The glass transition and molecular motions of poly(chlorotrifluoroethylene)

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Molecular motions in poly(chlorotrifluoroethylene) have been studied over the range -150 to $+200$°C by thermal/mechanical techniques with the specific intent of clarifying the glass transition (T_g) of this polymer. An extremely broad Γ relaxation, centred at ≈ -15°C and associated with an activation energy of 17 kcal mol^{-1}, is proposed to be a predominantly amorphous phenomenon involving small scale motions. A β relaxation peak at ≈ 95°C with an activation energy of 64 kcal mol^{-1} represents the amorphous segmental mobility and its onset at 75 ± 2°C is assigned as the T_g. This value for the T_g of poly(chlorotrifluoroethylene) is supported by dynamic mechanical, thermomechanical and differential scanning calorimetric techniques. We are unable to support the existence of an α relaxation at 140–150°C, i.e. $T_g < T < T_m$, occasionally cited in the literature.

(Keywords: poly(chlorotrifluoroethylene); glass transition; molecular motions)

INTRODUCTION

Poly(chlorotrifluoroethylene) (poly(CTFE)) is a very important polymer with a unique combination of chemical, mechanical, electrical and optical properties. One of the major applications of poly(CTFE) is in barrier technology in which advantage is taken of its transparency and the fact that its water vapour permeability is the lowest of all known plastics. The glass transition temperature, T_g, is an important parameter for understanding the structure–property relationships. Although poly(CTFE) has been a commercial material since 1957, no reliable value has been assigned to its T_g.

Conflicting views on the T_g of poly(CTFE) have been expressed in a recent review article[1]. Using specific volume *versus* temperature measurements, a T_g of 52°C has been reported for poly(CTFE)[2]. However, there is also general agreement that a relaxation at ≈ 95°C in mechanical and dielectric relaxation studies corresponds to the glass transition[3–5]. Thus the literature lacks a definite, reliable value for the T_g of poly(CTFE). The result of this study is to propose $T_g = 75 \pm 2$°C based on dynamic mechanical analysis (d.m.a.), thermomechanical analysis (t.m.a.) and differential scanning calorimetry (d.s.c.).

EXPERIMENTAL

Materials

Two commercial grade poly(CTFE) resins were used in this study. Resin A had a molecular weight $M_w = 8.5 \times 10^5$ and resin B had $M_w = 3 \times 10^5$. The two resins exhibited melt crystallization (T_{cc}) temperatures of 175–176°C and subsequent reheat melting temperatures (T_m) of 213–214°C. These values were obtained by d.s.c. at 10°C min^{-1} and are typical of a poly(CTFE).

All the characterization work was carried out on the moulded plaques. Resin A was compression moulded at ≈ 250°C into a plaque ≈ 1.25 mm thick and cooled in press (CIP). Resin B was moulded similarly but quick quenched in ice-cold water. The crystallinities of these samples have been estimated to be 30–50% by d.s.c.

Viscosity

The intrinsic viscosity $[\eta]$ of the samples was measured at 135°C with 2,5-dichlorobenzotrifluoride as the solvent. The intrinsic viscosity was converted to the weight average molecular weight (M_w) as follows:

$$[\eta] = 6.15 \times 10^{-5} (M_w)^{0.74}$$

Dynamic mechanical analysis

Two different instruments were used for d.m.a. A Rheometrics dynamic spectrometer, RDS-7700II, was operated in the torsion/rectangular geometry (shear mode) at a frequency of 10 rad s^{-1} (1.6 Hz) using a strain of 0.1%. The data was collected at 10°C intervals between -130 and 200°C. A Polymer Laboratories DMTA unit was operated in the bending deformation geometry (tension mode with shear correction) at a frequency of 1 Hz, a strain of ≈ 0.3% and a heating rate of 3°C min^{-1} over the range -130°C–200°C. Activation energies were calculated from two additional scans at 0.1 and 100 Hz.

