

Synthesis of Alternating Head-to-Head Copolymer of Methyl α -cyanoacrylate and 2,3-Dihydrofuran. Ring-Opening Polymerization of 3-Methoxy-4-cyano-2,9-dioxabicyclo [4.3.0]non-3-ene

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3-Methoxy-4-cyano-2,9-dioxabicyclo [4.3.0] non-3-ene (**1**) was prepared by (4 + 2) cycloaddition reaction of methyl α -cyanoacrylate with 2,3-dihydrofuran. Compound **1** was ring-open polymerized by cationic catalyst such as boron trifluoride etherate to obtain alternating head-to-head (H-H) copolymer (**2**) of methyl α -cyanoacrylate and 2,3-dihydrofuran. For comparison, head-to-tail (H-T) copolymer (**3**) was also prepared by free radical copolymerization of the corresponding monomers. The H-H copolymer exhibited minor differences in its $^1\text{H-NMR}$ and IR spectra, but in the $^{13}\text{C-NMR}$ spectra significant differences were observed between the H-H and H-T copolymers. All of the H-H and H-T copolymers were soluble in common solvents and the inherent viscosities were in the range 0.2-0.3 dl/g.

Introduction

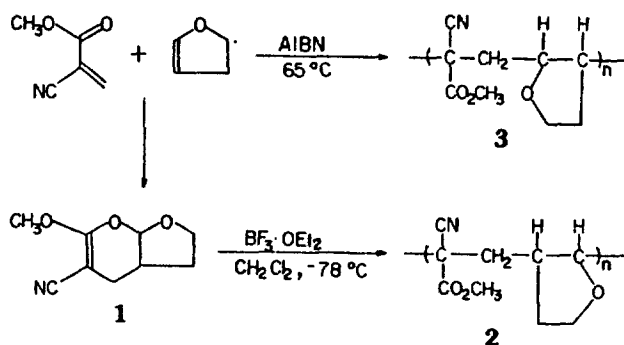
Extensive interest has been focused on the synthesis and properties of alternating head-to-head (H-H) polymers. Various H-H polymers have been prepared and their properties were found to differ significantly from those of the conventional head-to-tail (H-T) polymers.¹⁻⁸

In recent years, we have reported a new synthetic route to H-H alternating copolymers by cationic ring-opening polymerization of monocyclic pyrans.⁹⁻¹⁴ The substituted pyrans were prepared by (4 + 2) cycloaddition reaction of alkyl cyanoacrylates or vinyl ketons with alkyl vinyl ethers. These structures have cation-stabilizing groups at proper positions of the pyran ring. This work is now extended to the construction of H-H alternating copolymer of another pair of vinyl monomers. The present paper describes the synthesis and ring-opening polymerization of 3-methoxy-4-cyano-2,9-dioxabicyclo[4.3.0]non-3-ene (**1**). Properties of the resulting H-H copolymer were compared with those of the corresponding H-T copolymer which was prepared by free radical copolymerization of the corresponding monomers.

Results and Discussion

Compound **1** was prepared according to a procedure similar to that reported already^{9,15} from methyl α -cyanoacrylate and 2,3-dihydrofuran (Scheme 1). In dilute benzene solution, compound **1** was obtained in a rather low yield at 0°C under nitrogen. The chemical structure of the compound **1** was identified by $^1\text{H-NMR}$ (Figure 1) and IR spectra. All the spectral data confirmed the expected structure. Compound **1** was very reactive toward a cationic initiator polymerizing readily.

Compound **1** was polymerized with cationic catalyst such as boron trifluoride etherate to obtain H-H alternating copolymer **2** of methyl α -cyanoacrylate and 2,3-dihydrofuran. The polymerization results are summarized in Table 1. The values in Table 1 show that the ring-opening polymerizability of compound **1** is comparable to those of



Scheme 1

monocyclic pyrans⁸ or 2,3-dihydrofuran¹⁷⁻²⁰ and polymerized well with a cationic catalyst even at -78°C .

In the cationic polymerization as shown in Scheme 2, the catalyst initiates the polymerization by attacking a monomer molecule at C-4 thereby resulting in the formation of a cation that rearranges by ring opening to the well known alkoxy cation, which is usually involved in the cationic polymerization

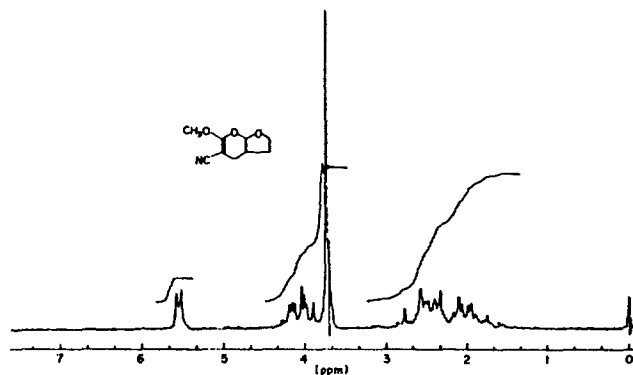


Figure 1. 60 MHz $^1\text{H-NMR}$ spectrum of 3-methoxy-4-cyano-2,9-dioxabicyclo[4.3.0]non-3-ene (**1**) taken in CDCl_3 at room temperature.

