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Ring-Opening Polymerization of 2,5,6-Trisubstituted-3,4-dihydro-2*H*-pyrans. Syntheses of Head-to-Head Alternating Vinyl Copolymers and Their Properties[1]

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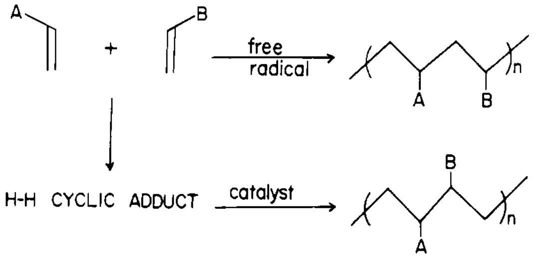
ABSTRACT: 2,6-Diethoxy-5-cyano-3,4-dihydro-2*H*-pyran (**1a**) and 2-*n*-butoxy-6-ethoxy-5-cyano-3,4-dihydro-2*H*-pyran (**1b**) were prepared by [4 + 2] head-to-head (H–H) cycloaddition reaction of ethyl α-cyanoacrylate with the corresponding vinyl ethers. 2-Ethoxy-6-methyl-3,4-dihydro-2*H*-pyran (**1c**), 2-*n*-butoxy-6-methyl-3,4-dihydro-2*H*-pyran (**1d**), and 2-methoxy-6-phenyl-3,4-dihydro-2*H*-pyran (**1e**) were prepared from the corresponding vinyl ketones and alkyl vinyl ethers. Compounds **1a–e** were ring-open polymerized by cationic or anionic catalysts to obtain high molecular weight polymers of H–H alternating sequence. For comparison, copolymers of head-to-tail (H–T) structure were also prepared by free radical copolymerization of the mixtures of the corresponding monomers. The H–H copolymers exhibited only minor differences in their ^{1}H NMR and IR spectra, but in the ^{13}C NMR spectra the H–H copolymers showed a significant difference, exhibiting the signal attributable to the extra backbone methylene carbon. Also noteworthy was that T_g values of the H–H copolymers were always higher than those of the corresponding H–T copolymers. Decomposition temperatures of the H–H copolymers were usually lower than those of the H–T copolymers. All of the H–H and H–T copolymers were soluble in common solvents.

Introduction

Vinyl polymers of head-to-head (H–H) structure are expected to show different physical and chemical properties from those of conventional head-to-tail (H–T) polymers, and to this subject much attention has been paid recently. Preparation of various H–H vinyl polymers has been reported, and some representative examples are the H–H structures of polypropylene,[2] polystyrene,[3] poly(vinyl chloride),[4] poly(vinylidene fluoride),[5] poly(methyl acrylate),[6] poly(methyl cinnamate),[7] etc.[8]

However, the synthetic schemes applied hitherto to prepare H–H polymers have been either by the reactions on polymers such as the chlorination of polybutadiene to H–H poly(vinyl chloride)[4] or by the copolymerization of stilbene with maleic anhydride, followed by esterification to H–H poly(methyl cinnamate).[7] In these synthetic methods, however, it is often difficult to get clean and complete reactions, leaving certain possibilities of contamination by undesired side products. Thus, it is of interest to find monomer-to-polymer synthetic routes that lead to the unequivocal and pure H–H vinyl polymers.

Our approach to this problem was based on the well-known chemistry in that certain monomer pairs which give one-to-one alternating copolymers upon free radical copolymerization often react in [2 + 2] H–H fashion to form cyclic adducts. A good example is the system consisting of vinylidene cyanide and alkyl vinyl ethers. If one can find a way to ring-open polymerize the H–H cycloaddition products by certain catalysts, it would be possible to obtain H–H alternating copolymers.



Stille and Chung[9] have prepared several 1,2-disubstituted cyclobutanes by [2 + 2] H–H cycloaddition reactions of certain monomer pairs and attempted their ring-opening polymerizations with various catalysts. However, all the substituted cyclobutanes failed to polymerize.

We also have prepared a series of cycloadducts and attempted their ring-opening polymerizations. Most of the cycloadducts again failed to polymerize. However, it has been reported recently that the particular adducts between ethyl α-cyanoacrylate and alkyl vinyl ethers were not cyclobutanes but 2,6-dialkoxy-5-cyano-3,4-dihydro-2*H*-pyrans,[13] and we found that these substituted dihydro-2*H*-pyrans polymerized well by ionic catalysts. The interesting feature of the ring-opening polymerizations of

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these substituted dihydro-2*H*-pyrans is that the polymers formed possess H–H alternating structures. Thus, we have found a unique system in which both H–H and H–T alternating copolymers can be prepared by a monomer-to-polymer method for comparative property studies.

