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New Copolymers of Styrene with Some Trisubstituted Ethylenes

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ABSTRACT: Novel trisubstituted ethylenes, 1,1-dicyanoethenes, methyl 2-cyanopropenoates, and 1,1-bis(methoxycarbonyl)ethenes, having cyclohexyl, 3-cyclohexenyl, 5-norbornenyl, phenyl, 1-naphthyl, 3-pyridinyl, 2-pyrrolyl, and 2-furyl substituents at the double bond have been prepared via Knoevenagel condensation of the corresponding aldehydes and active methylene compounds, malononitrile, methyl cyanoacetate, and dimethyl malonate. The trisubstituted ethylenes were copolymerized with styrene at equimolar monomer feed with the radical initiation. Relative reactivity of the trisubstituted ethylene monomers and radicals, estimated on the basis of the compositional data, increases in the same order as their acceptor properties: 1,1-dicyanoethenes > methyl 2-cyanopropenoates ≫ 1,1-bis(methoxycarbonyl)ethenes. 2-Pyrrolyl- and 2-furyl-substituted 1,1-dicyanoethenes, methyl 2-cyanopropenoates, and 1,1-bis(methoxycarbonyl)ethenes were unreactive in copolymerization with styrene.

Introduction

Early studies of substituted ethylenes showed that reactivity of the monomers in radical polymerization depends on their polarity, resonance stabilization, and steric effects.[1] 1,1-Disubstituted alkenes are generally more reactive than monosubstituted ethylenes due to resonance stabilization of the growing radical by both substituents. However, the ability of the monomer to polymerize is critically dependent on the bulkiness of the substituent, which leads to steric strain in the polymer and results in low ceiling temperatures.

1,2-Disubstituted ethylenes are significantly less reactive than the monosubstituted monomers. The propagation step is extremely slow due to steric interactions between the β-substituent of the propagating species and the two substituents of the incoming molecule.[1] Polymerization of trisubstituted ethylenes evidently should be further impeded on the grounds of both thermodynamic and kinetic factors encountered in the case of 1,1- and 1,2-disubstituted alkenes.

In copolymerization of trisubstituted ethylene monomers with monosubstituted olefins, influences due to steric hindrance are mostly minor compared to polarity and resonance stabilization.

Use of electron-deficient trisubstituted alkenes carrying two cyano, halo, and/or carboalkoxy substituents in copolymerization with electron-rich monosubstituted ethylenes made it possible to overcome steric problems observed in the homopolymerization.[2-4] Monomer polar interactions between dimethyl cyanofumarate or tricarbomethoxyethylene and α-methylstyrene, indene, furane, or benzofurane allowed even copolymerization of trisubstituted ethylenes with 1,1- and 1,2-disubstituted monomers.[5] On the other hand, in attempted copolymerization with monosubstituted comonomers of similar polarity such as methyl acrylate or acrylonitrile, these same trisubstituted carboxylate monomers gave no

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Table I
Copolymerization of Dicyanoethenes RCH=C(CN)$_2$ with Styrene

	R	solvent	time, h	yield, %	TSE mol fr in copolym	T_g, °C	$10^{-3}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1	cyclohexyl	ethyl acetate	1056	no polym				
2	3-cyclohexenyl	benzene	211	6.7	0.28	175	25[a]	1.47
3	5-norbornenyl	benzene	1056	2.7	0.40	170	24[a]	2.4
4	1-naphthyl	benzene	211	8.5	0.33	185	36[a]	1.56
5	3-pyridinyl	benzene + ethyl acetate	1416	14.1	0.42	175		
6	2-pyrrolyl	benzene	864	no polym				
7	2-furyl	ethyl acetate	1056	no polym				

[a] Eluent, chloroform.

copolymers[4] and monomers like ethyl 2-cyanopropenoate or 2-phenyl-1,1-dicyanoethene showed very low reactivity in copolymerization with acrylonitrile.[6]

Copolymerization of electron-deficient trisubstituted ethylene monomers with such electron-rich monomers as styrene,[3,4] vinyl acetate,[4,7] *N*-vinylcarbazole,[4] and *N*-vinylpyrrolidone[8] at equimolar comonomer feed results in copolymers of nearly 1:1 composition. The tendency toward alternation increases as the differences in polarity between the two monomers increases. The enhancement of reactivity of substituted ethylenes has been explained by considering the interaction between an electron-donor radical and an electron-acceptor monomer (or vice versa)[9,10] or homopolymerization of monomer donor–acceptor complexes.[11] Complex formation between electron-deficient trisubstituted ethylene monomers and electron-rich monosubstituted monomers was observed in a number of monomer pairs.[4,7]

In our earlier studies we applied terminal, penultimate, and monomer complex kinetic models for prediction of the copolymer composition in copolymerization of methyl 2-cyanopropenoate and 2-phenyl-1,1-dicyanoethene with vinyl acetate[7] and *N*-vinylpyrrolidone.[8,12]

In our investigation of the monomer reactivities in radical copolymerization of trisubstituted ethylenes, it was of interest to prepare new monomers and study the feasibility of their copolymerization with styrene. The electron-poor character of the prepared substituted 1,1-dicyanoethenes, methyl 2-cyanopropenoates, and 1,1-bis(methoxycarbonyl)ethenes should make them susceptible to attack by such electron-rich radicals as styrene.

Results and Discussion

Monomer Synthesis. The trisubstituted ethylene monomers were prepared according to the general procedure of Knoevenagel condensation[13] by reacting an appropriate aldehyde with malononitrile, methyl cyanoacetate, and dimethyl malonate, respectively, as described in the Experimental Section.

$$R^1CHO + R^2CH_2R^3 \rightarrow R^1CH{=}CR^2R^3$$

This reaction was used to synthesize three series of olefinic monomers with cyano and carbomethoxy electron-withdrawing groups on the α-disubstituted carbon and a number of β-substituents, which include cyclohexyl, cycloalkenyl structures with endo double bonds, 3-cyclohexenyl, and 5-norbornenyl, as well as aromatic, phenyl, naphthyl, and heteroaromatic six- and five-membered rings, 3-pyridinyl, 2-pyrrolyl, and 2-furyl.

