

Structure and Spontaneous Polarization in Fast-Quenched Copolymers of Vinylidene Fluoride and Trifluoroethylene

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ABSTRACT: Fast quenching from the melt was found to effect greatly the structures and ferroelectric properties of vinylidene fluoride and trifluoroethylene copolymers (P(VDF/TrFE)) in contrast to slow cooling. The results are discussed for high- and low-VDF content divided at about 50 mol% VDF. For the high-VDF copolymers, the quenched samples showed high T_c like poled samples, implying an ordered ferroelectric phase. Poling the quenched samples at elevated temperatures produced a ferroelectric polarization the direction of which was restored after cooling from above T_c . For the low-VDF copolymers, the quenched samples showed a crystalline phase different from that of the slow-cooled samples, which was found to exist in a metastable state. The quenched samples exhibited no ferroelectricity unlike the slow-cooled samples but poling at elevated temperatures induced pyroelectricity with anomalous temperature dependence. From the present results, the fast quenching seems to produce a phase stable at low temperatures and the poling at elevated temperatures causes crystal growth under an electric field resulting in thermally-stable spontaneous polarizations. Crystal structures of the low-VDF copolymers are also speculated based on the present results and published structure models.

KEY WORDS Vinylidene Fluoride-Trifluoroethylene Copolymers / Fast Quenching / Melt Crystallization / Ferroelectric Phase Transition / Spontaneous Polarization / Pyroelectricity /

Copolymers of vinylidene fluoride and trifluoroethylene (P(VDF/TrFE)) have been extensively studied since the discovery of ferroelectricity in samples with high-VDF content as the first clear example of a ferroelectric polymer.^{1,2} Ferroelectricity originates in the structural characteristics of the PVDF form I crystal, namely, the all-*trans* chain conformation for the highest polarization and the pseudo-hexagonal chain packing to facilitate chain rotation by 60° steps.^{3,4} The high-VDF copolymers are of great advantage to the formation of ferroelectricity because the form

I crystal is adopted by as-crystallized samples and a high degree of crystallinity is attained by heat treatment. On the other hand, copolymers with VDF content lower than 50 mol% have been found by our study to exhibit intricate ferroelectric behavior, for example, a *D—E* double hysteresis loop and an abnormally low amount of remanent polarization.⁵

Ferroelectricity is a crystal property which is expected to be strongly effected by a method of melt crystallization in semicrystalline polymers, *i.e.*, slow cooling or fast quenching. We have developed a method of fast quenching

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and applied it to the melt crystallization of PVDF and PTrFE.⁶⁻⁹ The fast quenching from the melt was found to have significant effects on crystal structures and morphology as well as crystallinity. In the case of PVDF, the form II crystal is normally obtained in melt crystallization, but the fast quenching results in the form I crystal instead of the form II.⁶ The formation mechanism of the form I crystal by fast quenching has been discussed based on nucleation kinetics that the fast quenching favors nucleation at low temperatures where nuclei of the form I are predominantly produced.⁶ In polytrifluoroethylene (PTrFE), a fast-quenched sample exhibits pyroelectricity by subsequent poling at elevated temperatures.⁷⁻⁹ The mechanism of producing a spontaneous polarization is that the process of simultaneous poling and crystal growth in the quenched sample leads to alignment of dipoles along the field in the growing crystalline regions.⁸ In this regard, a slow-cooled sample shows negligibly small pyroelectricity because no appreciable crystal growth is induced by poling at elevated temperatures.⁸ However, ferroelectricity has been revealed quite recently in the slow-cooled sample and not in the fast-quenched sample of PTrFE, which shows behavior similar to that in the low-VDF copolymers described above.¹⁰ As for the effects of quenching on ferroelectric properties in semicrystalline polymers, Tasaka and Miyata studied copolymers of vinylidene fluoride and tetrafluoroethylene (P(VDF/TFE)) and found that a coercive field is higher in quenched samples than in annealed samples.¹¹ They also found that the coercive field is inversely proportional to the long period.

The purpose of the present study is to elucidate the effects of fast quenching in P(VDF/TrFE) on the structures, spontaneous polarizations and the ferroelectric behavior in comparison with the results on samples slowly cooled from the melt.

