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Syntheses of Alternating Head-to-Head Vinyl Copolymers and Vinyl Terpolymers via Ring-Opening Mechanism. Ring-Opening Polymerization of Substituted-3,4-dihydro-2H-pyrans

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2-Ethoxy-6-methoxy-5-cyano-3,4-dihydro-2H-pyran ($\mathbf{1}_a$), 2-n-butoxy-6-methoxy-5-cyano-3,4-dihydro-2H-pyran ($\mathbf{1}_b$), 2-isobutoxy-6-methoxy-5-cyano-3,4-dihydro-2H-pyran ($\mathbf{1}_c$), and 2-ethoxy-6-methoxy-3-methyl-5-cyano-3,4-dihydro-2H-pyran ($\mathbf{1}_d$) were prepared by (4 + 2) cycloaddition reaction of methyl α-cyanoacrylate with the corresponding alkyl vinyl ethers. Compounds $\mathbf{1}_{a-d}$ were ring-open polymerized by cationic catalyst to obtain alternating head-to-head (H-H) copolymers. For comparison, head-to-tail (H-T) copolymer $\mathbf{3}_a$ was also prepared by free radical copolymerization of the corresponding monomers. The H-H copolymer exhibited minor differences in its ^{1}H NMR and IR spectra, but in the ^{13}C NMR spectra significant differences were observed between the H-H and H-T copolymers. Glass transition temperature (T_g) of H-H copolymer was higher than that of the H-T copolymer, but thermal decomposition temperature of the H-H copolymer was lower than that of the H-T copolymer. Compounds $\mathbf{1}_a$, $\mathbf{a}_b$, and $\mathbf{1}_c$ copolymerized well with styrene by cationic catalyst, but compound $\mathbf{1}_d$ failed to copolymerize with styrene. All of the H-H and H-T copolymers were soluble in common solvents and the inherent viscosities were in the range 0.2-0.4 dl/g.

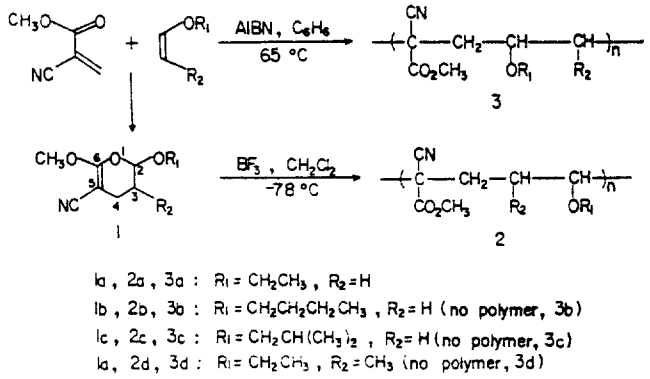
Introduction

Vinyl polymers of head-to-head (H-H) structure are expected to show different properties from those of conventional head-to-tail (H-T) polymers, and extensive interest has been focused on the synthesis and characterization of H-H polymers. So far, various H-H polymers have been prepared and their properities were found to differ significantly from those of H-T polymers[1-8]. The synthetic schemes hitherto applied to prepare H-H polymers have been by the reactions on polymers such as the radical 1,4-polymerization of 2,3-diphenylbutadiene, followed by selective hydrogenation to H-H polystyrene[2]. However, it is often difficult to get clean and complete reactions in these synthetic methods.

We have reported a new synthetic route to H-H alternating copolymers by cationic ring-opening polymerization of substituted-3.4-dihydro-2H-pyrans[9-13]. These substituted pyrans were prepared by (4 + 2) cycloaddition reaction of cyanoacrylate or vinyl ketones with alkyl vinyl ethers, and have various cation-stabilizing groups at proper positions of the pyran ring. This work is now extended to the construction of H-H copolymers of another pair of vinyl monomers. The present report describes the syntheses and ring-opening polymerization of 2,3,5,6-tetrasubstituted-3,4-dihydro-2H-pyrans. Properties of the resulting H-H copolymers were compared with those of the corresponding H-T copolymers which were prepared by free radical copolymerization of the corresponding monomers.

Results and Discussion

Compounds $\mathbf{1}_{a-d}$ were prepared according to a procedure similar to that reported earlier[12,14] from methyl α-cyanoacrylate and the corresponding alkyl vinyl ethers (Scheme 1). In dilute benzene solution, substituted 3,4-dihydro-2H-pyrans were obtained in high yield at room temperature and only a trace amount of poly(methyl α-cyanoacrylate) was formed. The chemical structures of the substituted pyrans were identified by ^{1}H NMR (Figure 1 and Figure 2) and IR spectra. Spectral data indicated that $\mathbf{1}_d$ was a mixture of the *cis*- and



Scheme 1

trans-isomer as shown in Figure 2. All the spectral evidence confirmed the expected structures. The pyrans $\mathbf{1}_{a-d}$ were very reactive toward a cationic initiator polymerizing readily.