We have now prepared and polymerized a series of substituted 3,4-dihydro-2*H*-pyrans and wish to report an account of the work.

Experimental Section

Materials. The reagent grade chemicals were purified by distillation or recrystallization before use. Dimethyl sulfoxide (Me_2SO) was dried over molecular sieves for several days and distilled before use. Sodium cyanide was recrystallized from ethanol–water (3:1 by volume) and stored in a desiccator. Benzene was purified by refluxing over sodium metal, distilled, and stored over molecular sieves under nitrogen. Boron trifluoride etherate was treated with a small amount of ethyl ether and distilled under reduced pressure. Methylene chloride was dried with $CaCl_2$, distilled over $CaSO_4$, and stored in a brown bottle with 4-Å molecular sieves. Chloroform was washed with water to remove the ethanol and refluxed with P_2O_5, followed by fractional distillation. Ethyl vinyl ether and *n*-butyl vinyl ether were dried over sodium metal and distilled under vacuum, taking the middle fraction. Technical grade ethyl α-cyanoacrylate for adhesive use was used without further purification. Anionic initiator solution was prepared by dissolving 0.1 g of purified sodium cyanide in 10 mL of Me_2SO.

Measurements. All measured temperatures were uncorrected. IR spectra were taken on a Perkin-Elmer Model 283B spectrophotometer. ^1H NMR spectra were obtained on a Varian Model T-60A spectrometer (60 MHz). ^{13}C NMR spectra were obtained on a Varian FT 80-A NMR spectrometer at room temperature. The glass transition temperatures (T_g) were measured on a 910 differential scanning calorimeter (DuPont Instrument, 990 thermal analyzer) in a N_2 atmosphere. A Perkin-Elmer TGS-1 thermobalance with a heating rate of 10 °C/min up to 500 °C was used for the thermal degradation study of the copolymers in a N_2 atmosphere. Melting points were taken on a Thomas-Hoover melting point apparatus.

Preparation of 2,6-Diethoxy-5-cyano-3,4-dihydro-2*H*-pyran (1a). 2-Alkoxy-6-ethoxy-5-cyano-3,4-dihydro-2*H*-pyrans **1a** and **1b** were prepared according to the known method[13] from ethyl α-cyanoacrylate and alkyl vinyl ethers. A solution of 25.0 g (0.20 mol) of ethyl α-cyanoacrylate in 120 mL of dry toluene was added slowly to the toluene (180 mL) solution of ethyl vinyl ether (18.0 g, 0.25 mol) under N_2. The mixture was stirred at room temperature for 3 days. Solvent and excess ethyl vinyl ether were then removed under reduced pressure, and the resulting viscous liquid was placed in a refrigerator (−20 °C) to crystallize. Colorless plate crystals were collected and washed a few times with cold CCl_4. **1a**: 36.2 g (92% yield); mp 16 °C; ^1H NMR ($CDCl_3$) δ 5.30 (1 H, t), 3.32–4.40 (4 H, m), 2.15–2.60 (2 H, m), 1.65–1.97 (2 H, m), 1.10–1.45 (6 H, m); IR (neat) 2200 ($C{\equiv}N$), 1640 ($C{=}C$) cm^{-1}.

Preparation of 2-*n*-Butoxy-6-ethoxy-5-cyano-3,4-dihydro-2*H*-pyran (1b). A solution of 18.8 g (0.15 mol) of ethyl α-cyanoacrylate in 80 mL of toluene was mixed with a toluene (120 mL) solution of *n*-butyl vinyl ether (20.0 g, 0.20 mol) under N_2. The mixture was allowed to stand at room temperature for 3 days. The trace amount of poly(ethyl α-cyanoacrylate) formed was separated by filtration. Solvent toluene and excess *n*-butyl vinyl ether were then removed under reduced pressure to give 29.0 g (86% yield) of **1b**: ^1H NMR ($CDCl_3$) δ 5.35 (1 H, t), 3.35–4.40 (4 H, m), 2.15–2.65 (2 H, m), 1.60–2.10 (2 H, m), 1.15–1.60 (4 H, m), 0.80–1.20 (3 H, d); IR (neat) 2200 ($C{\equiv}N$), 1640 ($C{=}C$) cm^{-1}.

