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Polymer 42 (2001) 4981–4987

polymer

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Annealing effects on the Curie transition temperature and melting temperature of poly(vinylidene fluoride/trifluoroethylene) single crystalline films

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Received 18 September 2000; received in revised form 24 November 2000; accepted 8 December 2000

Abstract

The effect of reannealing on the Curie transition temperature T_C, melting point T_m, and structures of single crystalline (SC) films of ferroelectric copolymer of poly(vinylidene fluoride/trifluoroethylene) (P(VDF/TrFE)) (75:25 mol%), which were prepared by uniaxial stretching of solvent cast films followed by crystallization/annealing at 140°C, was investigated using differential scanning calorimetry and X-ray diffraction. Accumulative reannealing in the ferroelectric phase just below T_C caused a large increase in T_C by 17°C without distinctive change in T_m, while prolonged reannealing in the hexagonal phase caused an increase in T_m by 5°C with a slight decrease in T_C. From the X-ray diffraction study it is found that the reannealing at a temperature below T_C removes the *gauche* conformational defects existing in molecular chains, and that the reannealing in the hexagonal phase for long periods leads to rearrangement of chain molecules through their sliding motion along the chain axis so as to eliminate crystal defects and to improve the preferential orientation distribution of the crystal axes perpendicular to the (110)/(200) planes in the film. The effects of such structural changes on T_C and T_m are explained on the basis of the Gibbs free energy-versus-temperature diagram.

Keywords: Vinylidene fluoride–trifluoroethylene copolymers; Single crystalline film; Annealing effect

1. Introduction

Copolymers of vinylidene fluoride and trifluoroethylene, P(VDF/TrFE), have attracted intense scientific and technological interest during the last two decades because of their unique structural phase transition between ferroelectric phase and paraelectric phase, and because of their strong piezoelectricity and pyroelectricity [1–3]. The crystal in the ferroelectric phase is orthorhombic, consisting of all-*trans* chains with their dipoles parallel to the *b*-axis, and in the paraelectric phase it is hexagonal, essentially consisting of a statistical combination of TT, TG, and TG$'$ rotational isomers [4]. In the hexagonal (paraelectric) phase the chain molecules are very mobile along the chain axis as in a one-dimensional liquid crystal [5]. Thick lamellar crystals (extended chain crystals) are grown extensively in the films when they are crystallized by annealing in the hexagonal phase, and poling treatment of the resulting films provides most effective piezoelectric polymer films [6–9]. Growth of thick lamellar crystals of P(VDF/TrFE) in the hexagonal phase is one of the typical examples that extended chain crystals can grow in a mobile hexagonal phase through sliding diffusion of chain molecules [10–12].

Recently, we succeeded in obtaining a single-crystal-like film of P(VDF/TrFE), which we call the ‘single crystalline’ (SC) film [13]. The SC film is composed of endlessly extended chain crystals only (no amorphous phase or lamellar crystals included). The *c*-axis of these crystals is highly oriented along the stretching direction, and the (200) and/or (110) planes are also preferentially oriented parallel to the film surface. Reflecting such unique structure, the SC film is optically very transparent, and has a high Young’s modulus (121 GPa at 10 K) in the stretching direction, and large piezoelectric constants [14].

In contrast to organic crystals of low molecular weight, macromolecular crystals are, in general, far from perfect, even if they are seemingly perfect: various disordered structures in the arrangement of molecular chains are included in polymer crystals [15]. From this viewpoint, the SC film of P(VDF/TrFE) may contain many structural defects in the crystals. Therefore, it is expected that elimination of these defects will improve functional properties of the SC film. For the purpose of making the crystal more perfect, we

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0032-3861/01/$ - see front matter
PII: S0032-3861(00)00937-X

studied in this paper the reannealing effects of the SC film on the phase transition and melting behaviors, and accompanying structural changes by using differential scanning calorimetry (DSC) and X-ray diffraction. The annealing was performed in two ways: one was that the SC film, which had been well crystallized by annealing in the hexagonal phase, was reannealed at various temperatures in the orthorhombic phase, where chain motions may be localized on the chain and macroscopic chain displacement is not permissible, and the other was that the SC film was reannealed at a temperature near the melting point in the hexagonal phase for various periods, where the chain molecules are mobile along their chain axis, and large displacement of chain molecules may be permissible during a long period.

