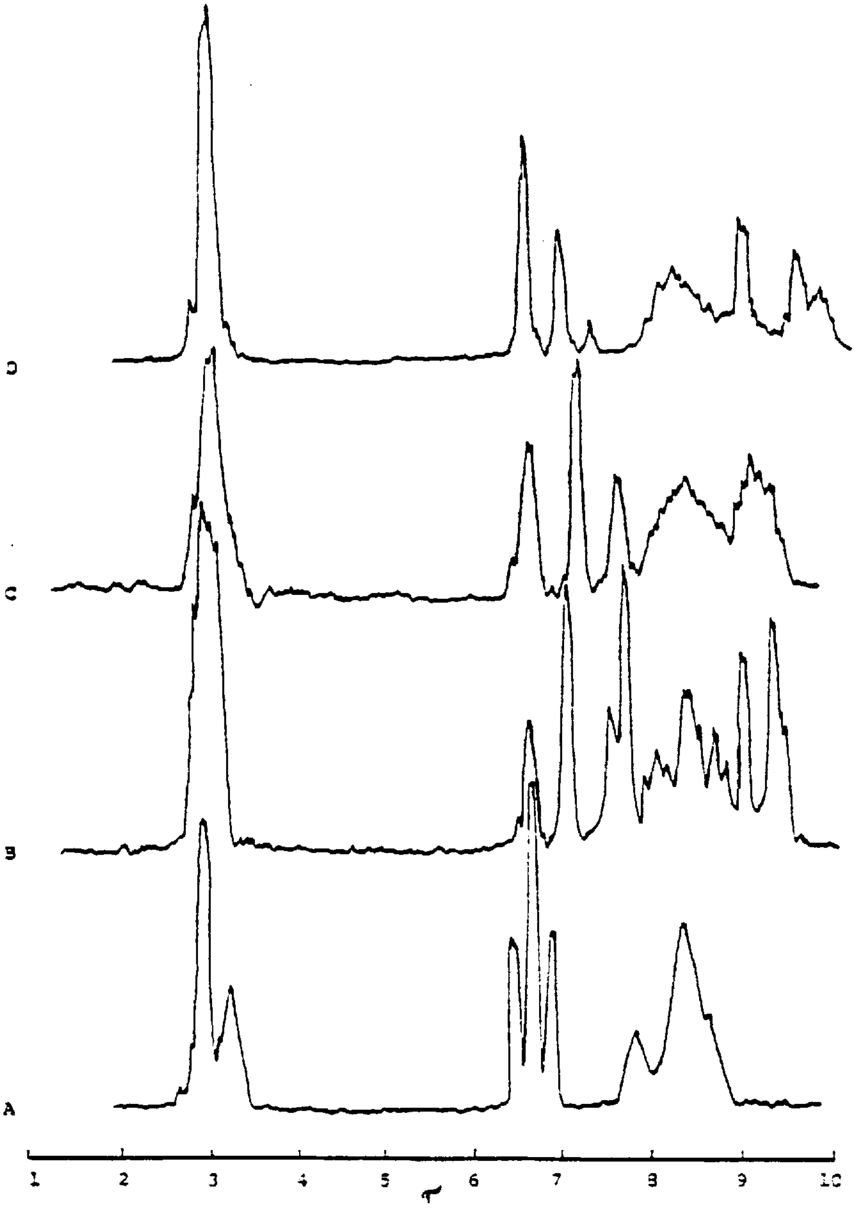

FIG. 1. NMR spectra of (A) S-MA, (B) S-MMA, (C) MS-MA, and (D) MS-MMA alternating copolymers prepared in the presence of EASC.

complexed to $SnCl_4$ via the carbonyl oxygen and that the complexation of styrene occurs at the MMA unit [25, 26]. Similar conclusions have also been reached from NMR studies of the benzene-MMA . . . $EtAlCl_2$ system [27]. NMR studies of the S-MMA . . . $SnCl_4$ system indicate that the carbomethoxy and the cis vinyl protons of the complexed MA monomer are considerably shielded by the aromatic ring. The participation of a second styrene unit, i.e., formation of 2:1:1 S-MMA-$SnCl_4$ complex, is also indicated from the spectral data.

The tacticity does not appear to be dependent upon the relative acid strength of the metal halide since the relative order is $BF_3 > AlCl_3 > SnCl_4 > ZnCl_2$ [28]. This is also reflected in the copolymers prepared in the presence of the various aluminum compounds since copolymers of the same tacticity were obtained although $AlCl_3$ > EASC > $AlEt_3$.

Similarly, the relative donor and acceptor strengths of the monomers do not appear to control the cotacticity in the copolymers. The relative monomer acceptor strengths are MCA > MA > MMA and the monomer donor strengths are MS > S. Thus, whereas the alternating MS-MMA copolymer was much more cosyndiotactic than the alternating MS-MA copolymer, the S-MCA copolymer was more cosyndiotactic than the S-MA copolymer.

It is possible that the bulkiness of the metal halide contributes toward the larger cosyndiotactic fraction in the S-MMA copolymer prepared in the presence of $SnCl_4$. The contributions of such steric factors associated with the structure of the donor-acceptor complex is also evident in the cotacticity distributions in the α-methylstyrene copolymers. Thus the cosyndiotactic fractions in the alternating MS-MA and MS-MMA copolymers prepared in the presence of EASC are 0.39 and 0.53, respectively, which are considerably higher than that observed with the S-MA and S-MMA copolymers (ca. 0.25) prepared under similar conditions. This observation is also supported from a comparison of the cosyndiotactic fractions obtained in S-MA (0.25) and S-MCA (0.30) where chlorine substitution at the α-position of methyl acrylate contributes to the increase in the cosyndiotactic fraction and the decrease in the coisotactic fraction, the coheterotactic fraction being almost unchanged. Thus the steric factors that influence the structure of the donor-acceptor complex are responsible for the cotacticity distribution in the alternating copolymer.

It is thus evident that both steric and polar factors derived from the comonomer pair determine the reactivity and the nature of the product in the polymerization of the DA complex. Steric factors based on the substituents in the comonomer pair appear to determine the cotacticity distribution of the copolymers.

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