References and Notes

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Electron-Deficient Trisubstituted Olefins. A New Class of Reactive Comonomers

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ABSTRACT: Four electron-deficient trisubstituted ethylenes, tricyanoethylene (**5**), ethyl 2,3-dicyanoacrylate (**7**), dimethyl 1-cyano-1,2-ethylenedicarboxylate (**10**), and trimethyl ethylenetricarboxylate (**13**), copolymerized readily with monosubstituted electron-rich vinyl monomers under free-radical conditions. Monomer **13** was actually more reactive than methyl acrylate in copolymerization with styrene. Copolymer compositions were approximately 1:1. Best yields and molecular weights were obtained from **10** and **13**; side reactions presumably involving electron transfer caused lower yields and molecular weights from the extremely electrophilic **5** and **7**. Also, **10** and **13** gave alternating copolymers with *N*-vinylcarbazole, whereas **5** and **7** induced its cationic homopolymerization. In general, the most electron-rich comonomers gave highest yields, molecular weights, and rates of copolymerization. Electron-poor vinyl compounds such as methyl methacrylate did not copolymerize with the trisubstituted ethylenes. For steric reasons, no homopolymerizations or copolymerizations with electron-rich disubstituted olefins occurred. Charge-transfer complexes and spontaneous initiation were observed in many of these reactions. The copolymers exist as brittle glasses possessing high T_g values owing to conformational immobility and dipolar repulsion.

1,1-Disubstituted ethylenes are generally more reactive in free-radical polymerization than the monosubstituted olefins.[1,2] The intermediate radical is stabilized by resonance interaction with both substituents. Steric effects are not evident in reactivity, although they make themselves felt in low ceiling temperatures for the resulting polymers.

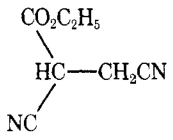
1,2-Disubstituted olefins, on the other hand, are markedly less reactive than the monosubstituted derivative. The β substituent gives no resonance stabilization and sterically hinders the attacking radical. Homopolymerization of 1,2-disubstituted olefins is difficult at best, and often impossible.[1,3] Their copolymerization is possible in two ways, however. A 1,2-disubstituted monomer will form random copolymers with a comonomer of similar polarity. As an example, dimethyl fumarate copolymerizes randomly with electron-deficient vinyl chloride.[4] On the other hand, comonomers of opposite polarity tend to give 1:1 alternating copolymers. Electron-poor maleic anhydride and electron-rich styrene give an altering copolymer.[5] Even a pair of 1,2-disubstituted monomers can copolymerize if they are of large, opposite polarities; the well-known copolymerization of maleic anhydride and stilbene is one example.[6] Polar interaction in the transition state overcomes the steric strain.

Few experimental investigations concerning the polymerization of trisubstituted olefins have been reported. This may reflect a belief that the steric effects encountered in the 1,2-disubstituted olefins would be worse for trisubstituted olefins. However, this should not be the case. The third substituent, located at the radical site, provides extra stabilization in the transition state, without any additional steric hindrance. Morever, if electron-withdrawing substituents such as cyano or carbomethoxy are involved, the extremely electron deficient double bond should be very susceptible to attack by electron-rich radicals. This analysis indicates that trisubstituted, electron-deficient olefins should copolymerize readily with electron-rich monomers to give alternating copolymers.

The small amount of data which we have found in the literature supports the view that a trisubstituted olefin can act as a free-radical monomer. Studies of the reactivity of several free radicals with the various chloroethylenes[7–9] indicated that trichloroethylene was as reactive toward an electron-rich polystyryl radical as was vinyl chloride (Table I). 1,1-Dicyano-2-phenylethylene and ethyl 1-cyano-2-phenylacrylate were more reactive toward styrene radicals than was *trans*-cinnamonitrile.[10]

In small amounts, these same compounds have also been shown to copolymerize with acrylonitrile,[11] as has α-cyanocinnamamide.[12]

Trisubstituted olefins carrying cyano and carboalkoxy groups are very electron-poor olefins which should copolymerize with electron-rich comonomers, leading to alternating copolymers with interesting and potentially useful properties. The first paper in this series briefly examined the copolymerization of tricyanoethylene (**5**) and ethyl 2,3-dicyanoacrylate (**7**) with styrene.[13] In this paper we have broadened this study to two other trisubstituted olefins, dimethyl 1-cyano-1,2-ethylenedicarboxylate (**10**) and trimethyl ethylenetricarboxylate (**13**), and to a wide variety of comonomers.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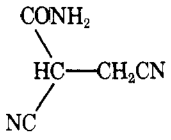
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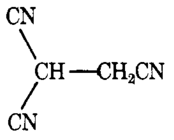
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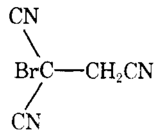
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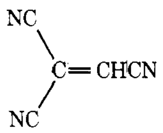
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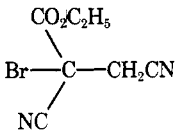
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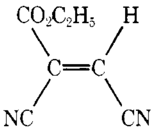
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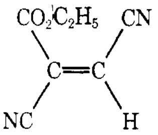
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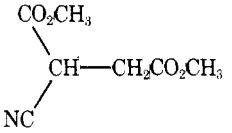
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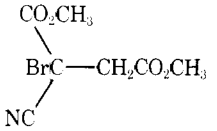
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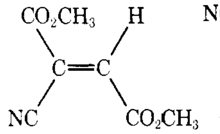
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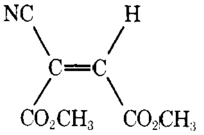
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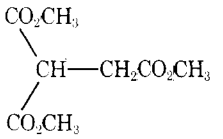
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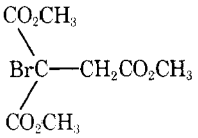
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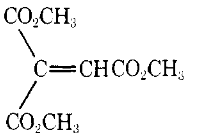
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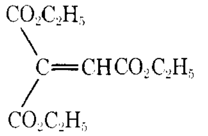
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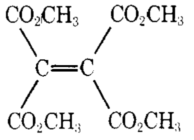
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Results

The trisubstituted ethylenes **5**, **7**, **10**, and **13** were synthesized by conventional alkylations of malonic or cyanoacetic esters, halogenation, and dehydrohalogenation, as described in the Experimental Section.

Copolymerizations with Electron-Rich Monosubstituted Comonomers. Tricyanoethylene. In the absence of solvent, **5** formed copolymers with *p*-methoxystyrene, *p*-methylstyrene, styrene, *p*-bromostyrene, and *p*-chlorostyrene. Red-brown solutions formed when the colorless monomers were mixed. AIBN caused copolymerization in 10–20 min at 72°. Colored low molecular weight impurities could be removed by dissolving the polymers in dimethylformamide and precipitating into methanol. Styrene copolymers could be prepared in acetonitrile and acetic acid but the polymers were inferior to the materials formed in bulk; solution polymerizations in benzene, acetonitrile, and tetramethylene sulfone of the styrene comonomers gave low yields of very low molecular weight copolymer or no copolymer at all (Table II). The compositions of the copolymers, determined from the elemental analysis, were approximately 1:1 in all cases.

Ethyl 2,3-Dicyanoacrylate. Monomer **7** was also active under free-radical initiation. Copolymers could be formed with the previously mentioned substituted styrenes, as well as with *p*-phenylstyrene and *p*-fluorostyrene (Table III). In this case the orange solutions formed by mixing the monomers either in the absence of solvent or in acetonitrile led in the presence of free radicals to copolymer formation.

These copolymers were obtained in better yields and with higher viscosities than the corresponding copolymers of **5**, and the composition by elemental analysis was 1:1.

Table I
Relative Reactivity of Chloroethylenes[a]

	Radical		
Olefin	Acrylonitrile	Vinyl acetate	Styrene
Vinyl chloride	1.0	1.0	1.0
Vinylidene chloride	3.6	10	9.2
cis-1,2-Dichloroethylene		0.05	0.08
trans-1,2-Dichloroethylene		0.3	0.46
Trichloroethylene	0.05	0.45	1.0
Tetrachloroethylene	0.007	0.04	0.09

[a] References 7-9.

Dimethyl 1-Cyano-1,2-ethylenedicarboxylate. *p*-Methoxystyrene and *p*-methylstyrene reacted immediately and exothermically with **10** to give initially deep yellow-orange solutions and then colorless clear glasses within 3 and 15 min, respectively, of mixing. These spontaneous reactions led to copolymers in essentially quantitative yields and high inherent viscosities (Table IV). Another spontaneous copolymerization occurred when *N*-vinylcarbazole was mixed with **10**. In this case, both monomers are solids, the polymerization was not homogeneous, and the copolymer was obtained in low yield.

