Formation of Unoriented Form I Poly(vinylidene fluoride) by High-Rate Quenching and its Electrical Properties

Yoshio OKA and Naokazu KOIZUMI

Unoriented form I poly (vinylidene fluoride) (PVDF) was found to be produced by high-rate quenching from the melt coexisting with form II of a common crystalline form in melt-crystallization. A content of form I in the crystallin region could be as much as 90% in a well-quenched sample and a content ratio of forms I and II remained unchanged by further annealing. A critical quenching rate to produce an appreciable amount of the form I crystal was found to be $800°Cs^{-1}$. It is proposed as a formation mechanism of form I based on nucleation kinetics that high-rate quenching favors a low-temperature nucleation process in which form I nuclei are predominantly generated. Poling of the quenched sample induced large pyroelectricity while heat-treatment to grow form I crystal before poling suppressed the formation of the pyroelectricity. In the quenched and poled sample a simultaneous poling and crystallization process caused the alignment of the new crystallites along the field leading to a high spontaneous polarization.

I. INTRODUCTION

Poly (vinylidene fluoride) (PVDF) has been extensively studied both experimentally and theoretically since the discovery of strong piezo-[1] and pyroelectricity[2] in poled uniaxially drawn PVDF consisting of the form I crystal. The strong piezo- and pyroelectric activities are related to a large spontaneous polarization due to the alignment of C-F dipoles in the crystalline region perpendicular to the film plane in a high electric field. Therefore, the most favorable chain conformation to produce a high spontaneous polarization in PVDF is considered to be an all-trans or a planar zigzag conformation of the form I crystal. However, PVDF is a semicrystalline polymer which shows many crystalline polymorphs being refered to as forms I, II, IIp and III or β, α, δ and γ phases, respectively. The crystalline structures of these polymorphs are depicted in Fig. 1. Form I has a chain conformation of slightly deflected all-trans and the chains are so packed that all the dipoles in the unit cell point in the b-axis direction.[3] The component of the dipole moment of the form I crystal perpendicular to the chain axis is calculated to be 6.9×10^{-30} Cm (2.1 D), which produces the spontaneous polarization of 132 $mCm.^{-2}$ At present the form I crystal is regarded as a ferreolectric crystal.[4] As is seen in Fig. 1, both forms II and IIp have the same chain conformation of trans-gauche-trans-gauche' (TGTG') and the difference between the two forms is the way of packing the chains in the unit cell.[3,5] That is, the chains are packed in an anti-

---

岡与志男, 小泉直一 : Laboratory of Dielectrics, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

I (β)　　　　　　　Ⅱ (α)

Ⅱp(δ)　　　　　　　Ⅲ (γ)
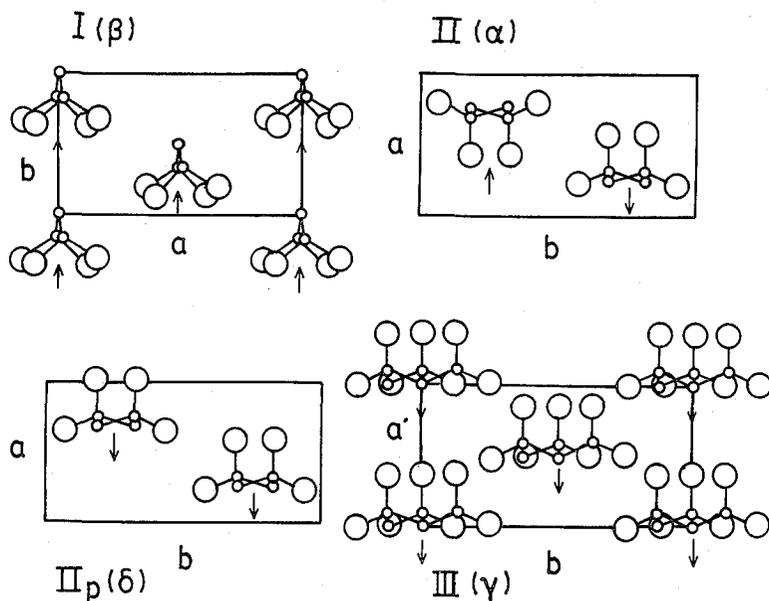
Fig. 1. Crystal structures of PVDF for forms I, II, IIp and III projected along the c-axis. Large circles are fluorine atoms and small circles carbon atoms. The arrow indicates the direction of dipoles.

parallel array along the a-aixs in form II so that the dipole moments cancel out in this direction resulting in an antipolar crystal with no net polarization while in form IIp the chains are packed in a parellel array along the a-axis resulting in a polar crystal. The component of the dipole moment of form IIp crystal perpendicular to the chain axis is approximately 60% of that of form I. Form III is a less-common crystal polymorph with a chain conformation of T_3GT_3G' and the chains are packed parallel to the a-axis resulting in a polar crystal.[6]

Form II is the most common crystalline form in a melt-crystallization process of PVDF, which is easily obtained by just cooling the melt. Form IIp is derived from form II by poling in a high electric field in excess of 100 MVm^{-1}.[5] Form III is a high-temperature phase which is transformed from form II by annealing around 170°C for a prolonged time or is produced directly from the melt by slow cooling and annealing.[7] Form I is normally obtained in an oriented form by deformation of form II which is performed by stretching uniaxially to more than four times the original length below 120°C.[8] Unoriented form I is obtained by the high-pressure quenching method in which the melt is solidified instantaneously by applying high pressure.[9] Also unoriented form I can be transformed from form II through form IIp by applying an extremely high field of 500 MVm^{-1}.[5] The overall phase relation of the four polymorphs based on a melt-crystallization process is summarized in Fig. 2.