Thermomechanical analysis

A Perkin–Elmer TMS-2 was used in the expansion mode. The sample was heated in a helium atmosphere at 10°C min^{-1} from 0 to 200°C.

Differential scanning calorimetry

A Perkin–Elmer DSC-2C was used to measure the specific heat over range 0–170°C at a heating rate of 10°C min^{-1} with a sample of 25 mg. A DuPont 9900 DSC was used to obtain the transition temperatures under the following conditions: argon atmosphere, ≈ 10 mg sample crimped in an aluminium pan and rates of 10°C min^{-1} for melting/crystallization and 20°C min^{-1} for glass transition determination.

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RESULTS AND DISCUSSION

The two poly(CTFE) resins, $M_w = 3 \times 10^5$ and 8.5×10^5, were characterized by two types of d.m.a. unit to obtain the relaxation patterns. The materials were also characterized by t.m.a. and d.s.c. techniques. All the methods suggest $T_g = 75 \pm 2°C$ for poly(CTFE).

Dynamic mechanical analysis

D.m.a. of resin A on the Rheometrics dynamic spectrometer (1.6 Hz, torsional deformation) exhibits two relaxations based on the shear modulus (G') and damping ($\tan \delta$) curves (*Figure 1*). Similar analysis on the Polymer Laboratories DMTA unit (1 Hz, bending deformation) provides an identical relaxation pattern (*Figure 2*).

Γ Relaxation

The Γ relaxation peak is quite broad and extends over a range of 150°C (*Figures 1* and *2*). Obviously, it must involve contributions from several components. It is pointed out in the literature that the Γ peak is a composite of both crystalline (lower temperature component) and amorphous peaks[5]. While we confirm the composite nature of the Γ peak (e.g. $\tan \delta$ curves in *Figure 3*), we stress that the Γ peak originates predominantly from the amorphous phase. For example, consider a substantial drop in the Γ relaxation strength on annealing, i.e. a change in shear modulus ($\Delta G'$) between −100 and +75°C (*Figure 3*). We believe that the Γ peak involves the following types of motion: small units of the polymer chain, perhaps 3–4 carbon atoms long[6]; loose chain ends within the amorphous and crystalline phases; and small scale or local motion of the amorphous segments, perhaps up to 10 carbon atoms long[6,7]. This transition is known to occur at $\approx 0.75T_g$ (references 6 and 7). With a T_g of 75°C for poly(CTFE), the local chain motion would occur at −12°C, which is about the maximum in the Γ relaxation.

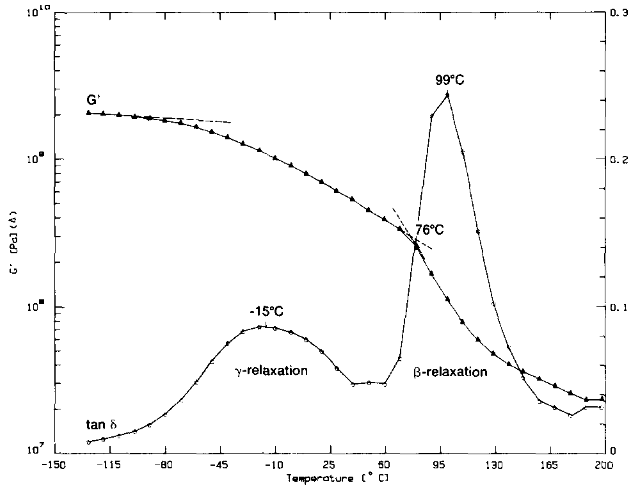

Figure 1 Dynamic mechanical analysis of poly(CTFE) resin A using Rheometrics dynamic spectrometer

