

TRANSITION IN THE MELT OF FEP COPOLYMER

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ABSTRACT

The nature of the transition in molten FEP copolymer was examined in relation to the enthalpy change, mechanical damping and melt viscosity. For a pre-heat-treated FEP copolymer sample a small endothermic peak appeared at 309–312 °C in DSC trace with enthalpy change 0.03–0.05 cal/g. A peak was also detected in damping versus temperature curve at the same temperature range. The rheological property of FEP copolymer melt was similar to that of liquid crystal, but no birefringence was viewed in the melt. Therefore the transition was explained as the melting of small crystallites which persist in typical copolymer beyond its melting temperature. These crystallites can act as nuclei for crystallization upon cooling.

INTRODUCTION

The melt phase transition of polymers has been of considerable research interest during recent years. First of all, the mesomorphic transitions in rigid chain polymers have been detected and investigated comprehensively^[1-2]. Furthermore, evidences for a transition above T_m in *n*-alkanes and crystalline polymers were reported by Kruger, Boyer and other authors^[3-6].

The high melting point of PTFE, its low solubility, and the high viscosity of its melt are generally considered to be indicative of extra-ordinary stiffness of the PTFE chain^[7]. It seems probable that PTFE melts to a mesomorphic phase which conceivably may be nematic. But none has detected this type transition in the melt of PTFE and related copolymers.

We have shown previously that the morphology of fluorinated ethylene-propylene (FEP) copolymer, melt-crystallized upon cooling, is critically dependent on the melt temperature in the range of 310–320°C^[8]. This finding leads us to detect a transition above T_m , the thermodynamic melting temperature of FEP copolymer^[9]. In this paper, the nature of the transition in molten FEP copolymer was examined in relation to the change of enthalpy, mechanical damping and melt viscosity. A structure model of the melt is also suggested to explain the results we have obtained.

EXPERIMENTAL

The copolymer samples were prepared by emulsion and suspension copolymerization of tetrafluoroethylene and hexafluoropropylene in pilot plant of our institute and some FEP

grade samples were purchased from du Pont de Nemours & Company.

A Perkin-Elmer Differential Scanning Calorimeter DSC-2 was employed to measure the transition temperature and enthalpy change. Mechanical damping was carried out on a homemade torsional braid analyzer. In order to prepare sample for TBA study, a thin film of FEP copolymer was hot-pressed on the glass fiber braid. The melt viscosity was measured by means of a micro-parallel type rheometer attached to Perkin-Elmer Thermo-mechanical Analyzer TMS-2. The melt viscosity was calculated from the usual relation^[10]

$$\eta = -\frac{8\pi F}{3V^2} \left(d \frac{1}{h^4} / dt \right)^{-1}, \quad (1)$$

where η is viscosity, F is applied force, V is volume, h is separation of the two parallel plates and t is time.

RESULTS AND DISCUSSION

Fig. 1 shows typical DSC traces for the FEP copolymer, two different patterns above T_m are observed. The as-received samples do not have any thermal effect or slope change at $T > T_m$ region. A small endothermic peak, appeared after fusion is detected only after heat-treatment. The typical procedure for heat-treatment is heating the sample to the temperature range above T_m and below 310°C for several minutes.

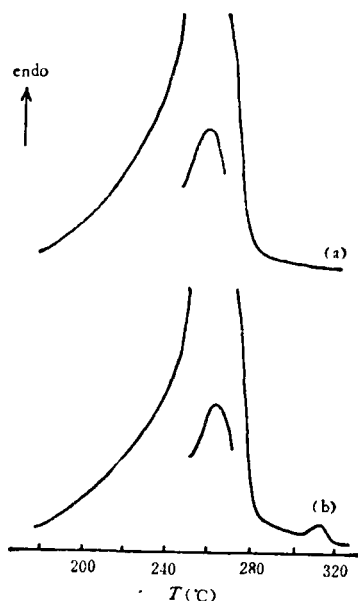


Fig. 1 DSC traces of FEP copolymer
(a) original sample;
(b) heated to 300 °C, then cooled.

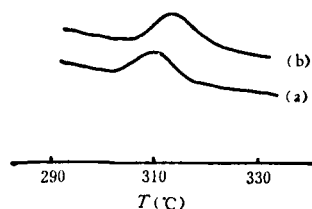


Fig. 2 The change of transition temperature T_u of FEP copolymer with heat-treatment temperature
(a) 295°C; (b) 300°C.

The heat of transition is about 0.03–0.05 cal/g or about the tenth of the enthalpy change of nematic phase transition. It is so small that a higher heating rate ($\geq 20^\circ\text{C}/\text{min}$) in DSC scan should be used, otherwise the endothermic peak will be missed.