Preparation of 2-Ethoxy-6-methyl-3,4-dihydro-2*H*-pyran (1c). 2-Alkoxy-6-alkyl(or aryl)-3,4-dihydro-2*H*-pyrans **1c–e** were preparad by known methods[10,11,15] from the corresponding vinyl ketones and alkyl vinyl ethers. Methyl vinyl ketone (35.0 g, 0.50 mol), 43.2 g (0.60 mol) of ethyl vinyl ether, and 0.2 g of hydroqinone were placed in a stainless steel bomb. The bomb was then placed in an oven kept at 200 °C. After 10 h the bomb was cooled and opened. The reddish product was distilled fractionally under vacuum to give 29.8 g (42% yield) of **1c**: bp 52–54 °C (15 mm) (lit.[11] bp 51–52 °C (14 mm); ^1H NMR (CCl_4) δ 4.90 (1 H, t), 4.40 (1 H, m), 3.20–4.05 (2 H, m), 1.55–2.20 (7 H, m), 1.15 (3 H, t); IR (neat) 1690 ($C{=}C$) cm^{-1}.

Preparation of 2-*n*-Butoxy-6-methyl-3,4-dihydro-2*H*-pyran (1d). Methyl vinyl ketone (31.5 g, 0.45 mol), 55.0 g (0.55 mol) of *n*-butyl vinyl ether, and 0.3 g of hydroquinone were placed in a bomb. The bomb was then placed in an oven kept at 200 °C. After 12 h the bomb was cooled and opened. Fractional distillation of the product under vacuum gave 30.6 g (40% yield) of **1d**: bp 80–82 °C (15 mm); ^1H NMR (CCl_4) δ 4.90 (1 H, t), 4.45 (1 H, m), 3.20–3.95 (2 H, m), 1.15–2.20 (11 H, m), 0.95 (3 H, d); IR (neat) 1690 ($C{=}C$) cm^{-1}.

Preparation of 2-Ethoxy-6-phenyl-3,4-dihydro-2*H*-pyran (1e). Phenyl vinyl ketone (42.2 g, 0.32 mol), 27.4 g (0.38 mol) of ethyl vinyl ether, and 0.3 g of hydroquinone were placed in a bomb and heated to 150 °C. After 10 h the bomb was opened, and the resulting black product was distilled fractionally through a helix column. **1e**: 15.0 g (23% yield); bp 88–90 °C (0.9 mm); ^1H NMR ($CDCl_3$) δ 7.05–7.60 (5 H, m), 5.30 (1 H, t), 5.10 (1 H, t), 3.30–4.05 (2 H, m), 1.95–1.40 (2 H, m), 1.55–1.95 (2 H, m), 1.15 (3 H, t); IR (neat) 1695 ($C{=}C$), 1660 ($C{=}C$ of the benzene ring) cm^{-1}.

Anionic Polymerization of 2,6-Dialkoxy-5-cyano-3,4-dihydro-2*H*-pyrans 1a and 1b. A representative anionic polymerization procedure (the case of **1a**) was as follows: In a rubber septum stopper capped glass ampule were placed a solution of dihydro-2*H*-pyran **1a** (1.97 g, 10 mmol) and 3.6 mL of dry Me_2SO, and dry N_2 gas was passed through the solution by a syringe needle for 30 min. The solution was then cooled in a dry ice–acetone bath, and to it was added 0.75 mL of initiator solution (0.20 M NaCN in Me_2SO) by a microsyringe. The ampule was then evacuated and sealed under vacuum. The sealed ampule was taken out of the dry ice–acetone bath and allowed to stand at room temperature. As polymerization proceeded, a red color developed and the viscosity of the solution increased. After 4 days the ampule was opened and the viscous polymer solution was poured into a large volume of cold Et_2O. Precipitated polymer was collected and reprecipitated from $CHCl_3$ into Et_2O. Thus obtained polymer was then dried in a vacuum oven at room temperature. **2a**: 1.75 g (89% yield); η_{inh} = 0.19 dL/g (*c* 0.5 g/dL in $CHCl_3$ at 20 °C). The ^1H NMR spectrum indicated that the composition of the copolymer was approximately 1.0:1.0.

