

## Syntheses and characterizations of copolymers of dicyanoquinone methides with $\alpha$ -acetoxystyrenes

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### Summary

7,7-Dicyanoquinone methides (**1a-b**) copolymerized spontaneously with substituted  $\alpha$ -acetoxystyrenes (**2a-b**) in benzene at 60 °C to give alternating copolymers (poly(**1a-b-co-2a-b**)) with the molecular weights of 8-60 x 10<sup>4</sup> in 42-66% yields. When these copolymers were heated under nitrogen, they eliminated acetic acid quantitatively at around 200 °C to be converted to the copolymers (poly(**3a-d**)) with olefinic bonds, which were characterized by infrared and nuclear magnetic resonance spectroscopy. Alternating copolymers and the corresponding copolymers with olefinic bonds were amorphous, and capable of being cast from their chloroform solutions into transparent, tough films.

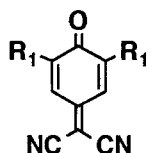
### Introduction

Piezoelectric polymers are of current interest (1,2). Crystalline poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoroethylene exhibit a strong piezoelectric effect when poled under a strong electric field (3-6). The large C-F dipole moments and details of the crystal structure are well known to play an important role in determining the electric properties associated with these fluoropolymers. Some nonfluorinated polymers containing large dipoles such as cyano group also have been shown to possess piezoelectric properties. Miyata *et al.* reported that an alternating copolymer of vinylidene cyanide (VDC) with vinyl acetate (VAc) (poly(VDC-co-VAc)) and highly alternating copolymers of VDC with vinyl esters of fatty acids are amorphous and exhibit fairly high piezoelectric activity after poling (7-9). The origin of the piezoelectricity in these copolymers has been attributable to the ability of the vinyl esters unit to assist in dipole orientation of cyano group under poling condition (10). Hall *et al.* reported preparations and homopolymerizations of novel monomers with three- and four-membered ring carrying cyano substituents in order to obtain piezoelectric polymers containing large concentration of dipoles, but solution-cast films were brittle due to low molecular weights (11-14). Previously we found that 7,7-dicyanoquinone methide (**1a**) could copolymerize with a donor monomer styrene in a perfectly alternating fashion (15). When  $\alpha$ -acetoxystyrenes such as  $\alpha$ -acetoxystyrene (**2a**) and *p*-acetoxy- $\alpha$ -acetoxystyrene (**2b**) are used instead of styrene, 7,7-dicyanoquinone methides such as **1a** and 2,6-dimethyl-7,7-dicyanoquinone methide (**1b**) are expected to copolymerize with them to give perfectly alternating copolymers, which have structures similar to poly(VDC-co-VAc) possessing high piezoelectric property and would have high glass

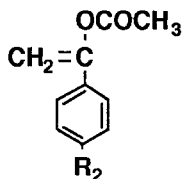
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transition temperatures due to the existence of aromatic rings. Therefore, these are interesting copolymers as one of good candidates for new materials with piezoelectric property.

In this work we describe the preparation of copolymers from the **1a-2a**, **1a-2b**, **1b-2a**, and **1b-2b** systems and their characterization and some properties.



**1a** :  $R_1 = H$   
**1b** :  $R_1 = Me$



**2a** :  $R_2 = H$   
**2b** :  $R_2 = OAc$

## Experimental

Copolymer compositions were established by the elemental analysis.  $^1H$ - and  $^{13}C$ -NMR measurements were carried out in chloroform-*d* with tetramethylsilane as an internal standard. The number-average molecular weights,  $M_n$ , of the copolymers were determined by gel permeation chromatography (GPC) using standard polystyrenes as a reference and tetrahydrofuran (THF) as an eluent without correction. UV-vis measurement was carried out in THF at room temperature. Glass transition temperature ( $T_g$ ) and decomposition temperature ( $T_d$ ) of the copolymers were determined by thermogravimetry (TG) and differential scanning calorimetry (DSC), respectively, at a scanning rate of  $+10\text{ }^\circ\text{C}/\text{min}$  under nitrogen (100 mL/min). Crystallinity of the copolymers was determined by X-ray diffraction measurement, which was carried out in the range of  $2\theta = 10\text{-}90^\circ$  at a scanning rate of  $5^\circ/\text{min}$ , using Cu-K $\alpha$  radiation. Refractive index values of the copolymers were measured by using mixture solutions of carbon disulfide ( $n_D = 1.6380$ ) and ethanol ( $n_D = 1.3614$ ) (16).