Substituted pyrans $\mathbf{1}_{a-d}$ were polymerized with a cationic catalyst such as boron trifluoride etherate to obtain H-H alternating copolymers $\mathbf{2}_{a-d}$ of methyl α-cyanoacrylate and alkyl vinyl ethers. The polymerization results are summarized in Table 1. The values in Table 1 show that the ring-opening polymerizability of tetrasubstituted pyran $\mathbf{1}_d$ is comparable to those of trisubstituted pyrans $\mathbf{1}_{a-c}$, and polymerized well with a cationic catalyst even at $-78°C$.

In the cationic polymerization, as proposed before[10], 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 known alkoxy cation, which is usually involved in the cationic polymerization of alkyl vinyl ethers. Thus, the driving force of the cationic polymerization is probably the stability of the ring-opened cation. Nevertheless, the highly reactive nature of ketene acetal structure of those pyrans contributes to a great extent to their high polymerizability.

For the purpose of comparison, the corresponding H-T alternating copolymers were prepared by conventional free radical copolymerization of the monomer mixtures. The results are summarized in Table 2. Methyl α-cyanoacrylate, a strong electron-acceptor, was copolymerized radically well with ethyl vinyl ether to give the one-to-one alternating H-T copolymer. However, H-T copolymers were not obtained in the free radical copolymerization of α-cyanoacrylate with sterically hindered alkyl vinyl ethers such as n-butyl vinyl ether, isobutyl vinyl ether, and ethyl 1-propenyl ether under the same conditions as shown in Table 2. This observation seems to indicate that steric hindrance at the polymerization reaction site remarkably decreases the copolymerizability of vinyl ethers. According to our experience the copolymerizability of ethyl

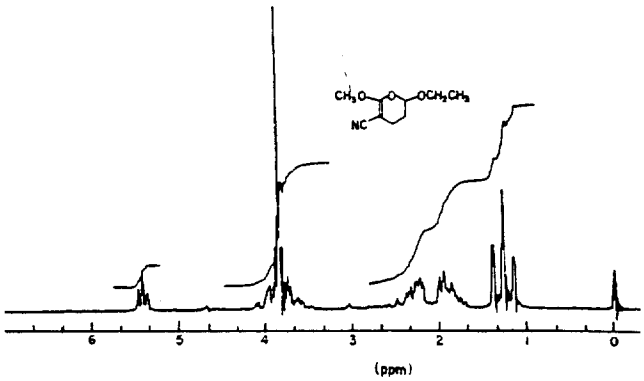


Figure 1. 60 MHz ^{1}H NMR spectrum of 2-ethoxy-6-methoxy-5-cyano-3,4-dihydro-2H-pyran ($\mathbf{1}_a$) taken in $CDCl_3$ at room temperature.

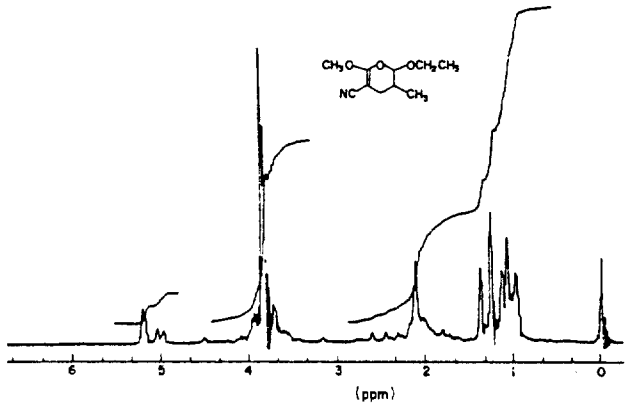


Figure 2. 60 MHz ^{1}H NMR spectrum of 2-ethoxy-6-methoxy-3-methyl-5-cyano-3,4-dihydro-2H-pyran ($\mathbf{1}_d$) taken in $CDCl_3$ at room temperature.

