The tumbling behavior of nitroxide probes of different sizes, as observed by ESR spectrometry in a limited number of polymers, is qualitatively, and even semiquantitatively, related to ΔV^{+}. An extensive study of seven probes in six polymers should clarify this subject when completed.

Meanwhile, the correlation shown in Figure 3 is new and may have application in areas other than the ESR work which prompted this study.

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Trisubstituted Ethylenes Containing Halo, Cyano, and Carbomethoxy Substituents. New Reactive Comonomers

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ABSTRACT: New electron-poor trisubstituted olefins were synthesized by dechlorocarbomethoxylation reactions, a Wittig reaction, and substitution of activated chloroolefins by potassium fluoride in the presence of a crown ether. These new monomers, along with several trisubstituted olefins from the literature, copolymerized with electron-rich monosubstituted ethylenes and bicyclobutane monomers under free radical conditions. Charge-transfer complexes of *p*-methoxystyrene were observed with every trisubstituted olefin except **16** and **18**. Spontaneous cationic homopolymerization of *p*-methoxystyrene, caused by several of the electrophilic olefins, occurred simultaneously with their radical-induced copolymerizations, and only dimethyl 2-cyanoethylene-1,1-dicarboxylate gave strictly 1:1 copolymers. 1-Chloro-olefins gave copolymers approaching 1:1 composition whereas 2-chloro- and 2-fluoroolefins were less satisfactory comonomers.

Electron-poor trisubstituted olefins bearing cyano and/or ester substituents are excellent comonomers for electron-rich monosubstituted olefins,[1,2] as well as for bicyclobutane monomers.[3] The adverse steric effect of the 2 substituent is largely counteracted by the two 1 substituents, which strongly stabilize the intermediate electron-poor radical. Moreover, the electron-poor character of these olefins makes them very susceptible to attack by electron-rich radicals. It was of interest to see if the replacement of either cyano or ester group by chloro substituents would still allow them to copolymerize with electron-rich olefins. Early work on the copolymerization of the chloroethylenes with styrene had already shown trichloroethylene to be more reactive than vinyl chloride to the polystyryl radical.[4]

Our purposes in introducing chloro substituents were threefold: (1) ready synthesis of monomers; (2) nonflammability of resulting copolymers, and (3) processability of resulting copolymers. The cyano- and ester-containing monomers synthesized earlier gave copolymers of too high T_g to be processable, and it was thought that substitution of ester or cyano groups by chloro might lead to more tractable materials.

During this study, investigation of one fluorine-containing analogue appeared warranted, as did the synthesis of one new monomer containing only cyano and carbomethoxy groups.

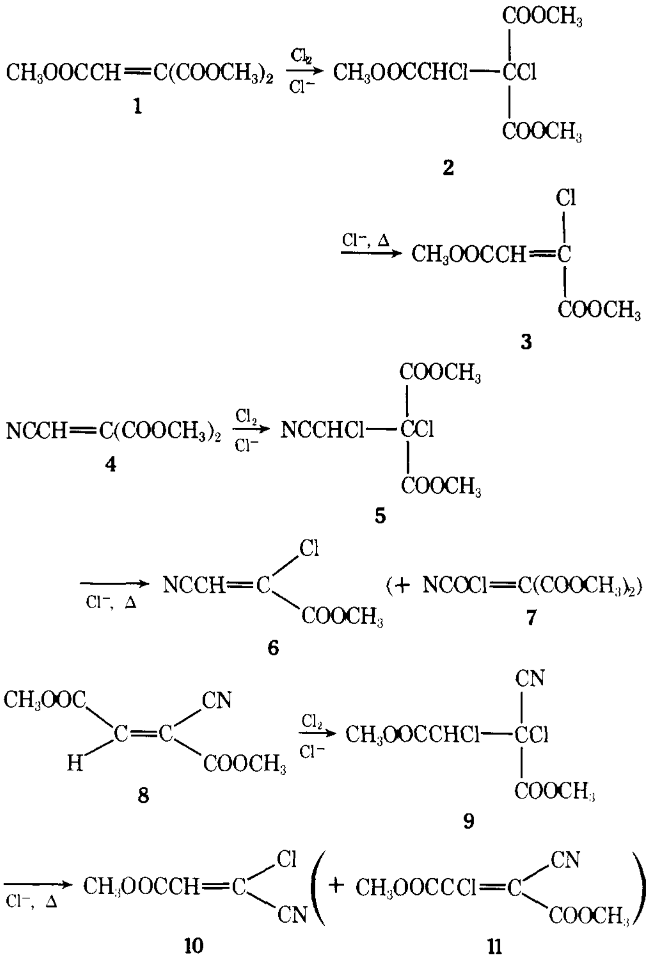
Results

Synthesis and Copolymerization of 1-Chloroolefins 3, 6, and 10. The desired monomers were synthesized from available trisubstituted monomers by our new de(chlorocarbomethoxylation) reaction,[5] demonstrating its generality (Scheme I). (No doubt **3** could also be prepared from dimethyl maleate by chlorination–dehydrochlorination.)

