

p-(2,2,3-트리시아노-3-카르보메톡시시클로프로필) 페닐 아크릴레이트와 메타크릴레이트의 합성 및 라디칼 중합

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Synthesis and Radical Polymerization of p-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)Phenyl Acrylate and Methacrylate

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요 약 : p-아크릴로일옥시벤질리덴 시안화초산 메틸(2a) 또는 p-메타크릴로일옥시벤질리덴 시안화초산 메틸(2b)을 각각 브로모말로노니트릴과 반응시켜 p-(2,2,3-트리시아노-3-카르보메톡시시클로프로필)페닐 아크릴레이트(3a)와 p-(2,2,3-트리시아노-3-카르보메톡시시클로프로필)페닐 메타크릴레이트(3b)를 합성하였다. 단량체 3a와 3b를 자유 라디칼 개시제로 중합시켜 시클로프로판고리에 시아노기가 다수 치환된 펜단트기를 갖는 폴리아크릴레이트(4a)와 폴리메타크릴레이트(4b)를 얻었다. 얻어진 중합체 4a와 4b는 아세톤에 녹았으며 고유점도는 0.2~0.3 dL/g을 보였다. 중합체의 용액으로부터 얻어진 필름은 투명하고 취약성을 보였으며, 폴리아크릴레이트 4a의 유리전이온도는 약 170°C였다.

Abstract : p-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenyl acrylate(3a) and methacrylate(3b) were prepared by the reaction of bromomalononitrile with methyl p-acryloyloxybenzylidenecyanoacetate(2a) or methyl p-methacryloyloxybenzylidenecyanoacetate(2b), respectively. Monomers 3a and 3b were polymerized with free-radical initiators to obtain the polymers with multicyno functionalities in the cyclopropane ring. The resulting polymers(4a and 4b) were soluble in acetone and the inherent viscosities were in the range of 0.2~0.3 dL/g. Solution-cast films were clear and brittle, and the T_g value of polyacrylate 4a was around 170°C.

INTRODUCTION

Piezoelectric polymers have long been the subject of curiosity and have caused recent interest.¹

It is well-known that crystalline polymers such as poly(vinylidene fluoride) with a large dipole moment exhibit the piezoelectric effect. Amorphous polymers with a high concentration of permanent

dipoles also exhibit piezoelectric properties after poling if the main chain has an all planar zigzag conformation. The copolymer of vinylidene cyanide and vinyl acetate is such a case.² Poly(acrylonitrile) has high concentrations of nitrile dipoles, but the helical structure of the polymer main chains causes the radiating dipoles to cancel each other.³ In the case of poly(1-bicyclobutanecarbonitrile), the rigid ring structure prevents helix formation and this polymer also shows a piezoelectric behavior.⁴

A potentially piezoelectric polymer must contain a large concentration of dipoles and also be mechanically very strong. These polymers have to be film-forming and be able to withstand high voltages without breakdown. We have recently proposed that three- and four-membered rings with several cyano substituents held rigidly in alignment will have large dipole moments⁵ and that these polymers are potentially piezoelectric materials. We have previously prepared a series of polymers containing 1,1,2,2-tetracyanocyclopropane,⁵⁻⁶ 1,1,2-tricyano-2-carbomethoxycyclopropane,⁷ 1,2-dicyano-1,2-dicarbomethoxycyclopropane,⁸ and 1,1,2,2-tetracyanocyclobutane units.⁹

This work is now extended with the synthesis of another polymer containing multicyanocyclopropane rings. The present report describes the synthesis and radical polymerization of *p*-(2,2,3-tricyano-3-carbomethoxycyclopropyl)phenyl acrylate and methacrylate **3a-b**.