Table 1. Cationic Ring-Opening Polymerization[a] of 2,3,5,6-Tetrasubstituted-3,4-dihydro-2H-pyrans $\mathbf{1}_{a-d}$ under Various Conditions

monomer	solvent	monomer/ solvent, g/ml	initiator[b] to monomer, mol %	temp, °C	time, h	yield of product polymer	η_{inh}, dl/g[c]
$\mathbf{1}_a$	CH_2Cl_2	0.30	0.8	-78	36	92	0.31
$\mathbf{1}_a$	$CHCl_3$	0.33	0.7	-30	48	90	0.30
$\mathbf{1}_b$	CH_2Cl_2	0.30	0.9	-78	40	80	0.23
$\mathbf{1}_b$	$CHCl_3$	0.33	0.8	-30	48	82	0.22
$\mathbf{1}_c$	CH_2Cl_2	0.40	0.7	-78	48	78	0.20
$\mathbf{1}_c$	$CHCl_3$	0.33	0.8	-30	60	81	0.20
$\mathbf{1}_d$	CH_2Cl_2	0.30	0.9	-78	56	68	0.19
$\mathbf{1}_d$	$CHCl_3$	0.35	0.80	-30	62	65	0.18

[a] The copolymer compositions were estimated to be 1.0:1.0 by ^{1}H NMR spectra. [b] Initiator: Boron trifluoride etherate. [c] Concentration of 0.5 g/dl in chloroform at 20°C.

Table 2. Free Radical Copolymerization[a] of Methyl α-Cyanoacrylate with Alkyl Vinyl Ethers by AIBN in Benzene at 65°C

monomer[b]		A/B, mol	AIBN, mol %	(A+B)/ benzene, g/ml	temp, °C	time h	% yield[c]		η_{inh},[d] dl/g
A	B						substituted pyrans **1**	copolymer	
MCA	EVE	0.66	0.70	0.50	65	16	66	24	0.36
MCA	EVE	0.60	0.75	0.55	65	12	68	20	0.38
MCA	BVE	0.60	0.80	0.60	65	10	74	18[e]	0.42[f]
MCA	BVE	0.50	0.85	0.50	65	12	76	16[e]	0.40[f]
MCA	IVE	0.55	0.80	0.55	65	12	78	15[e]	0.35[f]
MCA	IVE	0.60	0.70	0.50	65	13	80	14[e]	0.40[f]
MCA	EPE	0.50	0.85	0.66	65	14	77	18[e]	0.36[f]
MCA	EPE	0.60	0.80	0.60	65	16	74	20[e]	0.38[f]

[a] The copolymer compositions were estimated to be 1.0:1.0 by ^{1}H NMR spectra. [b] MCA = methyl α-cyanoacrylate; EVE = ethyl vinyl ether; BVE = n-butyl vinyl ether; IVE = isobutyl vinyl ether; EPE = ethyl 1-propenyl ether. [c] Yields of substituted pyrans and copolymers were calculated with respect to the comonomer present in smaller molar ratio. [d] Inherent viscosity of copolymer: concentration of 0.5 g/dl in chloroform at 20°C. [e] Homopolymer of methyl α-cyanoacrylate was formed. [f] Inherent viscosity of poly(methyl α-cyanoacrylate): concentration of 0.5 g/dl in acetone at 20°C.

α-cyanoacrylate toward the alkyl vinyl ethers is greater than that of methyl α-cyanoacrylate. Ethyl α-cyanoacylate copolymerized readily with n-butyl vinyl ether, but methyl α-cyanoacrylate did not copolymerize with n-butyl vinyl ether under the same polymerization reaction conditions.

The chemical structures of the resulting H-H and H-T copolymers were identified by IR, ^{1}H NMR, and ^{13}C NMR spectra. Representative spectra are shown in Figures 3-6. The IR spectra confirmed the expected chemical structures, exhibiting all the absorption bands attributable to the functional groups comprising the copolymers. The main 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 structure. In the H-T orientation all of the methylene groups are chemically equivalent. Thus, some differences were observed in the IR and ^{1}H NMR spectra of H-H and H-T copolymers as shown in Figure 3 and Figure 4, respectively.

As we have reported before[12], significant difference was observed in their ^{13}C NMR spectra. Representative ^{13}C NMR spectra of H-H and H-T copolymers are shown in Figure 6. Assignments of the chemical shifts were made on the basis

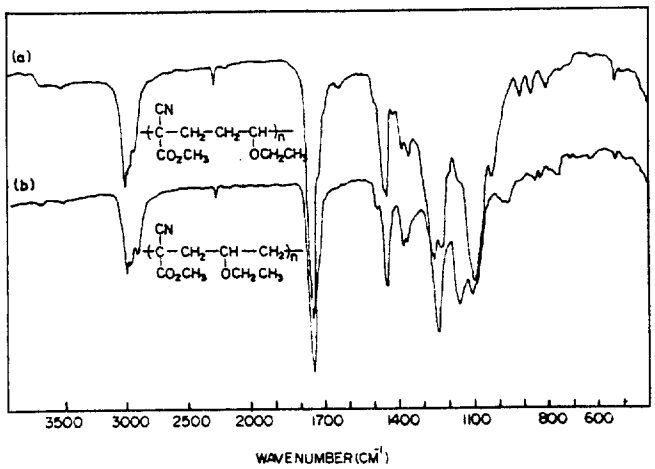


Figure 3. IR spectra of 1:1 alternating copolymers of methyl α-cyanoacrylate and ethyl vinyl ether: (a) head-to-head; (b) head-to-tail.