The phase transition behaviors of P(VDF/TrFE) are strongly dependent on the molar composition ratio of VDF and TrFE [1,2,7,9,16–18]. Furthermore, even the films having the same VDF/TrFE molar ratio still exhibit different thermal behaviors depending on the crystallization and/or annealing treatment conditions to which they have been subjected. Although much work has been devoted to clarify the thermal behaviors and structural changes induced by crystallization and annealing [19–29], the complicated thermal behaviors are not clearly understood yet. The SC film is more suitable for studying the annealing effects than lamellar crystalline films hitherto used, that is, the films composed of variously oriented lamellar crystals.

2. Experimental

The P(VDF/TrFE) copolymer used in this study was of 75 mol% VDF, which was kindly supplied from Daikin Industries, Ltd. The SC film was prepared by uniaxial stretching of a solution cast film, followed by crystallization by annealing in the hexagonal phase at 140°C for 2 h, maintaining the film surfaces free from contact with solid materials during crystallization. (Hereafter we call the resulting film the original SC film.) The preparation procedure of the P(VDF/TrFE) SC film is described in more detail elsewhere [30].

The original SC films were reannealed in two ways. For investigation of the effect of annealing in the orthorhombic phase, the original SC film was reannealed accumulatively at temperatures (T_a) below T_C as was done in the previous work [22,23]. The starting reannealing temperature (110°C) was chosen sufficiently lower than the T_C of the original SC film (125°C) and the film was reannealed for 3 h. A part of the reannealed sample was cut off to take the DSC and X-ray diffraction measurements for this first reannealing condition. The residual part of the sample was reannealed at a temperature (T_a) slightly higher than the previous temperature for the same period (3 h), and again a part of this reannealed sample was cut off for the DSC and X-ray measurements. This procedure was continued until the reannealing temperature was raised higher than T_C. (We call this reannealing procedure 'accumulative reannealing' [22,23], while Kim et al. called it 'consecutive annealing' [24].) To investigate the effect of annealing in the hexagonal phase, the original SC films were reannealed at a constant temperature (140°C) for various periods ranging from 2 up to 340 h.

Curie transition and melting point were observed by a differential scanning calorimeter (MAC Science, DSC 3100), with the sample weight of 5 mg and the heating rate of 5.0°C/min for every measurement. The scanning temperature range was from 50 to 180°C. Wide-angle X-ray diffraction (WAXD) profiles were obtained in the transmission mode by using CuK$_\alpha$ radiation ($\lambda = 0.15418$ nm) from a rotating anode X-ray generator (Rigaku RU-3SH) operated at 40 kV and 70 mA. The thickness of SC films used in this study was 50 ± 3 μm.

3. Results

Fig. 1 illustrates the endothermic DSC curves for the P(VDF/TrFE) SC film reannealed below T_C. The Curie transition temperature T_C increases with increasing reannealing temperature T_a and the reannealing treatment makes the Curie transition sharper. When the sample is reannealed at higher temperature than ca. 126°C, a broad peak ($T_{C'}$) appears below T_C and its peak strength becomes larger with increasing T_a, while the peak intensity at T_C correspondingly decreases, and disappears in the film reannealed

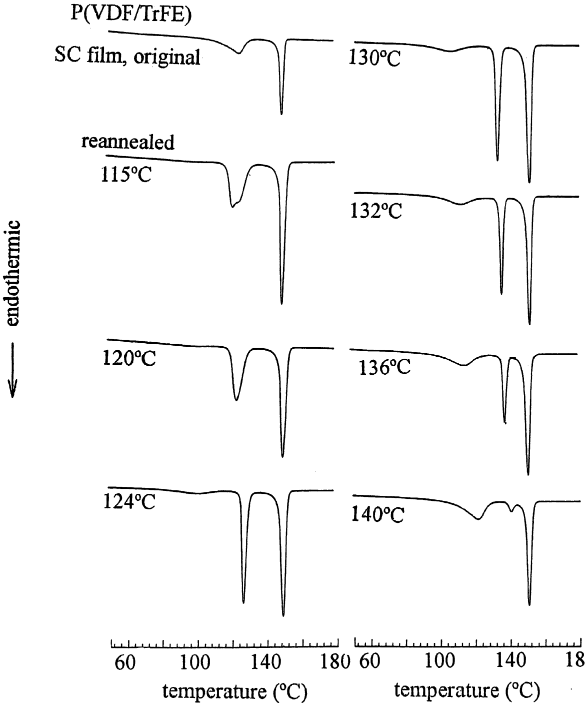

Fig. 1. DSC heating thermograms of the P(VDF/TrFE) (75:25) SC films reannealed accumulatively at various temperatures in the orthorhombic phase. The annealing temperature is indicated on each curve.

