

Dynamic Mechanical Dispersion in Copolymers of Vinylidene Fluoride and Trifluoroethylene

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(Received May 21, 1984)

ABSTRACT: Copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) with TrFE content ranging from 48 to 100 mol% were studied by dynamic mechanical measurements in a temperature range of 173 to 373 K at 3.5 Hz. The α and β dispersions were observed around 313 and 250 K in decreasing order of temperature and the T_g dispersion occurred at higher temperature above the α dispersion for copolymers with 48 to 71 mol% TrFE. It was inferred for copolymers with 48 to 71 mol% TrFE from the dependence of these dispersions on degree of crystallinity that the α and β dispersions were due to micro-Brownian molecular motions of TrFE rich and VDF rich sequences respectively in amorphous regions and that the T_g dispersion was connected to the phase transition in crystalline regions. It was noted that the β dispersion in copolymer with higher TrFE content was related to the local molecular motions in amorphous and crystalline regions.

KEY WORDS Vinylidene Fluoride-Trifluoroethylene Copolymers /
Mechanical Dispersion / Glass Transition / Ferroelectric Phase Transition /

Attention has recently been directed to poly(vinylidene fluoride) (PVDF) and its copolymers with other fluorocarbons for their piezoelectric and pyroelectric properties. PVDF has three crystalline modifications, form I, II, and III.¹⁻³ In form I, the molecular chains take a planar zigzag conformation and the dipole moments do not cancel out (polar crystal). It was shown by Lando *et al.* that the copolymer of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) with TrFE content higher than 17 mol% crystallizes in polar form I.⁴ Yagi *et al.* prepared these copolymers^{5,6} over the entire range of comonomer content and observed the phase transition T'_m below the melting point by differential scanning calorimetry (DSC) for copolymers with TrFE content less than 46 mol%.⁷ In dynamic mechanical measurements, they found the phase transition T'_m only for copolymer with 46 mol% TrFE.⁷ Following

this work, it was revealed by many authors⁸⁻¹⁵ that the origin of this phase transition was related to the ferroelectric to paraelectric transition accompanied by change in chain conformation in the crystalline regions. Higashihata *et al.*⁸ observed that the dielectric and piezoelectric constants for these copolymers showed anomalous peaks above room temperature, the size of which was maximum at an intermediate content of the comonomer and that the peak temperature of these constants agreed with the phase transition temperature for copolymers with 18 to 51 mol% TrFE. For copolymers with TrFE content of 63 and 87 mol%, the phase transition was observed around 318 K in X-ray measurements, being ascribed to the ferroelectric to paraelectric phase transition.¹⁶ In dynamic mechanical and DSC measurements, no phase transition behavior was observed in these copolymers with TrFE content higher than 46

mol%.⁷ Yagi *et al.* observed two relaxation processes except for T'_m and assigned them to the glass transitions of chain backbone rich in TrFE and VDF units for copolymers with 40 to 64 mol% TrFE.⁷ They studied the dependence of these relaxations on the degree of crystallinity for copolymer with 56 mol% TrFE.

In this work, dynamic mechanical measurements were carried out on VDF-TrFE copolymers with TrFE content ranging from 48 to 100 mol% with varied crystallinity. The ferroelectric to paraelectric phase transition was observed in copolymers with 48 to 71 mol% TrFE. The phase transition and glass transition are discussed in connection with the dynamic mechanical behavior of copolymers with high TrFE content.

EXPERIMENTAL

The samples used in this investigation were poly(trifluoroethylene) (PTrFE) and copolymers of VDF and TrFE with TrFE content ranging from 48 to 87 mol% and supplied from Daikin Kogyo Co. Ltd. The samples were heat pressed at 523 K into films about 100 μm in thickness. To prepare films of different crystallinity, two cooling conditions were used: quenching specimens from 523 K into water and slow cooling from 523 to 323 K. PTrFE was annealed at 453 K for 22 h after slow cooling. For a copolymer with 48 mol% TrFE, another specimen was prepared by annealing the quenched film at 373 K for 2 h and cooling it to room temperature in air. Dynamic mechanical measurements were carried out at 3.5 Hz in a temperature range from 173 to 373 K, using a Toyo Baldwin Model DDV-II-C Rheovibron. The degree of crystallinity was determined from an X-ray diffraction intensity curve in a diffraction angle range of 5 to 35°.¹⁷ The density was measured in mixtures of 1,1,2-tetrabromoethane and carbon tetrachloride by the buoyancy method. The degrees of crystallinity and density are listed in Table I.