These 1-chloroolefins copolymerized readily with several styrene monomers under free-radical conditions. The copolymers, obtained in 61–80% yields, had inherent viscosities 0.37–0.73 dl g^{-1} and formed fibrous precipitates when their solutions were poured into methanol. The electron-rich comonomers *p*-methoxystyrene and styrene gave approximately 1:1 compositions, while the more electron-poor 2,5-dichlorostyrene incorporated significantly less of the electron-poor olefin. Charge-transfer complexation of *p*-methoxystyrene with the three ethylenes took place as evidenced by the transient formation of bright colors on mixing the ingredients.

Thermal Behavior. The glass transition and thermal decomposition temperatures were determined on a differential scanning calorimeter (Table I). In most cases clearly defined T_g's were visible. These lay between 150 and 225 °C. While high, they were much lower than those noted previously[2] for

Scheme I



the carbomethoxy/cyano copolymers made earlier, which decomposed before their T_g's could be observed.

The present copolymers were reasonably thermally stable, decomposing in the range 225–300 °C.

Solubility. The copolymers were soluble in the conventional organic solvents. For example, copolymers containing only ester groups were soluble in acetone, while dimethylformamide was required to dissolve some of the nitrile-containing copolymers.

Flammability. Films were cast from acetone solutions of the copolymers of **3**, **6**, and **10** with styrene. They were brittle. They were found to be flammable.

Synthesis and Copolymerization of 2-Chloroolefins 15, 16, and 17. These compounds were readily prepared as follows:

$$\underset{\mathbf{12,\,13,\,14}}{CH_2YZ} \xrightarrow[CH_3OH]{CH_3OK} K^+\,O^-CH{=}CYZ \xrightarrow[\text{or }POCl_3]{PCl_5} \underset{\mathbf{15,\,16,\,17}}{ClCH{=}CYZ}$$

12, 15, Y = Z = CN

13, 16, Y = Z = COOCH$_3$

14, 17, Y = CN; Z = COOCH$_3$

Compounds **15**[6] and **16**[7] were known already; for the preparation of the latter we preferred to adapt the experimental procedure used for the corresponding diethyl ester.[8] Compound **17**, which is new, was synthesized analogously to **15**.

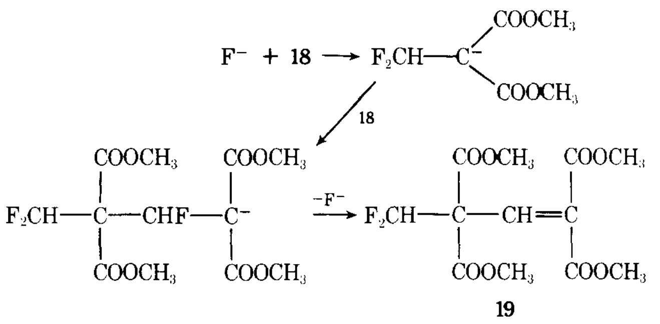
The 2-chloroolefins gave less satisfactory copolymerization results than their 1-chloro analogues. Yields, inherent viscosities, and incorporation of electron-poor trisubstituted ethylenes were all lower than the above results.

While the percentage of incorporated electron-poor olefins increased as before with increased electron-rich character of the styrene comonomer, a discontinuity was found with p-methoxystyrene. The polymer formed from this comonomer possessed very little (0–8%) of the trisubstituted ethylene, and in the case of **16** spontaneous polymerization occurred. Again charge-transfer complex behavior with p-methoxystyrene was noted.

Synthesis and Copolymerization of Dimethyl 2-Fluoroethylene-1,1-dicarboxylate (18). We thought that the mediocre results obtained with the 2-chloroolefins might be due to the large steric effect and inadequate inductive effect of a 2-chloro substituent. It appeared that the corresponding 2-fluoroolefins should be better in both respects. Synthesis difficulties hampered our investigation of these compounds, but we succeeded in synthesizing one representative as follows. Reacting **16** with anhydrous potassium fluoride in sulfolane or 2,4-dimethylsulfolane in the presence of dicyclohexyl-18-crown-6 at reduced pressure (140 mm) and elevated temperature (170°) under distillation conditions allowed us to isolate crude dimethyl 2-fluoroethylene-1,1-dicarboxylate (**18**). Redistillation gave the desired olefin in 23% yield.

$$\underset{\mathbf{16}}{ClCH{=}C(COOCH_3)_2} \xrightarrow[\substack{\text{sulfolane}\\ 170\ {}^\circ\text{C (140 mm)}}]{\text{KF, crown}} \underset{\mathbf{18}}{FCH{=}C(COOCH_3)_2}$$