Cationic Polymerization of 2,5,6-Trisubstituted-3,4-dihydro-2*H*-pyrans 1a–e. A representative cationic polymerization procedure (the case of **1c**) was as follows: A solution of **1c** (2.84 g, 20 mmol) was placed in a rubber septum stopper capped glass ampule under dry N_2. The resulting solution was flushed with N_2 for 20 min. The ampule was then placed in dry ice–acetone bath under N_2, and 0.015 mL of $BF_3{\cdot}OEt_2$ was added to the solution. After 4 h the ampule was taken out and the polymerization mixture was poured into a large volume of water. The precipitated white polymer was collected and reprecipitated from acetone into water. Thus obtained polymer was then dried in a vacuum oven at 40 °C. **2c**: 2.50 g (88% yield); η_{inh} = 0.38 dL/g (*c* 0.5 g/dL in $CHCl_3$ at 25 °C).

Preparation of H–T Alternating Copolymers 3a–e. All of the H–T alternating copolymers were prepared by conventional free radical copolymerization at 60 °C in benzene with AIBN. A representative polymerization procedure (the case of **3a**) was as follows: In a rubber septum stopper capped glass ampule were placed a solution of ethyl vinyl ether (0.96 g, 12.5 mmol) and 20 mg of AIBN in 10 mL of benzene. The resulting solution was flushed with N_2 for 30 min. The ampule was then placed in a dry ice–acetone bath, and the solution was allowed to freeze. To it was added 1.25 g (10 mmol) of ethyl α-cyanoacrylate, and the ampule was sealed under vacuum. The ampule was then placed in an oil bath kept at 60 °C. After 10 h the ampule was opened and the viscous solution was poured into a large volume of Et_2O. The precipitated polymer was collected and reprecipitated three times from $CHCl_3$ into Et_2O. **3a**: 0.50 g (30% yield); η_{inh} = 0.50 dL/g (*c* 0.5 g/dL in $CHCl_3$ at 25 °C). The ^1H NMR spectrum of **3a** indicated that the composition of the copolymer was approximately 1.0:1.0.

Results and Discussion

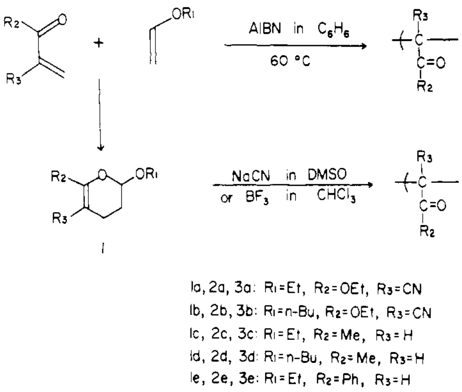
Preparation of Substituted 3,4-Dihydro-2*H*-pyrans 1a–e. It is rather well-known that electron-rich olefins and

Table I
Ring-Opening Polymerization[a] of 2,5,6-Trisubstituted-3,4-dihydro-2*H*-pyrans 1a–1e under Various Conditions

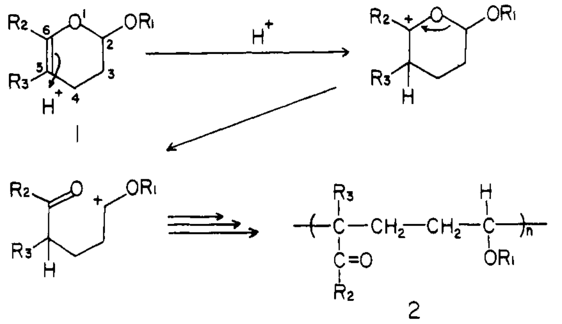
monomer	solvent	monomer/ solvent, g/mL	initiator to monomer, mol %	temp, °C	time, h	yield of product polymer	η_{inh}, dL/g
1a	$CHCl_3$	0.20	BF_3, 0.5	−30	20	95	0.37[b]
1a	CH_2Cl_2	0.10	BF_3, 0.7	−78	20	92	0.37[b]
1b	$CHCl_3$	0.18	BF_3, 0.7	−30	22	91	0.27[b]
1b	CH_2Cl_2	0.16	BF_3, 0.7	−78	24	88	0.35[b]
1a	Me_2SO	0.55	NaCN, 1.5	25	96	89	0.19[b]
1b	Me_2SO	0.40	NaCN, 1.9	25	144	60	0.15[b]
1c	CH_2Cl_2	0.28	BF_3, 0.6	−78	4	88	0.38[c]
1c	$CHCl_3$	0.30	BF_3, 0.7	−30	5	90	0.31[c]
1d	CH_2Cl_2	0.32	BF_3, 0.6	−78	4	80	0.32[c]
1d	$CHCl_3$	0.20	BF_3, 0.6	−30	3	87	0.27[c]
1e	CH_2Cl_2	0.32	BF_3, 0.7	−78	4	90	0.19[c]
1e	$CHCl_3$	0.22	BF_3, 0.6	−30	5	90	0.31[c]

[a] The copolymer compositions were estimated to be 1:1 by ^1H NMR spectra. [b] Concentration of 0.5 g/dL in $CHCl_3$ at 20 °C. [c] Concentration of 0.5 g/dL in $CHCl_3$ at 25 °C.