$^1H$ - and  $^{13}C$ -NMR spectra were taken on a JEOL JNM-EX 270 FT NMR spectrometer. Infrared and UV-vis measurements were made on JASCO IR-700 and UVIDEK-430B spectrometers, respectively. Melting points were measured on a Yanaco micro melting point apparatus and are uncorrected. Elemental analysis was performed by a Yanaco CHN Corder MT-3. The number-average molecular weights ( $M_n$ ) of the copolymers were measured on a Tosoh HLC-803D with a series of two columns, Tosoh TSK-GELG4000H and G6000H. Rigaku TAS 200 thermal analysis system was used for TG and DSC measurements. Rigaku Rotaflex RU-200B X-ray system was used for X-ray diffraction measurement. Elma Abbe refractometer was used for refractive index measurement.

## Materials

7,7-Dicyanoquinone methide (**1a**): **1a** was prepared in a 29.7% yield according to the method reported by Hyatt (17) and recrystallized from a mixture of dichloromethane and hexane; mp  $145\text{-}146\text{ }^\circ\text{C}$ ;  $^1H$  NMR( $CDCl_3$ ):  $\delta$  7.67 (d,  $J = 9.6$  Hz, 2H), 6.67 (d,  $J = 9.6$  Hz, 2H); IR(KBr):  $\nu_{CN}$  2232,  $\nu_{C=O}$  1650,  $\nu_{C=C}$  1596  $\text{cm}^{-1}$ .

2,6-Dimethyl-7,7-dicyanoquinone methide (**1b**): 2,6-Dimethylbenzoquinone(18) (0.74 g, 5.4 mmol), malononitrile (0.88 g, 13.3 mmol), and pyridine (2.12 g, 26.8 mmol) were dissolved in 50 mL of dichloromethane and cooled to  $0\text{ }^\circ\text{C}$ . Into the mixture was added dropwisely a solution of titanium tetrachloride (2.56 g) in 50 mL of dichloromethane under nitrogen, and then, the resulting mixture was stirred at  $0\text{ }^\circ\text{C}$

for 15 h. Water (100 mL) was added into the reaction mixture, and then, organic layer was separated and dried over anhydrous magnesium sulfate. The filtrate was placed under reduced pressure to remove the solvent to give a black oil, which was dissolved in a small amount of dichloromethane. The resulting solution was passed through silica gel column using dichloromethane as an eluent. The first yellow elution band portion was collected and placed under reduced pressure to remove the solvent to give a yellow solid, which was recrystallized from hexane to give 0.40 g (43% yield) of **1b** as a golden needles; mp 134.5-135 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.38 (s, 2H), 2.16 (s, 6H); IR (KBr):  $\nu_{\text{CH}}$  3000-2924,  $\nu_{\text{CN}}$  2204,  $\nu_{\text{C=O}}$  1603,  $\nu_{\text{C=C}}$  1561  $\text{cm}^{-1}$ .

$\alpha$ -Acetoxystyrene (**2a**): **2a** was prepared in a 30.2% yield according to the method reported by Noyce *et al.* (19); bp 88-90 °C / 3 mmHg;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.48-7.43 (m, 2H), 5.47 (d,  $J = 2.3$  Hz, 1H), 5.02 (d,  $J = 2.3$  Hz, 1H), 2.26 (s, 3H); IR (NaCl):  $\nu_{\text{CH}}$  3016,  $\nu_{\text{C=O}}$  1721,  $\nu_{\text{C=C}}$  1612  $\text{cm}^{-1}$ .

*p*-Acetoxy- $\alpha$ -acetoxystyrene (**2b**): **2b** was prepared in a 9% yield according to the method reported by Montheard *et al.* (20); bp 140 °C / 1 mmHg;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.38 (d,  $J = 8.25$  Hz, 2H), 7.08 (d,  $J = 8.24$  Hz, 2H), 5.44 (d,  $J = 2.31$  Hz, 1H), 5.03 (d,  $J = 2.3$  Hz, 1H), 2.26 (s, 3H); IR (NaCl):  $\nu_{\text{CH}}$  3020,  $\nu_{\text{C=O}}$  1720,  $\nu_{\text{C=C}}$  1609  $\text{cm}^{-1}$ .