EXPERIMENTAL

Materials. *p*-Hydroxybenzaldehyde was crystallized from water containing a small amount of sulfuric acid and dried under vacuum. Acryloyl chloride and methacryloyl chloride (Aldrich) were distilled and used immediately. Triethylamine was refluxed over potassium hydroxide and distilled. Methyl cyanoacetate was purified by drying with anhydrous sodium sulfate and distilled. Acetonitrile was refluxed with calcium hydride and fractionally distilled. Benzene was purified by refluxing

over sodium metal, distilled, and stored over molecular sieves (**4A**) under nitrogen. β -Butyrolactone was dried with anhydrous calcium sulfate and fractionally distilled. 2,2-Azobisisobutyronitrile (AIBN) was recrystallized from methanol and stored at 5°C. Bromomalononitrile was prepared according to a literature¹² and recrystallized twice from chloroform. *p*-Acryloyloxybenzaldehyde (**1a**) and *p*-methacryloyloxybenzaldehyde (**1b**) were prepared by a published procedure.⁸ Methyl *p*-acryloyloxybenzylidenecyanoacetate (**2a**) and methyl *p*-methacryloyloxybenzylidenecyanoacetate (**2b**) were prepared by a published procedure.⁸

Measurements. 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). Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The glass transition temperature (*T_g*) was measured on a DuPont 910 differential scanning calorimeter in nitrogen atmosphere. DuPont 951 thermogravimetric analyzer was used for the thermal degradation study of polymers up to 700°C under nitrogen atmosphere with a heating rate of 10°C/min. Melting points were measured on a Buchi 512 melting point apparatus and were corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

Preparation of *p*-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenyl acrylate (3a**).** Methyl *p*-acryloyloxybenzylidenecyanoacetate (1.54 g, 0.006 mol) and bromomalononitrile (1.30 g, 0.009 mol) were dissolved in 20 ml of 85% aqueous ethanol with stirring at 0°C. After stirring for 6 h at 0°C, the product was filtered and rinsed once with 20 ml of 85% aqueous ethanol and twice with 20 ml of cold ethanol. The obtained white crystals were recrystallized from ethanol/acetone (90/10, vol./vol.) mixtures to give 1.16 g (60% yield) of **3a** (an isomeric mixture of *Z*-/*E*-). M.p. 82-84°C. ¹H-NMR (acetone-*d*₆) δ 3.97 (s, 3H), 4.36 (s, 1H), 5.93-6.28 (m, 1H), 6.34-6.74 (m, 2H), 7.24-7.53 (d, 2H), 7.67-7.98 (d, 2H). IR (KBr) 2267 (m, CN), 1757, 1737 (vs, C=O), 1638, 1613 (m, C=C) cm⁻¹. Anal. Calcd. for

$C_{17}H_{11}N_3O_4$: C, 63.57 ; H, 3.42 ; N, 13.08. Found : C, 63.48 ; H, 3.37 ; N, 13.02.

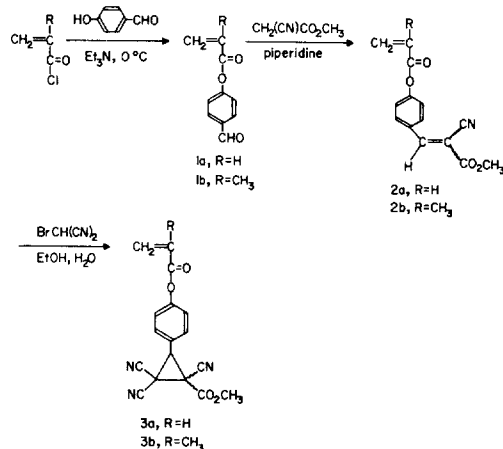
Preparation of p-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenyl methacrylate(3b). Methyl p-methacryloyloxybenzylidenecyanoacetate(1.17 g, 0.008 mol) and bromomalononitrile(1.74 g, 0.012 mol) were dissolved in 25 ml of 85% aqueous ethanol with stirring at 0°C. The resulting solution was stirred for 5 h at 0°C. The product was filtered and rinsed once with 20 ml of 85% aqueous ethanol and twice with 25 ml of cold ethanol. The obtained white crystals were recrystallized from ethanol/acetone(90/10, v/v) mixtures to give 1.74 g(65% yield) of **3b**(an isomeric mixture of Z-/E-). M.p. 138~140°C. 1H -NMR(acetone- d_6) δ 2.03 (s, 3H), 3.98(s, 3H), 4.35(s, 1H), 5.73~5.89(m, 1H), 6.22~6.33(m, 1H), 7.20~7.47(d, 2H), 7.65~7.95(d, 2H). IR(KBr) 2268(m, CN), 1758, 1737(vs, C=O), 1640, 1614(m, C=C) cm^{-1} . Anal. Calcd. for $C_{18}H_{13}N_3O_4$: C, 64.50 ; H, 3.88 ; N, 12.53. Found : C, 64.42 ; H, 3.84 ; N, 12.48.

