Polymer Bulletin 20, 449–453 (1988)

Polymer Bulletin

A study on the correlation between rigid and oriented amorphous fractions in uniaxially drawn poly(ethylene-2,6-naphthalene dicarboxylate)

Stephen Z. D. Cheng*, James J. Janimak, Anqui Zhang, Jiayu Guan***, and Ang-Ling Chu******

Institute and Department of Polymer Science, College of Polymer Science and Polymer Engineering, University of Akron, Akron, OH 44325, USA

Summary

Stress-induced crystallization occurs when one uniaxially draws amorphous poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) films at a certain temperature, drawing ratio and speed. The rigid amorphous fractions of the PEN samples were measured by differential scanning calorimetry (DSC), and their oriented amorphous fractions were detected by wide angle X-ray diffraction (WAXD). It has been shown that there is a close correlation between these two amorphous fractions.

Introduction

Thermal properties of poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) have been studied[1]. The glass transition temperature, T_g, for quenched PEN is at 390 K with the heat capacity increase at T_g of 80.1 J/(K mol). The equilibrium heat of fusion of PEN is found to be 25 kJ/mol at 610 K.

PEN also provides a new example of a polymer that may possess in the semicrystalline state a rigid amorphous fraction[1]. The rigid amorphous fraction does not contribute to the increase in heat capacity at T_g and devitrifies only at higher temperature. Similar behavior was found in several high-melting temperature polymers with phenylene groups in the main chain[2-4]. The overall "rigid fraction", f_r, is computed from C_p by setting

$$f_r = 1-[\Delta C_p(m)/\Delta C_p(a)] \qquad (1)$$

where $\Delta C_p(m)$ and $\Delta C_p(a)$ represent the measured and totally amorphous heat capacity increase at T_g, respectively. The weight crystallinity, in turn, is determined by differential scanning calorimetry (DSC):

$$w^c = \Delta H_f(m)/\Delta H_f(c) \qquad (2)$$

where $\Delta H_f(m)$ and $\Delta H_f(c)$ are the measured and 100% crystalline heat of fusion, respectively.

---

*To whom offprint requests should be sent

**Visiting Professor from China Textile University, Shanghai, PRC

***Visiting Professor from China Academia Sinica, Bejing, PRC

****Permanent address: Polymer Research, Key-tech Inc., RI 02920, USA

If the crystallinity model (two phase model) is valid, f_r is equal to w^c. If $f_r > w^c$, a rigid amorphous fraction exists about T_g and can be quantitatively studied.

To obtain the oriented amorphous fraction in a uniaxial drawn semicrystalline polymer, one may adopt the procedure of computational resolution of WAXD intensity of the oriented polymer, and separate the contributions of individual diffraction peaks of crystal planes, and isotropic and oriented amorphous components of diffuse scattering[5].

In this paper, we report our new results of which a close correlation between rigid and oriented amorphous fractions in uniaxially drawn PEN has been established.

Experimental

The PEN for our research was supplied by Academia Sinica, China. The intrinsic viscosity of the PEN at 298.2 K in phenol/o-dichlorobenzene (0.6/0.4) was 0.593 dL/g. The amorphous PEN film samples were then uniaxially drawn at different temperatures, drawing speeds, and drawing ratios as listed in Table I.

Table I. The Uniaxially Drawn PEN Samples

Sample Assignment	Drawing Ratio (λ)	Drawing Temperature (K)	Drawing Speed (m/min)
PEN 1	2	416.2	1.9
PEN 2	3	416.2	1.9
PEN 3	5	416.2	1.9
PEN 4	3	416.2	0.79
PEN 5	3	423.2	1.9
PEN 6	5	423.2	1.9
PEN 7	3	416.2	6.7
PEN 8	5	416.2	6.7

All the samples were measured with an updated computer-interfaced Perkin-Elmer DSC2. The heat capacity measurements were performed in the temperature range of 240 to 600 K. The DSC was calibrated following the standard procedures[1].