Styrene and **10** did not spontaneously (thermally) copolymerize at room temperature in the dark or at 40° but did so at 65°.

Spontaneous bulk polymerizations with less reactive monomers did not occur; AIBN was required. Under these conditions high molecular weight copolymers were obtained with *p*-fluoro-, *p*-chloro-, *p*-bromo-, and *p*-phenylstyrenes.

Radical initiators were required for solution copolymerizations of even the most reactive comonomers, though colored complexes could still be observed. The speed of copolymerization depended on the substituent on styrene. Using *p*-methoxystyrene as the comonomer the polymerization solution became rigid in approximately 5 min; styrene took almost 20 min, and *p*-chlorostyrene had not become rigid after 3 hr. Tetramethylene sulfone was the best solvent for these copolymerizations; acetonitrile and acetic acid were also satisfactory. It was noteworthy that solution copolymerization of *N*-vinylcarbazole with **10** formed an alternating copolymer, whereas monomers **5** and **7** (above) had given only homopolyvinylcarbazole. It is also of interest that our alternating copolymer of **10** (and of **13** (see below)) with *N*-vinylcarbazole is only the second reported example of alternating *N*-vinylcarbazole copolymers. Dimethyl fumarate and fumaronitrile give copolymers with *N*-vinylcarbazole in benzene at 60–80° using AIBN as an initiator.[14,15] Copolymers of this comonomer are rare due to its propensity to polymerize cationically, as seen with **5** and **7**.

A few photochemical initiations were carried out. Photoirradiation of a mixture of styrene and **10** at −78 and −30° did not produce copolymer but did so at 0°. The 1:1 copolymer of **10** and *N*-vinylcarbazole formed on irradiation of a solution of the monomers in acetonitrile.

Vinyl acetate, whose electronic condition is ambiguous, copolymerized with **10** to give copolymers containing a large excess of vinyl acetate units. Except for vinyl acetate, all copolymers of **10** formed in high yields and high inherent viscosities. Elemental and nmr analysis showed the co-

Table II
Tricyanoethylene (5) Copolymers[a]

Comonomer	Initiation[b]	Solvent[c]	Conversion, %	η_{inh}[d]	C	H	N	O	X	Composition, 5-Co.
					Elemental composition,[e] %					
$C_6H_5CH{=}CH_2$	I		59	0.42	76.76	3.98	19.26			1:1.13
					(75.35)	(4.38)	(20.28)			
	I	$TMSO_2$	No polymer							
	I	CH_3CN	No polymer							
	I	CH_3CO_2H	65	0.27	76.38	4.88	19.74			1:1.08
	II		55	0.37	76.14	4.28	19.58			1:1.05
p-$CH_3OC_6H_4$-$CH{=}CH_2$	II		60	0.41	71.67	4.25	17.21	6.87		1:1.07
					(70.87)	(4.67)	(17.71)	(6.74)		
p-$CH_3C_6H_4$-$CH{=}CH_2$	II		32	0.25	77.02	4.86	18.12			1:1.11
					(76.00)	(5.01)	(19.00)			
p-BrC_6H_4-$CH{=}CH_2$	II		35	0.12	54.73	2.67	13.93		28.67	1:1.09
					(54.57)	(2.82)	(14.69)		(27.93)	
p-ClC_6H_4-$CH{=}CH_2$	II		25	0.09	64.90	3.50	16.50		15.10	1:1.10
					(64.61)	(3.33)	(17.39)		(14.67)	
N-Vinylcarbazole					86.80	5.70	7.50			Homopoly NVK, spontaneous
					(77.02)	(4.08)	(18.90)			
		C_6H_6			86.84	5.71	7.45			Homopoly NVK, spontaneous

[a] Polymerization feed in 1:1, 5 mmol of 5 and 5 mmol of comonomer. [b] Initiation I: AIBN (0.005 g), 72°, 24 hr. Initiation II: AIBN (0.005 g), 40°, photoirradiation for 24 hr. [c] Solvent volume in 5 ml. [d] Viscosities were performed in DMF at 30° at a concentration of 0.5 g of polymer in 100 ml of solution. [e] Numbers in parentheses are the theoretical elemental analysis for a 1:1 copolymer.

Table III
Ethyl 2,3-Dicyanoacrylate (7) Copolymers

Comonomer	Feed,[a] 7-Co.	Initiation[b]	Solvent[c]	Conversion, %	η_{inh}[d]	C	H	N	O	X	Composition, 7-Co.
						Elemental analysis,[e] %					
$C_6H_5CH{=}CH_2$	1:1	I		62	0.40	70.68	5.50	10.99	12.83		1:1
						(70.85)	(5.55)	(11.01)	(12.58)		
	2:1	I		52		70.72	5.55	11.22	12.51		1:1
	1:2	I		85		76.77	6.08	7.97	9.18		1:1.65
	1:1	I	$TMSO_2$	No polymer							
	1:1	I	CH_3CN	67	0.41	70.75	5.54	11.10	12.61		1:1
	1:1	II	CH_3CN	47	0.24	70.64	5.52	11.05	12.79		1:1
p-$CH_3C_6H_4CH{=}CH_2$	1:1	II	CH_3CN	70	0.37	71.84	6.19	10.19	11.88		1:1
						(71.62)	(6.01)	(10.44)	(11.93)		
p-$CH_3OC_6H_4CH{=}CH_2$	1:1	I	CH_3CN	63	0.48	67.80	5.47	9.49	17.14		1:1
						(67.59)	(5.67)	(9.85)	(16.88)		
	1:1	I		48	0.42	67.61	5.63	(9.60	17.16		1:1
p-$ClC_6H_4CH{=}CH_2$	1:1	I		64	0.34	62.59	4.47	9.51	11.34	12.09	1:1
						(62.40)	(4.54)	(9.70)	(11.08)	(12.28)	
p-$BrC_6H_4CH{=}CH_2$	1:1	I	CH_3CN	94	0.40	53.91	3.86	8.33	9.80	24.10	1:1
						(54.07)	(3.93)	(8.41)	(9.60)	(23.98)	
p-$FC_6H_4CH{=}CH_2$	1:1	I	CH_3CN	89	0.23	65.90	4.98	9.77	11.81	7.54	1:1.1
						(66.17)	(4.81)	(10.79)	(11.75)	(6.98)	
p-$C_6H_5C_6H_4CH{=}CH_2$	1:1	I	CH_3CN	85	gel	76.58	5.69	8.08	9.65		1:1
						(76.35)	(5.49)	(8.48)	(9.69)		
2,5-$Cl_2C_6H_3CH{=}CH_2$	1:1	I	CH_3CN	65	0.30	56.15	3.88	8.49	9.44	22.04	1:1
						(55.75)	(3.74)	(8.67)	(9.90)	(21.94)	

[a] A 1:1 feed means 5 mmol of 7 and 5 mmol of comonomer. A 2:1 feed means 10 mmol of 7 and 5 mmol of comonomer. A 1:2 feed means 5 mmol of 7 and 10 mmol of comonomer. [b] Initiation I: AIBN (0.005 g) at 72° for 24 hr. Initiation II: AIBN (0.005 g) at 40° under photoirradiation for 24 hr. [c] Solvent volume was 5 ml. [d] Viscosities were performed in DMF at 30° at a concentration of 0.5 g of polymer in 100 ml of solution. [e] Numbers in parentheses are the theoretical elemental analysis for a 1:1 copolymer.

polymers to be 1:1 in composition and are alternating. Examination of the aromatic region of the styrene copolymer spectra shows no shoulder at τ 3.78 which would have corresponded to a block of polystyrene. Failure of the trisubstituted ethylenes to homopolymerize (see below) also required that a 1:1 copolymer be alternating.

