

MELTING BEHAVIOR OF γ -IRRADIATED ETHYLENE-alt-TETRAFLUOROETHYLENE COPOLYMER*

FU Tiejuan (傅铁垣), ZHANG Lifeng (张丽峰)**,
QI Yuchen (基玉臣) and CHEN Donglin (陈东霖)

(*Institute of Applied Chemistry, Academia Sinica, Changchun*)

ABSTRACT

The melting behavior of poly(ethylene-alt-tetrafluoroethylene) γ -irradiated in air and vacuum was studied by DSC. From the results of DSC and density measurements the equilibrium heat of fusion, ΔH_m° , and the density of the amorphous phase, ρ_a , of the polymer were estimated as 172J/g and 1.63g/cm³ respectively. Thereby the degree of crystallinity of this copolymer can be evaluated by both density and calorimetric methods. The crystal structure was damaged gradually and eventually completely destroyed with the increase in radiation dose from 0.3 to 900 Mrads. Exclusion of air was advantageous in lessening the damage of the crystal while increase in the degree of vacuum favored the formation of crosslinks. Small peaks appearing both on the DSC endotherm (600K) and on the exotherm (540K) resulted from the presence of small amount of tetrafluoroethylene blocks along the main chain of poly(ethylene-alt-tetrafluoroethylene).

Poly(ethylene-alt-tetrafluoroethylene), P(E-alt-TFE), is isomeric with polyvinylidene-fluoride (PVDF), the former being a head-to-head configuration of the latter. The alternating copolymer features high melting temperature, about 100°C higher than that of PVDF, and low dielectric dissipation, about one thousandth that of PVDF^[1]. It is also excellent in mechanical properties and fabrication performance^[2]. Especially, among all the fluoro-containing polymers, P(E-alt-TFE) is one of the most γ -irradiation stable polymer and is widely applied in nuclear industry.

Although a great deal of works concerning the physical properties of PVDF has been reported during the recent years^[4-6], literature on that of P(E-alt-TFE) is scarce. In the present work, differential scanning calorimeter (DSC) was used to study the effect of thermal treatment and γ -irradiation on the melting and crystallization behavior of P(E-alt-TFE). At the same time, the deterioration of crystal structure caused by γ -radiation was also studied by WAXD technique.

EXPERIMENTAL

Sample

A P(E-alt-TFE) granular sample (G81-81) containing 48 mole% of ethylene was kindly

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** Thesis student of the Chemical Engineering Department, Jilin Institute of Technology, 1983.

supplied by the Shanghai Institute of Organic Chemistry, Academia Sinica. The granules were pressed into sheets or films at $305 \pm 5^\circ\text{C}$ for 3 mins. Thereafter, they were cooled under different conditions (see Tab. 1). The samples were subjected to γ -irradiation in a ^{60}Co radiation source at room temperature both in air (series A) and in vacuum (series V, 10^{-2} torr) with a dose rate of $5.5 \cdot 10^5$ röntgen/hour. Radiation dose are tabulated in Tab. 2.

Table 1 Cooling conditions of P(E-alt-TFE) samples

No.	Treatment after pressing at $305 \pm 5^\circ\text{C}$
0	Removed from the press, cooled at ambient temperature
1	Cooled in the press from 300°C to room temperature at a rate of $0.1^\circ\text{C}/\text{min}$
2	Turn off the power, cooled to room temperature in the press
3	Sample #0 annealed in a muffle furnace (240°C) for 14 hours
4	Quenched in ice water

Table 2 Irradiation conditions for P(E-alt-TFE) samples

No.	Series A	A ₁	A ₃	A ₅	A ₇	A ₈	A ₉	A ₁₀	A ₁₁
	Series V	V ₁	V ₃	V ₅	V ₇	V ₈	V ₉	V ₁₀	V ₁₁
Radiation dose (Mrads)		0.3	3	10	60	120	240	400	900

