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Compositional variation of the glass transition and the associated dielectric relaxation in copolymers of vinylidene fluoride and trifluoroethylene

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The glass transition temperature (T_g) of a series of statistical copolymers of vinylidene fluoride and trifluoroethylene has been determined experimentally. Its variation as a function of the chemical composition of the copolymers has been discussed based on the Fox, Di Marzio and Couchman equations. Using $T_g = -42°C$ for poly(vinylidene fluoride) and a value of T_g usually reported for polytrifluoroethylene ($T_g = 31°C$), a significant discrepancy has been obtained between experimental and predicted values. Thus, it has been suggested that the glass transition temperature for polytrifluoroethylene is located in the range of −20 to −10°C, which is consistent with Wunderlich's thermal analysis data.

(Keywords: fluorinated copolymers; glass transition; mixing laws)

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) and related copolymers are interesting materials with regard to their electroactive properties. Indeed, since the discovery of piezoelectricity[1] and pyroelectricity in PVDF[2], the latter has been applied to the development of a large variety of transduction mechanisms between electrical, mechanical and thermal phenomena[3,4].

Random copolymers of vinylidene fluoride (VDF, $-CH_2-CF_2-$) and trifluoroethylene (TrFE, $-CHF-CF_2-$) are a great advantage over PVDF homopolymer when technical applications are concerned. Piezoelectricity and pyroelectricity can be produced by poling films from melt or solution, whereas PVDF has to be stretched prior to poling. Moreover, high-crystallinity materials can be achieved[5].

These properties of PVDF and its copolymers are related to the ferroelectricity of the crystalline β phase (all-*trans*): the direction of polarization can be changed by the application of a high electric field[6,7].

P(VDF/TrFE) copolymers exhibit the characteristic behaviour of ferroelectrics: for VDF unit content in the range 60–80 mol%, a clear and reversible first-order Curie transition has been observed[8,9].

Since these electroactive properties are based on polarization specific to the crystalline phase, many studies have been undertaken to characterize the crystalline structure and morphology of these polymers, and to establish relationships with ferroelectricity and related properties. Extensive reviews have been published recently on these subjects [10–12]. The semicrystalline morphology of these polymers is considered through a biphasic model in which the polar crystalline phase is embedded in an amorphous matrix with high mechanical compliance and thermal expansion.

Up to now, the amorphous phase of these semicrystalline polymers has not been fully characterized, especially for P(VDF/TrFE) copolymers. To our knowledge, only few data on the glass transition of such materials have been reported[13]. The behaviour of the amorphous phase has a direct influence on piezoelectric[14] and pyroelectric[15,16] coefficients through an increase of the slope of their dependence as a function of temperature.

The aim of this work is to investigate the glass transition and related dielectric relaxation in a series of P(VDF/TrFE) copolymers, including PVDF. The dependence of the glass transition temperature as a function of the chemical composition has been analysed based on several relationships established for compatible blends and for random copolymers, using the characteristics of PVDF and PTrFE homopolymers.

EXPERIMENTAL

PVDF and P(VDF/TrFE) copolymer films 30–50 μm thick were supplied by Solvay & Co. The investigated materials were unstretched. Thus, PVDF was in the α crystalline form. The investigated copolymers were constituted of 75/25, 65/35 and 50/50 mol% of VDF and TrFE units, respectively.

All calorimetric analyses were performed with a DSC7 differential scanning calorimeter from Perkin–Elmer. Samples (15–20 mg) were enclosed in aluminium pans. The temperature range measurement was from −80 to

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+100°C. All runs were performed at a heating rate of 20°C min^{-1} in a dry helium environment.

Dielectric relaxations were characterized by thermo-stimulated current (t.s.c.) spectroscopy. The procedure of this technique was described elsewhere[17,18]. The principle is briefly recalled here.

A static electrical field ($E_p = 5\,MV\,m^{-1}$) is applied at a temperature T_p for a time $t_p = 2$ min, in order to orient dipoles that have a relaxation time $\tau < t_p$, at T_p. Then, the temperature is decreased till $T_0 \ll T_P$ in order to freeze this dipolar orientation. The sample is then subjected to a linear heating rate at 7°C min^{-1} from T_0 to $T_f > T_p$. Upon heating, the electrodes of the film are short-circuited under an ammeter with a precision of 10^{-16} A, and the depolarization current is recorded as a function of the temperature: its variation constitutes the complex t.s.c. spectrum. 'Complex' means that the obtained relaxation modes are described by a distribution of overlapping relaxation times.

T.s.c. spectra can be compared with those obtained by dielectric dynamical analysis (d.d.a.) by considering the low equivalent frequency of the t.s.c. technique ($\approx 10^{-3}$ Hz).