Table 1. Ring-Opening Polymerization^a of 3-Methoxy-4-cyano-2,9-dioxabicyclo[4.3.0]non-3-ene under Various Conditions

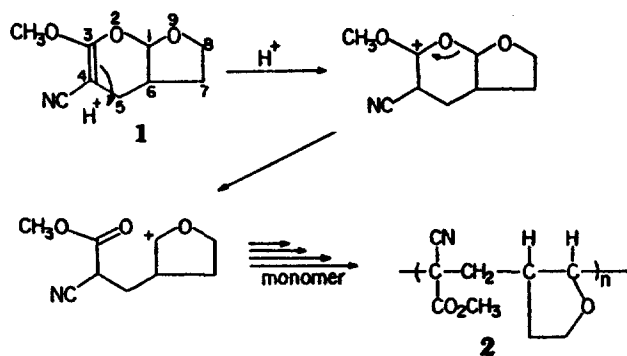
monomer	solvent	monomer/ solvent, g/ml	initiator to monomer, mol %	temp, °C	time, h	yield of product polymer, %	η_{inh} , dl/g ^b
1	CHCl ₃	0.33	BF ₃ , 0.7	-30	48	88	0.24
1	CHCl ₃	0.20	BF ₃ , 0.08	-30	24	86	0.20
1	CH ₂ Cl ₂	0.33	BF ₃ , 0.8	-78	40	90	0.25
1	CH ₂ Cl ₂	0.25	BF ₃ , 0.8	-78	30	85	0.22

^aThe copolymer composition was estimated from ¹H-NMR spectra to be 1.0:1.0. ^bInherent viscosity of copolymer: concentration of 0.5g/dl in chloroform at 20°C.

Table 2. Free Radical Copolymerization^a of Methyl α -cyanoacrylate with 2,3-Dihydrofuran 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							
MCA	DHF	0.50	0.80	0.83	65	10	15	0.28
MCA	DHF	0.67	0.85	0.65	65	8	18	0.30
MCA	DHF	0.60	0.70	0.50	65	9	14	0.25

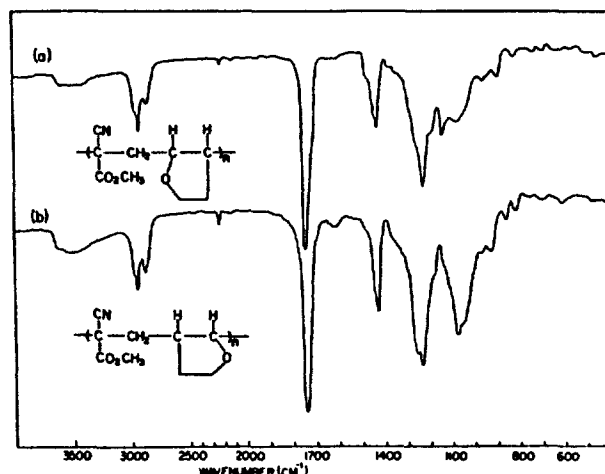
^aThe copolymer compositions were estimated to be 1.0:1.0 by ¹H-NMR spectra. ^bMCA = methyl α -cyanoacrylate; DHF = 2,3-dihydrofuran. ^cYield of copolymer was calculated with respect to the comonomer present in smaller molar ratio. ^dInherent viscosity of copolymer: concentration of 0.5g/dl in chloroform at 20°C.

**Scheme 2**

of 2,3-dihydrofuran. Thus, the driving force of the cationic polymerization is probably the stability of the ring-opened cation. The highly reactive nature of ketene acetal structure of the bicyclic compound should also contribute to a great extent to its high polymerizability.

For the purpose of comparison, the corresponding H-T alternating copolymer was prepared by conventional free radical polymerization of the monomer mixtures. The results are summarized in Table 2. Under the polymerization reaction conditions H-T alternating copolymer was obtained readily in a rather low conversion.

The chemical structures of the resulting H-H and H-T copolymers were identified by IR, ¹H-NMR, and ¹³C-NMR spectra. Representative spectra are shown in Figure 2-4. 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 sequences of the pendant groups. Thus, some differences were observed in the IR and ¹H-NMR spectra of H-H and H-T copolymers as shown in Figure 2 and Figure 3 respectively.

