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Analysis

DSC Studies on the Transitions in Poly(Vinylidenefluoride) and some Related Copolymers

C. Leonard, J. L. Halary, L. Monnerie and F. Micheron

Laboratoire P.C.S.M., Ecole Supérieure de Physique et Chimie Industrielles de la Ville de Paris,
10, rue Vauquelin, 75231 Paris Cedex 05, France
THOMSON-CSF, Laboratoire Central de Recherches, Domaine de Corbeville,
91401 Orsay Cedex, France

Summary

The transition properties of poly(vinylidenefluoride) and of some related copolymers, either semicrystalline or amorphous, were studied by differential scanning calorimetry in the temperature range from 200 K to 500 K. The amorphous copolymers exhibit a single glass transition. Melting endotherms and a lower glass transition [Tg(L)] are systematically observed in the semicrystalline materials as well as an upper glass transition [Tg(U)] for certain thermal and mechanical histories of the samples. Conditions for [Tg(U)] existence are related to solid state morphology of the macromolecules and loop length in the folded chains.

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) has attracted much interest in recent years as a result of the piezoelectric properties which it possesses and the technological applications to which it increasingly gives rise. Although the monomer unit is simple, PVDF is in fact a complicated polymer for three main reasons : 1/ it presents at least four crystal forms α, β, γ and α_p, which are all stable at room temperature. 2/ its microstructure exhibits a substantial content of head-to-head units (WILSON and SANTEE, 1965; GÖRLITZ et al., 1973) the extent of which depends on the polymerization conditions and 3/ its relaxational behavior has been viewed in terms of four or five transition temperatures interpreted as local mode relaxations, lower [Tg(L)] and upper [Tg(U)] glass transitions and premelting process (BOYER, 1975; Mc BRIERTY et al., 1976, ENNS and SIMHA, 1977). Both location and assignment of some transitions have been a subject of controversy for some time(PETERLIN and ELWELL, 1967; YANO, 1970; OSAKI and ISHIDA, 1974). In fact, it appears clearly that both thermal history of the samples and nature of the investigation technique may have a considerable effect on the observed behavior.

As for us, being involved in solid state dynamic studies on PVDF and some related copolymers (LEONARD et al, 1982), we decided first to determine the transition properties of the same samples by differential scanning calorimetry (DSC) for temperatures ranging from 200 K to 500 K. The purpose of this paper is to analyze the transition phenomena thus observed as well as their dependence on the thermal and mechanical histories of the samples under study.

EXPERIMENTAL

Materials

Experiments were performed on commercially available materials. PVDF KF-1000 was supplied by KUREHA Chem. Industry Co.. Three random PVDF copolymers were additionally investigated : Kynar grad 7201, a VDF/TFE copolymer containing 30 wt % of tetrafluoroethylene units, from PENNWALT Chem. Corp., and two VDF/CTRFE copolymers, provided by P.C.U.K. (France) under the trade names Voltalef 3700 and Voltalef 5500 and containing 30 wt % and 50 wt % of chlorotrifluoroethylene units, respectively.

Thermal and mechanical histories of the samples

Powders or granules of PVDF, VDF/TFE copolymer and Voltalef copolymers were molten at 473 K, 453 K and 443 K, respectively, and pressed in the form of films. The films were either quenched in a water-ice mixture or slowly cooled down inside the pressing machine. Drawing of PVDF samples till an extension ratio $\lambda = 4$ was achieved on quenched films using a calendering machine JOLLIOT operating with a speed of 100 %. Experiments were systematically performed at rolling temperatures of 293 K and 348 K and subsequent annealing temperatures in the range 353-393 K for 1-5 hrs. The experimental conditions relative to the results analyzed in this paper are given in table I. All the samples were left free during the annealing step or alternatively attached on a frame. In table I, only the samples C' and C" were annealed at constant length.

Table I

Drawing and annealing conditions of PVDF samples

Sample	Rolling temperature (K)	Subsequent annealing	
		Temperature (K)	Duration (hrs)
A	348	353	2
A'	348	373	2
B	348	353	1
B'	348	353	5
C	293	393	2
C'	293	393	2
C"	293	393	5

DSC measurements

Transition temperatures were determined using a DUPONT 1090 differential scanning calorimeter. The heating rate was 20 K.min^{-1}, and the measurements were performed on 20 - 30 mg samples. Temperature calibration of the instrument was achieved by the melting of high-purity DUPONT standards.