RESULTS

Differential scanning calorimetry

Figure 1 shows the d.s.c. thermograms of PVDF and related copolymers obtained in the temperature range of −60 to +80°C. The classical C_p jump associated with the glass transition is observed for all polymers in the low-temperature side of the diagram. When the TrFE content is increased, a slight shift of the glass transition towards high temperature is observed. The values of T_g, defined at the midpoint of the C_p jump, are listed in *Table 1*.

Another thermal event is observed between 40 and 70°C. For PVDF, a clear endothermic peak occurs. The thermogram shown in this figure corresponds to α-PVDF, but this endothermic peak has also been observed for β-PVDF[19], obtained by stretching α-PVDF films to several times their original length. A thermal event has been obtained by d.s.c. in this temperature domain, specially for α-PVDF, and it has been interpreted as an endothermic phenomenon, a C_p jump, or both [20–22]. From thermograms shown in *Figure 1*, both phenomena occur.

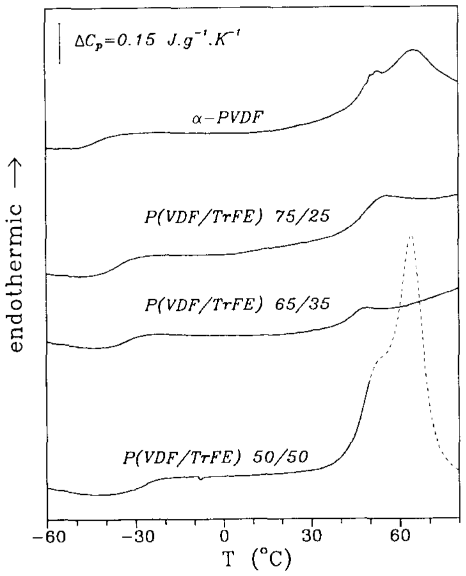

Figure 1 D.s.c. thermograms of PVDF and P(VDF/TrFE) copolymers

Table 1 Glass transition (T_g, ΔC_p) and associated relaxation mode (T_β) for PVDF and P(VDF/TrFE) copolymers

Sample (mol%)	T_g (°C)	$\Delta C_p (10^{-2}\,J\,g^{-1}\,K^{-1})$	T_β (°C)
α-PVDF	−42	5.5	−42
P(VDF/TrFE) 75/25	−36	4.0	−34
P(VDF/TrFE) 65/35	−33	3.4	−33
P(VDF/TrFE) 50/50	−28	5.2	−28

For P(VDF/TrFE) copolymers, the endotherm is detectable, although its magnitude is reduced. In the case of P(VDF/TrFE) 50/50, the α process is not observed because of the occurrence of the ferroelectric–paraelectric transition (dotted endothermic peak) in this temperature domain.

In order to further characterize this transiton (designated α), its evolution as a function of the thermal history of the sample has been considered. Results obtained for various thermal treatments of P(VDF/TrFE) 75/25 are shown in *Figure 2*. The thermogram (a) corresponds to the as-received sample. It has been recorded by heating the sample up to 100°C. The temperature was then decreased from 100°C down to −80°C, at a fast cooling rate, and the thermogram (b) was subsequently obtained. The sample was then maintained at room temperature for 20 h, and the thermogram (c) was recorded.

In *Figures 2a* to *2c*, we observe no significant evolution of the C_p jump associated with the glass transition: the temperature of the sample did not exceed 100°C during these measurements, and the glass transition temperature as previously defined is invariably −36°C for this copolymer. Contrarily, the α process observed at higher temperature is sensitive to these thermal treatments.

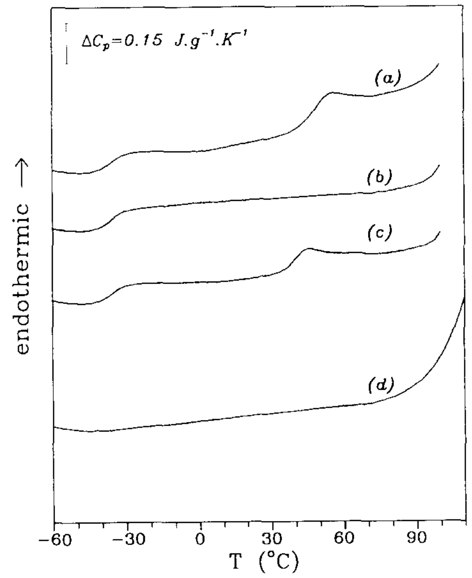

Figure 2 D.s.c thermograms of P(VDF/TrFE) 75/25 as a function of thermal history: (a) as-received sample; (b) second heating after fast cooling; (c) after room-temperature annealing for 20 h; (d) after annealing at 140°C

Indeed, it disappears when the temperature is increased above T_α prior to the measurement. Upon annealing for 20 h at room temperature, the α process is practically restored, both in temperature position and in magnitude. We have shown that this phenomenon behaves in the same way for α-PVDF and β-PVDF[19]. Thus, it is not an intrinsic property of the α phase of PVDF.