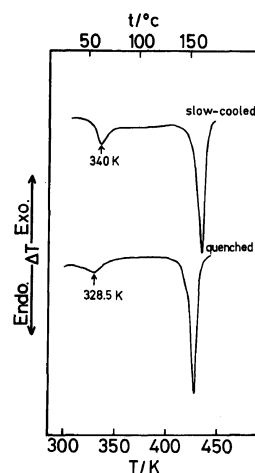


Figure 1. DTA curves for slow-cooled and quenched samples 9 and 11 with 48 mol% TrFE.

A higher degree of crystallinity was found for slow-cooled samples 1, 3, 5, 7, and 9. Quenched and annealed sample 10 gave lower degrees of crystallinity than slow-cooled sample 9. Thermal analysis was performed on a film specimen of about 10 mg at a heating rate of 10 K min^{-1} by a differential thermal analyzer (DTA). An endothermic peak connected with the phase transition was observed at 340 and 328.5 K for slow-cooled and quenched samples 9 and 11 with 48 mol% TrFE respectively, as shown in Figure 1.

RESULTS AND DISCUSSION

X-Ray diffractograms are shown for PTrFE and VDF-TrFE copolymers in Figure 2. A single peak was observed for quenched samples and a double peak for slow-cooled samples around 18–19° at a diffraction angle of 2θ . This peak may be due to the crystal structure of the planar zigzag conformation.^{14,18} For the double peak, there are two different interpretations: a crystal structure of the planar zigzag conformation containing skew bonds as presented by Tashiro *et al.*¹⁸ and a mixture of two crystal structures, disordered planar zigzag and 3/1 helix, taken by

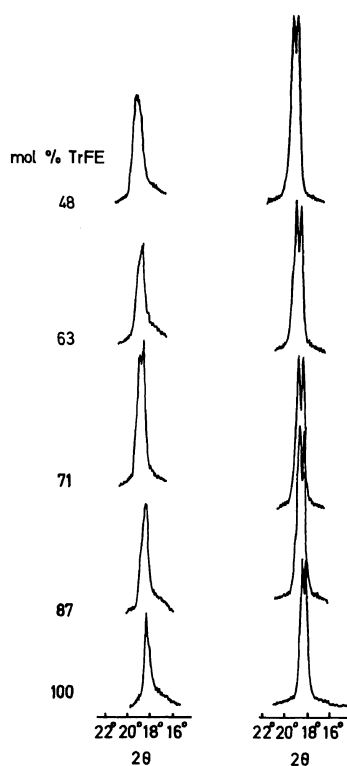


Figure 2. X-Ray diffractograms for quenched (left) and slow-cooled (right) samples of the VDF-TrFE copolymers and PTrFE.

Lovinger *et al.*¹⁴

The dynamic tensile modulus E' and mechanical loss tangent $\tan \delta$ are shown as a function of temperature in Figures 3 and 5 to 8. For PTrFE, two peaks of $\tan \delta$, α and β at 323 and 257 K, were observed with decrease in temperature between 173 to 373 K. The magnitude of the α peak in quenched sample 2 was larger than that in slow-cooled sample 1. Thus, the α dispersion is due to micro-Brownian molecular motion of the chain backbone in the amorphous regions.^{5,19} On the other hand, the β peak of quenched sample 2 was smaller in size and took place at a higher temperature compared to that of slow-cooled sample 1. This suggests that the β dispersion consists of two component dispersions^{5,19} assigned to the amorphous and crystalline regions schematically illustrated in Figure 4. In this figure, the

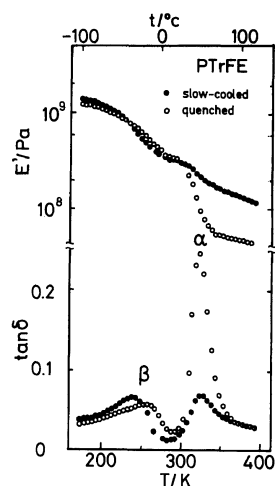


Figure 3. Temperature dependence of tensile modulus E' and mechanical loss tangent $\tan \delta$ at 3.5 Hz for PTrFE.

