Curie transition study in a 70/30 mol% copolymer of vinylidene fluoride and trifluoroethylene by mechanical spectrometry

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Vinylidene fluoride/trifluoroethylene statistical copolymer is a ferroelectric system with one observable Curie transition (in the case of 70/30 mol% composition). Data obtained by mechanical spectrometry show that the loss angle varies weakly with temperature in the transition range. We also observe a large decrease in modulus in this temperature range. These results are discussed in terms of a mixture of two crystalline phases in the transition range. The coexistence of these phases (ferroelectric and paraelectric) around the Curie transition point leads to hysteresis characteristic of a first-order transition. The purpose of this paper is to characterize the material modulus from the mixture formula for a two-phase system in the range of the Curie transition. Complementary results from differential scanning calorimetry and dielectric spectrometry are in agreement with such a hypothesis.

(Keywords: Curie transition; copolymer; mechanical spectrometry)

INTRODUCTION

The statistical copolymer of vinylidene fluoride (VF_2) and trifluoroethylene (TrFE) (70 mol% and 30 mol% respectively) has the same structure as the poly(vinylidene fluoride) (PVDF) β phase at room temperature and also presents a Curie transition temperature lower than its melting temperature[1–4].

Through studies of X-ray diffraction, Lovinger[5] and Tashiro[6] showed recently that the ferro–paraelectric transition is associated with a conformational change in chains and therefore with a disorder of the molecular electric dipoles. This disorder results from the crystalline transformation of the *trans* polar low-temperature phase to the non-polar high-temperature phase.

After characterizing the material by X-ray diffraction and differential scanning calorimetry (d.s.c.) techniques, we study the mechanical, dielectric and piezoelectric properties of the copolymer. For these studies, our attention was focused on the Curie transition range.

Thus, the purpose of this paper is to characterize the material from the mixture formula for a two-phase system in the range of the Curie transition.

EXPERIMENTAL

The copolymer of vinylidene fluoride and trifluoroethylene (VF_2/TrFE 70/30) was a statistical polymer supplied by Atochem in powder form and having the following characteristics: reference P2031, $M_n = 93\,000$, $M_w = 173\,000$. Samples 100 μm to 1 mm thick were obtained by the following method: hot compression and quenching in water, called 'F'. Samples 'F' were annealed at 413 K for 3 h in an oven. They are then called F413.

The dynamic modulus was measured using a mechanical spectrometer[7] developed in our laboratory; it works in torsion mode at very low frequencies (10^{-5} to 5 Hz) in the temperature range of 100 to 400 K. Data on the complex shear modulus are reported, using the real part G' and $\tan \phi$ ($= G''/G'$).

X-ray diffraction measurements were carried out in reflection mode using monochromatic Cu Kα radiation from a Rigaku diffractometer.

Specific heat, temperatures and enthalpies of Curie transition, melting and crystallization are determined by using d.s.c. performed with a Mettler TA 3000 system at a heating or cooling rate of 10 K min^{-1}.

After metallization of sample faces with silver, an impedance meter (autoranging digital impedance meter, from Electro Scientific Industries, model 253) was used for the measurements of relative dielectric permittivity at 1 kHz in the temperature range 200–425 K.

In order to determine the piezoelectric coefficient d_{33}, we polarized the sample with an electric field of 30 kV mm^{-1} (for 30 min at 373 K) in a silicone oil bath; the material was then cooled, under the field, down to 333 K. The piezoelectric coefficient d_{33} was measured by the direct method, consisting of applying a stress σ on the faces of the samples; the electric charges Q thus generated at the surface are then measured using a piezometer (from Berlincourt), to obtain $d_{33} = Q/\sigma$.

