Deformation in thin films of amorphous and semicrystalline isotactic polystyrene

C. J. G. Plummer* and H.-H. Kausch
Laboratoire de Polymères, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland
(Received 3 September 1992; revised 23 November 1992)

Transmission electron microscopy investigations of deformation in films of amorphous and semicrystalline isotactic polystyrene have shown crazing to dominate up to the glass transition temperature, T_g, the craze fibrils becoming more crystalline as the strain rate is lowered and the temperature raised. Above T_g semicrystalline films show fibrillar shear.

(Keywords: isotactic polystyrene; transmission electron microscopy; thin films; crazing; fibrillar shear)

Investigations using transmission electron microscopy (TEM) of deformation in semicrystalline isotactic polystyrene (iPS), using the 'copper-grid' technique[1], have confirmed that at room temperature, both amorphous and semicrystalline iPS show similar craze microstructures to those seen in amorphous atactic polystyrene (αPS)[2]. The object of the current work has been to extend these observations to cover temperatures up to and above the glass transition temperature, T_g. iPS ($M_w = 590\,000$, $M_w/M_n = 3.4$; supplied by Polymer Laboratories Ltd) was refluxed overnight in methyl ethyl ketone to remove atactic material. Amorphous films of approximately 0.5 μm in thickness were cast from dichlorobenzene at 60°C onto cleaved NaCl crystals. After evaporation of the solvent, the films were bonded to annealed copper grids by heating to 120°C, and dried under vacuum at 90°C. Subsequent crystallization under vacuum at 180°C gave a fine sheaf-like crystallite morphology, for which selected-area electron diffraction (s.a.e.d.) indicated random crystallite orientation. To obtain a spherulitic structure, the films were heated to 250°C under nitrogen prior to bonding to the grids and heat treatment. The resulting radial growth rate at 180°C was 0.15 μm min^{-1}, consistent with the literature[2-6]. The spherulites comprised a central sheaf containing *c*-axis orientation parallel to the plane of the film, surrounded by plates of perpendicular *c*-axis orientation, as reported previously[2,5]. The samples were strained in tension using the Polymer Laboratories Minimat tensile test apparatus equipped with an environmental chamber: individual grid squares were then removed for examination by TEM (Phillips 300 at 100 keV).

Craze microstructures in all types of film deformed below T_g were similar to those in amorphous αPS[2,7], with fibril spacings of approximately 20 nm. The crazes grew perpendicular to the direction of principal stress, although local distortions of the craze–bulk interface were seen in semicrystalline films, believed to be a consequence of their uneven thickness and of local variations in the craze extension ratio, λ_{craze}, associated with variations in the crystallite orientation[2]. Bundles of lamellae lying parallel to the advancing craze often became incorporated in the craze body. Considerable systematic thickness variations were observed in spherulitic films, spherulite boundaries, for example, tending to be relatively thin. However, although there was some tendency for crazes to run along the spherulite boundaries where these were at high angles to the principal stress direction, they passed readily into the bulk of adjacent spherulites, and showed little tendency to avoid regions of particular crystallite orientation.

As the temperature was raised towards T_g, crazing continued to dominate in both amorphous and semicrystalline films as in *Figure 1*, which shows a craze in an amorphous film strained at 80°C at a deformation rate of $10^{-2}\,s^{-1}$. As the strain rate was lowered at temperatures above 80°C, however, the extent of crazing appeared to diminish, such that at strain rates of $10^{-5}\,s^{-1}$ or less, the films deformed homogeneously up to the breaking strain of the copper grid (between 10 and 20%). This was in contrast to the behaviour of αPS of the same molecular weight, in which similar conditions led to a sharp drop in crazing stress and profuse crazing. Above T_g, amorphous films deformed homogeneously at all strain rates. In semicrystalline films, however, a second type of localized deformation became apparent above T_g, as shown in *Figure 2*. At low magnification, the deformation is similar to the shear deformation zones seen in amorphous glassy polymers[7] but, unlike the latter, appears fibrillar at low magnification. At higher magnifications, as in *Figure 2*, the fibrillar texture is nevertheless coarser and less well defined than in the case of crazes, hence we prefer to use the term 'fibrillar shear', applied previously to similar features in thin semicrystalline films of nylon[8] and poly(ether ether ketone) (PEEK)[9]. The deformation zone in *Figure 2* also shows a pronounced lamellar structure running parallel to its length. This is a result of high temperature recrystallization rather than break-up of the original lamellae. The corresponding s.a.e.d. pattern (*Figure 2*) indicates strong orientation of the *c*-axis along the stress axis, similar to that obtained in homogenous deformation of amorphous films to high strains above T_g[5].

