Structure and properties of amorphous piezoelectric vinylidene cyanide copolymers

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Dielectric properties, X-ray diffraction and differential scanning calorimetry were investigated up to the glass transition temperature (T_g) for six kinds of vinylidene cyanide copolymers with vinyl acetate, vinyl isopropionate, vinyl benzoate, vinyl pivarate, isobutene and methyl methacrylate. The copolymers with vinyl ester comonomers showed a large dielectric relaxation strength of ~ 100 and strong enthalpy relaxation around T_g, and revealed a sharp X-ray diffraction of spacing 10–13 Å below T_g. A paracrystalline or mesophase glass structure is proposed for the copolymer glass to allow cooperative motion over at least several monomers.

INTRODUCTION

Since high piezoelectric activity was observed in poled amorphous poly(vinylidene cyanide–vinyl acetate), P(VDCN–VAc)[1,2], such amorphous polymers have been attracting much attention as a new type of piezoelectric material. This copolymer has special features[1-4], as follows: (1) perfect alternating copolymer; (2) amorphous polymer with high glass transition temperature; (3) strong piezoelectric activity; (4) high dielectric relaxation strength; and (5) large enthalpy relaxation. According to the results of n.m.r. in P(VDCN–VAc)[5-7], a combination of several factors involving microstructure and conformation may be responsible for the piezoelectricity, which should be due to the residual polarization based on the orientation of C–CN dipoles. The anomalously large dielectric relaxation strength (~ 100), which was reported by Furukawa et al.[4,8], may be attributable to cooperative motion of several C–CN dipoles. Such a large dielectric relaxation strength in the glass transition region allows a sample to form a large remanent polarization, inducing piezoelectricity. Further, Wang et al.[9] suggested the possibility of amorphous ferroelectrics in P(VDCN–VAc) from linear and non-linear dielectric behaviour.

As regards chemical structure, VDCN monomers with a large dipole moment have a tendency to alternate during copolymerization with electron-accepting comonomers. Therefore, we considered that the alternation of polar symmetric monomer and non-polar asymmetric comonomer, like P(VDCN–VAC), may have a fundamental significance to amorphous structure and piezoelectric properties. Actually, some new copolymers of VDCN and bulky vinyl esters gave good piezoelectric properties.

In this paper, we report the relationship between the physical properties and amorphous structure of VDCN copolymers on the basis of detailed structural information obtained by X-ray diffraction.

EXPERIMENTAL

Powdered samples of VDCN copolymers with vinyl acetate (VAc), vinyl isopropionate (VPr), vinyl benzoate (VBz) and vinyl pivarate (VPiv) were generously supplied by Mitsubishi Petrochem Co. Ltd. The copolymers with isobutene (IB) and methyl methacrylate (MMA) were synthesized by normal radical polymerization. All the polymers were confirmed as alternating copolymers by elemental analysis and n.m.r. The chemical structure of these copolymers is shown in Figure 1. All samples were dissolved in dimethylacetamide (DMA), and then cast at 120°C to get a firm sample. Drawn samples were obtained by uniaxial drawing at a temperature 20°C below T_g. Poling was carried out under a d.c. electric field of 30 MV m^{-1} at a temperature 10°C below T_g. Annealing to induce an enthalpy relaxation was carried out in vacuum below T_g. The thermal behaviour at T_g was investigated by differential scanning calorimetry (d.s.c.) (Rigaku TG-DSC). Dielectric and piezoelectric measurements were carried out using the equipment developed by Furukawa et al.[10]. X-ray diffraction was obtained with a diffractometer (Rigaku FG-9) with nickel-filtered Cu Kα radiation. Density was measured pycnometrically at 25°C by a floating method using a mixture of toluene and carbon tetrachloride.

RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of dielectric constant of the VDCN copolymers at 10 Hz. The

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copolymers without α-methyl groups (VAc, VBz, VPr, VPiv) have a large apparent dielectric relaxation strength of more than 80, which is related to the cooperative motion of large segments as suggested by Furukawa *et*
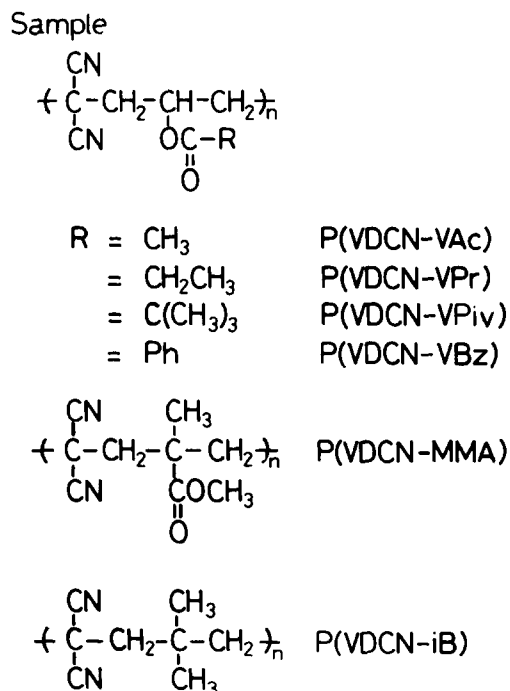

Sample

R = CH₃   P(VDCN-VAc)
  = CH₂CH₃   P(VDCN-VPr)
  = C(CH₃)₃   P(VDCN-VPiv)
  = Ph   P(VDCN-VBz)

P(VDCN-MMA)

P(VDCN-iB)

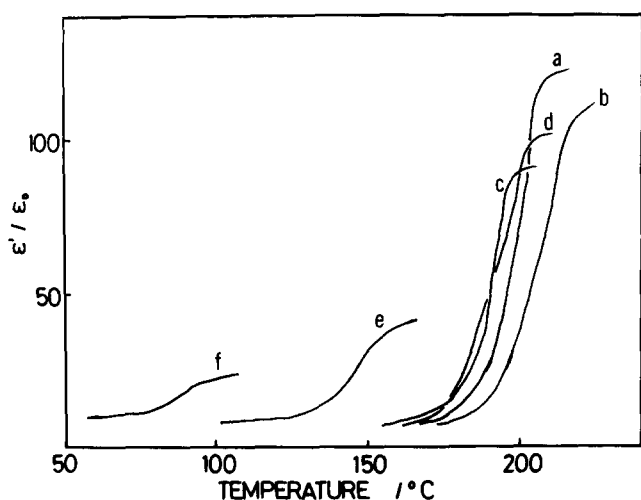**Figure 1** Chemical structure of vinylidene cyanide copolymers

Figure 2 Temperature dependence of dielectric constant for VDCN polymers at 10 Hz: (a) P(VDCN–VAc); (b) P(VDCN–VBz); (c) P(VDCN–VPr); (d) P(VDCN–VPiv); (e) P(VDCN–MMA); (f) P(VDCN–IB)

al.[4]. On the other hand, copolymers with α-methyl groups have a smaller dielectric relaxation strength.

The physical properties of the VDCN copolymers are listed in *Table 1*. The samples that possess higher glass transition temperatures show larger piezoelectric constants and large dielectric relaxation strength, leading to large residual polarization (P_r).

Figure 3 shows d.s.c. curves of the copolymers annealed at a temperature 10°C below T_g. We have already reported a large energy absorption during isothermal annealing in P(VDCN–VAc)[3]. A large enthalpy relaxation was also observed in VDCN copolymers with vinyl esters, except P(VDCN–MMA) and P(VDCN–IB), corresponding to high electric and piezoelectric activities. Net energy absorption (Q_t) was obtained from peak integration of the d.s.c. curves: the $5.3\,\mathrm{cal\,g^{-1}}$ for P(VDCN–VPiv) is one of the largest values ever obtained. When the samples are quenched from a temperature above T_g to room temperature, the d.s.c. trace around T_g becomes a simple step like that of normal glassy polymers. The loss of the excess enthalpy is characteristic of the non-equilibrium nature of the glassy state relaxing to the equilibrium state. The relaxation involves not only densification in the liquid-like packing but also a change in conformational energy. As shown in *Table 2*, however, the densification is less than 0.7% upon annealing. Especially, the density of P(VDCN–VPiv) with bulky side-chains does not increase in spite of the increase in net energy absorption. Therefore, we should mainly consider the effect of small conformational changes upon annealing. On increasing the annealing period, of course, the molecules with compact packing are probably arranged with a conformational change, so that the mobility of dipoles may be suppressed by reducing the free volume. Therefore, piezoelectricity and its thermal stability relating to macroscopic dipole rotation are influenced by annealing[3]. However, dielectric relaxation strength is little affected by thermal history. Consequently, the dielectric properties of these copolymers may essentially be intramolecular in nature, including a mesophase cooperative interaction between dipoles. The effect of annealing on physical properties may be due to intermolecular interaction.

