Differential Scanning Calorimetry Evidence for the Existence of a First-Order Thermal Transition in Ultraoriented at-Poly(acrylonitrile)

Daisuke Sawai and Tetsuo Kanamoto*

Department of Applied Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

Roger S. Porter

Department of Polymer Science & Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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Introduction. It has been shown that gel films of ultrahigh molecular weight (UHMW) atactic poly(acrylonitrile) (at-PAN) are ultradrawable to a total draw ratio (DR_t) <110−160 by a two-stage draw technique.[1,2] DR_t is the product of draw ratios in the two stages. Such highly drawn samples show an extreme morphology, indicated by a high chain orientation function (f_c = 0.996) and a high tensile modulus (28 GPa), comparable to the uncertain X-ray crystal modulus.[3] Such ultraoriented samples are found to exhibit a crystal/crystal transition from orthorhombic to hexagonal chain packing around 150 °C, as determined from the temperature variations of the X-ray equatorial reflections around 2θ = 17° (Cu Kα radiation).[1]

The relaxation and/or thermal transitions in this polymer have been extensively studied by several techniques, including dynamic mechanical analysis (DMA),[4,5] dielectric measurements,[6] infrared absorption spectroscopy,[7] birefringence,[8] and X-ray diffraction.[9−11] These studies report the existence of relaxations around 100 and 150 °C, which correspond to the molecular motion in (para)crystalline regions and that in noncrystalline regions (glass transition), respectively. However, no report has been published on any first-order thermal transition in at-PAN, studied by DSC.

In this Communication, we report differential scanning calorimetry (DSC) and DMA studies on at-PAN films having a wide range of DR_t (1−100). A first-order thermal transition was clearly found at 142−150 °C on DSC heating scans only in ultradrawn samples of DR_t ≥ 60. This transition is ascribed to the reversible crystal/crystal transition, revealed by an X-ray diffraction study.[1] The contribution of this transition to the dynamic storage modulus, E', and tan δ peak is also discussed.

Experimental Section. Samples. The UHMW at-PAN used was prepared by suspension polymerization of acrylonitrile and had a viscosity average molecular weight of $2.3 \times \sim 10^6$, calculated according to an intrinsic viscosity/molecular weight relation.[12] A gel film, prepared from a 1 wt % solution in *N*,*N*′-dimethylformamide, was completely dried by extraction with methanol and then water, followed by drying in vacuo to constant weight.

A uniaxial two-stage draw technique[1,2] was used to prepare the highly drawn samples. The dry gel film was positioned within split billets of high-density polyethylene. This first draw was by solid-state coextrusion at 125 °C to a draw ratio (EDR) of 16. This extrudate was further drawn by a tensile force at 200 °C. The DR_t, after two-stage draw, is defined by DR_t = (first-stage EDR) × (second-stage *DR*).

Table 1. Characteristics of Nascent Powder, Gel, and Drawn Films of UHMW at-PAN

	E' (GPa)[a]	ρ (g/cm^3)[b]	f_c[c]
powder		1.155	∼0
gel (1 wt %)	2.1	1.160	∼0
EDR = 16	19.4	1.169	0.976
DR_t = 60	23.2	1.178	0.987
DR_t = 100	28.6	1.179	0.996

[a] Dynamic storage modulus at room temperature. [b] Density at 30 °C. [c] Crystal chain orientation function at room temperature from WAXD.

Measurements. DMA was made on an Orientec Rheovibron DDV-II-EP viscoelastomer, operated at a frequency of 110 Hz and a heating rate of 2 °C/min. DSC measurements were performed on a Seiko Denshi DSC-220C differential scanning calorimeter at a heating or cooling rate of 10 °C/min under a N_2 gas flow. The transition temperature and heat of transition were calibrated by using an indium standard.

Crystalline chain orientation was evaluated by the Herman orientation function,[13] f_c, calculated from the azimuthal intensity distribution of the equatorial X-ray reflection.[1,2] Densities of samples were measured at 30 ± 0.1 °C in a density gradient column consisting of mixtures of *n*-heptane and carbon tetrachloride.

Results and Discussion. PAN is an unusual polymer in that even an atactic sample can crystallize. The crystal of at-PAN has only two-dimensional order in the chain packing,[14−16] and significant disorder along the chain axis, due to the existence of heterotactic chain configurations.