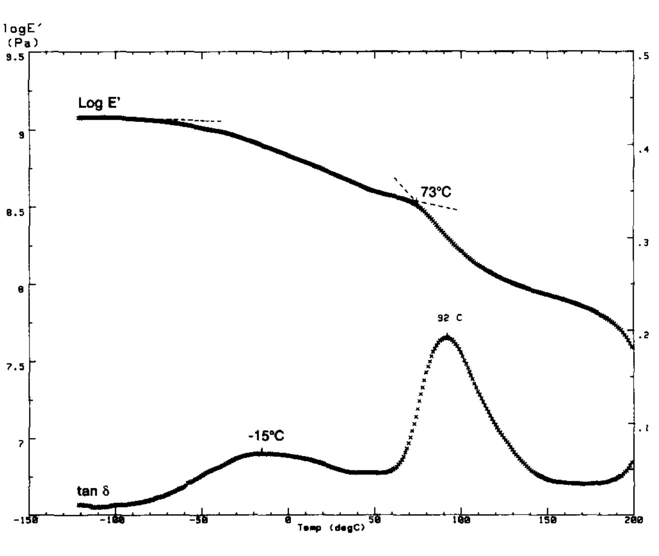

Figure 2 Dynamic mechanical analysis of poly(CTFE) resin A using Polymer Laboratories DMTA unit

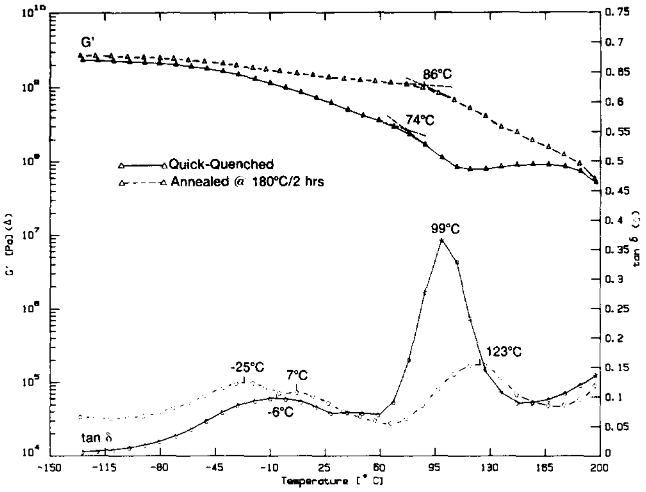

Figure 3 Effect of thermal history on relaxation strengths for Γ and β processes in poly(CTFE) resin B

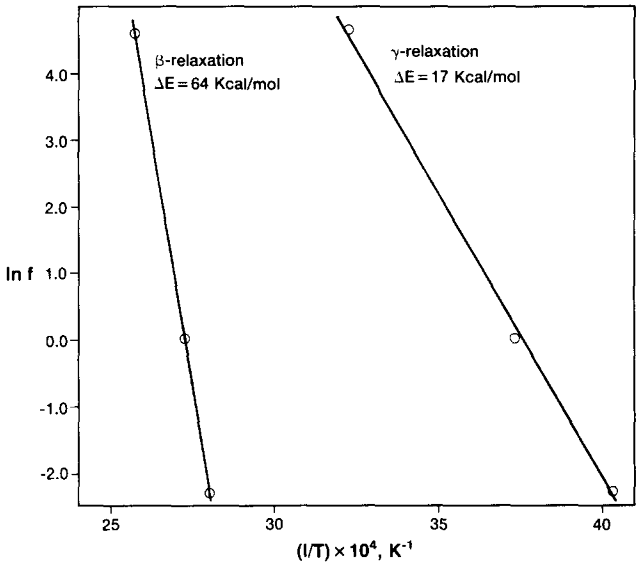

Figure 4 Activation energies for Γ and β relaxations of poly(CTFE) resin B

In addition to the motions of the moieties mentioned above, chemical heterogeneities (e.g. head–tail and tacticity) at the short chain level may also contribute to the extreme broadness of the Γ relaxation. From the frequency (f) dependence of the relaxation temperatures (*Figure 4*), an activation energy (ΔE) of 17 kcal mol^{-1} has been established for the Γ peak. This is in line with the ΔE values for relaxations involving small scale motions[8].