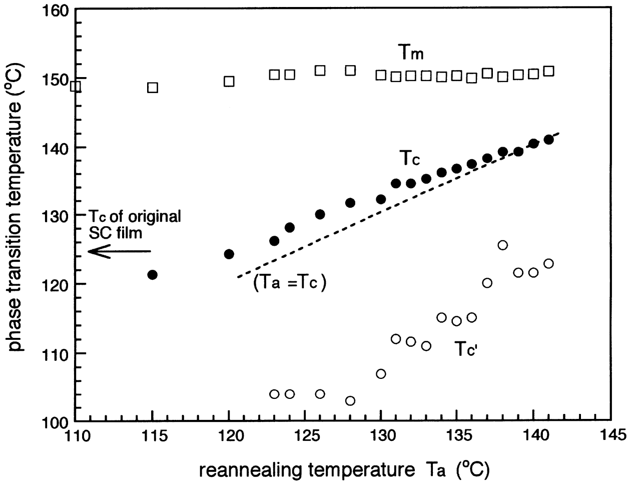

Fig. 2. Plots of Curie transition temperatures T_C and $T_{C'}$, and melting temperature T_m against accumulative reannealing temperature T_a for the P(VDF/TrFE) (75:25) SC film. The dotted line represents the relationship $T_C = T_a$.

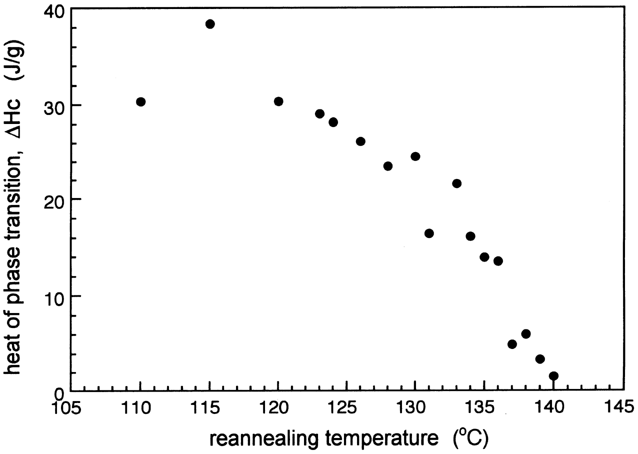

Fig. 3. Heat of phase transition ΔH_C at T_C for the P(VDF/TrFE) (75:25) SC film as a function of reannealing temperature T_a.

at temperatures higher than 141°C. In Fig. 2, T_C, $T_{C'}$ and melting temperature T_m are plotted as a function of reannealing temperature T_a. The Curie temperature T_C increases linearly with T_a, and reaches 140.4°C at $T_a = 140$°C, while T_m is practically independent of T_a. Fig. 3 shows the enthalpy change ΔH_C at T_C as a function of T_a. It is noted that the DSC curve for $T_a = 140$°C is almost the same as that of the original SC film except for a weak T_C peak at 140.4°C. These results are very similar to those obtained for lamellar crystalline films of P(VDF/TrFE) (75:25) [22–24].

The increase in T_C with increasing T_a is most possibly attributable to a decrease in the *gauche* defect density, that is, a decrease in the number of *gauche* defects which have been introduced in all-*trans* chains on cooling from the hexagonal phase to the orthorhombic phase: reannealing just below T_C removes the *gauche* defects through localized thermal motions of chain molecules and increases long *trans* sequences in the chain. However, during reannealing at temperatures higher than ca. 130°C, *gauche* defects enter again into the molecular chain, which is responsible for the broad peak ($T_{C'}$) appearing below T_C. Therefore, it is suggested that the accumulative reannealing at around 126°C produces the SC film with the least *gauche* defect density in the case of the copolymer of VDF 75 mol%.

To confirm if the reannealing reduces the number of *gauche* defects, X-ray diffraction measurements were performed for the SC film accumulatively reannealed at 126°C, which is considered to include the least number of *gauche* defects, and for the original SC film. Fig. 4 shows the X-ray diffraction profiles obtained by scanning the scattering vector S along the c^*-axis of the reciprocal lattice. The profile of the original SC film (Fig. 4(a)) shows, in addition to the sharp and strong 001 reflection ($2\theta = 35.3°$), a very weak and diffuse scattering peak at angle $2\theta \approx 40°$. The broad peak is similar to that observed for an SC film in the hexagonal phase, which has been assigned to the diffraction from the chain molecules composed of TGTG′ sequences undergoing the flip-flop motion along the chain axis and the rotational motion around the chain axis without correlation with neighboring chains [5]. Therefore, the broad peak at $2\theta \approx 40°$ in the original SC film is also attributable to the defects of short sequences of TGTG′ units. The diffuse peak disappears after reannealing treatment at $T_a = 126$°C (Fig. 4(b)), which indicates a considerable decrease in the number of *gauche* defects in the orthorhombic phase.

