

# Anomaly in dielectric relaxation in alternating copolymers of vinylidene cyanide and fatty acid vinyl ester

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Dielectric relaxation spectra at 10 Hz to 1 MHz for five vinylidene cyanide–vinyl ester copolymers were studied as functions of temperature and length of aliphatic side-chain in the comonomer unit. Three unusual phenomena in their dielectric behaviours were found: (1) extremely large dielectric relaxation strength; (2) dielectric transition phenomena whose strength changed suddenly at a critical temperature; and (3) unusual temperature dependence of the strength above the transition temperature. The dielectric transition temperature depends upon length of the side-chain and corresponds well with enthalpy peak temperature in the differential scanning calorimetry study. It was also found that the thermal history strongly affects the dielectric behaviours.

(Keywords: vinylidene cyanide copolymer; dielectric relaxation; dielectric anomaly; transition phenomena)

## INTRODUCTION

An alternating copolymer of vinylidene cyanide and vinyl acetate, P(VDCN/VAc), which is a non-crystalline polar polymer with large dipoles on its skeleton, has been reported to show several unusual dielectric behaviours. High piezoelectric activity has been found in its poled films<sup>1,2</sup>. However, no satisfactory explanation for the origin of large remanent dipoles in a non-crystalline polymer has yet been given. Furukawa and coworkers<sup>3</sup> showed that P(VDCN/VAc) copolymer exhibited unusually large relaxation strength above its  $T_g$ . Wang and Takase<sup>4</sup> pointed out the ferroelectric-like nature of this copolymer based on third-order dielectric susceptibility measurements.

Neither the large dielectric relaxation strength at high temperatures nor the large remanent polarization in poled films can be explained simply in terms of the large dipole moment of cyano groups, if one assumes a complete amorphous polymer structure and independent motion of cyano dipoles on polymer skeletons. Thus, the presence of some kind of order in the aggregated structure of P(VDCN/VAc) has been pointed out. Although X-ray diffraction analyses did not give any distinct sign of crystallinity, a large enthalpy relaxation<sup>5</sup> and a casting-solvent dependence of thermal behaviours<sup>6</sup> suggested the presence of order in P(VDCN/VAc) films.

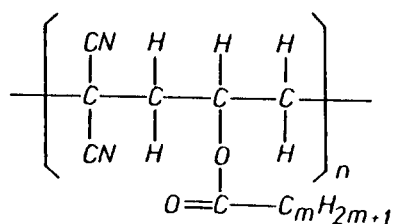
Vinylidene cyanide (VDCN) can easily be copolymerized with a variety of vinyl comonomers to form

alternating copolymers<sup>7</sup>. Dielectric behaviours of VDCN–vinyl ester copolymers have been investigated<sup>8,9</sup>. Some copolymers were found to exhibit unusually large dielectric constants and losses, very similar to the case of P(VDCN/VAc), but other copolymers showed ordinary dielectric behaviours like conventional non-crystalline polymers. These observations indicate that the interactions between the cyano groups and comonomer units may play important roles in the dielectric behaviours of VDCN copolymers. Then, one expects that detailed dielectric studies of VDCN–vinyl ester copolymers with different side-chain structures will contribute to a better understanding of the unusual dielectric behaviours in VDCN alternating copolymers.

In this paper, we studied the dielectric behaviours of five VDCN–fatty acid vinyl ester copolymers (*Figure 1*). The length of aliphatic chains in vinyl ester comonomers went from one (VAc) to eight (VOc). Frequency dispersions of complex permittivity (10 Hz–1 MHz) in the temperature range from room temperature to 250°C were examined. Anomalous jumps of dielectric constants within very narrow temperature regions, which corresponded well with the so-called  $T_g$  of P(VDCN/VAc), were clearly observed in the samples with longer side-chains, and above these anomalous transition temperatures another dielectric relaxation appeared. The temperatures of the anomalous transitions and the effect of thermal history on dielectric anomalies were dependent on the chain length of comonomers.