As described above, the crystal form obtained by cooling the melt had been believed to be exclusively form II until quite recently Hsu and Geil observed independently of us the formation of the crystalline form different from form II in the ultra-quenched sample. They succeeded to obtain the completely amorphous PVDF by quenching thin
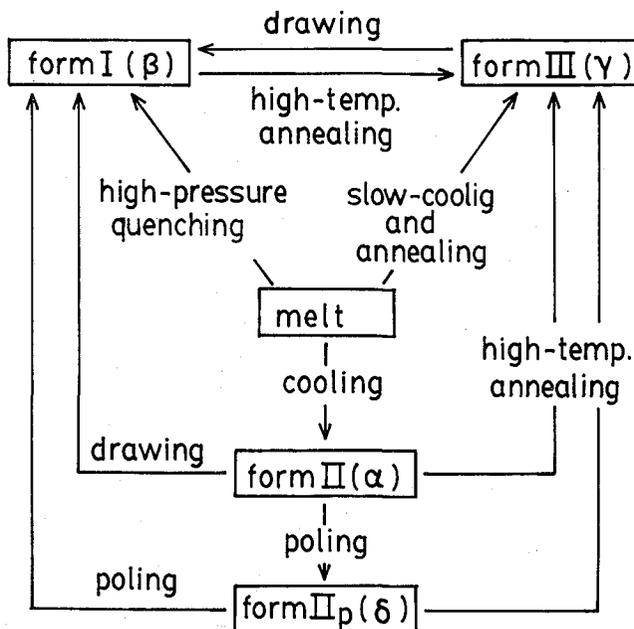
Fig. 2. Phase relation of PVDF in a melt-crystallization process.

films of less than 1000 Å thick into −160°C using either isopentane or Freon 12 as quenchant and observed the developement of a new crystal as raising temperatute to room temperature. They presumed the new crystal to be form I from the lattice spacings observed by x-ray diffraction. Thus form II is not a unique crystal form produced by cooling the melt at atmospheric pressure.

In the present study, the high-rate quenching method was employed in the melt-crystallization of PVDF and the form I crystal was found to coexist with form II in the quenched sample. The quenching conditions to obtain form I were examined. The mechanism to produce form I by high-rate quenching is discussed based on the nucleation rate concept. The quenched sample thus obtained was subjected to simultaneous poling and crystallization at elevated temperatures and rather high pyroeletric activity for unoriented PVDF resulted.

II. EXPERIMENTAL

PVDF samples were supplied from Daikin Kogyo Co., Ltd. and KF200 from Kureha Chemical Industry Co., Ltd. Powder samples were heat-pressed at 250°C into films of thickness 10 to 15μm, and were subjected to the following quenching procedure. The film was again heat-pressed on an Al foil of thickness 15μm as a support, and the Al foil carrying the film on it was held between annular frames in order to expose the film in the center of the frames. The brass frames were heated to 220°C in a heat press and was plunged rapidly into ice water. In this manner a high-quenching rate was attained because the film came into contact directly with the quenchant on one side and through the 15 μm Al foil on the other side when quenching. The quenched film was then immersed in a cold sodium hydroxide solution to remove the Al foil.

A quenching rate was altered by using Al plates of different thickness to sandwitch the film instead of an Al foil. Relative quenching rates were measured as follows. A chromel–alumel thermocouple of 50 μm diam was mounted in a sample film of ～100 μm thick, and the film was sandwiched by Al foils or plates of different thickness for different quenching rates. The Al foils or plates sandwitching the film were subjected to the above-mentioned quenching procedure, that is, they were placed between the brass frames and were heated to 220°C followed by plunging into ice water. The temperature change in quenching was measured by recording an emf change of the thermocouple mounted in the sample with a Nicolet model 2090 didital oscilloscope.

IR spectra were obtained with a Hitachi model 260-50 infrared spectrometer and x–ray diffraction patterns with a Rigaku RU 200 x–ray diffractometer using monochromatized CuKα radiaton.