Benzene (bp 80 °C) was washed with sulfuric acid, water, 5% aqueous sodium hydroxide solution, and again water, dried over sodium metal chips, and distilled. Tetrahydrofuran (THF) (bp 66 °C) was refluxed over lithium aluminum hydride for 12 h, and then distilled.

#### Polymerization procedure

Given amounts of **1a** (or **1b**), **2a** (or **2b**) as a comonomer, and benzene were placed in a glass ampule, which was degassed by the freeze-thaw method (repeated three times) and sealed. The ampule was placed in a bath thermostated at 60 °C for 24 h, and then, opened. The reaction mixture was poured into an excess of methanol to deposit a polymeric product, which was dissolved again in a small amount of dichloromethane and the resulting solution was poured into an excess of methanol. This procedure was repeated three times or more for purification. The polymeric product obtained was dried under reduced pressure until a constant weight was reached.

#### Dielectric constant measurement

The gold-film-gold sandwich type specimens were prepared as follows: The copolymers were dissolved in chloroform, and then the resulting solution was passed through a Teflon-coated filter with a pore size of 1.0  $\mu\text{m}$  to remove small suspended dust particles. The solution was spread uniformly on a cover glass carrying gold electrode and then the solvent was removed at a slow rate to obtain a film, on which a gold electrode ( $4 \times 10^{-6} \text{ m}^2$ ) was deposited by a vacuum evaporating technique. The film has a thickness of 3  $\mu\text{m}$ . Capacity of the film was measured at room temperature before and after poling treatment by applying d.c. electric fields of 33 V/m for 1 h at 100 °C on General Radio Precision Capacitance measurement system.

## Results and Discussion

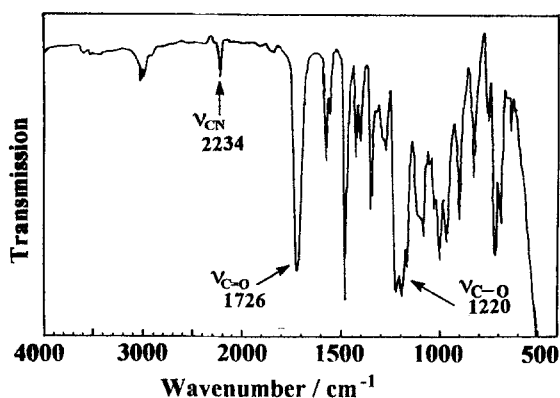
#### Copolymerization and copolymer structure

The copolymerizations for the **1a-2a**, **1a-2b**, **1b-2a**, and **1b-2b** systems were carried out in benzene at 60 °C without initiator. The results of the copolymerizations are summarized in Table 1. All copolymers were obtained as white powders, which have the molecular weights of  $8-60 \times 10^4$ . From the elemental analysis, the copolymers obtained were found to consist of one to one composition of **1a** and **2a** units, of **1a** and **2b** units, of **1b** and **2a**, and of **1b** and **2b** units. The IR spectrum and  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra in chloroform-*d* of a

Table 1 Copolymerizations of **1a** with **2a**, **1a** with **2b**, **1b** with **2a**, and **1b** with **2b** in benzene at 60 °C

	Monomer Feed			Solv.	Yield	Conv.	Copolymer Compn				$M_n^a$ /10 <sup>4</sup>
	<b>1a-b</b> mg	<b>2a-b</b> mg	<b>1a-b</b> mol%				mL	mg	%	%H	
<b>1a</b>	156.3	<b>2a</b> 162.4	50.0	2.0	210.2	66.0	4.51	72.35	8.88	50.6	23
<b>1a</b>	183.8	<b>2b</b> 259.3	50.0	2.0	185.6	41.9	4.47	66.78	7.50	50.4	11
<b>1b</b>	178.4	<b>2a</b> 168.1	48.3	0.4	223.1	64.4	5.34	73.13	8.51	52.8	8
<b>1b</b>	176.9	<b>2b</b> 221.8	48.7	0.4	258.0	64.7	5.22	68.04	7.05	50.8	60

a) Measured by GPC using THF as an eluent and polystyrenes as standards.