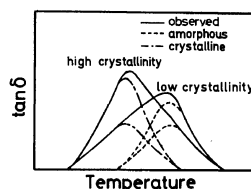


Figure 4. Schematic illustration of the relation between observed and component loss curves.

observed $\tan \delta$ vs. temperature curves are represented as the sum of two component loss curves, although, strictly speaking, the additivity of $\tan \delta$ does not hold for an overlapped loss peak. Therefore, this figure approximately exhibits the dependence of $\tan \delta$ on crystallinity for observed dispersions. Similar results were observed for the γ relaxation of poly(chlorotrifluoroethylene) (PCTFE) in which the two component relaxations assigned to molecular motions in the amorphous and crystalline regions overlap with each other.^{20,21} The component relaxation in the amorphous regions was attributed to the crankshaft molecular motions or the local mode molecular motions; the relaxation in the crystalline regions was related to the chain end defects in the crystallites.²¹ Therefore, the re-

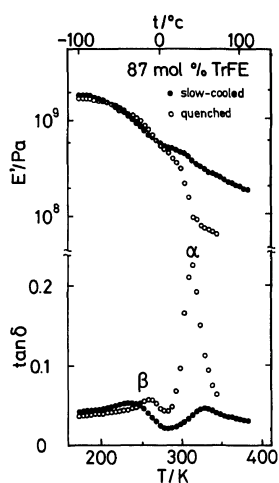


Figure 5. The same as Figure 3 for VDF-TrFE copolymer with 87 mol% TrFE.

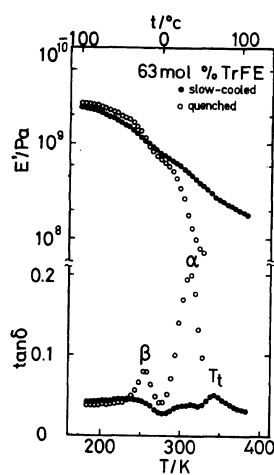


Figure 7. The same as Figure 3 for VDF-TrFE copolymer with 63 mol% TrFE.

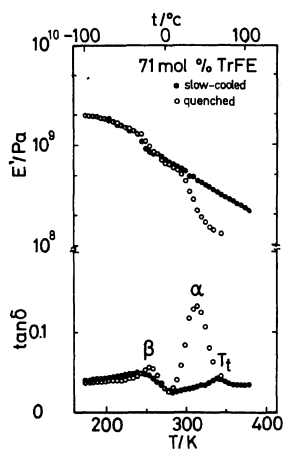


Figure 6. The same as Figure 3 for VDF-TrFE copolymer with 71 mol% TrFE.

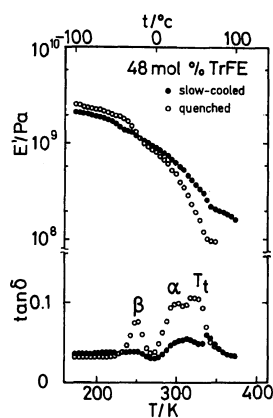


Figure 8. The same as Figure 3 for VDF-TrFE copolymer with 48 mol% TrFE.

laxations in the β dispersion of PTrFE may be due to local molecular motions similar to those in the γ relaxation of PCTFE. The details of the molecular mechanism of the β dispersion related to the crystalline regions are still open to question at this stage.