RESULTS

Material characterization

X-ray diffraction. Figure 1 shows the X-ray diffraction patterns of specimens F and F413. The peak at 2θ in each spectrum characterizes the composite (1 1 0, 2 0 0)

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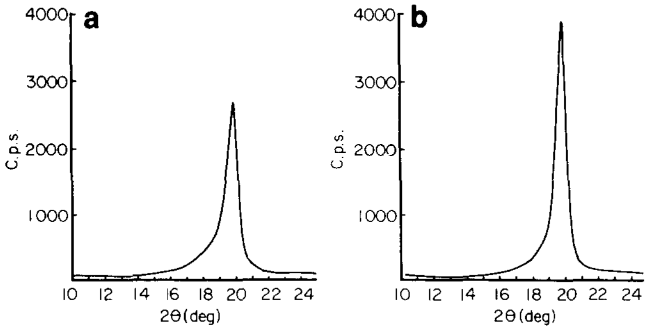

Figure 1 X-ray diffraction plots of copoly(VF_2/TrFE 70/30) samples: (a) F, (b) F413

reflection of the β phase[3,6,8], which is composed of *trans* zig-zag chain conformations. These spectra show the characteristic reflections of the monoclinic structure[3,9], whose unit-cell parameters are as follows: $a = 0.918$ nm, $b = 0.512$ nm, $c = 0.255$ nm and $\beta = 91°52'$.

The X-ray diffractograms of specimens 'F' show a weak reflection of the crystalline phase, which may be assigned to the β phase. Under the effect of annealing at 413 K, i.e. higher than the Curie temperature T_C, the amorphous phase transforms partially into the β phase[10]. It was mentioned in the literature[3,10] that annealing treatment could result in a reduction of imperfections in crystallites and in an increase of the crystallite ratio as well as of the crystallite size. Thus we have verified how far such a change may occur in our experiment. If one considers the diffraction intensity profile, the half-width $\Delta(2\theta)$ of the composite reflection is related to the crystallite thickness L by the Scherrer formula[11]:

$$\Delta(2\theta) = \frac{0.9\lambda}{2L\cos\theta}$$

where λ = used wavelength, $\Delta(2\theta)$ = width of θ diffraction line and L = the lamellar thickness.

One can estimate as a first approximation that L is an average value following the normal to the planes in the Bragg position. We present in *Table 1* information concerning the composite reflection (1 1 0, 2 0 0). These results show that annealing only slightly enhances the size of the crystallites.

Differential scanning calorimetry. In order to study the thermal properties, sample F413 is submitted to a first heating, from room temperature up to 393 K (*Figure 2A*), followed by cooling to room temperature (*Figure 2B*), in the experimental set-up at the rate of $10\,\mathrm{K\,min^{-1}}$. *Figure 2A* shows two endothermic peaks corresponding to the ferroelectric–paraelectric transition. In the first cooling process, two exothermic peaks appear at the paraelectric–ferroelectric transition temperatures, which is indicative of a first-order transition between these two phases. In order to stabilize the thermal properties, another heating and cooling process of the sample, as previously described, is undertaken. D.s.c. thermograms presented in *Figure 3* are plotted during this second process. *Figure 3A* shows, at the Curie point, two endothermic peaks ($T_{C1^+} = 365$ K, $T_{C2^+} = 375$ K), which correspond to that seen in *Figure 2A* (but shifted to higher temperature) and a melting peak at $T_M = 426$ K. The low-temperature peak could be related to the crystalline phase and the high-temperature peak to the amorphous phase[12]. This hypothesis is in agreement with the results obtained by Hirschinger *et al.*[2], who emphasized from n.m.r. spectrometry that an increase of the amorphous phase ratio is associated with the Curie transition, in the temperature range corresponding to the high-temperature peak in d.s.c., while the structural change (paraelectric phase ratio) corresponds to the low-temperature peak. Moreira[4] suggests that the low-temperature peak corresponds to the Curie transition (T_{C1}) in imperfectly crystallized crystalline regions, whereas the high-temperature peak (T_{C2}) could result from well formed crystallites. During the cooling experiment, an exothermic peak appears at the crystallization or solidification temperature $T_s = 404$ K, and two other peaks appearing around T_C ($T_{C1} = 324$ K, $T_{C2} = 333$ K) characterize the existence of a strong thermal hysteresis

Table 1 X-ray data of the (1 1 0, 2 0 0) reflection for VF_2/TrFE 70/30. L is the size of the crystallites calculated from the Scherrer formula

	2θ (deg)	$\Delta(2\theta)$ (deg)	L (nm)	Intensity	d_{hkl} (nm)
Sample F	19.84	0.85	10	2686	0.447
Sample F413	19.86	0.7	12	3889	0.446