Figure 1. IR spectrum of poly(**1a-co-2a**) (film)

copolymer of **1a** and **2a** (poly(**1a-co-2a**)) were shown in Figures 1, 2a, and 3, respectively. The IR spectrum shows absorption peaks at 2234 cm<sup>-1</sup> due to stretching vibration of the nitrile group and at 1726 and 1220 cm<sup>-1</sup> due to stretching vibration of the ester group, indicating that the copolymer contains both the **1a** and the **2a** units. In the <sup>1</sup>H NMR spectrum, each peak is assignable to the respective protons of the chemical structure illustrated therein. The methylene protons of the **2a** units of the copolymer appear in the 3.80 and 3.15 ppm regions, indicating that they are much more subject to deshielding than the corresponding ones of a homopolymer of **2a**, appearing at around 1.5 ppm region (20). Presumably, the deshielding arises from an electron withdrawal by the neighboring oxygen atom and dicyanomethylene group when the **2a** unit is sandwiched between **1a** units in the copolymer. And also, each peak in the spectra is very sharp, suggesting that all monomer units are arranged in only head-to-tail placement. In the <sup>13</sup>C NMR spectrum, each peak is assignable to the respective carbons of the chemical structure illustrated therein. The quaternary carbon (f) of **2a** unit of the copolymer were observed as two peaks at 103.63 ppm and 103.68 ppm, due to asymmetric carbon. It is concluded, therefore, that **1a** copolymerizes with **2a** in a perfectly alternating fashion, and it reacts at the exocyclic oxygen and carbon sites. The spectral features observed for poly(**1a-co-2a**) were also found in the copolymers of **1a** with **2b** (poly(**1a-co-2b**)), of **1b** with **2a** (poly(**1b-co-2a**)), and of **1b** with **2b** (poly(**1b-co-2b**)). It is, therefore, concluded that poly(**1a-co-2b**), poly(**1b-co-2a**), and poly(**1b-co-2b**) are also alternating copolymers.

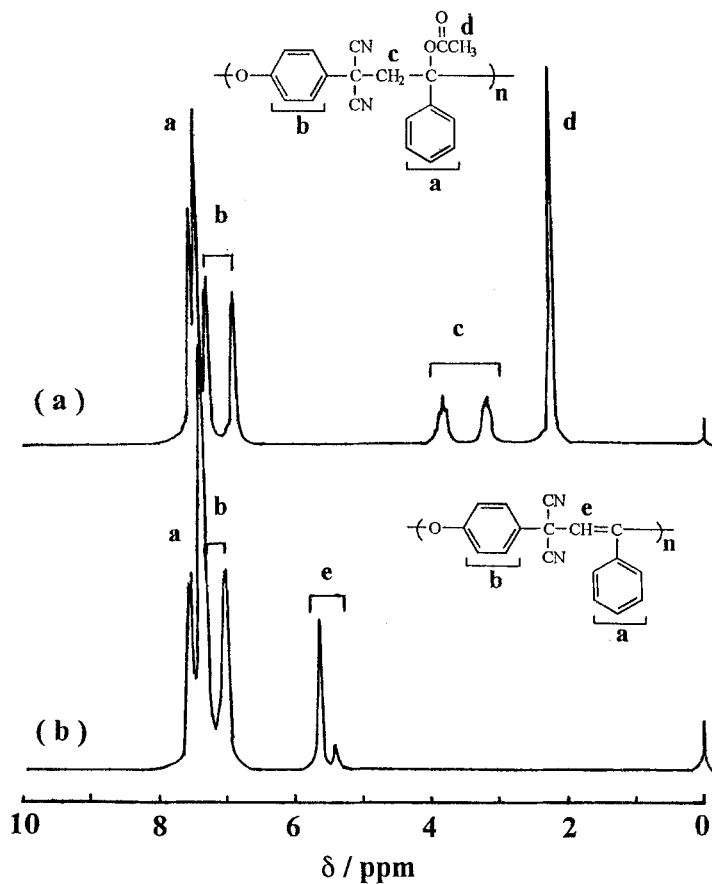


Figure 2.  $^1\text{H}$  NMR spectra of (a) poly(1a-co-2a) and (b) poly(3a) in chloroform- $d$ .