Radical polymerization of 3. A representative polymerization procedure(the case of **3a**) was as follows : A γ -butyrolactone(3.0 ml) solution of **3a** (0.96 g, 0.003 mol) was placed in a polymerization tube, and 0.0044 g(2.7×10^{-5} mol) of AIBN was added under nitrogen. The mixture was degassed by a freeze-thaw process under vacuum. After the mixture was warmed to room temperature, it was placed in an oil bath kept at 65°C. After 12 h, the polymerization tube was opened and the viscous product was poured into 400 ml of methanol. The precipitated polymer was collected and reprecipitated from acetone into methanol. The obtained polymer **4a** was dried in a vacuum oven at 30°C. Yield : 0.82 g(85%) ; $\eta_{inh} = 0.25$ dl/g(c : 0.5 g/dl in acetone at 25°C). **4a** : 1H -NMR(acetone- d_6) δ 6.88~7.93(m, 4H), 4.28(s, 1H), 4.02(s, 3H), 1.95~3.42(m, 3H). IR(KBr) 2249(m, CN), 1748 (vs, C=O), 1602(m, C=C) cm^{-1} . Anal. Calcd. for $(C_{17}H_{11}N_3O_4)_n$: C, 63.57 ; H, 3.42 ; N, 13.08. Found : C, 63.48 ; H, 3.37 ; N, 13.01. **4b** : 1H -NMR(acetone- d_6) δ 6.98~7.96(m, 4H), 4.33(s, 1H), 4.01(s, 1H), 2.10~3.38(m, 2H), 1.03~2.03

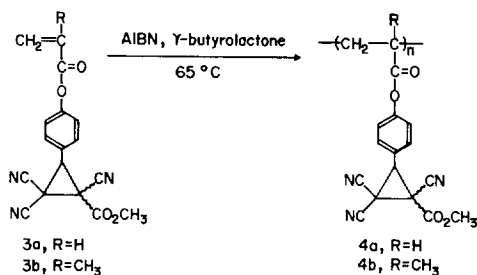
(m, 3H). IR(KBr) 2249(m, CN), 1746(vs, C=O), 1603(m, C=C) cm^{-1} . Anal. Calcd. for $(C_{18}H_{13}N_3O_4)_n$: C, 64.50 ; H, 3.88 ; N, 12.53. Found : C, 64.41 ; H, 3.82 ; N, 12.49.

RESULTS AND DISCUSSION

p-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenyl acrylate(**3a**) and p-(2,2,3-tricyano-3-carbomethoxycyclopropyl)phenyl methacrylate(**3b**) were prepared by cyclopropane formation from bromomalononitrile and methyl p-acryloyloxybenzylidenecyanoacetate(**2a**) or methyl p-methacryloyloxybenzylidenecyanoacetate(**2b**), according to a variation of the Wideqvist reaction.¹⁰ Compound **2a** and **2b** were prepared by the condensation of methyl cyanoacetate with p-acryloyloxybenzaldehyde(**1a**) or p-methacryloyloxybenzaldehyde(**1b**).¹¹