The thermogram (d) shown in *Figure 2* was obtained for P(VDF/TrFE) annealed at 140°C for 2 min. Then, the C_p jump associated with the glass transition is no longer observable within experimental precision.

P(VDF/TrFE) copolymers are characterized by a ferroelectric–paraelectric (Curie) transition below their melting point for TrFE unit content in the range 50–80 ml%[8,9]. For P(VDF/TrFE) 75/25, the endothermic peak corresponding to this transition has a maximum at 130°C[23]. The investigation of this transition is beyond the scope of this paper. However, when annealed above their Curie transition, these copolymers undergo a strong increase of their crystallite thickness[5], resulting in an increase of crystallinity. Thus, crystallinity as high as 80–90% may be achieved upon annealing the copolymers at a temperature intermediate betwen their Curie transition and their melting point[5,24]. The disappearance of the manifestation of the glass transiton as revealed by d.s.c. is a consequence of this crystallinity increase.

Thermo-stimulated current spectroscopy

Figure 3 shows the t.s.c. spectrum of α-PVDF obtained with a polarization temperature $T_p = 80$°C. Two relaxation modes appear in this spectrum. The higher-temperature one has a maximum at about 50°C. It has been designated as α relaxation mode. This mode appears at the same temperature as the d.s.c. transition (cf. *Figure 1*). Thus, both processes probably have the same molecular origin. The lower-temperature mode has been designated as β relaxation. Its maximum is close to the glass transition temperature as defined by d.s.c. Therefore, the β relaxation corresponds to the dielectric manifestation of the glass transition of α-PVDF.

The complex t.s.c. spectra obtained in P(VDF/TrFE) 75/25 with a polarization temperature $T_p = 100$°C are shown in *Figure 4*. The full spectrum corresponds to the as-received sample; the dotted one has been obtained after annealing the sample at 140°C for 2 min. The peak observed in the full thermogram corresponds to the β relaxation of the copolymer. In a similar way as for PVDF, the maximum temperature of the β mode is close to the glass transition of the copolymer. Upon annealing (dotted spectrum), a strong decrease of the β mode is observed, as well as a slight shift of the maximum temperature towards high temperatures. Although the glass transition of the copolymer cannot be detected upon annealing (cf. *Figure 1d*), the β mode can, because of the high sensitivity of the t.s.c. technique.

In this spectrum, an additive relaxation mode appears as a shoulder at ≈ 10–15°C. A change in the slope of the pyroelectric coefficient has been observed at the same temperature[25]. The shoulder appearing at about 10°C in *Figure 4* has been associated with an upper component of the glass transition involving the amorphous phase constrained by crystallites[25].

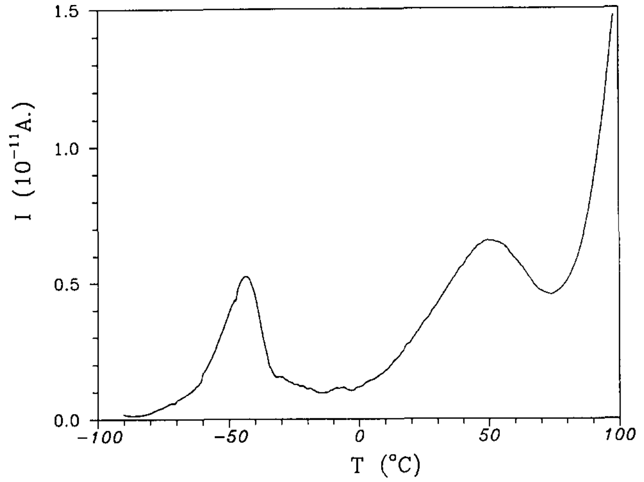

Figure 3 T.s.c. spectrum of PVDF. $T_p = 100$°C; field = 5 MV m^{-1}; $t_p = 2$ min

Figure 5 shows the complex t.s.c. spectra of P(VDF/TrFE) 65/35 and 50/50 mol%. For P(VDF/TrFE) 65/35, the polarization temperature was $T_p = 50$°C. Under these conditions, the α mode appears at about 35°C. Higher polarization temperatures would result in an overlapping of this mode by the relaxation mode associated with the Curie transition of the copolymer. The β relaxation mode of P(VDF/TrFE) 65/35 has a maximum at −33°C. Therefore, it is associated with the glass transition of this copolymer. For P(VDF/TrFE) 50/50 (dotted spectrum), the maximum temperature of the β mode is −28°C, and corresponds, here also, to the glass transition found by d.s.c.