To conclude our view on the Γ relaxation in poly(CTFE), we propose that it originates predominantly from the amorphous phase and involves small scale motions of the polymer chain.

β Relaxation

There is general agreement that the β relaxation at ≈ 95°C is associated with the glass transition. Our own results fully support this. For example, the β relaxation strength reflected by $\tan\delta$ is severely reduced upon annealing (*Figure 3*). An activation energy of 64 kcal mol^{-1} (*Figure 4*) is in the range for the glass transition of polymers[8]. We attribute the onset of β relaxation at 75 ± 2°C to the T_g of poly(CTFE) based on the modulus–temperature curves. If the T_g of a polymer is defined as the onset of segmental motion, it would manifest itself in a sudden increase in specific heat (c_p) in d.s.c., an increase in expansion coefficient in t.m.a. and a sudden loss of stiffness in d.m.a. Thus an onset temperature of softening from the modulus (E', G')–temperature (T) curve in d.m.a. experiment should appropriately define the T_g. While we will substantiate the use of T_g from (E', G')–T curves in a later section, note that the T_g obtained from the $\tan\delta$ peak is not reliable. For example, the $\tan\delta$–T_g peak broadens and shifts to higher temperatures with an increase in crystallinity and orientation for almost all polymers, whereas the T_g onset from (E', G')–T curves is not much affected[9].

To conclude our view on the β relaxation in poly(CTFE), we support the view that the β relaxation process is associated with the glass transition but propose its onset at 75 ± 2°C as the T_g value.

α Relaxation

It is pointed out in the literature that there is an α relaxation at 140–150°C, but only for very high crystallinity samples (e.g. 80%)[3–5]. Although we have not analysed samples of such high crystallinity and, therefore, have not confirmed the α relaxation, we doubt the existence of a real α relaxation in poly(CTFE).

As the crystallinity of a polymer increases, the $\tan\delta$–T_g peak broadens and becomes unsymmetrical towards the upper temperature[9]. At a very high level of crystallinity (achieved, for example, through extended annealing close to the melting temperature), fractional amorphous phase constrained by crystalline phase and possibly by cross-linking might relax at a temperature higher than the T_g. However, this does not have to be treated as a separate relaxation mechanism. In polymers showing α relaxation, it is observed at even lower crystallinities and one of its characteristics is to occur at higher temperatures with increase in crystallinity and crystallite thickness[9,10].

To conclude our view on the α relaxation in poly(CTFE), we doubt its existence since it does not have the characteristic features of a typical α relaxation associated with the mobility of interfacial amorphous phase, e.g. polyethylene[10] and 1:1 alternating copolymer of ethylene/CTFE[8].

Thermomechanical analysis

T.m.a. of resin A exhibits a linear expansion up to 74°C, at which point the expansion probe tends to sink into the sample (*Figure 5*). This is being interpreted as due to the T_g related softening at 74°C, which would also be supported by a loss in stiffness (*Figure 1*). Upon reheating the same sample, a break in the thermal expansion coefficient occurs at ≈ 85°C, an increased expansion coefficient being associated with the T_g (*Figure 5*). Note that the reheat T_g is higher, probably due to increased crystallinity during the initial t.m.a. scan. The same trend is also indicated by d.m.a. in *Figure 3*, suggesting that the T_g of poly(CTFE) is crystallinity dependent.