Besides the dielectric measurements, differential scanning calorimetric (d.s.c.) measurements were also carried out to help the understanding of the unusual transitions.

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m=	
1	P(VDCN/VAc)
2	P(VDCN/VPr)
3	P(VDCN/VBu)
5	P(VDCN/VHe)
7	P(VDCN/VOc)
13	P(VDCN/VMy)

Figure 1 Chemical structures of polymers used

## EXPERIMENTAL

Films about 10  $\mu\text{m}$  in thickness were prepared by casting from dimethylacetamide solutions. Cast films were immersed in methanol for about 48 h to eliminate residual dimethylacetamide and then dried at 125°C under vacuum for 24 h. Au electrodes were attached on both sides of films by vacuum evaporation. In order to avoid the influence of chemical degradation, all measurements were carried out under constant heating or cooling runs by using a Hewlett–Packard 4192A LF impedance analyser controlled by a computer. The rates of ascending or descending temperature were about 2°C min<sup>-1</sup>. Because the frequency dependence of dielectric constant and loss at each temperature was obtained within 15 s, pseudo-isothermal frequency dispersion curves were obtained.

D.s.c. measurements were carried out by using a Seiko I&E SSC/575 thermal analyser with an ascending temperature rate of 10°C min<sup>-1</sup>. About 10 mg of sample was used for each measurement.

## RESULTS AND DISCUSSION

### Temperature dependence of dielectric constant

Dielectric behaviours of the vinylidene cyanide copolymers were largely dependent on thermal histories of sample films. We will mainly show and discuss the dielectric data obtained for ascending temperatures for freshly prepared cast films, which had not sustained temperatures above 125°C before measurements (as-cast films), because the dielectric data for as-cast films gave the most typical and reproducible results. In the final section of this paper, we deal separately with the effects of thermal histories on dielectric properties.

Figure 2 shows the temperature dependence of the real part of dielectric constants at four different frequencies for five copolymers. Very sharp increase of dielectric constants was observed in each sample. The temperature ranges of the abrupt increase are within 5°C, except for the case of P(VDCN/VAc). The frequency dependence

of this dielectric anomaly was very small, giving a clear contrast to the case of well known dielectric relaxations in common polymers. Therefore, this dielectric anomaly can never be explained in terms of the usual dipole relaxations of polymer chains, and may be ascribed to some kind of thermodynamic transition. Thus, we tentatively call the temperatures at which the dielectric anomaly occurred 'transition temperatures'.

Below the transition temperatures, dielectric constants were low and almost independent of temperature, indicating that the movement of cyano dipoles is completely frozen. On the other hand, dielectric constants were very large, exceeding 90 in P(VDCN/VAc) and P(VDCN/VPr), above the transition temperatures. As was pointed out before, these large dielectric constants cannot be explained if one simply considers free rotation of independent cyano dipoles.