Poling of the sample film was performed as follows. An Al electrode was vacuum evaporated onto both surfaces of the film. The film was placed in an electrode designed for a thermally stimulated current (TSC) measurement. Biased a dc field E_p at room temperature, the sample was then heated up to a desired temperature T_p and kept at T_p for a certain time, followed by rapid cooling to room temperature before swiching off E_p where the poling time t_p was taken from applying E_p to just before cooling. The poled sample was subsequently heated to T_p to depolarize an irreversible polarization such as a space charge polarization. After eliminating the irreversible polarization, only reversible currents were measured upon heating and cooling. This current arises from
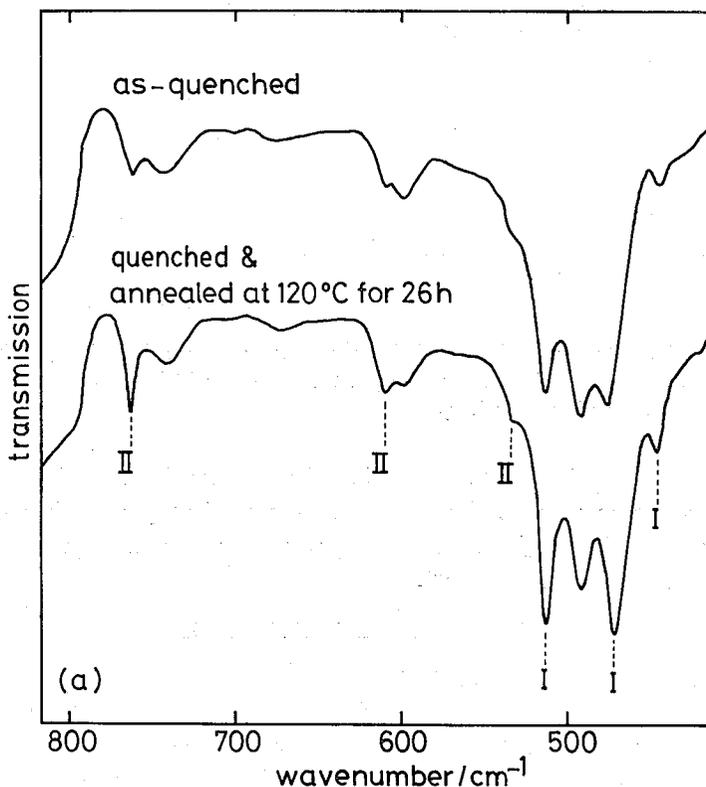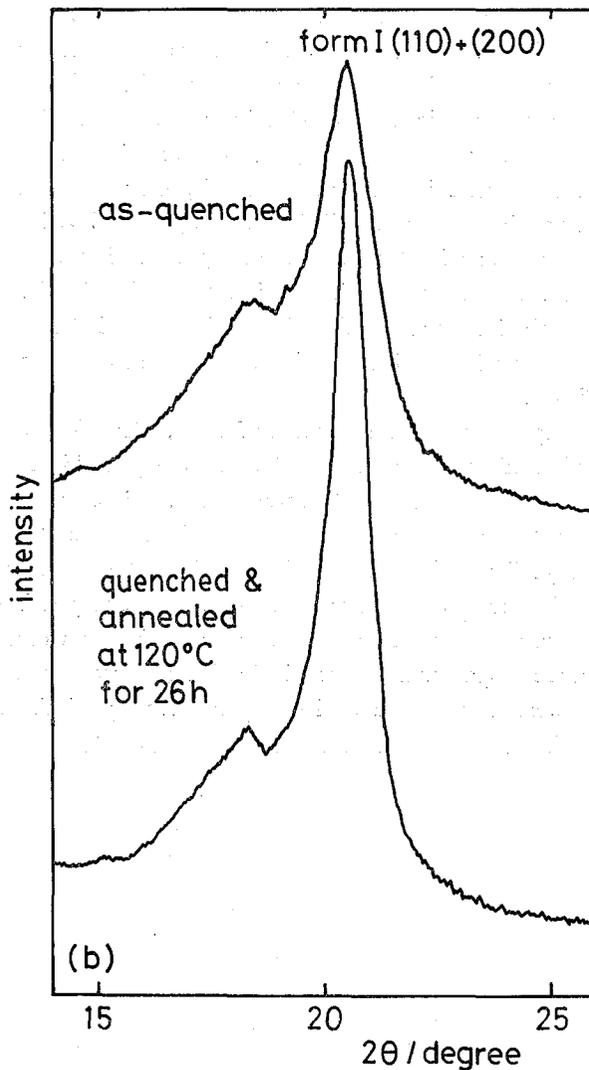
Fig. 3. IR spectra (a) and x-ray diffraction patterns (b) for PVDF crystallized by
the present high-rate quenching method; as-quenched and annealed at 120°C
for 26 h after quenching.

a temperature change of a spontaneous polarzation induced by the poling procedure and
is called a pyroelectric current. The pyroelectric coefficient p was obtained from the
pyroelectric current density j and the heating rate β through the equation $p = j/\beta$. The
heating rate was fixed at 3.3 Kmim^{-1}.

III. RESULTS AND DISCUSSION

3-1 Crystalline phases of quenched PVDF

Figure 3 shows IR spectra and x-ray diffraction patterns for PVDF samples sub-
mitted to the present quenching procedure and also to subsequent annealing at 120°C
for 26 h. In the IR spectrum of the as-quenched sample the bands at 762, 612 and

535 cm^{-1} are assigned to the crystalline bands characteristic of form II which is expected to be present in a melt-crystallized sample. It is noticed that in the IR spectrum of the as-quenched sample the new bands other than those for form II are observed at 512, 478 and 445 cm^{-1}, indicating that the quenched sample consists of at least two crystalline phases. The new bands can be assigned to those for form I according to the detailed IR study on PVDF by Kobayashi et al.[11]

The x-ray diffraction pattern for the as-quenched sample has a strong peak at $2\theta =$ 20.6° and a broad one around $2\theta = 18°$. The peak at 20.6° can be assigned to the unresolved (110) and (200) reflections of form I and the broad one around 18° may be mainly amorphous scattering and partly the (110) and (020) reflections of form II. Heat treatment of the quenched sample makes the crystalline components in the IR and x-ray figures become clearer as is seen from the changes in the IR spectra and the x-ray diffraction patterns due to annealing. That is, the IR bands for both forms I and II crystals became larger after annealing and correspondingly the x-ray peak of form I (110, 200) stronger and sharper. Also the amorphous scattering around 18° in the x-ray patterns became smaller indicating the reduction of an amount of the amorphous region. The annealing effect will be described in detail in the next section.