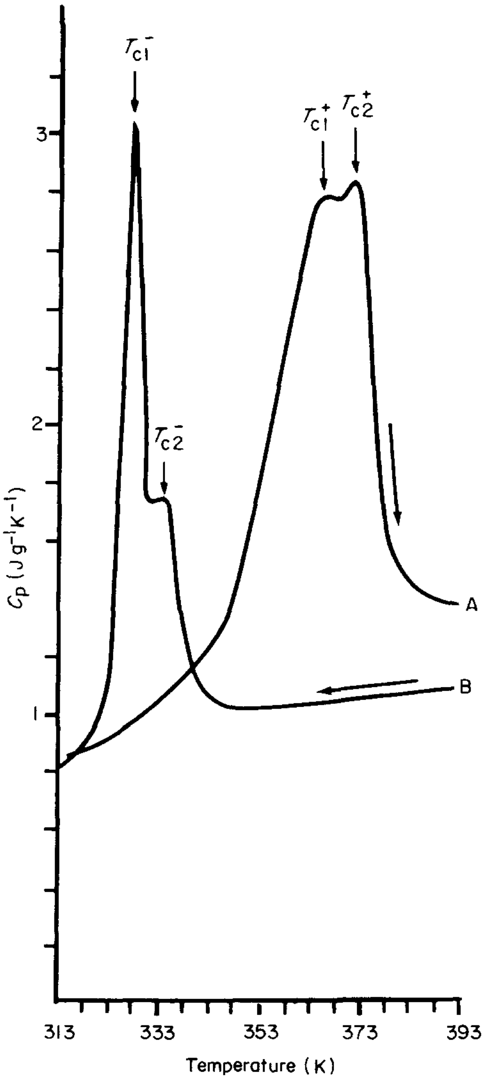

Figure 2 Specific heat as a function of temperature for sample F413. Heating and cooling rate of $10\,\mathrm{K\,min^{-1}}$. (A) Heating from 313 to 393 K. (B) Cooling from 393 to 313 K

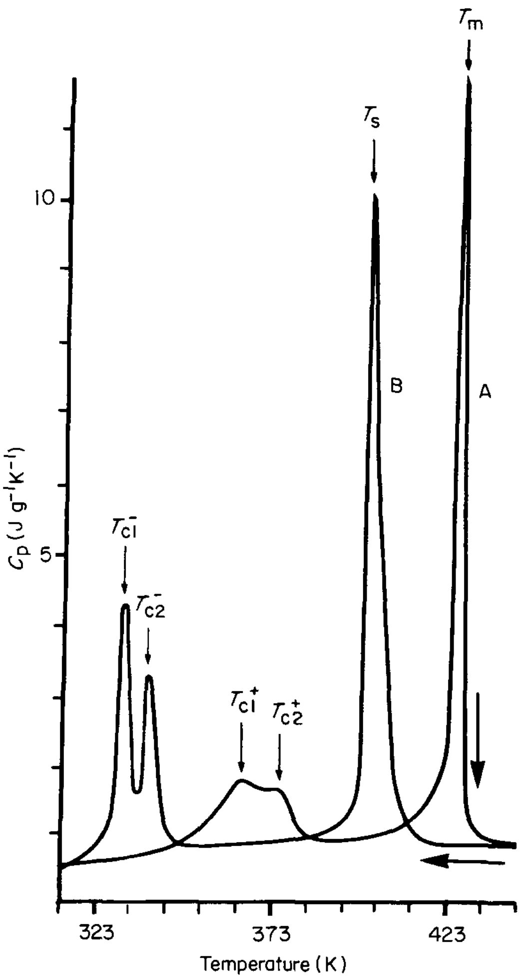

Figure 3 As *Figure 2* for second process. (A) Heating from 313 to 443 K. (B) Cooling from 443 to 313 K

Table 2 Thermal properties of VF_2/TrFE 70/30 (sample F413)

Heating			
T_C (K)	ΔH_C (J g^{-1})	T_M (K)	ΔH_M (J g^{-1})
365–375	22	426	31
Cooling			
T_s (K)	ΔH_s (J g^{-1})	T_C (K)	ΔH_C (J g^{-1})
404	27	324–333	17

$\Delta T = 40$ K (*Figure 3B*). Chalumeau[12] observes a third peak associated with the metastable β pseudo-phase, which does not appear during heating. Koga *et al.*[10] explain these peaks by the presence of conformational defects in lamellae obtained during cooling from high temperature ($T > T_C$) to a temperature below T_C. We summarize the thermal properties of this copolymer in *Table 2*.