This transition, which is designated as T_u , can be detected in almost all FEP copolymer samples, despite their origin or polymerization method.

Table 1 gives values of T_m , T_u and heat of transition for a variety of samples, annealed for several minutes at 295°C. T_u slightly depends on annealing temperature as shown in Fig. 2.

Table 1 Transition temperatures and heat of transition of FEP copolymer

Sample No.	Polymerization method	C_3F_6 (%wt.)	T_m (°C)	T_u (°C)	$\Delta H \times 10^3$ (cal/g)
809	suspension	17.1	271	312	3.9
11	emulsion	17.1	269	312	4.9
FEP100	du Pont	18.6	267	310	5.3
FEP140	du Pont	17.6	264	311	4.5
FEP160	du Pont	18.6	266	310	3.0
549	suspension		266	311	4.2
06	emulsion	17.6	261	312	3.9
315	suspension	20.5	250	312	4.0
107	suspension	26.1	246	309	2.5

The transition T_u can also be detected by torsional braid analyzer with concordant results. Fig. 3 shows the damping versus temperature curves for the original samples and those annealed at 300°C. It is clear that the damping versus temperature curves exhibit quite similar behavior, except that the peak at T_u is much wider than that in the DSC trace.

It is interesting to know the temperature dependence of melt viscosity of FEP copolymers. The variation of the melt viscosity of common polymers with temperature can be described

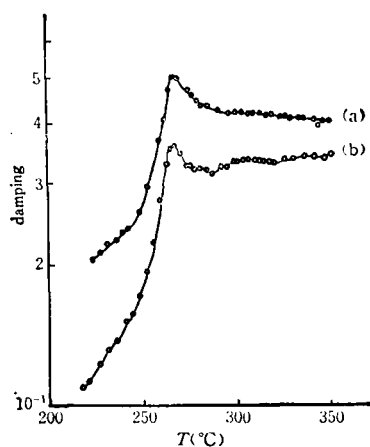


Fig. 3 Plot of damping versus temperature for FEP copolymer
(a) original sample;
(b) heated to 300°C, then cooled.

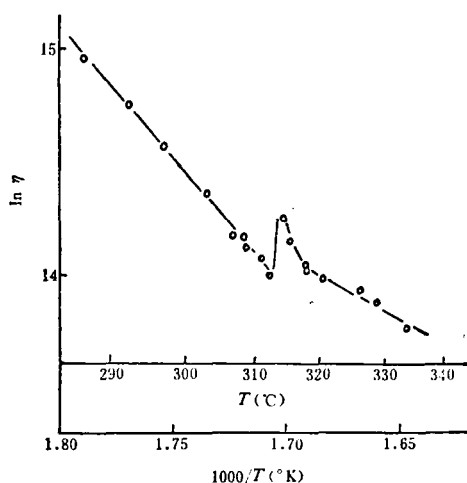


Fig. 4 The change of melt viscosity of FEP copolymer with temperature

by the Arrhenius equation

$$\eta = A \exp \left(-\frac{E_\eta}{RT} \right), \quad (2)$$

where A is the preexponential factor, E_η is the activation energy, R is the gas constant and T is the absolute temperature. If $\ln \eta$ is plotted as a function of $1/T$, a straight line should be obtained. But if a mesomorphic or other structural transition happens, an anomalous increase in viscosity occurs at the transition temperature.

A microparallel-plate rheometer was used to measure the melt viscosity of FEP copolymer. The height h of sample between two parallel plates was measured continuously as a function of time at a given temperature. $\left(d \frac{1}{h^4} / dt \right)$ was obtained from the plot of $\frac{1}{h^4}$ against time, which actually obey the straight linear relationship up to 4×10^3 sec in our experiments. The melt viscosity was calculated by using Eq. (1).

The temperature dependence of melt viscosity for the FEP copolymer after heat-treatment is shown in Fig. 4. Instead of a linear relationship between the logarithm of viscosity and $1/T$ an anomalous increase in viscosity occurs when the temperature is increase above 310°C , which is quite similar to that of liquid crystal^[11]. But no birefringence was observed in this melt. This is a good indication that liquid crystallinity is absent in the FEP copolymer.