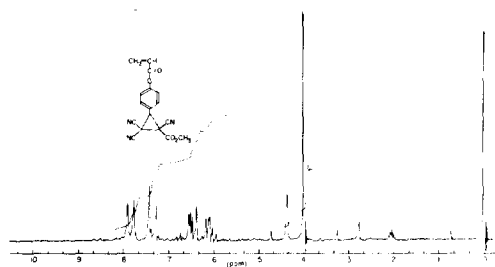
Scheme 1



Scheme 2

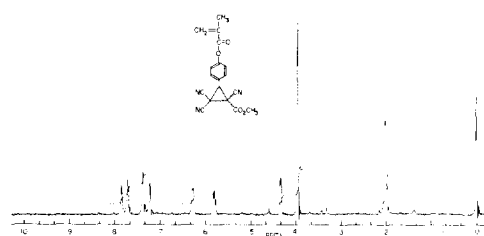
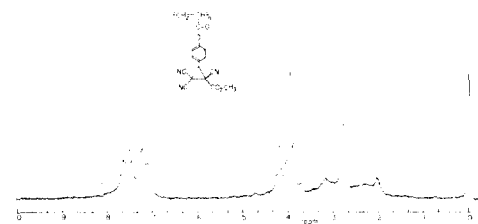
Table 1. Free Radical Polymerization of **3**^a by AIBN^b at 65°C

Monomer	solvent (vol./vol.)	Wt. of monomer	Time (h)	Conversion (%)	η_{inh}^c (dL/g)
		vol. of solvent(g/mL)			
3a	γ -butyrolactone	0.32	12	85	0.25
3a	γ -butyrolactone	0.25	10	82	0.22
3a	γ -butyrolactone	0.40	18	83	0.20
3a	C ₆ H ₆ /CH ₃ CN, 1/1	0.20	10	80	0.20
3b	γ -butyrolactone	0.34	12	92	0.30
3b	γ -butyrolactone	0.30	15	95	0.24
3b	γ -butyrolactone	0.25	10	90	0.25
3b	C ₆ H ₆ /CH ₃ CN, 1/2	0.20	12	88	0.22

^a **3a** = p-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenyl acrylate ;**3b** = p-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenyl methacrylate.^b Concentration : 0.9 mol-%.^c Concentration : 0.5 g/dL in acetone at 25°C.**Fig. 1.** ¹H-NMR spectrum(60 MHz) of p-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenyl acrylate(**3a**) taken in acetone-d₆ at room temperature.

Compounds **1a** and **1b** were prepared by the well-known Schotten-Baumann method. The chemical structure of the compounds was confirmed by ¹H-NMR(Fig. 1 and Fig. 2), IR, and elemental analyses. Compounds **3a-b** were quite stable when heated up to 100°C.

Monomers **3a** and **3b** were polymerized by free radical mechanism using AIBN as initiator to obtain the polymers **4a** and **4b**. Polymerizations were carried out in solution at 65°C. The polymerization results are summarized in Table 1. Monomers **3a-b** were quite reactive toward the free radical initiator and polymerized readily. The free radical initiator did not attack the cyclopropane ring during polymerization. The polymerizability of

**Fig. 2.** ¹H-NMR spectrum(60 MHz) of p-(2,2,3-Tricyano-3-carbomethoxycyclopropyl)phenyl methacrylate (**3b**) taken in acetone-d₆ at room temperature.**Fig. 3.** ¹H-NMR spectrum of polymer **4a**. 60 MHz, room temperature, arbitrary concentration in acetone-d₆.

monomer **3b** was higher than that of **3a**, and yield and inherent viscosity of polymer **4b** were higher than those of polymer **4a**, as shown in Table 1. In most cases, conversions were quite high, but the molecular weights were rather low.