Figure 4 shows X-ray diffraction patterns for non-stretched and annealed copolymers. All the samples show two broad peaks around 15° and 30°, as reported previously in P(VDCN–VAc)[11,12]. However, only the copolymers with vinyl esters give a peak at lower diffraction angle, which corresponds to the dimension of the side-chain. The diffraction patterns of non-annealed or as-drawn copolymers with vinyl esters have a small peak at lower angle (lower than $2\theta \sim 10°$). The peak

Table 1 Physical properties of VDCN polymers[a]

	T_g (°C)	$\varepsilon(20°C)$	$\Delta\varepsilon$	d_{31} (pC N⁻¹)	e_{31} (mC m⁻²)	P_3 (μC K⁻¹ m⁻²)	P_r (mC m⁻²)
P(VDCN–VAc)	178	5.6	120	7.0	14.5	10	35
P(VDCN–VBz)	184	5.6	115	5.2	8.6	10	21
P(VDCN–VPr)	176	5.8	85	9.8	16.6	30	28
P(VDCN–VPiv)	172	5.8	100	7.0	14.0	12	33
P(VDCN–MMA)	146	5.4	30	2.2	5.4	7	12
P(VDCN–IB)	75	5.0	16	1.0	1.8	3.5	6

[a] T_g from d.s.c.; and P_3 (pyroelectric constant) and P_r (residual polarization) from t.s.d.c. (thermally stimulated depolarizing current)
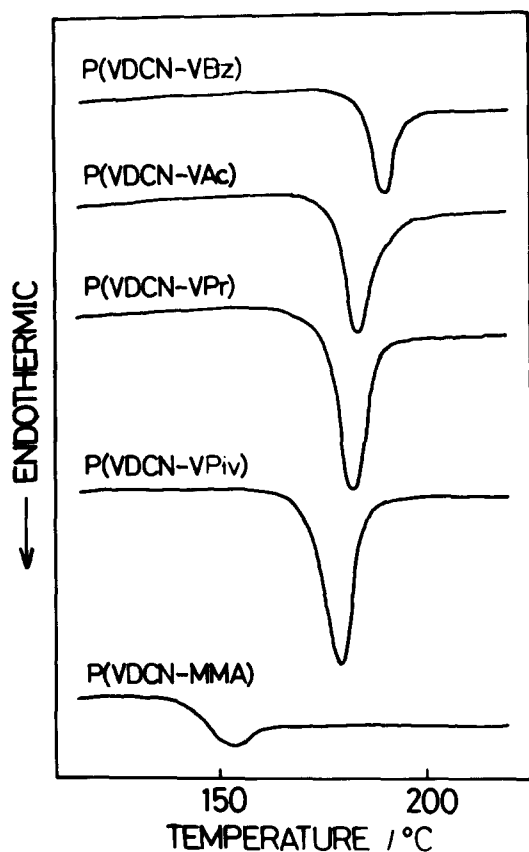
Figure 3 D.s.c. curves for VDCN polymers annealed for 8 h at $T_g - 10°C$. Net energy absorptions Q_t (cal g^{-1}) are: 1.5, P(VDCN–VBz); 1.8, P(VDCN–VAc); 3.2, P(VDCN–VPr); 5.3, P(VDCN–VPiv); and 0.5, P(VDCN–MMA)

Table 2 Density changes by annealing for VDCN copolymers[a,b]

		Density (g cm^{-3})	T_g (°C)	Q_t (cal g^{-1})
P(VDCN–VAc)	Quenched	1.215	168	–
	Annealed	1.222	180	1.8
P(VDCN–VPiv)	Quenched	1.131	154	–
	Annealed	1.133	173	5.3