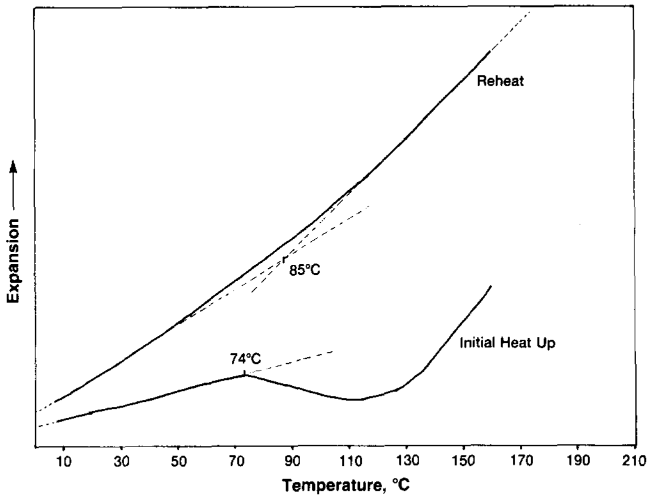

Figure 5 Thermomechanical analysis of poly(CTFE) resin A in the expansion mode

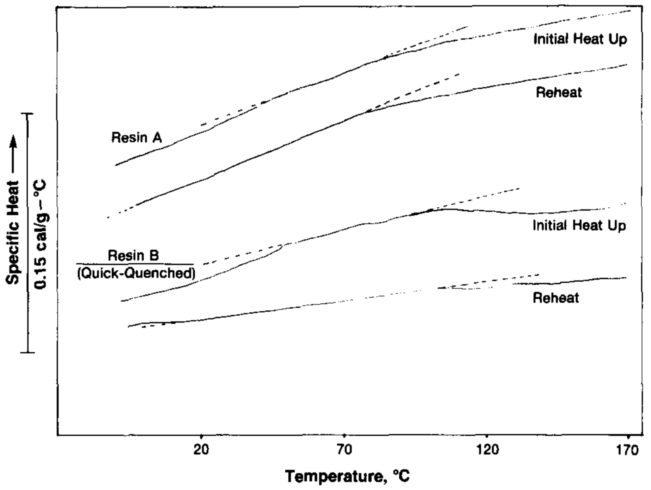

Figure 6 Specific heat *versus* temperature curves by d.s.c. for the two poly(CTFE) resins

Differential scanning calorimetry

The specific heat (c_p) of an amorphous or semicrystalline polymer should exhibit a step increase at the T_g followed by a faster rate of increase. For reasons not clearly understood, the T_g of poly(CTFE) cannot be identified readily from the c_p–T curves (*Figure 6*). Apart from there being no step increase in the c_p, the specific heat begins to decrease in the range 80–110°C even in the reheat scan (slow crystallization?). One of the main reasons for the failure of c_p–T curves to reveal the T_g is the high level crystallinities in poly(CTFE), at least 30–50% in our samples. The literature also reveals high crystallinities even for quenched samples, e.g. 40% (reference 4).

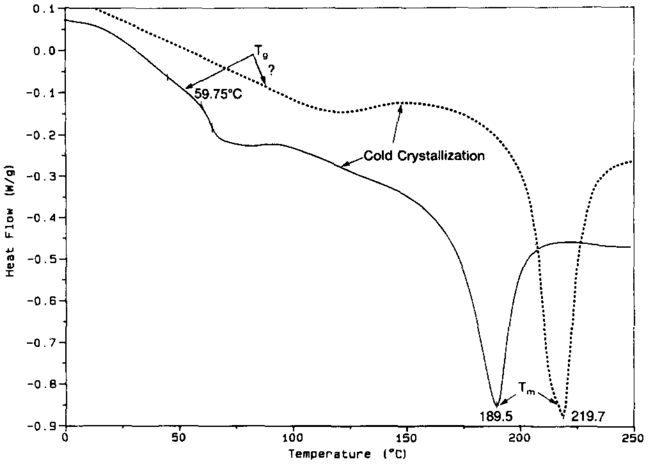

Figure 7 D.s.c. thermogram showing the T_g of a random copolymer of CTFE(96%) and VF2(4%). ······, Quick quenched poly(CTFE) resin B

Table 1 Comparison of T_g values obtained by d.s.c. and d.m.a.