The effect of reannealing in the hexagonal phase at 140°C for a long period on the phase transition and melting temperature is quite different from the effect of reannealing below T_C. The DSC thermograms of the SC films reannealed at 140°C for various periods are shown in Fig. 5, and their melting temperature T_m and Curie transition temperature T_C are plotted in Fig. 6 as a function of reannealing time in logarithmic scale. The melting point increases with increasing reannealing time, and the T_C peak becomes broad, shifting to the lower temperature side. Since the Curie transition temperature range is spread rather widely as seen in Fig. 5, the transition temperature range defined by the width at half-maximum of the endothermic peak is shown with a dotted bar on each T_C plot in Fig. 6. The melting point increases by about 5°C from T_m (149°C) of the original SC film after reannealing for 340 h at 140°C. The heat of fusion ΔH_m of the SC film annealed at 140°C is shown in Fig. 7 as a function of reannealing time: the value of ΔH_m markedly increases with annealing time within 100 h, and reaches a constant value for a longer annealing time.

A prominent structural change was observed in the SC film reannealed for a long period. Fig. 8 shows the rocking curves of X-ray diffraction intensity of the 110/200 reflections at $2\theta = 20.0°$ for the original SC film and for the film reannealed for 340 h at 140°C. (In an unpoled P(VDF/TrFE) SC film, the axis perpendicular to the (110) or (200) plane of

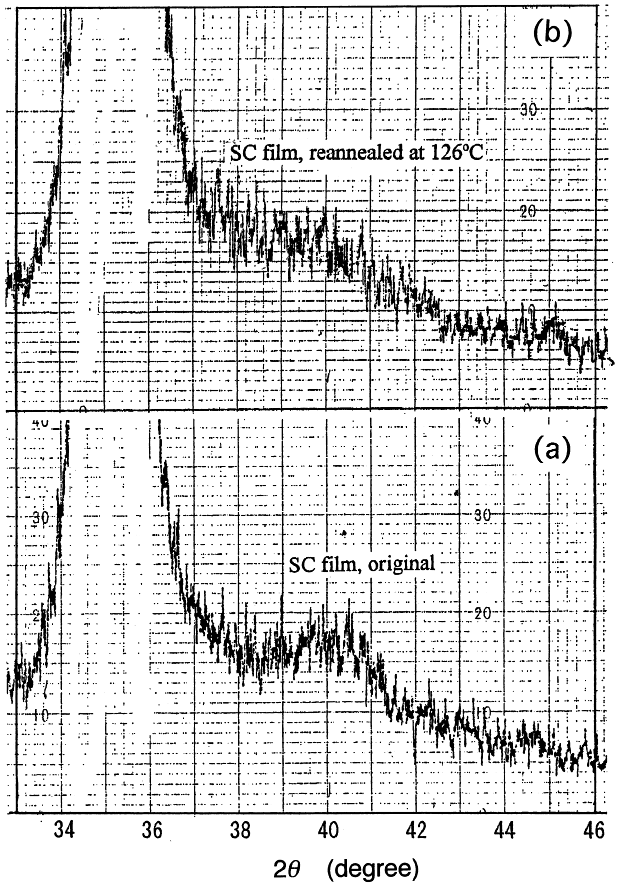

Fig. 4. X-ray diffraction profiles for (a) the original SC film, and (b) the SC film reannealed in the orthorhombic phase ($T_a = 126$°C). The scattering vector is scanned along the c^*-axis of the reciprocal lattice. For the original SC film, the peak intensity of the 001 reflection ($2\theta = 35.3$°) is about 300 times stronger than the diffuse scattering intensity at $2\theta \approx 40$°.