**Figure 2.** IR spectra of 1:1 alternating copolymers of methyl α -cyanoacrylate and 2,3-dihydrofuran: (a) head-to-tail, (b) head-to-head.

Significant differences were observed in their ¹³C-NMR spectra. Representative ¹³C-NMR spectra of H-H and H-T alternating copolymers are shown in Figure 4. Assignments of the chemical shifts were made on the basis of the predicted chemical shifts.¹⁶

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 0.2-0.3 dl/g.

We are now in the process of polymerization of other bicyclic alkenes and the results will be reported later.

Experimental

Materials. The reagent grade chemicals used in this work were purified by distillation before use. 2,3-

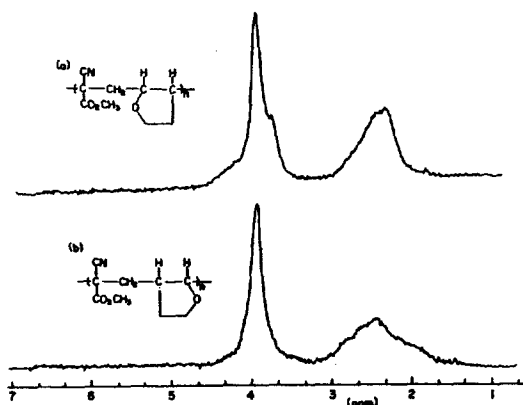


Figure 3. $^1\text{H-NMR}$ spectra of 1:1 alternating copolymers of methyl α -cyanoacrylate and 2,3-dihydrofuran: (a) head-to-tail, (b) head-to-head; 60 MHz, room temperature, arbitrary concentration in CDCl_3 .

Dihydrofuran was dried with anhydrous sodium carbonate, followed by fractional distillation. 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 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. $^1\text{H-NMR}$ spectra were obtained on a Varian Model T-60A spectrometer (60 MHz). $^{13}\text{C-NMR}$ spectra were obtained on a Bruker AS-200 NMR spectrometer at room temperature. Melting points were taken on a Buchi-512 melting point apparatus.

Preparation of 3-Methoxy-4-cyano-2,9-dioxabicyclo[4.3.0] non-3-ene (1). A solution of methyl α -cyanoacrylate (5.55g, 50 mmol) was added slowly to a benzene (50ml) solution of 2,3-dihydrofuran (7.0g, 100 mmol) with stirring under nitrogen at 0°C . The mixture was stirred at room temperature for 3 days. Poly(methyl α -cyanoacrylate) formed was removed by filtration. Solvent and excess 2,3-dihydrofuran

were then evaporated under vacuum at 0°C . Thus obtained crude crystal was recrystallized twice from diethyl ether to give 2.72g (30% yield) of **1**: mp $79\text{--}80^\circ\text{C}$; $^1\text{H-NMR}$ (CDCl_3) δ 1.58-2.25 (2H, m), 2.26-2.95 (3H, m), 3.81 (3H, s), 3.96 (2H, m), 5.70 (1H, d); IR (KBr) 2200 ($\text{C}\equiv\text{N}$), 1640 ($\text{C}=\text{C}$) cm^{-1} .

Cationic Polymerization of 3-Methoxy-4-cyano-2,9-dioxabicyclo[4.3.0] non-3-ene (1). A representative cationic polymerization procedure was as follows: A methylene chloride solution of **1** (1.81g, 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 placed in a dry ice-acetone bath under nitrogen, and 0.01ml of boron trifluoride etherate was added to the solution. After 40 hours the ampule was taken out and 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 . **2**: 1.63g (90% yield); $\eta_{inh} = 0.25$ dl/g (C 0.5 g/dl in chloroform at 20°C).

Preparation of H-T Alternating Copolymer (3). The H-T alternating copolymer was prepared by usual free radical copolymerization at 65°C in benzene with AIBN. A representative polymerization procedure was as follows: In a rubber septum stopper capped pyrex glass ampule were placed a solution of 2,3-dihydrofuran (14.0g, 0.20mol) and 0.26g of AIBN in benzene (30ml). The resulting solution was flushed with dry nitrogen for 20 min. The ampule was then placed in a dry ice-acetone bath and the solution was allowed to freeze. To it was added 11.1g (0.10mol) 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 10 hours the ampule was opened and the precipitated poly(methyl α -cyanoacrylate) was separated by suction filtration. The filtrate was concentrated by rotary evaporator. The resulting viscous product was poured into a large volume of methanol. The precipitated white polymer was collected and reprecipitated from chloroform into methanol. Thus obtained polymer was dried in a vacuum oven at 40°C . **3**: 2.72g (15% yield); $\eta_{inh} = 0.28$ dl/g (C 0.5g/dl in chloroform at 20°C). The $^1\text{H-NMR}$ spectrum of **3** indicated that the composition of the copolymer was approximately 1.0:1.0.