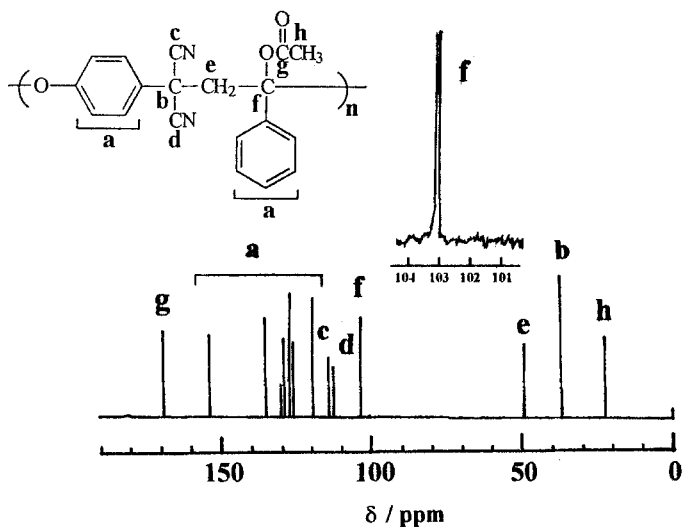


Figure 3.  $^{13}\text{C}$  NMR spectrum of poly(1a-co-2a) in chloroform- $d$ .

### Properties of polymers

The poly(**1a-co-2a**), poly(**1a-co-2b**), poly(**1b-co-2a**), and poly(**1b-co-2b**) are soluble in chloroform, dichloromethane, acetone, and benzene, but insoluble in methanol, ethanol, diethyl ether, and hexane, and they are capable of being cast from chloroform solutions to give tough films, which have excellent transparency. UV-vis spectra of these copolymers measured in THF at room temperature show no absorption bands in the 300-800 nm range. The refractive index values ( $n_D$ ) of poly(**1a-co-2a**), poly(**1a-co-2b**), poly(**1b-co-2a**), and poly(**1b-co-2b**) were measured to be 1.554, 1.554, 1.553, and 1.554, respectively, which are larger than that of a homopolymer of **2a** ( $n_D = 1.516-1.537$ ) prepared under same polymerization condition and poly(methyl methacrylate) ( $n_D = 1.4893$ )(21).

The TG measurement was performed to investigate the thermal stability of the copolymers. As the typical example, Figure 4a shows a TG curve for the poly(**1a-co-2a**), where weight loss took place in two steps, beginning at about 150 °C ( $T_{d1}$ ) and 320 °C ( $T_{d2}$ ). The weight loss from 150 to 300 °C amounted to 18 %, which approximately corresponds to the weight percent of the acetic acid (18.9 %). The IR spectrum of the product obtained at 200 °C shows no absorption bands at 1726 and 1220  $\text{cm}^{-1}$  due to the ester group and instead an absorption band at 1609  $\text{cm}^{-1}$  due to the stretching vibration of carbon-carbon double bond. The  $^1\text{H}$  NMR spectrum of