WAXD experiments were carried out on a Rigaku X-ray generator with a 12kW rotating anode as a source of the incident X-ray beam. The photographs were taken on a vacuum camera (point-focused X-ray beam). The crystallinity determinations were performed on a D/Max-B X-ray powder diffractometer after the oriented samples were grounded. The method of separating oriented amorphous fractions from other contributions described in ref. 5 was applied, and the software was provided by Dr. H. Jiang at the John Hopkins University.

Results and Discussions

Figure 1 shows the DSC melting traces for PEN 1-3, as an example, and the results of all the samples are listed in Table II. From DSC measurements one can find that the glass transition temperature, T_g, is almost independent of mechanical and thermal histories in these samples. A slight change of the melting temperature, T_m, is related to those histories. For other parameters listed in Table II, however, there exists a strong dependence upon drawing conditions. The heat capacity increase at T_g decreases with increasing drawing ratio, drawing speed and decreasing temperature. A similar tendency can also be found at the peak temperature of crystallization, T_c, and the heat of crystallization, ΔH_c, indicating that uniaxial drawing enhances nucleation, and therefore, leads to a fast overall crystallization[6]. On the other hand, the heats of fusion of the samples, ΔH_f, increase with increasing the drawing ratio and decreasing drawing temperature, but, in our experiments, are not sensitive to the drawing speed.

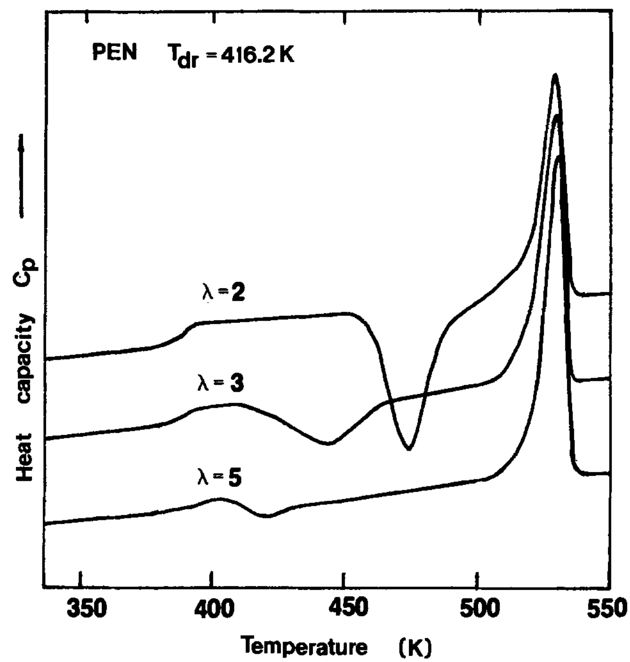

Figure 1. A set of DSC melting traces of uniaxially drawn PEN samples at 416.2 K and different drawing ratio (λ).

The stress-induced crystallinity, w^c, before heating can be obtained by substracting the heat of crystallization from the heat of fusion. These values of w^c are also checked by WAXD method, and the two sets of data obtained from DSC and WAXD are very close. Finally, the rigid amorphous fractions of the PEN samples can be calculated by applying $f_r - w^c$ (Eq. 1 for f_r).

WAXD results are listed in the last column of Table II, and detailed X-ray photographs are shown in Fig. 2 (a,b) for PEN 2 and 3 as examples. One can find that the oriented amorphous fraction, f_{or}, measured by WAXD is closely correlated with the rigid amorphous fraction, $f_r - w^c$, determined by DSC. The ratio between rigid or oriented amorphous fraction and crystallinity decreases with increasing the crystallinity, w^c.

To explain such a correlation, one has to invoke the microscopic descriptions of these two amorphous fractions, although these descriptions

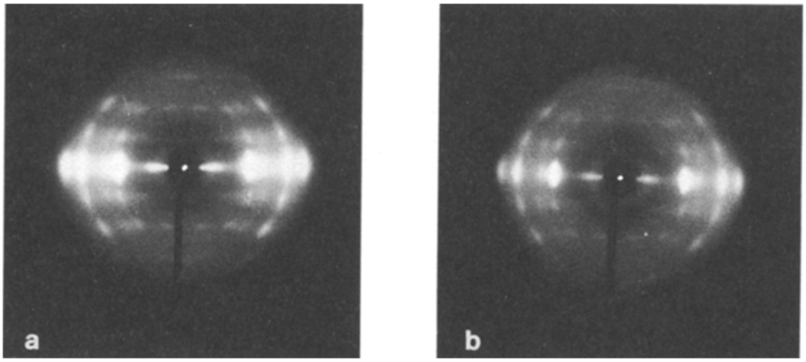

Figure 2. WAXD photographs of uniaxially drawn PEN samples at 416.2 K and 1.9 m/min. (a) $\lambda=3$, and (b)$\lambda=5$.