$R^1CH{=}C(CN)_2$ dicyanoethenes $R^1CH{=}C(CN)CO_2CH_3$ 2-cyanopropenoates

$R^1CH{=}C(CO_2CH_3)_2$ 1,1-bis(methoxycarbonyl)ethenes

R^1 = cyclohexyl, 3-cyclohexenyl, 5-norbornenyl, phenyl, 1-napthyl, 3-pyridinyl, 2-pyrrolyl, and 2-furyl

The condensation reaction proceeded smoothly, yielding crystalline or liquid products, which were purified by conventional techniques. The existence of double peaks for $^{13}C{\equiv}N$ in the carbon-13 NMR spectra of substituted 1,1-dicyanoethenes and $^{13}C{=}O$ in the spectra of 1,1-bis(methoxycarbonyl)ethenes indicates that the prepared monomers are mixtures of *E* and *Z* isomers. It was not possible to obtain separately the *E* and *Z* isomers in a pure form. The carbon-13 NMR analysis of methyl 2-cyanopropenoates showed the presence of a single *E* isomer with the ester group trans to the β-substituent, which is consistent with the NMR data on a variety of cyanocinnamate compounds.[14]

Homopolymerization. Polymerization of substituted 1,1-dicyanoethenes, methyl 2-cyanopropenoates, and 1,1-bis(methoxycarbonyl)ethenes under free radical initiation was not successful. No polymer was isolated upon precipitation of polymerization mixtures in methanol. Polymerizations were also run at room temperature with photoirradiation in an attempt to overcome possible low ceiling temperatures, but no polymers formed. Inability of these TSE monomers to polymerize is associated with steric difficulties encountered in homopolymerization of 1,1- and 1,2-disubstituted ethylenes. This type of steric hindrance would increase the activation energy required for an addition reaction and slow down the rate of propagation to such an extent as to favor the occurrence of a chain-transfer or termination step instead.

Homopolymerization of styrene under conditions identical with those used in copolymerization experiments (solvent, concentrations of the monomer and initiator, and temperature) yielded 26.8 and 22.8 wt % of polystyrene in benzene ($\bar{M}_w$ 45 200, $\bar{M}_w/\bar{M}_n$ 1.38) and ethyl acetate ($\bar{M}_w$ 39 600, $\bar{M}_w/\bar{M}_n$ 1.33), respectively, when polymerized for 320 min.

Copolymerization. All three groups of novel electrophilic trisubstituted ethylene monomers were mixed with styrene at equimolar feed ratios and copolymerized at 70 °C in the presence of AIBN in ethyl acetate, benzene, or chloroform (Tables I–III). The choice of the solvent was based on solubility of the electrophilic monomer at 1 mol/L concentration. AIBN was chosen due to its low susceptibility to transfer.[15]

Copolymerization of 2-(3-cyclohexenyl)-, 2-(5-norbornenyl)-, 2-(1-naphthyl)-, and 2-(3-pyridinyl)-1,1-dicyanoethenes resulted in formation of copolymers, whereas no styrene copolymers were obtained with cyclohexyl-, 2-pyrrolyl-, and 2-furyl-substituted dicyanoethenes (Table I). According to elemental analysis of the copolymers, a substantial amount of trisubstituted ethylene monomer is present in the copolymers, which is indicative of quite high reactivity of these monomers toward styrene. Conversion data, although obtained in different solvents, suggested that these copolymerizations run much slower (~0.03–0.003 %/h) than earlier studied 2-phenyl-1,1-dicyanoethene (~7 %/h)[3] or 2-(carboethoxy)-1,1-dicyano-

Table II
Copolymerization of Methyl 2-Cyanopropenoates RCH=C(CN)(CO_2CH_3) with Styrene

	R	solvent	time, h	yield, %	TSE mol fr in copolym	T_g, °C	$10^{-3}\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
8	cyclohexyl	benzene	120	7.4	0.06	102	16[b]	1.67
9	3-cyclohexenyl	benzene	90	14.9	0.14	133	25[b]	1.58
10	5-norbornenyl	ethyl acetate	140	3.9	0.26	120	19[c]	1.8
11	1-naphthyl	ethyl acetate	90	17.8	0.33	127	29[b]	1.63
12	3-pyridinyl	chloroform	16.5	20.5	0.40	a		
13	2-pyrrolyl	chloroform	100	no polym				
14	2-furyl	benzene	620	no polym				

[a] The copolymer decomposed when heated above 120 °C. [b] Eluent, tetrahydrofuran. [c] Eluent, chloroform.

Table III
Copolymerization of 1,1-Bis(methoxycarbonyl)ethenes RCH=C(CO_2CH_3)$_2$ with Styrene

	R	solvent	time, h	yield, %	TSE mol fr in copolym	T_g, °C	$10^{-3}\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
15	cyclohexyl	ethylbenzene	100	13.0	0.02	80	34[a]	1.85
16	3-cyclohexenyl	benzene	206	18.0	0.01	102	33[a]	1.78
17	5-norbornyl	benzene	206	17.1	0.03	103	36[a]	1.78
18	phenyl	benzene	90	14.7	0.06	105	37[a]	1.88
19	1-naphthyl	benzene	206	19.6	0.03	104	75[a]	2.6
20	3-pyridinyl	benzene	600	0.7	0.11	107		
21	2-pyrrolyl	benzene	1120	no polym				
22	2-furyl	ethyl acetate	1080	no polym				

[a] Eluent, tetrahydrofuran.

ethene (3%/h),[4] at equimolar monomer feed. These differences are due to polar and steric factors related to the nature of the β-substituent.

It is not obvious why cyclohexyl-substituted dicyanoethene failed to copolymerize with styrene. Availability of allylic hydrogen in the monomer would lead to a degradative chain transfer. However, this is not the case, since both 3-cyclohexenyl- and 5-norbornenyl-substituted dicyanoethenes give styrene copolymers in spite of the presence of allylic hydrogen in their molecule. Steric requirements are similar for all three monomers with cyclic substituents, whereas only cyclohexyldicyanoethene does not have an endocyclic double bond. The differences in reactivity might be attributed to the inability of the cyclohexyl-substituted monomer to achieve a completely coplanar conformation in the transition state, a requirement for resonance stabilization of the newly formed radical by the substituents,[16] or due to favorable polar interactions between styrene and monomers with endocyclic double bond, which might enhance reactivity of these monomers in comparison with cyclohexyldicyanoethene. Another explanation could be also that 3-cyclohexyl-1,1-dicyanoethene participates in side reactions that limit its copolymerization ability. This is thought to involve the formation of a cycloadduct composed of one molecule of styrene and two molecules of 3-cyclohexyl-1,1-dicyanoethene, similar to the one formed in the copolymerization of styrene and vinylidene cyanide.[17] 2-(3-cyclohexenyl)-, 2-(5-norbornenyl)-, 2-(1-naphthyl)-, and 2-(3-pyridinyl)-1,1-dicyanoethene behaved similarly in copolymerization with styrene. The heterocyclic substituted dicyanoethenes with 2-pyrrolyl and 2-furyl groups gave no copolymers with styrene at equimolar monomer feed. The inability of 2-pyrrolyl-substituted monomers of dicyanoethene, methyl 2-cyanopropenoate, and 1,1-bis(methoxycarbonyl)ethene to copolymerize with styrene (Tables I–III) is most likely associated with chain-transfer reaction to the pyrrolyl ring. Thus, in the homopolymerization of 2-vinylpyrrole, substantial chain transfer to the monomer was observed.[18] The furan ring in furyl-substituted monomers dicyanoethene, methyl cyanopropenoate, and 1,1-bis(methoxycarbonyl)ethene apparently acts as a radical trap, resulting in a strong inhibiting effect on copolymerization. This phenomenon is known for radical polymerizations involving monomers that give poorly stabilized growing species. Simple furans, e.g., 2-methylfuran, quench the growth of styrene macroradicals.[19] Apparently, this is the cause of the inability of styrene to homopolymerize in the presence of cyclohexyldicyanoethene and trisubstituted ethylenes with 2-pyrrolyl and 2-furyl substituents.

