

# Synthesis of Alternating Head-to-Head Copolymer of Methyl $\alpha$ -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  $\alpha$ -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  $\alpha$ -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

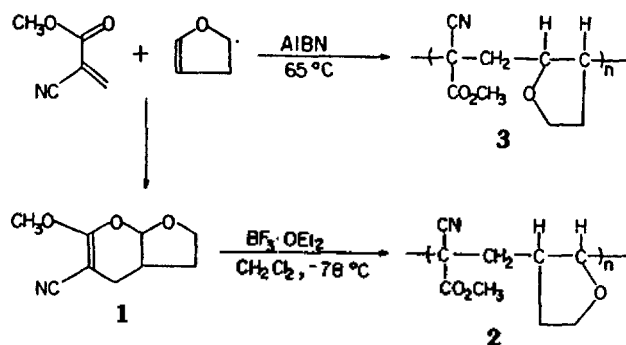
Extensive interest has been focused on the synthesis and properties of alternating head-to-head (H-H) polymers. Various H-H polymers have been prepared and their properties were found to differ significantly from those of the conventional head-to-tail (H-T) polymers.<sup>1-8</sup>

In recent years, we have reported a new synthetic route to H-H alternating copolymers by cationic ring-opening polymerization of monocyclic pyrans.<sup>9-14</sup> 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<sup>9,15</sup> from methyl  $\alpha$ -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  $\alpha$ -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 pyrans<sup>8</sup> or 2,3-dihydrofuran<sup>17,20</sup> and polymerized well with a cationic catalyst even at  $-78^\circ\text{C}$ .

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

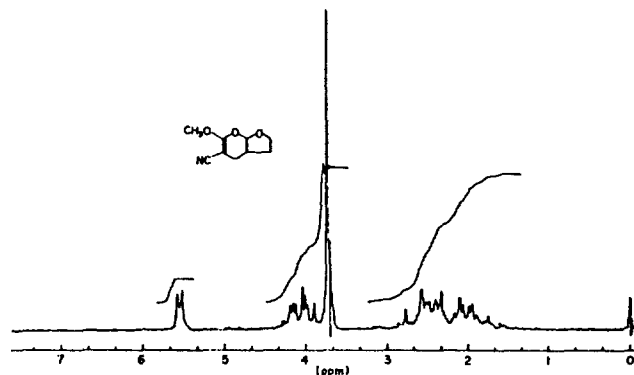


Figure 1. 60 MHz  $^1\text{H-NMR}$  spectrum of 3-methoxy-4-cyano-2,9-dioxabicyclo[4.3.0]non-3-ene (**1**) taken in  $\text{CDCl}_3$  at room temperature.

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

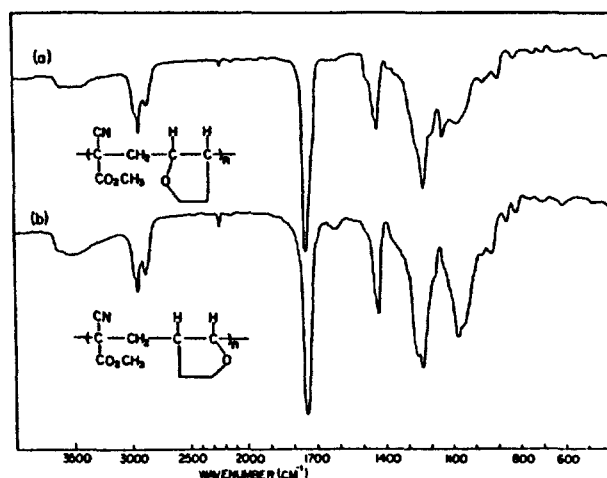
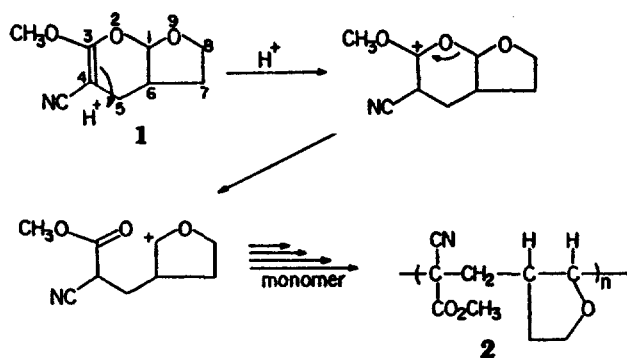
monomer	solvent	monomer/ solvent, g/ml	initiator to monomer, mol %	temp, °C	time, h	yield of product polymer, %	$\eta_{inh}$ , dl/g <sup>b</sup>
1	CHCl <sub>3</sub>	0.33	BF <sub>3</sub> , 0.7	-30	48	88	0.24
1	CHCl <sub>3</sub>	0.20	BF <sub>3</sub> , 0.08	-30	24	86	0.20
1	CH <sub>2</sub> Cl <sub>2</sub>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