Table II Thermal and Defraction Properties of Uniaxially Drawn PEN Samples

Samples	T_g (K)	ΔC_p [J/(K mol]	T_c (K)	ΔH_c (kJ/mol)	T_m (K)	ΔH_f (kJ/mol)	w^c	f_r-w^c	f_{or}
PEN 1	387	72	471	-8.0	529.7	8.7	0.03	0.07	0.10
PEN 2	388	56	448	-5.2	530.2	9.5	0.17	0.13	0.18
PEN 3	388	42	418	-1.0	530.8	10.8	0.39	0.08	0.07
PEN 4	388	54	445	-5.1	530.2	9.5	0.18	0.15	0.20
PEN 5	388	66	438	-6.3	528.8	9.0	0.08	0.10	0.13
PEN 6	388	49	417	-2.3	530.1	9.8	0.30	0.08	0.05
PEN 7	388	47	449	-4.8	530.3	9.6	0.19	0.22	0.25
PEN 8	389	37	421	-0.2	531.1	10.7	0.42	0.12	0.11

are still qualitative and even hypothetical. The rigid amorphous fraction is usually formed in a semicrystalline polymeric system due to the existence of stress-concentrated interface connections[1-4]. A size of perhaps 1-2 nm is expected in-between amorphous and crystalline states. A gradual loss of chain-order should be observed in the rigid amorphous region from the boundary of crystals towards the mobile amorphous portion.

On the other hand, the oriented amorphous fraction is caused by deformations in the early stage of stress-induced crystallization[6-8]. Further uniaxial drawing leads to the formation of crystals from such a fraction, and in return, the crystals retain the rest of the oriented amorphous portion by playing a role similar to physical cross-linking. Qualitatively, therefore, these two fractions should be correlated after crystallization. A possible explanation of the decrease of the ratio between rigid or oriented amorphous fraction and crystallinity with increasing w^c is that small and imperfect crystals (low w^c) may provide large interfacial tension and introduce internal stresses. With increasing size and perfection of the crystals through exhausting those fractions and release of internal stress, as a result, the ratio thus decreases. A generally higher value of the oriented amorphous fraction compared to the rigid amorphous fraction (see Table II) may indicate that the later one is perhaps more restricted and close to the interface region.

To fully understand the correlation between these two amorphous fractions, one needs to further study morphology and molecular motion in the drawn solid state.

Acknowledgment

This work was supported by the Research Challenge Grant of Ohio State Regent through The University of Akron.

References

1. S. Z. D. CHENG and B. WUNDERLICH, Macromolecules 21, 789 (1988).
2. S. Z. D. CHENG, M.-Y. CAO and B. WUNDERLICH, Macromolecules 19, 1868 (1986).
3. S. Z. D. CHENG and B. WUNDERLICH, Macromolecules 20, 1630 (1987).
4. S. Z. D. CHENG, Z. Q. WU and B. WUNDERLICH, Macromolecules 20, 2082 (1987).
5. G. LEMANSKA and A. NAREBEKA, J. Polym. Sci., Polym. Phys. Ed. 18, 917 (1980).
6. B. WUNDERLICH, "Macromoleculer Physics, Crystal Nucleation Growth, Annealing," Chapter 6.3.2, Academic Press, New York (1976).
7. J. H. SOUTHERN, Special issue of Polym. Eng. Sci. on stress-induced crystallization, 16 (1976).
8. W. B. BLACK, Special issue of Polym. Eng. Sci. on stress-induced crystallization, 17 (1978).

Accepted September 20, 1988 K