If **18** is not distilled out as formed, the only product isolated was tetramethyl 4,4-difluorobut-1-ene-1,1,3,3-tetracarboxylate (**19**), formed by fluoride-ion catalyzed dimerization of **18**:



Analogous dimerization of methyl trifluoroacrylate under the influence of fluoride ion has been reported by England, Solomon, and Krespan.[9] Once obtained, **18** was difficult to handle. The olefin is very sensitive to moisture, hydrolyzing with loss of fluoride ion to **20**. The olefin has to be kept in sealed ampules at −78 °C.

$$\mathbf{18} \xrightarrow[-2HF]{H_2O} \underset{\mathbf{20}}{(CH_3OOC)_2C{=}CHOCH{=}C(COOCH_3)_2}$$

The fluoroolefin **18** was slightly better in radical copolymerization than the corresponding chloro derivative, but with bicyclobutancarbonitrile it was a very poor comonomer.

Because fluorine is not much larger than hydrogen, it was thought that **18** might homopolymerize. Attempted radical homopolymerization of **18** at 70 °C, or 28 °C under UV irradiation, in both cases in the presence of AIBN, failed.

Attempted anionic homopolymerization of the olefin initiated by 1,4-diazabicyclo[2.2.2]octane or triphenylphosphine at 28 °C gave no polymer. Attempted anionic homopolymerization initiated by tetraethylammonium fluoride in acetonitrile at − 20 °C gave **19** (90%) and **20** (10%). Attempted polymerization initiated by n-butyllithium in THF at − 78 °C also did not give polymer.

Dimethyl 2-Cyanoethylene-1,1-dicarboxylate (23). To complete our series of trisubstituted olefins containing only cyano and carbomethoxy substituents, we synthesized **23** as shown:

Table I
Copolymerization Results

Electron-poor trisubstituted olefin	Comonomer	Reaction conditions	Yield, %	Elemental Anal.				^{c}	$\eta_{inh}{}^{a,b}$	T_g, deg	T dec, deg
				C	H	N	Other				
Chloroolefins											
Methyl 1-chloroethylene-1,2-carboxylate (**3**)	*p*-Methoxystyrene	13.7 h, 72 °C	61	58.52	5.60		Cl, 10.90	47	0.72, fibrous	188	244
	Styrene	13.7 h, 72 °C	64	59.83	5.47		Cl, 11.17	47	0.73, fibrous	None visible	250
Methyl 1-chloro-2-cyanoethylene-1-carboxylate (**6**)	*p*-Methoxystyrene	13.0 h, 70 °C	63	59.96	5.13	4.65	Cl, 13.55	50	0.52, fibrous	None visible	225
	Styrene	16.5 h, 70 °C	77	64.04	5.07	5.15	Cl, 13.07	46	0.37, fibrous	224	293
Methyl 1-chloro-1-cyanoethylene-2-carboxylate (**10**)	*p*-Methoxystyrene	13.0 h, 70 °C	68	60.46	5.17	4.67	Cl, 12.34	48	0.63, fibrous	164 156	240 257
	Styrene	16.5 h, 70 °C	80	64.13	5.05	5.08	Cl, 13.23	46	0.56, fibrous	262	231
	2,5-Dichlorostyrene	13.2 h, 68 °C	61	51.04	2.95		Cl, 34.83	37	0.44, fibrous	217	266
2-Chloroolefins											
1,1-Dicyano-2-chloroethylene (**15**)	*p*-Methoxystyrene	13.0 h, 28 °C	34	78.94	7.28	1.30	Cl, 0.96	4	0.19^c		
	Styrene	17.2 h, 70 °C	44	69.30	4.49	11.53	Cl, 14.57	44	0.20	190	215
	p-Fluorostyrene	13.0 h, 68 °C	70	62.14	3.95	11.25	Cl, 13.11	44	0.29^b	206	225
	p-Chlorostyrene	13.0 h, 70 °C	55	59.47	3.44	8.96		42	0.16	198	269
	2,5-Dichlorostyrene	14.0 h, 67.5 °C	53	52.66	2.92	5.32	Cl, 38.44	32	0.21		
Dimethyl 2-chloroethylene-1,1-dicarboxylate (**16**)	*p*-Methoxystyrene	19.3 h, 28 °C	33	80.58	7.52		Cl <0.3	0	0.20		
	Styrene	20.7 h, 70 °C	14	73.04	6.39		Cl, 7.11	25	0.25		
	p-Chlorostyrene	13.0 h, 70 °C	33	63.10			Cl, 24.36	17	0.28	184	237
	2,5-Dichlorostyrene	14.0 h, 67.5 °C	46	55.88			Cl, 39.05	7	0.37	193	207
Methyl 2-Chloro-1-cyanoethylene-1-carboxylate (**17**)	*p*-Methoxystyrene	18.7 h, 28 °C	26	77.00	7.01	0.80	Cl, 1.74	8	0.18		270
	Styrene	19.0 h, 67.5 °C	73	65.34	5.05	5.08	Cl, 12.68	44	0.70, fibrous		235
	p-Fluorostyrene	13.0 h, 68 °C	63	60.02	4.33	4.75	Cl, 11.65	44	0.38		
	p-Chlorostyrene	13.0 h, 70 °C	51	57.77	4.09	3.99		40	0.32	187	250
	2,5-Dichlorostyrene	14.0 h, 67.5 °C	57	52.01		2.34	Cl, 36.93	28	0.39	None visible	220
Other olefins											
Dimethyl-2-fluoroethylene-1,1-dicarboxylate (**18**)	*p*-Methoxystyrene	12.9 h, 70 °C	39	80.05	7.53		F, <0.10	0	0.27		
	Styrene	19.7 h, 70 °C	58	72.35	6.31		F, 4.78	31	0.38		
	Bicyclobutan-1-carbonitrile	1.2 h, 63 °C	24	71.28	6.17	15.78	F, 0.95	6	2.05,^{b} fibrous		
Dimethyl 2-cyanoethylene-1,1-dicarboxylate (**23**)	*p*-Methoxystyrene	19.0 h, 28 °C	27	62.83	5.68	4.63		50	0.26	160	249
	Styrene	21.0 h, 70 °C	65	66.04	5.45	4.97		50	0.37	160	240
	p-Fluorostyrene	13.0 h, 68 °C	62	61.86	4.90	4.74		48	0.33	163	198
	p-Chlorostyrene	13.0 h, 70 °C	43	59.31		4.14	Cl, 12.54	46	0.31	170	234
	2,5-Dichlorostyrene	14.0 h, 67.5 °C	31	53.85		2.34	Cl, 29.67	28	0.37	180	255
	Bicyclobutan-1-carbonitrile	13.5 h, 70 °C	43	66.15	5.47	14.36		22	1.25,^{b} fibrous	224	297
	Bicyclobutan-1-carbonitrile	16.7 h, 28 °C	38	68.05	5.74	15.17		16	1.96,^{b} fibrous	127	240