<sup>a</sup>The copolymer composition was estimated from <sup>1</sup>H-NMR spectra to be 1.0:1.0. <sup>b</sup>Inherent viscosity of copolymer: concentration of 0.5g/dl in chloroform at 20°C.

**Table 2. Free Radical Copolymerization<sup>a</sup> of Methyl  $\alpha$ -cyanoacrylate with 2,3-Dihydrofuran by AIBN in Benzene at 65°C**

monomer <sup>b</sup>		A/B, mol	AIBN, mol %	(A + B) benzene, g/ml	temp. °C	time, h	% yield <sup>c</sup>	$\eta_{inh}$ , <sup>d</sup> 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

<sup>a</sup>The copolymer compositions were estimated to be 1.0:1.0 by <sup>1</sup>H-NMR spectra. <sup>b</sup>MCA = methyl  $\alpha$ -cyanoacrylate; DHF = 2,3-dihydrofuran. <sup>c</sup>Yield of copolymer was calculated with respect to the comonomer present in smaller molar ratio. <sup>d</sup>Inherent viscosity of copolymer: concentration of 0.5g/dl in chloroform at 20°C.



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

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, <sup>1</sup>H-NMR, and <sup>13</sup>C-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 <sup>1</sup>H-NMR spectra of H-H and H-T copolymers as shown in Figure 2 and Figure 3 respectively.

Significant differences were observed in their <sup>13</sup>C-NMR spectra. Representative <sup>13</sup>C-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.<sup>16</sup>

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-

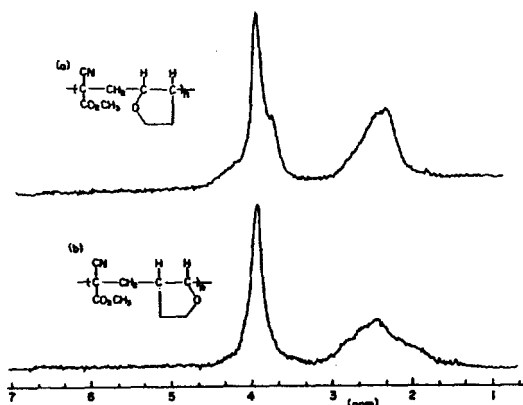


Figure 3.  $^1\text{H-NMR}$  spectra of 1:1 alternating copolymers of methyl  $\alpha$ -cyanoacrylate and 2,3-dihydrofuran: (a) head-to-tail, (b) head-to-head; 60 MHz, room temperature, arbitrary concentration in  $\text{CDCl}_3$ .

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  $\alpha$ -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  $\alpha$ -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  $0^\circ\text{C}$ . The mixture was stirred at room temperature for 3 days. Poly(methyl  $\alpha$ -cyanoacrylate) formed was removed by filtration. Solvent and excess 2,3-dihydrofuran

were then evaporated under vacuum at  $0^\circ\text{C}$ . Thus obtained crude crystal was recrystallized twice from diethyl ether to give 2.72g (30% yield) of **1**: mp  $79\text{--}80^\circ\text{C}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  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 ( $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ .

**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  $40^\circ\text{C}$ . **2**: 1.63g (90% yield);  $\eta_{\text{inh}} = 0.25 \text{ dl/g}$  (C 0.5 g/dl in chloroform at  $20^\circ\text{C}$ ).