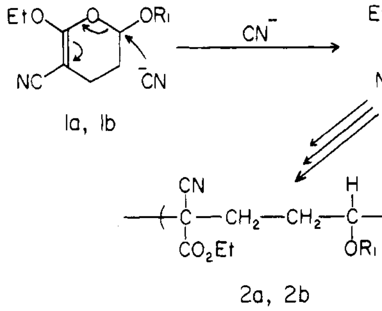
Scheme I



Scheme II



Scheme III



electron-poor olefins react under mild conditions to form cyclic adducts,[9,12] and most of these adducts are cyclobutanes. However, the particular adducts between ethyl α-cyanoacrylate and alkyl vinyl ethers were not cyclobutanes but 2,6-dialkoxy-5-cyano-3,4-dihydro-2*H*-pyrans (**1a,b**) as reported recently by Hall and co-workers.[13] Similar intramolecular Diels–Alder reactions of α-substituted unsaturated carboxylic esters were reported also by Snider and co-workers.[14] Also known is that α,β-unsaturated aldehyde and ketone heterodienes react with electron-rich olefins such as alkyl vinyl ethers at high temperatures to give 2,6-disubstituted-3,4-dihydro-2*H*-pyrans (**1c–e**).[10,11,15]

We have confirmed these reactions and prepared cyclic monomers **1a–e** according to the reported procedures. All of the pyrans prepared were found to be very reactive toward electrophiles or nucleophiles, polymerizing readily.

Ring-Opening Polymerization of 1a–e. Cyclic monomers **1a,b** were polymerized with either anionic or cationic catalyst to obtain H–H alternating copolymers **2a,b** of ethyl α-cyanoacrylate and alkyl vinyl ethers. Monomers **1c–e** were polymerized with cationic cataysts to obtain H–H alternating copolymers of alkyl vinyl ketones and alkyl vinyl ethers. The results are summarized in Table I.

Kern and co-workers[16] reported cationic polymerization of unsubstituted dihydropyran itself. Under all of the conditions they employed, the resulting polymers were the products of mixed modes of polymerization, addition and ring opening. However, the presently investigated substituted dihydro-2*H*-pyrans **1a–e** are activated by the proper substitutions and polymerize cleanly in ring-opening fashion (Scheme I).

In the cationic polymerization depicted in Scheme II the catalyst initiates the polymerization by attacking a monomer molecule at C_5, thereby resulting in formation of a cation that rearranges by ring opening to the well-investigated alkoxy cation, which is usually involved in the cationic polymerization of vinyl ethers. Vinyl-type polymerization of those dihydro-2*H*-pyrans without ring opening are obviously not favored for steric reasons.

When anionic catalysts were used, only **1a** and **1b** were polymerizable. As shown in Scheme III, the driving force of the anionic polymerization is probably the stability of the ring-opened anion, which is well-known in the polymerization of α-cyanoacrylates. Nevertheless, the highly reactive nature of ketene acetal structure of those pyrans contributes to a great extent to their high polymerizability.

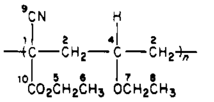
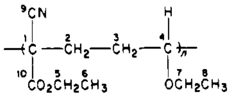
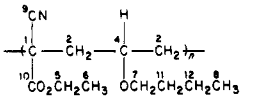
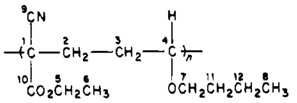
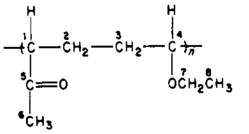
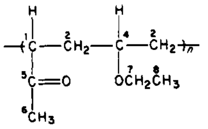
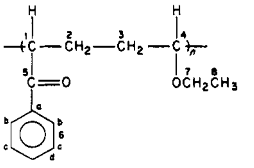
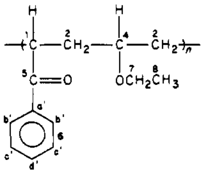
For comparison, H–T alternating copolymers were prepared by the usual free radical copolymerization of the monomers. The results are shown in Table II. As expected, ethyl α-cyanoacrylate, a strong electron-acceptor molecule, was copolymerized radically well with alkyl vinyl ethers which are electron-rich monomers to give the one-to-one alternating H–T copolymers. This was observed also in the copolymerization of vinyl ketones with vinyl ethers. It must be noted here that during these radical