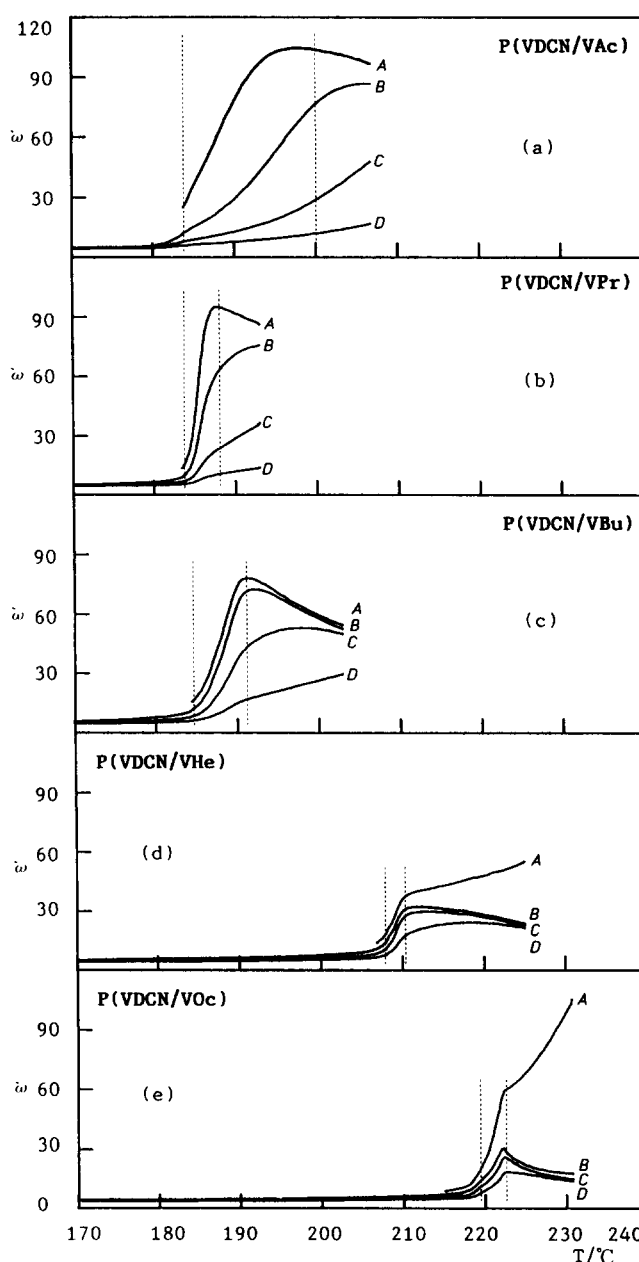


Figure 2 Temperature dependences of dielectric constants at four frequencies (A, 0.1 kHz; B, 1 kHz; C, 10 kHz; D, 100 kHz) for five copolymers

The copolymers with longer side-chains, P(VDCN/VHe) and P(VDCN/VOc), possessed higher transition temperatures. This tendency gives a clear contrast to the usual plasticizing effect of side-chains on dielectric relaxations; the longer the side-chains are, the more the temperature of relaxations move to lower temperature. The increase of local order in polymer chains with the aid of long aliphatic chains may play a major role in the transition.

#### Frequency dependences of dielectric constant and loss

Although the abrupt changes of dielectric constants could be clearly demonstrated by the temperature dependences of dielectric constants, frequency spectra at fixed temperatures are much more helpful for separating several overlapping phenomena in temperature spectra. Figures 3 and 4 show two examples of the frequency dependences of the real and imaginary parts of dielectric constants. At temperatures below the transition, dielectric losses were very small and the low-frequency parts were completely covered by large d.c. conduction due to impurity ions, which increased with the increase of temperature. Although the losses due to d.c. conduction increased with the increase of temperature, they did not interfere with our observations of dielectric phenomena due to dipoles at higher temperatures because of the marked difference of activation energies.

Below the transition temperatures, no dielectric absorption was observed, and dielectric constants were kept small. At around the transition temperatures, very large absorption peaks suddenly emerged except for the case