Apparatus and Techniques

Differential Scanning Calorimetry — A Perkin-Elmer Model DSC-2C differential calorimeter was used to study the melting and crystallization behavior. The temperature scale of the calorimeter was calibrated over a temperature range of 150 – 300°C by standard In, Sn and Pb calibrants, and the ΔH was calculated by comparing with the heat of fusion of a known weight of standard In. The irradiated samples were heated twice in DSC. The first heating was used to erase the processing history. Unless otherwise stated, all the melting data were taken from the second heating endotherms. Measurements were carried out under the following conditions: sample weight, 25 ± 0.2 mg; heating (cooling) rate, $10^\circ\text{C}/\text{min}$; chart speed, 20 mm/min; atmosphere, flowing nitrogen.

WAXD — The X-ray diffraction measurements of P(E-alt-TFE) samples were made using a Rigaku Model 2028 X-ray diffractometer with nickel foil filtered CuK_α source. 2θ value was recorded in $0.1^\circ/\text{division}$ with a scanning rate of $2^\circ/\text{min}$ and calibrated with a standard silicon sheet.

Density Measurement — Density of the samples was determined by heavy liquid-variable temperature method^[3]. Heavy liquid: tribromomethane (sp. gr. ~ 2.89); light liquid: trichloromethane (sp. gr. ~ 1.47).

RESULTS AND DISCUSSION

After irradiation the crystalline structure of P(E-alt-TFE) was damaged irrespective of the atmosphere in which the sample was subjected to irradiation. Therefore, both the heat of fusion, ΔH_m , and the melting point, T_m , were lowered with the increase in radiation dose. On the other hand, the crosslinking effect induced by irradiation inhibited both the reorganization of imperfect crystals during melting and the alignment of macromolecules in the melt during crystallization. Thus the crystallization temperature during constant cooling rate, T_c , and its corresponding heat of crystallization, ΔH_c , were also affected and shifted to lower values. The DSC endotherms and exotherms during melting and crystallization of series A samples are shown in Figs. 1 and 2.

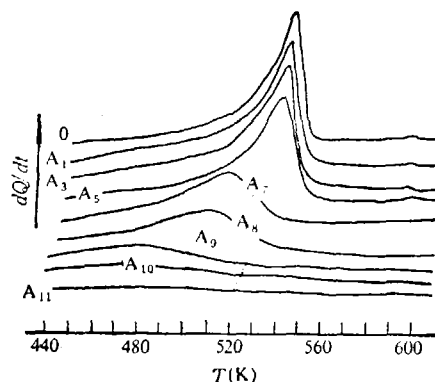


Fig. 1 Melting endotherms of series A samples

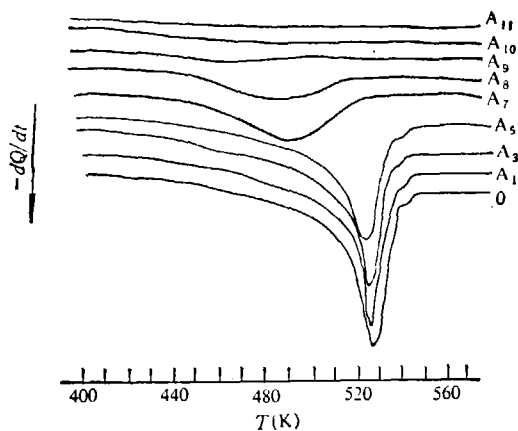


Fig. 2 Crystallization exotherms of series A samples

With the increase in radiation dose, DSC melting endotherms and crystallization exotherms shifted gradually to lower temperatures, and the peak area diminished accordingly. When the radiation dose reached as high as up to 900 Mrads, both endo- and exotherms degenerated nearly into horizontal lines, the thermal event owing to the melting or crystallization of crystals could hardly be observed. It means that at such a high radiation dose, the crystals had

been completely destroyed, and the highly crosslinked macromolecules was no longer capable of recrystallization. The same trend holds true for samples of series V (see Fig. 3 and Fig. 4). However, since there was not enough amount of oxygen to combine with the radicals generated during irradiation, molecular scission was inhibited somewhat and crosslinking was enhanced. As can be seen from Figs. 5 and 6, for the same amount of radiation dose, all the values of T_m , T_c and ΔH_m were higher than the corresponding values in series A.