Table II
Free Radical Copolymerization[a] of Ethyl α-Cyanoacrylate and Vinyl Ketones with Alkyl Vinyl Ethers by AIBN in Benzene at 60 °C

monomer[d]		A/B, mol	AIBN, mol %	(A + B)/ benzene, g/mL	temp, °C	time, h	% yield[b]		η_{inh},[c] dL/g
A	B						substituted pyrans 1	copolymer	
ECA	EVE	0.70	0.55	0.86	60	10	63	27	0.54
ECA	EVE	0.75	0.60	0.62	60	10	59	30	0.50
ECA	BVE	0.67	0.40	0.95	60	12	56	25	0.52
ECA	BVE	0.80	0.50	0.75	60	12	51	31	0.49
MVK	EVE	0.25	0.70	1.50	60	8	trace	80	0.51
MVK	EVE	0.20	0.50	2.00	60	10	trace	85	0.72
MVK	BVE	0.25	0.75	2.00	60	9	trace	75	0.46
MVK	BVE	0.20	0.55	nil	60	10	trace	83	0.69
PVK	EVE	0.20	0.0	3.00	60	9	3	70	0.25
PVK	EVE	0.20	0.55	nil	60	10	5	75	0.29

[a] The copolymer compositions were estimated to be 1:1 by ^{1}H NMR spectra. [b] Yields of substituted pyrans and copolymers were calculated with respect to the comonomer present in smaller molar amount. [c] Inherent viscosity of copolymer: concentration of 0.5 g/dL in chloroform at 25 °C. [d] ECA = ethyl α-cyanoacrylate; EVE = ethyl vinyl ether; BVE = n-butyl vinyl ether; MVK = methyl vinyl ketone; PVK = phenyl vinyl ketone.

Table III
^{13}C NMR Spectra of Copolymers[a]

compd	observed chemical shift (calcd)[b]											
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
	44.2 (44.0)	42.7 (44.3)		73.5 (75.2)	62.5 (59.5)	13.8 (12.8)	64.9 (65.2)	14.6 (11.4)	118.5	168.6		
	55.0 (42.6)	30.2 (31.8)	27.5 (19.4)	81.4 (79.5)	63.0 (59.8)	14.0 (12.8)	67.9 (65.7)	15.2 (11.4)	117.2	167.7		
	44.6 (44.0)	42.7 (44.3)		73.5 (75.2)	62.6 (59.5)	13.8 (12.8)	69.6 (72.3)	13.8 (14.4)	118.8	168.8	31.3 (29.7)	19.0 (21.9)
	54.7 (42.6)	30.1 (31.8)	27.7 (19.4)	81.5 (79.5)	62.9 (59.8)	13.8 (12.8)	72.3 (72.8)	13.8 (14.4)	117.3	167.6	31.7 (29.7)	19.0 (21.9)
	55.4 (55.6)	23.7 (25.4)	31.0 (28.4)	80.2 (79.5)	211.0	29.5	64.9 (66.0)	15.4				
	45.5 (47.9)	36.6 (32.5)		75.9 (77.9)	211.1	29.2	64.1 (66.0)	15.0				
	49.5 (47.5)	23.8 (25.4)	28.5 (28.4)	80.5 (79.5)	203.1	C_a, 138.0; C_b, 127.8; C_c, 128.2; C_d, 132.3	65.2 (66.0)	14.9				
	39.5 (43.8)	37.5 (32.5)		75.4 (77.9)	203.3	$C_{a'}$, 136.8; $C_{b'}$, 128.0; $C_{c'}$, 128.2; $C_{d'}$, 132.5	63.9 (66.0)	14.9				

[a] All of the spectra were taken in $CDCl_3$ on a Varian FT 80-A NMR spectrometer. [b] For the method of calculation, see: Levy, G. C.; Nelson, C. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972.