EXPERIMENTAL

Samples of P(VDF/TrFE) with 13–78 mol% VDF and PTrFE were kindly provided by Daikin Kogyo Co., Ltd. The powder samples were heat-pressed into films of 10–15 μm thick followed by different melt-cooling procedures. A sample designated as slow-cooled was obtained by cooling the melt at a rate of approximately 2 K min^{-1} . The other sample designated as quenched was obtained by the fast-quenching method described in detail in the previous paper,⁶ where the sample film stuck on a 15 μm thick Al foil was plunged into ice water from 220–250°C. Densities of the samples were measured at 25°C by a buoyancy method using a mixture of 1,1,2,2-tetrachloroethane and 1,1,2,2-tetrabromoethane. X-Ray diffraction patterns were obtained by using a Rigaku RU200 X-ray diffractometer with a monochromatized Cu-K_α radiation and IR spectra by using a Hitachi model 260-50 IR spectrometer. A DTA measurement was carried out using a Rigaku Thermoflex TG-DTA at a heating rate of 10 K min^{-1} .

Al electrodes of 6.5 or 10 mm in diameter were vacuum-evaporated onto both surfaces of the sample film for poling and electrical measurements. Poling was performed by the following procedure. A dc electric field E_p was applied at room temperature and then the sample was heated to a desired temperature T_p and kept at T_p for a certain time followed by rapid cooling to room temperature with E_p applied, where poling time t_p was taken from switching on E_p to just before cooling. The poled sample was heated above T_p in order to depolarize an irreversible polarization prior to the pyroelectric measurement. The pyroelectric coefficient p_y was obtained from the reversible pyroelectric current on heating and cooling at a rate of 3.3 K min^{-1} . Here, p_y is taken as a positive value for simplicity. A measurement of thermally stimulated currents (TSC) was conducted by a conventional method¹² with a heating rate β of 3.3 K min^{-1} .

RESULTS

Differences in Structures and Ferroelectric Behavior between Quenched and Slow-Cooled Samples

Variation of Density with VDF Content. The variation of density with VDF content in P(VDF/TrFE) is presented in Figure 1 for samples with the highest and lowest densities obtained in the present study by melt crystallization at an atmospheric pressure. The highest density was attained in a sample slowly cooled from the melt and annealed near a crystallization temperature for a prolonged time and the lowest density was in a sample subjected to the fast-quenching method. A linear relation holds between the density and VDF content for both annealed and quenched samples except for a range of VDF content higher than 80 mol%. Here, the quenched

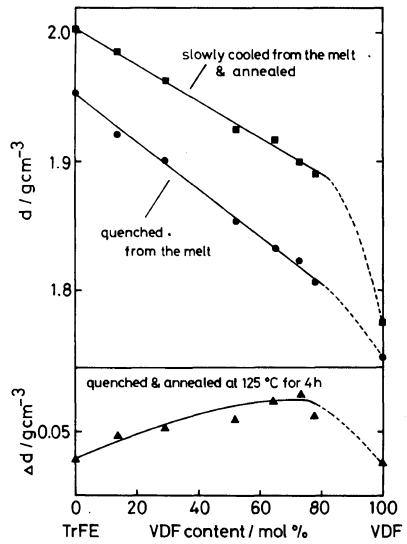


Figure 1. Variation of density with VDF content in annealed and quenched samples for P(VDF/TrFE) and increase in density in quenched samples by annealing at 125°C for 4 h.

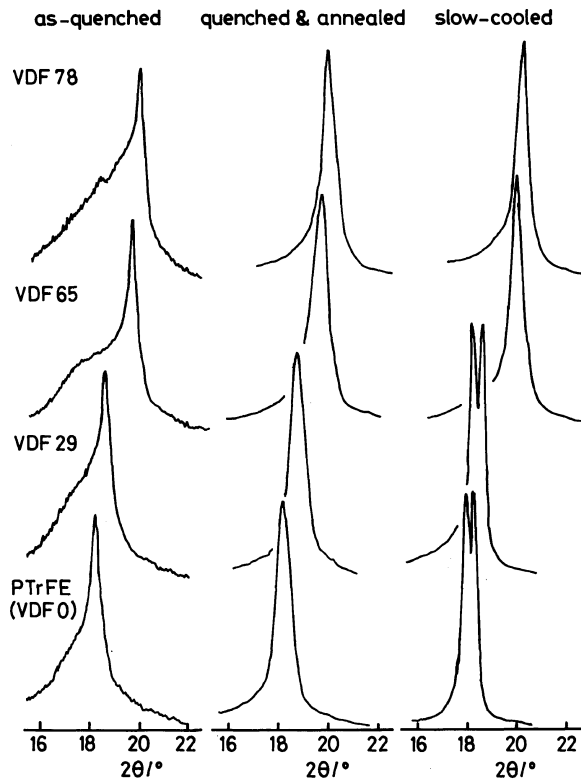


Figure 2. X-ray diffraction profiles of P(VDF/TrFE) for samples under different melt-crystallization conditions: as quenched, quenched and annealed at 120°C for 20 h, and slow cooled.

sample of PVDF shows mostly the form I crystal identical to the crystal structure of the high-VDF copolymers while the annealed one shows a mixture of the forms II and III. The deviation from the linear relation in the vicinity of PVDF may be due to the degree of crystallinity which tends to become small as VDF content comes close to 100 mol%. Figure 1 also shows the increment of density in the quenched sample by annealing at 125°C for 4 h. The increment of density becomes maximum at about 70 mol% VDF, implying that the rate of crystal growth is high in P(VDF/TrFE) as compared with that in homopolymers of PVDF and PTrFE.