Trimethyl Ethylenetricarboxylate. No spontaneous copolymerizations were observed with **13.** In bulk, AIBN

Table IV
Dimethyl 1-Cyano-1,2-ethylenedicarboxylate (10) Copolymers

Comonomer	Feed,[a] 10-Co.	Initiation[b]	Solvent[c]	Conversion, %	η_{inh}[d]	Elemental analysis,[e] %					Composition, 10-Co.
						C	H	N	O	X	
$C_6H_5CH{=}CH_2$	1:1	I		80	0.81	65.80	5.48	4.99	23.73		1:1
						(65.92)	(5.59)	(5.13)	(23.42)		
	1:1	II		65	0.65	65.99	5.52	5.02	23.46		1:1
	2:1	I		58		65.02	5.48	4.84	24.66		1.04:1
	1:2	I		73		70.69	5.98	3.74	19.86		1:1.60
	1:1	I	$TMSO_2$	100	2.12	65.76	5.32	4.87	24.05		1:1
	2:1	I	$TMSO_2$	63		65.10	5.82	4.79	24.19		1:1
	1:2	I	$TMSO_2$	81		70.82	6.03	3.70	19.45		1:1.65
	1:1	I	CH_3CN	93	0.80	66.16	5.42	5.00	23.52		1:1
	1:1	I	$C_6H_5CH_3$	86	1.14	65.62	5.78	5.04	23.56		1:1
p-$CH_3OC_6H_5CH{=}CH_2$	1:1			92	1.55	63.26	5.71	4.52	26.51		1:1 spontaneous
						(63.36)	(5.65)	(4.62)	(26.37)		
	2:1			60		62.22	5.38	4.74	27.66		1.04:1 spontaneous
	1:2			87		66.68	5.63	3.74	24.95		1:1.23 spontaneous
	1:1	I	$TMSO_2$	85	0.91	63.14	5.51	4.59	26.76		1:1
p-$ClC_6H_4CH{=}CH_2$	1:1	I		67	0.68	58.24	4.61	4.28	21.00	11.47	1:1
						(58.54)	(4.59)	(4.55)	(20.80)	(11.52)	
	1:1	I	$TMSO_2$	87	1.44	58.54	4.68	4.30	20.58	11.90	1:1.06
p-$BrC_6H_5CH{=}CH_2$	1:1	I		78	0.32	51.09	4.13	3.98	18.15	22.65	1:1
						(51.15)	(4.45)	(3.98)	(18.17)	(22.69)	
	1:1	I	$TMSO_2$	82	0.40	51.02	4.06	3.90	18.17	22.85	1:1
p-$CH_3C_6H_4CH{=}CH_2$	1:1			91	1.55	66.81	5.98	4.92	22.29		1:1 spontaneous
						(66.89)	(5.96)	(4.88)	(22.27)		
	1:1	I	$TMSO_2$	97	1.27	66.68	5.99	4.64	22.69		1:1
p-$FC_6H_4CH{=}CH_2$	1:1	I		87	0.89	60.82	4.70	4.98	22.47	7.03	1:1.1
						(61.85)	(4.85)	(4.81)	(21.97)	(6.52)	
	1:1	I	$TMSO_2$	95	0.97	61.65	4.70	4.72	22.18	6.75	1:1
p-$C_6H_5C_6H_4CH{=}CH_2$	1:1	I	$TMSO_2$	77	gel	72.09	5.31	4.20	18.40		1:1
						(72.19)	(5.48)	(4.01)	(18.32)		
4-Vinylpyridine	1:1	I		No polymer							
	1:1	I	$TMSO_2$	No polymer							
N-Vinylcarbazole	1:1			20	0.12	70.11	5.10	7.64	17.15		1:1.06 spontaneous
						(69.60)	(5.01)	(7.73)	(17.66)		
	1:1	II	THF	79	0.18	69.43	5.07	7.69	17.81		1:1
Methyl vinyl ether	1:1	II	$TMSO_2$	54	0.41	51.02	6.17		42.81		1:1
						(50.77)	(6.20)		(43.04)		
Methyl vinyl sulfide	1:1	I	$TMSO_2$	21	0.25	54.13	6.70		25.79	13.38	1:1
						(54.08)	(6.60)		(26.20)	(13.12)	
Butadiene	1:1	I	$TMSO_2$	65							Rubbery, unable to purify
Vinyl acetate		I	$TMSO_2$	57	0.34	52.74	5.72	4.00	37.54		1:2
						(51.76)	(5.12)	(5.47)	(37.65)		

[a] 1:1 feed represents 0.005 mol of **10** and 0.005 mol of comonomer. A 2:1 feed represents 0.010 mol of **10** and 0.005 mol of comonomer. A 1:2 feed represents 0.005 mol of **10** and 0.010 mol of comonomer. [b] Initiation I: AIBN (0.005 g) at 72° for 24 hr. Initiation II: AIBN (0.005 g) at 40° under photoirradiation for 24 hr. [c] Solvent volume was 5 ml. [d] Viscosities were performed in chloroform at 30° at a concentration of 0.5 g of polymer in 100 ml of solution. [e] Numbers in parentheses are the theoretical elemental analysis for a 1:1 copolymer.

initiation produced copolymers of **13** with each of the substituted styrenes (Table V). The electron-rich styrenes, *p*-methoxy and *p*-methyl, gave 1:1 copolymer, but the less electron-rich styrenes formed copolymers containing an excess of the styrene. Again the rate of reaction was faster with more electron-rich styrenes.

Copolymers of **10** could be synthesized by radical copolymerization in solution with the various styrenes, as well as

Table V
Trimethyl Ethylenetricarboxylate (13) Copolymers

Comonomer	Feed[a] 13-Co.	Initiation[b]	Solvent[c]	Conversion, %	η_{inh}[d]	Elemental analysis,[e] %					Composition, 13-Co.
						C	H	N	O	X	
$C_6H_5CH=CH_2$	1:1	I		96	0.67	63.02	6.00		30.98		1:1
						(62.74)	(5.92)		(31.34)		
	2:1	I		52		62.79	5.85		31.36		1:1
	1:2	I		70		68.84	6.07		25.09		1:1.74
	1:1	I	$C_6H_5CH_3$	94	0.21	64.10	6.13		29.77		1:1.14
	1:1	I	CH_2Cl_2	80	0.32	64.05	6.00		29.95		1:1.13
	1:1	I	THF	47	0.15	64.25	5.98		29.79		1:1.15
	1:1	I	CH_3CN	94	0.20	64.45	5.97		29.58		1:1.17
	1:1	I	$TMSO_2$	99	0.70	64.07	6.14		29.79		1:1.14
	1:1	II	$C_6H_5CH_3$	71	0.55	64.22	6.15		29.63		1:1.15
	1:1	II		63	0.55	63.85	6.02		30.13		1:1.12
	1:1	III		55	0.79	66.78	5.98		27.24		1:1.44
p-$CH_3OC_6H_4CH=CH_2$	1:1	I		87	0.50	61.00	5.95		33.05		1:1
						(60.71)	(6.00)		(33.29)		
	1:1	I	$TMSO_2$	92	0.57	60.92	5.94		33.14		1:1
	2:1	I	$TMSO_2$	53		61.05	5.97		32.98		1:1
	1:2	I	$TMSO_2$	90		66.05	6.54		27.41		1:1.11
p-$CH_3OC_6H_4CH=CH_2$	1:1	II	$TMSO_2$	65	0.52	61.02	5.96		33.02		1:1.04
p-$CH_3C_6H_4CH=CH_2$	1:1	I	$TMSO_2$	72	0.26	63.52	6.47		30.01		1:1
						(63.74)	(6.29)		(29.97)		
p-$ClC_6H_4CH=CH_2$	1:1	I		70	0.40	58.42	4.99		24.59	12.00	1:1.3
						(56.40)	(5.03)		(28.17)	(10.40)	
	1:1	I	$TMSO_2$	73	0.45	58.40	5.00		24.58	12.02	1:1.3
	2:1	I		45		57.91	5.05		25.74	11.30	1:1.17
	1:2	I		52		59.35	5.02		21.69	13.94	1:1.77
p-$BrC_6H_4CH=CH_2$	1:1	I		55	0.20	50.37	4.32		22.21	23.12	1:1.25
						(49.89)	(4.45)		(24.92)	(20.74)	
	1:1	I	$TMSO_2$	55	0.25	50.47	4.51		21.52	23.50	1:1.28
p-$FC_6H_4CH=CH_2$	1:1	I	$TMSO_2$	56	0.31	61.47	5.80		25.86	6.89	1:1.33
						(59.08)	(5.27)		(29.51)	(5.84)	
p-$C_6H_5C_6H_4CH=CH_2$	1:1	I	$TMSO_2$	70	0.49	72.25	6.06		21.69		1:1.43
						(69.10)	(5.80)		(25.10)		
4-Vinylpyridine	1:1	I	$TMSO_2$	No polymer							
N-Vinylcarbazole	1:1	I		65		67.04	5.40	3.60	23.96		1:1
						(66.82)	(5.35)	(3.54)	(24.28)		
	1:1	II	CH_3CN	70	0.19	66.66	5.41	3.47	24.46		1:1
	2:1	II	CH_3CN	63		65.91	5.40	3.31	25.38		1.04:1
	1:2	II	CH_3CN	71		69.86	5.39	4.09	20.66		1:1.56
Methyl vinyl ether	1:1	II	$TMSO_2$	84	0.55	69.13	5.93		24.94		1:1
						(69.10)	(5.80)		(25.10)		
tert-Butyl vinyl ether	1:1	I		46	0.24	55.42	7.33		37.25		1:1
						(55.62)	(7.34)		(37.04)		
Methyl vinyl sulfide	1:1	I	$TMSO_2$	63	0.47	47.60	5.76		34.63	12.01	1:1
						(47.82)	(5.84)		(34.74)	(11.60)	
Vinyl acetate	1:1	I	$TMSO_2$	85	0.35	51.34	6.00		42.67		1:2.00
						(50.00)	(5.60)		(44.41)		
N-Vinylpyrrolidone	1:1	I	$TMSO_2$	65	0.35	53.82	6.15	4.23	35.80		1:1
						(53.67)	(6.11)	(4.47)	(35.75)		