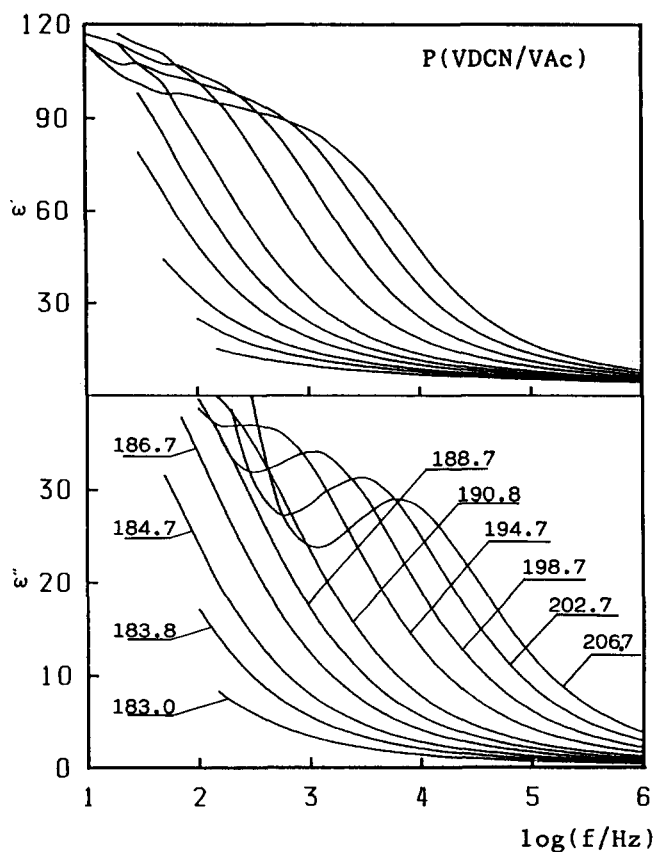


Figure 3 Frequency spectra of dielectric constant and loss for P(VDCN/VAc)

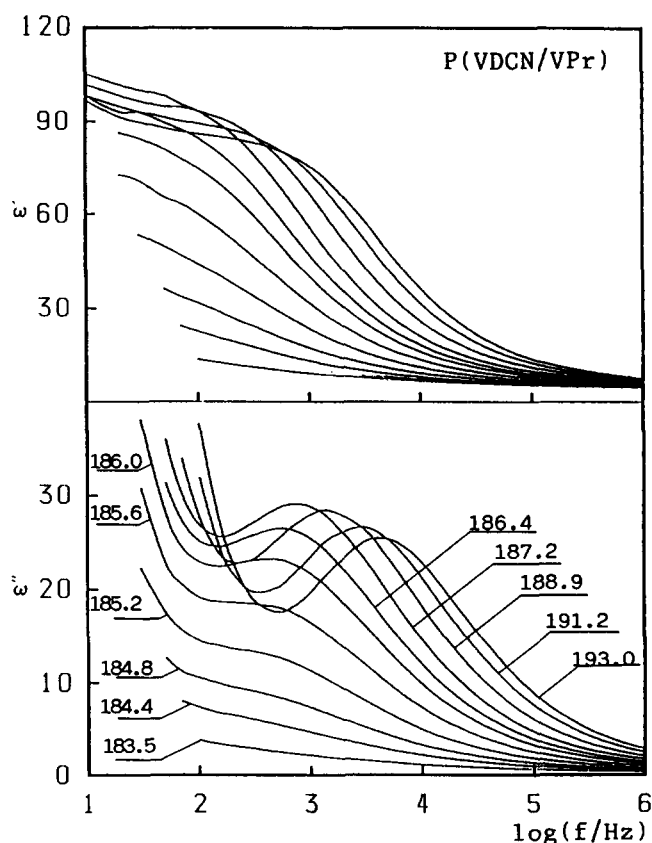


Figure 4 Frequency spectra of dielectric constant and loss for P(VDCN/VPr)

of P(VDCN/VAc) in which large d.c. conduction in the lower frequency region covered up the details of the appearance of a large absorption peak. For instance, as shown in Figure 4, the absorption intensity increased abruptly within a narrow temperature range (184–187°C). Above the transition temperatures, the absorption peaks shifted towards higher frequencies with increasing temperature and the magnitudes of the loss peaks decreased with increasing temperature. These behaviours are very similar to that of primary absorptions of common amorphous polymers.

From the observation of both temperature and frequency dependences of dielectric constants and losses, we succeeded in separating the unusually complicated dielectric behaviours of the copolymers into three well defined dielectric phenomena: d.c. conduction due to impurity ions; anomalous dielectric transitions (large change of absorption intensity within a narrow temperature range); and ordinary dielectric relaxations at higher temperatures.