For VDF-TrFE copolymers with a TrFE content of 48 to 87 mol%, two or three peaks in $\tan \delta$ were observed between 173 and 373 K and designated as T_t , α and β in descending order of temperature. The α peak of $\tan \delta$

observed at 303 K (48 mol% TrFE) to 313 K (87 mol% TrFE) resembles the α dispersion of PTrFE in size of loss peak and crystallinity dependence. For the β dispersion of the copolymers, the size of $\tan \delta$ peak was larger for the quenched than the slow-cooled samples and increased with decreasing TrFE content. Thus the β dispersion is likely to be related to VDF sequences in the amorphous regions. In the PVDF homopolymer, there are two relaxation processes, β and γ , assigned to the amorphous regions between 173 and 273 K.²²

The former, due to micro-Brownian molecular motion of the chain backbone,²² was located at 235 K and 3.5 Hz,²³ and occurred at a somewhat lower temperature than the β peak of these copolymers. The shape of the β peak for quenched copolymers with 48 to 71 mol% TrFE resembles that of PVDF homopolymer. It thus seems that the α and β dispersions of these copolymers are due to micro-Brownian molecular motion of the TrFE rich and VDF rich sequences respectively. Yagi *et al.* pointed out that there may be two glass transitions in these copolymers, on the basis of the α and β dispersions in their dynamic mechanical measurements.⁷ Two glass transitions have been found for blended polymers and block copolymer composed of incompatible or partially compatible components, each forming two separated amorphous phases.²⁴ If no phase separation occurs, one glass transition is observable. Therefore, it is considered that VDF-TrFE copolymers with 48 to 71 mol% TrFE for which the β peak is similar to that of PVDF homopolymer are block-like copolymers consisting of incompatible or partially compatible TrFE rich and VDF rich sequences which formed the respective amorphous phases. In these copolymers, the values of $\tan \delta$ below 250 K for slow-cooled samples were higher than those for quenched samples. Thus, the molecular motions in the crystalline regions contribute to the loss process at low temperature. The β dispersion of the copolymer with 87 mol% TrFE is likely related to the local molecular motions of TrFE rich sequences in the amorphous and crystalline regions, because of the similarity of the β dispersion between PTrFE and this copolymer in shape of the loss peak and dependence of peak temperature on the degree of crystallinity.

Above the α dispersion, another peak of $\tan \delta$ T_i was seen for slow-cooled copolymers with 48 to 71 mol% TrFE and for a quenched one with 48 mol% TrFE. The temperature of this peak is consistent with that of the anomalous peak T'_m in dielectric and piezoelectric

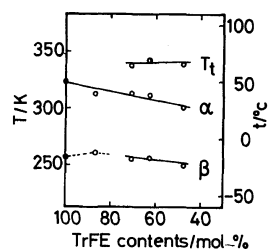


Figure 9. Variation in temperature for loss peak of the T_i , α and β dispersions with TrFE content.

constants observed by Higashihata *et al.*⁸ Thus, the T_i dispersion may be due to the ferroelectric to paraelectric phase transition. Yagi *et al.* did not observe the phase transition for copolymers with TrFE content higher than 46 mol% by dynamic mechanical measurements.⁷ This may be due to the low crystallinity of their samples.

The temperature of the T_i , α and β loss peaks are plotted against TrFE contents in Figure 9, in which the curve for the β dispersion is drawn with a broken line in comonomer content of 87 to 100 mol% TrFE, since the β dispersion for the copolymer with 87 mol% TrFE is connected mainly with the local molecular motion of TrFE rich sequences in the amorphous and crystalline regions. The α and β dispersions were found to depend slightly on TrFE content. This may indicate that the number of VDF units slightly increases in the TrFE rich and VDF rich sequences with decreasing TrFE content. The T_i peak of $\tan \delta$ was depressed at 71 mol% TrFE and disappeared at 87 mol% TrFE, suggesting the T_i dispersion to be related to the VDF rich sequences in the crystalline regions. The T_i loss peak for slow-cooled copolymer with 48 mol% TrFE was sharp in comparison with those of copolymer with 63 and 71 mol% TrFE. In the DTA measurements, the phase transition was found only for a copolymer with 48 mol% TrFE, as shown in Figure 1 but not for copolymers with 63 and 71 mol% TrFE. Thus, the molecular motion in the T_i dispersion may be cooperative for the copolymer with 48

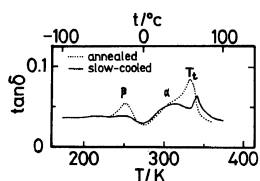


Figure 10. Temperature dependence of $\tan \delta$ at 3.5 Hz for slow-cooled and annealed samples 9 and 10 with 48 mol% TrFE.