Polymer	Thermal[a] history	T_g (°C) D.s.c.[b]	T_g (°C) D.m.a.[c]
Polystyrene	CIP	86	92
Polycarbonate	CIP	146	144
Poly(ethylene terephthalate)	Quenched	77	74
	Annealed 150°C, 1 h	85	82
Poly[CTFE(96)/VF$_2$(4)]	?	58±3	60±2
Poly(CTFE)	CIP	?	75±2
	Annealed 180°C, 2 h	?	≈85

[a] CIP: moulded plaque cooled in press, providing a thermal history between quenching and annealing treatments
[b] Onset of step increase in c_p
[c] Onset of step loss in stiffness

Another problem could be a large Γ relaxation (predominantly amorphous phenomenon) just preceding the T_g.

D.s.c. of a quenched copolymer (≈15–20% crystallinity) of 96% CTFE/4% vinylidene fluoride (VF2), however, exhibits a clear T_g at ≈58°C (*Figure* 7). Sibilia and Paterson[11] plotted the intensities of the infrared (i.r.) bands at 3.33 and 3.38 μm (antisymmetric and symmetric -CH- stretching vibrations in the VF2 units of the copolymer) against the annealing temperature. A sharp decrease occurred at 52°C and this was assigned to the T_g of the CTFE(96)/VF2(4) copolymer. Note that a T_g of 52°C obtained by the i.r. method[11] is close to our T_g of 58°C obtained by d.s.c. for the same copolymer. The T_g of the same copolymer obtained by d.m.a. based on the E'–T curve is the same as that from d.s.c. *Table 1* provides data for some common polymers to demonstrate that the T_g obtained by d.s.c is very similar to that obtained by d.m.a. using the E'–T curves.

Having established a T_g of 58°C for the CTFE(96)/VF2(4) copolymer, we should expect a $T_g > 58$°C for the poly(CTFE) since the homopolymer of VF2 is known to have a T_g of −45°C (reference 9). Thus the T_g of 52°C reported earlier[2] and used thereafter is definitely low for poly(CTFE). We strongly support a T_g of 75±2°C as revealed by d.m.a. This value of T_g for poly(CTFE) is supported by t.m.a. Although d.s.c. cannot support the d.m.a. value for reasons mentioned above, we have shown good general agreement between d.s.c. and d.m.a. on the T_g of several other common polymers.

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REFERENCES

1 Chandrasekaran, S. in 'Encyclopedia of Polymer Science and Engineering' (Eds H. Mark, N. Bikales, C. Overberger and G. Menges), Vol. 3, John Wiley & Sons, New York, 1985, p. 463
2 Hoffman, J. D. and Weeks, J. J. *J. Res. Natl. Bur. Stand.* 1958, **60**, 465
3 Hoffman, J. D., Williams, G. and Passaglia, E. *J. Polym. Sci. C* 1966, **14**, 173
4 Scott, A. H., Scheiber, D. J., Curtis, A. J., Lavritzen, J. I. and Hoffman, J. D. 1962, **66A**, 269
5 Sacher, E. *J. Polym. Sci. C* 1980, **18**, 333
6 McCrum, N. G. in 'Molecular Basis of Transitions and Relaxations' (Ed. D. J. Meier), Gordon and Breach, New York, 1978
7 Boyer, R. F. in 'Encyclopedia of Polymer Science and Technology', Vol. 2, John Wiley & Sons, New York, 1977, p. 745
8 Khanna, Y. P., Sibilia, J. P. and Chandrasekaran, S. *Macromolecules* 1986, **19**, 2426
9 Khanna, Y. P. unpublished data, Allied-Signal Inc., Morristown, NJ, 1983–1989
10 Khanna, Y. P., Turi, E. A., Taylor, T. J., Vickroy, V. V. and Abbott, R. F. *Macromolecules* 1985, **18**, 1302
11 Silibia, J. P. and Paterson, A. R. *J. Polym. Sci. C* 1965, **8**, 41