It shoud be checked whether form I is the only polymorph coexisting with form II obtained by high-rate quenching. PVDF shows two more polymorphs, forms IIp and III, other than forms I and II. Form IIp is exclusively obtained from form II by high-
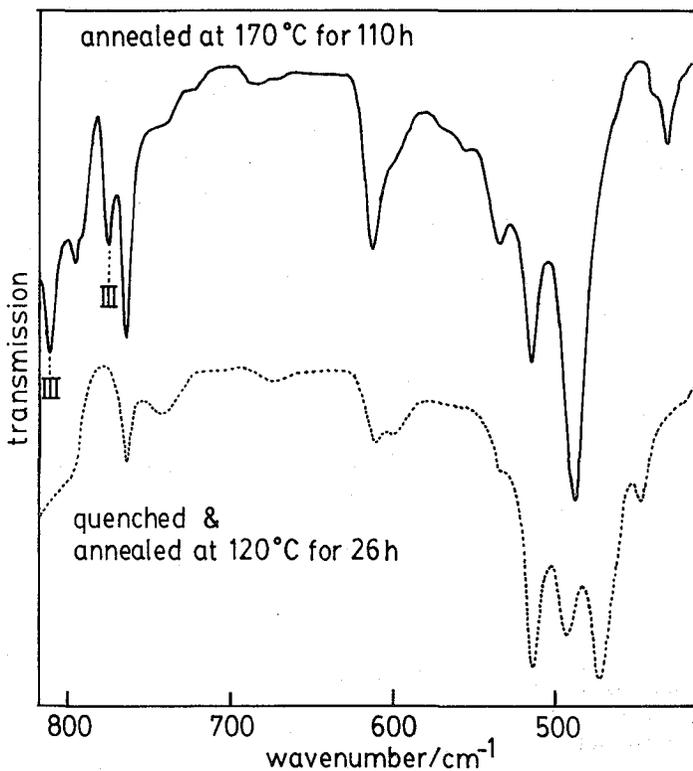
Fig. 4. IR spectra for PVDF containing form III crystal crystallized by high-temperature annealing (solid line) and qenched and annealed sample in Fig. 3 (broken line).

field poling and so the presence of form IIp is ruled out. The presence of form III is considered to be possible in the melt-crystallization process. In order to examine the presence of form III in the quenched sample, the IR spectrum of the quenched and annealed sample in Fig. 3 is compared with that of the sample containing form III which was prepared by annealing at 170°C for 110 h as shown in Fig. 4. The IR spectrum of the long-annealed sample consists of the crystalline bands for both forms II and III and the bands at 775 and 811 cm^{-1} are characteristic of form III[12] which are well separated from other bands. As is seen in Fig. 4, the IR spectrum of the quenched and annealed sample has no sign of the presence of form III because the 775- and 811-cm^{-1} bands are definitely missing. Therefore, the presence of form III is ruled out in the quenched sample and form I is confirmed to be a unique crystalline phase coexisting with form II.

3-2 Crowth of crystalline region in quenched PVDF by annealing

In order to obtain the rate of growth of the crystalline region in the quenched
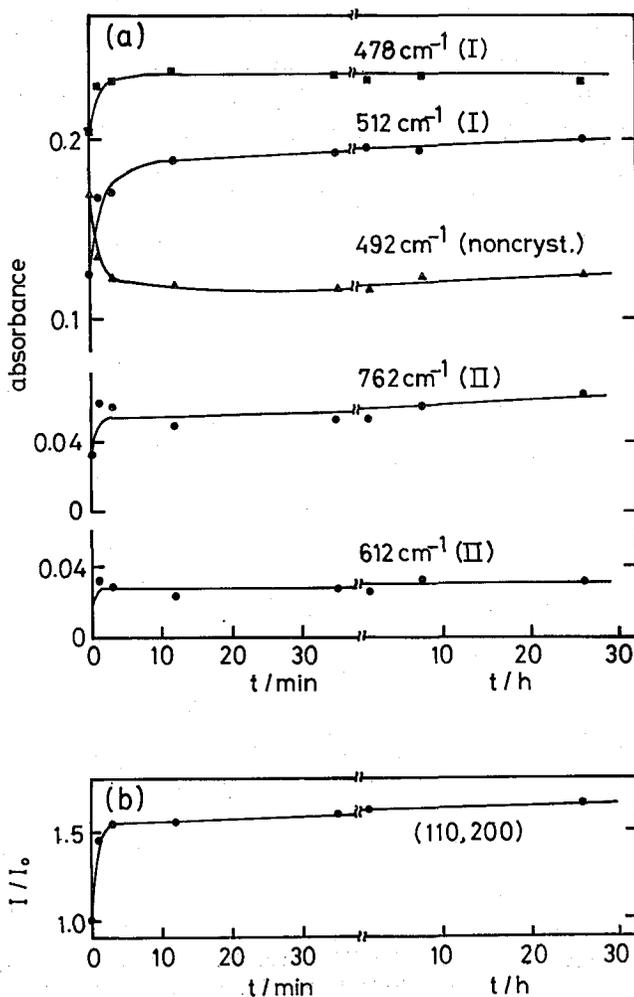
Fig. 5. Time dependence of IR absorbances (a) and x-ray peak intensities (b) by annealing at 120°C for quenched PVDF.

sample by annealing, IR and x-ray measurements were carried out on a sample which was quenched and subsequently annealed at 120°C. The changes in the relative absorbances of the IR bands and the x-ray peak intensity of (110, 200) reflection with annealing time are presented in Fig. 5. As shown in Fig. 5a, the absorbances of the crystalline bands at 478 and 512 cm^{-1} for form I increase sharply in 4 min and tend to saturate after 12 min annealing. The same result was obtained for the 612-cm^{-1} band which is characteristic of form II. On the other hand the absorbance of the 492-cm^{-1} band decreases with annealing time in contrast to the increase of the crystalline bands. It is also noted that the decrease of the 492-cm^{-1} band is well related to the increase of the crystalline bands. This band is assigned by Kobayashi et al.[11] mainly to the gauche form in the noncrystalline region and hence the decrease in its absorbance by annealing is consistent with the band assignment. The change in the intensity of the x-ray (110, 200) peak for the quenched sample by annealing shown in Fig. 5b is well corresponding to the results of the IR study. That is, the growth of the peak was almost completed in 4 min annealing at 120°C and the small increase in the peak intensity was observed by further annealing.