[a] A feed of 1:1 represents 0.010 mol of **13** and 0.010 mol of comonomer. A feed of 2:1 represents 0.020 mol of **13** and 0.010 mol of comonomer. A feed of 1:2 represents 0.010 mol of **13** and 0.020 mol of comonomer. [b] Initiation I: AIBN (0.010 g) at 72° for 24 hr. Initiation II: AIBN (0.010 g) at 40° with photoirradiation for 24 hr. Initiation III: emulsion polymerization using AIBN (0.005 g) in 10 ml of 10% sodium laurylsulfate solution. [c] Solvent volume was 5 ml. [d] Viscosities were determined in chloroform at 30° at a concentration of 0.5 g of polymer in 100 ml of solution. [e] Numbers in parentheses are the theoretical elemental analysis of a 1:1 copolymer.

with methyl vinyl ether, *tert*-butyl vinyl ether, methyl vinyl sulfide, *N*-vinylcarbazole, and *N*-vinylpyrrolidone. Vinyl acetate copolymerized with **13** to yield copolymers rich in the former.

Copolymer yields and inherent viscosities were slightly lower than for **10**. Elemental and nmr analyses showed that all of the copolymers, except those of the electron-poor styrenes and vinyl acetate, were 1:1 and alternating.

Attempted Copolymerizations with Electron-Rich Disubstituted Olefins. No copolymers of **10** or **13** with electron-rich disubstituted olefins, including isopropenyl acetate, isobutene, α-methylstyrene, ketene diethyl acetal, *trans*-stilbene, and 1,1-diphenylethylene, were obtained.

Attempted Copolymerizations with Electron-Poor Olefins. None of the electron-poor monomers methyl acrylate, methyl methacrylate, acrylonitrile, methyl vinyl ketone, or vinyl bromide gave copolymers. In a few cases a small amount of homopolymers could be isolated.

Attempted Copolymerizations of Tetramethyl Ethylenetetracarboxylate. Monomer **15** did not copolymerize with *p*-methoxystyrene, styrene, *p*-chlorostyrene, and/or vinyl acetate.

Attempted Homopolymerization. None of the trisubstituted olefins **5, 7, 10,** or **13** nor the tetrasubstituted monomer **15** homopolymerized under free-radical initiation. Polymerization was unsuccessful in bulk and in solution. Neither BPO nor AIBN initiated polymerization after heating or uv irradiation. Initiation at −30° or at −70° using uv irradiation was also unsuccessful.

In another mode of initiation, a series of samples of styrene with these esters, but without AIBN, was photoirradiated at 40° for 48 hr. Copolymer was formed in high yield with **13** as comonomer but no polymer was formed from the other mixtures.

Physical Properties of Polymers. The high molecular weight copolymers such as **10**–styrene and **10**–*p*-methoxystyrene could be cast into films from chloroform solution. The films were brittle when the plasticizing solvent was removed. They were optically clear, colorless, and showed no crystallinity in a polarizing microscope. Attempts to orient the films at temperatures up to 270° were unsuccessful. The DSC of the **10**–styrene film showed no T_g to 300°; decomposition set in at 330°. Even on lower viscosity samples which were not filmforming, no T_g was observed to 250° where decomposition began.

The copolymers of **13** also showed no T_g. In an attempt to obtain a moldable polymer the triethyl ester **14** was prepared and copolymerized. The larger alkyl group should make for a more flexible copolymer. However, no T_g was observed for the **14**–styrene and **14**–*p*-methoxystyrene copolymers.

The **10** and **13** copolymers were soluble in chloroform, acetonitrile, and dimethyl sulfoxide. Copolymers of **7** were only slightly soluble in chloroform but dissolved readily in acetonitrile and dimethylformamide. Copolymers of **5** were soluble only in polar aprotic solvents such as dimethylformamide.

Discussion

Scope of the Copolymerizations. The electrophilic trisubstituted ethylenes **5, 7, 10,** and **13** described in the present work represent a new class of reactive comonomers. Trimethyl ethylenetricarboxylate (**13**) copolymerizes more rapidly than methyl acrylate with styrene. Such copolymerization, brought about by favorable polar interactions in the transition state, is expected to be general for their combinations with electron-rich, monosubstituted olefins.

The four monomers show different reactivities. Since cyano is a better electron withdrawing group than carbomethoxy, **5** is the most electrophilic, and therefore the most reactive monomer. However, **5** and also **7** are perhaps too reactive, and undergo side reactions which limit their polymerization abilities. These are thought to involve oligomerization through the cyano groups to form conjugated (-C=N-)$_x$ systems, and may be initiated by transient anion radicals. Experimentally, **10** produced the best copolymers at the highest rates, and **13** was almost as good.

The four monomers also differed in their abilities to copolymerize in various solvents. Monomer **5** could not be copolymerized in any nonprotolytic solvent; **7** was intermediate in behavior; **10** or **13** copolymerized in a variety of solvents including benzene, tetrahydrofuran, acetonitrile, and tetramethylene sulfone.

The more electron-rich comonomers copolymerized with the highest rates in all cases. Large steric effects can overcome favorable electronic effects. Even very electron-rich 1,1-disubstituted olefins such as α-methylstyrene or ketene diethyl acetal did not form copolymers with the trisubstituted olefins. The failure of *trans*-stilbene to form a copolymer with **13**, although it reacts readily with maleic anhydride, gave another indication of the steric requirements for copolymerization.

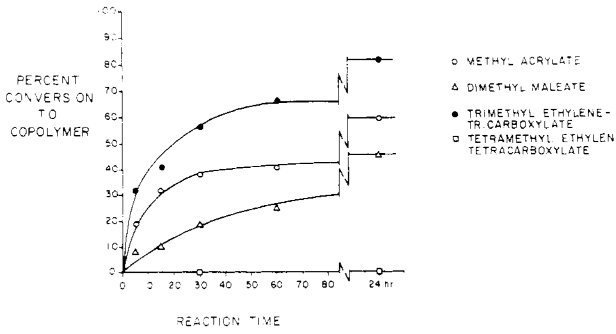


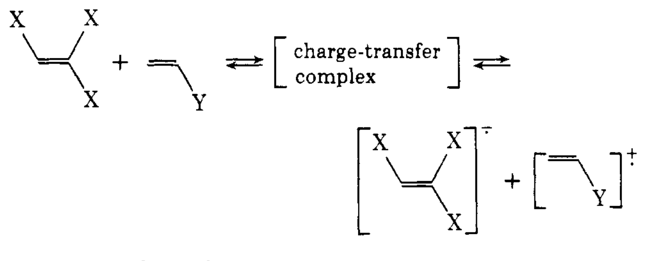
Figure 1.

Steric effects in the tetramethyl ester, **15**, were too large to allow copolymerizations even with reactive comonomers.

Finally, steric effects, uncompensated by favorable polar influences, prevented the homopolymerization of our monomers. No homopolymers were obtained at 70 or 90° using AIBN as an initiator. Low-temperature initiations with AIBN and light were run in an attempt to overcome possible low ceiling temperatures, but no polymers formed.

Mechanisms. The AIBN-initiated copolymerizations, either thermal or photolytic, appear to proceed by the conventional mechanism. Initiation consists of generation of radicals from AIBN by heat or light. Propagation involves successive addition of the growing radical to monomers in alternating sequence, as directed by strong polar influences in the transition state. We have no information concerning termination.