Table I (Continued)

Electron-poor trisubstituted olefin	Comonomer	Reaction conditions	Yield, %	Elemental Anal. C	H	N	Other	[c]	η_{inh} [a,b]	T_g, deg	T dec, deg
	Methyl bicyclobutanecarboxylate	16.5 h, 28 °C	56	57.71	5.92	3.47		34	1.51, fibrous		

[a] All viscosities were performed in chloroform at 30 °C (0.5% solutions) except as indicated. [b] Viscosity performed in DMF. [c] It was of interest that this polymer was yellow, whereas the copolymer with styrene was white, as was the copolymer of **16** with *p*-methoxystyrene. [c] Mol % of electron-poor trisubstituted olefin.

$$\underset{\mathbf{21}}{(C_6H_5)_3P{=}CHCN} + \underset{\mathbf{22}}{O{=}C(COOCH_3)_2} \rightarrow \underset{\mathbf{23}}{NCCH{=}C(COOCH_3)_2}$$

Inverse addition of **21** to dimethyl oxomalonate (**22**) gave **23** in 50% yield. Similar results have been found by Trippett[10] in the reaction of **21** with tetracyanoethylene.

This new monomer **23** was as active as the best of the cyano/carbomethoxy-containing monomers studied previously.[2] It copolymerized with various styrenes, including the *p*-methoxy derivative, to yield almost perfectly alternating copolymers, while a drop in its extent of incorporation was observed with the more electrophilic styrenes.

Again charge-transfer complexation was noted in the case of *p*-methoxystyrene.

The new monomer **23** also copolymerized well with two bicyclobutane comonomers. High molecular weight products were formed from both bicyclobutane-1-carbonitrile and methyl bicyclobutane-1-carboxylate. However, the yields and percentage incorporation of **23** were not very high. Incorporation of the bicyclobutane ester exceeded that of the nitrile, as before.[3]

Discussion

This work has presented eight new electrophilic trisubstituted ethylenes as potential new monomers. They copolymerize readily with styrene and bicyclobutane comonomers under free-radical conditions, but interesting individual variations in behavior were found.

The three 1-chloroolefins **3**, **6**, and **10**, and the cyano/carbomethoxy monomer **23**, are satisfactory new materials for copolymerization studies. With various styrenes they gave almost perfectly alternating copolymers in high yields and molecular weights. This can be attributed to the ability of the 1-Cl to stabilize the growing radical, which outweighs its only moderate inductive effect.

The three 2-chloroolefins were less satisfactory comonomers in terms of yields, incorporation of electrophilic trisubstituted ethylene, and molecular weight. Here the 2-Cl again contributes only moderately to the overall electron deficiency but now is not able to offer resonance stabilization of the growing radical. Moreover, it probably gives more steric hindrance to the approaching radical than cyano or carbomethoxy can provide.