The crystalline morphology of FEP copolymer, prepared with different polymerization

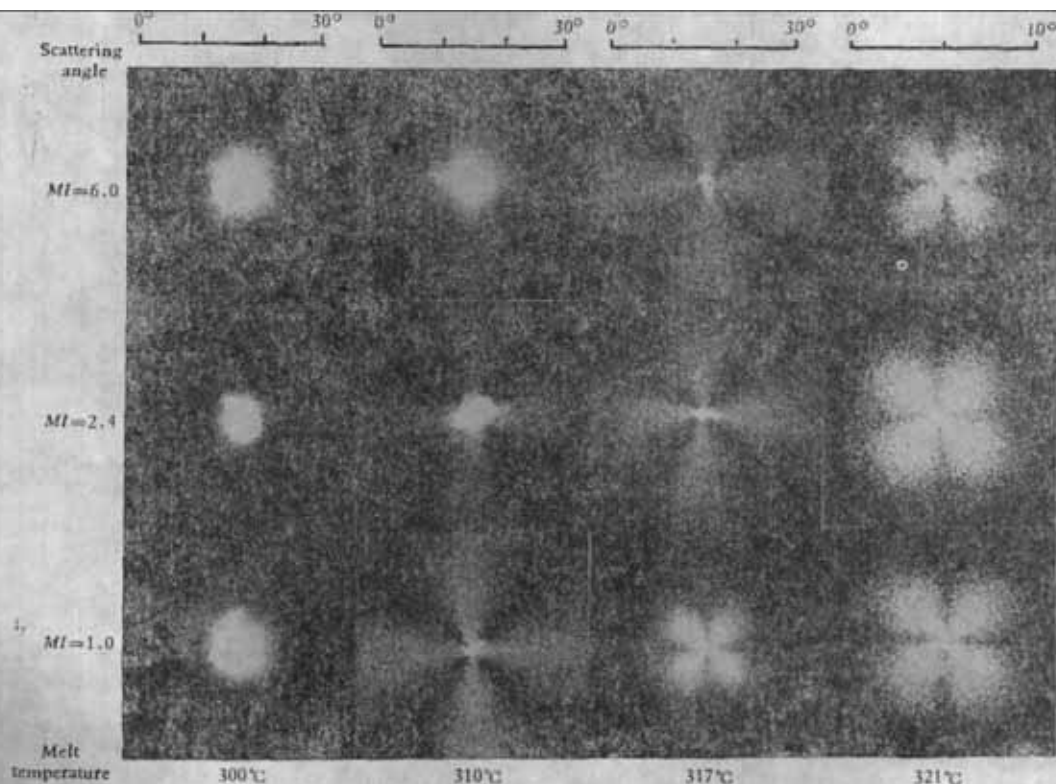


Fig. 5 The H_v scattering patterns of FEP copolymer, cooled from different melt temperatures.

methods, with different hexafluoropropylene contents and different melt indexes (molecular weights) was studied by small angle light scattering technique. The results obtained also show that the main factor which affects the crystalline morphology of the copolymer is the melt temperature in the range 310–320°C. The morphological structure of the copolymer could change from randomly arranged lamellae through rod-like to spherulitical as the temperature increased from 310 to 320°C under usual cooling condition. Fig. 5 shows the typical H_v scattering patterns of three FEP copolymer samples with different melt indexes, which were cooled from different melt temperature. The H_v scattering pattern of melt-crystallized sample, cooled down from melt temperature below 310°C, is circularly symmetric and can be assigned as randomly arranged lamellae morphology. The H_v patterns of FEP copolymers, cooled down from melt temperature above 320°C, have four-leaf patterns which are those from the spherulitic morphology. When the melt temperature was held in the temperature range between 310–320°C, the + type scattering pattern was obtained. The intensity is azimuthally dependent and has four-fold symmetry, but the maximum is at the center and the intensity monotonically decreases with increasing scattering angle. The light scattering patterns of this type are assigned as rod-like morphology.

In order to understand the origin of the change of morphology with melt temperature, the crystallization behavior of copolymer was studied. Crystallization studies were carried out in the Perkin-Elmer DSC-2, both isothermally and under definite cooling rate. As shown in Fig. 6 the variation of crystallization curve with melt temperature occurs in the same temperature range as that of morphology. In fact, three types of crystallization curves, corresponding to the three types of morphology, were obtained.

The crystallization curve, obtained from melt temperature above 320°C under 5°C/min cooling rate has a sharp exothermic peak, which is typical for spherulitic crystallization

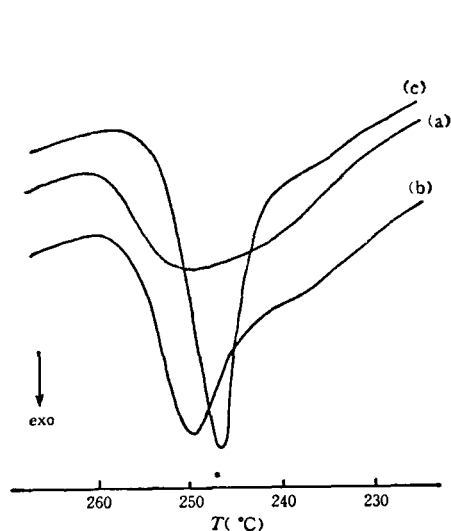


Fig. 6 DSC cooling curves of FEP copolymer, cooled from different temperature regions
(a) 280–300°C; (b) 312°C; (c) 320–330°C.