Mechanical spectrometry

Before studying the mechanical properties, sample F413 is heated in the set-up at the rate of 2 K min^{-1} from 175 to 400 K, and cooled at the same rate from 400 to 175 K (*Figure 4*). *Figure 5*, plotted after such a thermal cycle in order to stabilize the properties, shows the

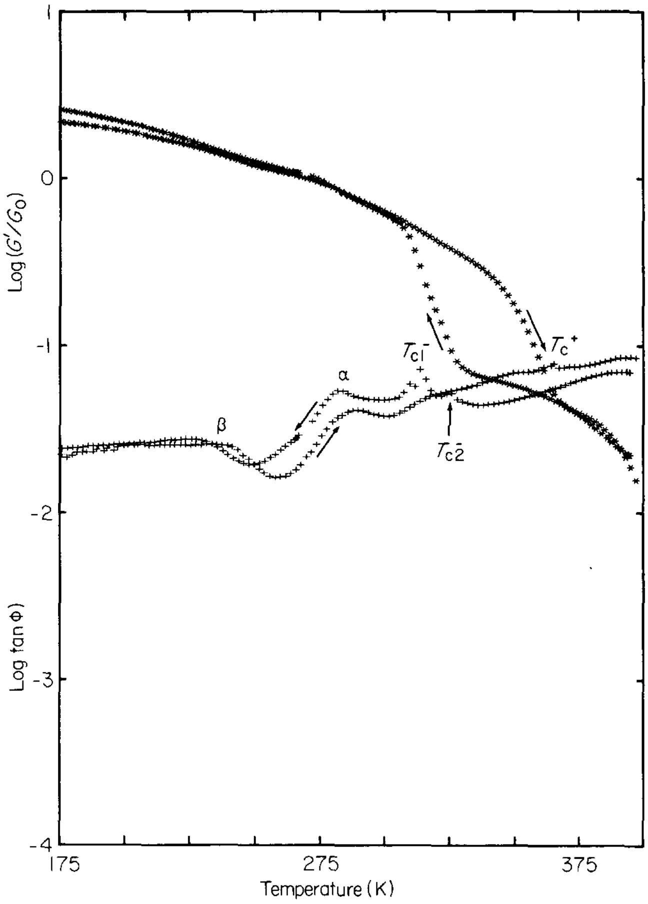

Figure 4 Plots of modulus and tan ϕ as functions of temperature for sample F413 at 1 Hz. Heating and cooling rate 2 K min^{-1}

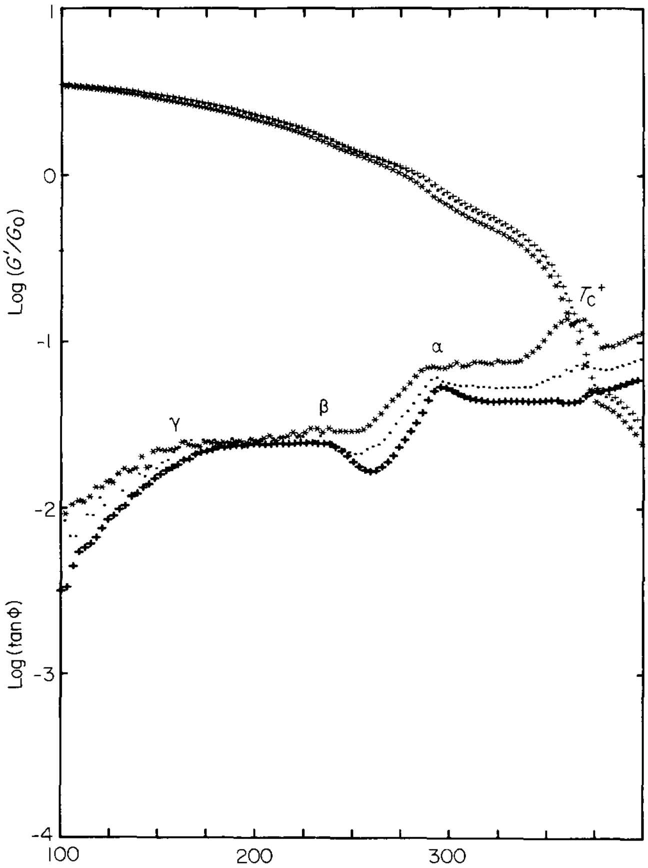

Figure 5 Plots of tan ϕ and log(G'/G_0) as functions of temperature for sample F413: (+), 1 Hz, (●) 0.1 Hz and (∗) 0.01 Hz. Heating rate 0.25 K min^{-1}, $G_0 = 10^9$