All methyl 2-cyanopropenoates except 2-pyrrolyl- and 2-furyl-substituted compounds readily copolymerized with styrene (Table II). Cyclohexyl-substituted cyanopropenoate, unlike the dicyano monomer, gave copolymer with styrene, although with low content of the electrophilic monomer in the copolymer. Conversion data on copolymerization of substituted methyl 2-cyanopropenoates indicate generally higher yields than for dicyanoethenes, which is consistent with results on copolymerization of styrene with analogous 1,1-disubstituted monomers. Thus methyl cyanoacrylate copolymerizes with styrene[20] faster than vinylidene cyanide.[21] Since the order of monomer reactivities corresponds to the order of increased resonance stabilization by substituents, the 1,1-disubstituted dicyano monomer should be more reactive than methyl α-cyanoacrylate, due to higher resonance stabilization of the formed radical by the two cyano groups. On the other hand, the methyl cyanoacrylate radical should be much more reactive than the more stable dicyano radical, because the effect of a substituent on radical reactivity is considerably larger than its effect on monomer reactivity.[22] In radical copolymerization of hindered trisubstituted alkenes, these effects should be less prominent because of differences in the entropies of activation for monomer–radical reactions.

The group of 1,1-bis(methoxycarbonyl)ethenes displays an interesting discontinuity in the behavior of these three series of trisubstituted ethylene monomers. Although conversion values for 1,1-bis(methoxycarbonyl)ethenes are similar or higher than those of substituted dicyanoethenes and 2-cyanopropenoates, copolymer composition data (Table III) indicate very small incorporation of the electrophilic olefin into the copolymer.

Low reactivities of these monomers toward the electron-rich styrene radical resulted in an increase of styrene homopropagation with the formation of a very small

Table IV
Relative Reactivity ($1/r_1$) of Styrene with Trisubstituted Ethylene Monomers

R	RCH=C(CN)$_2$	RCH=C(CN)CO$_2$CH$_3$	RCH=C(CO$_2$CH)$_2$
cyclohexyl		0.1	0.02
3-cyclohexenyl	0.6	0.2	0.01
5-norbornenyl	2.0	0.5	0.03
phenyl			0.07
1-naphthyl	0.9	1.0	0.03
3-pyridinyl	2.6	2.0	0.14

number of isolated dicarboxylate monomer units. The highest electrophilic monomer content in the copolymer was 11 mol % for 2-(3-pyridinyl)-1,1-bis(methoxycarbonyl)ethene. A drop in reactivity though not as large as for the monomers in Table III, was also observed in the copolymerization behavior of trisubstituted ethylene monomers containing halo, cyano, and carbomethoxy substituents.[23] Styrene copolymers with 2-chloro-1,1-bis(methoxycarbonyl)ethene had compositions of 25 mol % of the trisubstituted ethylene, whereas both 2-chloro-1,1-dicyanoethene and 3-chloro-2-cyanopropenoate gave almost equimolar (44 mol %) copolymers.

In an attempt to qualitatively correlate the observed monomer reactivities, we considered copolymer composition data obtained at equimolar monomer feed. The relative reactivity of styrene in copolymerization with these monomers can be estimated by assuming applicability of the copolymer composition equation (1) of the terminal copolymerization model.[1]

$$m_1/m_2 = [M_1](r_1[M_1] + [M_2])/[M_2]([M_1] + r_2[M_2]) \quad (1)$$

m_1 and m_2 are mole fractions of styrene and trisubstituted ethylene monomer units in the copolymer, respectively; $[M_1]$ and $[M_2]$ are the concentrations of styrene and trisubstituted ethylene in the monomer feed, respectively; $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are reactivity ratios for styrene and trisubstituted ethylene, respectively. In the absence of trisubstituted ethylene self-propagation ($k_{22} = 0$, $r_2 = 0$) and at equimolar monomer feed ($[M_1]/[M_2] = 1$), eq 1 yields

$$r_1 = m_1/m_2 - 1 \quad (2)$$

or the equation for the relative reactivity of styrene radical k_{12}/k_{11} with TSE monomers:

$$1/r_1 = 1/(m_1/m_2) - 1 \quad (3)$$

Consideration of monomer reactivities according to eq 3 involves also the assumption of minimal copolymer compositional drift at equimolar monomer feed and given conversion. This nonrigorous kinetic treatment nevertheless allows estimation of the reactivity of a styrene-ended polymer radical in reaction with an electrophilic monomer. Relative reactivity data for substituted dicyanoethenes, methyl 2-cyanopropenoates, and 1,1-bis(methoxycarbonyl)ethenes in copolymerization with styrene as calculated from copolymer composition data of Tables I–III according to eq 3 are presented in Table IV. The values in the horizontal rows of the table give the general order of reactivity for the three series of trisubstituted ethylene monomers: dicyanoethenes > methyl 2-cyanopropenoates > 1,1-bis(methoxycarbonyl)ethenes. The order of monomer reactivities is approximately the same in each vertical column irrespective of the β-substituent. This order corresponds to the order of increased resonance stabilization by both α-substituents of the radical formed from the monomer.

$$\sim CH(R)C^{\bullet}(CN)_2 > \sim CH(R)C^{\bullet}(CO_2CH_3)(CN) > \sim CH(R)C^{\bullet}(CO_2CH_3)_2$$

Unlike mono- and 1,1-disubstituted monomers where substituents are much more effective in decreasing radical reactivity than increasing monomer reactivity, the reactivity of trisubstituted ethylene radicals increases on the same order as the reactivity of the monomers, apparently due to donor–acceptor interactions between electron-poor trisubstituted ethylene radicals and electron-rich styrene. Thus the reactivity of trisubstituted ethylene monomers and radicals increases on the same order as their acceptor properties.

