SHORT COMMUNICATIONS

Curie Transition in Copolymers of Vinylidene Fluoride and Tetrafluoroethylene

Yukinobu MURATA* and Naokazu KOIZUMI

Institute for Chemical Research, Kyoto University,
Uji, Kyoto-fu 611, Japan
*Osaka Prefectural Technical College,
26–12, Saiwai-cho, Neyagawa 572, Japan

A typical ferroelectric copolymer of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) shows the Curie transition where dielectric anomaly,[1-4] change in remanent polarization,[1,5,6] mechanical relaxation[2,7] and endothermic peak[2-4,7] in differential scanning calorimetry (DSC) are observed. These properties were connected with the change in the chain conformation from all *trans* zigzag to contracted *gauche* forms in the crystalline regions.[8-12] Copolymers of VDF and tetrafluoroethylene (TeFE) also exhibited ferroelectric[13] and piezoelectric[14,15] properties. Recently, Lovinger studied a VDF–TeFE copolymer with 19 mol% TeFE by X-ray measurement and found that the conformational change similar to that of VDF–TrFE copolymer took place at 110—115°C, being ascribed to the Curie transition.[16] We studied dielectric behavior of VDF–TeFE copolymers with 10.7 to 30.7 mol% TeFE in which no Curie transition was observed.[17] The present work was undertaken to find out the Curie transition for VDF–TeFE copolymers used in the previous work. For this purpose dynamic mechanical and thermal properties were examined for these copolymers with varied degrees of crystallinity.

The samples used were the same VDF–TeFE copolymers with 17.8, 25.1, and 30.7 mol% TeFE as those employed in the previous work.[17] The samples were heat pressed at 523 K into films 100—200 μm in thickness and listed in Table I. Samples 1, 3, and 5 were prepared by cooling specimens from 523 to 320 K in air. Samples 2 and 4 were prepared by quenching specimens into cold water. The density measured by the floating method in mixtures of carbon tetrachloride and 1,1,2,2-tetrabromoethane are shown in Table I. For the 30.7 mol% TeFE copolymer, no significant difference was found in density between slow cooled and quenched samples. Thermal analysis was made on film specimens of about 10 mg at a heating rate of 10K min^{-1} using a

Table I. VDF–TeFE copolymer samples

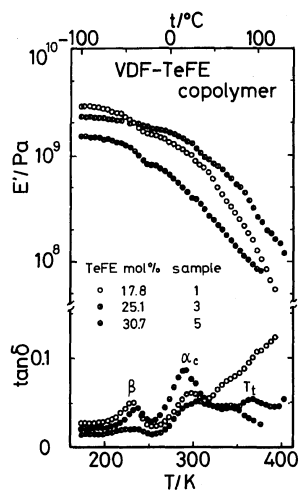| Sample No.	TeFE content mol%	Density g cm^{-3}
1	17.8	1.865
2	17.8	1.849
3	25.1	1.940
4	25.1	1.890
5	30.7	1.896

Figure 1. Temperature dependence of tensile modulus E' and mechanical loss tangent $\tan\delta$ at 3.5 Hz for slow cooled samples 1, 3, and 5.
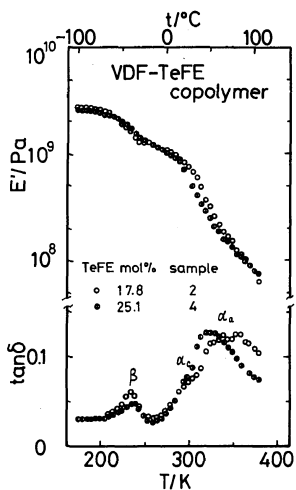

Figure 2. The same as Figure 1 for quenched samples 2 and 4.

Figure 3. DTA curves for slow cooled samples 1, 3, and 5.

high sensitivity of $\pm 50\,\mu$V by a Rigaku Denki differential thermal analyzer Thermoflex TG-DTA. Dynamic mechanical measurements were carried out at a frequency of 3.5 Hz in a temperature range of 173 to 393 K using a Toyo Baldwin Model DDV-II-C Rheovibron. X-Ray measurements were performed by a Rigaku Denki diffractometer Geigerflex 2012. The diffraction patterns for slow cooled sam-
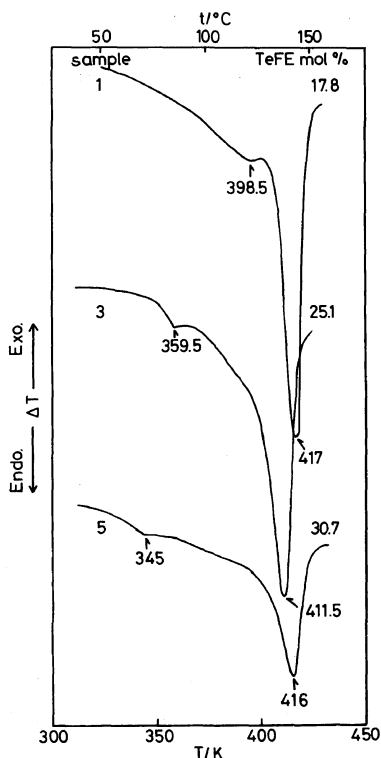
ples 1, 3, and 5 indicated the same crystal structure of all *trans* zigzag conformation as that of VDF–TrFE copolymer.[8-12]