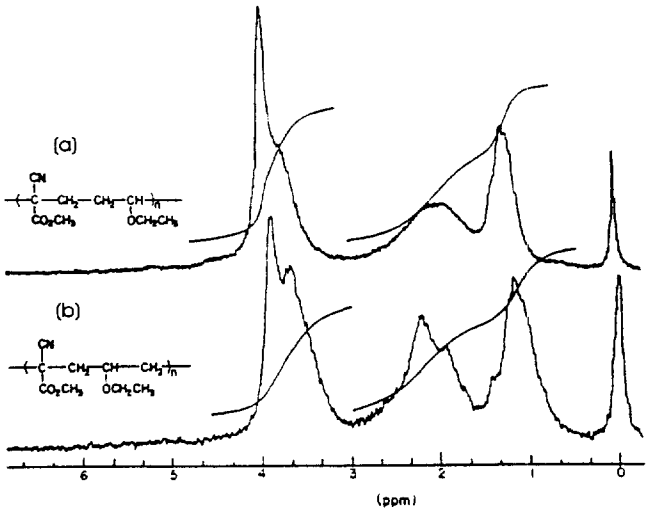


Figure 4. ^{1}H NMR spectra of 1:1 alternating copolymers of methyl α-cyanoacrylate and ethyl vinyl ether: (a) head-to-head; (b) head-to-tail, 60 MHz, room temperature, arbitrary concentration in $CDCl_3$.

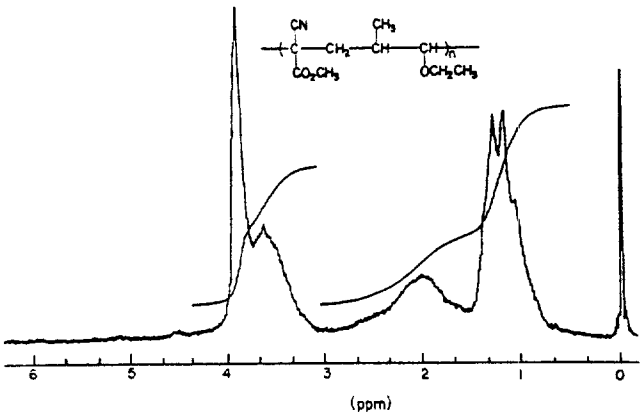


Figure 5. 60 MHz ^{1}H NMR spectrum of 1:1 alternating copolymer of methyl α-cyanoacrylate and ethyl 1-propenyl ether taken in $CDCl_3$ at room temperature.