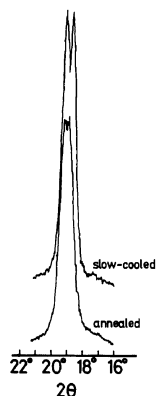


Figure 11. X-Ray diffractograms for slow-cooled and annealed samples 9 and 10 with 48 mol% TrFE.

mol% TrFE and less so for copolymers with 63 and 71 mol% TrFE.

For the copolymer with 48 mol% TrFE, temperature dependence of $\tan \delta$ and X-ray diffractograms for annealed and slow-cooled samples are shown in Figures 10 and 11, respectively. The α peak in $\tan \delta$ for annealed sample 10 had the same size as that for slow-cooled sample 9, while the β peak for the former was larger than that of the latter. These results indicate that the amounts of TrFE rich sequences in amorphous regions are the same between annealed sample 10 and slow-cooled sample 9, while the amounts of VDF rich sequences in the amorphous regions are larger for annealed sample 10 than for slow-cooled sample 9. The degree of crystallinity is lower for annealed sample 10 than for slow-cooled sample 9, as evident from Table I. The difference in crystallinity between samples 9 and 10 may be due to the amounts of VDF rich

Table I. Degree of crystallinity and density of VDF-TrFE copolymers

Sample No.	TrFE content	Degree of crystallinity	Density
	mol%	%	g cm^{-3}
1	100 ^a	52	2.018
2	100 ^b	26	1.967
3	87 ^c	41	1.981
4	87 ^b	26	1.934
5	71 ^c	39	1.959
6	71 ^b	31	1.928
7	63 ^c	43	1.940
8	63 ^b	26	1.888
9	48 ^c	48	1.916
10	48 ^d	40	1.905
11	48 ^b	29	1.886

^a Slow-cooled and annealed at 453 K.

^b Quenched in water.

^c Slow-cooled.

^d Quenched and annealed at 373 K.

sequences in the crystalline regions. Lovinger *et al.*¹⁴ consider that VDF rich and TrFE rich sequences take disordered planar zigzag and 3/1 helix forms, respectively, in the melt-crystallized copolymer with the same comonomer content as in this work. This consideration cannot be applicable to an annealed sample, since the X-ray pattern of such a sample shows a single peak due to the planar zigzag. However the VDF rich and TrFE rich sequences are considered to be more or less separately aggregated in the crystallites.

CONCLUSION

Alpha and β -dispersions were observed around 313 and 250 K, respectively, for copolymers with 48 to 100 mol% TrFE in dynamic mechanical measurements. These dispersions were connected with micro-Brownian molecular motion of TrFE rich and VDF rich sequences respectively in the amorphous regions for copolymers with 48 and 71 mol% TrFE. In the copolymer with higher TrFE content, the β dispersion was related to the

local molecular motion of TrFE rich sequences in the amorphous and crystalline regions. The T_1 dispersion occurred at higher temperature above the α dispersion for copolymers with 48 to 71 mol% TrFE and was related to the ferroelectric to paraelectric phase transition in the crystalline regions. The behavior of the α , β , and T_1 dispersions suggests that VDF rich and TrFE rich sequences aggregate separately in the amorphous and crystalline regions.

Acknowledgements. The authors wish to thank Dr. Y. Kubouchi and Mr. S. Koizumi of Daikin Kogyo Co., Ltd., Osaka for providing copolymer samples. The present work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan for which the authors are thankful.

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