Charge-transfer complexes form during many of these copolymerizations, as shown by the occurrence and disappearance of bright colors during the reactions. In most cases they do not appear to be involved in the copolymerization mechanism. However, when very electron-rich olefins are involved, the charge-transfer complex can proceed on to complete electron transfer. That ion radicals are formed is indicated by several facts. Their occurrence would explain the spontaneous bulk copolymerizations observed for **10** and **13**. The presence of cation radicals is responsible for the homopolymerization of *N*-vinylcarbazole induced by **7** and **5**.[16,17] Finally, the permanent dark colors found in the reactions of tricyanoethylene could be caused by the formation of anion radicals (this monomer is exceptionally base sensitive). Use of acetic acid as solvent, which could protonate such anion radicals, gave significantly improved results.

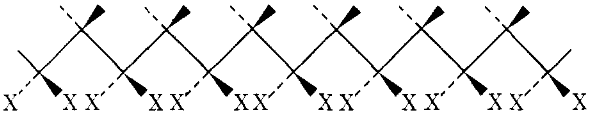


Copolymer Compositions. The copolymers resulting from these experiments were generally 1:1. Thus among the copolymers of **13** (Table V), electron-rich styrene gave 1:1 copolymers among the few marginal comonomers, electron-poor halostyrenes gave copolymers containing excess styrene, and vinyl acetate, more electron-deficient, gave copolymers containing still less **13**. Finally, extremely electron-poor comonomers such as methyl acrylate did not react with the triester **13**, or with the other electrophilic trisubstituted ethylenes.

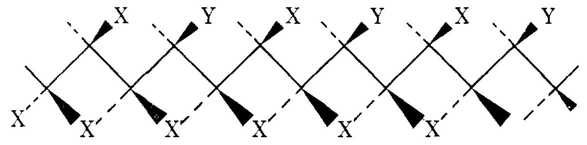
The 1:1 composition of the copolymers, along with inability of the trisubstituted ethylenes to homopolymerize, shows that the copolymers must be highly alternating in structure.

Our inability to mold these copolymers along with the lack of an observable T_g by differential scanning calorimetry indicates that these copolymers are extremely rigid glasses. High T_g's are caused by steric crowding and/or dipolar repulsions. Thus, the T_g's of poly(methyl acrylate), poly(methyl methacrylate), and poly(methyl α-cyanoacrylate) are 279, 378, and 440°K, respectively.[18] A second nonpolar substituent causes further interchain attraction and adopts a preferred orientation to minimize dipole interaction with chain companions.

Models indicate that our copolymers have fewer steric interactions than 1,1-disubstituted homopolymer. The threo diisotactic copolymer was chosen as a model because its steric strains are more severe than those of the erythro form and compared with the 1,1-disubstituted model. In the all-trans forms there are two 1,3-eclipsed interactions in the homopolymer but only one in the copolymer. The high T_g's indicated for our copolymers may therefore be attributed to the dipolar repulsions among the three ester groups.



homopolymer of a 1,1-disubstituted monomer



threo diisotactic copolymer (present work, one possible structure)

Conclusion

Electron-deficient trisubstituted olefins are a new class of reactive comonomer. Their copolymerization with monosubstituted electron-rich olefins to give rigid glassy materials is general. At present they have not been homopolymerized or copolymerized with electron-poor monomers or with 1,1-disubstituted electron-rich monomers.

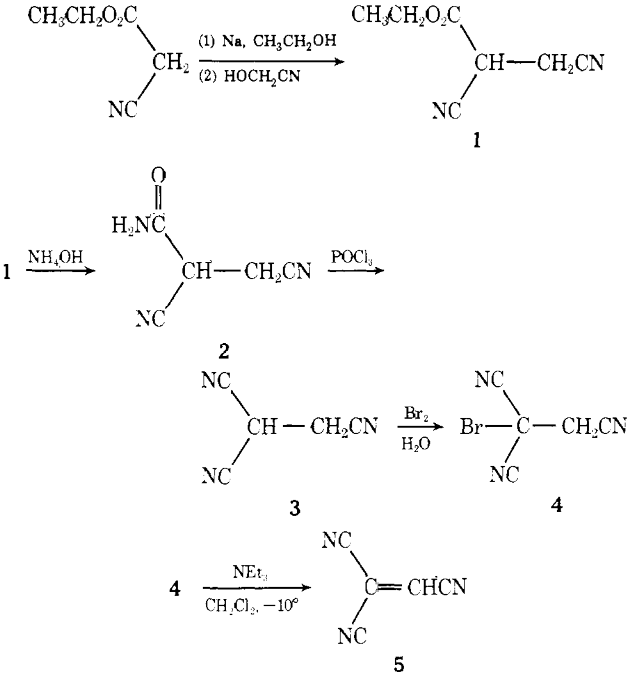
Study of these monomers is continuing.

Experimental Section

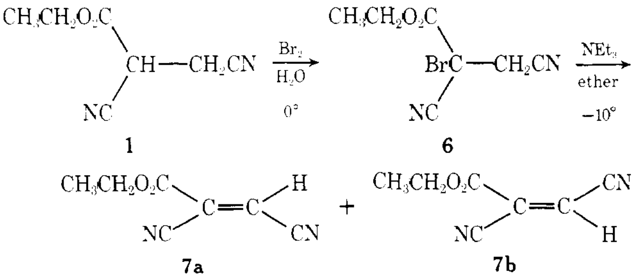
Instrumentation. Melting and boiling points are uncorrected. Melting points of intermediates and monomers were determined in capillaries. Infrared spectra were taken on a Perkin-Elmer 337 spectrophotometer and nmr spectra were obtained on a Varian T60. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E double focusing instrument. Thermal studies were performed on a Perkin-Elmer DSC 18. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Viscosities were run in $CHCl_3$ or DMF at 30° at a concentration of 0.5 g of polymer in 100 ml of solution. The purity of intermediates and monomers was checked on a Varian Aerograph 1700 gas chromatograph on the following columns: (1) 3% SE 30 80–100 mesh Chromosorb W, AW/DMCS HP, 5 ft × 0.25 in.; (2) 15% Fluorosilicon QF-1-0065 on 80–100 mesh Anakron SD, 5 ft × 0.25 in.

Solvents. *All of the polymerization solvents were fractionally distilled before use, degassed with argon, and then stored under argon. Toluene, chlorobenzene, and tetrahydrofuran were distilled from metallic sodium.* Tetramethylene sulfone was initially stirred over 3A molecular sieves and then distilled from calcium hydride. Acetonitrile was also distilled from calcium hydride.

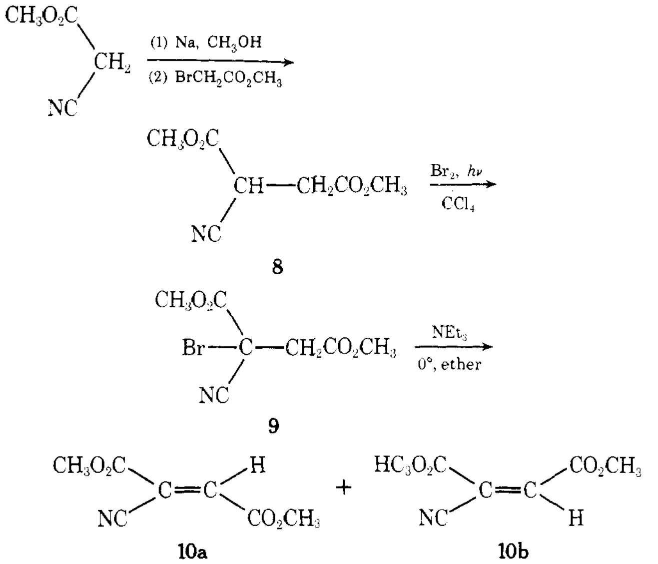
Tricyanoethylene. Monomer **5** was prepared by the method of Dickinson, Wiley, and McKusick[19] except for the final dehydrohalogenation which was run in dichloromethane at −10° in order to reduce the amount of product decomposition which occurred. Tricyanoethylene is sensitive to even catalytic amounts of base and care must be taken to avoid high local concentrations of base. Acid-washed equipment and storage vials should be used. Monomer purity material was obtained by melting the olefin at 65° (0.2 mm) and collecting the white crystals which formed on a cold finger. The process was repeated and the crystals, mp 39–40°, were stored under nitrogen at −78° until used.



Ethyl 2,3-Dicyanoacrylate. Monomer **7** was prepared by the method of Noren and Hall.[13] Dehydrohalogenation of **6** at −10° and distillation at 78–81° (0.1 mm) gave a distillate which at 0° solidified, mp 25–29°. This was approximately a 15:1 mixture of the two isomers, **7a** and **7b**. The assignment of **7a** as the predominent isomer was made from analysis of the nmr.[13-15] Recrystallization at −78° from ether gave what appears to be exclusively the cis isomer, **7a**, mp 30–32°.