But the influence of the presence of oxygen on the thermogram prevails only in the dose range from 10 to 400 Mrads. For radiation dose lower than 10 Mrads, much the same T_m , T_c and ΔH_m values were obtained for both series A and V samples. After then, with the increase in radiation dose, the difference in thermal properties between the two series of samples was getting larger and larger. For example, at 240 Mrads of irradiation, the lowering of

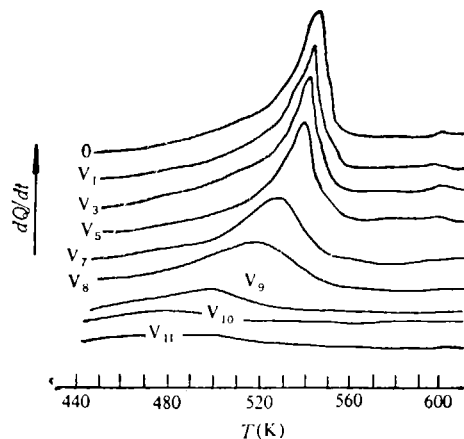


Fig. 3 Melting endotherms of series V samples

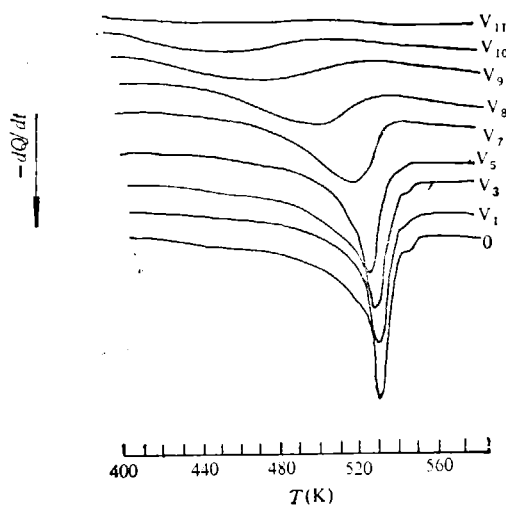
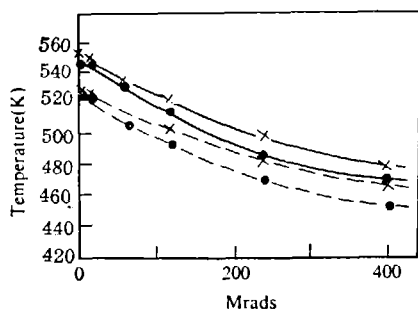
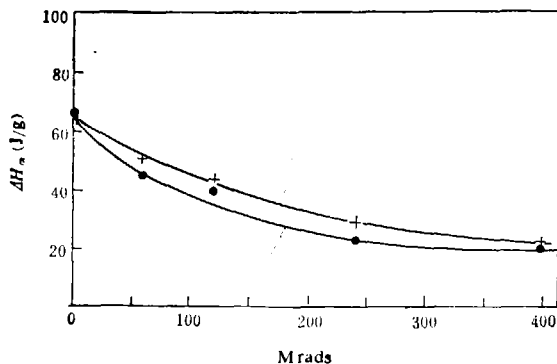


Fig. 4 Crystallization exotherms of series V samples

Fig. 5 Dependence of T_m and T_c upon radiation dose

× series V — T_m ;
● series A --- T_c .

Fig. 6 Dependence of ΔH_m upon radiation dose

● series A;
× series V.