X-Ray and IR Figures of Quenched and Slow-Cooled Samples. X-Ray diffraction patterns of P(VDF/TrFE) are shown in Figure 2 for the samples of as-quenched, quenched-and-annealed at 120°C for 20 h and slow-cooled. The

main peak located at 2θ of 18–20° is presented in Figure 2, which is indexed as (110, 200) reflecting the mode of chain packing. The results of the X-ray work are discussed separately for high- and low-VDF copolymers. For the high-VDF copolymers, VDF 78 and VDF 65 in Figure 2, no difference is seen in the X-ray profiles between the quenched and slow-cooled samples which give single peaks characteristic of the PVDF form I crystal type. For the low-VDF copolymers, VDF 29 and VDF 0 in Figure 2, the slow-cooled samples show a double peak while the quenched samples show a single peak. This tendency was observed for VDF content lower than 52 mol%. Here, the phases with a single and a double X-ray peaks for the low-VDF copolymers are tentatively called S and D phases, respectively. It is also noted that the as-quenched samples exhibit large amorphous scattering on the lower- 2θ

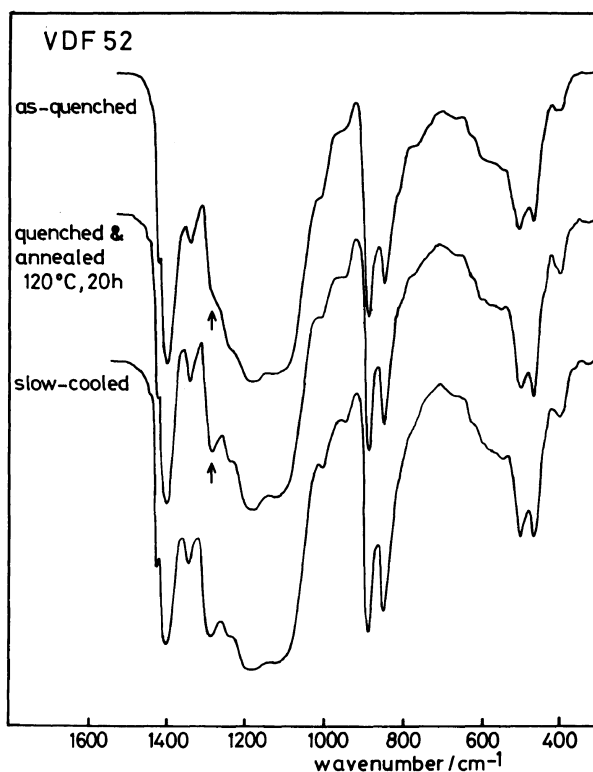


Figure 3. IR spectra of 52 mol% VDF copolymer for samples under different melt-crystallization conditions as in Figure 2.

side of the peak indicating low crystallinity, which is considerably diminished due to crystal growth by annealing.

In Figure 3 are shown IR spectra of the samples subjected to the crystallization treatments identical to those in Figure 2. The results of 52 mol% VDF copolymer are presented as an example of the copolymers showing different X-ray profiles between the quenched and slow-cooled samples. The IR spectra are essentially the same for the three samples in spite of the differences in the X-ray profiles. It should be noticed in Figure 3 for the as-quenched sample that the 1288-cm^{-1} band indicated by an arrow appears as a shoulder which becomes a clear peak after annealing. This band is assigned to a *trans* band in the crystalline regions by Tashiro *et al.*¹³ This band is considered to be sensitive to the crystal perfection. The copolymers with no difference between the quenched and slow-cooled samples in the X-ray peak gave the same IR patterns for the two samples.

