Macromolecules 1993, 26, 1318–1323

Side-Chain Order in Poly(3-alkylthiophenes)

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Received August 7, 1992; Revised Manuscript Received November 16, 1992

ABSTRACT: The structures of unoriented films of poly(3-alkylthiophenes) were studied by X-ray diffraction, infrared spectroscopy, and organic vapor sorption. Side-chain crystallization takes place in these films when the alkyl groups contain 12 or more carbon atoms. The disordering of the side chain upon melting results in a large increase in the amount of hexane vapor absorbed by poly(3-tetradecylthiophene) (PTDT) when the temperature is raised to above the melting point. The effective distance of side-chain overlap, as measured by hexane as the diffusional probe, is estimated to be 6.7 Å along the *a*-axis. The distance of overlap is about 2.6 Å for poly(3-octylthiophene) (POT). When the conformational information obtained from infrared spectroscopy is combined with the results of X-ray and vapor sorption studies, a model can be constructed which accounts for all the experimental observations.

Introduction

Side-chain substitution at the 3-carbon position of the rings in poly(thiophenes) renders the otherwise insoluble polymer soluble in organic solvents[1] and is an important step in the advancement of conductive polymer technology. However, structural information for long side-chain substituted polythiophenes is still incomplete. It is generally accepted that the substitution induces a layer structure in which the main chains are separated by the side chains acting as spacers. The layered sheets are assembled into three-dimensional structures by stacking the backbone chains in a regular array one on top of another. The layered structure[2–4] is often represented schematically by Figure 1. The position of the R groups depicted in the figure has been referred to as the "up–down" or "α–α" arrangement, but a recent X-ray diffraction study[5] invoked "up–up–down–down" configurations.

As early as 1948, it was reported by Kaufman et al.[6] that polymers derived from long-chain esters of acrylic and methacrylic acids exhibited a sharp X-ray diffraction ring corresponding to a spacing of about 4.2 Å. Since the spacing is similar to that observed in paraffin hydrocarbons, the results suggest that the long alkyl side chain can pack into paraffin-like crystallites. Subsequently, the crystallization of long side chains attached to both flexible and rigid backbones has been the subject of many investigations.[7–11] Although the phenomenon of side-chain crystallization is not in dispute, a consensus about the detailed structures has yet to be reached.

The melting temperatures of the crystallized alkyl side chains fall in many cases between 37 and 70 °C, a convenient range for experimental study. Therefore, it occurred to us that the degree of side-chain ordering in poly(3-alkylthiophenes) in the crystalline state and the loss of such order in the molten state can be studied by using a diffusional probe. Both the equilibrium sorption and the rate of diffusion of the probe molecule should be sensitive to chain packing. Furthermore, if the schematic representation of Figure 1 is taken literally, one would expect the conventional method of calculating the statistics of random mixing to be almost certainly inapplicable because the side chains are essentially fixed in their spatial positions below the melting point. A study of penetrant diffusion into such a structure has not been undertaken previously and therefore has merit of its own.

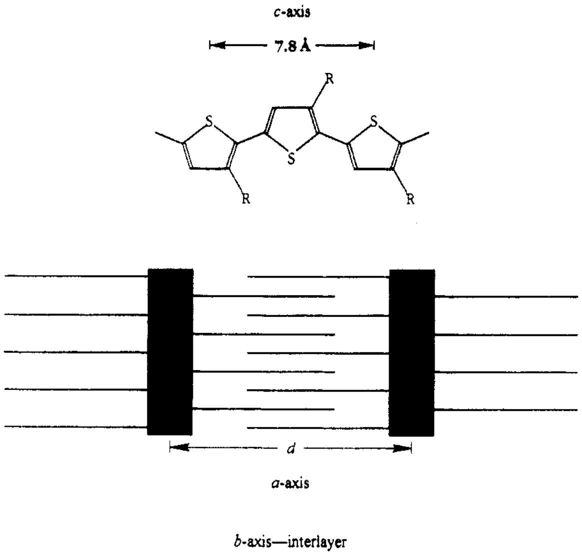

Figure 1. Chemical structure of poly(3-alkylthiophenes) (top); schematic diagram of the layer structure (bottom). Taken from ref 2.