ΔH_m was about 56% for V₉, while 66% for A₉. But if the dosage was larger than 400 Mrads, the discrepancy between these two series becomes negligible again. Based on the experimental results, the relationship between ΔH_m and radiation dose R below 400 Mrads can be expressed as follows:

$$\Delta H_m(A) = (1.7 \cdot 10^{-3}R + 2.7 \cdot 10^{-1})^{-1} \quad (\text{J/g})$$

$$\Delta H_m(V) = (1.5 \cdot 10^{-3}R + 2.6 \cdot 10^{-1})^{-1} \quad (\text{J/g})$$

where $\Delta H_m(A)$ and $\Delta H_m(V)$ are the heat of fusion of γ -irradiated series A and V samples respectively. R is in the unit of Mrads.

P(E-alt-TFE) is a semicrystalline polymer. Its crystalline structure belongs to monoclinic crystallographic system with a planar zigzag molecular conformation^[7]. On the wide angle X-ray diffraction pattern over a span of 65° Bragg angle, there are two crystalline diffraction peaks, c_1 and c_2 as shown in Fig. 7, and the X-ray crystallinity of P(E-alt-TFE) samples can be evaluated by means of method suggested by reference [8]. This is the only way to measure the crystallinity of this polymer, because so far no characteristic constants such as equilibrium heat of fusion, ΔH_m^0 , or density of completely amorphous phase at 23°C, ρ_a , of this polymer are available in the literature for calorimetric or density method. By plotting ΔH_m from the first run DSC endotherms against corresponding specific volumes (V_{sp}) of the thermally treated samples listed in Tab. 3, a straight line could be obtained (Fig. 8). Through

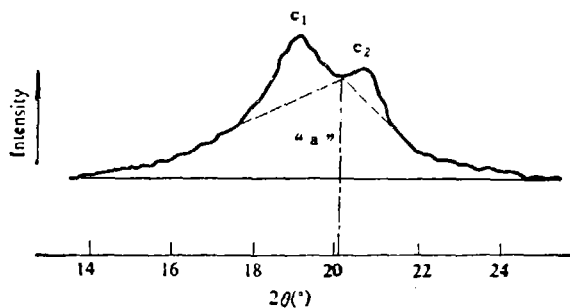
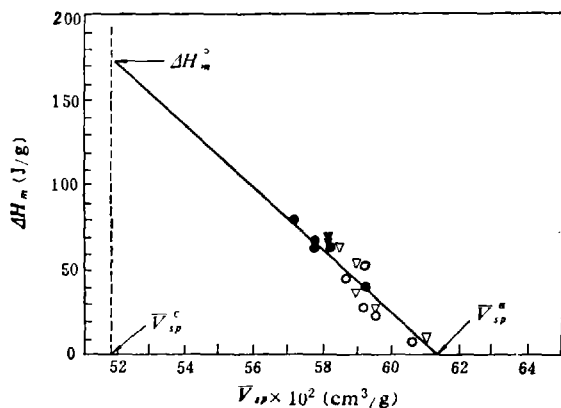


Fig. 7 Resolution of X-ray diffraction pattern of P(E-alt-TFE)

Fig. 8 Relationship between ΔH_m and V_{sp} at 23°C

● onnealed; ○ series A; ▽ series V

linear regression, an expression in the following form with a correlation factor of -0.98 was deduced.

$$\Delta H_m = 1127 - 1843 V_{sp} \quad (\text{J/g})$$

Substituting boundary conditions into the above equation, we obtained $V_{sp}^a = 0.612 \text{ cm}^3/\text{g}$ (or $\rho_a = 1.63 \text{ g/cm}^3$) when $\Delta H_m = 0$; and $\Delta H_m^0 = 172 \text{ J/g}$ when $V_{sp}^c = 0.518 \text{ cm}^3/\text{g}$ (or $\rho_c = 1.93 \text{ g/cm}^3$)^[7]. If all the ΔH_m and V_{sp} data of both A and V series listed in Tab. 3 were plotted as above, values of $\Delta H_m^0 = 197 \text{ J/g}$ and $V_{sp}^a = 0.610 \text{ cm}^3/\text{g}$ were calculated with a poor correlation coefficient of -0.91 . Although there are only a few data points available to derive the values of ΔH_m^0 and V_{sp}^a from thermally treated samples, we recommend the values obtained from these samples because not only it is theoretically more sound and shows a higher correlation coefficient, but the crystallinities calculated by the use of $\Delta H_m^0 = 172 \text{ J/g}$ agree better with those obtained by density or X-ray method than when $\Delta H_m^0 = 189 \text{ J/g}$ is used.