The values in any vertical column in Table IV give the order of monomer reactivities within each series. In the dicyano series, the substituents increase reactivity of a trisubstituted ethylene monomer toward styrene radical in the following order: 3-pyridinyl > 5-norbornenyl > 1-naphthyl > 3-cyclohexenyl. For methyl 2-cyanopropenoates the order of monomer reactivity is somewhat different: 3-pyridinyl > 1-naphthyl > 5-norbornenyl > 3-cyclohexenyl > cyclohexyl. All 1,1-bis(methoxycarbonyl)ethenes, except the 3-pyridinyl-substituted monomer, have very low reactivity, which increases in the following order: 3-pyridinyl > phenyl > 5-norbornenyl > 1-naphthyl > cyclohexyl > 3-cyclohexenyl. 3-pyridinyl-substituted ethylenes appear to be the most reactive trisubstituted monomers of all three series, which might be associated with their aromatic character. It was observed that 2-phenyl-1,1-dicyanoethene[3] and methyl 3-phenyl-2-cyanopropenoate[24] are very reactive monomers in copolymerizations with styrene.

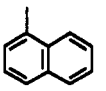
More detailed information on the copolymer composition at different monomer feed ratios would be necessary for the application of copolymerization models that would allow prediction of copolymer composition.

Physical Properties. The copolymers prepared in the present work are all amorphous powders, soluble in chloroform, DMF, and acetone and insoluble in methanol, heptane, and petroleum ether. IR and NMR data showed that these are true copolymers, composed of both trisubstituted ethylene and styrene monomer structural units. Molecular weights are approximately the same for the copolymers of dicyanoethenes and 2-cyanopropenoates and somewhat higher for 1,1-bis(methoxycarbonyl)ethenes (Tables I–III). For the last system they become comparable with that of polystyrene obtained under similar conditions. The polydispersity index (M_w/M_n) does not change significantly for the majority of the copolymerization pairs and remains close to that of polystyrene. Glass transition temperatures of the copolymers with substantial incorporation of trisubstituted ethylene monomer are raised by the substituents that have high dipolar character and restrict conformational mobility. Dicyanoethene–styrene copolymers have much higher T_g values (170–185 °C) than methyl cyanopropenoate based copolymers (127–133 °C). In the case of styrene copolymers with substituted 1,1-bis(methoxycarbonyl)ethenes, the electrophilic monomer content in the copolymers is too small to cause significant T_g changes.

Experimental Section

General Procedures. All boiling points and melting points are uncorrected. Capillary melting points were determined on a Gallenkamp melting point apparatus. Infrared spectra were determined with an IBM Model FT-IR-32 spectrometer in KBr or between NaCl plates (the wavelengths are given in reciprocal

Table V
Synthesis of Monomers

R^2; R^3	R^1 = 							
$R^2 = R^3 = CN$	1a	1b	1c		1d	1e	1f	1g
$R^2 = CN$; $R^3 = CO_2CH_3$	2a	2b	2c		2d	2e	2f	2g
$R^2 = R^3 = CO_2CH_3$	3a	3b	3c	3d	3e	3f	3g	3h

centimeters). ^1H and ^{13}C NMR spectra of monomers were obtained on a Bruker WP 270SY spectrometer. ^1H NMR spectra of the copolymers were recorded on a Varian EM-360L spectrometer. All NMR spectra were obtained on 10% solutions in deuteriochloroform at ambient temperature. Tetramethylsilane was used as the internal reference. Chemical shifts are reported on the δ scale in parts per million. Molecular weights of polymers were estimated by gel permeation chromatography using tetrahydrofuran and chloroform as eluents on a Waters GPC II liquid chromatograph equipped with a Waters 410 differential refractometer and with a set of 10^3-, 10^4-, 10^5-, and 10^6-Å Styragel columns. The retention times were calibrated against known polystyrene standards. Glass transition temperatures were recorded by using a Du Pont 9900 thermal analyzer with 910 DSC module. A sample of 5–10 mg was crimped in an aluminum pan and heated at a 10 °C/min rate. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY.

Synthesis of Monomers. Cyclohexanecarboxaldehyde (98%), 1,2,3,6-tetrahydrobenzaldehyde (99%), 5-norbornene-2-carboxaldehyde (95%), benzaldehyde (98+%), 1-naphthaldehyde (97%), 3-pyridinecarboxaldehyde (99%), pyrrole-2-carboxaldehyde (99%), 2-furaldehyde (99%), malonitrile (99%), methyl cyanoacetate (99%), dimethyl malonate (97%), and piperidine (98%) supplied from Aldrich Chemical Co. were used for monomer synthesis as received, without additional purification. The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of aldehyde and active methylene compound were mixed with a small amount of ethanol in an Erlenmeyer flask. A few drops of piperidine were added with stirring. The product of the reaction was isolated and purified by crystallization from ethanol or distillation (Table V).

2-Cyclohexyl-1,1-dicyanoethene (1a). Yield 62%; bp 90–93 °C (1 mmHg); ^1H NMR δ 7.2 (s, 1 H, CH=), 2.7 (s, 1 H, CHC=C), 1–2.3 (m, 10 H); ^{13}C NMR δ 160.0, 134.6, 130.6, 129.6, 113.7, 112.6, 82.7; IR (KBr) 2940, 2850 (s, C—H), 2240 (m, C≡N), 1600 (m, C=C), 1450 (m, CH_2). Anal. Calcd for $C_{10}H_{12}N_2$: C, 75.0; H, 7.50, N, 17.5. Found: C, 74.38; H, 7.45, N, 16.89.

2-(3-Cyclohexenyl)-1,1-dicyanoethene (1b). Yield 36.3%; bp 95 °C (0.4 mmHg); ^1H NMR δ 7.7 (d, 1 H, CH=), 5.8 (d, 2 H, CH=CH), 3.0 (s, 1 H, CHC=), 2.5–1 (m, 6 H); ^{13}C NMR δ 172.9, 127.0, 123.3, 112.0, 110.4, 88.2, 37.7, 28.8, 26.6, 22.9; IR (NaCl neat) 3032, 2923, 2841 (s, O—H), 2235 (m, C≡N), 960 (m, C=C). Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.95; H, 6.33; N, 17.72. Found: C, 75.90; H, 6.83, N, 17.31.