Dynamic tensile modulus E' and mechanical loss tangent $\tan\delta$ are plotted against temperature for slow cooled and quenched samples in Figures 1 and 2. The slow cooled samples showed three relaxations, designated as β, α_c, and T_t, in increasing order of temperature. The quenched samples exhibited the β, α_c, and α_a relaxations. The α_c relaxation was observed as a shoulder on the low temperature side of the large α_a loss peak. From the dependence of these relaxations on the degree of crystallinity, the α_a and β relaxations are connected to molecular motions in the amorphous regions and the T_t and α_c relaxations to those in the crystalline regions. The behavior of dynamic tensile modulus E' and mechanical loss tangent $\tan\delta$ near the T_t relaxation is similar to
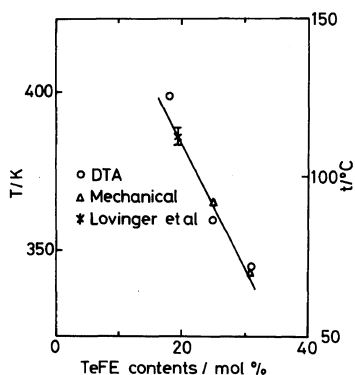
Figure 4. Variation of temperatures for the T_t mechanical loss peak and DTA endotherm in Curie transition with TeFE content.

that of VDF–TrFE copolymer[7] at the Curie transition. Hence, the T_t relaxation of VDF–TeFE copolymers was considered to be related with the Curie transition.

In DTA measurements as shown in Figure 3, a prominent endothermic peak corresponding to the melting point took place at 410—420 K. Below this temperature, a small endotherm was observed at 398.5, 359.5, and 345 K for samples 1, 3, and 5, respectively. The temperatures of these small peaks were consistent with those of the T_t mechanical relaxations for samples 3 and 5, so that the endotherms were attributable to the Curie transition. For the quenched samples 2 and 4, neither mechanical loss peak nor DTA endotherm indicating the Curie transition was observed because of the low degrees of crystallinity. The Curie temperatures for VDF–TeFE copolymers obtained by mechanical and DTA measurements decreased with increasing TeFE content, as plotted against TeFE content in Figure 4. In VDF–TrFE copolymer the Curie points decreased with increasing TrFE content.[2,4] The temperature of the Curie transition for the copolymer with 19 mol% TeFE obtained by Lovinger *et al.*[16,18] was consistent well with our results, as shown in Figure 4. It is inferred from the present results that the T_t mechanical relaxation and endotherm of VDF–TeFE copolymers are related to the

Curie transition.

The DTA endotherms at the Curie transitions are small and broad in comparison with those for VDF–TrFE copolymers.[7] This feature suggests the low degree of crystallinity and/or less cooperative molecular motions at the Curie transition which may arise from introduction of rigid and bulky TeFE units. In the previous work,[17] the dielectric anomaly similar to that for VDF–TrFE copolymers at the transition was not observed but dielectric constant and loss increased with increasing temperature and decreasing frequency, being attributed to the space charge polarization. It would be possible that the space charge polarization contributed to the dielectric constant was large enough to conceal the dielectric anomaly at the Curie transition. Further work on ferroelectric properties of this copolymer is in progress.

REFERENCES

1. T. Furukawa, M. Date, E. Fukada, Y. Tajitsu, and A. Chiba, *Jpn. J. Appl. Phys.*, **19**, L109 (1980).
2. T. Yagi, M. Tatemoto, and J. Sako, *Polym. J.*, **12**, 209 (1980).
3. T. Yamada, T. Ueda, and T. Kitayama, *J. Appl. Phys.*, **52**, 948 (1981).
4. N. Koizumi, N. Haikawa, and H. Habuka, *Ferroelectrics*, **57**, 99 (1984).
5. T. Furukawa, G. E. Johnson, H. E. Bair, Y. Tajitsu, A. Chiba, and E. Fukada, *Appl. Phys. Lett.*, **32**, 61 (1981).
6. T. Furukawa, A. J. Lovinger, G. T. Davis, and M. G. Broadhust, *Macromolecules*, **16**, 1885 (1983).
7. Y. Murata and N. Koizumi, *Polym. J.*, **17**, 385 (1985).
8. K. Tashiro, K. Takano, M. Kobayashi, Y. Chatani, and H. Tadokoro, *Polymer*, **22**, 1312 (1981).
9. K. Tashiro, K. Takano, M. Kobayashi, Y. Chatani,

and H. Tadokoro, *Polymer*, **25**, 195 (1984).

10. A. J. Lovinger, G. T. Davis, T. Furukawa, and M. G. Broadhust, *Macromolecules*, **15**, 323 (1982).

11. A. J. Lovinger, T. Furukawa, G. T. Davis, and M. G. Broadhust, *Polymer*, **24**, 1225 (1983).

12. A. J. Lovinger, T. Furukawa, G. T. Davis, and M. G. Broadhust, *Polymer*, **24**, 1233 (1983).

13. J. C. Hicks, T. E. Jones, and J. C. Logan, *J. Appl. Phys.*, **49**, 6093 (1978).

14. H. Stefanou, *J. Appl. Phys.*, **50**, 1486 (1979).

15. J. X. Wen, *Polym. J.*, in press.

16. A. J. Lovinger, *Macromolecules*, **16**, 1592 (1983).

17. N. Koizumi, J. Hagino, and Y. Murata, *Ferroelectrics*, **32**, 141 (1981).

18. A. J. Lovinger, G. E. Johnson, H. E. Bair, and E. W. Anderson, *J. Appl. Phys.*, **56**, 2412 (1984).