Taking the present observations together with previous investigations of nylon and PEEK[8,9], it appears clear that one of the crucial factors affecting the competition

* To whom correspondence should be addressed

0032-3861/93/091972-03

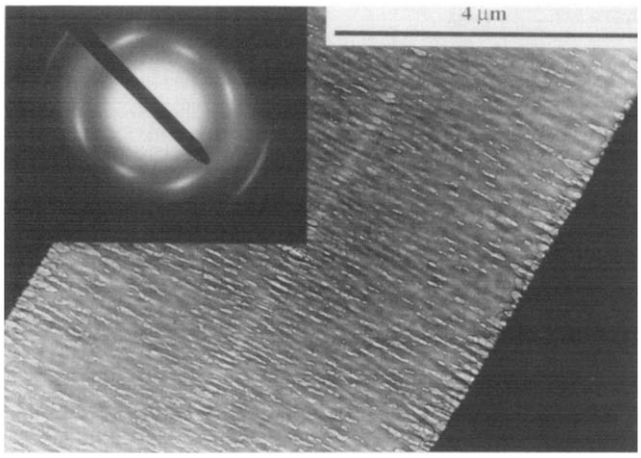

Figure 1 Craze in amorphous solution-cast iPS film deformed at 80°C at a strain rate of $10^{-2}\,s^{-1}$; inset, diffraction pattern from craze

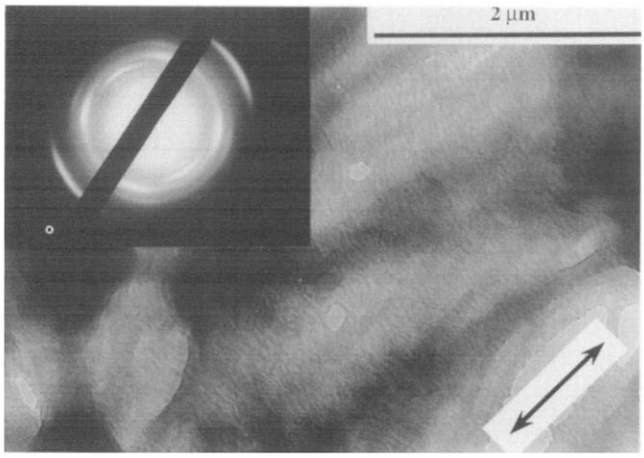

Figure 2 Detail from deformed region of localized deformation in solution-cast iPS, heat treated for 10 min at 180°C and deformed at 180°C, at a strain rate of $10^{-2}\,s^{-1}$; inset, corresponding diffraction pattern (arrow indicates tensile direction)

between crazing and shear deformation in glassy semicrystalline polymers is the entanglement density, v_e, as is known to be the case for amorphous glassy polymers below T_g[7]. Where entanglement loss during crazing is mediated by scission, the propagation stress for a craze, σ_{craze}, has been argued to depend on the effective surface tension, Γ, at the advancing craze void tips such that:

$$\sigma_{craze} \sim k\Gamma^{1/2} \sim k\left(\Gamma_0 + \frac{v_e d_e U}{4}\right)^{1/2} \quad (1)$$

where Γ_0 is the Van der Waals' surface energy of the polymer, k is a constant, d_e is the spatial separation of topologically adjacent entanglement points, and U is the bond energy[7]. In amorphous αPS, with $v_e = 4 \times 10^{25}\,m^{-3}$, $U = 6 \times 10^{-19}$ J and $d_e = 9.6$ nm. Γ is approximately $2\Gamma_0$, and crazing predominates[7]. In a high entanglement density amorphous polymer such as poly(ether sulfone) (PES), however, where v_e is an order of magnitude larger, σ_{craze} is greatly increased, and crazing is replaced by simple shear deformation; the number of bonds which must be broken to allow void tip advance is simply too high for scission crazing to occur in PES[10].

We suggest that it is for similar reasons that shear deformation appears to be the dominant deformation mechanism in semicrystalline PEEK (large v_e)[9], whereas crazing dominates in amorphous and semicrystalline iPS (small v_e). Moreover, in the latter case it has been possible to account quantitatively for the observed variations in craze extension ratio, λ_{craze}, as a function of the local lamellar orientation on the basis of the entanglement network model[2]. Neutron scattering suggests that the overall coil size remains unchanged during crystallization under the appropriate conditions[11], and further, the chains may be considered as divided into subunits consisting of a short block of three adjacent lamellar folds, and an equal length of a chain in a random conformation, incorporated in the amorphous interlamellar material[2,11]. The total length of chain representing such a subunit was estimated to be equal to the strand length, l_e, separating entanglement points in amorphous PS[2]. In the latter, the value of λ_{craze} is approximately l_e/d_e, where d_e is the spatial separation of the entanglement points. By considering the effect of the orientation of the chain-folded block on the effective d_e, it was possible to predict[2] the observed local variations in λ_{craze}.