The penetrant chosen for this study was hexane. The choice was based primarily on the ground that the enthalpy of mixing of two structurally similar molecules was usually small. For example, the enthalpy of mixing of *n*-heptane and *n*-hexadecane was only about 23 cal/mol.[12] Accordingly, the temperature coefficient of hexane sorption in poly(3-alkylthiophenes) should also be small, except for the effect of melting.

Our investigation centered on poly(3-tetradecylthiophene) (PTDT), in which side-chain melting occurred at around 35–40 °C. For the purpose of comparison, poly(3-octylthiophene) (POT) was also studied because it showed no sign of side-chain crystallinity as determined by calorimetry. Unoriented films were used in both cases. The sorption of hexane by unsubstituted polythiophene, in the form of powder, was also measured.

Experimental Section

1. **Materials.** Unsubstituted polythiophene (PT) and poly(3-alkylthiophenes) in which the alkyl groups were octyl (POT) and dodecyl (PDDT), respectively, were kindly supplied by Neste Co. Poly(3-tetradecylthiophene) (PTDT) and poly(3-hexadecylthiophene) (PHDT) were synthesized at Polytechnic.

Films of poly(3-alkylthiophenes) were cast from tetrahydrofuran solutions and dried in vacuum at room temperature for calorimetric and X-ray studies. For infrared measurements, thin films were cast directly onto KBr plates.

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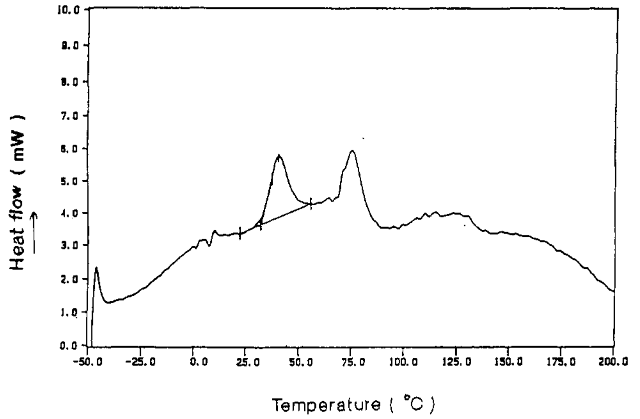

Figure 2. DSC scans of PTDT.

Table I
***d*-Spacings (Å) of Poly(3-alkylthiophenes)**

polymer	200 (*a*-axis)	transverse (*b*-axis)
POT, C8	17.40	3.61
PDDT, C12	21.71	3.97
PTDT, C14	24.73	3.82
PHDT, C16	24.74	4.21

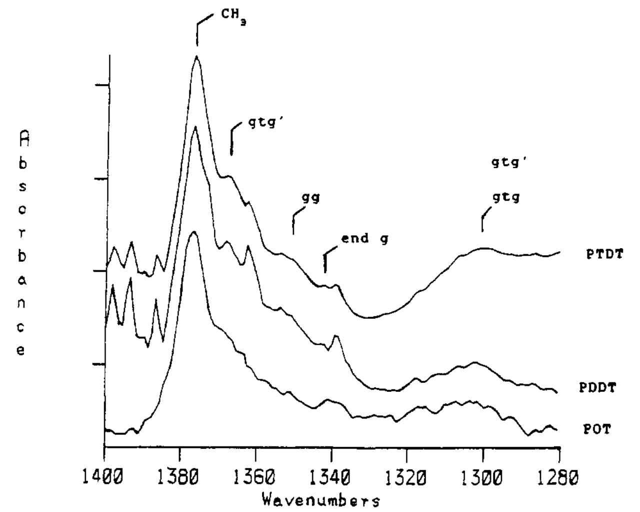

Figure 3. Infrared spectra of PTDT, PDDT, and POT in the 1280–1400-cm^{-1} region. Ordinate scale is 0.05 absorbance unit.