Ferroelectric Transition in Quenched Samples for High-VDF Copolymers. Although no difference between the quenched and slow-cooled samples is seen for the high-VDF copolymers in X-ray and IR profiles, a clear difference is detected in the behavior of the ferroelectric transition. Figure 4 shows DTA curves for the quenched and slow-cooled samples of 65 mol% VDF copolymer. An endothermic peak located at 60–100°C corresponds to a ferroelectric transition and a sharp one at about 160°C to the melting. The as-quenched sample shows a single peak of the ferroelectric transition at 93°C higher than a composite peak of the slow-cooled sample at 67–85°C. The DTA profile of the quenched sample gradually changes to that of the slow-cooled sample by annealing, *i.e.*, a shoulder appears on the lower temperature side of the peak after annealing at 120°C for 20 h and becomes a peak after annealing at 140°C for 20 h with the original peak being faded into a shoulder. The difference in the DTA curves be-

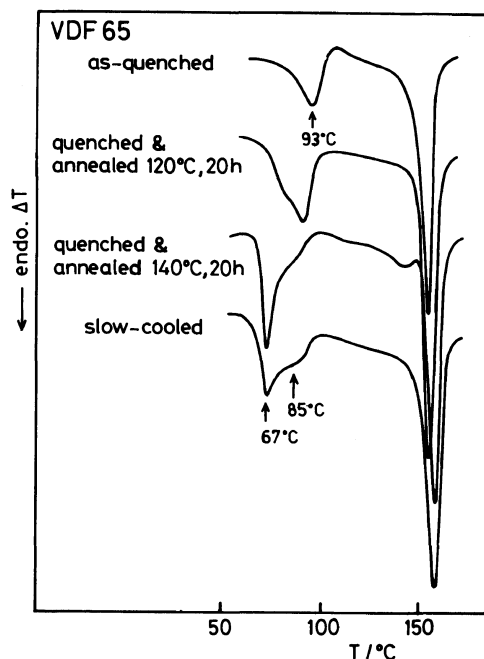


Figure 4. DTA curves of 65 mol% VDF copolymer for samples under different melt-crystallization conditions: as quenched, quenched and annealed 120°C for 20 h, quenched and annealed at 140°C for 20 h, and slow cooled.

tween the quenched and slow-cooled samples is quite similar to that between unpoled and poled samples studied by Davis *et al.*¹⁴ They observed that a double peak at 74 and 86°C in an unpoled sample was unified into a single one at a higher temperature of 99.6°C in a poled sample. It is thus considered that the quenched sample corresponds to the poled one in the behavior of the ferroelectric transition.

The results of the DTA measurements are further justified by TSC measurements as shown in Figure 5, where the depolarization of ferroelectric polarization is presented as a TSC curve for 65 mol% VDF copolymer. In order to obtain TSC curves of the slow-cooled samples for unpoled and poled with respect to the ferroelectric transition, the parameters of T_p and t_p to condition a sample were chosen as follows. For an unpoled sample, low T_p of 25°C and t_p of as short as 1 min were employed

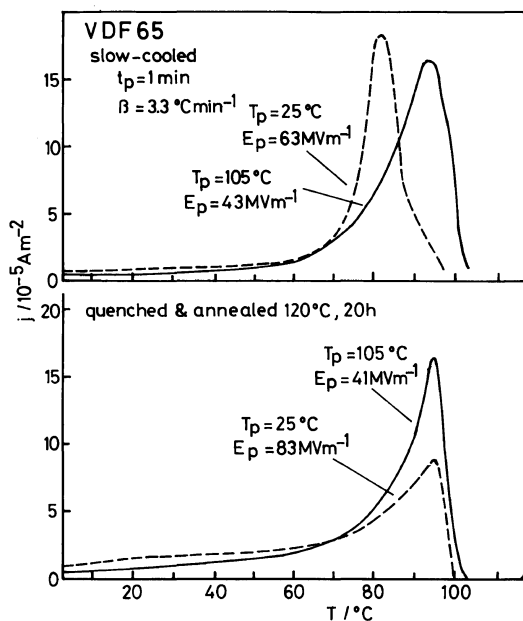


Figure 5. TSC curves of 65 mol% VDF copolymer for slow-cooled (top) and quenched (bottom) samples with T_p of 25°C (dashed line) and 105°C (solid line).

to avoid effects of poling on the structure. For a poled sample, a high T_p of 105°C above the Curie temperature T_c was adopted to make sure an adequate poling effect. E_p was always set above a coercive field E_c to induce a ferroelectric polarization. As shown in Figure 5, the unpoled slow-cooled sample with T_p of 25°C gives a peak of depolarization at a lower temperature than the poled sample with T_p of 105°C, implying that T_c is lower in the former than in the latter. On the other hand, the quenched sample for T_p of both 25 and 105°C gives the peak at a temperature as high as that of the poled slow-cooled sample. It is concluded from the results of the DSC and TSC measurements for the high-VDF copolymers that the quenched samples are in an ordered ferroelectric state similar to that of the poled samples while the slow-cooled samples are in a disordered ferroelectric state which changes to the ordered state by poling. The structure of the quenched samples, however, is gradually converted to that of the slow-cooled samples

