

NOTES

Melting of Ethylene–Tetrafluoroethylene Copolymer

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Equilibrium melting temperature T_m^0 and heat of fusion ΔH_m are important parameters to characterize a polymer crystal. Heat of fusion in polymer crystal is determined by the use of differential scanning calorimetry (DSC) or by calculating from Clapeyron–Clausius equation using pressure dependence of melting temperature.

Ethylene–tetrafluoroethylene (E–TFE) copolymer shows some characteristic physical properties, such as high melting temperature and high stiffness in the chain.¹ It is important to determine the melting parameters to discuss the melting phenomena in polymer crystals, but they are not still determined in E–TFE copolymer, because of the high melting temperature.

In this report, heat of fusion and entropy of fusion ΔS_m of E–TFE were determined by using DSC and Clapeyron–Clausius equation. Equilibrium melting temperature, pressure dependence of the melting temperature, and the volume change in the melting of the crystal were measured to calculate ΔH_m and ΔS_m . These values for E–TFE were compared with the values for polyethylene (PE) and two fluorine polymers, poly(tetrafluoroethylene) (PTFE), and poly(vinylidene fluoride) (PVDF). The melting behavior of E–TFE is discussed in comparison with the melting of PE, PTFE, and PVDF.

EXPERIMENTAL

The E–TFE original material was purchased from Scientific Polymer Products, Inc. The ethylene content of the sample was 46.3 mol% by the melting temperature method after Modena.² According to the infrared absorption method,³ the ethylene content was 47 mol%.

Pressure dependence of T_m of E–TFE was determined by high pressure DTA up to 30 MPa. The apparatus was described elsewhere.^{4,5}

The equilibrium melting temperature T_m^0 of E–TFE crystal was determined by plotting the melting temperature for reciprocal long period ($1/L$) using Gibbs–Thomson's equation.⁶ The long period (L) of the sample was determined by small angle X-ray scattering (SAXS) apparatus in Fukuoka University. Cu- K_α radiation was used as an incident beam.

Crystallization condition, L , $1/L$, and T_m of the samples were listed in Table I.

Volume change (ΔV_m) of the sample on melting was measured by using conventional dilatometer (capillary) made of pyrex glass. The sample part of the glass dilatometer was heated in a silicon oil bath. The height of the top of mercury was measured by cathetometer.

RESULTS AND DISCUSSION

DTA curve of melting of E–TFE at 0.1 MPa shows endothermic peak at 268.3°C. The endothermic peak shifted to high temperature with increasing pressure. Figure 1 shows pressure dependence of the peak melting temperature of DTA up to about 30 MPa. Pressure dependence of T_m of E–TFE (dT_m/dP) determined by linear approximation in this figure was 0.72 K MPa⁻¹ with the standard deviation of 0.82.

Figure 2 shows the change of T_m with $1/L$. Equilibrium melting temperature of E–TFE determined in the figure by linear approximation of T_m is 564.5 K. Melting temperature at 0.1 MPa of the same sample as used in the SAXS measurement was determined for the heating rate at 20 K min⁻¹ in DSC at 0.1 MPa.

Figure 3 shows temperature change of E–TFE volume around melting region. The heating rate was 6 K min⁻¹. The mercury height change at melting of E–TFE was 0.184 cm in the figure and the volume change was 0.077

Table I. Long period L , $1/L$, and T_m in the sample with different crystallization conditions in E–TFE

Sample	$L/\text{Å}$	$1/L/\text{Å}^{-1}$	T_m/K
24 h annealed	552.2	1.811×10^{-3}	554.8
10 h annealed	441.8	2.264	550.2
100°C quenched	346.5	2.886	544.0
0°C quenched	333.4	3.000	543.4
-50°C quenched	332.5	3.101	546.9
-100°C quenched	289.7	3.452	545.5
-170°C quenched	360.6	2.773	547.2

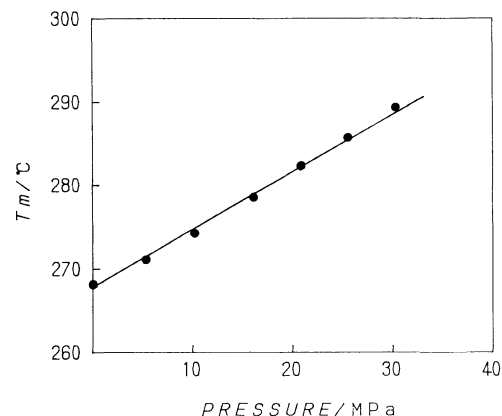


Figure 1. Pressure dependence of T_m of E–TFE copolymer.

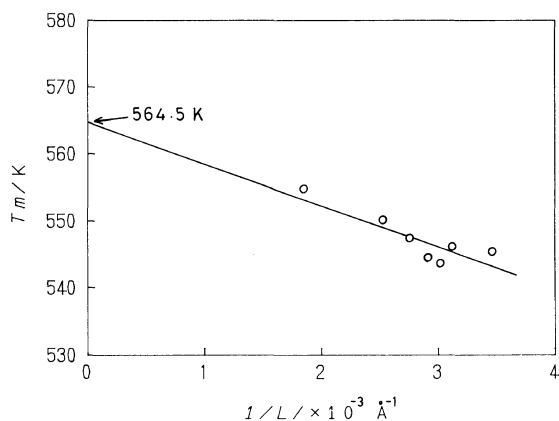


Figure 2. Plot of T_m with the reciprocal long period ($1/L$).