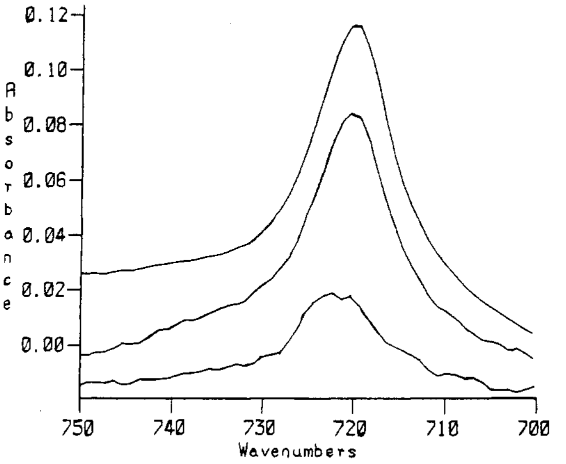

Figure 4. Infrared spectra of PTDT, PDDT, and POT (from top to bottom) in the 720-cm^{-1} region.

2. Thermal Analysis. A Perkin-Elmer differential scanning calorimeter (Model DSC-7) was used for thermal analysis. The sample, typically 10 mg in weight, was placed in a sealed aluminum pan, and the measurements were carried out in a nitrogen atmosphere using a heating rate of 20 °C/min.

3. X-ray Diffraction. A Phillips X-ray generator was used for diffraction studies. The films were placed on slides (or cast directly on the slides) and exposed to Cu/Ni radiation at 45 kV and 35 mA. Measurements were performed between 2 and 40° at 0.04° intervals with an exposure time of 50 s at each step.

4. Infrared Spectroscopy. Infrared spectra of the polymers were determined at ambient temperature with the use of a Digilab FTS-60 Fourier transform infrared spectrometer. Sixty-four scans were signal-averaged at a resolution of 2 cm^{-1}.

5. Vapor Sorption. The sorption of hexane vapor by a polymer film was monitored by the use of an electrobalance connected to a personal computer. Equilibrium sorption was determined when there was no further change in the weight of the sample for at least 2 h. The diffusion coefficient was calculated from the initial slope of the sorption curve (weight gain vs square root time) according to the standard method.[13]

Results and Discussion

1. Calorimetry. The DSC scan of PTDT is shown in Figure 2. The three thermal events noticeable in the scan for PTDT are side-chain melting at 40 °C, solid to liquid crystal transition at 75 °C, and liquid crystalline to isotropic transition at 125 °C. On the other hand, melting endotherms are always detectable when the alkyl groups contain 12 or more carbon atoms. From the endotherm in the PTDT scan, the heat of fusion for the side-chain melting process is obtained as 6 J/g.

2. X-ray Diffraction. The details of X-ray studies will be described in a separate publication. The results pertinent to this investigation are summarized in Table I. The *c*-axis spacing is 7.8 Å for all the polymers studied. The spacing between two neighboring backbone chains in the same layer increases with the length of the alkyl group up to C14. Further increase of the length to C16 does not seem to induce additional enlargement of the spacing. The spacing between adjacent layers (along the *b*-axis) shows little variation from C8 to C14; the values are between 3.61 and 3.97 Å. For the dodecyl side chain, the spacing 3.97 Å is in good agreement with that determined by Yoshino et al. for an oriented film having orthorhombic unit cell structures.[14] When the alkyl group is C16, the spacing increases to 4.21 Å, the same as the value observed for paraffin hydrocarbons.

3. Infrared Spectroscopy. The infrared spectra of POT, PDDT, and PTDT are shown in Figure 3. The spectra of PDDT are included in the figure because PDDT is the first member of the poly(alkylthiophene) series to show side-chain crystallinity under our film preparation conditions and a comparison of its spectra with that of PTDT might be useful.