#### Analysis of dielectric data

From the frequency spectra, the relaxation strength  $\Delta\epsilon$  at high temperature was determined by using Cole-Cole plots. On the low-temperature region, it is difficult to determine  $\Delta\epsilon$  from Cole-Cole plots because of the influence of d.c. conduction. Figure 5 shows the relation between the relaxation strength and temperature. Each curve has a sharp jump at around the transition temperature, except for the case of P(VDCN/VAc). The relaxation strength took maxima and gradually decreased with increasing temperature. The peak temperatures were

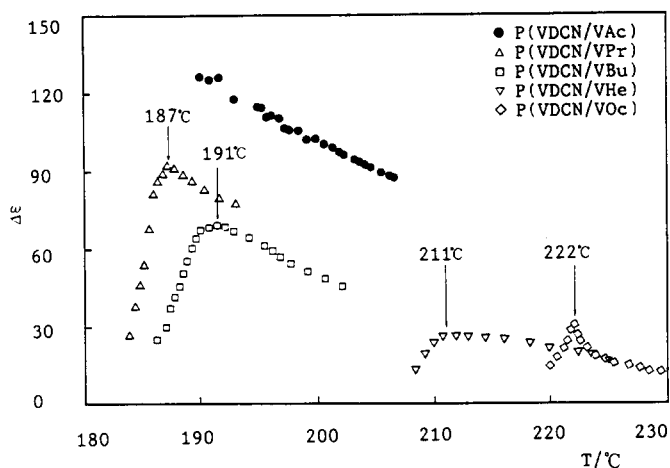


Figure 5 Temperature dependence of dielectric relaxation strength

187, 191, 211 and 222°C for P(VDCN/VPr), P(VDCN/VBu), P(VDCN/VHe) and P(VDCN/VOc), respectively. As shown later, they corresponded well to the temperatures of endothermic peaks in d.s.c. measurements. On P(VDCN/VAc), we failed to find a maximum of relaxation strength in our plotted temperature region.

Our  $\Delta\epsilon$  values of P(VDCN/VAc) went from 120 to 90 between 190 and 205°C. These values corresponded well with reported values<sup>3</sup> which were obtained through a curve-fitting procedure on dielectric data in the frequency range  $10^{-2}$  to  $10^4$  Hz. Extremely large relaxation strength above the transition temperatures implies the presence of cooperative motion of cyano dipoles even at temperatures above the transitions. The relaxation strength decreased with the increase of the length of side-chains. Because the density of cyano dipoles decreases with the increase of the chain length, that part of the decrease of  $\Delta\epsilon$  due to the increase of side-chain length should be reduced to a trivial density effect. However, one-quarter of the decrease of  $\Delta\epsilon$  from P(VDCN/VAc) to P(VDCN/VOc) cannot be accounted for fully with this correction. Undoubtedly, a more quantitative consideration including units of cooperative motion and modes of motion of cyano dipoles should be performed.

According to the theory of dielectric liquids, the relaxation strength of dipoles is inversely proportional to temperature. As shown in Figure 5, the relaxation strengths above the transition temperatures decrease with increasing temperature. The temperature dependences, however, are steeper than that expected from the inverse proportionality to temperature. This observation may indicate that the extent of cooperativity is dependent on temperature. In other words, the cooperative interaction decreases with the increase of temperature.

Figure 6 shows  $\log(f_{\max})$  vs.  $T^{-1}$  plots for the high-temperature relaxation peaks for five copolymers, where  $f_{\max}$  is the frequency at which  $\epsilon''$  becomes maximum. In each curve, except for that of P(VDCN/VAc), the transition temperature is indicated by an arrow. Below that temperature, accurate peak frequency was difficult to determine due to rapid freezing-in of molecular motions.

Owing to the limited accuracy of these curves, we did not dare to fit the curves to a WLF-type equation. Instead, we roughly estimated activation energies using the data points above the transition temperature. The activation energy ranged between 80 and 120 kcal mol<sup>-1</sup>.