Dimethyl 1-cyano-1,2-ethylenedicarboxylate (**10**) was synthesized in three steps starting with the condensation of methyl cyanoacetate with methyl bromoacetate.[20] It was necessary to use a molar excess of sodium and methyl cyanoacetate so that the monoalkylated product, **8**, *was formed in high yield rather than* the dialkylated product. This ethane was brominated under free-radical conditions to give the bromide **9**. The ionic bromination used to prepare **5** and **7** was not totally successful for **10** and was avoided. The dehydrohalogenation was again stereoselective and gave only a single isomer, **10a** or **10b**, in greater than 98% purity. Analysis of the nmr indicated that in all probability the fumarate, **10a**, *was the isomer formed.*[21-23]



8

9

10a

10b

Dimethyl Cyanosuccinate. One liter of anhydrous methanol was treated with 23 g (1.0 mol) of metallic sodium. The solution was cooled and 99 g (1.0 mol) of methyl cyanoacetate (Aldrich) was added. The pale yellow solution was cooled to 0° in an ice–salt bath. A second solution containing 76 g (0.5 mol) of methyl bromoacetate in 200 ml of absolute methanol was added slowly while the reaction temperature was maintained below 5°. The addition took about 1 hr.

Upon stirring overnight at room temperature, a dark purple solution resulted which was poured onto 1 kg of ice and water. Concentrated hydrochloric acid was added until the solution was acid to litmus. This aqueous solution was extracted with four 400-ml portions of methylene chloride. The combined organic phases were dried over $MgSO_4$ and decolorized with activated charcoal. The suspension was filtered to give a yellow solution and the methylene chloride was stripped away on the rotary evaporator. The orange oil remaining was distilled on a short-path apparatus and the material collected between 75 and 95° (0.12 mm) was redistilled on a spinning band column. The desired succinate, **8**, 50 g (58%), was obtained as a colorless liquid, bp 82–85° (0.13 mm): nmr ($CDCl_3$) τ 6.98 (d, 2 H), 6.21 (s, 3 H), 609 (s, 3 H), 5.98 (t, 1 H); ir (neat) 2940 (C–H), 2245 (m, $C\equiv N$), 1740 cm^{-1} (s, C=O); mass spectrum (70 eV) molecular ion *m/e* 171, calcd *m/e* 171.

Anal. Calcd for $C_7H_9NO_4$: C, 49.12; H, 5.30; N, 8.18; O, 37.39. Found C, 49.10; H, 5.25; N, 8.24; O, 37.41.

Dimethyl 1-Bromo-1-cyanosuccinate. Dimethyl cyanosuccinate (**8**) (17.1 g, 0.10 mol) was placed in 500 ml of carbon tetrachloride. The solution was stirred and 0.1 g of AIBN was added. Bromine (18 g, 0.11 mol) was added in small portions and irradiation was begun after the first addition. Other additions were made as the red-orange bromine color dissipated. Hydrogen bromide was evolved. Irradiation continued for another 2 hr. (Further irradiation caused the formation of another product which separated out of the carbon tetrachloride solution.) The carbon tetrachloride and excess bromine were stripped away to leave an organic oil which was the crude bromide, **9**, 19.5 g (80%): nmr ($CDCl_3$) τ 6.53 (d, 2 H), 6.24 (s, 3 H), 6.03 (s, 3 H); ir (neat) 3020 (m, C–H), 2975 cm^{-1} (s, C–H), 2250 (w, $C\equiv N$), 1750 cm^{-1} (s, ester C=O).

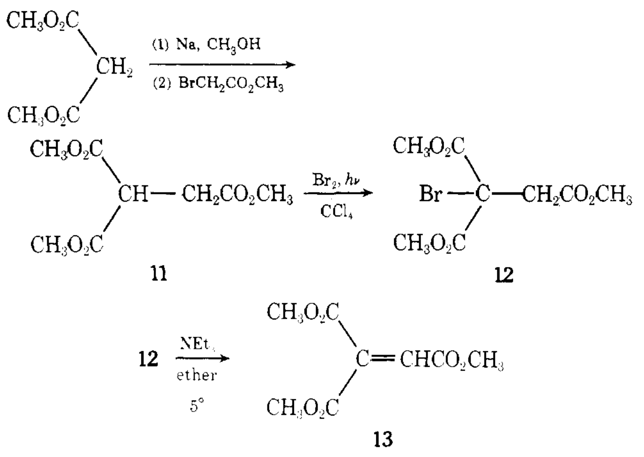
Dimethyl 1-Cyano-1,2-ethylenedicarboxylate. The crude bromide, **9** (17.9 g, 0.07 mol), was dissolved in 110 ml of anhydrous ether. The ether solution was cooled to 0° and stirred mechanically. Triethylamine (6.5 g, 0.065 mol) in 50 ml of ether was added dropwise to the bromide solution. The reaction temperature was maintained below 5° throughout the 1 hr addition. Cooled stirring continued for another hour. A pale orange precipitate formed immediately.

The cold ether solution was filtered to remove the triethylamine hydrobromide salts and the solid was washed with 100 ml of ether. The red-brown solution was concentrated to *ca.* 40 ml and then eluted through 35 g of acid alumina with ether. The ether was stripped away to leave a yellow oil which was distilled under vacuum, bp 82–86° (0.08 mm), 10.2 g (86%). The distillate solidified on cooling and was twice recrystallized from ether. The final product was 6.25 (51%) of a white crystalline solid, mp 59.0–60.5°.

The single isomer obtained appears from examination of the nmr to be the fumarate, **10a**, and this is substantiated by calculations using the characteristic shift assignments tabulated by Pascual, Meier, and Simon:[22] nmr ($CDCl_3$) τ 6.06 (s, 3 H), 6.83 (s, 3 H), 2.51 (s, 1 H); mass spectrum (70 eV) molecular ion *m/e* 169, calcd *m/e* 169; ir (neat) 3075 (w, C–H), 2970 (m, C–H), 2230 (w, $C\equiv N$), 1730 (5, ester C=O), 1635 cm^{-1} (m, C=C).

Anal. Calcd for $C_7H_7NO_2$: C, 49.71; H, 4.17; N, 8.28; O, 37.84. Found: C, 49.75; H, 4.10; N, 8.18; O, 37.97.

Trimethyl and Triethyl Ethylenetricarboxylates, 13 and 14. These monomers were synthesized as follows.



11

12

13

Trimethyl 1,1,2-Ethanetricarboxylate. A solution of sodium dimethyl malonate was prepared by adding 66 g (0.50 mol) of previously distilled dimethyl malonate (Aldrich) to 600 ml of absolute methanol containing 11.5 g (0.50 mol) of sodium. The resulting solution was cooled to 5°. A second solution containing 37.3 g (0.50 mol) of methyl chloroacetate (Matheson) dissolved in 150 ml of absolute methanol was added dropwise to the stirring malonate solution. The addition took approximately 1 hr and the pot temperature was maintained under 15°. A precipitate began to form after 2 hr. The system was stirred overnight at room temperature.

The resulting slurry was poured onto 600 g of ice and water. Hydrochloric acid was added until the solution was acidic. This aqueous solution was then saturated with potassium chloride and extracted with four 400-ml portions of ether. The combined layers were then backwashed with 100 ml of saturated potassium chloride solution and then dried over magnesium sulfate. The suspension was filtered and the ether evaporated.

The yellow organic residue was distilled through a short path apparatus and all materials boiling under 110° (0.11 mm) were collected and further fractionated on a spinning band. Fraction 2, bp 82–84° (0.23 mm), yielded 44.65 g (44%) of the desired trimethyl 1,1,2-ethylenetricarboxylate (**11**). The ester crystallied on cooling and a melting point of 34–35° was observed: nmr ($CDCl_3$) τ 6.17 (t, 1 H), 6.24 (s, 6 H), 6.34 (s, 3 H), 7.08 (d, 2 H); ir (neat 3005 (m, C–H), 2965 (s, C–H), 1750 cm^{-1} (s, ester C=O); mass spectrum (70 eV) molecular ion *m/e* 204, calcd *m/e* 204.

Anal. Calcd for $C_8H_{12}O_6$: C, 47.05; H, 5.93; O, 47.02. Found: C, 46.83, H, 5.93; O, 47.24.

Fraction 4, bp 101–104°C (0.11 mm), gave 20 g (40%) of the dialkylated product, tetramethyl 1,2,2,3-propanetetracarboxylate: nmr ($CDCl_3$) τ 6.27 (s, 6 H), 6.35 (s, 6 H), 6.83 (s, 4 H); mass spectrum (70 eV) molecular ion *m/e* 276.

