

3-Methoxy-4-cyano-2,9-dioxabicyclo[4.3.0]non-3-ene과 스티렌의 양이온 공중합 : 2,3-Tetrahydrofurandiyl기를 포함하는 비닐삼원 공중합체의 합성 및 그들의 성질

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Cationic Copolymerization of 3-Methoxy-4-cyano-2,9-dioxabicyclo [4.3.0]non-3-ene with Styrenes : Preparation of Vinyl Terpolymers containing 2,3-Tetrahydrofurandiyl Group and Their Properties

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요 약 : Methyl α -cyanoacrylate를 2,3-dihydrofuran과 (4+2) 고리 부가반응시켜서 3-methoxy-4-cyano-2,9-dioxabicyclo[4.3.0]non-3-ene (1)를 합성하였다. 2,3-Tetrahydrofurandiyl기를 포함하는 비닐 삼원공중합체를 합성하기 위해서 화합물 1을 스티렌과 양이온 공중합시켰다. 삼원 공중합체 2는 상용 용매에 녹았으며 고유점도는 0.2~0.4 dL/g을 나타냈다. 용액으로 부터 만들어진 중합체 필름은 투명하고 취약성을 보였으며, 유리전이 온도는 99.6°C였다.

Abstract : 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 copolymerized with styrene by cationic initiator to obtain vinyl terpolymers containing 2,3-tetrahydrofurandiyl group. Terpolymers 2 were soluble in common solvents and the inherent viscosities were in the range 0.2~0.4 dL/g. Solution-cast films were clear and brittle, showing T_g value of 99.6°C.

INTRODUCTION

Because tetrahydrofuran and its derivatives are stable under normal battery conditions and wettable by the solvent-electrolyte solution, the effort to incorporate tetrahydrofuran units into a polymer

chain was tried by several polymer chemists.¹ Thus the polymers containing tetrahydrofuran can be used as a effective battery separator. Poly(2,3-tetrahydrofurandiyl) may be obtained by the copolymerization of 2,3-dihydrofuran at low temperature using boron trifluoride gas or boron trifluo-

ride etherate as initiators.^{2~4}

In recent years, we have reported a synthetic route to vinyl terpolymers by cationic copolymerization of substituted pyrans with styrenes.^{5,6} This work is now extended to the construction of another type of vinyl terpolymers containing 2,3-tetrahydro-furandiyl unit. The present paper describes the synthesis of vinyl terpolymers composed of methyl α -cyanoacrylate, 2,3-dihydro-furan, and styrene. Properties of terpolymers were analyzed by thermal and spectroscopic methods.

EXPERIMENTAL

Materials

The reagent grade chemicals were purified by distillation or recrystallization before use. Dichloromethane was dried with anhydrous calcium chloride, distilled over anhydrous calcium hydride, and stored in a brown bottle. Chloroform was refluxed with phosphorus pentoxide, followed by fractional distillation. Benzene was purified by drying with calcium hydride, refluxed and distilled under nitrogen. Styrene was distilled from calcium hydride under reduced pressure and used immediately. 2,3-Dihydrofuran was dried with anhydrous sodium sulfate, followed by fractional distillation under nitrogen. Boron trifluoride etherate was treated with a small amount of diethyl ether and distilled under reduced pressure. 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. ¹H-NMR spectra were obtained on a Varian EM 360L NMR spectrometer (60 MHz). The glass transition temperatures (T_g) were measured on a DuPont 910 differential scanning calorimeter in a nitrogen atmosphere. DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min up to 500°C was used for the thermal degradation study of the terpolymers in a nitrogen atmosphere. Melting points were taken on

a Buchi 512 melting points apparatus.

Preparation of 3-Methoxy-4-cyano-2,9-dioxabicyclo[4.3.0]non-3-ene (1): Compound **1** was prepared by a known method⁷ from methyl α -cyanoacrylate and 2,3-dihydrofuran, and recrystallized twice from benzene. **1**: mp 79~80°C; ¹H-NMR (CDCl₃) δ 1.58~2.24 (2H, m), 2.26~2.95 (3H, m), 3.80 (3H, s), 3.95 (2H, m), 5.70 (1H, d); IR (KBr) 2200 (C \equiv N), 1640 (C=C) cm⁻¹.

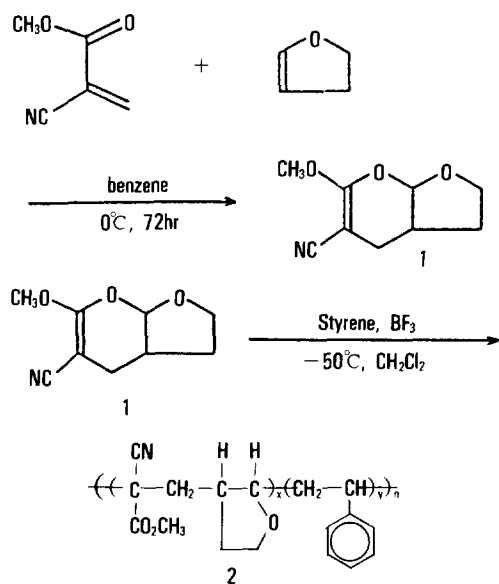
Cationic Copolymerization of 3-Methoxy-4-cyano-2,9-dioxabicyclo[4.3.0]non-3-ene (1) with Styrene. A representative cationic copolymerization procedure was as follows: In a rubber septum stopper capped polymerization tube was placed a dichloromethane solution of **1** (0.91g, 50mmole) and styrene (0.52g, 50mmole). The resulting solution was flushed with dry nitrogen for 20min. The polymerization tube was then placed at -50°C under nitrogen, and 0.01 mL of boron trifluoride etherate was added to the solution. After 89 hr the polymerization tube 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 room temperature. **2**: 1.0g (70% yield); η_{inh} = 0.32 dL/g (C = 0.5g/dL in chloroform at 25°C). ¹H-NMR (CDCl₃) δ 1.10~2.75 (m, 8H), 3.35~4.30 (m, 6H), 6.30~7.33 (m, 5H); IR (KBr) 3018 (aromatic C-H), 2240 (CN), 1640 (C=O), 707 (aromatic). The copolymer composition was calculated from ¹H-NMR spectra by the integration ratios of proton resonance peaks (δ = 6.30~7.33, phenyl group, 5H; δ = 3.35~4.30, -CO₂CH₃ and -CH-O-CH₂-, 6H).