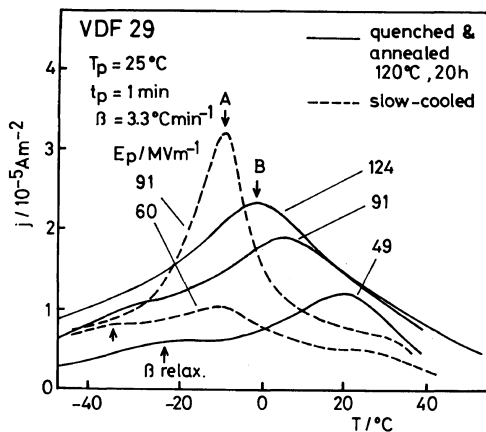


Figure 6. TSC curves of 29 mol% VDF copolymer for slow-cooled (dashed line) and quenched (solid line) samples with various E_p .

by annealing at high temperatures, e.g., 140°C annealing for 65 mol% VDF copolymer.

Absence of Ferroelectricity in Quenched Samples of Low-VDF Copolymers. As revealed in our previous study,¹⁵ the slow-cooled samples of the low-VDF copolymers exhibit ferroelectricity, the features of which were also such that the D phase is transformed into S phase by an electric field and the S phase is stabilized below a certain temperature T_1 . The field-induced S phase transforms into the D phase on heating through T_1 , which is regarded as a ferro-to-ferroelectric transition.¹⁵ For the quenched samples, however, no polarization reversal was observed, offering negative evidence for the ferroelectricity. To further check this point, TSC spectra were observed for the quenched and slow-cooled samples of 29 mol% VDF copolymer, as shown in Figure 6. The TSC curves for the slow-cooled samples show a marked change with increasing E_p through E_c of 72 MVm⁻¹. For E_p of 91 MVm⁻¹ higher than E_c , a large peak (peak A) appears at -10°C. This peak is assigned to the above-mentioned transition from the field-induced S phase to the D phase, and hence T_1 for 29 mol% VDF copolymer is -10°C in a heating process. The existence of the peak A, therefore, gives a criterion of ferroelectricity. In

the TSC curves of the quenched sample, no sign of the peak A was observed as E_p increased to 124 MVm^{-1} and a broad peak (peak B) is seen to shift to lower temperature with increasing E_p . The origin of peak B is not clear but may be related with a space-charge polarization judging from the shift in peak temperature and the nonlinear dependence of the peak intensity on E_p . A shoulder in the TSC curves below -25°C is assigned to the β relaxation of dipole origin.¹⁶ The results of the TSC measurements again rule out ferroelectricity in the quenched samples of the low-VDF copolymers.

Spontaneous Polarizations in Quenched Samples Induced by Simultaneous Poling and Crystal Growth

Types of Spontaneous Polarization for High- and Low-VDF Copolymers. Since the as-quenched samples have considerably low crystallinity as observed in the density and X-ray measurements, poling at elevated temperatures is expected to cause crystal growth at the same time. It is interesting to examine spontaneous polarizations thus induced in the quenched samples with reference to their structural and ferroelectric characteristics.

Figure 7 shows the results of the poling procedure on the quenched samples for 65 and 52 mol% VDF copolymers as examples of the high- and low-VDF copolymers, respectively. A long t_p of 15 h was employed for crystal growth. In Figure 7 are presented a depolarization current after poling and reversible pyroelectric currents on heating and cooling. A marked distinction is seen between the results of 65 and 52 mol% VDF copolymers. For 65 mol% VDF copolymer in Figure 7a, reversible pyroelectric currents appear with temperature hysteresis, the profile of which is identical to that of the depolarization current after poling. Since the depolarization current is induced by a decay of ferroelectric polarization, the pyroelectric currents arise from the ferroelectric phase. It is surprising that the direction