2-(5-Norbornenyl)-1,1-dicyanoethene (1c). Yield 37%; bp 93 °C (0.6 mmHg); ^1H NMR δ 7.3, 6.85 (d, 1 H, CH=), 5.7–6.3 (m, 2 H, endo CH=CH), 1.0–3.5 (m, 7 H, cyclic C–H); ^{13}C NMR δ 136.6, 136.0, 126.7, 121.0, 115.1, 113.2, 54.0, 40.3, 32.3, 27.5; IR (NaCl neat) 3057, 2939, 2853 (S, C—H), 2243 (m, C≡N), 1450 (s, CH_2 in plane), 756 (s, CH out of plane). Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.57; H, 5.88; N, 16.45. Found: C, 77.26; H, 5.82; N, 16.47.

2-(1-Naphthyl)-1,1-dicyanoethene (1d). Yield 73.2%; mp 172–173 °C; ^1H NMR δ 8.7 (s, 1 H, CH=), 7.5–8.5 (m, 7 H, naphthyl); ^{13}C NMR δ 157.6, 134.8, 131.0, 127.4, 125.3, 122.2, 113.6, 112.4, 85.1; IR (KBr) 3030 (m, C—H), 2228 (m, C≡N), 1566 (s, skeletal ring), 936 (m, C=C), 765, 779 (s, CH, out of plane). Anal. Calcd for $C_{14}H_8N_2$: C, 82.35; H, 3.92; N, 13.72. Found: C, 82.61; H, 4.30; N, 13.18.

2-(3-Pyridinyl)-1,1-dicyanoethene (1e). Yield 60.1; mp 125–126 °C; ^1H NMR δ 8.7 (s, 1 H, CH=), 7.8, 8.5, 8.9, 9.2 (m, 4 H, pyridyl); ^{13}C NMR δ 159.2, 154.7, 152.4, 136.7, 128.27, 124.8, 114.3, 113.4, 84.9; IR (KBr) 3030 (m, C—H), 2240 (m, C≡N), 1410 (s, CH_2 in plane), 800 (s, CH out of plane), 1450–1600 (s, pyridine ring). Anal. Calcd for $C_9H_4N_3$: C, 70.12; H, 2.6; N, 27.76. Found: C, 68.75; H, 3.3; N, 27.43.

2-(2-Pyrrolyl)-1,1-dicyanoethene (1f). Yield 68.8%; mp 132 °C (lit.[25] 134–135 °C); ^1H NMR δ 8.1 (s, 1 H, CH=), 7.7 (s, 1 H, CHN), 6.6, 7.5 (d, 2 H, =CHCH=), 12.2 (s, NH); ^{13}C NMR δ 147.8, 130.6, 127.7, 119.5, 116.3, 115.8, 114.6, 69.0; IR (KBr) 3350 (s, N—H), 3100 (m, C—H), 2218 (s, C≡N), 1587, 1348, 1327 (s, skeletal ring), 950, 930 (m, C=C), 773 (m, CH, out of plane). Anal. Calcd for $C_8H_5N_3$: C, 67.10; H, 3.49; N, 29.35. Found: C, 67.02; H, 3.14; N, 29.39.

2-(2-Furyl)-1,1-dicyanoethene (1g). Yield 67.8%; mp 73.4 °C (lit.[26] 72–73 °C); ^1H NMR δ 7.7 (s, 1 H, CH=), 7.45 (s, 1 H, CHO), 7.3, 6.6 (s, 2 H, =CHCH=); ^{13}C NMR δ 149.9, 148.1, 143.3, 124.2, 114.1, 112.8, 77.8, 77.4, 77.1, 76.9; IR (KBr) 3125, 3042 (m, C—H), 2231 (m, C≡N), 1606, 1458, 1398 (m, ring stretching), 1022, 767 (s, out-of-plane CH bend and ring), 935 (m, C=C). Anal. Calcd for $C_8H_4N_2O$: C, 66.70; H, 2.77; N, 19.44. Found: C, 66.49; H, 2.59; N, 19.59.

Methyl 3-Cyclohexyl-2-cyanopropenoate (2a). Yield 26%; mp 57 °C; ^1H NMR δ 7.5 (d, 1 H, CH=), 3.9 (s, 3 H, CH_3), 2.7 (s, 1 H, CHC=), 1.0–2.2 (m, cyclohexyl); ^{13}C NMR δ 168.1, 162.1, 113.7, 107.3, 53.1, 41.2, 31.1, 25.4, 24.9; IR (KBr) 2940, 2850 (s, C—H), 2240 (m, C≡N), 1720 (s, C=O), 1620, 980 (s, C=C), 1220 (s, C—O—CH_3). Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.39; H, 7.77; N, 7.25. Found: C, 68.52; H, 7.80; N, 7.25.

Methyl 3-(3-Cyclohexenyl)-2-cyanopropenoate (2b). Yield 25.6%; mp 56–57 °C; ^1H NMR δ 7.7 (d, 1 H, CH=), 5.8 (q, 2 H, CH=CH), 3.9 (s, 3 H, CH_3), 3.0 (m, 1 H, >CHC=), 1.5–2.3 (m, 10 H, cyclohexyl); ^{13}C NMR δ 167.2, 161.7, 127.0, 123.8, 113.4, 53.0, 36.7, 29.2, 26.9, 23.3; IR (KBr) 3030, 2920, 2841 (m, C—H), 2230 (m, C≡N), 1720 (s, C=O), 1240 (s, C—O—CH_3). Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.11; H, 6.80; N, 7.30. Found: C, 69.25; H, 6.72; N, 7.17.

Methyl 3-(5-Norbornenyl)-2-cyanopropenoate (2c). Yield 60.6; bp 100 °C (0.3 mmHg); ^1H NMR δ 7.1–7.6 (d, 1 H, CH=), 5.9–6.3 (t, 2 H, endo CH=CH), 3.8 (d, 3 H, CH_3), 0.8–3.2 (m, 7 H, cyclic CH); ^{13}C NMR δ 168.8, 167.9, 138.6, 137.6, 135.0, 131.5, 113.3, 107.3, 52.4, 49.3, 48.0, 45.11, 42.4, 41.4, 32.7; IR (KBr) 3039, 2920, 2840 (m, C—H), 2235 (w, C≡N), 1720 (s, C=O), 1240 (s, C—O—CH_3). Anal. Calcd. for $C_{12}H_{13}NO_2$: C, 70.93; H, 6.40; N, 6.89. Found: C, 68.86; H, 6.57; N, 7.10.

Methyl 3-(1-Naphthyl)-2-cyanopropenoate (2d). Yield 81.1; mp 108–109 °C; ^1H NMR δ 9.2 (s, 1 H, CH=), 8.5–7.5 (m, 7 H, naphthyl), 4.0 (s, 3 H, CH_3); ^{13}C NMR δ 162.7, 152.8, 133.4, 129.1, 128.1, 127.7, 126.7, 125.3, 122.7, 115.3, 105.1, 53.2; IR (KBr) 3040–2850 (m, C—H), 2226 (w, C≡N), 1740 (s, C=O), 1600 (s, C=C), 1420 (s, CH=C), 1250 (s, C—O—CH_3), 720 (s, CH out of plane). Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.95; H, 4.64; N, 5.90. Found: C, 75.76; H, 4.89; N, 5.69.