It is of interest to indicate that the V_{sp}^a values derived from both methods are practically the same (0.610 vs. 0.612). It seems that the γ -irradiation has basically no profound effect upon the density of the amorphous phase of P(E-alt-TFE) sample. Thereby this value can also be used to calculate the crystallinity of the irradiated P(E-alt-TFE) sample by density method. Besides, the value $V_{sp}^a = 0.612 \text{ cm}^3/\text{g}$ also seems to be reasonable because the ratio $\rho_c/\rho_a = 1.18$ is much the same as that of the related polymers, e.g. polyethylene, (1.18); polytetrafluoroethylene, (1.17); and PVDF, (1.15)^[9].

On the basis of the characteristic physical constants obtained above, in addition to X-ray

Table 3 Crystallinity of P(E-alt-TFE)

Sample		Density ρ_{23} (g/cm ³)	Heat of fusion ΔH_m (J/g)		Crystallinity (%)		
Series	No.		1st run	2nd run	Density method	Calorimetric method	X-ray method
	1	1.7529	79.2		44	46	58
	2	1.7345	63.2		38	37	40
	3	1.7351	61.6		38	36	37
	4	1.6910	28.5		21	22	24
A	1	1.7206	62.0	64.5	33	36	35
	3	1.7146	—	66.6	30	—	36
	7	1.7049	44.4	44.4	27	26	29
	8	1.6912	51.1	39.4	22	30	19
	9	1.6880	27.2	22.2	21	16	—
	10	1.6802	23.9	19.3	19	14	—
	11	1.6484	8.4	8.4	6	5	—
V	1	1.7196	64.5	64.1	32	38	37
	3	1.7200	66.2	64.9	33	38	39
	7	1.7103	62.0	50.7	29	36	34
	8	1.6951	55.3	43.6	24	32	22
	9	1.6948	32.6	28.1	23	19	—
	10	1.6808	26.8	20.5	18	16	—
	11	1.6403	11.0	10.9	3	6	—

Table 4 Influence of thermal treatment on the interplanar spacing

Sample No.	Diffraction peak c_1 d_1 (Å)	Diffraction peak c_2 d_2 (Å)
1	4.55	4.09
2	4.56	4.23
0	4.60	4.29
4	4.75	4.31

method, it is possible to calculate the crystallinity of the samples by calorimetric or density method. The results calculated by these three methods are shown in Tab. 3. As can be seen from the table, the values are different for different methods. This is because the different methods of measurement may be sensitive to different definitions of crystalline order.

However, the trend of the variation of crystallinity with radiation dose is the same despite of the different methods of measurement.

Listed in Tab. 4 are the values of interplanar spacing d_1 and d_2 , which reflect the size of unit cell for samples subjected to various thermal treatments. The cooling rate of sample No. 1 was the lowest; for other samples, the rate increased in the order of No. 2, 0 and 4. Since the sample No. 1 had the most favoured condition to crystallize, the crystallinity was the highest and the d value the lowest. With the increase in cooling rate, the crystallinity decreased and the interplanar spacing increased.

As to the influence of γ -irradiation on the crystal structure of P(E-alt-TFE), it can be seen from Figs. 9 and 10 that for both series A and V, the intensity of peak c_2 diminished gradually with the increase in radiation dose and eventually vanished when the radiation dose exceeded 240 Mrads. At the same time, peak c_1 also weakened appreciably. At high level of radiation dose, the superimposition of the intensity c_1 on the amorphous peak resulted in an abnormal single peak diffraction pattern, thus rendered the correct determination of crystallinity by X-ray method difficult. However, both calorimetric and density methods were still applicable at such a low degree of crystallinity (Tab. 3).