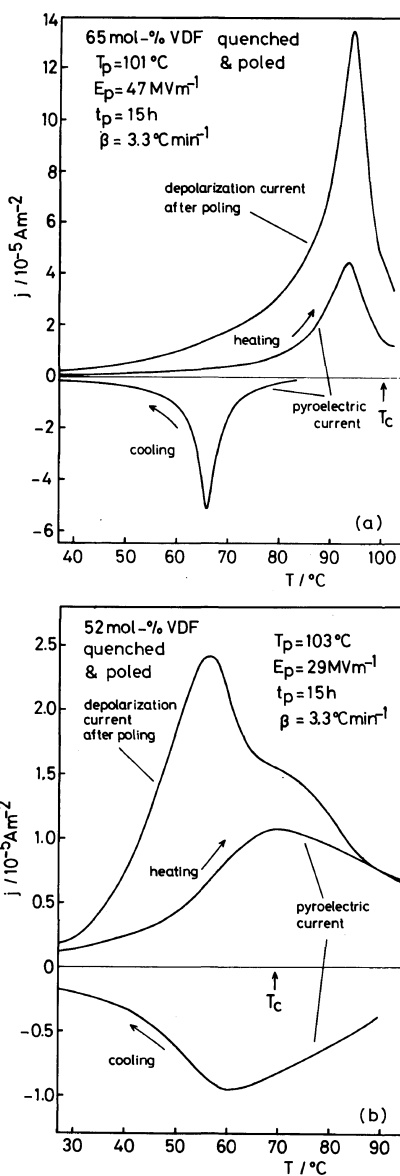


Figure 7. Profiles of depolarization current after poling and pyroelectric current on heating and cooling for quenched samples of 65 mol% (a) and 52 mol% VDF (b) copolymers.

of the ferroelectric polarization is memorized after cooling from above T_c . The amount of the polarization in the pyroelectric currents is estimated to be 10 mCm^{-2} and that in the first depolarization current is 32 mCm^{-2} .

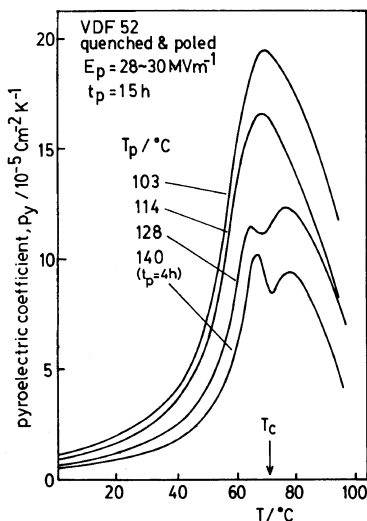


Figure 8. Temperature dependence of pyroelectric coefficient for quenched sample of 52 mol% VDF copolymer poled at various T_p .

About one third of the total ferroelectric polarization survives in the new crystalline regions after depolarization.

For 52 mol% VDF copolymer in Figure 7b, the depolarization current after poling exhibits a peak and a shoulder in the order of ascending temperature, indicating that two types of polarization are induced by the poling procedure. The peak arises from a decay of ferroelectric polarization and the shoulder from a new type of polarization which was not observable in the slow-cooled sample. Reversible pyroelectric currents were also observed with temperature hysteresis after depolarization. It is considered from the profiles of the depolarization and pyroelectric currents that the new polarization is an origin of the pyroelectric currents unlike the pyroelectricity in 65 mol% VDF copolymer.

The results in Figure 7 suggest that there are two types of spontaneous polarization induced in the quenched samples by the poling procedure depending on VDF content. This point becomes apparent in the 52 mol% VDF copolymer which has an intermediate VDF content between the high- and low-VDF copoly-

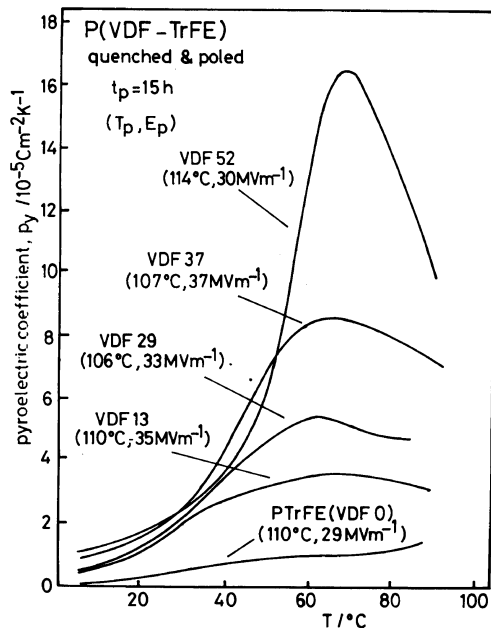


Figure 9. Temperature dependence of pyroelectric coefficient for quenched samples of a series of low-VDF copolymers.

mers. Figure 8 shows curves of p_y for 52 mol% VDF copolymer induced by the poling procedure with various T_p . For low T_p of 103 and 114°C, the p_y curves show a single peak. As T_p increases to 128°C, the single peak gradually changes to a double peak with an additional peak emerging on the lower temperature side of the original peak. For T_p of 140°C, the double-peak feature becomes clearer. Taking the results of Figure 7 into consideration, the low-temperature component of the double peak is ascribed to the ferroelectric polarization and the high-temperature one to the new polarization.