The reduction of the amount of amorphous region can be estimated quantitatively by observing the change in TSC peak areas of the primary dispersion for a quenched sample before and after annealing. For this purpose a TSC peak of the primary dispersion for the as-quenched sample is compared with that after annealing at 140°C for 20 h as shown in Fig. 6, where the sample was conditioned under 20 MVm^{-1} at room
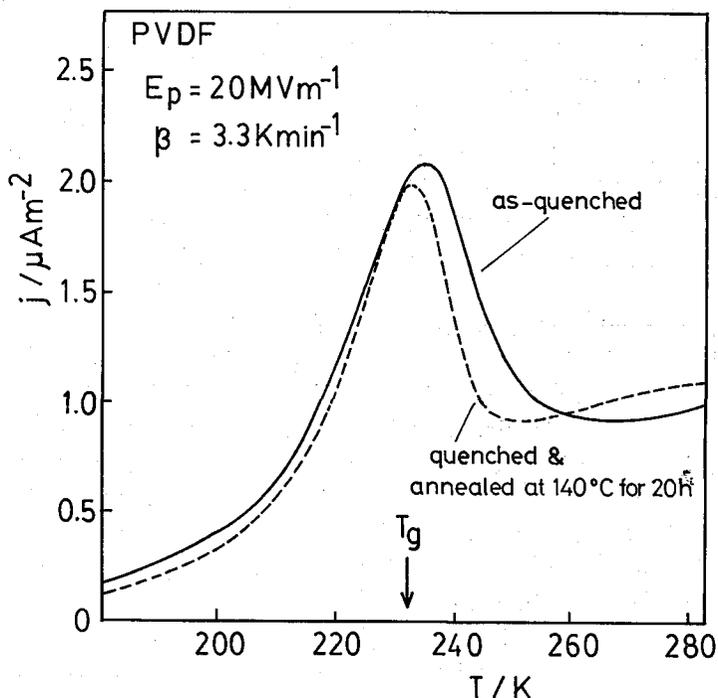
Fig. 6. TSC spectra for annealing effect of qeunched PVDF in the region of a primary dispersion; as-quenched (solid line) and quenched and annealed at 140°C for 20 h (broken line).

Table I. Change in $F(I)$ by succesive annealing for quenched PVDF with different initial form I contents

Annealing Condition	Sample 1	$F(I)$ Sample 2	Sample 3
As-quenched	0.85	0.61	0.43
60°C, 35h	0.85	0.65	0.43
90°C, 36h	0.86	0.64	0.40
140°C, 20h	0.86	0.64	0.42

temperature. The peak became smaller and narrower and shifted slightly to lower temperature as a result of annealing. The peak area of the primary dispersion is proportional to an amount of the amorphous region because the primary dispersion originates from the dipoles in the amorphous region only. The peak area for the as-quenched sample is estimated to be 1.4 mCm^{-2} and is reduced to 1.1 mCm^{-2} after annealing. Thus, 22% of the amorphous region was converted to the crystalline region by annealing.

As described above, a sample obtained by the present quenching method consists of two crystalline phases, forms I and II. The fraction of the amount of form I $F(I)$ in the total amount of forms I and II can be determined by using the absorbances of the bands at 512 cm^{-1} D_{512} and 535 cm^{-1} D_{535} characteristic of forms I and II, respectively, through the equation of $F(I) = D_{512}/(D_{512} + 0.81D_{535})$ proposed by Osaki et al.[7] The above equation has originally been introduced to determine the form III content in the system of forms II and III and is also applicable for the system of forms I and II in the present study.[13] The form I content was as much as 90% in a well-quenched sample estimated by the above method. Changes in $F(I)$ by annealing was examined for samples with different initial form I contents as altering annealing conditions and the results are listed in Table I. $F(I)$ remains unchanged with the crystal growth by annealing within an experimental error for the samples with different initial form I contents indicating that the two crystalline phases develop by annealing at nearly the same rate.

3-3 Formation mechanism of form I by high-rate quenching

Quenching rates in the present quenching method were measured with sample films sandwitched by Al foils or plates of different thickness to obtain various quenching rates and the results are shown in Fig. 7. It is noted that all the temperature vs time curves or the quenching curves in Fig. 7 have a point where slopes are changed, namely the slope becomes steeper passing through the point. The reason for the slope change is considered as follows. Immediately after the sample film sandwitched by Al supports is plunged into ice water, the quenchant of water is evaporated around the Al supports to deteriorate thermal transfer from the film to the quenchant and when the water vapor is condensed at the point of changing slopes the Al supports come into direct contact with the ice water resulting in high-rate thermal transfer. That is to say, the vaporized water generated just after quenching deteriorates high-rate quenching. Formation of form I was clearly observed when Al plates of less than 100μm were used and the thinner the Al plate the higher was the form I content. From the quenching
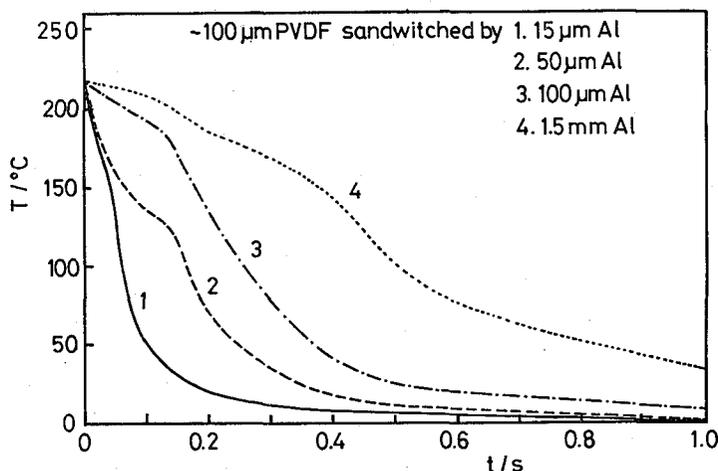
Fig. 7. Temperature vs time curves in a process of quenching from 220°C for~100 μm thick PVDF sandwiched by Al foils or plates of thickness 15 μm (curve 1), 50 μm (curve 2), 100 μm (curve 3) and 1.5 mm (curve 4).