The absorption peaks in the 1280–1400-cm^{-1} region are rich in conformational information. According to Snyder,[15] the characteristics for disordered paraffin chains are 1366 W (gtg′ kink), 1353 W (gg double gauche), 1341 W (gtt end gauche), and 1300 W (gtg, gtg′). A strong peak located at 1375 cm^{-1} can be assigned to methyl group absorption. Our spectra match Snyder's assignment to within 2 cm^{-1} for the methyl group, gtg′, and end gauche absorptions. The double-gauche conformation may also be present as weak shoulders at 1352 cm^{-1}. These peaks were also reported by Yoshino[14] for unoriented poly(3-hexylthiophene) (PHT) and for PHT and PDDT at high temperatures.

Between 700 and 800 cm^{-1}, all three spectra show strong absorptions at 720 cm^{-1} due to methylene rocking (Figure 4). This peak has been observed in other comblike polymers containing long alkyl side chains. There is no evidence of absorption at 730 cm^{-1} although the band has been reported frequently in the literature for oriented films. In this respect, the spectra of our polymers in this

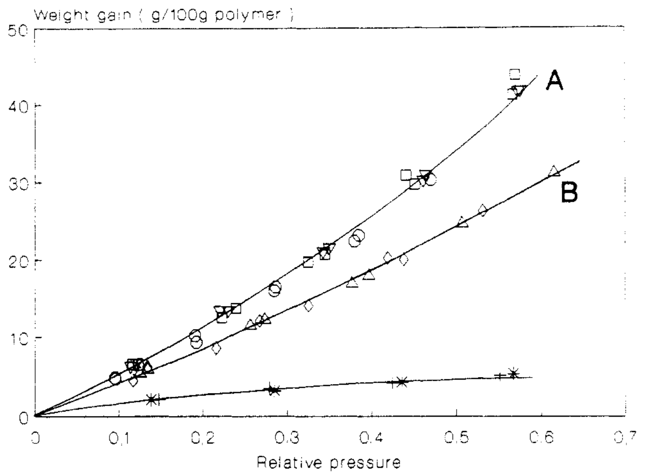

Figure 5. Sorption of hexane vapor by PTDT [(○) 45.1, (▽) 40.2, and (□) 35.1 °C, top curve; (◇) 30.2 and (△) 25.1 °C, middle curve] and by the unsubstituted polymer [(*) 39.9 and (+) 3.7 °C, bottom curve].

region resemble that of n-$C_{21}H_{44}$ in the disordered liquid state rather than in the crystalline state.[15]

For the all-trans n-$C_{21}H_{44}$, four weak peaks were listed by Snyder at 1326, 1288, 1254, and 1222 cm^{-1}. We detected a small peak at 1254 cm^{-1} in PTDT but were uncertain about the shoulder at 1327 cm^{-1}; the two other peaks were not seen. These peaks were absent in the POT spectra although there appeared to be a shoulder at 1320 cm^{-1}.

4. Vapor Sorption. The amount of hexane vapor sorbed by PTDT was determined at five temperatures, from 25.1 to 45.1 °C, and at relative vapor pressures ranging from 0.1 to 0.6. The results are shown in Figure 5; included in the same figure are the amounts absorbed by the unsubstituted polythiophene. Sorption by the latter polymer is only a fraction of the value for PTDT.

The sorption data measured at 25.1 and 30.2 °C can be represented by a single curve. Similarly, the data at 35.1, 40.2, and 45.1 °C fall on another common curve. The near-zero temperature coefficient of vapor sorption in each temperature regime is in line with our expectation of a very small enthalpy of mixing of two linear hydrocarbons, which we have mentioned earlier. The sudden increase in the amount of sorbed hexane between 30 and 35 °C can therefore be ascribed solely to the effect of side-chain melting. (The melting temperature deduced from sorption experiments is in good agreement with the DSC data if the onset of the endothermic event is taken as the melting point.) The difference between curves A and B in Figure 5 is then a direct measure of the fraction of the side chain which is unavailable for hexane sorption at 25 °C. To perform this calculation, we have subtracted the sorption by the backbone and calculated the amount of hexane vapor sorbed by the side chain. The results are depicted in Figure 6. When the sorbed amounts represented by the two curves are compared at the same relative vapor pressures, the values for the lower curve are 69–72% of the corresponding values for the upper curve. Therefore, about 30% of the hydrocarbon units in the unoriented PTDT film are arranged in such a way as to be effectively excluded from mixing with hexane.