RESULTS AND DISCUSSION

Voltalef copolymers exhibit the simplest DSC traces, because they belong to completely amorphous materials in which it is impossible to induce a crystallization by any way. As shown in fig. 1, the glass transitions (Tg) are pointed out at 260 K and 271 K for Voltalef 3700 and Voltalef 5500, respectively. These values agree roughly with an equation as simple as :

$$\frac{1}{Tg(\text{Voltalef})} = \frac{w(\text{VDF})}{233} + \frac{1-w(\text{VDF})}{318}$$

in which w(VDF) is the weight % of VDF units in the copolymer and 233 and 318 represent the Tg's(K) of pure VPDF (this study) and PCTRFE (WOOD, 1958) DSC traces representative of different thermal histories of pure PVDF are given in fig. 2. Samples quenched from the melt (a) exhibit unambiguously two transition regions below the melting point around 458 K, a first one at about 233 K and a second one in the range 313-323 K. An additional transition, sometimes observed at about 283 K, will not be discussed in this paper, because of its lack in reproducibility. Annealing at 403 K for 3 hrs of samples quenched from the melt (curve b) results in a decrease of the intensity of the transition at 318 K. Finally samples slowly crystallized from the melt (c) exhibit only a transition at 231 K and the melting peak at 458 K.

In these results, the position of the melting peak agrees well with the melting temperature of PVDF in α crystal form, as prepared from the melt (NAKAGAWA and ISHIDA, 1973). The transitions near 230 K and 315 K are referred to by ENNS and SIMHA (1977) as the lower Tg(L) and upper glass transition Tg(U), respectively. If the attribution of the transition near 230 K is unambiguous, some difficulties arise from that of the transition near 318 K. Indeed, previously reported Tg(U) values are scattered in the temperature range 283 K - 313 K (BOYER, 1975). In order to confirm the assignment of the transition at 318 K to Tg(U), we have performed additional measurements on drawn PVDF samples. It is well known that such a procedure leads to a destruction of the spherolitic structure as well as the change from α to β-crystal form. As shown in fig. 3, samples laminated at 350 K to an extension ratio λ = 4 do not exhibit any transition region at temperatures larger than Tg(L) = 233 K, excepted two melting endotherms. The large one at 458 K refers to as the normal melting process. The second endotherm may be assigned to a melting peak corresponding to a secondary crystallization process during the rolling step; indeed, additional experiments performed on drawn ma-

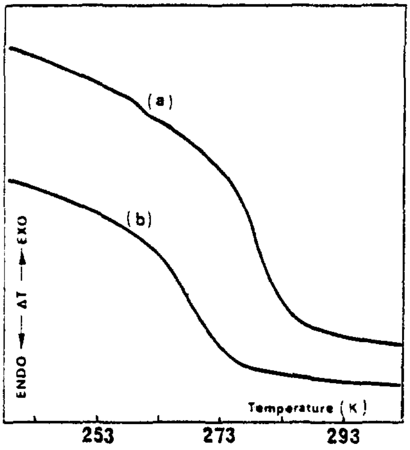

Fig. 1 - DSC traces of VOLTALEF copolymers in the glass transition region
a/ : VOLTALEF 5500; b/ VOLTALEF 3700

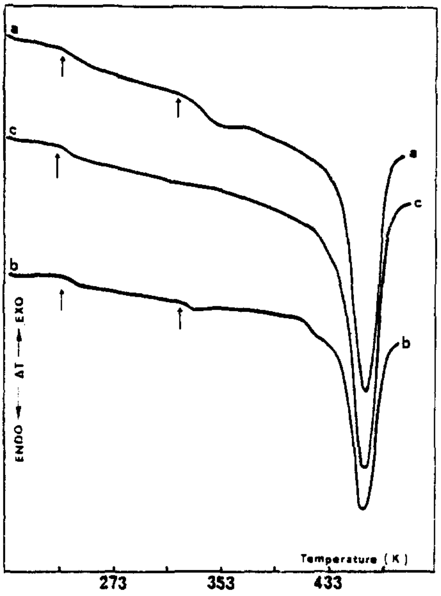

Fig. 2- DSC traces of PVDF samples. a/ quenched from the melt; b/ slowly crystallized from the melt;
c/ quenched from the melt and then annealed for 3 hrs at 403 K.

terials have shown that its location is a function of temperature and duration of a subsequent annealing.

Existence of the transition at 318 K depends on the experimental annealing procedure (fig. 4). Sharply contrasted effects are observed depending if the sample is annealed free or attached on a frame. For annealing at constant length, indeed, high temperatures and large durations are required for this transition to be detected (sample C"); otherwise, only Tg(L) is observed (sample C'). On the other hand, free annealing leads easily to the appearance of the transition at 318 K, even at moderate temperature and short duration. As a general rule, an increase in annealing temperature (samples A and A') as well as an increase in annealing duration at a given temperature (samples B and B') enhance this transition. The above observations give evidence that the transition at 318 K is related to the level of constraint of part of the amorphous chains in the vicinity of crystalline domains and support its assignment to Tg(U). However, we must allow that we did not find any significative dependence of Tg(U) temperature on crystallinity rate, as it should be (BOYER, 1982), probably because crystallinity of the PVDF samples under study does not vary enough as a function of our experimental conditions (from about 45 % to 60 %, as determined from X-rays).

