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Intermediate Angle Scattering Functions and Local Chain Configurations of Semicrystalline and Amorphous Polymers

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SUMMARY

Molecular scattering functions at intermediate scattering vectors, of $\mu=(4\pi/\lambda \sin\vartheta/2)$ in the range 0.03 to 1.0Å^{-1}, are found to be extremely sensitive to the local configurations of polymer chains in both semicrystalline and amorphous states. Available experimental results of intermediate angle neutron scattering (IANS) from melt-crystallized polyethylene and isotactic polypropylene provide compelling evidence that adjacent re-entry is rare. The rotational isomeric state model satisfactorily accounts for IANS and chain dimensions of polycarbonate in the amorphous state.

INTRODUCTION

The fact that the intensity of intermediate angle neutron scattering (IANS), i.e., scattering at intermediate scattering vectors $\mu=(4\pi/\lambda \sin \vartheta /2)>0.03\text{Å}^{-1}$, is extremely sensitive to local chain configurations is now well established. This has been demonstrated most strikingly for PMMA[1,2] and also for semicrystalline polyethylene.[3-6] The scattering function in the intermediate range should be especially sensitive to adjacency of deuterated stems in crystalline lamellae, the presence of which must enhance the incidence of pairs of scattering centers at distances comparable to the lamellar thickness.

With recent advances in experimental IANS methods it has been possible to extend the range of scattering vectors wherein reliable data can be obtained. Consequently, experimental results of molecular scattering functions are now available up to $\mu\simeq 1.0\text{Å}^{-1}$ for melt-crystallized polyethylene[6] and amorphous polycarbonate.[7] The IANS method has been applied recently to a number of other polymers including semicrystalline isotactic polypropylene.[8] The availability of these new experimental data has enabled us to investigate the local configurations of polymers in much greater detail than was previously possible.

In this paper, we first present scattering functions calculated for various models of semicrystalline polyethylene in the range of $0.03<\mu<0.4\text{Å}^{-1}$. In order to render the results applicable at these large scattering vectors, the scattering functions have been calculated from the positions of the interfering deuterium atoms in the lamellar morphology. Full account has been taken of the crystal lattice and of the unit cell structure. This refined procedure was then applied to semicrystalline isotactic polypropylene.

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Next we present calculations of scattering functions for amorphous polycarbonate in the range of scattering vectors up to $\mu=1.0\text{Å}^{-1}$. Exact geometrical parameters and realistic conformational energy profiles[9,10] have been employed to account for the interferences between deuterium atoms.

RESULTS AND DISCUSSIONS

The scattering function $F_x(\mu)$ defined by:

$$F_x(\mu) = (x+1)\mu^2\frac{I(\mu)}{I(0)} \tag{1}$$

for a polymer chain comprising x+1 repeat units was calculated through use of the relationship:[2]

$$F_x(\mu) = \frac{\mu^2}{(x+1)m^2}\left\{\sum_{k,1}^{m}\left[\frac{\sin(\mu r_{0,k1})}{\mu r_{0;k1}} + 2\sum_{t=1}^{x}(x+1-t)\left\langle\frac{\sin(\mu r_{t;k1})}{\mu r_{t;k1}}\right\rangle\right]\right\}, \tag{2}$$

where m is the number of D atoms per repeat unit, $r_{0;k1}$ is the distance between D atoms, k and 1, within the same repeat unit, and $r_{t;k1}$ is the distance between D atoms occurring in different units.

The experimental scattering function $F_x(\mu)$ defined by Eq. (1) was evaluated directly from the experimental scattering cross section $I(\mu)$ according to:[6]

$$F_x(\mu) = \frac{I(\mu)\mu^2 M_0}{c(1-c)\rho(a_D-a_H)^2 m^2 N_{Av}}, \tag{3}$$

where c is the volume fraction of deuterated chains, ρ is the density, a_D and a_H are the scattering cross sections of D and H atom, respectively, M_0 is the molecular weight of the repeat unit, and N_{Av} is the Avogadro's number.

MELT CRYSTALLIZED POLYETHYLENE

The scattering functions $F_n(\mu)$ for a deuterated polyethylene chain comprising n=750 bonds dispersed in protonated polyethylene having the lamellar morphology with alternating crystalline (100Å) and noncrystalline (50Å) layers are shown in Fig. 1. The calculations were carried out for various values of P_{ar}, the *a priori* probability of adjacent re-entry whereby the chain, upon emerging from the crystalline layer, adopts the conformation required for a tight fold with re-entry along (110) plane.[11] In order to render the density of deuterated atoms in the interfacial region consistent with the actual density, the degree of deuteration in this region was adjusted to meet this requirement. The effect of this adjustment was demonstrated to be otherwise inconsequential.

Comparison with experimental results in Fig. 1 shows that models with $P_{ar}\geq 0.5$ are incompatible with the experimentally observed profile, as well as with the absolute intensity. The experimental results shown in Fig. 1 do not depart significantly from scattering functions calculated for $P_{ar}=0$. Even with full allowance for possible errors, the experimental results require $P_{ar}<0.3$.