Table 1 shows characteristics of the as-polymerized powder, gel, and drawn films of UHMW at-PAN. The dynamic storage modulus (E') at 24 °C, density (ρ) at 30 °C, and crystalline chain orientation function (f_c) increase remarkably with DR_t. One may note the extreme morphological anisotropy of an ultradrawn film with a DR_t of 100, compared to samples used in prior studies by others on PAN.[3−11] The IR spectra of highly drawn samples confirmed that no chemical reaction took place during drawing.

Figure 1 shows DSC heating thermograms of an as-polymerized powder, a gel film, and drawn products with EDR = 16 and DR_t = 60 and 100. A sharp endothermic peak was observed at 142−146 °C on the first DSC heating scans, for the ultradrawn samples. The peak became broader and less prominent with decreasing DR_t. The undrawn samples and the extrudate showed no clear peak. However, a closer inspection of their thermograms suggests that each shows a small and broad endothermic peak around 150−160 °C, which almost merges into the thermogram baseline. The fact that a clear DSC peak was observed only in ultradrawn at-PAN is likely the reason that prior DSC studies failed to detect this transition.

A DSC thermogram was also recorded on a cooling scan for the film with DR_t = 100, following the first heating run up to 200 °C. Subsequently, a reheating

* Author to whom correspondence should be addressed.

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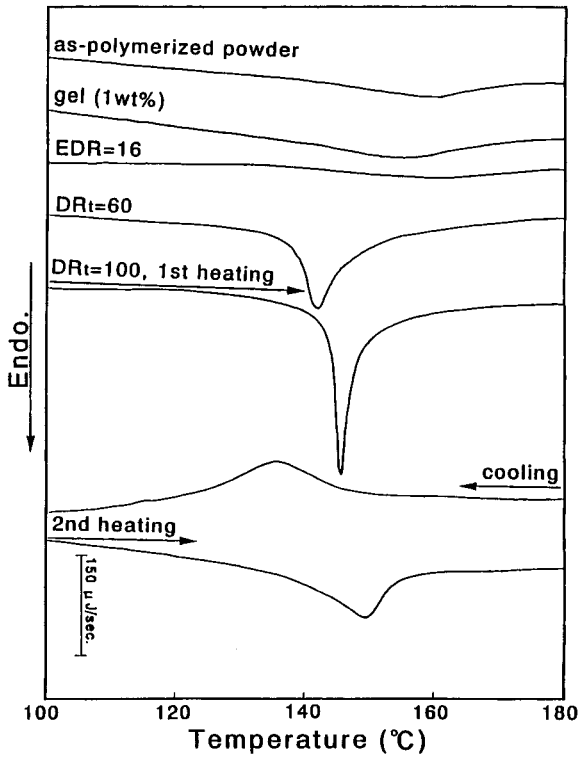

Figure 1. DSC thermograms for an as-polymerized powder, gel film, extrudate with an EDR of 16, and ultradrawn films with DR_t values of 60 and 100. Thermograms of a sample with the highest DR_t of 100 were recorded also on cooling and reheating scans. Heating and cooling rates were all 10 °C /min.

scan was made from 0 to 200 °C. These thermograms are also included in Figure 1. On the cooling scan, a broader exothermic peak appeared at ~134 °C, some 12 °C lower than the peak temperature (146 °C)observed on first heating. On the second heating scan, a broader endothermic peak was observed at 150 °C, slightly higher than the peak temperature on the first scan. These results suggest that the transition is a rate process and is affected by annealing during DSC scans. The transition peak temperature of 142−150 °C, observed on DSC heating scans, agrees well with the crystal/crystal transition[1] reported earlier by the X-ray diffraction.

The heat of transition for the ultradrawn samples with DR_t values of 60 and 100 was ~480 J/mol for the first heating scan. It decreased slightly to 370−420 J/mol for the cooling and the second heating scans. These values are remarkably lower than the heats of fusion (4−10 kJ/mol) for olefin polymers. However, it corresponds to 44−34% of the total heats (1.1 kJ/mol) of the two crystal/crystal transitions at 19 and 30 °C in a highly crystalline (X_c = 86%, calculated from the density), nascent powder of poly(tetrafluoroethylene).[17] These all infer that the observed DSC transition is more like a crystal/crystal transition. Consistent with this, on annealing of the highly drawn sample with DR_t = 100 at 180 °C, slightly above the transition temperature, for 20 min with the sample ends fixed, the chain orientation function decreased from the initial $f_c = 0.996$ to 0.920 due to the molecular motion in the hexagonal crystalline phase. However, on redrawing of the annealed sample, the chain orientation increased again.