The success of this approach is evidence for λ_{craze} which arises simply as a consequence of stretching of entangled strands. It also implies little change in the entanglement network parameters on crystallization, and complete unfolding of the original lamellae during deformation, as also suggested by the low degree of crystallinity present in iPS crazes at room temperature; here we found no evidence from s.a.e.d. for crystallinity in room temperature crazes in films deformed at $10^{-2}\,s^{-1}$. This unfolding presumably takes place in the fluid-like process zone of thickness h at the craze–bulk boundary, since λ_{craze} is constant within the craze body. Hence the main factors determining the surface energy Γ at the void tips ought to remain entanglement loss and the Van der Waals' surface energy. Equation (1) should therefore remain approximately valid for semicrystalline iPS, hence the craze fibril separation should remain similar to that in amorphous iPS or αPS, as we have observed in the present investigation.

The term 'fluid-like' process zone and the high chain mobility this implies, suggest that the deformed polymer may recrystallize during drawing. In films deformed at a strain rate of $5 \times 10^{-7}\,s^{-1}$, weak s.a.e.d. patterns resembling fibre patterns have been obtained from the craze fibrils[12,13]. The fact that the degree of crystallinity in the craze fibrils is likely to be a increasing function of the residence time of the polymer chains in the process zone[13], and hence to increase with decreasing strain rate, explains the absence of crystallinity in room temperature crazes formed at $10^{-2}\,s^{-1}$. The crystallinity nevertheless increases rapidly with T at this strain rate to give well defined s.a.e.d. images close to T_g, as in *Figure 1*. While we have not been able to obtain clear images of the lamellae in such crazes, we suspect these to be associated with cross-tie fibrils.

Another process intimately linked with this residence time is disentanglement[10,14–17], which has been argued to replace scission as the mechanism for entanglement loss during crazing at high temperatures and low strain rates. In this view, individual polymer chains may be 'pulled' out of the entanglement network under the influence of local stresses[16,17]. However, the transition from shear or scission crazing to disentanglement crazing as the temperature approaches T_g, shown by amorphous polymers of similar entanglement density such as PES[10],

is absent from amorphous quenched films of PEEK, shear being observed at all temperatures[9]. It is suggested that this might be due to strain-induced crystallization preventing disentanglement. The absence of crazing at low strain rates close to T_g (found here for iPS in contrast to the behaviour of αPS of the same molecular weight under such conditions), which are expected to favour disentanglement[15], might be taken as further evidence for crystallization preventing disentanglement.

References

1 Lauterwasser, B. D. and Kramer, E. J. *Phil. Mag.* 1979, **A39**, 469
2 Morel, D. E. and Grubb, D. T. *Polymer* 1984, **25**, 417
3 Boon, J., Challa, G. and Van Krevelin, D. W. *J. Polym. Sci.* 1968, **A2** (6), 1791
4 Suzuki, T. and Kovacs, A. J. *Polym. J.* 1970, **1**, 82
5 Edwards, B. C. and Phillips, P. J. *Polymer* 1974, **15**, 351
6 Lemstra, P. J., Postma, J. and Challa, G. *Polymer* 1974, **15**, 757
7 Kramer, E. J. in 'Advances in Polymer Science No. 52/53' (Ed. H.-H. Kausch), Springer Verlag, Berlin, 1983, Ch. 1
8 More, A. P. and Donald, A. M. Proc. 8th International Conference on Deformation Yield and Fracture of Polymers, Cambridge, April 1991, paper 11
9 Plummer, C. J. G. and Kausch, H.-H. *Polymer* 1993, **34**, 305
10 Plummer, C. J. G. and Donald, A. M. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 327
11 Guenet, J.-M. *Polymer* 1981, **22**, 313
12 Morel, D. E. and Grubb, D. T. *J. Mater. Sci. Lett.* 1984, **3**, 5
13 Krug, H., Karbach, A. and Petermann, J. *Polymer* 1984, **25**, 1687
14 Donald, A. M. *J. Mater. Sci.* 1985, **20**, 2630
15 Berger, L. L. and Kramer, E. J. *Macromolecules* 1987, **20**, 1980
16 McLeish, T. C. B., Plummer, C. J. G. and Donald, A. M. *Polymer* 1989, **30**, 1651
17 Kramer, E. J. and Berger, L. L. in 'Advances in Polymer Science No. 91/92' (Ed. H.-H. Kausch), Springer Verlag, Berlin, 1990, Ch. 1