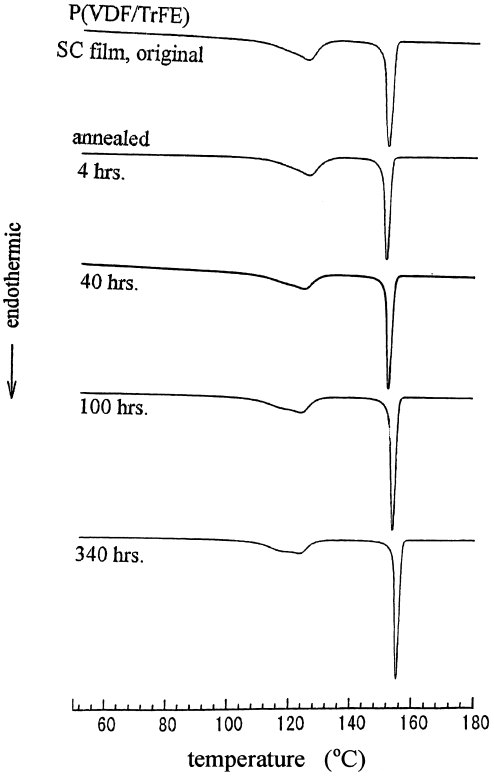

Fig. 5. DSC heating thermograms of the P(VDF/TrFE) (75:25) SC film reannealed in the hexagonal phase at 140°C for various periods. The reannealing period is shown on each thermogram.

an extended chain crystal orients to one of the six directions, i.e. the directions 0, ±60, ±120 and 180° from the film normal in the plane perpendicular to the stretching axis [13,31].) The rocking curves shown in Fig. 8 were obtained by rocking the scattering vector S around the 60°-direction from the normal of the film in the plane perpendicular to the stretching axis [30,31]. (ω in Fig. 8 is the angle between S and the normal to the film surface.) These rocking curves indicate that prolonged reannealing in the hexagonal phase makes the orientation distribution of the axes normal to the (110)/(200) planes much sharper. The full width at half-maximum (FWHM) ($\Delta\omega_{1/2\ 110/200}$) of the rocking curve becomes almost half as compared with that of the original SC film, whereas the FWHM of the orientation distribution of the [001] axis with respect to the stretching axis ($\Delta\chi_{1/2\ 001}$), which was also estimated from the rocking curve of the 001 reflection, is essentially unchanged by prolonged reannealing. (χ is the angle between the stretching axis and the [001] axis in the film plane.) The data obtained from the X-ray diffraction of SC films reannealed under various conditions are listed in Table 1. The crystal coherent lengths, $L_{110/200}$ and L_{001}, were estimated from the corrected linewidths of the 110/200 and 001 reflections, respectively.

4. Discussion

In an SC film of P(VDF/TrFE), there exist possibly two kinds of defects or irregular structures which affect its thermal behavior: one is those that may be removed by local motions of chain molecules, and the other is those that may be removed by displacement of chain molecules through some distance. The former may be such defects as conformational defects, domain boundaries, etc., and the latter may be, for example, kink bands, chain folding, various dislocations, etc. [15]. P(VDF/TrFE) copolymers, whose VDF content range is 65–82 mol%, exhibit large thermal hysteresis in Curie transition temperature; the Curie transition temperature in the cooling process ($T_C^{\downarrow}$) is much lower than that in the heating process ($T_C^{\uparrow}$). (For the P(VDF/TrFE) 75:25 mol%, $T_C^{\downarrow} = 57$–79°C, while $T_C^{\uparrow} \approx 124$°C [7]). Owing to large difference in the free energy between the hexagonal phase and orthorhombic phase at $T_C^{\downarrow}$, the phase transition in the cooling process proceeds very rapidly even if the film is cooled very slowly, and, therefore, TGTG′ sequences in the hexagonal phase are quenched partly in the orthogonal crystals as conformational defects. This is

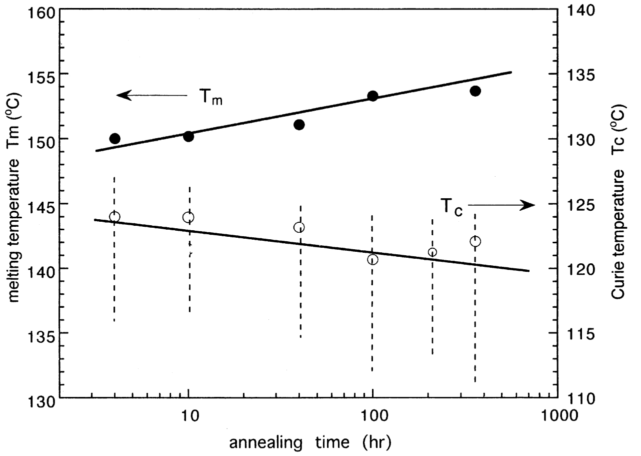

Fig. 6. Plots of the melting temperature T_m and Curie transition temperature T_C of the P(VDF/TrFE) SC film reannealed in the hexagonal phase (T_a = 140°C) as a function of annealing time.