DISCUSSION

Several relationships have been proposed in the literature to predict the glass transition temperature of compatible blends, or statistical copolymers. They are basically derived from either free-volume theories, or from thermodynamic considerations.

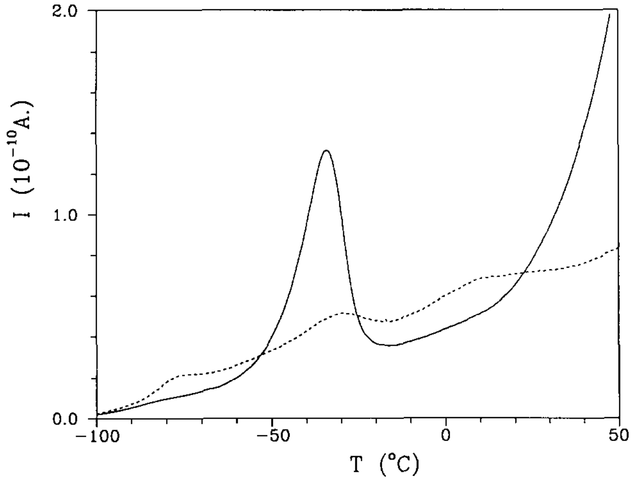

Figure 4 T.s.c. spectra of Al-metallized P(VDF/TrFE) 75/25. $T_p = 100$°C; full line, as-received sample; dotted line, after annealing at 140°C

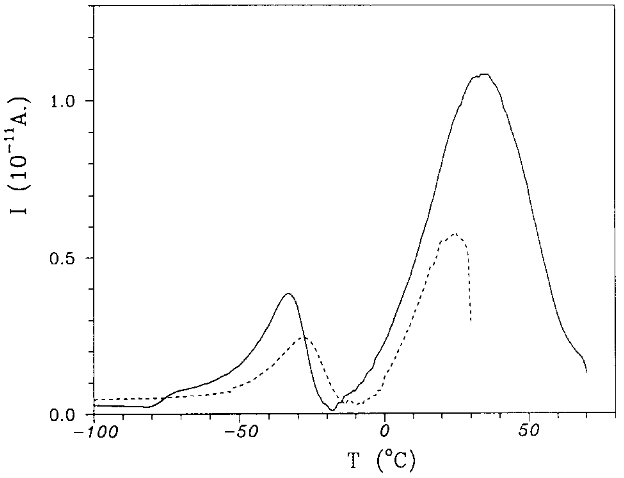

Figure 5 T.s.c. spectra of P(VDF/TrFE) 65/35 (full line, $T_p = 50°C$) and P(VDF/TrFE) 50/50 (dotted line, $T_p = 20°C$)

The well known equation of Fox[26] gives the glass transition temperature T_g *versus* composition:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (1)$$

where T_{gi} are the glass transition temperatures of the homopolymers, and w_i are their weight fractions. It is based on volume additivity.

Gordon and Taylor[27] have proposed an equation based on volume and free-volume additivity:

$$T_g = \frac{w_1 T_{g1} + K w_2 T_{g2}}{w_1 + K w_2} \qquad (2)$$

where K is given by the ratio $\rho_1 \Delta\alpha_2 / \rho_2 \Delta\alpha_1$. Here ρ_i and $\Delta\alpha_i$ are the densities and the increment at T_{gi} of the thermal expansion coefficients, respectively.

Recently, Di Marzio[28] derived the glass transiton of a binary system, based on the entropy theory of glasses[29]. The free-volume effects have been neglected, and the configurational entropy of the chains has been related to the number of flexible bonds in the units. The derived expression is the same as equation (2), but the K parameter is replaced by:

$$K' = \gamma_2 \omega_1 / \gamma_1 \omega_2 \qquad (3)$$

where γ_i are the number of flexible bonds per monomer unit, and ω_i are the weights of the units. The advantage of this theory is that it only requires the chemical structure of the copolymer.

By considering the glass transition as an Ehrenfest second-order transition, Couchman and Karasz[30] and Couchman[31,32] derived a series of equations from continuity of either the volume, the entropy, or the enthalpy, at the glass transition. The entropic relation leads to the following equation for a binary system[31]:

$$w_1 \int_{T_{g1}}^{T_g} \frac{\Delta C_{p1}}{T} \mathrm{d}T + w_2 \int_{T_{g2}}^{T_g} \frac{\Delta C_{p2}}{T} \mathrm{d}T = 0$$

This equation requires the heat capacity increment ΔC_{p_i} between the liquid and solid states of the homopolymers.