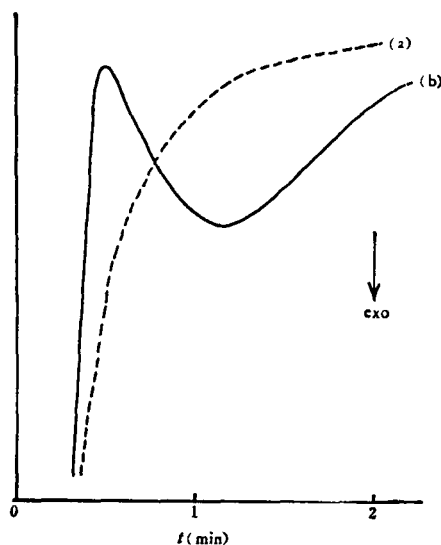


Fig. 7 Effect of melt temperature on isothermal crystallization of FEP copolymer
Crystallization temperature: 247°C;
Melt temperature: (a) 310°C; (b) 320°C.

usually observed in major semi-crystalline polymer. That obtained from melt temperature below 310°C has a flat peak. An intermediate width peak is recorded from melt temperature of 312°C. Comparing the three typical crystallization curves, the difference in onset temperature of crystallization was noted. The sample cooled from melt temperature above 320°C has lower onset temperature of crystallization than that cooled from melt temperature below 310°C.

It is important to know how the crystallization rate of copolymer varies with the melt temperature. The crystallization rate can be estimated by the time to reach maximum crystallization rate $t_{\max}$ at isothermal mode. A Perkin-Elmer DSC-2 was also employed to measure $t_{\max}$. When the sample was heated to temperature above 320°C, then crystallized isothermally at small undercooling, i.e. $\Delta T \approx 15-20^\circ\text{C}$, $t_{\max}$ were in the 30-70 sec range. When the sample was heated to temperature below 310°C, then crystallized isothermally in DSC-2 the exothermic crystallization peak could not be obtained (Fig. 7), even if the isothermal crystallization temperature was varied widely. It means that in this case the crystallization rate is so high that crystallization has taken place during the rapid cooling process before the equilibrium temperature in DSC-2 sample holder is reached. These crystallization behaviors exhibit that small amounts of crystalline material may persist in FEP copolymer beyond the temperature at which most of the melting occurs. These crystallites or aggregates can act as nuclei for crystallization upon cooling. Hence, the overall crystallization is very fast and the character of the crystal obtained depends critically on these embryonic crystallites.

It is not difficult to understand how the crystallites can be formed in the melt of FEP copolymer. Eby has shown that crystalline phase of FEP copolymer is the solid solution of TFE and HFP units and the comonomer HFP units produce defects in the crystalline TFE lattice^[12]. When the temperature is raised beyond the m.p. of FEP copolymer, the comonomer-containing crystals will melt and the longer TFE segments tend to aggregate into crystallites, and heat-treatment enhance the size and amount of the crystallites, the melting of which is then detected. Moreover, the fact that T_u (310-320°C) is somewhat lower than T_m of PTFE (327°C) gives added evidence.

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REFERENCES

- [1] Samulski, E. T., Dupre, D. B., in "Advances in Liquid Crystals", edited by Brown, G. H., Academic Press, New York, 1979, p. 132-138.
- [2] Warner, S. B., Jaffe, M., *J. Crystal Growth*, 1980, 48, 184.
- [3] Krüger, J. K., *Solid State Communications*, 1979, 30, 43.
- [4] Krüger, J. K., Peetz, L., Wildner, W., Pietralla, M., *Polymer*, 1980, 21, 620.
- [5] Pietralla, M., Krüger, J. K., *Polymer Bulletin*, 1980, 2, 663.
- [6] Denny, L. R., Boyer, R. F., *Polymer Bulletin*, 1981, 4, 527.
- [7] Flory, P. J., "Statistical Mechanics of Chain Molecules", Interscience Publishers, New York, 1969, p. 153.
- [8] 史观一、张国光、乐俊士, 高分子通讯, 1981(5), 355.
- [9] 史观一、乐俊士, 科学通报, 1982(3), 168.
- [10] Cessna, L. C., Jabloner, H., *J. Elastomers and Plastics*, 1974, 6, 103.
- [11] Porter, R. C., Johnson, J. F., *J. Appl. Phys.*, 1963, 34, 51.
- [12] Eby, R. K., *J. Appl. Phys.*, 1966, 37, 3511.