Methyl 3-(3-Pyridinyl)-2-cyanopropenoate (2e). Yield 74.2; mp 125–126 °C; ^1H NMR δ 8.9 (s, 1 H, CH=), 8.8, 7.5 (m, 4 H pyridyl), 4.0 (s, 3 H, CH_3); ^{13}C NMR δ 162.1, 153.5, 152.8, 136.0, 127.4, 124.0, 114.8, 105.2, 53.6; IR (KBr) 3030, 2840 (s, C—H), 2230 (w, C≡N), 1720 (s, C=O), 1620 (s, C=C), 1240 (s, C—O—CH_3). Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.8 H, 4.26; N, 14.89. Found: C, 64.01; H, 4.26; N, 14.75.

Methyl 3-(2-Pyrrolyl)-2-cyanopropenoate (2f). Yield 50.5; mp 139–140 °C; ^1H NMR δ 9.9 (s, 1 H, NH), 8.0 (s, 1 H, CH=), 7.4, 6.9, 6.4 (m, 3 H, pyrrolyl); ^{13}C NMR δ 164.0, 142.7, 128.7, 126.7, 124.3, 118.3, 112.9, 91.3, 52.9; IR 3300 (s, N—H), 3100–2800 (w, C—H), 2225 (m, C≡N), 1700 (s, C=O), 1600 (s, C=C), 1250 (s, C—O—CH_3). Anal. Calcd for $C_9H_8N_2O_2$: C, 61.36; H, 4.55; N, 15.91. Found: C, 61.60; H, 4.75; N, 15.74.

Methyl 3-(2-Furyl)-2-cyanopropenoate (2g). Yield 83.7; mp 91–92 °C; ^{1}H NMR δ 8.0 (s, 1 H, CH=, vinyl), 7.8 (s, 1 H, =CHO), 7.4, 6.7 (d, 2 H, =CH—CH=); ^{13}C NMR δ 163.0, 148.7, 139.6, 121.9, 114.8, 113.9, 98.2, 53.3; IR (KBr) 3100–2800 (w, C—H), 2230 (w, C≡N), 1720 (s, C=O), 1620 (s, C=C), 1250 (s, C—O—CH_3). Anal. Calcd for $C_9H_7NO_3$: C, 61.02; H, 3.95; N, 7.91. Found: C, 60.56; H, 4.08; N, 7.95.

2-Cyclohexyl-1,1-bis(methoxycarbonyl)ethene (3a). Yield 74.6%; bp 106 °C (0.6 mmHg); ^{1}H NMR δ 6.8 (d, 1 H, CH=), 3.8 (d, 6 H, CH_3), 2.4 (s, 1 H, >CHC=) 1.8, 1.2 (m, 10 H, cyclohexyl); ^{13}C NMR δ 166.0, 164.6, 154.4, 126.1, 52.2, 39.1, 31.7, 25.6, 25.2; IR (NaCl neat) 2920 (s, C—H), 1720 (s, C=O), 1420 (s, C=C), 1250 (s, C—O—CH_3). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.72; H, 7.96. Found: C, 63.55; H, 8.04.

2-(3-Cyclohexyl)-1,1-bis(methoxycarbonyl)ethene (3b). Yield 48.3%; bp 90 °C (0.4 mmHg); ^{1}H NMR δ 6.9 (d, 1 H, CH=), 5.8–6.3 (m, 2 H, CH=CH), 3.8 (m, 6 H, CH_3), 2.9 (s, 1 H, >CHC=); ^{13}C NMR δ 166.7, 165.7, 164.3, 153.4, 126.8, 124.6, 52.1, 34.7, 29.8, 27.4, 23.6; IR (NaCl neat) 3020–2800 (s, C—H), 1740 (s, C=O), 1440 (m, C=C), 1250 (s, C—O—CH_3). Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.28; H, 7.14. Found: C, 63.19; H, 7.11.

2-(5-Norbornenyl)-1,1-bis(methoxycarbonyl)ethene (3c). Yield 39.1%; bp 100 °C (0.1 mmHg); ^{1}H NMR δ 7.0–6.4 (q, 1 H, CH=), 6.3–5.8 (d, 2 H, endo CH=CH), 3.7 (s, 6 H, CH_3), 3.5–1.0 (m, 7 H, cyclic CH); ^{13}C NMR δ 169.9, 168.7, 166.1, 165.9, 164.3, 155.5, 154.9, 148.7, 138.5, 137.7, 135.7, 134.0, 132.3, 126.6, 110.3, 52.9, 52.1, 49.7, 48.1, 45.5, 42.8, 42.4, 39.4, 39.0, 33.5, 31.7; IR (NaCl neat) 2950 (s, C—H); 1738 (s, C=O), 1440 (s, C=C), 1250 (s, C—O—CH_3). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.02; H, 6.77. Found: C, 65.13; H, 7.01.

2-Phenyl-1,1-bis(methoxycarbonyl)ethene (3d). Yield 63.4%; bp 110 °C (0.3 mmHg) (lit.[27] bp 120 °C (0.9 mmHg)); ^{1}H NMR δ 7.7 (s, 1 H, CH=), 7.2 (s, 5 H, phenyl), 3.7 (s, 6 H, CH_3); ^{13}C NMR δ 166.9, 164.4, 142.7, 132.8, 130.8, 129.4, 128.9, 125.7, 52.5; IR (NaCl, neat) 2950 (w, C—H), 1730 (s, C=O), 1640 (m, phenyl), 1430, (m, C=C), 1250 (s, C—O—CH_3), 690 (m, phenyl). Anal. Calcd for $C_{12}H_{11}O_4$: C, 65.75; H, 5.02. Found: C, 65.62; H, 5.49.

2-(1-Naphthyl)-1,1-bis(methoxycarbonyl)ethene (3e). Yield 47.3; mp 68–69 °C; ^{1}H NMR δ 8.5 (s, 1 H, CH=), 8.0–6.2 (m, 7 H, naphthyl), 3.9, 3.6 (d, 6 H, CH_3); ^{13}C NMR δ 166.5, 164.2, 141.7, 133.4, 131.3, 130.6, 128.7, 127.0, 126.2, 125.2, 123.8, 52.4; IR (KBr) 2780 (s, C—H), 1740 (s, C=O), 1430 (m, C=C), 1250 (s, C—O—CH_3), 806, 780 (m, Ar). Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.03; H, 5.19. Found: C, 71.11; H, 5.15.