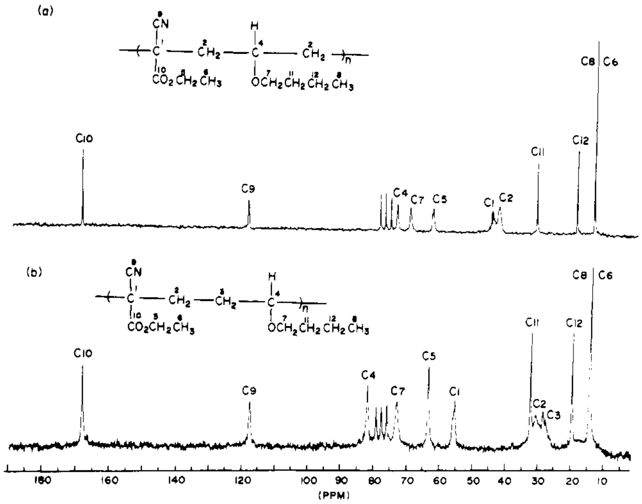


Figure 1. ^{13}C NMR spectra of 1:1 alternating copolymers of ethyl α-cyanoacrylate and *n*-butyl vinyl ether: (a) head-to-tail; (b) head-to-head. 20 MHz, room temperature, arbitrary concentration in $CDCl_3$. Chemical shifts are referenced to $CDCl_3$ (δ 77.0).

polymerizations, cyclic adducts were always formed as byproducts.

Structure Identification of H–H Alternating Copolymers. The chemical structures of the copolymers were identified by IR, ^1H NMR, and ^{13}C NMR spectra. The IR spectra confirmed the chemical structures, exhibiting all the absorption bands attributable to the functional groups comprising the copolymers. However, only a minor difference was observed in the spectra of the H–H and H–T copolymers, thus failing to identify the H–H and H–T orientations of copolymers.

The chief structural difference between the H–H and H–T alternating copolymers is the presence of an extra polymer backbone methylene group in the H–H orientation. In the H–T orientation all of the methylene groups are chemically identical. It was expected that a significant difference would be observed in the ^1H NMR spectra. The only difference observed in the ^1H NMR spectra was that the chemical shift of the backbone methylene protons was shifted toward higher field appearing as two peaks in the case of the H–H copolymer. Thus, even in the ^1H NMR spectra the evidence did not conclusively identify the H–H orientation.

Stille and Chung[9] have discussed extensively the microstructure determination of H–H alternating copolymers by ^{13}C NMR spectroscopy. ^{13}C NMR spectra of the copolymers were determined at 20 MHz on a Varian FT 80-A NMR spectrometer with the hydrogen noise decoupled. As we have reported before,[17] significant differences were observed in their ^{13}C NMR spectra. Representative ^{13}C NMR spectra of the H–H and H–T copolymers are shown in Figure 1. Assignments of the signals, summarized in Table III, were made on the basis of predicted chemical shifts.[18] As expected, the most significant difference between the ^{13}C NMR spectra of the H–H and H–T copolymers is that the H–H copolymer exhibited two signals corresponding to two different methylene carbons (C_2 and C_3 in Figure 1), while the H–T copolymer exhibited only one signal. Furthermore, the signals of C_2 and C_3 of H–H are shifted toward higher magnetic field than those of C_2 of H–T, while those of C_1 and C_4 of H–H are shifted to lower field compared with those of C_1 and C_4 of H–T.

With this spectral evidence we are now certain that we have indeed the H–H alternating copolymers and are able to compare the properties of the H–H copolymers with those of the corresponding traditional H–T copolymers.

Table IV
Thermal Properties of H–H and H–T Copolymers

copolymer	type	T_g,[a] °C	degrad temp,[b] °C		residue[b] at 500 °C, %
			initial	half-loss	
2a	H–H	58	324	385	7.8
3a	H–T	47	347	417	4.2
2b	H–H	39	275	353	3.3
3b	H–T	30	317	412	2.1
2c	H–H	1	276	366	1.0
3c	H–T	–4	360	422	1.1
2d	H–H	–12	245	350	7.1
3d	H–T	–22	263	376	1.3
2e	H–H	47	254	379	5.5
3e	H–T	38	287	385	5.1

[a] Determined from DSC curves measured on a 910 differential scanning calorimeter (DuPont Instrument, 990 thermal analyzer) with a heating rate of 10 °C/min in a N_2 atmosphere. [b] Determined from TGA curves measured in a Perkin-Elmer TGS-1 thermobalance with a heating rate of 10 °C/min in a N_2 atmosphere.

Properties of H–H Alternating Copolymers. All of the copolymers we prepared were soluble in common solvents such as chloroform and acetone, and the inherent viscosities of the copolymers measured in chloroform were in the range 0.2–0.7 g/dL. All of the copolymers irrespective of their orientation appeared to be noncrystalline. It is interesting to note that H–H copolymers **2c** and **2d** were leathery, while the corresponding H–T copolymers **3c** and **3d** were quite rubbery at room temperature.