The diffusion coefficient of hexane vapor in PTDT was plotted as a function of hexane concentration in the film in Figure 7. We notice that the diffusion coefficients at 30 °C are higher than the values determined at 25 °C although the amounts absorbed at equilibrium are the same at the two temperatures. In contrast to the relatively large differences in the magnitude of diffusion coefficients at 25 and 30 °C, the data at 40 and 45 °C fall within a much narrower range. The data at 35 °C are close to the 30 °C values and therefore not shown in the figure. The results seem to suggest that the diffusional probe already experiences an increase in side-chain mobility at 30 °C which facilitates transport. The disordering phenomenon which has its onset at about 30 °C is nearly complete at 40 °C (aside from the normal thermal effects).

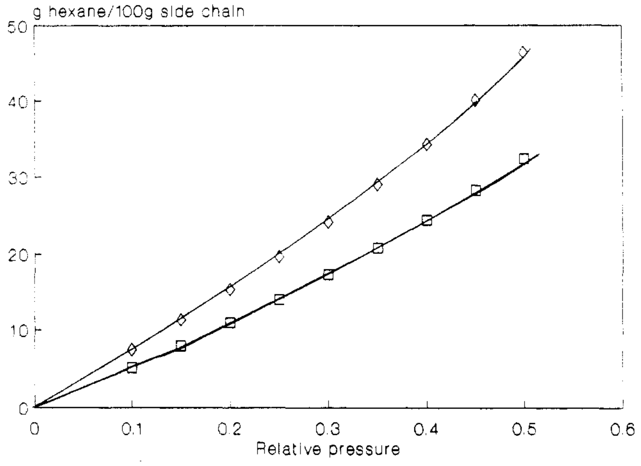

Figure 6. Sorption of hexane by the alkyl groups: 40.1 (top) and 30.2 °C (bottom).

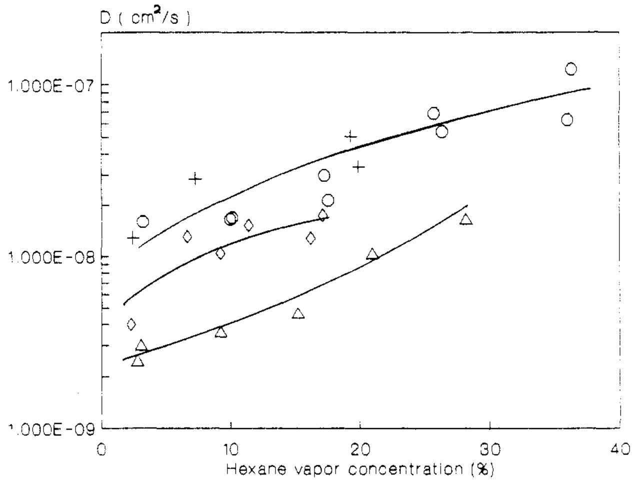

Figure 7. Diffusion coefficients of hexane vapor in PTDT: (+) 45.1, (○) 40.2, (◇) 30.2, and (△) 25.1 °C.

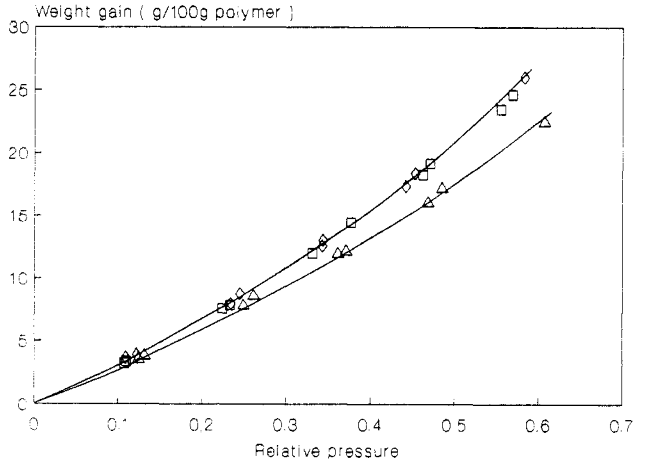

Figure 8. Sorption of hexane by POT: (□) 40.1 and (◇) 35.2 °C (top); (△) 30.1 °C (bottom).