Pyroelectricity in Low-VDF Copolymers. The poling procedure was employed in a series of the low-VDF copolymers including PTrFE. All the quenched samples of the low-VDF copolymers exhibited appreciable pyroelectricity as presented by the curves of p_y in Figure 9. Since the single-peak feature of 52 mol% VDF copolymer is retained for the low-VDF copolymers as can be seen in Figure 9, the ori-

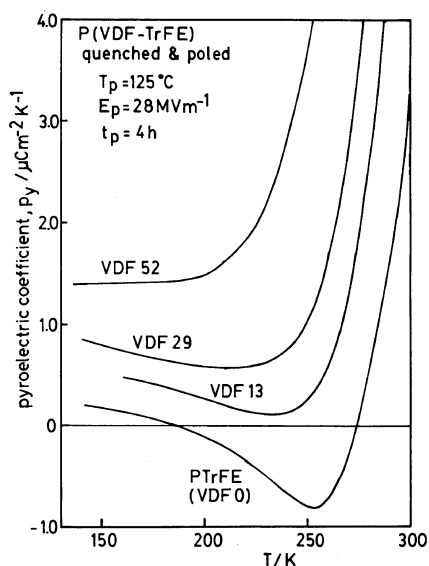


Figure 10. Temperature dependence of pyroelectric coefficient in low-temperature region for quenched samples of low-VDF copolymers.

gin of the pyroelectricity in the low-VDF copolymers is the new polarization described above. It is noted that the amounts of spontaneous polarization estimated from the p_y curves are considerably reduced as the VDF content is lowered.

The other feature of p_y in the low-VDF copolymers is seen in a low-temperature region below room temperature as shown in Figure 10. The curve of p_y for 29 mol% VDF copolymer has a minimum at 215 K, which becomes apparent in 13 mol% VDF copolymer and PTrFE with a minimum at 235 and 255 K, respectively.

DISCUSSION

P(VDF/TrFE) is grouped into high- and low-VDF content at around 50 mol% as to structural, ferroelectric and pyroelectric characteristics in the quenched and slow-cooled samples. The high-VDF copolymers show no difference between the two samples in the X-ray and IR figures, which have the structure of

the PVDF form I crystal type. On the other hand, the low-VDF copolymers exhibit S and D phases for the quenched and slow-cooled samples, respectively. The difference between S and D phases is seen in the X-ray peak of (110, 200) reflection as a single peak for S phase and a double peak for D phase. The IR spectra are essentially the same for the two phases. Taking into consideration that X-ray is sensitive to chain packing and IR to chain conformation, the above results imply that a chain packing is pseudohexagonal for S phase and orthorhombic for D phase with the same chain conformation.

According to the study on the structures of the low-VDF copolymers by Tashiro *et al.*,¹⁷ the D phase corresponds to the cooled phase of their study with a disordered all-*trans* conformation and the S phase to the low-temperature phase with an ordered all-*trans* conformation. Their structure models are unacceptable from the fact that the density of the cooled phase calculated from the reported lattice parameters is always *smaller* than the density observed at 25°C. For example, in the slow-cooled sample of 13 mol% VDF copolymer, the former is 1.961 g cm⁻³ and the latter is 1.975 g cm⁻³. The crystal density has to be *larger* than the sample density in semicrystalline polymers having lower density for lower crystallinity. This discrepancy may arise from their value of 2.53 Å for a fiber period of the all-*trans* conformation. It should be ~2.30 Å which yields 2.157 g cm⁻³ for the crystal density of 13 mol% VDF copolymer. This value is considered to be reasonable because it gives 55% crystallinity using 1.749 g cm⁻³ for the amorphous density estimated by Van Krevelen's method,¹⁸ which is comparable with the observed value of 42% by the X-ray method. As was reported elsewhere,²⁵ the change in the amount of polarization accompanied by the transition from the field-induced S phase to the D phase or from the low-temperature phase to the cooled phase in their nomenclature is much larger than that esti-

mated from their structure models based on the all-*trans* conformation. This again leads to the inadequacy of the all-*trans* conformation for the low-VDF copolymers. It is claimed that the chain conformation of S and D phases consists of T and G sequences with polar nature to give a fiber period of ~ 2.3 Å. Conformations of TGT \bar{G} and T₃GT₃ \bar{G} are examples of a polar chain with a period of 2.3 Å as adopted by the in PVDF forms II and III, respectively. The TGT \bar{G} conformation was, however, found energetically unfavorable for PTrFE or 0 mol% VDF copolymer.¹⁹ Although an energy calculation for the T₃GT₃ \bar{G} conformation is not available, we consider that some conformation based on T₃GT₃ \bar{G} would be likely for S and D phases.