This value meant that the relaxations with which we are dealing should be ascribed to primary relaxations due to micro-Brownian segmental motions of polymer chains.

The relaxation peak moved to lower temperature or higher frequency with increase of side-chain length in P(VDCN/VAc), P(VDCN/VPr) and P(VDCN/VBu). This tendency is reminiscent of the well known side-chain length effect on primary relaxations in amorphous polymers with long side-chains, such as polyacrylates, polymethacrylates and poly(vinyl ethers). The plots of P(VDCN/He) and P(VDCN/VOc) fall on the extrapolated line of P(VDCN/VBu). Coincidence of the three curves might mean the saturation of side-chain effect. The chain length effect on the high-temperature relaxations gave clear contrast to that on the anomalous transition temperatures. Thus, we can conclude that molecular origins and mechanisms of the high-temperature relaxations and the dielectric anomalous transitions were quite different.

#### Comparison with thermal behaviour

Examination of thermal behaviours of the copolymers helps our understanding of the transition phenomena observed in dielectric measurements. Figure 7 shows the d.s.c thermograms of six copolymers (a new copolymer with longer side-chain was added). Each sample gave an endothermic peak. The observed peaks undoubtedly do not originate from a glass transition phenomenon, and should rather be classified as 'enthalpy relaxations' reported for several VDCN copolymers<sup>5,8</sup>.

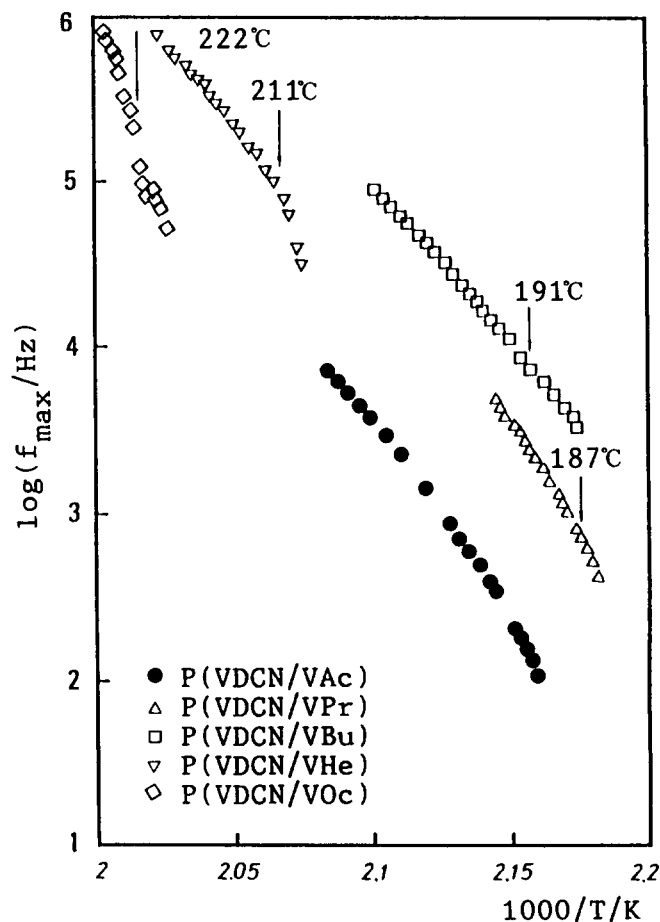


Figure 6 Temperature dependences of the relaxation frequency above the transition temperature