curves in Fig. 7, an effective rate to obtain form I is estimated to be more than 800 $°Cs^{-1}$ and the highest rate to be $4000°Cs^{-1}$. It is noted that the sample film used in the rate measurements was about 100 μm thick which was thicker than those of 10 to 15 μm thick used for the IR and x–ray studies and so the rates observed are considered to be much or less slower than those for the thinner films.

Two possible causes are considered for a formation mechanism of form I, i. e., a stress and high–rate quenching. A stress which is generated in an interface between a sample film and an Al support at solidiflcation of the sample due to mismatch of the thermal expansions may play a role on the form I formation because form I is transformed from form II in a strained state. However, this is not the case because quenching without using an Al support or in a sress–free condition also resulted in substantial formation of form I. Accordingly a formation mechanism of form I is discussed on the basis of high–rate quenching and a nucleation rate concept. A nucleation rate for form II may have a maximum around 140°C where a crystallization temperature of form II is located in a DSC thermogram and that for form I is assumed to have a maxium somewhere below 140°C. Based on the above supposition, a schematic diagram of the relation betweeen nucleation rate and temperature for forms I and II is illustraited in Fig. 8, where the nucleation rate vs temperature curves have a maximum at T_I and T_{II} for forms I and II, respectively. A nucleation rate of form I has a significant magnitude in the temperature region between T_1 and T_2 centered at T_I and that for form II in the region between T_3 and T_4 centered at T_{II}. To explain the formation mechanism of form I by high–rate quenching, Fig. 9 again shows the temperature vs time curves for fast and slow quenching with the above-mentioned temperature regions of nucleation for forms I and II. In the case of slow quenching a time for a sample to pass through the region from T_3 to T_4, indicated as t_{II} in Fig. 9, is long enough to complete the nucleation of form II and there is no room in a sample for the nucleation of form I in
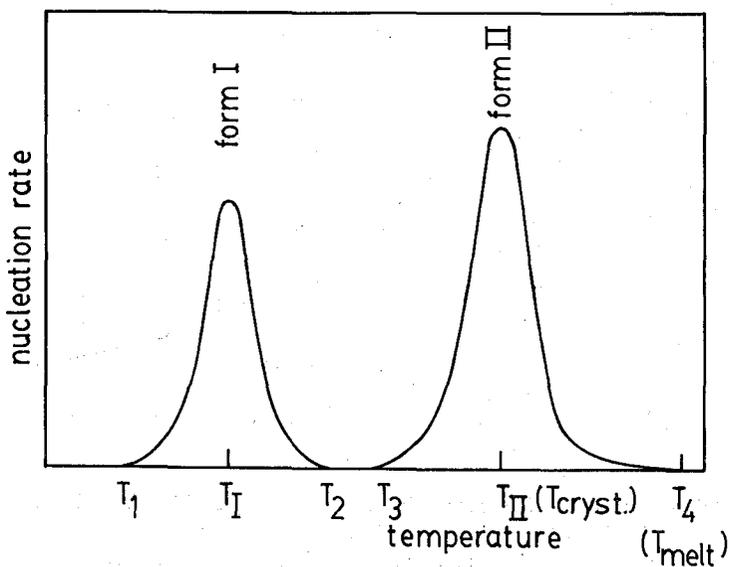
Fig. 8. A schematic illustration of temperature dependence of nucleation rate for forms I and II PVDF.
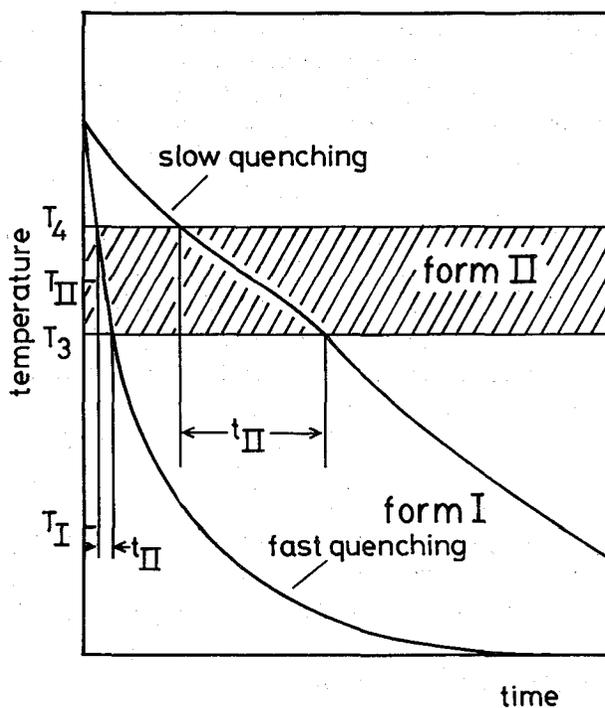
Fig. 9. A schematic diagram of quenching curves for slow and fast processes. The hatched region indicates a temperature range for nucleation of form II crystal.