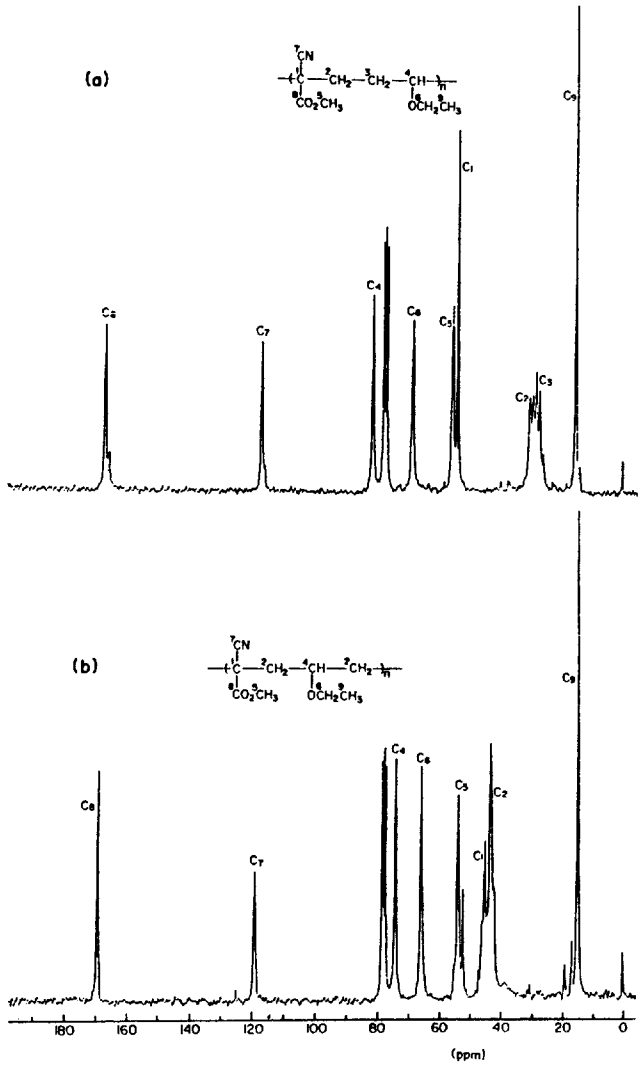


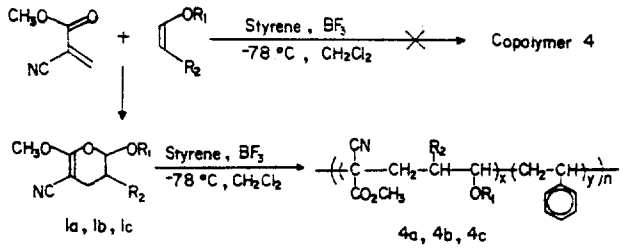
Figure 6. ^{13}C NMR spectra of alternating copolymers of ethyl α-cyanoacrylate and ethyl vinyl ether: (a) head-to-head; (b) head-to-tail. 20 MHz, room temperature, arbitrary concentration in $CDCl_3$. Chemical shifts are referenced to $CDCl_3$ (δ 77.0).

Table 3. 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	
2$_a$	H-H	79	270	326	1.5
3$_a$	H-T	67	305	247	1.0

[a] Determined from DSC curves measured on a Perkin-Elmer DSC-2 differential scanning calorimeter with a heating rate of 10°C/min in a nitrogen atmosphere. [b] Determined from TGA curves measured on a 910 thermogravimetric analyzer (DuPont Instrument, 990 thermal analyzer) with a heating rate of 10°C/min in a nitrogen atmosphere.

of the predicted chemical shifts[15]. As expected, the remarkable 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, while the H-T copolymer exhibited only one signal.



Scheme 2

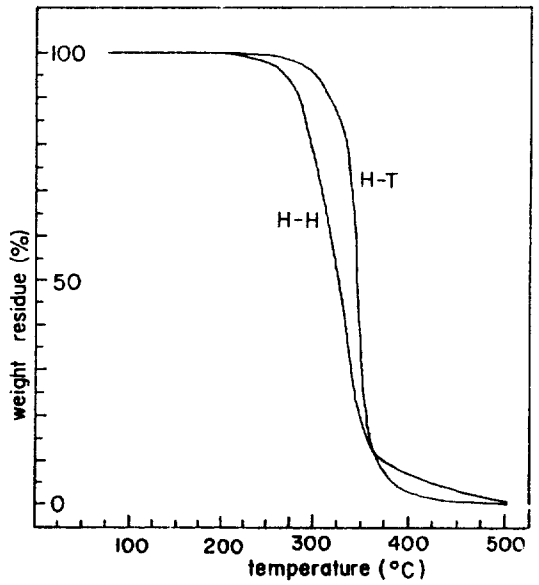


Figure 7. TGA thermograms of 1:1 alternating copolymers of methyl α-cyanoacrylate and ethyl vinyl ether (10°C/min, N_2).

Another observation to note is that the resonance peaks of H-H copolymers reveal the unusual splitting patterns in the ^{13}C NMR spectra as shown in Figure 6. These spectral evidence seems to indicate that the copolymers are mixtures of several stereoisomers.

All the copolymers of H-H and H-T copolymers were soluble in common solvents such as chloroform and acetone and the inherent viscosities measured in chloroform were in the range 0.2-0.4 dl/g.

The thermal behavior of H-H and H-T copolymers was investigated by DSC at scanning rate of 10°C/min to determine the glass transition temperature (T_g). The results are shown in Table 3. The T_g value of the H-H structure was higher than that of the H-T copolymer, as reported previously[10]. However, thermal stability of H-H copolymer was lower than that of the conventional H-T copolymer, and the H-H structure exhibited initial degradation and half-weight loss temperatures much lower than that of the H-T copolymer (Figure 7). These results are resonable in a view of the sterically crowded nature of H-H orientation. Similar observations were reported for poly(methyl cinnamate)[6].