The group of 2-chloroolefins displayed an interesting discontinuity in their behavior toward the styrene comonomers. The incorporation of the electrophilic olefin increased with the increasing electron-rich nature of the styrene (greater alternation tendency). However, when *p*-methoxystyrene is reached, the incorporation suddenly drops to 0–8%. This tendency toward homopolymer formation does not correlate with the occurrence or absence of charge-transfer colors. We suggest that a mechanistic change in the direction of competing cationic polymerization accounts for these observations. However, the exact nature of the initiating species remains to be elucidated.

2-Fluoroolefin. Finally, dimethyl 2-fluoroethylene-1,1-dicarboxylate (**18**) behaved more like methyl α-cyanoacrylate than like the other olefins reported here. Its high susceptibility to nucleophilic attack by fluoride ion and by moisture made it difficult to synthesize and store. Anionic polymerization was not successful owing to termination by ready loss of fluoride ion. With styrene under free-radical conditions it gave results comparable to the 2-methoxystyrene, only homopolymer of the latter was formed.

Physical Properties. The copolymers prepared in the present work are more tractable materials than the rigid glasses obtained in the earlier study.[2] Glass transition temperatures are raised by substituents which have high dipolar character and restrict conformational mobility. Chlorine shows less of these characteristics than either cyano or carbomethoxy groups. Therefore, its introduction into the trisubstituted ethylene units brings the T_g down to observable and useful range. As cast, films were brittle. The films were found to be flammable, probably owing to insufficient chlorine in the copolymers.

Experimental Section

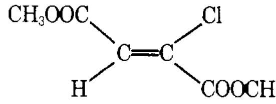
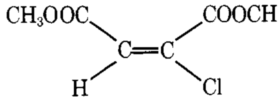
General. All boiling points and melting points are uncorrected. Capillary melting points were determined on a Thomas-Hoover melting point apparatus. Infrared spectra were determined with a Perkin-Elmer Model 337 spectrophotometer in KBr or between NaCl plates (the wavelengths are given in cm^{-1}). NMR spectra were obtained on a Varian T60 spectrometer. Chemical shifts are reported on the τ scale. The gas chromatograms were obtained on a Varian Aerograph 1700 instrument using the following column: 3% SE 30 on 80–100 mesh Chromosorb W AW/DMCS HP, 5 ft × 0.25 in.

The thermal scans were taken on a Perkin-Elmer DSC1-B instrument. The sample size was ~30 mg, the scan rate was 10° min^{-1}, and the sensitivity setting was 2. Each sample was run from 30 to 220 °C or more and was done at least once by two different operators. The T_g's were observed as characteristic "dog-leg's" in the traces. The results were checked by following the thermal behavior visually on a Fischer-Johns melting point block. Good general agreement was observed.

Dimethyl 1-Chloroethylene-1,2-dicarboxylate (3). To 10.1 g (50 mmol) of trimethyl ethylene-1,1,2-tricarboxylate[2] (**1**) and 0.5 g of tetraethylammonium chloride in 50 ml of dry acetonitrile was added while cooling with an ice–methanol bath 5.30 ml (102 mmol) of chlorine. The reaction was monitored by NMR (disappearance of the olefinic absorption and appearance of the CHCl absorption at τ 5.47). At the end of the reaction, the solvent was evaporated and the residue was distilled at an initial pressure of 4 mm. The pressure rose to 8 mm, then decreased to 6 mm, and dimethyl 1-chloroethylene-1,2-dicarboxylate (**3**) distilled. The first fractions (bp up to 83 °C (5 mm)) had an isomer ratio of 66 Z:34 E; the last one (bp 83° (5 mm)), 3.6 g, had a Z:E ratio of 85:15. Yield 5.2 g (58%); IR (NaCl neat) 3055 (=C—H), 1730 (COOCH$_3$), 1635 (C=C), and 755 (C-Cl). Anal. Calcd for $C_6H_7ClO_4$: Cl, 19.85. Found: Cl, 20.02. The structure assignment was made by NMR.

NMR of Dimethyl Chloroethylenedicarboxylates. Olefinic Proton (CDCl$_3$). See Chart I.