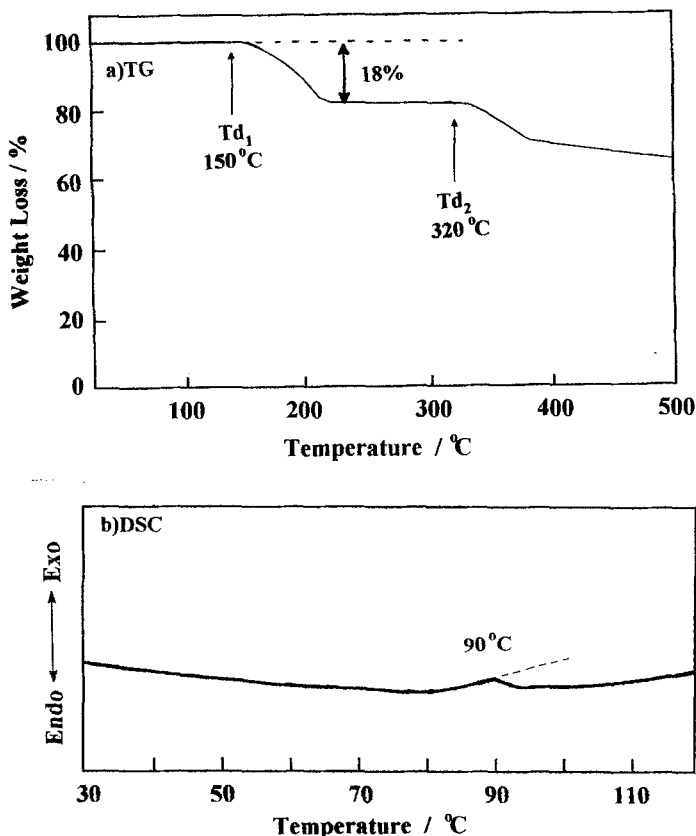
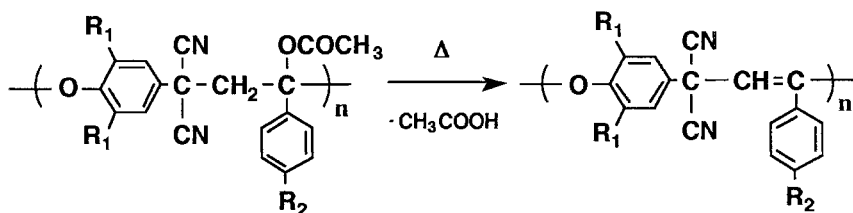


Figure 4. TG (a) and DSC (b) curves of the poly(**1a-co-2a**).

the product obtained at 200 °C is shown in Figure 2b, where the peaks at 3.80 and 3.15 ppm due to the methylene protons and at 2.0 ppm due to the methine proton observed for the poly(**1a-co-2a**) in Figure 2a disappear and instead the new two peaks appear at 5.63 and 5.42 ppm assignable to olefinic protons. Thus, the thermal degradation starting at 150 °C is ascribed to elimination of acetic acid. Moreover, the peaks at 5.63 ppm and at 5.42 ppm in Figure 2b are assignable to cis and trans configurations, respectively, because the chemical shift of a olefinic proton due to cis and trans configurations for a trisubstituted ethylene could be calculated according to the method reported by Pasucual *et al.* (22) to be 5.63 and 5.56 ppm, respectively, and also the ratio of cis to trans was estimated to be 9 to 1 on the basis of their peak area. Similar degradation profile was also observed for poly(**1a-co-2b**), poly(**1b-co-2a**), and poly(**1b-co-2b**). Therefore, all alternating copolymers eliminate acetic acid quantitatively at around 200 °C to give the copolymers with olefinic bond (poly(**3a-d**)) (Scheme). DSC measurement was performed to determine the glass transition temperature ( $T_g$ ) of the copolymers. As the typical example, Figure 4a shows a DSC curve for poly(**1a-co-2a**), where  $T_g$  was found to be 90 °C. Table 2 summarized the values of  $T_g$ ,  $T_{d1}$ , and  $T_{d2}$  for all copolymers. The  $T_g$  values of poly(**1a-co-2a**), poly(**1a-co-2b**), poly(**1b-co-2a**), and poly(**1b-co-2b**) and poly(**3a-d**) are around 90-99 °C, which are lower than that of poly(VDC-co-VAc) ( $T_g = 150$  °C) (23).

The X-ray diffraction pattern of the transparent, tough poly(**1a-co-2a**) and poly(**3a**) films exhibited no peaks, indicating that they are amorphous as well as poly(VDC-co-VAc)(7).

#### Scheme



poly(**1a-co-2a**)  $R_1=R_2=H$   
 poly(**1a-co-2b**)  $R_1=H, R_2=OAc$   
 poly(**1b-co-2a**)  $R_1=Me, R_2=H$   
 poly(**1b-co-2b**)  $R_1=Me, R_2=OAc$

poly(**3a**)  $R_1=R_2=H$   
 poly(**3b**)  $R_1=H, R_2=OAc$   
 poly(**3c**)  $R_1=Me, R_2=H$   
 poly(**3d**)  $R_1=Me, R_2=OAc$

Table 2 Glass transition temperatures ( $T_g$ ) and thermal degradation temperatures ( $T_d$ ) of the polymers