RESULTS AND DISCUSSION

Compound **1** was prepared according to a procedure similar to that reported already.⁷ In dilute benzene solution, compound **1** was obtained in a rather low yield and always contaminated by the homopolymer of methyl α -cyanoacrylate. After poly(methyl α -cyanoacrylate) was removed by suction

filtration, the crude product was recrystallized twice from benzene. Monomer **1** is thermally unstable and isomerized to ring-opened compound⁷ at room temperature within a few days. Monomer **1** is very reactive toward cationic initiator polymerizing readily.^{7,8}

We have tried cationic copolymerization of monomer **1** with styrene and p-methoxystyrene (Scheme 1). Copolymerizations of **1** with styrene



Scheme 1

were carried out in dichloromethane solution with boron trifluoride etherate at -50°C . The copolymerization results are summarized in Table 1. The copolymer composition was analyzed by $^1\text{H-NMR}$ and IR spectra. Representative $^1\text{H-NMR}$ spectrum is shown in Figure 1. The IR spectra confirmed the expected chemical structures, exhibiting all the absorption bands attributable to the functional groups comprising the copolymers. The ca-

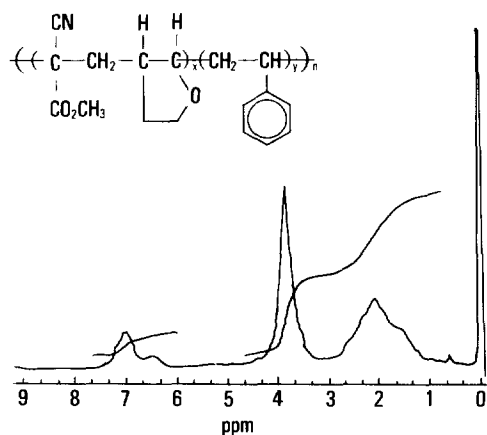


Fig. 1. $^1\text{H-NMR}$ spectrum of the copolymer containing approximately 37.5 mol % of methyl α -cyanoacrylate, 37.5 mol % of 2,3-dihydrofuran, and 25 mol % of styrene. 60 MHz, room temperature, arbitrary concentration in CDCl_3 .

Table 1. Cationic Copolymerization of 3-Methoxy-4-cyano-2,9-dioxabicyclo[4.3.0]non-3-ene (**1**) with Styrene under Various Conditions

Monomer		A/B mol	Solvent	(A + B)/ Solvent g/mL	Initiator ^a to Monomer mol %	Temp, $^{\circ}\text{C}$	Time, h	Yield of Polymer %	Copolymer Composition ^b A/B, mol/mol	η_{inh}^c
A	B									
1	St	1.00	CH_2Cl_2	0.57	0.8	-50	89	70	77/23	0.32
1	St	1.25	CH_2Cl_2	0.53	0.9	-50	92	78	75/25	0.29
1	St	0.50	CHCl_3	0.78	0.5	-30	45	50	60/40	0.28
1	d	1.00	CH_2Cl_2	0.80	0.7	-50	60	88	48/52	0.26
1	d	0.50	CHCl_3	0.90	0.5	-30	72	92	25/75	0.30

^a Initiator : Boron trifluoride etherate.

^b Copolymer composition estimated from $^1\text{H-NMR}$ and IR spectra.

^c Concentration of 0.5 g/dL in chloroform at 25°C .

^d p-Methoxystyrene.

Table 2. Thermal Properties of Terpolymer 2

Terpolymer	T_g^a , °C	Degrad Temp, ^b °C		Residue ^b at 500°C, %
		10%-loss	half-loss	
c	99.6	278	364	26.8
d	84.4	309	387	13.2

^a Determined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10°C/min in a nitrogen atmosphere.

^b Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min in a nitrogen atmosphere.

^c Terpolymer composition (mol/mol/mol) : methyl α -cyano-acrylate/2, 3-dihydrofuran/styrene = 38.5/38.5/23.0.

^d Terpolymer composition (mol/mol/mol) : methyl α -cyano-acrylate/2, 3-dihydrofuran/*p*-methoxystyrene = 24.0/24.0/52.0.

tionic polymerizability of compound **1** is higher than that of styrene, and the copolymer always has lower styrene contents as shown in Table 1. However, the reactivity of *p*-methoxystyrene toward cationic polymerization is similar to that of monomer **1**. The striking feature of the copolymerization is that it provides a synthetic route to terpolymer composed of three vinyl monomers. The terpolymer cannot be prepared from the mixtures of three vinyl monomers. Thus, we prepared vinyl terpolymers containing 2, 3-tetrahydrofurandiyl units.

The thermal behavior of terpolymer was investigated by DSC at scanning rate of 10°C/min to de-

termine the glass transition temperature (T_g). The results are shown in Table 2. Solution-cast films were clear and brittle, showing T_g value of 99.6°C. The terpolymers 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.

We are exploring the perparation of various terpolymers and the results will be reported later.

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