Chart I

	Exptl	Calcd[11]
$ClCH{=}C(COOCH_3)_2$ **16**	2.53	2.20
 **3Z**	2.88	2.83
 **3E**	3.73	3.33

Methyl 1-Chloro-2-cyanoethylene-1-carboxylate (6). To 5.07 g (30 mmol) of dimethyl 2-cyanoethylene-1,1-dicarboxylate (**23**) and 0.35 g of tetraethylammonium chloride in 40 ml of dry acetonitrile was added, while cooling in an ice–methanol bath, 2.50 ml (45 mmol) of chlorine. The solution was stirred overnight, at which time NMR showed CHCl at 4.30. The solvent was evaporated and the residue was distilled at an initial pressure of 3 mm. Thermolysis of the intermediate dichloride[5] caused the pressure after rising to 6 mm (bath temperature 105 °C) to decrease to 1 mm. Redistillation gave 1.45 g of methyl 1-chloro-2-cyanoethylene-1-carboxylate (**6**) (two isomers, bp 48–55 °C (0.1 mm), GC 98% pure, yield 36%) and a mixture of **6** and dimethyl 2-chloro-2-cyanoethylene-1,1-dicarboxylate (**7**) (bp 61–80 °C (0.6 mm). **6**: IR (NaCl neat) 3050 (=C—H), 2220 (C≡N, v.s.), 1720 ($COOCH_3$), and 1600 (C=C); NMR ($CDCl_3$) 3.32 and 3.85 (2s, sum 1, =C—H), 6.08 and 6.13 (2s, sum 3, $COOCH_3$); 3.85 absorption corresponding to the 6.08 absorption, minor isomer, 18%. Anal. Calcd for $C_5H_4ClNO_2$: Cl, 24.36; N, 9.62. Found: Cl, 24.17; N, 9.74.

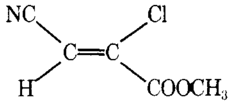
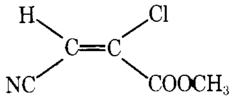
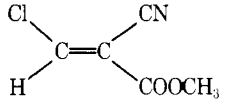
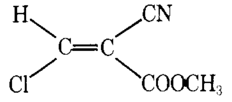
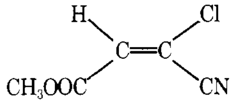
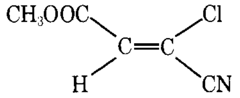
Methyl 1-Chloro-1-cyanoethylene-2-carboxylate (10). To dimethyl 1-cyanoethylene-1,2-dicarboxylate[2] (**8**) (16.9 g, 100 mmol) and 1.0 g of tetraethylammonium chloride in 100 ml of dry acetonitrile was added 6.8 ml (130 mmol) of chlorine while cooling in an ice–methanol bath. The reaction was finished after one night (NMR 5.20, CHCl). Evaporation of the solvent and distillation at reduced pressure were performed. The thermolysis[5] began at a bath temperature of 95 °C, clearly indicated by a strong rise in pressure from 2 mm to more than 10 mm. The first fraction was taken to 98° (4 mm) and consisted mostly of methyl 1-chloro-1-cyanoethylene-2-carboxylate (**10**). The second fraction (bp 105° (1 mm)) consisted of dimethyl 1-chloro-2-cyanoethylene-1,2-dicarboxylate (**11**) (5.8 g, 28% yield). Redistillation of the first fraction gave one pure isomer of methyl 1-chloro-1-cyanoethylene-2-carboxylate (**10**) as a solid (5.27 g, 36%), which on recrystallization (ether) melted at 37–37.5 °C (NMR C-H 3.28). A second fraction contained the minor isomer (NMR C-H 3.30), with the major isomer and some dimethyl 1-chloro-2-cyanoethylene-1,2-dicarboxylate (**11**). From calculation[11] the Z isomer would absorb at 3.24 and the E at 3.09; because our two isomers absorb nearly at the same position, an NMR structure assignment cannot be made. IR of the solid (KBr): 3030 (=C—H), 1710 ($COOCH_3$), and 1605 (C=C). Anal. Calcd for $C_5H_4ClNO_2$: Cl, 24.36; N, 9.62. Found: Cl, 24.50; N, 9.76.

Methyl 2-Chloro-1-cyanoethylene-1-carboxylate (17). Potassium metal, 80 g (2 mol), was added in small portions to 1500 ml of anhydrous methanol. To the refluxing solution of potassium methoxide was added 198 g (2 mol) of methyl cyanoacetate. After the end of addition refluxing was continued for 30 min. Methyl formate, 246 ml (4 mol), was added in portions and refluxing was continued for 2 h. The abundant precipitate was filtered warm. The filtrate was cooled and additional precipitate was collected. The precipitated potassium salt of hydroxymethylene methylcyanoacetate (**14**) was dried at 55 °C at aspirator pressure overnight, yield 233 g (70%).