To examine further the ring-opening polymerization of substituted pyrans we have attempted cationic copolymerization of pyrans with styrene. The results are summarized in Table 4. From the data shown in Table 4 it was found that 2,5,6-trisubstituted pyrans **1**$_{a-c}$ copolymerized well with styrene. However, contrary to its homopolymerizability

Table 4. Cationic Copolymerization of 2,3,5,6-Tetrasubstituted-3,4-dihydro-2H-pyrans with Styrene under Various Conditions

monomer A	monomer B	A/B, mol	solvent	(A+B)/ solvent, g/ml	initiator[a] to monomer, mol %	temp, °C	time, h	yield of polymer, %	copolymer composition[b] A/B, mol/mol	η_{inh},[c] dl/g
$\mathbf{1}_a$	St	1.00	CH_2Cl_2	0.60	0.8	−78	48	62	60/40	0.30
$\mathbf{1}_a$	St	0.80	CH_2Cl_2	0.50	0.9	−30	40	60	54/46	0.28
$\mathbf{1}_b$	St	1.00	CH_2Cl_2	0.66	0.8	−78	60	54	20/80	0.25
$\mathbf{1}_b$	St	0.80	$CHCl_3$	0.60	0.7	−30	72	51	18/82	0.22
$\mathbf{1}_c$	St	1.00	CH_2Cl_2	0.55	0.8	−78	60	52	16/84	0.23
$\mathbf{1}_c$	St	2.00	CH_2Cl_2	0.50	0.8	−78	72	42	48/52	0.20
$\mathbf{1}_d$	St	1.00	CH_2Cl_2	0.66	0.9	−78	55	nil		
$\mathbf{1}_d$	St	0.80	$CHCl_3$	0.50	0.8	−30	48	18[d]		0.14

[a] Initiator: Boron trifluoride etherate. [b] Copolymer composition estimated from ^{1}H NMR and IR spectra. [c] Concentration of 0.5 g/dl in chloroform at 20°C. [d] Homopolymer of pyran ($\mathbf{1}_d$) was formed.

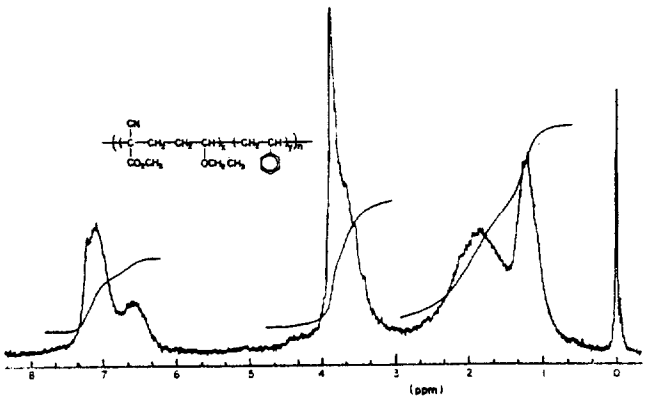


Figure 8. ^{1}H NMR spectrum of the copolymer containing approximately 30 mol % of methyl α-cyanoacrylate, 30 mol % of ethyl vinyl ether, and 40 mol % of styrene. 60 MHz, room temperature, arbitrary concentration in $CDCl_3$.

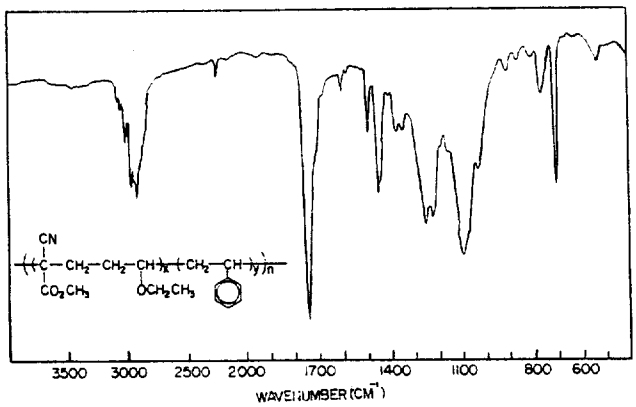


Figure 9. IR spectrum of the copolymer containing approximately 30 mol % of methyl of methyl α-cyanoacrylate, 30 mol % of ethyl vinyl ether, and 40 mol % of styrene.

2,3,5,6-tetrasubstituted pyran $\mathbf{1}_d$ did not copolymerize with styrene when treated under identical conditions. Representative ^{1}H NMR and IR spectra of the copolymers are shown in Figure 8 and Figure 9, respectively. The striking feature of the copolymerization of substituted pyrans is that it provides a synthetic route to terpolymers composed of three vinyl monomers (Scheme 2).

We are now in the process of extending the polymerization of substituted pyran system to the syntheses of other types of H-H alternating copolymers and the results will be reported on shortly.