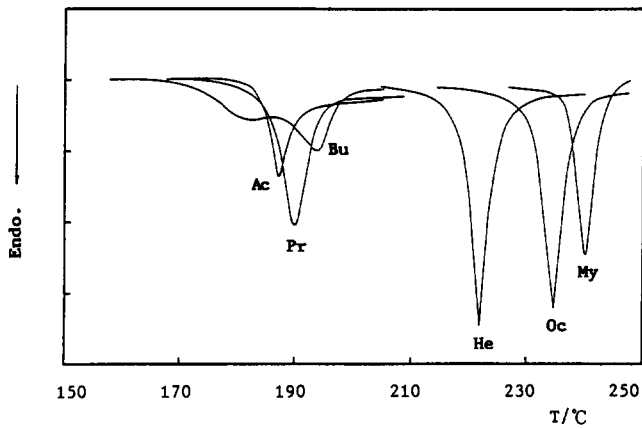


Figure 7 D.s.c. thermograms for six copolymers

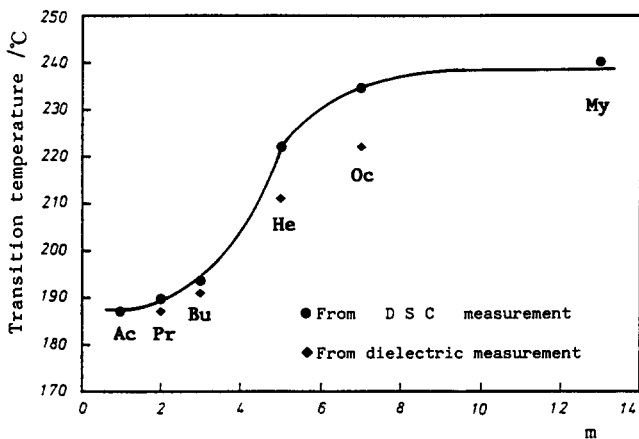


Figure 8 Side-chain length dependence of transition temperatures obtained by d.s.c. and dielectric measurements

Figure 8 shows the side-chain length dependence of the endothermic peak temperatures. The peak temperature increased with increasing side-chain length, and levelled off when the side-chain is sufficiently long. The transition temperatures determined from dielectric measurements corresponded well with the endothermic peaks. This implies that the dielectric anomalous transitions had the same origin as the endothermic peaks. Thus, we reach the viewpoint that the observed dielectric transitions belong to a kind of thermodynamic transition accompanied by order-disorder transformation of large cyano dipoles. Transition temperatures might be broadened considerably owing to imperfect order of dipole arrangements.

*Influence of thermal history*

Figure 9 shows three typical examples of thermal histories on dielectric constants. Arrows in the figure represent the first heating run and following cooling run. Thermal history strongly affected the dielectric behaviours, probably because highly ordered aggregated structures preserved in the as-cast film cannot be restored by a simple cooling process. From the figures, one can also see that the appearances of thermal histories depended on the side-chain lengths. Longer aliphatic chains in comonomer units help to weaken influences of thermal history and clear transition phenomena in VDCN copolymers emerge.

In Figure 10, the temperature dependences of the

relaxation strength in P(VDCN/VPr) obtained in first heating and cooling runs are shown. The curves obtained in the cooling run did not possess a sharp change of  $\Delta\epsilon$ , and rather resembled that of P(VDCN/VAc). High values above the transition temperature persisted down to 170°C in the cooling run. This finding suggests that the primary relaxation can persist at further lower tempera-

