Observation of Local Order in Poly(di-*n*-alkyl itaconate)s

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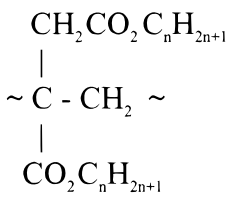
Itaconic acid is a versatile precursor to polymeric materials, and a series of polyitaconate derivatives have been prepared, such as monoalkyl,[1] di-*n*-alkyl,[1−3] cycloalkyl,[4−6] and mixed alkyl esters.[7] The poly(di-*n*-alkyl itaconate)s have unusual thermal properties in comparison with their poly(*n*-alkyl methacrylate) analogues, and these have been studied in some detail by Cowie and co-workers.[3,8−10] The poly(di-*n*-alkyl itaconate)s have the following structure:



where *n* is the number of side chain atoms. Polymers with $n < 6$ display a single T_g which decreases with increasing *n* due to the internal plasticization effect. In contrast, polymers with 7−11 side chain carbons exhibit two major relaxations which correlate with two distinct and separate step changes in the heat capacity (C_p);[10] i.e., these structures exhibit two calorimetric glass transitions (T_g). The higher temperature transition (T_g^u) is identified with cooperative main chain motion, whereas the lower transition (T_g^l) is attributed to decoupled independent relaxation of the side chains. Statistical themodynamic calculations,[11] along with dynamic mechanical and C_p data from copolymers,[10] confirmed that T_g^l is due to the onset of rotational freedom of the *n*-alkyl side chains. Calorimetrically, T_g^u is actually the more pronounced of the two transitions, involving as it does the greater change in C_p.

Multiple T_gs are a feature usually observed in phase-separated blends and block copolymers, while homopolymers are expected to show a single T_g. This led Cowie's group[10] to postulate that a form of microphase separation occurs in poly(di-*n*-alkyl itaconate)s where the nonpolar side chains tend to segregate from the more polar backbone to form discrete regions with their own glass transition T_g^l. To test this hypothesis, we have carried out combined wide-angle and small-angle X-ray scattering measurements on poly(di-*n*-alkyl itaconate)s with side chain lengths from $n = 1$ to $n = 12$. Structural order in these systems is reported here for the first time.

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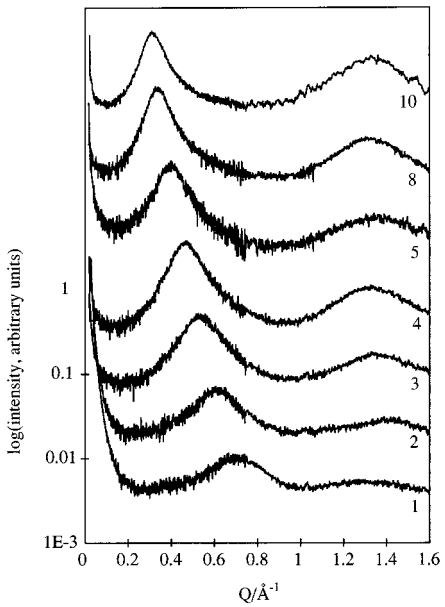

Figure 1. Combined wide-angle and small-angle X-ray scattering curves for poly(di-*n*-alkyl itaconate)s with $n = 1−5$, 8, and 10 as indicated. Intensity is shown on a logarithmic scale, and curves are shifted vertically for clarity.

Dialkyl itaconate esters with side chain length $n = 1−5$, 8, and 10 were prepared by esterification of itaconate acid using the appropriate alcohol.[2,3] Bulk polymerizations using α,α′-azobisisobutyronitrile as initiator were carried out under nitrogen, and polymers were isolated by precipitation into methanol. Combined SAXS−WAXS measurements were performed on the SAXS beam-line at synchrotron ELETTRA in Trieste, Italy. The X-ray beam was monochromatized by a double crystal Si(1,1,1) and focused on the 2 mm thick samples by a toroidal mirror.[12] The wavelength was 1.54 Å and the beam size 0.5 × 0.5 mm^2. A sample−detector distance of 0.5 m was used to merge the SAXS to the WAXS Q ranges. Calibration of the *Q*-axis was made with wet rat tail tendon for the SAXS region and with an isotactic polypropylene standard for the WAXS region, thus covering a *Q* range from 0.02 to 1.6 Å^{-1} ($Q = 4\pi/\lambda \sin\theta$, 2θ being the scattering angle). Measurements on polymers with $n = 1$, 2, and 3 were carried out over the temperature range 298−473 K at a heating rate of 6 K min^{-1}; the remaining polymers were examined at 298 K only. Each frame is an average over 10 s data accumulation.