Experimental

Materials. The reagent grade chemicals used in this work were purified by distillation before use. Ethyl vinyl ether and n-butyl vinyl ether were dried over sodium metal and distilled under vacuum, taking the middle fraction. Isobutyl vinyl ether and styrene were distilled from calcium hydride under reduced pressure and stored under nitrogen at −10°C. Ethyl 1-propenyl ether was purchased from Fluka as *cis-trans* mixture, and dried over sodium metal, followed by distillation under vacuum. Thiophene-free benzene was refluxed over sodium metal, distilled, and stored over molecular sieves under nitrogen. Boron trifluoride etherate was treated with a small amount of diethyl ether and distilled under reduced pressure. Methylene chloride was dried with anhydrous calcium chloride, distilled over anhydrous calcium sulfate, and stored in a brown bottle with 4-A° molecular sieves. Chloroform was washed with water to remove the ethanol and refluxed with phosphorus pentoxide, followed by fractional distillation. Technical grade methyl α-cyanoacrylate for adhesive use was used without further purification.

Measurements. All measured temperatures were uncorrected. IR spectra were taken on a Hitachi Model 260-30 infrared spectrophotometer. ^{1}H NMR spectra were obtained on a Varian Model T-60A spectrometer (60 MHz). ^{13}C NMR spectra were obtained on a Brucker AS-200 NMR spectrometer at room temperature. The glass transition temperatures (T_g) were measured on a Perkin-Elmer DSC-2 differential scanning calorimeter in a nitrogen atmosphere. A DuPont 910 thermogravimetric analyzer with a heating rate of 10°C/min up to 500°C was used for the thermal degradation study of the polymers in a nitrogen atmosphere.

Preparation of 2-Ethoxy-6-methoxy-5-cyano-3,4-dihydro-2H-pyran ($\mathbf{1}_a$). A solution of methyl α-cyanoacrylate (5.55 g, 0.05 mol) in 50 m*l* of dry benzene was added slowly to a benzene (80 m*l*) solution of ethyl vinyl ether (7.2 g, 0.10 mol) with stirring under nitrogen. The mixture was stirred at room temperature for three days. The trace amount of poly(methyl α-cyanoacrylate) formed was removed by filtration. Solvent and excess ethyl vinyl ether were then evaporated

under vacuum to give 8.4 g (92% yield) of $\mathbf{1}_a$: ^{1}H NMR ($CDCl_3$) δ 1.10–1.28 (3H, t), 1.62–1.98 (2H, m), 2.15–2.50 (2H, m), 3.42–4.06 (5H, m), 5.33 (1H, t); IR (neat) 2200 (C≡N), 1640 (C=C) cm^{-1}.

Preparation of 2-n-Butoxy-6-methoxy-5-cyano-3,4-dihydro-2H-pyran ($\mathbf{1}_b$). A solution of 4.44 g (0.04 mol) of methyl α-cyanoacrylate in 30 m*l* of dry benzene was mixed slowly with a benzene (70 m*l*) solution of n-butyl vinyl ether (8.0 g, 0.08 mol) with stirring. The reaction mixture was stirred at room temperature for three days. The trace amount of poly(methyl α-cyanoacrylate) formed was removed by filtration. Solvent and excess n-butyl vinyl ether were then evaporated under reduced pressure to give 7.6 g (90% yield) of $\mathbf{1}_b$: ^{1}H NMR ($CDCl_3$) δ 0.78–1.16 (3H, m), 1.17–1.65 (4H, m), 1.65–2.04 (2H, m), 2.05–2.58 (2H, m), 3.39–3.95 (5H, m), 5.33 (1H, t); IR (neat) 2200 (C≡N), 1640 (C=C) cm^{-1}.

Preparation of 2-Isobutoxy-6-methoxy-5-cyano-3,4-dihydro-2H-pyran ($\mathbf{1}_c$). A solution of methyl α-cyanoacrylate (4.44 g, 0.04 mol) in 30 m*l* of dry benzene was added slowly to a benzene (90 m*l*) solution of isobutyl vinyl ether (8.0 g, 0.08 mol) with stirring under nitrogen. The reaction mixture was stirred at room temperature for three days. The trace amount of poly(methyl α-cyanoacrylate) formed was separated by filtration. Solvent and excess isobutyl vinyl ether were then removed under vacuum to give 7.3 g (86% yield) of $\mathbf{1}_c$: ^{1}H NMR ($CDCl_3$) δ 0.85–0.98 (6H, d), 1.47–2.02 (3H, m), 2.08–2.55 (2H, m), 3.13–3.78 (2H, m), 3.80 (3H, s), 5.32 (1H, t); IR (neat) 2200 (C≡N), 1640 (C=C) cm^{-1}.