According to the functional dependence of $\Delta C_{p_i}(T)$, several equations have been derived[31,33]:

$$\ln(T_g) = \frac{w_1 \Delta C_{p1} \ln(T_{g1}) + w_2 \Delta C_{p2} \ln(T_{g2})}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \qquad (4)$$

by considering $\Delta C_{p_i}(T)$ as a constant.

Under the approximation that $T\Delta C_{p_i}(T)$ = constant, the obtained variation is:

$$T_g = \frac{w_1 \Delta C_{p1} T_{g1} + w_2 \Delta C_{p2} T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \qquad (5)$$

where ΔC_{p_i} corresponds to the heat capacity jump at T_{g_i}.

Applicability of the relationships

The compositional dependences of the glass transition temperatures reviewed above constitute simplified expressions. Indeed, these relations should take into account not only the contributions of the pure components, but also the specific interactions between components[34-37].

These interactions are responsible for the departure of the experimental glass transition temperature from the predicted value in various systems[34,35]. Some of the strongest differences have been observed in blends where the interactions between the components induce the formation of either electron donor–acceptor complexes, or hydrogen bonds[35].

In order to take these interactions into account, several parameters have been introduced, such as mixing entropy[31,35], or various empirical parameters characterizing the strength of the interaction[32,37].

The deviation of the experimental glass transition temperature from the predicted value may also arise from inhomogeneous mixing of the components in blends.

For random copolymers such as the P(VDFTrFE) system, non-random mixing is avoided. Indeed, Tashiro *et al.*[8] have successfully shown the randomness of these copolymers by i.r. spectroscopy.

Copolymers involve not only physical interactions between components, but also chemical bonds. Therefore, the glass transition of the copolymer can be sensitive to the stereoregularity of the units in the chains[34]. However, PVDF and PTrFE have analogous chemical structures. Moreover, the configurational entropies of fluorinated vinyl polymers, as calculated by Tonelli[38], are close, except for PTFE (polytetrafluoroethylene). Thus, PVDF and PTrFE have similar conformational characteristics, and the overall equations related to the glass transition are expected to be valid for their random copolymers.

Another parameter that should be taken into account is the semicrystalline character of both PVDF, PTrFE and related copolymers. The real chemical composition of the amorphous phase could be affected by the tendency of units of one of the components to enter the crystallites at the expense of the other component. Because of the randomness of the copolymers, one expects that the chemical compositions of the crystalline and amorphous phases are the same. So, the inhomogeneous morphology of the copolymers does not induce an inhomogeneous chemical structure.

Crystallinity could also play a role through a shift of the glass transition towards high temperatures. We have shown that the β mode of P(VDF/TrFE) 75/25 as revealed by t.s.c. (cf. *Figure 4*) has a maximum temperature that slightly increases upon annealing, i.e. upon increase of the crystallinity from about 60% to 80%. A similar behaviour was observed for the other copolymers. However, this shift does not exceed a few degrees, even for relatively high crystallinities.

Homopolymer parameters

The application of these rules requires some additive parameters about PVDF and PTrFE, and first of all their glass transition temperatures. For PVDF, it is well defined, as shown in *Figure 1*.

Since we did not investigate PTrFE, the value of its T_g has been checked in the literature. The most often adopted value is $T_g = 31°C$[39,40]. It was obtained from volumetric analysis[41,42]. However, d.s.c. measurements reported by Loufakis and Wunderlich[22] have shown that the glass transition is not well defined for PTrFE: the specific heat increases in a broad temperature range, from about −40°C to 70°C. The half-vitrification point has been located at −8°C.

Dynamic techniques (either mechanical or dielectric) are more sensitive for the investigation of the molecular mobility associated with the glass transition. By d.m.a. and d.d.a., two relaxation modes have been observed in PTrFE[39,43]. The β mode has been found at −20°C at 35 Hz[39] by d.m.a. It has been associated with local molecular motions in both the amorphous and crystalline regions. The α mode appears at 50°C (at 35 Hz) and has been associated with the dielectric manifestation of the glass transition based on volumetric analysis previously mentioned.

The Gordon–Taylor equation (2) requires knowledge of the increment of the thermal expansion coefficient of both homopolymers. However, these data are not available in the literature.

The Di Marzio rule is applicable to P(VDF/TrFE) copolymers, because it requires only the molecular weight of the VDF ($64\,\mathrm{g\,mol^{-1}}$) and TrFE ($82\,\mathrm{g\,mol^{-1}}$) units, and the number of flexible bonds per unit: two for VDF and for TrFE units according to Di Marzio's criteria[36].