The fast quenching was found to exert a considerable effect on crystal structures for the high- and low-VDF copolymers. The effect of the fast quenching on the structure was also found in PVDF by our previous study that the form I crystal is obtained in most part instead of the form II.⁶ It is concluded as a common feature of the quenched samples that a phase or structure stable at low temperatures is obtained by the fast quenching: an ordered ferroelectric phase for high VDF and S phase for low VDF. A mechanism for producing a phase stable at low temperatures has been proposed based on a concept of nucleation kinetics in our previous study on PVDF.⁶ In the fast quenching, a sample passes through a high-temperature region too fast to induce nucleation in an appreciable amount and hence nucleation mostly proceeds at low temperatures. In slow cooling, on the other hand, a sample stays in a high-temperature region during cooling long enough to complete nucleation at high temperatures. Therefore, the fast quenching favors the low-temperature nucleation and the slow cooling favors the high-temperature nucleation resulting in the different crystalline phases between the quenched and slow-cooled samples.

The fast quenching strongly effects mor-

phology as well as structure, that is, the size of crystallite and the thickness of lamellae in the quenched samples should be fairly small as compared with those in the slow-cooled samples. In fact, the quenched samples are transparent even after prolonged annealing at high temperatures and the slow-cooled samples are translucent. As the thickness of lamellae becomes small, the number of folds in a chain increases, which tends to hinder cooperative motion of chains. For the low-VDF copolymers, this morphological feature of the quenched samples is considered to result in the stability of S phase and the absence of the ferroelectricity. As revealed in the slow-cooled samples that the field-induced S phase transforms to the D phase at T_1 below room temperature, the D phase is an equilibrium state. In the quenched samples, the morphological feature suppresses the S-to-D phase transition and consequently the S phase appears in a metastable state up to a melting point. We found that the S-to-D phase transition under an electric field is indispensable for polarization reversal, that is, S phase with a higher polarization transforms into D phase by a depolarization process and further transforms into S phase with the reversed polarization.¹⁰ This two-step process indicates that S phase is essentially a ferroelectric phase as well as D phase. For the S phase in the quenched samples, however, it is difficult to exhibit the ferroelectricity because the S-to-D phase transition is suppressed, resulting in the absence of the ferroelectricity. It is also noted that annealing the quenched samples fails to change the S phase to the D phase. For the high-VDF copolymers, the morphological and ferroelectric features of the quenched samples are gradually changed to those of the slow-cooled samples by annealing at high temperatures as has been shown in Figure 4. This is due to the characteristics of the high-VDF copolymers, namely, the greater increase in crystallinity by annealing, less bulky chains and a higher polarization as compared to the low-VDF

copolymers, which facilitate cooperative motion even in the quenched samples.

Types of spontaneous polarization induced in the quenched samples by the poling procedure are also different between the high- and low-VDF copolymers in connection with structural and morphological characteristics. Spontaneous polarizations are mainly created in the crystalline regions developed during the poling procedure which are the ferroelectric phase for the high-VDF and the metastable S phase for the low-VDF copolymers. A ferroelectric polarization is thus formed in the quenched samples of the high-VDF copolymers as a thermally-stable spontaneous polarization. It is interesting in the case of typical ferroelectric polymers such as the high-VDF copolymers to note that the direction of the ferroelectric polarization is restored after cooling the sample from above T_c resulting in a pyroelectric current of a polarization process on cooling. This fact indicates that the ferroelectric domains in the developed crystalline regions are oriented along the field and do not take on random orientation by cooling from the paraelectric phase. The exact mechanism is unknown but this may be due to the size of the domain in the developed ferroelectric phase being too small to be divided into multiple domains.

For the low-VDF copolymers, a thermally-stable polarization is formed in the metastable S phase of the quenched samples. The profile of the pyroelectric current shows a broad peak in contrast to that in the high-VDF copolymers with a sharp peak coming down to zero at a Curie point, reflecting the difference in the types of polarization. The temperature dependence of the pyroelectric coefficient is not a monotonously-increasing function in a low temperature region, which shows a minimum at a certain temperature leading to the anomalous pyroelectricity in PTrFE.⁷⁻⁹ Thus the already-reported pyroelectricity in PTrFE arises from the metastable S phase. Clarification of the exact conformation and structure

of S and D phases is required to reveal the mechanism of the anomalous ferroelectric and pyroelectric behavior of the low-VDF copolymers.

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