X-ray data at 298 K are reported in Figure 1 where the scattering patterns show two distinct peaks in the high *Q* region: peak I in the region 1.0 Å^{-1} < *Q* < 1.6 Å^{-1} and peak II at lower *Q* whose position varies with the number of CH_2 units in the side chain. The presence of such broad scattering features is consistent with the amorphous nature of these polymers. Although there is no unambiguous relationship between scattering maxima and characteristic distances within a noncrystalline polymer sample,[13] "equivalent Bragg" spacings corresponding to the position of the scattering maxima may be obtained by means of the Bragg relation ($d = 2\pi/Q$). Peak maxima were determined by fitting the data to Gaussian functions, and the equivalent *d* spacings for peaks I and II (d_I and d_{II}) are plotted in Figure 2a

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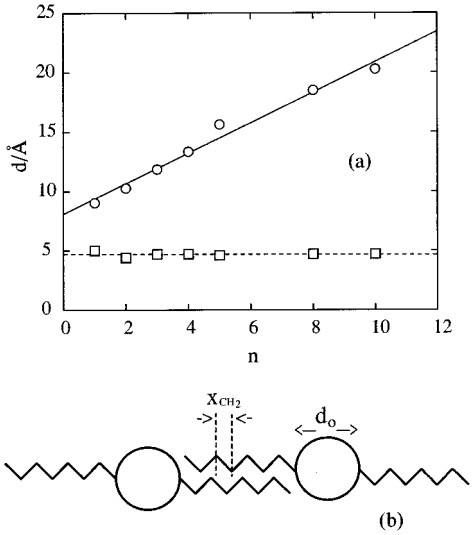

Figure 2. (a) Bragg distances, d_I (squares) and d_{II} (circles), obtained from SAXS−WAXS data at 298 K from poly(di-*n*-alkyl itaconate)s as a function of side chain length *n*. The full line is the best linear fit to d_{II} data. (b) Idealized model for the local structure in poly(di-*n*-alkyl itaconate)s. Shaded circles represent the "effective cores", diameter $d_0 \approx 8$ Å, which are separated by distance $x_{CH_2} \approx 1.25$ Å per side chain CH_2 unit.

as a function of side chain length. The dependencies of the two spacings are very different. The *d* spacing d_I, representing ~5 Å, is independent of alkyl chain length and corresponds to the amorphous halo resulting from the mean van der Waals (VDW) separation of nonbonded atoms.[13] In contrast, the dependence of d_{II} on *n* in Figure 2a indicates a correlation with the number of CH_2 units in the side chain. It is also noteworthy that the intensity of the d_{II} peak exceeds that of the VDW peak. Expressing the dependence of d_{II} on *n* as

$$d_{II} = d_0 + nx_{CH_2} \quad (1)$$

we can relate the intercept (d_0) and slope (x_{CH_2}) to the chemical structure of the poly(di-*n*-alkyl itaconate)s by following the proposals of Miller and co-workers,[13] who suggest d_{II} measures the average spacing between adjacent chain segments, which increases per CH_2 by an amount x_{CH_2}, and that d_0 is an "effective core diameter" for the polymer. Our data give a least-squares intercept $d_0 = 8.1_5$ Å and slope $x_{CH_2} = 1.2_7$ Å. Modeling the core as a cylinder having the length of a repeat unit (2.51 Å), the value of d_0 translates to a core molar volume of 130 Å^3. This matches a core comprising the main chain repeat unit, plus both its ester units, which has a calculated[14] volume of 126 Å^3. Figure 2b shows an idealized model, where the side chains "interdigitate" between adjacent core backbones, consistent with our experimental slope of 1.27 Å per side chain increment. This latter value is close to the increase in *d* spacing per *one* CH_2 unit (1.25 Å), indicative of the layer arrangement shown rather than other packing forms such as end-on contact of the side chains. The model is one which maximizes like−like contacts among the side chains, the basis of an energy-minimized domain structure, and is in accord with that proposed earlier[10] from the analysis of dynamic mechanical and C_p data. As interpreted above, the value $x_{CH_2} = 1.27$ Å suggests a conformation close to all-trans for the side side chains. A closely related model for side-chain packing has been employed by Cervinka[15] for polyesters and McCreight[16] and co-workers in a series of polyimides.