As for the Couchman equation, we have used data from Wunderlich *et al.*[22,40,44] on the heat capacity of linear fluoropolymers. The additive scheme derived for all liquid fluoropolymers gives[22]:

$$C_{pl} = N_f(55 + 0.162T) + (1 - N_f)(37.7 + 0.0829T)$$

(C_p in $\mathrm{J\,K^{-1}\,mol^{-1}}$ and T in K) for the investigated temperature range. N_f is the fraction of fluorination: 0.5 for PVDF, and 0.75 for PTrFE. The solid heat capacity was derived from a Tarasov model, and the calculated data are listed in ref. 40.

Figure 6 shows the variation, as a function of temperature, of the heat capacity of PVDF and PTrFE, in the liquid and solid states. From this figure, it is shown that the ΔC_p = constant approximation used in equation (4) is not appropriate. Thus, we have plotted in *Figure 7* the values of $T\Delta C_p$ as a function of temperature, for both PVDF and PTrFE. A quasi-constant value of $T\Delta C_p = 72.7\,\mathrm{J\,g^{-1}}$ and $51.6\,\mathrm{J\,g^{-1}}$ was obtained for PVDF and PTrFE, respectively, in the considered temperature range of 200 to 320 K. These averaged values correspond to the dotted lines. They have been used in the Couchman equation (5).

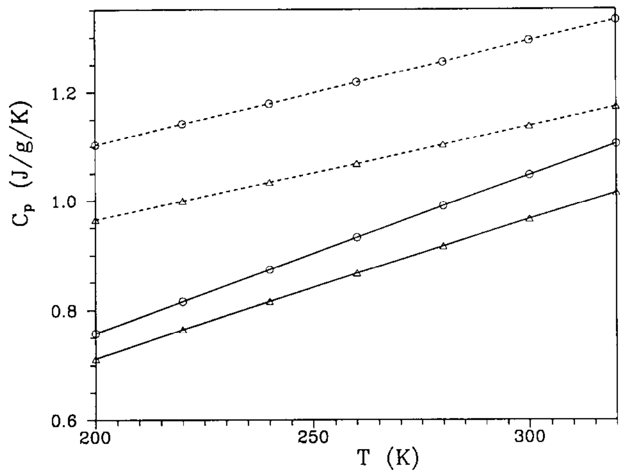

Figure 6 Theoretical heat capacities as a function of temperature in the liquid (dotted line) and solid (full line) states, for PVDF (circles) and PTrFE (triangles). Data from refs. 22, 40 and 44

Extrapolated T_g *of PTrFE*

In *Figure 8a*, the predicted variations of the glass transition temperature of P(VDF/TrFE) copolymers have been plotted as a function of the weight fraction of the TrFE units. The glass transition temperatures adopted for PVDF and PTrFE are −42°C and 31°C respectively. The experimental glass transition temperatures of the copolymers are also reported and correspond to circles.

Note that using $T_g(\mathrm{PTrFE}) = 31°C$, the Fox and Di Marzio relations give practically the same T_g variation for the copolymers. The equality of the corresponding equations is obtained under the condition that:

$$K' = \frac{T_{g1}}{T_{g2}} = \frac{\gamma_2\omega_1}{\gamma_1\omega_2} \tag{6}$$

For the investigated system, the value of T_{g1}/T_{g2} (=1.32) is close to ω_1/ω_2 (=1.28), so that the variations predicted by the Fox and Di Marzio equations cannot be practically distinguished.

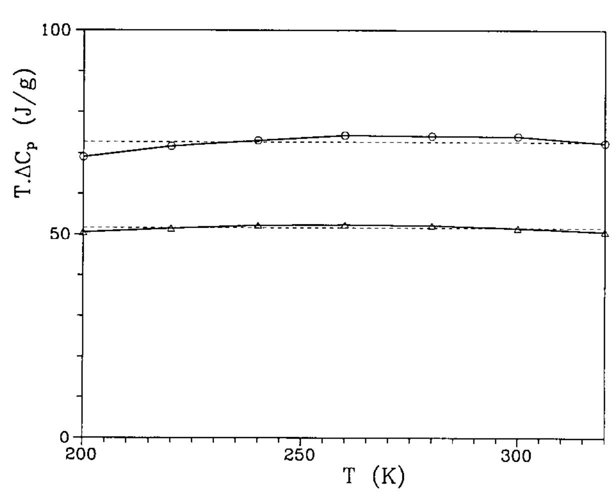

Figure 7 $T\Delta C_p$ *versus* temperature deduced from *Figure 6*. The dotted lines correspond to averaged values; PVDF, circles; PTrFE, triangles