Anal. Calcd for $C_{11}H_{16}O_8$: C, 47.82; H, 5.84; O, 6.34. Found: C, 47.97; H, 5.95; O, 46.08.

The desired triester may also be prepared in 40% yield under similar conditions using methyl bromoacetate rather than the chloroacetate.[20]

Trimethyl 1-Bromo-1,1,2-ethylenetricarboxylate. A solution containing 44.65 g (0.22 mol) of dimethyl 1,1,2-ethylenetricarboxylate (**11**) and 0.2 g of azobisisobutyronitrile in 400 ml of carbon tetrachloride was treated with 38 g (0.24 mol) of bromine. Irradiation with a sunlamp was begun with the first bromine addition. After a short induction period, hydrogen bromide began to evolve and the red bromine color dissipated to a bright yellow. Further addition followed each time the red color disappeared. Stirring and irradiation continued for 16 hr. (Addition of dilute bromine in carbon tetrachloride gave very erratic results.)

The carbon tetrachloride and excess bromine was stripped away on the rotary evaporator to leave 59 g (0.21 mol) of the crude bromide, 12, a viscous golden liquid. Gas chromatographic analysis indicated no residual starting material and the nmr indicated high purity. The material was used in this crude state as further purification attempts resulted in decomposition: nmr ($CDCl_3$) τ 6.20 (s, 6 H), 6.34 (s, 3 H), 6.58 (s, 2 H); ir (neat) 3005 (m, C–H), 2960 (s, C–H), 1750 cm^{-1} (s and b, ester C=O).

Trimethyl Ethylenetricarboxylate. The crude bromide, **12,** (59 g, 0.21 mol), was dissolved in 400 ml of dry ether and the solution cooled to 0° in an ice–salt bath. Triethylamine, 20 g (0.20 mol), previously distilled from P_2O_5, was dissolved in 150 ml of ether and added dropwise to the cold stirring bromide solution. Trimethylamine hydrobromide immediately began to precipitate. The amine was added slowly enough so that the temperature of the reaction vessel did not rise above 5°. Stirring and cooling was maintained for 12 hr more.

Water, 200 ml, was added to the reaction mixture in order to dissolve all of the salts and the two phases were separated. The aqueous layer was extracted with two 200-ml portions of ether and the combined organic phases were washed with 50 ml of distilled water and then dried over $MgSO_4$. The dry suspension was filtered and the ether evaporated away in order to give a viscous yellow oil.

This crude triester, **13,** was then distilled under vacuum through a short-path apparatus to give a single colorless fraction, bp 80–83° (0.3 mm), which solidified on standing, mp 37–40°. The solid was recrystallized from ether to give 29 g (65% from the ethane) of colorless crystals, mp 38–40°. Repeated recrystallization from ether gave a sample, mp 40–41°, suitable for analysis and polymerization: nmr ($CDCl_3$) τ 3.12 (s, 1 H), 6.12 (s, 3 H), 6.16 (s, 3 H), 6.21 (s, 3 H); ir (neat) 3005 and 2950 (m and s, C–H), 1740 (s, ester C=O), 1650 cm^{-1} (w, C=C); mass spectrum (70 eV) molecular ion *m/e* 202, calcd *m/e* 202.

Anal. Calcd for $C_8H_{10}O_6$: C, 47.51; H, 5.11; O, 49.16. Found: C, 47.45; H, 5.17; O, 49.16.

Triethyl Ethylenetricarboxylate. The triethyl ester, **14,** was prepared with exactly the same procedures as the preceding trimethyl ester except that the final product was not a solid at room temperature and had to be distilled repeatedly on a spinning band to obtain monomer grade material. The spectral and physical properties for the intermediates and monomer are as follows.

Triethyl 1,1,2-Ethanetricarboxylate: bp 100–104° (2.0 mm); nmr ($CDCl_3$) τ 5.80 (q 4 H), 5.86 (q, 2 H), 6.20 (t, 1 H), 7.12 (d, 2 H), 8.75 (t, 9 H); ir (neat) 2980 and 2940 (s and m, C–H), 1750 cm^{-1} (s, ester C=O); mass spectrum (70 eV) molecular ion *m/e* calcd 246.

Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37; O, 38.98. Found: C, 53.52; H, 7.40; O, 39.08.

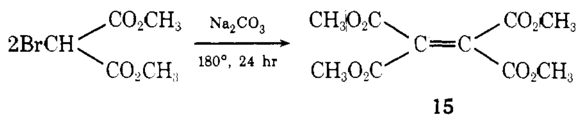
Triethyl 1-bromo-1,1,2-ethanetricarboxylate: nmr ($CDCl_3$) τ 5.71 (q, 4 H), 5.82 (q, 2 H), 6.58 (s, 2 H), 8.69 (t, 6 H), 8.74 (t, 3 H); ir (neat) 2990 and 2945 (s and m, C–H), 1745 cm^{-1} (s, ester C=O).

Triethyl ethylenetricarboxylate: bp 80–82° (0.20 mm); nmr ($CDCl_3$) τ 3.20 (s, 1), 5.75 (m, 6), 8.70 (t, 9); ir (neat) 2990 and 2945 (s and w, C–H), 1735 (s, ester C=O), 1645 cm^{-1} (w, C=C); mass spectrum (70 eV) molecular ion *m/e* 244, calcd *m/e* 244.

Anal. Calcd $C_{11}H_{16}O_6$: C, 54.09; H, 6.60; O, 39.31. Found: C, 54.19; H, 6.67; O, 39.14.

Tetramethyl Ethylenetetracarboxylate. The tetramethyl ester, **15,** was prepared analogously to the tetraethyl ester listed in Organic Syntheses.[24] The white crystalline solid, mp 118.5–119.5°, was recrystallized from an ether–ethyl acetate mixture. Spectral data are as follows: nmr ($CDCl_3$) τ 6.13 (s); ir ($CHCl_3$ solution) 2960 (m, C–H), 1750 cm^{-1} (s, ester C=O); mass spectrum (70 eV) Calcd *m/e* 260.

Anal. Calcd for $C_{10}H_{12}O_8$: C, 46.16; H, 4.65; O, 49.19. Found: C, 46.15; H, 4.64; O, 49.21.



$$2BrCH(CO_2CH_3)_2 \xrightarrow[180°,\ 24\ hr]{Na_2CO_3} (CH_3O_2C)_2C{=}C(CO_2CH_3)_2$$

15

Comonomers. Each of the substituted styrene comonomers (Aldrich) were passed through a basic Woelm alumina column and then distilled at appropriate pressures in a nitrogen atmosphere. The monomers were degassed and then stored at −20° under argon. The same procedure was used for α-methylstyrene, methyl vinyl sulfide, and 1,1-diphenylethylene. Isopropenyl acetate (Aldrich), vinyl acetate, vinyl bromide, methyl methacrylate, methyl acrylate, and acrylonitrile were distilled twice, taking the center cut each time. Methyl vinyl ether (Matheson) and isobutylene were used directly from the gas cylinder. *N*-Vinylcarbazole (Pfaltz and Bauer) was recrystallized three times from methanol and dried for 72 hr under vacuum. Zone-refined *trans*-stilbene (Aldrich) was used directly as obtained.

Sample Copolymerizations. Thermal Initiation. A typical copolymerization involved charging a 10-ml flask with 0.52 g (0.005 mol) of styrene and 0.85 g (0.005 mol) of dimethyl 1-cyano-1,2-ethylenedicarboxylate (**10**). Five milliliters of tetramethylene sulfone was added along with 0.005 g of AIBN. The sample was flushed with nitrogen and sealed. The polymerization vessel was placed in a heating bath at 72° for 24 hr.

A clear, colorless solid plug resulted which was dissolved in 10 ml of chloroform. The polymer solution was then added dropwise to 250 ml of methanol being churned in a Waring blender. A white polymer resulted which was ground in the blender and then collected on a sintered glass filter. The polymer was dried in a drying pistol under vacuum at 80° for 72 hr. The polymer, 1.32 g (96%), analyzed as a 1:1 composition and gave an inherent viscosity of 2.07 in chloroform at 30°.

Photoinitiation. For gaseous or very low-boiling conomers it was necessary to run the polymerizations in thick-walled, bottle-capped tubes which were photoirradiated. A thick-walled tube was charged with 2.02 g (0.01 mol) of trimethyl ethylenetricarboxylate (**13**), 0.005 g of AIBN, and 5 ml of tetramethylene sulfone. A magnetic stirrer was added and the bottle was capped. Holes in the metal cap allowed syringe needles to be inserted through the septum. The system was freed from oxygen through several freeze–thaw cycles under vacuum and then nitrogen. Finally the tube was flushed with nitrogen.