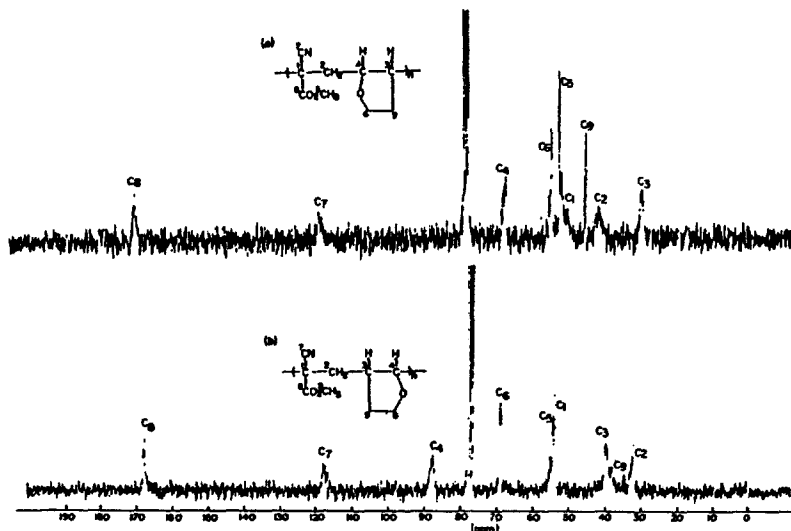


Figure 4. $^{13}\text{C-NMR}$ spectra of 1:1 alternating copolymers of methyl α -cyanoacrylate and 2,3-dihydrofuran: (a) head-to-tail, (b) head-to-head; 20 MHz, room temperature, arbitrary concentration in CDCl_3 . Chemical shifts are referenced to CDCl_3 (δ 77.0).

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Correlation Between Cross Interaction Constant and Bond Length in the S_N2 Transition State

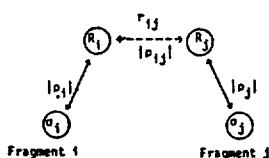
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A simple correlation between cross interaction constants ρ_{ij} and bond lengths in the transition state was obtained; it has been shown that ρ_{ij} corresponds to force constant of activation, which in turn is related to bond length by Badger's rule involving only universal constants. A satisfactory correlation between 4-31G ab initio calculated values of bond length and force constant for C-X stretching in the transition state of the methyl transfer reaction, $X^- + CH_3X = XCH_3 + X^-$, indicated that Badger's rule can be extended to bonds in the transition state. Independence of ρ_{ij} values from the variable charge transmission of reaction centers has been demonstrated with nearly constant, experimentally determined $|\rho_{XY}|$ values, and hence similar degree of bond formation, for various S_N2 reactions.

Introduction

Transition states (TS) can not be directly observed experimentally simply because reacting molecules do not remain near their TSs long enough to be accurately measured.¹ Selectivity parameters obtained by linear free energy relationships have, however, provided indirect measure of the TS structure within a series of reactions; Brønsted β values from rate-equilibrium relationships^{2,3} and Hammett ρ values from structure-reactivity relationships⁴ have been used as useful means of assessing relative bond tightness or looseness in the TS.



Scheme 1

The magnitude of a Hammett ρ_i reflects the intensity of interaction, relative to that for the benzoic acid dissociation

equilibria, between substituents (σ_j) and the reaction center (R_i) on fragment i ⁵ (e.g. in S_N2 reactions, a fragment refers to a nucleophile, substrate or leaving group)⁶ in the TS of a reaction; the stronger the interaction, the larger is the magnitude of $|\rho_i|$. Likewise $|\rho_j|$ reflects the intensity of interaction between substituents (σ_j) and the reaction center (R_j) on fragment j . However, the efficiency of charge transmission between reaction centers, R_i and R_j , in bond formation or bond cleavage may differ for different reaction series so that $|\rho_i|$ can at most serve as a relative measure of bond length r_{ij} within a series of reactions; $|\rho_i|$ values for different reaction series e.g. for different R_j such as R_k or R_b , can not be compared to assess relative bond length (r_{ij}) between two reaction centers which corresponds to the bond being formed or broken in the TS.⁷

On the other hand, the magnitude of cross interaction constant, ρ_{ij} in eq (1), reflects the intensity of indirect interaction between two substituents on fragments i and j through the reaction centers, R_i and R_j , in the TS when both substituents interact with their respective reaction centers simultaneously in the TS of a reaction i.e., when R_i and R_j form a partners