[a] T_g: apparent value from d.s.c.
[b] Annealing conditions: P(VDCN–VAc), 160°C, 8 h; P(VDCN–VPiv), 145°C, 8 h

appears to increase after annealing. In particular, P(VDCN–VPiv) gave a strong peak. The fibre of stretched and annealed P(VDCN–VPiv), with a draw ratio of 3, shows diffraction as in *Figure 5*. As indicated in the photograph, the sample seems not to be completely amorphous. In the innermost halo the equatorial arcs are extremely sharp, like in a crystal, indicating that the sample is highly oriented. However, the second and third haloes are still wide and diffuse, as in typical amorphous materials. The haloes are not those of a highly oriented sample. Further, the absence of a meridional diffraction spot indicates disorder along the molecular chain axis, which is similar to polyacrylonitrile[13]. This behaviour may be due to the alternation of symmetrical VDCN and atactic vinyl esters along the chain.

Figure 6 shows the temperature dependence of the X-ray diffraction pattern for annealed P(VDCN–VPiv). The lower-angle diffraction peak around 10° disappears above the glass transition temperature. With decreasing

temperature, the diffraction peak appears again. The change was reversible. If this diffraction peak is due to a crystal formed on annealing below T_g, the crystal would be required to melt at T_g. Further, the transition, which was assumed as T_g, behaved like a second-order transition. According to the analysis of common enthalpy relaxation, the relaxation time for P(VDCN–VPiv) will be much shorter than that of glassy polymers. Therefore, we propose that these polymers with a large dipole
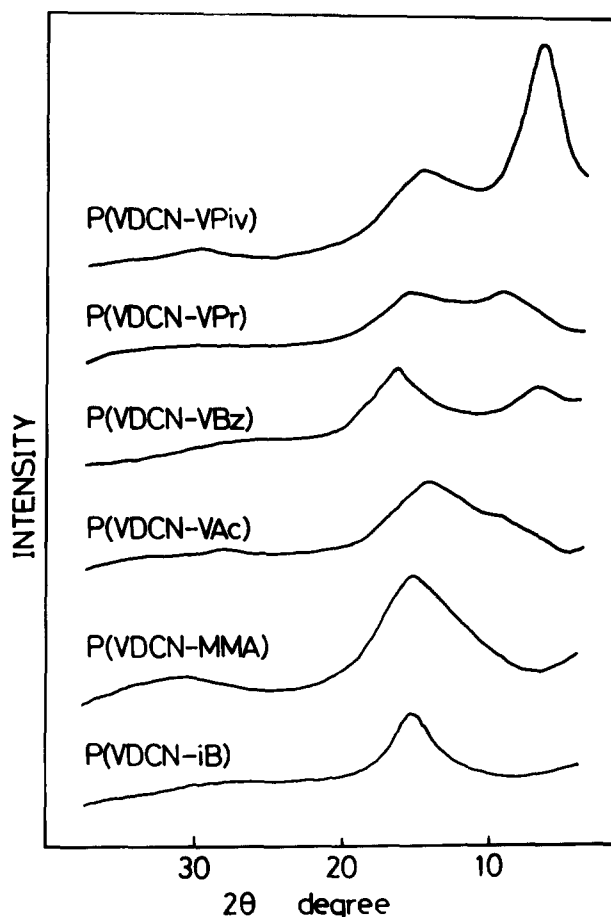

Figure 4 X-ray diffraction pattern of VDCN polymers annealed at $T_g - 10°C$ for 2 h
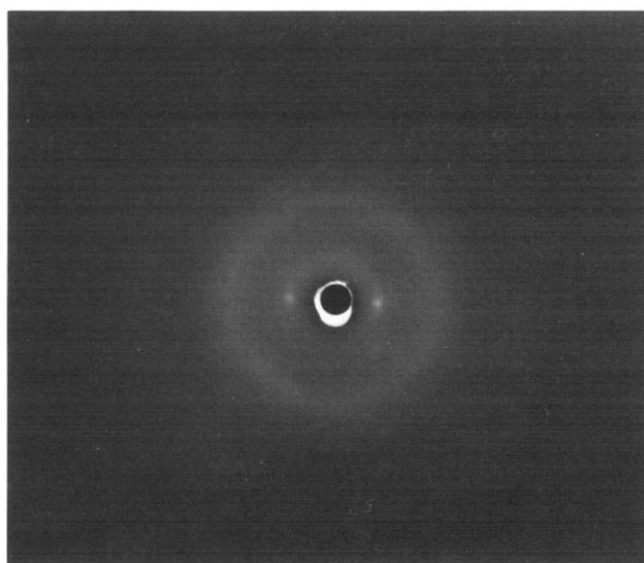