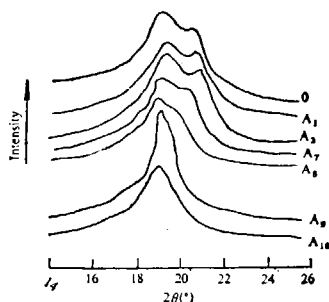


Fig. 9 X-ray diffraction patterns of series A samples

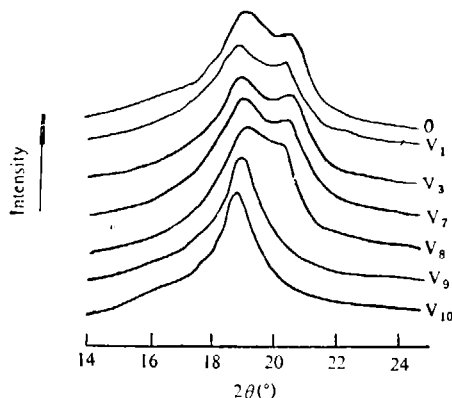


Fig. 10 X-ray diffraction patterns of series V samples

Fig. 11 shows the radiation dose dependence of interplanar spacing d_1 and d_2 . The values of d_1 were nearly independent of radiation dose, while d_2 varied only a little before 30 Mrads

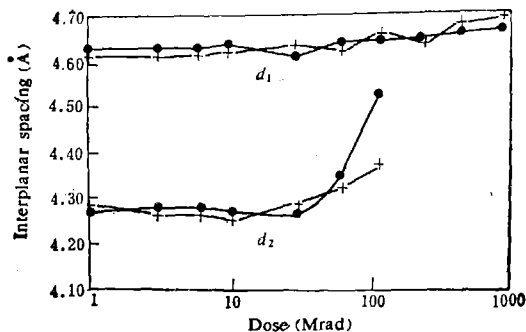


Fig. 11 Radiation dose dependence of the interplanar spacing of P(E-alt-TFE)

● series A; ⊕ series V.

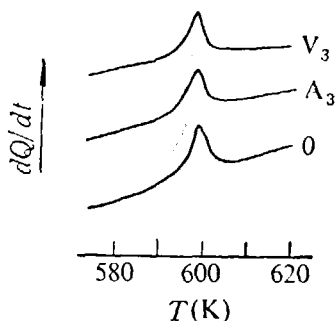


Fig. 12 Magnification of 600K small endothermic peaks (sensitivity: 1 mcal/sec full scale)

was reached. Above 30 Mrads, d_2 increased rapidly, i.e. for both series of samples, it was only above this level of radiation dose, that the crystal structure would be damaged appreciably.

As shown in Figs. 1 and 2, there was a small endothermic peak at 600 K on the DSC melting curve for samples A_1 — A_5 and V_1 — V_7 . At the same time, a corresponding small exothermic peak appeared on the DSC crystallization curve at 540 K. Fig. 12 is a magnification of the 600 K peak with a range of 1 mcal / sec full scale for samples No. 0, A_3 and V_3 . By means of a computerized TADS interfaced with the DSC-2C, the heat of fusion of this small peak was evaluated to be only about one thousandth the total thermal effect of the sample. There are three possibilities responsible for the occurrence of this small thermal effect, i.e. the T_u transition of fluoro-containing polymers in the range of $(1.1-1.42) T_m^{[10]}$, the presence of homopolymer impurity, i.e. polytetrafluoroethylene (PTFE), and the formation of PTFE block along the alternating main chain. We exclude the first two possibilities, because for some other P(E-alt-TFE) samples, such as DI-91-47, no such small peaks are discernible on the thermogram (see Fig. 13). For a deliberately mixed sample, which was prepared by blending small amount of PTFE with sample DI-91-47, and the content of PTFE was adjusted in such a way that it would yield the same amount of thermal effect as that of sample G81-81, although both the small T_m and T_c peaks appeared on the thermograms, the location of them were in