**Preparation of H-T Alternating Copolymer (3).** The H-T alternating copolymer was prepared by usual free radical copolymerization at  $65^\circ\text{C}$  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  $\alpha$ -cyanoacrylate and the ampule was sealed under vacuum. The ampule was then placed in an oil bath kept at  $65^\circ\text{C}$ . After 10 hours the ampule was opened and the precipitated poly(methyl  $\alpha$ -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  $40^\circ\text{C}$ . **3**: 2.72g (15% yield);  $\eta_{\text{inh}} = 0.28 \text{ dl/g}$  (C 0.5g/dl in chloroform at  $20^\circ\text{C}$ ). The  $^1\text{H-NMR}$  spectrum of **3** indicated that the composition of the copolymer was approximately 1.0:1.0.

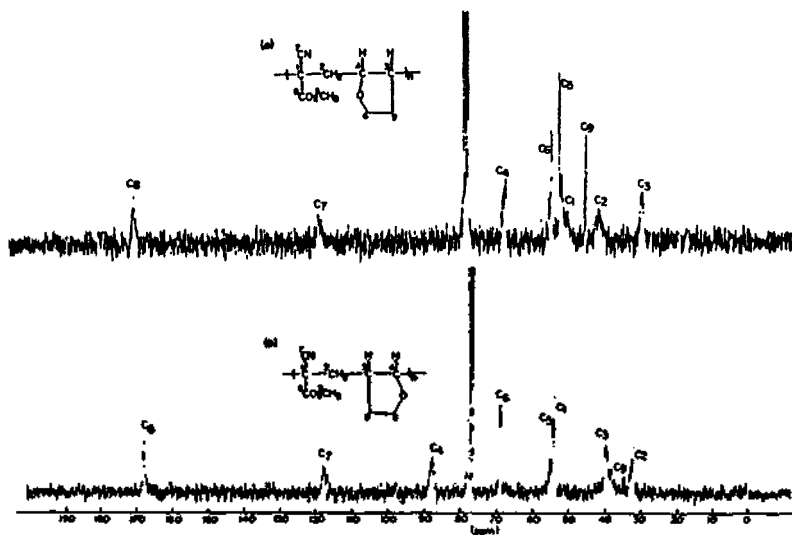


Figure 4.  $^{13}\text{C-NMR}$  spectra of 1:1 alternating copolymers of methyl  $\alpha$ -cyanoacrylate and 2,3-dihydrofuran: (a) head-to-tail, (b) head-to-head; 20 MHz, room temperature, arbitrary concentration in  $\text{CDCl}_3$ . Chemical shifts are referenced to  $\text{CDCl}_3$  ( $\delta$  77.0).

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

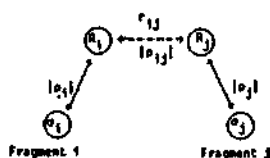
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A simple correlation between cross interaction constants  $\rho_{ij}$  and bond lengths in the transition state was obtained; it has been shown that  $\rho_{ij}$  corresponds to force constant of activation, which in turn is related to bond length 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  $\rho_{ij}$  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.<sup>1</sup> Selectivity parameters obtained by linear free energy relationships have, however, provided indirect measure of the TS structure within a series of reactions; Brønsted  $\beta$  values from rate-equilibrium relationships<sup>2,3</sup> and Hammett  $\rho$  values from structure-reactivity relationships<sup>4</sup> have been used as useful means of assessing relative bond tightness or looseness in the TS.



Scheme 1

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

equilibria, between substituents ( $\sigma_j$ ) and the reaction center ( $R_i$ ) on fragment  $i$ <sup>5</sup> (e.g. in  $S_N2$  reactions, a fragment refers to a nucleophile, substrate or leaving group)<sup>6</sup> 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 ( $\sigma_j$ ) 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  $|\rho_j|$  can at most serve as a relative measure of bond length  $r_{ij}$  within a series of reactions;  $|\rho_j|$  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.<sup>7</sup>

On the other hand, the magnitude of cross interaction constant,  $\rho_{ij}$  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