2-(3-Pyridinyl)-1,1-bis(methoxycarbonyl)ethene (3f). Yield 98.6; mp 50–51 °C; ^{1}H NMR δ 8.8–7.2 (m, 5 H, CH= and pyridyl), 3.7 (s, 6 H, CH_3); ^{13}C NMR δ 191.0, 166.3, 163.9, 154.7, 152.0, 151.3, 150.6, 139.2, 135.8, 135.6, 128.8, 127.7, 124.1, 123.7, 52.8; IR (KBr) 3028, 2955, 2849 (w, C—H), 1730 (s, C=O), 1430 (m, C=C), 1220 (s, C—O—CH_3), 830, 812 (m, Ar). Anal. Calcd for $C_{11}H_{11}NO_4$: C, 59.72; H, 4.98; N, 6.33. Found: C, 60.14; H, 4.97; N, 7.02.

2-(2-Pyrrolyl)-1,1-bis(methoxycarbonyl)ethene (3g). Yield 97.4; bp 118 °C (0.5 mm Hg (lit.[27] bp 128 °C (0.08 mmHg)); ^{1}H NMR δ 7.6 (s, 1 H, CH=), 7.2–6.1 (t, 3 H, pyrrolyl), 3.7 (s, 6 H, CH_3); ^{13}C NMR δ 168.3, 166.9, 138.0, 127.0, 126.5, 123.4, 112.4, 111.6, 52.4, 52.2; IR (NaCl, neat), 3329 (m, N—H), 2953 (m, C—H), 1716 (s, C=O), 1440 (s, C=C), 1269, 1230 (s, C—O—CH_3). Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.42; H, 5.26; N, 6.70. Found: C, 57.51; H, 5.58; N, 6.90.

2-(2-Furyl)-1,1-bis(methoxycarbonyl)ethene (3h). Yield 64.9%; bp 115 °C (0.6 mmHg); ^{1}H NMR δ 7.5 (s, 2 H, CH= and CHO), 6.6, 6.4 (d, 2 H, =CHCH=), 3.8 (s, 6 H, CH_3); ^{13}C NMR δ 166.7, 164.5, 148.9, 146.7, 128.1, 121.3, 118.5, 112.9, 52.5; IR (NaCl, neat) 3100, 3000, 2950 (m, C—H), 1730 (s, C=O), 1420 (s, C=C), 1250 (s, C—O—CH_3). Anal. Calcd for $C_{10}H_{10}O_5$: C, 57.14; H, 4.76. Found: C, 56.74; H, 4.74.

Homopolymerization. Polymerizations of trisubstituted ethylene monomers or styrene (2 mol/L) were conducted in glass tubes at 70 °C in benzene or ethyl acetate for 240 h with AIBN as an initiator (0.0045 mol/L). Polymerization tubes were also irradiated at room temperature. The solutions then were precipitated in 800 mL of methanol. Polystyrene was isolated by filtration and dried in a vacuum oven.

Copolymerization. In the typical copolymerization procedure, a 100-mL glass tube was charged with equimolar amounts of a trisubstituted ethylene (TSE) monomer and styrene (ST) ([TSE] + [ST] = 2 mol/L), AIBN (0.0045 mol/L), and solvent; purged with nitrogen; and sealed. The mixture was polymerized at 70 °C. After a predetermined time, the copolymerization mixture was cooled to room temperature and precipitated dropwise in methanol. Polymer was collected by suction, redissolved in chloroform or DMF, and reprecipitated in methanol. Filtered polymers were dried in a vacuum oven at 60 °C to constant weight. Compositions of the copolymers were estimated on the basis of the elemental analysis and ^{1}H NMR spectra.

Characterization of Copolymers (Tables I–III). No. 2: Yield 6.7%; IR (KBr) 3080–2800, 2242, 1678, 1603, 1495, 1452, 756, 700; ^{1}H NMR δ 7.5–6.3, 3.2–0.5. Anal. C, 85.04; H, 7.35; N, 6.56.

No. 3: Yield 2.7%; IR (KBr) 3080–2800, 2243, 1601, 1493, 1452, 758, 698, 542; ^{1}H NMR δ 7.6–6.2, 3.6–0.5. Anal. C, 87.78; H, 7.91; N, 3.4.

No. 4: Yield 8.5%; IR (KBr) 3080–2800, 2241, 1672, 1585, 1512, 1495, 1454, 1396, 1074, 1030, 783, 700, 538; ^{1}H NMR δ 8.0–5.5, 3.5–0.5. Anal. C, 85.63; H, 6.10; N, 6.82.

No. 5: Yield 14.1%; IR (KBr) 3080–2800, 2240, 1666, 1495, 1456, 1429, 1093, 760, 700; ^{1}H NMR δ 7.5–6.0, 2.8, 2.2, 1.2, 0.8. Anal. C, 79.01; H, 6.39; N, 12.41.

No. 8: Yield 7.4%; IR (KBr) 3080–2800, 2242, 1700, 1602, 1495, 1450, 1030, 754, 702, 542; ^{1}H NMR δ 7.3–6.0, 2.8, 2.3–0.8. Anal. C, 90.22; H, 8.24; N, 1.16.

No. 9: Yield 14.9%; IR (KBr) 3000, 2243, 1740, 1600, 1495, 1450, 1230, 755, 700, 540; ^{1}H NMR δ 7.3–6.0, 3.8–2.6, 2.3–0.6. Anal. C, 87.57; H, 7.56; N, 1.64.

No. 10: Yield 3.9%; IR (KBr) 3080–2800, 2244, 1740, 1495, 1450, 1240, 750, 700, 545; ^{1}H NMR δ 7.4–6.2, 3.8, 3.2–0.5. Anal. C, 83.01; H, 7.13; N, 2.83.

No. 11: Yield 17.8%; IR (KBr) 3080–2800, 2242, 1745, 1600, 1500, 1450, 1240, 1030, 780, 750, 700, 540; ^{1}H NMR δ 8.0–5.5, 3.4–0.5. Anal. C, 88.13; H, 6.48; N, 3.14.

No. 12: Yield 20.5%; IR (KBr) 3080–2800, 2245, 1745, 1495, 1450, 1240, 1030, 755, 695, 540; ^{1}H NMR δ 8.3–5.5, 3.3–0.5. Anal. C, 74.66; H, 6.16; N, 8.10.

No. 15: Yield 13.0%; IR (KBr) 3080–2800, 1725, 1600, 1495, 1450, 1030, 755, 700; ^{1}H NMR δ 7.2–5.8, 2.5–0.5. Anal. C, 91.25; H, 7.71.