A small, graduated gas trap containing a boiling chip was attached to the cylinder of methyl vinyl ether. The trap was placed in a Dry Ice–acetone bath while being flushed with nitrogen. The methyl vinyl ether cylinder was opened and the ether was condensed into the trap. The cylinder was closed after 3 ml of the ether had been collected.

The trap was then connected to the tared polymerization tube. The tube was cooled in a Dry Ice–acetone bath. The cooling bath around the trap was lowered, allowing the methyl vinyl ether to distill into the polymerization tube. After 1.5 ml of ether has distilled out of the trap the needles were removed from the tube. The outside of the polymer tube was then cleaned and allowed to return to room temperature. Weighing the tube showed that 0.62 g (0.013 mol) of methyl vinyl ether had been added.

The sealed tube was then photoirradiated at 40° for 24 hr. At the end of this time the tube was cooled to −78° and opened. Ten milliliters of chloroform was added and after 2 hr the polymer had dissolved.

The chloroform solution was added dropwise to 200 ml of rapidly stirring hexane. The white polymer was collected on a sintered glass filter and reprecipitated from chloroform into hexane. The white polymer was dried at 40° for 8 days under vacuum. The polymer, 2.1 g (84%), had a viscosity of 0.55 in chloroform at 30° at a concentration of 0.5 g in 100 ml of solution.

Spontaneous Initiation. A small erlenmeyer flask was fitted with a magnetic stirrer and 1.34 g (0.01 mol) of *p*-methoxystyrene was added. Dimethyl 1-cyano-1,2-ethylenedicarboxylate (**10**) (1.69 g, 0.01 mol) was then poured into the *p*-methoxystyrene. As **10** dissolved an orange color formed and the polymerization mixture became hot. Within 1 min of addition all of the **10** had dissolved or melted and stirring was difficult. Within 3 min stirring had ceased and the polymer was a deformable glass. After 10 min the polymer was a hard, brittle, orange glass. The reaction was spontaneous in air or under nitrogen.

The glassy polymer was dissolved in 10 ml of chloroform and precipitated into 200 ml of methanol. The methanol suspension was stirred in a Waring blender. The polymer was collected on a sintered glass filter funnel and dried for 72 hr at 80°. The 1:1 alternating copolymer (2.73 g, 92%) has an inherent viscosity of 1.55 in chloroform at 30° at a concentration of 0.5 g in 100 ml of solution.

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Synthesis and Optical Properties of Asymmetric Polyamides Derived from Optically Active Dicarboxylic Acids and Spirodiamine

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ABSTRACT: Optically active polyamides derived from either (+)-(*S*)-*trans*-1,2-cyclopropanedicarboxylic acid [(+)-C3] or (+)- and (−)-*trans*-1,2-cyclohexanedicarboxylic acids [(+)- and (−)-C6] with 2,6-diazaspiro[3.3]heptane (DSH) were prepared by interfacial polycondensation reactions. Several model compounds, (±)-*trans*-2-methylcyclopropanecarboxylic acid azetidide (I), (+)-*trans*-cyclopropanedicarboxylic acid diazetidide (II), 2,6-di[(±)-*trans*-2-methylcyclopropanecarbonyl]-2,6-diazaspiro[3.3]heptane (III), IV, V, and (+)-*trans*-1,2-cyclohexanedicarboxylic acid dipiperidide (VI), were also made for studying the conformation of the polymers. The optical rotatory dispersion (ORD) and circular dichroism (CD) of these compounds indicated that the polyamide [(+)-C3 · DSH] and the model compounds, II, IV, and V, derived from (+)-C3 did not change their conformations in various solvents. Solvents used were 2,2,2-trifluoroethanol (TFE), water, methanesulfonic acid (MSA), and sulfuric acid. The conformation of the carbonyl groups of a cyclopropane ring in all compounds may be the same. Model compound VI may have a different conformation in strong acids and nonacidic solvents (water and TFE), whereas the polyamide (C6-DSH) derived from C6 showed no variance in conformation in the above solvent systems. Optically active and racemic polyamides derived from C6 and C6 had the same solution viscosities in TFE and in sulfuric acid. All polymers had melting points higher than 300°.

Poly(L-proline) is known to exist in two different regular forms in solution without hydrogen bonds, and extensive studies on this polymer have been done.[1] Theoretical calculations have attributed the cause of the regularity of poly(L-proline) mainly to steric hindrance to rotation around the peptide bond and to the geometric restriction on the polymer backbone.[2] A regular conformation may exist in a synthetic asymmetric polyamide derived from a rigid monomer as well. We have been studying this problem by making various optically active polyamides with rigid structures.[3–5]

In the present study, we prepared optically active polyamides derived from either (+)-(*S*)-*trans*-1,2-cyclopropanedicarboxylic acid [(+)-C3] or (+)- and (−)-*trans*-1,2-cyclohexanedicarboxylic acid [(+)- and (−)-C6] with rigid spirodiamine, 2,6-diazaspiro[3.3]heptane (DSH). We also prepared several model compounds, I–VI, as shown below.

The conformations of the polymers and the model compounds were investigated by means of ORD, CD, and hydrodynamic methods.

Experimental Section

(+)-(*S*)-*trans*-1,2-Cyclopropanedicarboxylic Acid. The synthesis of optically pure (+)-(*S*)-*trans*-1,2-cyclopropanedicarboxylic acid was reported previously.[4] The dicarboxylic acid was prepared by ozonolysis of optically active (+)-(*S*)-*trans*-2-phenylcyclopropanecarboxylic acid:[6] mp 172.5–173.5° (lit.[4] mp 172–173°); $[\alpha]^{20}\mathrm{D}$ +258° (water, *c* 1.0 g/dl); $[\alpha]^{20}\mathrm{D}$ +250° (water, *c* 1.0 g/dl).

(+)- and (−)-*trans*-1,2-Cyclohexanedicarboxylic Acids. *trans*-1,2-Cyclohexanedicarboxylic acid (Aldrich Chemical Co.) was recrystallized twice from methanol–water (1:1). Activated charcoal was used in the recrystallizations. Optical resolution was carried out according to the procedure of Nishimura[7] and Applequist and Werner.[8] The quinine salt of the diacid was recrystallized from 95% ethanol. Free (+)-diacid liberated from the quinine salt was recrystallized from water again using charcoal: mp 181.5–182.5° (lit.[7] mp 179.5–181.5°); $[\alpha]^{20}\mathrm{D}$ +19.4° (acetone, *c* 1.0 g/dl); $[\alpha]^{25}\mathrm{D}$ +20.0 (acetone, *c* 2.0 g/dl).

The (−)-isomer-rich diacid recovered from the quinine salt was dissolved in acetone, in which the racemic acid was insoluble: mp 181–182.5° (lit.[7] mp 175–180°); $[\alpha]^{20}\mathrm{D}$ −18.9° (acetone, *c* 1.0 g/dl); $[\alpha]^{25}\mathrm{D}$ −19.5° (acetone, *c* 2.0 g/dl).

(±)-*trans*-2-Methylcyclopropanecarboxylic Acid. This was synthesized according to the method of Applequist and Peterson:[9] bp 104–105° (22 mm) [lit.[9] 91–91.5° (14 mm)]. The melting point of the amide derived from the above acid and aqueous ammonia was 110–111° (lit.[9] 111.3–112.0°).

Acid Chlorides. The acid chlorides of (+)-(*S*)- and (±)-*trans*-1,2-cyclopropanedicarboxylic acid, (+)-, (−)-, and (±)-*trans*-1,2-cyclohexanedicarboxylic acid, and *trans*-2-methylcyclopropanecarboxylic acid were prepared by treating the acids with an excess of purified thionyl chloride:[4] (+)-C3 bp 29.5–30° (0.12 mm), mp 32–33° [lit.[4] bp 40° (0.08 mm)]; $[\alpha]^{24}\mathrm{D}$ +252° (CCl_4, *c* 1.0 g/dl); (±)-C3 bp 38–39° (0.8 mm); (+)-C6 bp 65–66° (0.15 mm) (lit.[7] bp 61–62° (0.04 mm)), $[\alpha]^{24}\mathrm{D}$ −19.5° (CCl_4 *c* 2.6 g/dl), $[\alpha]^{25}\mathrm{D}$ −18.2° [CCl_4, *c* 2.0 g/dl)]; (−)-C6 bp 61–62° (0.10 mm), $[\alpha]^{24}\mathrm{D}$