the region from T_1 to T_2, and consequently a single crystalline phase of form II results. On the other hand, in the case of fast quenching a time to pass through the region from T_3 to T_4 is too short for the nucleation of form II to occur in an appreciable amount and the nucleation mainly proceeds in a low temperature region leading to form I-rich crystal. Therefore, the content ratio of forms I and II in the crystalline region is determined by the time of passing through the region from T_3 to T_4 when cooling the sample from the melt. Thus the low-temperature nucleation is regarded as a main mechanism for the formation of form I by high-rate quenching. This is also supported by the finding made by Hsu and Geil that crystallization directly from glassy state as raising temperature to room teperature in PVDF produces form I crystal.[10]

3-4 Pyroelectricity in quenched PVDF by simultaneous poling and crystallization

Poling procedure on samples containing form I polar crystal render a spontaneous polarization due to realignment of dipoles in the crystalline region along an electric field and thus the samples become piezo- and pyroelectric. The as-quenched sample in this study has a high content of form I in the crystalline region and hence a large
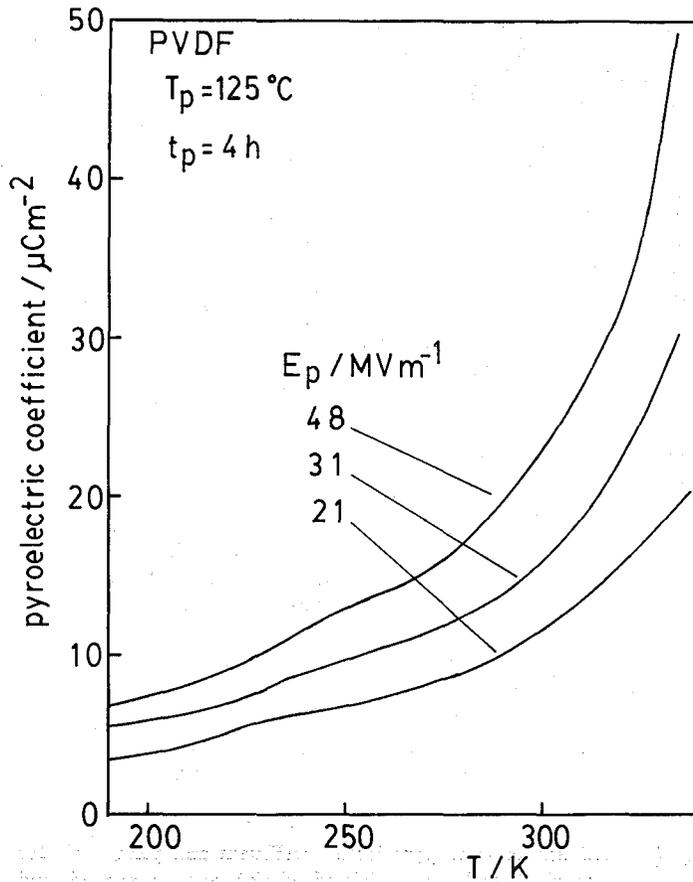
Fig. 10. Pyroelectric coefficient vs temperature curves for quenched
PVDF poled at 125°C for 4 h under 21, 31 and 48 MVm⁻¹.

spontaneous polarization is expected to be induced by a method of forming thermoelec-
trets or poling at high temperatures. Actually high-temperature poling produced the
pyroeletricity in the quenched sample as shown in Fig. 10, where temperature depend-
ence of a pyroelectric coefficient for the samples poled in various flelds at 125°C for
4 h is presented. The pyroelectric coefficient increases monotonically with increasing
temperature like that in ordinary pyroelectric polymers. Figure 11 shows the relation
between a poling field and a pyroelectric coefficient at 25°C for the quenched sample
and the sample of quenched and annealed at 130°C for 10 h before poling with other
poling conditions being fixed as $T_p=125°C$ and $t_p=4$ h. It should be noted that the
quenched and poled sample exhibits rather strong pyroelectricity while the sample sub-
mitted to annealing before poling exhibits considerably small pyroelectricity. Concerning
an amount of form I crystal, the annealed sample may have a larger amount than the
quenched and poled sample because the former was conditioned by annealing at the
temperature higher than the poling temperature. Suppose the pyroeletric activity is
propotional to an amount of the form I crystal, the annealed sample should have a
larger pyroelectricity than the quenched and poled sample but the results in Fig. 11 are
opposite. To clarify the discrepancy, the following polarization mechanism is put forth
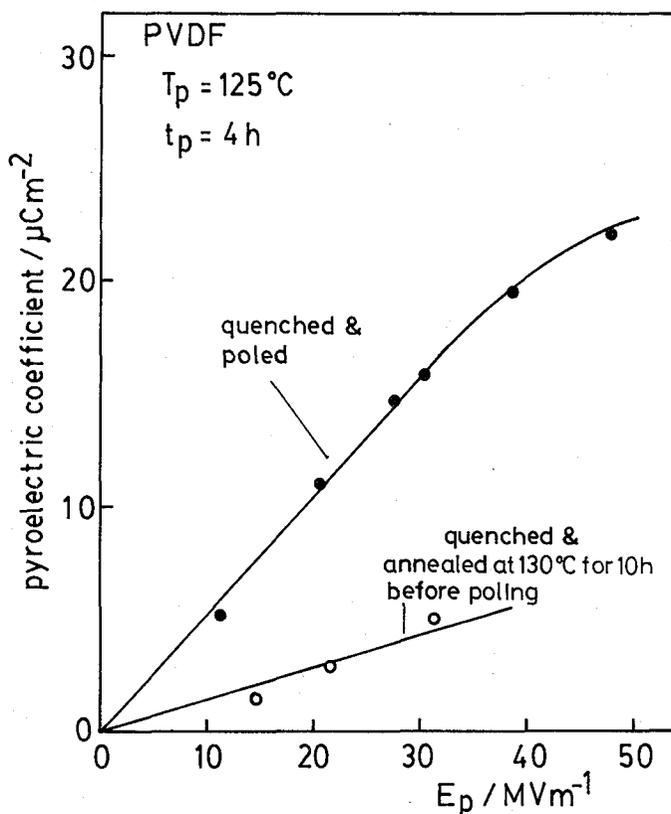
Fig. 11. Relation between pyroelectric coefficient and poling field for
quenched and poled (closed circle) and quenched and
annealed at 130°C for 10 h before poling (open circle);
$T_p=125$ °C and $t_p=4$h.