The thermal behavior of all H–H and H–T copolymers was investigated by DSC at a scanning rate of 10 °C/min to determine the glass transitoin temperatures (T_g). The results are shown in Table IV. The T_g values of the H–H samples were always higher than those of the respective H–T copolymers and the most significant 11 °C difference in T_g was observed for **2a** and **3a**. This observation seems to indicate that the introduction of the H–H orientation into the polymer chain strengthens the dipole–dipole interactions of polar substituents, stiffening the polymer chains. Similar observations were reported for poly(methyl crotonate)[19] and poly(methyl cinnamate).[7]

This steric repulsion is further reflected by the lower thermal stability of the H–H copolymers compared with that of the conventional H–T copolymers. The results of thermogravimetric analyses of the copolymers are summarized in Table IV. All of the H–H copolymers exhibited initial degradation and half-weight loss temperatures much lower than those of the H–T copolymers. These results are reasonable in view of the sterically crowded nature of H–H orientation.

Somewhat similar observations have been reported for poly(methyl crotonate)[19] and poly(methyl cinnamate),[7] where the decreases were reported for initial and maximum degradation temperatures for H–H structures.

We are now in the process of extending the polymerization of the dihydro-2*H*-pyran system to the syntheses of other types of H–H alternating copolymers, and the results will be reported at a later date.

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Registry No. **1a** homopolymer, 83693-34-9; **1b** homopolymer, 83693-36-1; **1c** homopolymer, 85967-75-5; **1d** homopolymer, 85967-74-4; **1e** homopolymer, 85967-73-3; **2a**, 86163-03-3; **2b**, 83693-30-5; **2c**, 86163-05-5; **2d**, 86163-06-6; **2e**, 86163-07-7; ECA–EVE copolymer, 83693-31-6; ECA–BVE copolymer, 83693-32-7; MVK–EVE copolymer, 86163-08-8; MVK–BVE copolymer, 86163-09-9; PVK–EVE copolymer, 86163-10-2.

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Fire- and Heat-Resistant Laminating Resins Based on Maleimido-Substituted Aromatic Cyclotriphosphazenes

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ABSTRACT: A novel class of flame- and heat-resistant polymers has been synthesized by the thermal polymerization of maleimido-substituted aromatic cyclotriphosphazenes. The polymer obtained from tris(aminophenoxy)tris(maleimidophenoxy)cyclotriphosphazene has good thermal stability and is noteworthy for its high char yield, viz., 82% at 800 °C in nitrogen and 81% at 700 °C in air. Graphite-fabric laminates prepared with this polymer did not burn in pure oxygen (limiting oxygen index 100%), even at 300 °C, and were tested for mechanical properties. Hexakis(4-maleimidophenoxy)cyclotriphosphazene and some fluorine-containing monomers have also been synthesized. The structures of these cyclic phosphazene precursors and polymers were characterized by FT IR spectrophotometry, ^{1}H NMR, ^{19}F NMR, and ^{31}P solid-state magic angle spinning NMR spectroscopy, and mass spectrometry. The curing behavior of the polymer precursors and the thermal stabilities of the polymers were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA).

Introduction

Considerable interest exists in the use of high-strength lightweight composites for the construction of both new and retrofitted aerospace vehicles. These composites are made by embedding various types of fibers or fabrics in a resin matrix. The polymer used for such a matrix is most commonly an epoxy resin, although other resins such as phenolic, poly(ether sulfone), poly(phenyl sulfone), and bismaleimide resins have also been used for certain applications.

Graphite–epoxy composites, however, suffer disadvantages where structural integrity and fire retardancy at higher temperatures are of prime importance. This is more or less true with other resin systems also. Many of these resins burn to give smoke and toxic gases and also have processing problems.

The principal objective of the present work is to provide greatly improved new fire- and heat-resistant binders having high anaerobic char yields useful for reinforced composites.

Inherent in our approach is the synergism of the phosphorus–nitrogen combination in respect to fire retardation[1] and the fact that this combination, especially when in the form of phosphazene, does not form toxic products upon oxidative thermal decomposition.[2] In addition, the maleimido substitution on the cyclotriphospazene ring has been made in view of our[3] recent work with bismaleimides and the fact that this would result in polymers having high anaerobic char yields.[4]

Several high-temperature polymers based on cyclotriphosphazenes have been reported in the literature,[5,18] but few have been used for composites. In another series,

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