close agreement with pure PTFE rather than G81-81 (T_m was 5K and T_c , 47K higher than that of G81-81, see Fig. 13 (a) and (b)). All the above mentioned experimental results suggest that the small peak on the thermogram of sample G81-81 should be attributed to the presence of small amount of $-(CF_2CF_2)_n-$ blocks along the alternating main chain. As the molecular weight of the blocks is not high enough and the blocks are covalent-bonded with the main chain, the melting point is lowered and more super-cooling is needed for crystallization. A further confirmation of the above point of view is given by the fact that after the sample had been subjected to higher radiation dose, the small peaks disappeared completely on the thermograms (see Figs. 1 and 2), since it is well-known that PTFE molecule is very liable to radiation dose.

Fig. 15 illustrates the TMA curves of P(E-alt-TFE) samples before and after irradiation.

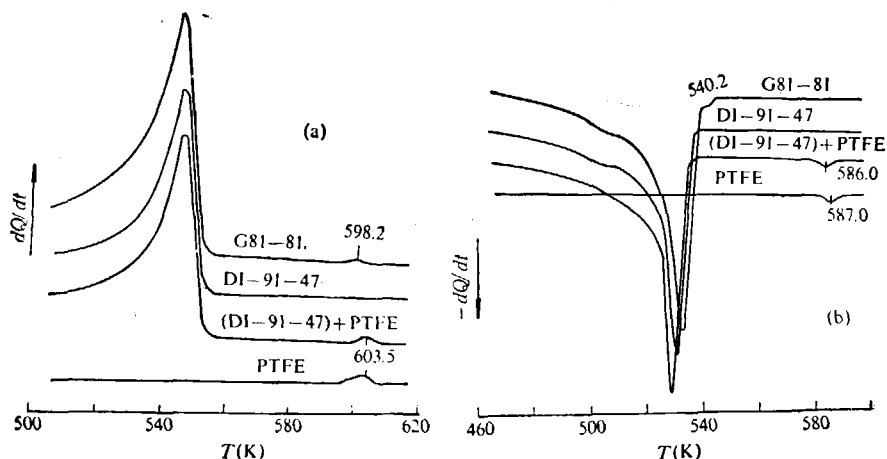


Fig. 13 The occurrence and location of 600K small peaks on DSC thermograms for various samples

(a) endotherms, (b) exotherms.

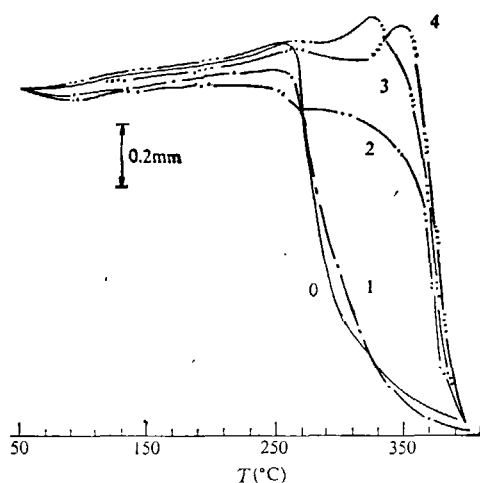


Fig. 14 TMA curves of P(E-alt-TFE) samples
0. unirradiated; 1. $1 \cdot 10^{-5}$ torr, $1 \cdot 10^6$ rads;
2. $1 \cdot 10^{-5}$ torr, $1 \cdot 10^7$ rads; 3. A_5 ; 4. V_5 .

with different amount of radiation dose in different atmospheres. It is obvious that only above $1 \cdot 10^3$ rads and in high vacuum a distinct rubbery elastic state will appear. Therefore, it is important to keep high degree of vacuum to increase the efficiency of irradiation cross-linking of this copolymer.

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