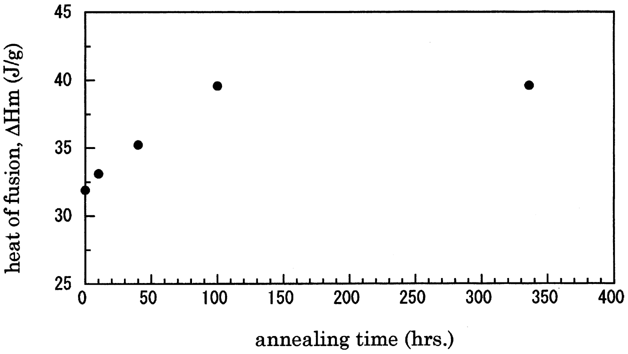

Fig. 7. Heat of fusion ΔH_m at T_m for the SC film reannealed in the hexagonal phase at T_a = 140°C as a function of reannealing time.

proved by the presence of diffuse X-ray scattering from the *gauche* chain sequences (Fig. 4(a)). Owing to a variety of these defects, which may arise from such differences as that in the length of the TGTG′ sequences, in local fluctuation of the VDF/TrFE ratio, etc., the phase transition temperature range is spread widely on heating, as can be seen in Fig. 1. These defects may be removed by reannealing at temperatures below 126°C. This prediction is proved to be valid by the disappearance of the X-ray diffraction from the TGTG′ sequences as shown in Fig. 4(b). The decrease in the conformational defect density will bring the growth of the domain size or a longer coherent length of X-ray diffraction. The X-ray coherent length L_{001} along the [001] axis is really longer for the SC film accumulatively reannealed at 126°C than for the original SC film (Table 1). A similar result has been reported by Kim et al. [24]. (The coherent length $L_{110/200}$ cannot be estimated correctly, because the line shape of the composite 110/200 reflections is considerably broadened by the difference in lattice spacings of the (110) and (200) planes [31].) As shown in Table 1, the width of the orientation distribution, $\Delta\omega_{1/2\ 110/200}$ is unchanged by the accumulative reannealing when T_a is below 130°C, which indicates that the displacement of chain molecules in the orthorhombic phase occurs within very limited regions.

The effect of reannealing in the hexagonal phase is very different from the effect of reannealing in the orthorhombic phase. As described before, chain molecules in the hexagonal phase are very mobile along their chain axis. Diffusive chain motions along the chain axis will rearrange chain arrays to make more stable packing in the hexagonal crystal, eliminating such various crystal defects as kink bands, chain folding, chain entanglements, stacking faults, and dislocations, which results in a lower free energy of the hexagonal phase and, consequently, a higher melting temperature T_m. Several experimental results supporting the rearrangement of chain molecules, which become prominent in the SC film reannealed for periods longer than 100 h, are as follows: (1) the preferential orientation distribution of the axes normal to the (110)/(200) planes becomes much sharper compared to the distribution in the original SC film (Fig. 8; Table 1); (2) the coherent length L_{001} is much longer than that for the SC film reannealed in the orthorhombic phase (Table 1); and (3) both T_m and ΔH_m increase with increasing reannealing time (Figs. 6 and 7).

Annealing effects on the phase transition behaviors in the SC film of P(VDF/TrFE) are most easily understood by using the Gibbs free energy diagram for the orthorhombic, hexagonal and liquid phases. A schematic representation of the Gibbs free energy against temperature is shown in Fig. 9(a) and (b) for the SC films reannealed in the orthorhombic phase, and in the hexagonal phase, respectively. The free energy G_i at pressure P and temperature T is defined by

$$G_i = U_i + V_iP - S_iT,$$

where U_i, V_i and S_i are the internal energy, volume and entropy per unit mass, respectively, and suffix i represents the orthorhombic (i = o), hexagonal (i = h), or liquid phase (i = m). For simplicity, the free energy for each phase is expressed by a straight line.

When the film is reannealed in the orthorhombic phase, only G_o shifts downwards because reannealing in the hexagonal phase reduces the concentration of chain conformational defects only, and leaves G_h unchanged. In this case, T_C, at which $G_o = G_h$, shifts upwards, but T_m, at which $G_h = G_m$, remains constant.