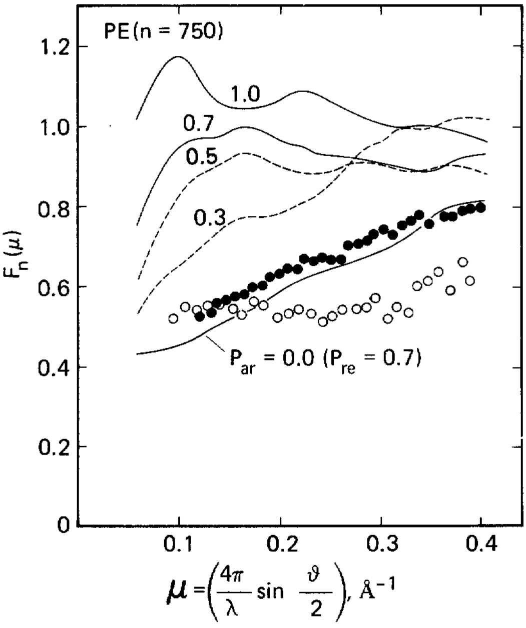

Figure 1. The scattering functions $F_n(\mu)$ for polyethylene chains of n=750 bonds in the melt-crystallized state, computed for various values of the *a priori* probability of adjacent re-entry P_{ar}. Experimental points are from Stamm et al. (filled circles)[6] and Sadler et al. (open circles).[5]

MELT CRYSTALLIZED ISOTACTIC POLYPROPYLENE

The scattering functions $F_x(\mu)$ for isotactic polypropylene chains of x=2,000 repeat units (n=4000 bonds) dispersed in crystalline (170Å) and noncrystalline (75Å) lamellae are presented in Figure 2. The calculations were carried out for various values of P_{ar}, the *a priori* probability of tight adjacent re-entry along the (010) plane.[12] Since the calculations are restricted to $\mu < 0.1$Å^{-1}, it was legitimate to take the α-carbon atoms as the scattering loci for each repeat unit. Comparison with experimental results of Ballard et al.[8] shows no intimation of significant departure from calculations carried out with complete exclusion of adjacent re-entry. They are irreconcilable with a value of $P_{ar} > 0.3$.

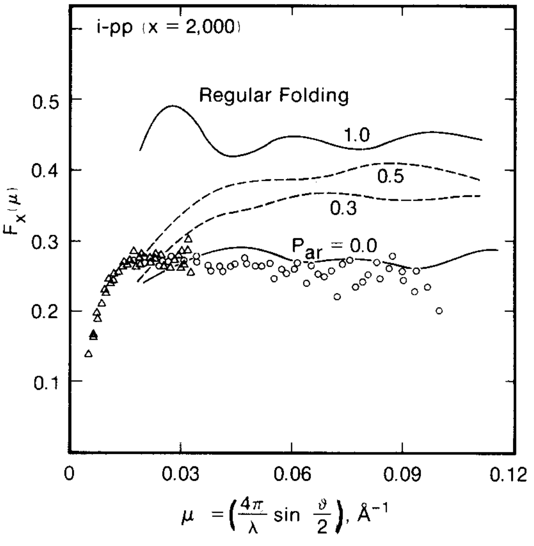

Figure 2. The scattering functions $F_x(\mu)$ for isotactic polypropylene chains of x=2,000 repeat units in the melt-crystallized state, computed for various values of the *a priori* probability of adjacent re-entry P_{ar}. Experimental points are from Ballard et al.[8]

AMORPHOUS POLYCARBONATE

The scattering function $F_x(\mu)$ for polycarbonate chains of x=50 repeat units, converted to $I(\mu)\ \mu^2/c\ (1\text{-}c)$ according to Eq. (3), are shown in Fig. 3 for $\mu \leq 1.0$Å^{-1}. Each D-atom in the benzene ring was taken as a scattering locus; the three D-atoms in each CD_3 group were represented as a point scatterer located at the mean position of the three D-atoms. Geometrical parameters derived from the crystal structure of diphenyl carbonate[9] have been employed in conjunction with the conformational energy profile calculated for diphenyl propane[10] and phenyl acetate.[13] The experimental results of Gawrisch et al.,[7] shown in the same figure, are satisfactorily accounted for by the unperturbed chain model of polycarbonate over the entire range of scattering vector μ up to 1.0Å^{-1}. Also, the chain extension thus calculated, $\langle r^2\rangle/M_w \simeq 1.1$, is in satisfactory agreement with the experimental value of $\langle r^2\rangle/M_w \simeq 1.3$ for amorphous polycarbonate.[7] The inadequacy of the Debye equation is also demonstrated in Fig. 3.

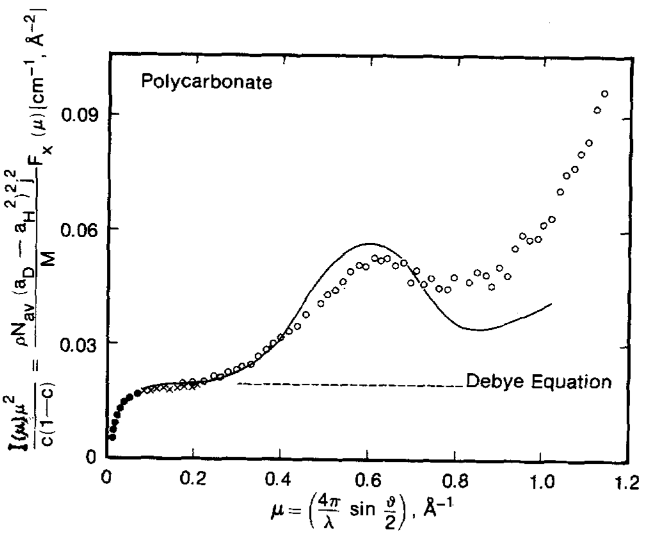

Figure 3. The scattering function $F_x(\mu)$, converted to $I(\mu)\ \mu^2/c(1\text{-}c)$ for polycarbonate chains of $x=50$ repeat units in the amorphous state. The experimental points are from Gawrisch et al.[7]

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