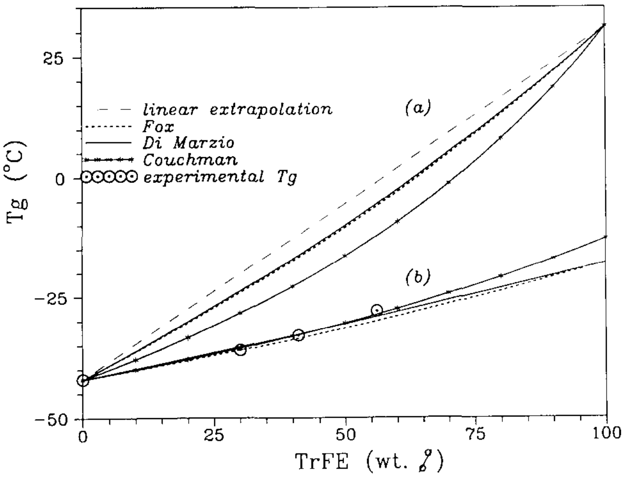

Figure 8 Glass transition temperature *versus* weight per cent TrFE predicted by the Fox, Di Marzio and Couchman equations, using T_g(PTrFE) = 31°C (a), and T_g(PTrFE) = −18 to −12°C (b)

Equation (6) is consistent with the Schneider and Di Marzio postulate that a proportionality exists between the glass transition of an infinite-molecular-weight polymer, and its molecular weight per flexible bonds[36]. However, in the present case, the 'universal' constant $C = T_g\gamma/\omega$ is about 7.3, whereas the value of C obtained from more than 50 polymers[36] is between 8 and 12.

It appears in *Figure 8a* that, for all the applied variation rules, the predicted glass transition temperatures differ from the experimental values. The discrepancy is about 15–20°C for P(VDF/TrFE) 50/50 mol% (57/43 wt%). In the applied equations, the most uncertain parameter is the glass transition temperature of PTrFE. Moreover, this discrepancy seems too strong to be explained by a hypothetical interaction parameter. So, we have extrapolated a new T_g value for PTrFE, based on experimental results on copolymers, and we discuss it below with reference to previous work on PTrFE.

The best fit of experimental T_g data on copolymers is obtained for the Fox and Di Marzio rules using T_g(PTrFE) = −18°C. With the Couchman equation (5), we obtained T_g(PTrFE) = −12°C. The corresponding variations are shown in *Figure 8b*, and data used in the Couchman equation are listed in *Table 2*.

Relation with previous work on relaxations

The application of the various equations to the determination of the glass transition temperature of PTrFE shows that the predicted value would be in the range of −20 to −10°C. If this was so, the β relaxation mode of PTrFE observed by d.m.a. and d.d.a.[39,43] would be associated with the relaxation of main chains rather than with local molecular motions (secondary relaxation).

Some of the characteristics of the β mode of PTrFE are not typical of a secondary relaxation:

(i) By d.m.a.[39,43], the decrease of the modulus for the α and β relaxation is about one decade for both relaxations. This decrease seems rather strong for a secondary relaxation.

(ii) As pointed out by Yagi[39], the activation energy associated with the β relaxation ($\Delta H_\beta = 1.2\,\mathrm{eV}$) is rather strong for a secondary relaxation of any linear polymer.

Table 2 Parameters used in the Couchman equation (5) for the T_g *versus* composition variation shown in *Figure 8*

	T_g (°C)	ΔC_p ($\mathrm{J\,g^{-1}\,K^{-1}}$)
PVDF	−42	0.315
PTrFE	+31	0.170
PTrFE	−12	0.210

(iii) The dielectric α relaxation on $\epsilon''(T)$ of PTrFE appears only as a shoulder with a magnitude that is nearly one decade lower than that of the β mode. This behaviour appears inconsistent with (a) the well defined dielectric relaxation associated with the glass transition of PVF $(\text{–CH}_2\text{–CHF–})_n$ and PVDF for example[45,46], and (b) the relative intensities of the primary (β) and secondary (γ) relaxations in these polymers.

(iv) Finally, semicrystalline polymers are generally characterized by a relaxation mode that is associated with—or at least requires—the crystalline phase. In PTrFE, the α relaxation mode is the highest-temperature one[39,43]. If it really corresponds to the manifestation of T_g, then the crystalline relaxation would not appear in PTrFE. Contrarily, for polymers with similar structures, PVDF (see *Figure 3*), PVF[47], PE[48], PCTFE $(\text{–CFCl–CF}_2\text{–})_n$[49] and PVDC $(\text{–CH}_2\text{–CCl}_2\text{–})_n$[50], this relaxation has been observed. The lack of such a mode in the relaxation spectrum of PTrFE is all the more improbable that its crystalline phase is characterized by a high degree of conformational disorder[22,51].