Preparation of 2-Ethoxy-6-methoxy-3-methyl-5-cyano-3,4-dihydro-2H-pyran ($\mathbf{1}_d$). A solution of methyl α-cyanoacrylate (5.5 g, 0.05 mol) in dry benzene (40 m*l*) was added slowly to a benzene (100 m*l*) solution of ethyl 1-propenyl ether (8.6 g, 0.10 mol) with stirring under nitrogen. The reaction mixture was stirred at room temperature for three days. The precipitated poly(methyl α-cyanoacrylate) was removed by filtration. Solvent and excess ethyl 1-propenyl ether were removed under vacuum to give 7.1 g (84% yield) of $\mathbf{1}_d$: ^{1}H NMR ($CDCl_3$) δ 0.90–1.40 (6H, m), 1.55–2.58 (3H, m), 3.40–4.08 (5H, m), 4.85–5.18 (1H, m); IR (neat) 2200 (C≡N), 1640 (C=C) cm^{-1}.

Cationic Polymerication of 2,3,5,6-Tetrasubstituted-3,4-dihydro-2H-pyrans $\mathbf{1}_{a-d}$. A representative cationic polymerization procedure (the case of $\mathbf{1}_a$) was as follows: A methylene chloride solution of $\mathbf{1}_a$ (1.83 g, 10 mmol) was placed in a rubber septum stopper capped pyrex glass ampule under nitrogen. The resulting solution was flushed with dry nitrogen for 20 min. The ampule was then placed in dry ice-acetone bath under nitrogen, and 0.01 m*l* of boron trifluoride etherate was added to the solution. After 36 hours the ampule was taken out and the polymerization mixture was poured into a large volume of diethyl ether. The precipitated white polymer was collected and reprecipitated from chloroform into diethyl ether. Thus obtained polymer was dried in a vacuum oven at 40°C. $\mathbf{2}_a$: 1.69 g (92% yield); η_{inh} = 0.31 dl/g (c 0.5 g/dl in chloroform at 20°C).

Preparation of H-T Alternating Copolymer ($\mathbf{3}_a$). The H-T alternating copolymer was prepared by usual free radical copolymerization at 65°C in benzene with AIBN. All the attempt to prepare the H-T copolymers $\mathbf{3}_{b-d}$ failed under polymerization reaction conditions so far. A representative polymerization procedure (the case of $\mathbf{3}_a$) was as follows: In a rubber septum stopper capped pyrex glass ampule were placed a solution of ethyl vinyl ether (4.32 g, 0.06 mol) and 0.11 g of AIBN in benzene (17.5 m*l*). The resulting solution was flushed with dry nitrogen 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 4.44 g (0.04 mol) of methyl α-cyanoacrylate, and the ampule was sealed under vacuum. The ampule was then placed in an oil bath kept at 65°C. After 16 hours the ampule was opened and the viscous product was poured into a 500 m*l* of diethyl ether. The precipitated polymer was collected and repecipitated from chloroform into diethyl ether. $\mathbf{3}_a$: 1.76 g (24% yield); η_{inh} = 0.36 dl/g (c 0.5 g/dl in chloroform at 20°C). The ^{1}H NMR spectrum of $\mathbf{3}_a$ indicated that the composition of the copolymer was approximately 1.0:1.0.

Cationic Copolymerization of 2,3,5,6-Tetrasubstituted-3,4-dihydro-2H-pyrans $\mathbf{1}_{a-d}$ with Styrene. 2,3,5-Trisubstituted pyrans $\mathbf{1}_{a-c}$ were copolymerized well with styrene to give vinyl terpolymers. However, 2,3,5,6-tetrasubstituted pyran $\mathbf{1}_d$ did not copolymerize when treated under identical conditions. A representative cationic copolymerization procedure (the case of $\mathbf{1}_a$) was as follows: In a rubber septum stopper capped pyrex glass ampule were placed a methylene chloride solution of $\mathbf{1}_a$ (0.93 g, 5 mmol) and styrene (0.52 g, 5 mmol). The resulting solution was flushed with dry nitrogen for 20 min. The ampule was then placed in a dry ice-acetone bath under nitrogen, and 0.01 m*l* of boron trifluoride etherate was added to the solution. After 48 hours the ampule was taken out and the polymerization mixture was poured into a large volume of diethyl ether. The precipitated white polymer was collected and reprecipitated from chloroform into diethyl ether. Thus obtained polymer was dried in a vacuum oven at 40°C.: 0.90 g (62% yield); η_{inh} = 0.31 dl/g (c 0.5 g/dl in chloroorm at 20°C).

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