To a slurry of 82.5 g (0.5 mol) of dry salt (**14**) in 275 ml of dichloromethane was added 104 g (0.5 mol) of phosphorus pentachloride. The mixture was refluxed for 5 h with strong stirring and filtered. The precipitate was thoroughly washed with dichloromethane. Dichloromethane was evaporated and the residue was distilled at aspirator pressure through a 20 cm vigreux column to give 54.35 g (74%) of methyl 2-chloro-1-cyanoethylene-1-carboxylate **17** (GC 99.5% pure; bp 113–116° (27 mm): IR (NaCl neat) 3055 (=C—H), 2225 (s, C≡N), 2210 (m, C≡N), 1720 ($COOCH_3$) and 1635 (w, C=C); NMR ($CDCl_3$) 1.98 and 2.45 (2s, 1, ratio 66:34, =C—H), 6.12 (s, 3, $COOCH_3$). Anal. Calcd for $C_5H_4ClNO_2$: C, 41.26; H, 2.77; Cl, 24.36; N, 9.62. Found: C, 41.03; H, 2.72; Cl, 24.30; N, 9.77.

NMR of Chlorocyanoethylene Monocarboxylates. Olefinic Proton. See Chart II.

Chart II

	Exptl	Calcd[11]
 **6Z**	3.32	3.34
 **6E**	3.85	3.84
 **17E**	1.98	2.11
 **17Z**	2.45	2.46
 **10E**	3.28	3.24
and/or		
 **10Z**	3.30	3.09

Dimethyl 2-Fluoroethylene-1,1-dicarboxylate (18). In a 200-ml, three-necked flask fitted with a constant-pressure addition funnel, a thermometer and a 14 cm vigreux column leading to a short-path distillation apparatus were put a Teflon-coated stirring bar, 1.35 g of technical dicyclohexyl-18-crown-6 (Aldrich), 20.88 g (0.36 mol) of anhydrous potassium fluoride, and 120 ml of dry 2,4-dimethylsulfolane. In the addition funnel was put 16.05 g (90 mmol) of dimethyl 2-chloroethylene-1,1-dicarboxylate (**16**). The pressure was kept at 140 mm and the inside temperature was allowed to reach 170 °C while stirring. Under strong stirring the olefin was added dropwise (addition time 3 min). The pressure was then carefully lowered. The product began to distill at 40 mm and 105 °C. The distillation was continued until a temperature of 155 °C and a pressure of 28 mm was reached. GC analysis showed only the starting material, some solvent, and the desired olefin. Spinning band column distillation gave 3.39 g (23%) of 98% pure **18** and some less pure fractions. Redistillation afforded pure **18** (bp 88–90 °C (28 mm)): IR (NaCl neat) 3080 (=C—H), 1755–1700 (several absorptions, $COOCH_3$), 1655 and 1630 (C=C); NMR ($CDCl_3$) 2.38 (d, J = 77 Hz, 1, =CH(F), 6.15 and 6.22 (2s, 6, $COOCH_3$). Anal. Calcd for $C_6H_7FO_4$: C, 44.45; H, 4.35; F, 11.72. Found: C, 44.34; H, 4.47; F, 11.67.

The source of the potassium fluoride played a role in the success of this experiment. Potassium fluoride dihydrate (Mallinckrodt) was dehydrated at 120 °C under high vacuum for 24 h and was thereafter handled under nitrogen. Use of similarly dried anhydrous potassium fluoride (Ventron) gave identical results on a 10 mmol scale, but on a larger scale only **19** was formed. This latter KF is too reactive at the temperature required to distill out **18** as formed and caused its dimerization.

Tetramethyl 4,4-Difluorobut-1-ene-1,1,3,3-tetracarboxylate (19). Dimer **19** could be isolated in purity and characterized as follows: To pure dimethyl 2-fluoroethylene-1,1-dicarboxylate (**18**) (0.81 g, (5 mmol)) in 2 ml of dry acetonitrile cooled at −20 °C was added by syringe a solution of tetraethylammonium fluoride (0.05 g, 0.33 mmol) in 0.5 ml of dry acetonitrile. The solution was stirred at −20 °C for 6 h and was then allowed to warm to room temperature. An NMR spectrum showed **19**, approximately 10% of **20**, and traces of starting olefin. After evaporation of the solvent the residue was taken in dichloromethane (10 ml), washed twice with 10 ml of water, dried over magnesium sulfate, filtered, and evaporated. Removal of **20** by crystallization from dichloromethane–ether left **19** in purity as a colorless oil; IR (NaCl neat) 3050 (w, =C—H), 1755 and 1720 ($COOCH_3$), 1655 (C=C); NMR ($CDCl_3$) 2.67 (s, 1, =C—H), 3.58 (t, J = 54 Hz, 1, CF_2H), 6.22 and 6.27 (2s, 12, $COOCH_3$). Anal. Calcd for $C_{12}H_{14}F_2O_8$: C, 44.45; H, 4.35. Found: C, 44.24; H, 4.54.