The reannealing in the hexagonal phase for a long period shifts the free energy of the hexagonal phase downward as discussed above, which necessarily increases T_m. At the same time, the free energy G_o may also decreases to some extent because of the reduced number of crystal defects, even though a comparative number of chain conformational defects are still included as in the original SC film. Therefore, the T_C of the SC film reannealed in the hexagonal phase may depend on the extent of decrements in G_o and G_h. The observed T_C slightly decreases with increasing annealing time, which indicates that the decrement in G_h is larger than that in G_o. The broadened DSC peak of the SC films

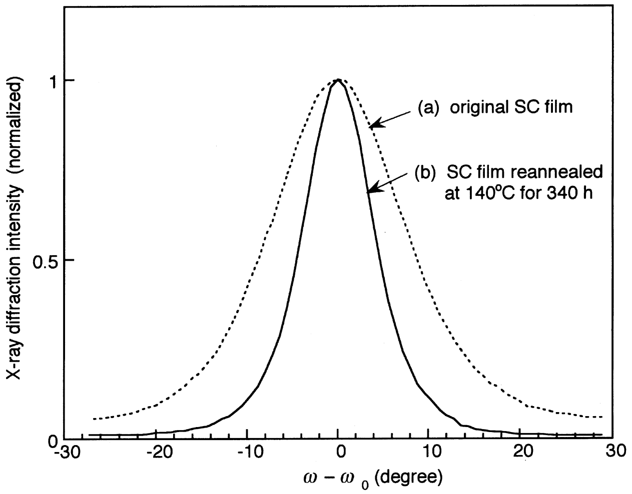

Fig. 8. Angular distribution (rocking curve) of X-ray diffraction intensity of the 110/200 reflections for (a) the original SC film, and (b) for the SC film reannealed in the hexagonal phase at 140°C for 340 h. The X-ray scattering vector S ($2\theta = 20.0°$) is scanned as a function of ω in the plane (a^*b^* plane) perpendicular to the stretching axis, where ω is the azimuthal angle between S and the normal of the film surface ($\omega_0 = 60°$).

annealed in the hexagonal phase (Fig. 5), however, suggests that there is a rather wide distribution in G_o, probably because of various defects included in the crystals.

As shown in Fig. 2, the Curie temperature T_C increases almost linearly with increasing annealing temperature T_a. It is noted that the maximum T_C attainable by accumulative reannealing in the orthorhombic phase (140.4°C) equals the cross-point of the observed T_C-versus-T_a plots and the virtual line of $T_C = T_a$ (see Fig. 2). This behavior is very similar to the Hoffman–Weeks plots often used to estimate the thermal equilibrium melting point [32]. Therefore, we may regard $T_C = 140.4°C$ as the equilibrium phase transition temperature or Curie transition temperature of the P(VDF/TrFE) (75:25) crystal.

The above-mentioned equilibrium phase transition temperature is very high compared with the T_C generally observed in this copolymer: the Curie temperature T_C of the original film was observed to increase up to 131°C after it was poled by applying a high electric field. For the SC film having a T_C peak higher than 131°C, the T_C peak and $T_{C'}$ peak, which appeared at a lower temperature than 125°C, coalesced into a single peak around 131°C, as reported in previous papers [22,23]. Considering that poling treatment eliminates almost all TGTG$'$ defects in the crystal, it seems unreasonable to attribute the presence of such high T_C as 130–140°C to crystal perfection. To discuss the Curie transition temperature of ferroelectric polymer crystals we have to take into account the additional free energy, which includes the polarization energy, domain wall energy, and depolarization energy. The increase in T_C in the temperature range higher than ca. 130°C is most probably attributable to the formation of ferroelectric domains (180° domains or 60° domains) to minimize the additional free energy [22,23]. The crystals or crystal regions that have missed forming such stable domains have a phase transition temperature $T_{C'}$ much lower than T_C. For such crystal regions, the reannealing at a temperature just below T_C is really the reannealing in the hexagonal phase. The decreased orientation distribution width $\Delta\omega_{1/2\ 110/200}$ observed for the SC film reannealed at 132°C (Table 1) is a result of reannealing in the hexagonal phase. The lower phase transition temperature $T_{C'}$ increases with increasing reannealing temperature, the reason for which is still unclear.

The melting point of well-crystallized P(VDF/TrFE) of 75:25 mol% ratio is around 150°C [7,9,16–18]. The present study shows that the melting point is increased up to 154°C by prolonged annealing in the hexagonal phase. Recently we also showed that the melting point of the SC film of P(VDF/TrFE) (75:25) is further increased up to 157°C by reannealing under high pressure at high temperature (400 MPa, 290°C), where the film is still in the hexagonal phase [33]. These facts suggest that a polymer crystal, in general, would potentially exhibit a melting point much higher than that presently accepted, if various defects in the crystal could be removed.