Figure 2 shows the temperature dependence of the dynamic storage modulus (E') and loss tangent (tan δ) for a gel film and drawn films with EDR = 16 and DR_t = 100. Two mechanical relaxations were observed around 100 and 150 °C for each sample, as reported.[4,5] Minami[5] and Hayakawa et al.[6] conclude that the lower temperature transition is due to the molecular motion in paracrystalline regions and the higher one to the glass transition in amorphous regions. Some authors[9−11] found that the thermal expansion coefficient, calculated from the lattice spacing of an X-ray equatorial reflection, increased rapidly above ~100 °C, consistent with the assignment of the lower temperature relaxation by Minami[5] and Hayakawa et al.[6] No DSC peak was observed around 100 °C, where the relaxation in crystalline regions was observed by DMA[5] and X-ray diffraction.[9−11]

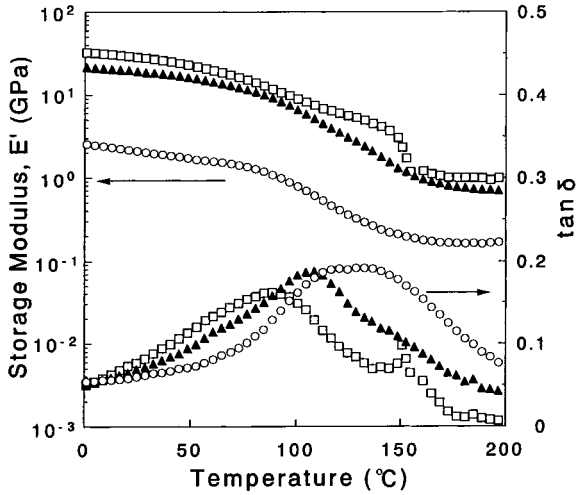

Figure 2. Dynamic storage modulus (E') and loss tangent (tan δ) vs. temperature for a series of at-PAN samples, measured in the draw direction at 110 Hz: (○) original gel film; (▲) extrudate with an EDR of 16; (□) ultradrawn film with a DR_t of 100.

We focus our attention here only on the higher temperature tan δ peak at ~150 °C, to discuss the relationship between this relaxation and the thermal transition detected by DSC. The intensity of the tan δ peak significantly decreases with increasing DR_t, corresponding to an increase in sample density, as shown in Table 1. The crystallinity cannot be calculated from a sample density, since the theoretical densities of neither the crystal nor the amorphous regions are known for at-PAN, nonetheless, the increase in sample density can be a measure of crystallinity increase. Thus, the observed decrease in intensity of the tan δ peak at ~150 °C on draw is consistent with the prior assignment of this relaxation to the molecular motion in noncrystalline regions.

However, the origin of the tan δ peak at ~150 °C in a highly drawn sample cannot be simply ascribed only to the molecular motion in noncrystalline regions. The ultradrawn film with a DR_t of 100 of an extreme morphology (Table 1) exhibits a significantly sharp drop in E' and a correspondingly small and sharp tan δ peak at ~150 °C. Samples with a lower DR_t show a gradual decrease in E' and a correspondingly broad tan δ peak. This is consistent with a relaxation phenomenon in nocrystalline regions. The fact that a sharp drop in E' occurred only for the ultradrawn sample suggests that this is coupled to the molecular motion in crystalline regions, rather than that in noncrystalline regions alone, consistent with this DSC evidence, and with our prior X-ray study,[1] which reports a reversible crystal/crystal transition at ~150 °C in a highly drawn at-PAN.

Conclusion. An ultradrawn, highly oriented (f_c = 0.996) film with a DR_t of 100 exhibits a sharp DSC endothermic peak with a transition heat of 480 J/mol at 146 °C. On a subsequent cooling run, a broader exothermic peak is observed at ~134 °C. Such a reversible transition is less prominent in samples of lower DR_t.

This first-order thermal transition, detected by DSC, seems to correspond to the crystal/crystal transition, previously observed by wide-angle X-ray diffraction study on a highly drawn at-PAN.[1] Thus, the dynamic mechanical tan δ peak at ~150 °C, observed at 110 Hz in drawn at-PAN films, likely consists of contributions from both the molecular motion in noncrystalline regions, as reported,[5,6] and from the crystal/crystal transition detected by DSC and X-ray diffraction.[1] The magnitude of contribution of the former mechanism decreases with increasing DR_t, while the latter increases with DR_t.

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