making use of the formation mechanism of the pyroelectricity in polytrifluoroethylene (PTrFE) revealed by the present authors.[14] The high pyroelectric activity in the quenched and poled sample is considered to be due to simultaneous poling and crystallization. That is, the new crystallites growing by annealing under an electric field in the quenched sample align the polar axis along the field to have a high spontaneous polarization. In the quenched and annealed sample, on the other hand, the orientation of crystalline region is totally random and no crystal growth takes place in a poling process. Also a coercive field in the quenched and annealed sample was observed at about 100 MVm^{-1} as a broad and small peak of a polarization reversal current in our preliminary study, which is fairly higher than a coercive field of 50 MVm^{-1} in uniaxially stretched form I PVDF.[4] This high coercive field and low remanent polarization in the quenched and annealed sample may be due to small-size crystallites grown by quenching and annealing treatment. To sum up, the random orientation of crystallites, the high coercive field and the low remanent polarization suppress the formation of high spontaneous polarization in the quenched and annealed sample. In a well-poled sample of quenched and poling, a pyroelectric coefficient goes up over 20 $\mu Cm^{-2} K^{-1}$ which is regarded as rather high activity for unoriented PVDF by taking into account that the pyroelectric coefficient in uniaxially oriented PVDF lies in 20 to 40 $\mu Cm^{-2} K^{-1}$.

IV. SUMMARY

Form I PVDF was found to be produced in a melt-crystallization process by the high-rate quenching procedure. It was believed so far that form II was the only polymorph formed by cooling from the melt. The as-quenched sample has a low degree of crystallinity and subsequent heat-treatment leads to growth and perfection of crystallites where the rate of crystal growth is considerably high, i. e., annealing for 4 min at 120°C almost completes the crystal growth. Form I coexists with form II in the quenched sample and the fraction of an amount of form I in the crystalline region depends on the quenching rate but remains unchanged by subsequent annealing. The form I content in the crystalline region is estimated to be as much as 90% in a well-quenched sample and decreases with decreasing the quenching rate. A mechanism of forming form I by high-rate quenching is proposed as follows. Assuming that a nucleation rate of form I has a maxium at lower temperature than that of form II, the nucleation of form I is predominant at low temperature and that of form II at high temperature. For high-rate quenching, high-temperature nucleation is suppressed and nucleation proceeds mostly at low temperature resulting in formation of form I.

Poling of the quenched sample produces large pyroeletricity whereas heat-treatment to grow form I crystal prior to poling leads to unexpectedly small pyroeletricity. A mechanism of simultaneous poling and crystallization operates for high pyroelectric activity in the quenched and poled sample. On the other hand, in the quenched and annealed sample the small pyroelectricity is due to the random orientation of crystallite, the high coercive field and the small remanent polarization.

ACKNOWLEDGEMENTS

REFERENCES

(1) H. Kawai, *Jpn. J. Appl. Phys.*, **8**, 975 (1969).
(2) J. G. Bergman, J. H. McFree and G. R. Crane, *Appl. Phys. Lett.*, **18**, 203 (1971).
(3) R. Hasegawa, Y. Takahashi, Y. Chatani and H. Tadokoro, *Polym. J.*, **5**, 600 (1972).
(4) T. Furukawa, M. Date and E. Fukada, *J. Appl. Phys.*, **51**, 1135 (1980).
(5) G. T. Davis, J. E. McKinney, M. G. Broadhurst and S. C. Roth, *J. Appl. Phys.*, **49**, 4998 (1978).
(6) S. Weinhold, M. H. Litt and J. B. Lando, *Macromolecules*, **13**, 1178 (1980).
(7) S. Osaki and Y. Ishida, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1071 (1975).
(8) J. B. Lando, H. G. Olf and A. Peterlin, *J. Polym. Sci., Part A-1*, **4**, 941 (1966).
(9) J. Scheinbeim, C. Nakafuku, B. A. Newman and K. D. Pae, *J. Appl. Phys.*, **50**, 4399 (1979).
(10) C. C. Hsu and P. H. Geil, *J. Appl. Phys.*, **56**, 2404 (1984).
(11) M. Kobayashi, K. Tashiro and H. Tadokoro, *Macromolecules*, **8**, 158 (1975).
(12) M. A. Bachmann, W. L. Gordon, J. L. Koenig and J. B. Lando, *J. Appl. Phys.*, **50**, 6106 (1979).
(13) S. Osaki, private communication.
(14) Y. Oka and N. Koizumi, *Jpn. J. Appl. Phys.*, **23**, 948 (1984).