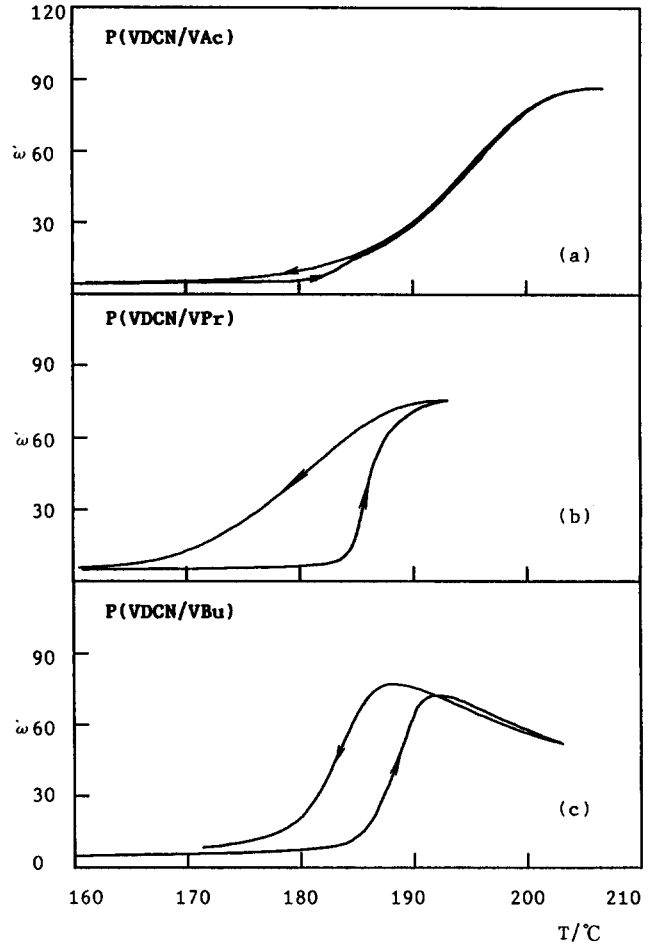


Figure 9 A comparison of temperature dependences of dielectric constant at 1 kHz determined at ascending and descending temperatures for P(VDCN/VAc), P(VDCN/VPr) and P(VDCN/VBu)

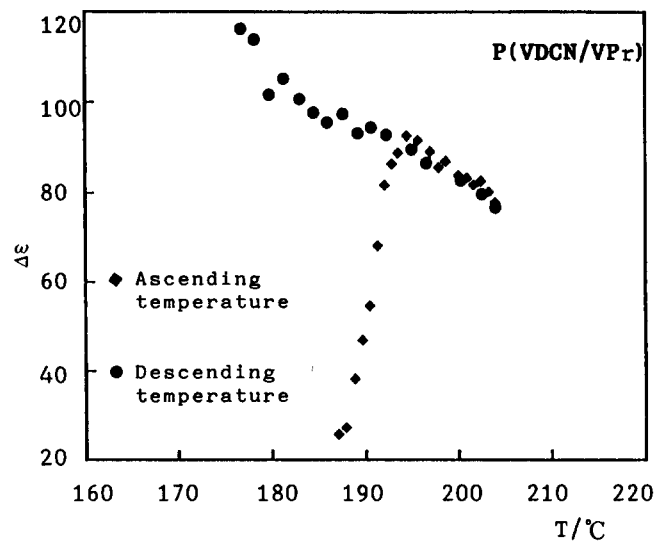


Figure 10 Influence of thermal history on relaxation strength of P(VDCN/VPr)

tures, if the transition that brings about rapid freezing-in of segmental motions does not occur. Thus it is recognized that the molecular mechanisms of thermodynamic transition and primary relaxations have independent origins.

One can point out several reasons for thermal histories in dielectric behaviours. First, the possibility that the thermodynamic transitions themselves hold thermal hysteresis, as is well known in ferroelectric materials, should be considered. Secondly, irreversible changes of aggregated structures can occur, when samples are caused to cross the transition temperatures. Finally, the possibility of irreversible chemical degradations should be examined. At present, we do not possess enough experimental evidence to discriminate among the above three effects. At least, we can assume that chemical degradations did not play a major role in observed thermal histories, because dielectric data on second ascending runs were influenced by neither highest temperatures nor time intervals at which sample films were exposed before second runs.

## CONCLUSIONS

Dielectric properties of five vinylidene cyanide alternating

copolymers were investigated. Although the detailed dielectric behaviour of each copolymer was different from each other, characteristics common in the five copolymers were summarized. First, there is a thermodynamic transition with latent heat at which the dielectric constant abruptly jumps. Secondly, above this transition temperature, an ordinary primary relaxation with large relaxation strength is found. Finally, the increase of side-chain length in comonomer units contributes to the appearance of sharp transition phenomena.

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