The transition behavior of the VDF/TFE copolymer is quite similar to that of pure PVDF. The DSC trace of a sample quenched from the melt (fig. 5,a) shows an endothermic peak near 415 K plus two transitions at about 238 K and 318 K. On the other hand, if a molten sample is cooled down at a rate of 10 $K.min^{-1}$ till 378 K and then allowed to crystallize at this temperature for 8 hrs, the transition at 318 K is no longer detected (fig. 5, b). For such a copolymer, KOIZUMI et al. (1981) reported that Tg values range between 234 K and 238 K irrespective of the VDF content of the copolymer. Such an observation is supported by taking into account that the Tg(L) value for PVDF, given in this paper, and the hypothetic Tg for a completely amorphous PTFE (BOYER , 1975) are very close with each other. By analogy with crystallisation influence on pure PVDF transitions, as discussed above, one can assume that the transitions at 238 K and 318 K are the Tg(L) and Tg(U) of the copolymer, respectively.

One must notice that the double glass-transition behavior was observed on materials crystallized in α-form-isotropic PVDF- as well as in β-form - drawn PVDF and copolymer VDF/TFE (LANDO and DOLL, 1968). This means that no relationship exists between the existence of Tg(U) and the nature of the crystal phase.

Crude arguments are enough to understand the influence of thermal and mechanical histories on the transition behavior reported here above. As recently recalled by BOYER (1982), amorphous segments of a semi-crystalline polymer which could give rise to a glass transition are mainly : a/ chains free at both ends or segments restricted at one end by crystallites (cilia) and b/ segments restricted on both ends (loose loops or tie molecules).

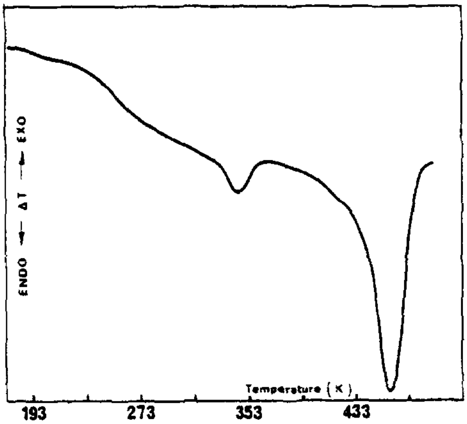

Fig. 3 - DSC trace of a PVDF sample drawn up to λ = 4 at 350 K

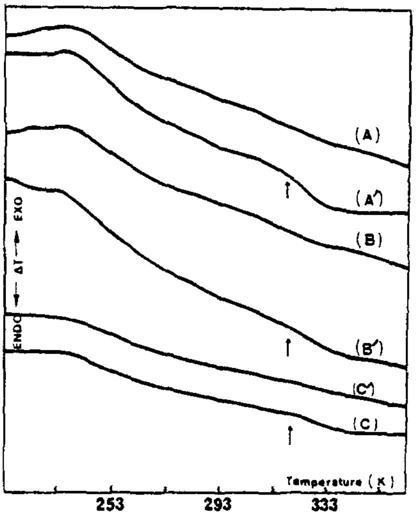

Fig. 4 - DSC traces of some PVDF samples drawn and annealed in the conditions given in Table I.

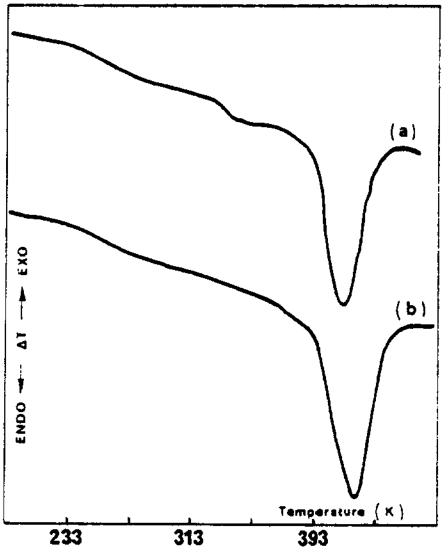

Fig. 5 - DSC traces of (VDF/TFE) copolymer samples. a/ : quenched from the melt - b/ : slowly crystallized from the melt.

a/ would be believed responsible for Tg(L) and b/ for Tg(U). In fact, existence of these transitions needs both appropriate segment length and large enough intermolecular co-operativity volumes. For isotropic materials, all these conditions are satisfied after quenching from the molten state and both Tg(L) and Tg(U) are observed. Further annealing leads to a growth of crystal domains mainly to the detriment of the loops, so that Tg(U) intensity decreases. Finally, slow crystallization from the melt leads to chain foldings which generate too short loops for Tg(U) to exist. According to PETERLIN (1971), drawing of the samples induces a transformation of lamellar to fibrous structure, characterized by the formation of elongated crystal domains and the decrease in loop quantity. As a consequence, Tg(U) desappears in markedly anisotropic materials. Free annealing of the samples permits some shrinkage to occur[in the range 2-12 % at $\lambda = 4$, as determined by BROUSSOUX (1982)]and some loops to develop in the amorphous phase. Therefore, existence of Tg(U) is again possible. On the contrary, when annealing at constant sample length does not allow such a molecular reorganization, Tg(U) does not occur.

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