variation in tan ϕ and in log G' as functions of temperature at frequencies of 1, 0.1 and 0.01 Hz (the heating rate was 0.25 K $\min^{-1}$). The internal friction spectrum exhibits three relaxations, so-called α, β and γ at about 287, 237 and 150 K respectively. The α relaxation is associated with the existence of a crystalline phase[13,14]; the β relaxation is related to the glass transition in the amorphous phase[13,14]; and the γ relaxation is connected with local movements on molecular chains below the glass transition temperature[13,14].

At higher temperature, internal friction varies slowly in the transition region, while the modulus G' presents an important decrease between 325 and 375 K.

Peak position was located in agreement with the work by Koizumi *et al.*[13,14]. Generally, the γ peak is observable for all polymers containing CH_2 groups. This peak has been clearly observed on nylon-12[15] and polyethylene[16]. In the case of our materials, the crystallinity ratio being very high (60% before and 80% after annealing), the β and γ peaks in *Figure 5* are not clearly observed.

Results reported in *Figure 4* show a large hysteresis around 325 K; this behaviour is due in part to thermal hysteresis of the set-up as shown on α and β relaxations, but mainly due to the material itself. The large decrease in modulus and this hysteresis should be associated with the Curie transition in this temperature range; this will be discussed in the final section.

It is observed experimentally that, during heating, the tan ϕ peak temperature (T_{C^+}) is similar to the one measured from the inflection point of the $\log(G'/G_0)$ curve and corresponds to T_{C1^+}. This remark is valid on cooling as well (T_{C1}).

The different Curie temperatures obtained from d.s.c. and mechanical spectrometry should certainly be due to (i) the differences of heating and cooling rates and (ii) the thermal hysteresis of the set-up during cooling.

It is worth noting that the modulus decreases with frequency (*Figure 5*) and the β relaxation peak in tan ϕ shifts towards low temperatures: the apparent activation energy is about 470 kJ mol^{-1}. Such a result is commonly encountered for mechanical relaxation through the glass–rubber transition of an amorphous polymer. Furthermore, the α relaxation maximum as a function of temperature increases with decreasing frequency; a similar feature has been mentioned for polypropylene[17].

Dielectric spectrometry

Figure 6 shows the dielectric constant and loss measurements at 1 kHz for the sample F413 after the first thermal cycle. Dielectric relaxation measurements have shown that the ferroelectric–paraelectric transition of a 70/30 copolymer of $VF_2/TrFE$ is accompanied by a peak in ε_r' (heating and cooling). *Figure 6* clearly shows a large thermal hysteresis (connected with the first-order character of the transition). It is observed experimentally that the temperature at the inflection point of the ε_r' Curie transition peak corresponds to the temperature of the maximum low-temperature peak (T_{C1}) observed by d.s.c. The dielectric loss behaviour shows, at increasing temperatures, a β relaxation that is attributed to the amorphous phase of the polymer (movement of chains associated with the glass transition) and a peak associated with the ferro–paraelectric transition (cooling), but those corresponding to T_{C^-} appear less clearly during heating, because of the spreading of the ε_r' peak and electrical conduction phenomena at high temperature.