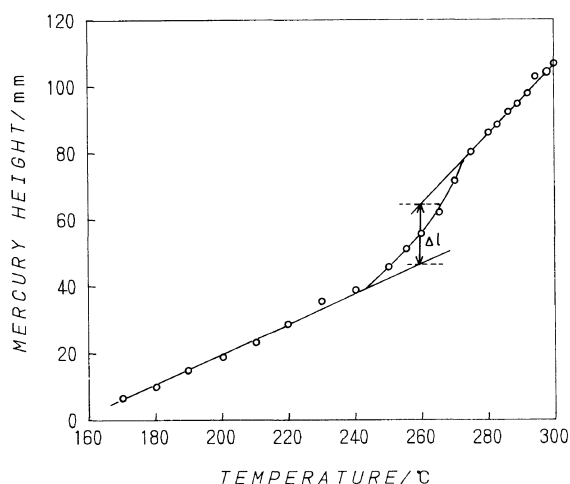


Figure 3. Thermal expansion curve of E-TFE.

($\text{cm}^3 \text{g}^{-1}$). In calculation of the heat of fusion from Clapeyron–Clausius eq 1

$$\Delta H_m = \frac{T_m \cdot \Delta V_m}{dT_m/dP} \quad (1)$$

crystallinity of the sample should be known.

Crystallinity of E-TFE sample used in dilatometry was determined by density measurement. The value of 1.757 g cm^{-3} as E-TFE crystal density and 1.684 g cm^{-3} as amorphous density by the data from Tanigami *et al.*⁷ were used to determine the sample crystallinity. The density measured by density column was 1.716 g cm^{-3} and the sample crystallinity was 45%. Heat of fusion of E-TFE calculated from eq 1 was 98.4 J g^{-1} .

Heat of fusion was also obtained by DSC. The value of ΔH_m for E-TFE determined by DSC was 96.0 J g^{-1} which is close to the value determined by eq 1.

Table II lists the values of the equilibrium melting temperature, pressure dependence of T_m^0 , ΔH_m and ΔS_m obtained by dividing ΔH_m by T_m^0 in E-TFE in this study and the literature values of ΔH_m and ΔS_m for PE,⁶ PTFE,⁸ and form II of PVDF⁶ which resembles to E-TFE in molecular component. Heat of fusion of E-TFE is much smaller than that of PE and it is close to that of PTFE. Order–disorder transition occurs at about 100°C in E-TFE¹ and the hexagonal phase (mesophase) appears. PTFE also shows hexagonal

Table II. Melting parameters of E-TFE (this work) and reference data of PE, PTFE, and form II of PVDF

	E-TFE	PE ⁶	PTFE ⁷	PVDF ⁶
$dT_m/dP/\text{K MPa}^{-1}$	0.72	0.30^5	0.97	0.38
$\Delta V/\text{cm}^3 \text{g}^{-1}$	0.077	—	—	—
T_m^0/K	564.5	414.6	600.2	480
Crystallinity/%	45	—	—	—
$\Delta H/\text{J g}^{-1}$	98.6	291	93	52.3
$\Delta S/\text{J g}^{-1} \text{K}^{-1}$	0.175	0.702	0.155	0.108
ΔH_m by DSC/ J g^{-1}	96.0	—	—	—
ΔS_m by DSC/ $\text{J g}^{-1} \text{K}^{-1}$	0.171	—	—	—

transition at 30°C at atmospheric pressure. PVDF crystal becomes soft above about 87°C by changing to condic crystal.⁹ The entropy change ΔS_m at melting for E-TFE, PTFE, and PVDF is very small compared to the change in PE. Melting in these fluorine polymers occurs from soft mesophase to liquid state, so that the entropy change is small. On the contrary, PE melts from the solid orthorhombic phase to the liquid state at 0.1 MPa and the entropy change is large. PE melting occurs through hexagonal phase resemble to liquid crystal under high pressure but it appears above 300 MPa. The value of pressure coefficients of T_m (dT_m/dP) at 0.1 MPa of E-TFE is very large among polymer crystals.

Equilibrium melting temperature T_m^0 of E-TFE crystal is very large among polymer crystals and is close to that of PTFE, not to that of PVDF. The E-TFE molecular chain has sequence of two CF_2 and two CH_2 units, contrary to the alternating sequence of CF_2 and CH_2 units in PVDF molecule, even though small amount head to head or tail to tail linkage exists in PVDF molecule. Existence of CF_2 sequence might decrease the molecular mobility around chain axis and result in the different melting behavior between E-TFE and PVDF molecules, considering that PTFE composed of only CF_2 shows high melting temperature among polymer crystals.

Very large pressure coefficient of T_m of E-TFE and PTFE is thought to be caused from large compressibility of the supercooled melt just below the melting temperature of these polymers. This consideration is supported by the comparison of the storage modulus (E') in the dynamic mechanical testing. In PE, the value of E' just below melting of single crystal mats¹⁰ is about 100 MPa. The value of E' in E-TFE at 200°C is 25 MPa and it decreases drastically around 200°C with temperature,¹ so that the extrapolated value at 250°C (below melting temperature) becomes about 9 MPa. The value of E' in PTFE at 150°C is 60 MPa¹¹ and the value extrapolated to 320°C (just below the melting temperature) becomes about 20 MPa. Temperature dependence of E' of PVDF is also reported by Imken *et al.*¹² The value at 80°C is 600 MPa and the extended value at 160°C becomes about 200 MPa. The smaller value of E' means larger compressibility about an order of decade just below the melting temperature.

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