5. Conclusions

In this paper we investigated the reannealing effect on the Curie transition temperature T_C, melting temperature T_m,

Table 1
Coherent length (L) of crystals and their orientation distribution ($\Delta\omega_{1/2}$) in the P(VDF/TrFE) SC film reannealed under various conditions

	SC film (reannealing condition)		$L_{110/200}$ (nm)	L_{001} (nm)	$\Delta\omega_{1/2\ 110/200}$ (°)	$\Delta\chi_{1/2\ 001}$ (°)
A	Original SC film		12.7	12.9	16.6	6.4
B	Reannealed in orthorhombic phase					
	T_a (°C)	110°C	13.1	12.7	16.0	6.4
		124°C	13.5	19.3	17.0	6.3
		126°C	13.0	20.1	16.6	6.2
		128°C	11.1	15.2	18.6	6.3
		132°C	12.7	18.8	13.6	7.2
C	Reannealed in hexagonal phase					
	140°C, 340 h		13.9	22.1	9.2	7.9

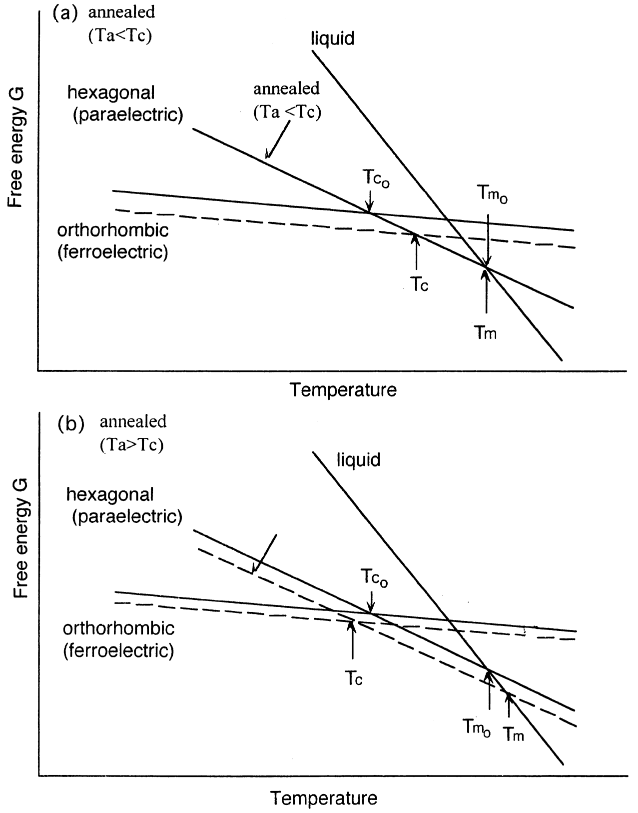

Fig. 9. Schematic representation of the Gibbs free energy diagram for the SC film of P(VDF/TrFE) as a function of temperature for explaining the annealing effects on T_C and T_m: (a) the SC film reannealed in the orthorhombic phase, and (b) the SC film annealed in the hexagonal phase. T_{C_o} and T_{m_o} are the phase transition temperature and the melting temperature, respectively, of the original SC film.

and structures of the P(VDF/TrFE) (75:25) SC film. The reannealing in the hexagonal phase (140°C), where the chain molecules are very mobile along the chain axis, improves the chain arrangement and removes the defects in the hexagonal crystals through the sliding motion of the chains. Owing to such an annealing effect, the melting point increases considerably, and the preferential orientation distribution of the axes normal to the (110)/(200) planes becomes very sharp.

The reannealing in the orthorhombic phase at temperatures below T_C, where only the local motions of the chain molecules are permissible, removes the *gauche* defects in the molecular chains, which results in an increase in T_C, but leaves the melting temperature essentially unchanged. The highest T_C attained by the accumulative annealing is 140.4°C. For explaining such a high Curie transition temperature, the mechanisms for stabilization of the crystal, that is, the formation of domains, must be taken into consideration.

Elimination of crystal defects in the P(VDF/TrFE) SC film by annealing in the hexagonal phase is expected to improve its mechanical and piezoelectric properties. A preliminary experiment really showed that the SC film reannealed in the hexagonal phase for a long period and then poled in the orthorhombic phase has the Young's modulus along the chain axis much higher than that of the poled original SC film. The detailed results will be reported in the near future.

Acknowledgements

We thank Daikin Industries, Ltd for kindly supplying P(VDF/TrFE) copolymers. This work was supported in part by Grants-in-Aid for Scientific Research (No. 08455448 and No. 10450357) from the Ministry of Education, Science, Sports and Culture, Japan.

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