Another point that should be stressed is that dielectric measurements on copolymers in the whole composition range revealed that the β mode displays a continuous shift towards high temperatures as the TrFE unit content is varied from 0 (PVDF homopolymer) to 100% (PTrFE)[52,53]. Moreover, the mean relaxation time associated with this mode displays a WLF-like[54] temperature dependence, which is characteristic of a relaxation mode associated with a glass transition. This behaviour constitutes a strong support for ascribing the β relaxation of PTrFE with the dielectric manifestation of its glass transition.

Relation with previous work on transitions

From Loufakis and Wunderlich's measurements[22], the experimental heat capacity of PTrFE has nearly reached at 30°C the theoretical value for liquid PTrFE. This behaviour is an indication that the glass transition temperature—as defined in this work for PVDF and P(VDF/TrFE) copolymers—is located below 30°C for PTrFE.

The value of $T_g = -8°\mathrm{C}$ for PTrFE reported by Wunderlich was obtained from the half-vitrification point taken on a wide temperature range variation of the heat capacity between the solid and liquid states of the polymer. This slow variation gives a poorly defined glass transition. However, the temperature proposed by Wunderlich falls practically in the temperature range we have suggested.

As previously noticed, the glass transition temperature of PTrFE usually reported is based on dilatometric measurements only[41,42]. For polymers with analogous chemical composition, a change in the slope of the volume vs. temperature plot occurs not only for the glass transition, but also for the crystalline transition/relaxation. This behaviour was observed for PVDF[47,55] and PVF[47]. In that case, the change in slope can be even more pronounced than for the glass transition.

Additional comments on the glass transition–relaxation of polymers

As shown in *Figure 4*, the t.s.c. technique is a powerful tool for observing and dissociating relaxation modes in polymers. This characteristic is mainly due to the low equivalent frequency of the t.s.c. technique. For example, the glass transition of annealed P(VDF/TrFE) cannot be detected by d.s.c. (cf. *Figure 2*) while its dielectric manifestation is clearly observed.

A specific procedure of the t.s.c. technique, fractional polarizations[18,55,56], allows one to resolve the complex t.s.c. spectrum into a set of elementary spectra, and to obtain, by a subsequent analysis, the distribution in relaxation times characterizing a relaxation mode. By applying this technique to the resolution of the β relaxation of PVDF[19] and P(VDF/TrFE) copolymers[16,23], we obtained a series of Arrhenius-like relaxation times that obey a compensation law, i.e. a linear relationship exists between the activation enthalpy and entropy. This behaviour is generally observed for the relaxation mode associated with the glass transition of polymers, either amorphous[57] or semicrystalline[58]. Contrarily, the α mode of PVDF (cf. *Figure 3*) is characterized by iso-enthalpic relaxation times[19].

The application of the technique of fractional polarizations to the resolution of the α and β modes of PTrFE would be of great interest for further knowledge of the precise origin of these modes.

The investigation undertaken in this work on the glass transition of P(VDF/TrFE) copolymers and the extrapolation for PTrFE could be applied to another semicrystalline fluorinated polymer, PTFE $(-CF_2-CF_2-)_n$, for which the glass transition temperature is still controversial. According to Wunderlich[59] and Lovinger *et al.*[60], it has been located in the range of −95 to −70°C. Contrarily, some workers[49,61], assigned the α relaxation—located above 100°C—to the glass transition. The T_g for a P(VDF/TFE) 81/19 mol% copolymer has been found at −45°C[60], i.e. slightly lower than for PVDF. This tendency of the TFE unit to shift the glass transition towards low temperatures is an indication that T_g for PTFE is below that of PVDF.

CONCLUSION

The glass transition of a series of P(VDF/TrFE) copolymers has been determined experimentally by differential scanning calorimetry. The associated dielectric relaxation mode (β) has been observed by thermo-stimulated current spectroscopy. Also the high-temperature (α) transition/relaxation has been observed.

The glass transition temperature of these copolymers increases slightly as the TrFE unit content increases. Based on the glass transition temperature of PVDF (−42°C) and PTrFE (31°C), it has been found that a significant lag exists between the experimental data on T_g, and the values predicted by the Fox, Di Marzio and Couchman equations.

Because of the randomness of the copolymers, and of the similar chemical structure of the components, this lag has been interpreted by an overestimated value of T_g for PTrFE, rather than to specific interactions between the components.

It was proposed that the glass transition of PTrFE lies in the range of its β relaxation mode: −20 to −10°C. This result is consistent with Loufakis and Wunderlich's data based on the determination of the absolute C_p variations of this polymer.

An investigation of PTrFE by fractional polarizations is suggested for ascertaining this result.

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