Figure 5 X-ray diffraction photograph of P(VDCN–VPiv) stretched and annealed at 155°C
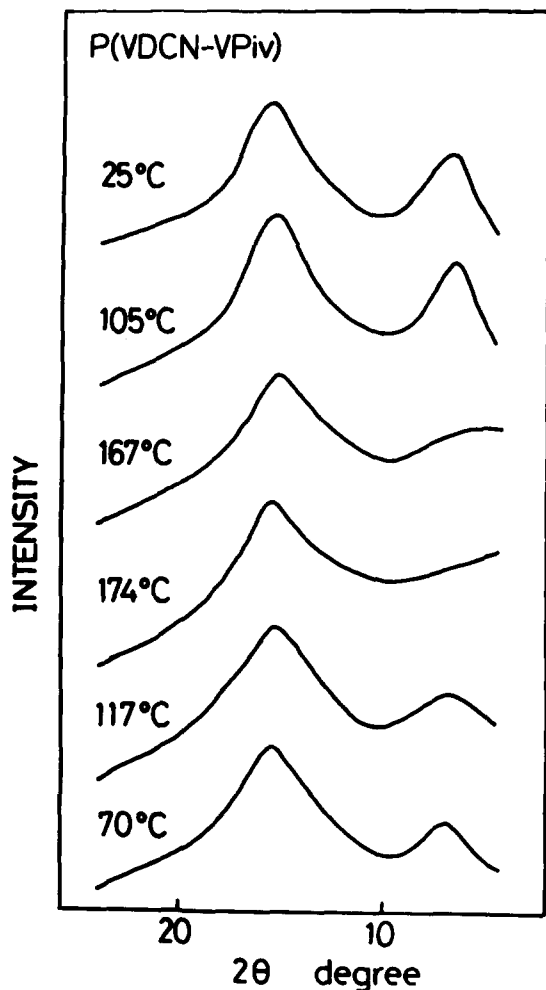
Figure 6 Temperature dependence of X-ray diffraction patterns for P(VDCN-VPiv) annealed for 2 h at 155°C

moment, rigid chain and bulky side-chains may form a kind of mesophase[14]. In such a mesophase, cooperative motion will be permitted between intermolecular segments. Consequently, the X-ray behaviour may be explained by the existence of a mesophase glass or a paracrystal, which is related to some interaction between chains of a copolymer. This interaction may play a role in the stabilization of the polarization formed by the poling process. Therefore, the piezoelectric activity of these polymers may be markedly stable below T_g.

We carried out observations with a polarizing microscope to elucidate an optical domain texture like in a liquid crystal. However, we were not able to observe such a texture. The size of ordered structure may be less than 1 μm.

It was assumed that the diffraction at low angle was due to hexagonal packing of rigid cylindrical chains, as reported in liquid-crystalline polyesters[14] or poly(di-

isopropyl fumarate)[15]. The apparent lattice constant calculated from the diffraction angle, for example, is $a = 15.2$ Å for P(VDCN-VPiv), which suggests that there are three chains in the hexagonal unit lattice from the results of density $(1.13\,\mathrm{g\,cm^{-3}})$ and *trans*-rich conformation[7] $(c \simeq 4.6\,\text{Å})$. Consequently, these VDCN copolymers probably have a special layered packing and a lateral interaction to give the resulting micro-order.

CONCLUSIONS

Several VDCN copolymers with vinyl esters were good piezoelectric materials, and gave significant enthalpy relaxations and special X-ray diffraction after annealing, Owing to non-stereoregularity of vinyl esters, these copolymers have been considered to be amorphous. However, the large dipole interaction of the cyanide group makes aggregation between chain molecules possible and the weak micro-ordering is destroyed by micro-Brownian motion above T_g. This ordering may be useful to stabilize the remanent polarization by poling. However, the origin of dielectric and piezoelectric polarization may be attributed to the intramolecular interaction of these polymers, concerning a mesophase cooperative motion around T_g.

ACKNOWLEDGEMENTS

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