No. 16: Yield 18.0%; IR (KBr) 3080–2800, 1730, 1600, 1490, 1450, 1240, 755, 700; ^{1}H NMR δ 7.5–6.0, 2.5–0.5. Anal. C, 91.63; H, 7.55.

No. 17: Yield 17.1%; IR (KBr) 3080–2800, 1734, 1601, 1493, 1452, 1028, 906, 756, 648, 540; ^{1}H NMR δ 7.3–6.2, 2.3–0.5. Anal. C, 90.77; H, 7.55.

No. 18: Yield 14.7%; IR (KBr) 3080–2800, 1740, 1600, 1490, 1450, 1240, 1030, 750, 690, 540; ^{1}H NMR δ 7.3–6.0, 2.2–0.5. Anal. C, 89.08; H, 7.71.

No. 19: Yield 19.6%; IR (KBr) 3080–2800, 1734, 1601, 1493, 1452, 1068, 1028, 906, 756, 698, 538; ^{1}H NMR δ 7.3–6.0, 2.3–0.5. Anal. C, 90.77; H, 7.69.

No. 20: Yield 0.7%; IR (KBr) 3420, 3026–2920, 1734, 1603, 1493, 1452, 1205, 756, 698; ^{1}H NMR δ 8.3–5.5, 2.3–0.5. Anal. N, 1.35.

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Registry No. 1a, 73776-46-2; **1b**, 99071-52-0; **1c**, 22629-10-3; **1d**, 2972-83-0; **1e**, 7424-56-8; **1f**, 15031-03-5; **1g**, 3237-22-7; **2**, 115324-39-5; **2a**, 121125-87-9; **2b**, 121125-89-1; **2c**, 121125-91-5; **2d**, 121125-93-7; **2e**, 121125-95-9; **2f**, 121142-19-6; **2g**, 69513-10-6; **3**, 121125-86-8; **3a**, 67498-35-5; **3b**, 100257-85-0; **3c**, 121125-97-1; **3d**, 6626-84-2; **3e**, 115324-50-0; **3f**, 74299-85-7; **3g**, 96238-10-7; **3h**, 74299-84-6; **4**, 115324-42-0; **5**, 115324-43-1; **8**, 121125-88-0; **9**, 121125-90-4; **10**, 121125-92-6; **11**, 121125-94-8; **12**, 121125-96-0; **15**, 115324-45-3; **16**, 115324-46-4; **17**, 121125-98-2; **18**, 115324-49-7; **19**, 115324-51-1; **20**, 121125-99-3; styrene, 100-42-5.

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Living Cationic Polymerization of Vinyl Monomers by Organoaluminum Halides. 4. Polymerization of Isobutyl Vinyl Ether by $EtAlCl_2$ in the Presence of Ether Additives

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ABSTRACT: In the presence of added ethers (1,4-dioxane, tetrahydrofuran, and diethyl ether), living cationic polymerization of isobutyl vinyl ether was achieved in *n*-hexane at 0 to +40 °C with the use of the 1-(isobutoxy)ethyl acetate ($CH_3CH(O\text{-}i\text{-}Bu)OOCCH_3$, 1)/ethylaluminum dichloride ($EtAlCl_2$) initiating system. In particular, 1,4-dioxane as an ether additive permitted a living process operable even at +70 °C. The optimum amount of the added ethers needed for the living polymerization depended on their basicity, increasing in the order THF (1–2 vol %) > 1,4-dioxane (5–10 vol %) > Et_2O (70 vol %); diisopropyl ether, less basic and more sterically hindered than diethyl ether, was unable to induce a similar living process even when employed as solvent at 0 °C. Under these living conditions the polymers exhibited very narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n \leq 1.1$), and the number-average molecular weights ($\bar{M}_n$) increased in direct proportion to monomer conversion as well as to the reciprocal of the initial concentration of 1 (as cationogen). In the polymerization with added 1,4-dioxane below +40 °C, the $\bar{M}_n$ also increased on addition of a second monomer feed to a polymerized reaction mixture. For comparison, polymerizations by $H_2O/EtAlCl_2$ and $CH_3CO_2H/EtAlCl_2$ initiating systems were also carried out in the presence of the ethers.

Introduction

We have recently established a method for truly living cationic polymerizations of vinyl monomers, for the first time, based on the concept of stabilization of unstable propagating carbocations by suitably nucleophilic counteranions.[2] Another concept for living cationic polymerization, which has also proved successful more recently, invokes added inert bases for stabilization of growing carbocations associated by less nucleophilic counteranions that are per se unable to stabilize their cationic partners.[3] For example, in the presence of a large excess of an ester[4] or ether,[5] the polymerization of isobutyl vinyl ether (IBVE) with ethylaluminum dichloride ($EtAlCl_2$), in conjunction with a protogen or cationogen, yields well-defined living polymers, whereas the absence of the added base results in a transfer-dominant nonliving polymerization with other reaction conditions the same.

For esters and related carbonyl compounds, our latest study[6] has further clarified in detail which types of such oxygen bases fit for stabilizing growing cations, as well as the optimum reaction conditions for the $EtAlCl_2$-mediated living processes of IBVE in the presence of esters. It has been proposed that the basic carbonyl oxygen of an ester plays a critical role in stabilizing the otherwise unstable propagating carbocation so as to endow it with living character.

Following our preliminary report,[5] the present study is concerned with the use of a series of ethers (1,4-dioxane, tetrahydrofuran, diethyl ether, and diisopropyl ether) as basic additives that, similarly to esters, may effect living cationic polymerization of IBVE. The initiating systems employed herein are all based on $EtAlCl_2$, coupled with 1-(isobutoxy)ethyl acetate ($CH_3CH(O\text{-}i\text{-}Bu)OCOCH_3$, 1),[3] water, or acetic acid (CH_3CO_2H), as cationogen or protogen. Particular emphasis was placed on the relationship between the basicity (or structure) of the ethers and their cation-stabilizing ability.

Experimental Section

Materials. Commercial IBVE (Tokyo Kasei Kogyo) was washed with an aqueous alkaline solution and water and distilled twice over calcium hydride just before use.[4] $EtAlCl_2$ was commercially obtained as a *n*-hexane solution (1.0 M; Kanto Chemicals) and used without further purification. 1,4-Dioxane (DO), tetrahydrofuran (THF), diethyl ether (Et_2O), and diisopropyl ether (iPr_2O) (Wako Chemicals, all guaranteed reagents) were dried over calcium chloride and then distilled over calcium hydride before use. *n*-Hexane and toluene as polymerization solvents were purified by the usual method[3] and distilled twice over calcium

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