Tetramethyl 3-Oxa-1,4-pentadiene-1,1,5,5-tetracarboxylate (20). This compound was obtained when **18** was kept in closed vials for a while and is the major constituent of the residue of distillation of the olefin: IR (KBr) 3070 (=C—H), 1725 ($COOCH_3$), and 1615 (C=C); NMR ($CDCl_3$) 2.29 (s, 2, =C—H), 6.18 (s, 6, $COOCH_3$), and 6.22 (s, 6, $COOCH_3$); mass spectrum 302 ($M\cdot^+$, 13%), 143 ($(MeOOC)_2C{=}CH\cdot^+$) (100%); mp 156–158 °C. Anal. Calcd for $C_{12}H_{14}O_9$: C, 47.69; H, 4.67. Found: C, 47.82, H. 4.73.

Cyanomethylenetriphenylphosphorane (21). Triphenylphosphine (262 g, 1 mol) and chloroacetonitrile (75.5 g, 1 mol, 63 ml) were refluxed overnight in 500 ml of toluene. The crude salt was filtered and dissolved in 1800 ml of water with filtration. Chloroform, 800 ml, was added to the filtrate. To the strongly stirred mixture was added dropwise a solution of 40 g (1 mol) of sodium hydroxide in 270 ml of water. The reaction was followed with pH paper. When the mixture remained neutral, the addition was stopped and the two layers were separated. The water layer was washed with 500 ml of chloroform and the combined organic layers were backwashed with 500 ml of water, dried for several hours over magnesium sulfate, filtered, and evaporated. Crystallization of the residues from benzene gave 221.4 g (overall yield 73%) of cyanomethylenetriphenylphosphorane (**21**), mp 190–192 °C (lit.[12] 186–187 °C).

Dimethyl 2-Cyanoethylene-1,1-dicarboxylate (23). To an ice-water cooled solution of dimethyl oxomalonate (**22**) (14.6 g, 100 mmol) in 200 ml of benzene was added over 1 min cyanomethylenetriphenylphosphorane (**21**) (30.1 g, 100 mmol). After 20 min the benzene was evaporated and ether was added to crystallize as much triphenylphosphine oxide and side product as possible. When no further solid precipitated the remaining liquid was distilled to give, after some fractions containing the olefin and dimethyl oxomalonate, olefin **23** in purity (8.5 g, 50% yield, bp 97–100 °C (1.4 mm)); IR (NaCl neat) 2200 (C≡N), 1725 ($COOCH_3$), 1625 (C=C); NMR ($CDCl_3$) 3.45 (s, 1, C-H), 6.08 and 6.13 (2s, 6, $COOCH_3$). Anal. Calcd for $C_7H_7NO_4$: C, 49.71; H, 4.17; N, 8.28; O, 37.84. Found: C, 49.50; H, 4.16; N, 8.13; O, 38.12.

Copolymerizations. All copolymerizations were done in bulk working with 5 mmol of each monomer and 4 mg of AIBN. At the end of the polymerization the polymers were dissolved in chloroform or dimethyl formamide, precipitated in methanol, washed with methanol, and dried overnight at 54 °C.

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N,N′-Biisomaleimide. 2. Polyhydrazides[1]

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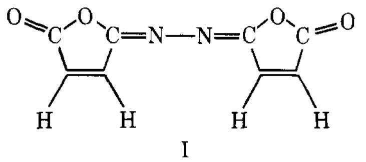
ABSTRACT: *N,N′*-Biisomaleimide undergoes a rapid ring-opening polymerization with a variety of dihydrazides in polar media to yield the corresponding polyhydrazides. These polyhydrazides are largely amorphous and exhibit many nylon-like properties. Upon heating at elevated temperatures, the hydrazide linkages in these polymers are converted to the corresponding 1,3,4-oxadiazole ring structure.

The synthesis of low molecular weight polyhydrazides was first reported in 1942 in a French patent[2] from the condensation of hydrazine with dicarboxylic acids in alcohol. A high-temperature solution polymerization technique developed by McFarlane and Miller[3] produced usually either insoluble polymeric products or low molecular weight materials. The low-temperature solution polymerization route using a dihydrazide and a diacylchloride, developed by Frazer and Wallenberger,[4] was shown to yield soluble polyhydrazides of much higher molecular weight. The polyhydrazides and their post-cyclization derivatives have been studied quite extensively both in this country[5] and abroad.[6,7]

The polymerization of *N,N′*-biisomaleimide with various dihydrazides, characterizations of the resulting polyhydrazides, and their post-cyclization reactions were studied in the present work.



I

Experimental Section

***N,N′*-Biisomaleimide (I)** was prepared from hydrazine and maleic anhydride and purified according to the procedures given in the literature.[8] The product used for polymerization had an mp of 260 °C (lit.[3] 260 °C). Anal. Calcd for $C_8H_4N_2O_4$: C, 50.00; H, 2.04; N, 14.58. Found: C, 50.15; H, 2.19; N, 14.68.

Dihydrazides were prepared from the reaction of dimethyl (or diethyl) ester of a dibasic acid and excess hydrazine hydrate in methanol. The crude product was purified by recrystalization from aqueous ethanol solution. Dihydrazides so prepared include: oxalyl dihydrazide