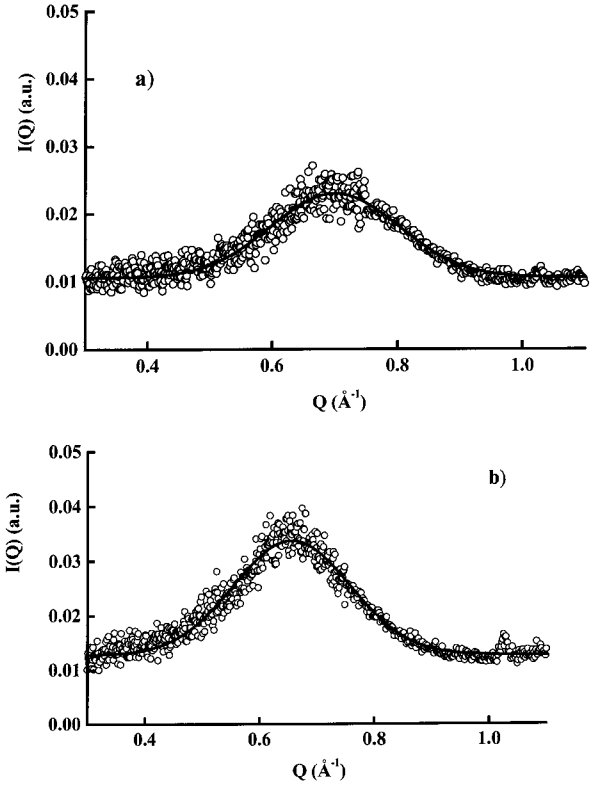

Figure 3. Temperature dependence of the SAXS−WAXS data for poly(di-*n*-methyl itaconate); the full lines are the best Gaussian fits at (a) 298 K and at (b) 473 K.

Strong d_{II} peaks are found at all side-chain lengths, whether the polymer has one T_g ($n \leq 6$) or two T_gs ($n > 6$), implying that a common structural element is the cause rather than a threshold side chain length. Also, the d_{II} peaks appear independent of molecular motion since the 298 K data involve samples either in the glassy ($n = 1, 2, 3$)[17] or in the liquid state ($n = 5, 8, 10$). We suggest the element is the "effective core" encompassing *two* carbonyl functions per main chain unit and making this a much more polar entity than, e.g., the main chain of the poly(*n*-alkyl methacrylates). The strong d_{II} intensity reflects a well-developed periodicity in these samples as a consequence.

The temperature dependence of the SAXS−WAXS pattern is illustrated in Figure 3 for poly(dimethyl itaconate). Similar studies have been performed on other poly(di-*n*-alkyl itaconate)s and will be reported in a future publication. As shown in both Figures 3 and 4 for poly(dimethyl itaconate), in the temperature range 298−473 K, the d_I and d_{II} peak widths are largely unaffected by temperature, and only small changes in peak position are observed. This indicates that, although changes due to thermal expansion occur,[18] these are relatively small. This conclusion justifies comparison between different itaconates at room temperature discussed in this work.

Although the high *Q* region is only slightly affected by temperature, this is not so at low *Q*. As shown in Figure 4a, poly(dimethyl itaconate) displays a low *Q* feature that appears to be a superposition of two peaks at ~0.03 and ~0.06 Å^{-1}. This feature remains constant in the temperature range 298−473 K. However, above the glass transition (370 K), the low *Q* signal intensity diminishes significantly (see Figure 4b). Analogous temperature behavior occurs for the diethyl and dipropyl polymers. Although the origin of the low *Q* signal is

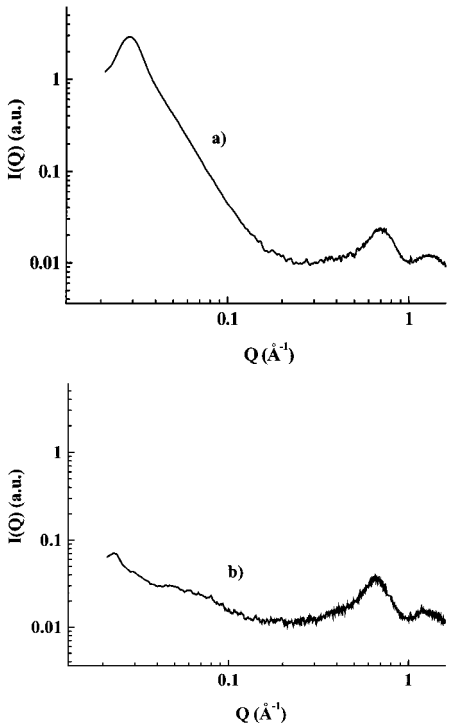

Figure 4. SAXS/WAXS patterns for poly(di-*n*-methyl itaconate) at (a) 298 K and (b) 473 K on a log−log scale.

presently unknown, it must be related to the presence of scattering objects, size at least 200 Å, which occur only in the glassy state. The absence of long-range ordering effects on the high Q region indicates that the low Q signal cannot be associated with crystallization. A possibility is some form of phase aggregation involving clustering of side chains.

The presence of domain structures in amorphous polymers is still controversial. Scattering maxima in the Q range covered by peaks II in Figure 1 have been reported for poly(*n*-alkyl methacrylate)s.[19,20] The *n*-alkyl itaconate scattering data reported here show a stronger tendency of the side chains to order compared to the poly(*n*-alkyl methacrylate)s analogues. This is demonstrated by a comparison between the relative intensities of the two amorphous peaks. It is possible that the higher ordering in the poly(di-*n*-alkyl itaconate)s may be responsible for the appearance of a low-temperature T_g in higher *n*-alkyl polymers. Further work is in progress on this matter and with regard to the low Q signal.

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