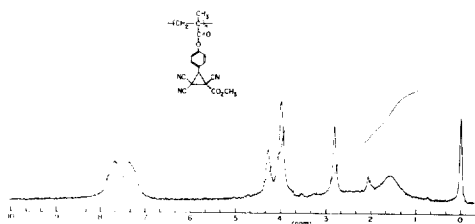


Fig. 4. ^1H -NMR spectrum of polymer **4b**. 60 MHz, room temperature, arbitrary concentration in acetone- d_6 .

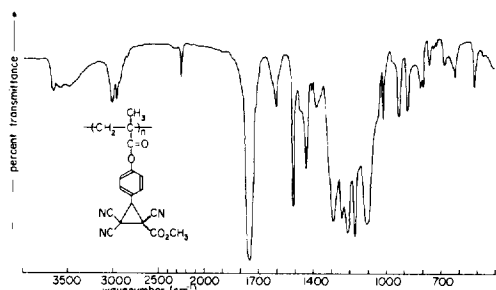


Fig. 5. IR spectrum of polymer **4b**.

The chemical structure of polymer **4a** and **4b** was confirmed by ^1H -NMR (Fig. 3 and Fig. 4) and IR spectroscopy (Fig. 5), and elemental analysis. The polymers were soluble in acetone but were not soluble in chloroform and diethyl ether. The inherent viscosity measured in acetone at 25°C was in the range of $0.2\sim 0.3$ dl/g. The thermal behavior of the polymer **4a** and **4b** was investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature (T_g), and the results are summarized in Table 2. Polymer **4b** shows a double phase degradation pattern in its TGA thermogram as shown in Fig. 6, probably due to the presence of two rings in the pendant group. The T_g value of polymer **4a** determined from DSC curve (Fig. 7) was found to be about 170°C . These T_g values are higher than those for poly(methyl acrylate) (10°C) and for poly(methyl methacrylate) (105°C). Films cast from polymer solution in acetone were brittle, and the-

Table 2. Thermal Properties of Polymers **4**

Polymer	T_g^a ($^\circ\text{C}$)	Degradation-temp. ($^\circ\text{C}^b$)			Residue ^b at 700°C (wt.%)
		5 %-loss	20 %-loss	40 %-loss	
4a	171	270	344	484	30.6
4b	—	257	278	367	34.8

^a Determined from DSC curves obtained on a DuPont 910 differential scanning calorimeter with a heating rate of $10^\circ\text{C}/\text{min}$ in N_2 atmosphere.

^b Determined from TGA curves obtained on a DuPont 951 thermogravimetric analyzer with a heating rate of $10^\circ\text{C}/\text{min}$ in N_2 atmosphere.

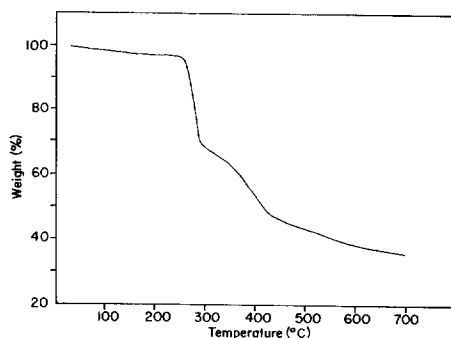


Fig. 6. TGA thermogram of polymer **4b** ($10^\circ\text{C}/\text{min}$, N_2).

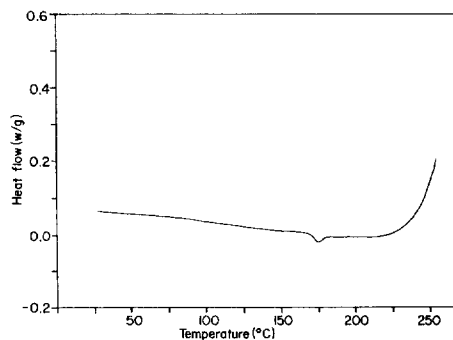


Fig. 7. DSC thermogram of polymer **4a** ($10^\circ\text{C}/\text{min}$, N_2).

refore, their piezoelectric activity has not been measured yet.

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