Polymers	$T_g / ^\circ C$	$T_{d1} / ^\circ C$	$T_{d2} / ^\circ C$
poly( <b>1a-co-2a</b> )	90	150	320
poly( <b>1a-co-2b</b> )	94	145	300
poly( <b>1b-co-2a</b> )	92	120	300
poly( <b>1b-co-2b</b> )	96	90	300
poly( <b>3a</b> )	99	320	
poly( <b>3b</b> )	92	300	
poly( <b>3c</b> )	96	300	
poly( <b>3d</b> )	99	300	

The dielectric constant values ( $\epsilon$ ) at room temperature for the poly(**1a-co-2a**), poly(**1a-co-2b**), and poly(**3a**) films were determined to be 2.71, 2.47, and 2.80, respectively, which are close to that for polystyrene ( $\epsilon = 2.40\text{--}2.65$ )(24). However, after applying an electric field of 33 V/m at 100 °C for 1 h, the  $\epsilon$  values were to be 2.46 for poly(**1a-co-2a**), 2.47 for poly(**1a-co-2b**), and 2.80 for poly(**3a**), respectively. On the other hand, it is reported that the  $\epsilon$  value of a poly(VDC-co-VAc) film increase from 5.6 to 120 on poling treatment (9). No change in the  $\epsilon$  values for the poly(**1a-co-2a**), poly(**1a-co-2b**), and poly(**3a**) films before and after poling indicates that orientation of dipoles in these polymer films is considerably difficult compared with the poly(VDC-co-VAc) film. Their piezoelectric behavior has not been measured yet.

### Acknowledgment

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### References

- Hall HK Jr (1988) *J Macromol Chem* A25: 729
- Wang TT, Herbert JM, Glass AM Ed (1988) *The Application of Ferroelectric Polymers* Blackie & Son Glasgow
- Kawai H (1969) *Jpn J Appl Phys* 8: 975
- Uchidoi M, Iwamoto T, Iwata K, Tamurs M (1979) *Rep Prog Polym Phys Jpn* 22: 345
- Furukawa T, Johnson GE, Bair HE, Tajitsu Y, Chiba A, Fukada E (1981) *Ferroelectric* 32: 61
- Koga K, Nakano N, Hattori T, Ohigashi H (1990) *J Appl Phys* 67: 965
- Miyata S, Yoshikawa M, Tasaka S, Ko M (1980) *Polym J* 12: 875
- Miyata S, Yoshikawa M, Tasaka S, Ko M (1984) *Ferroelectric* 57: 267
- Tasaka S, Inagaki N, Okutani T, Miyata S (1989) *Polymer* 30: 1639
- Jo YS, Inoue Y, Chujo R, Saito K, Miyata S (1985) *Macromolecules* 18: 1850
- Hall HK Jr, Chan RJH, Oku J, Hughes OR, Chelnbelm J, Newman B (1987) *Polym Bull* 17: 135
- Padias AB, Hall HK Jr (1990) *Polym Bull* 24: 195
- Lee JY, Padias AB, Hall HK Jr (1991) *Macromolecules* 24: 17
- Lee JY, Cho SO, Padias AB, Hall HK Jr (1991) *Polym Bull* 27: 25
- Iwatsuki S, Itoh T, Ishiguro K (1987) *Macromolecules* 20: 939
- Chem Soc of Jpn Ed (1990) *Jyiken Kagaku Koza* 4th ed vol 1 Maruzen Tokyo: 91-104
- Hyatt JA (1983) *J Org Chem* 48: 129
- Delgado M, Wolf RE Jr, Hartman JAR, McCafferty G, Yagbasan R, Rawle SC, Watkin DJ, Cooper SR (1992) *J Am Chem Soc* 114: 8983
- Noyce DS, Pollack RM (1969) *J Am Chem Soc* 91: 119
- Montheard JP, Camps M, Belfkira A, Steffan G, Lucas JM, (1984) *Polym Comm.* 25: 337
- Broussoux D, Chastaing E, Esselin S, Lebarney P, Robin P, Bourbin Y, Pocholle JP, Raffy J (1989) *Revue Technique THOMSON-CSF* 20/21: 1
- Pascual C, Meier J, Simon W (1966) *Helv Chem Acta* 49: 164
- Ohigashi H (1985) *Jpn J Appl Phys* 24: 23
- Budavari S Ed (1989) *The Merck Index* 11th ed Merck & Co Inc Rahway: 8833