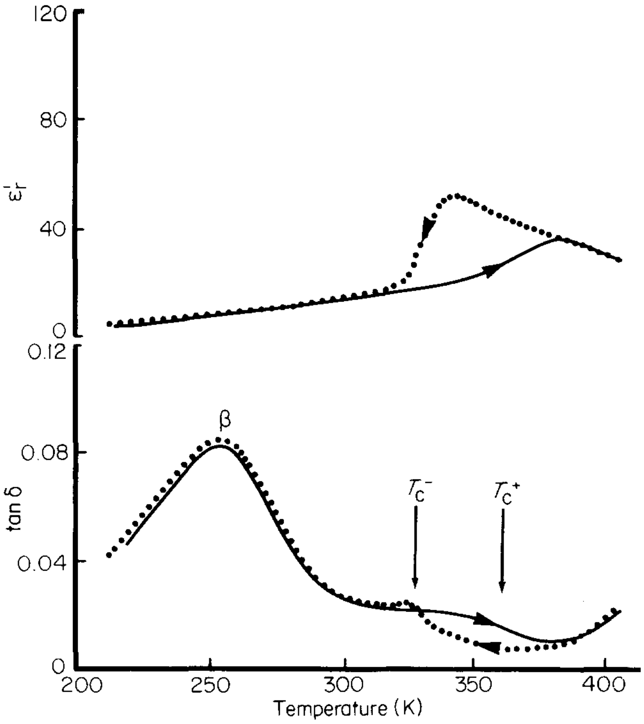

Figure 6 Dielectric constant and loss as functions of temperature for sample F413 at 1 kHz

Contrary to PVF_2, which in addition to β relaxation possesses an α relaxation whose origin is still being discussed, the $VF_2/TrFE$ copolymer does not exhibit dielectric α-relaxation, though some authors[18,19] attribute its origin to the crystalline phase.

DISCUSSION AND CONCLUSION

Using mechanical spectrometry, we have underlined the existence of three types of mechanical relaxations and a ferroelectric–paraelectric transition. Our discussion will be especially focused on the Curie transition range.

At T_C, one notes that the internal friction (tan ϕ) is only slightly dependent upon temperature and increases when the frequency is lowered (the domain boundaries are certainly mobile with a long relaxation time), while a strong variation of the modulus G' is observed (*Figure 5*). One cannot attribute this difference to thermal hysteresis of the experimental set-up, since such effects do not appear for the other relaxation processes.

We recall that, at $T > T_C$, the system is not polar, i.e. the dipoles are disordered on the microscopic scale, while the relative dielectric permittivity (susceptibility) increases in the vicinity of T_C due to the dipolar fluctuations. On the contrary at $T < T_C$, ferroelectric spontaneous domains exist whose order parameter varies continuously from 0 (fully paraelectric phase) to 1 (fully ferroelectric phase) as the temperature decreases. This suggests that, in the vicinity of T_C, we have a mixture of two crystalline phases whose proportion varies with temperature: (i) one ferroelectric with volume fraction x and (ii) one paraelectric with volume fraction $1 - x$. If we denote the ferroelectric and paraelectric phase moduli by E_1 and E_2 respectively, we can remark that the composite phase modulus can be written (as a first approximation):

$$E = E_1 x + E_2(1 - x) \qquad 0 < x < 1$$

Following these definitions, x could be considered as the order parameter. This equation shows that the modulus varies from E_1 to E_2 (E_2 to E_1) when x goes from 1 to 0 (0 to 1) for increasing (decreasing) temperature with a structure hysteresis. It is worth while to note the similar hysteresis between thermal measurements (*Figures 2* and *3*) and modulus measurements (*Figure 4*).

This interpretation is strengthened by the results obtained in dielectric measurements and presented in *Figure 6*. One sees that the temperature corresponding to the maximum of ε_r' is comparable to that where we observed a large decrease in modulus. Such an analysis is in agreement with that of Fukada *et al.*[1,20], who interpreted this phenomenon in terms of a transition between ferroelectric and paraelectric crystalline phases. In fact, the hysteresis ($35\,K < \Delta T < 40\,K$) shown in *Figures 4* and *6* is characteristic of a first-order transition[6,21]. Taking into account the probable distribution of Curie temperatures due to the distribution in size of crystallites[21], a difficulty results for a more quantitative interpretation of the measurement.

Because of its ferroelectric character and strong piezoelectric activity, the material studied in this paper (VF_2/TrFE 70/30) presents great interest, both scientifically and technologically. Measurements taken with F413 samples enable one to obtain values of the longitudinal piezoelectric coefficient d_{33} as high as $30\,pC\,N^{-1}$.

In conclusion, mechanical spectrometry constitutes a complementary technique for understanding the ferro–paraelectric transition.

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