The sorption isotherms of POT at different temperatures are shown in Figure 8. We had initially thought that, since POT showed no side-chain melting endotherm

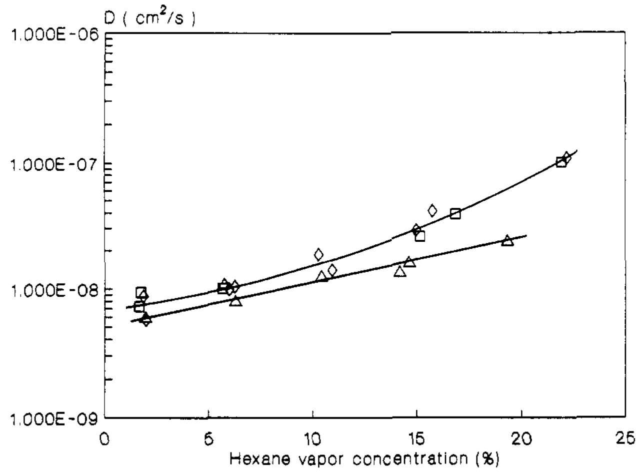

Figure 9. Diffusion coefficients of hexane vapor in POT: (□) 40.1 and (◇) 35.2 °C (top); (△) 30.1 °C (bottom).

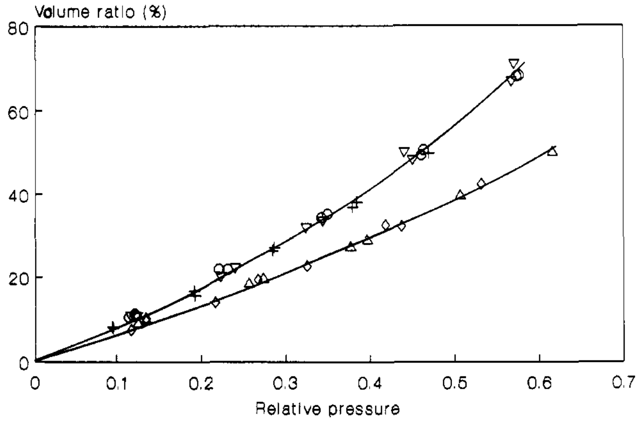

Figure 10. Sorption isotherms, expressed in volume ratios, for PTDT: (+) 45.1, (○) 40.2, and (▽) 35.1 °C (top); (◇) 30.2 and (△) 25.1 °C (bottom). The volume ratios are calculated from the densities of the solvent and the polymer.

in the thermal scan, all the hydrocarbon units were available for hexane sorption and the experimental sorption data collected at different temperatures would coalesce into a single curve. This turns out not to be the case. Sorption at 30 °C is less than the values measured at 35 and 40 °C; the two latter sets of data, however, do fall on a single curve. Consequently, we arrive at the conclusion that although side-chain crystallinity in our unoriented POT film is too low to be detected by calorimetry, there is nevertheless some degree of order in the side-chain arrangement which restricts vapor sorption at 30 °C. Again, if the sorbed amount is recalculated as the weight gain by the side chain, the fraction of hydrocarbon units available for hexane sorption at 30 °C is estimated to be 84 ± 2% from the two curves in Figure 8. To the extent that some degree of ordering or constraint may be present in the polymer, it reduces sorption by about 16%. The diffusion coefficients are also smaller at 30 °C than the values determined at 35 and 40 °C which again can be represented by a single curve (Figure 9).

5. Mechanism for Sorption. We have alluded earlier to a different mechanism of sorption and diffusion being operative in our system. It appears doubtful that conventional statistics of random placement of molecules is applicable to a constrained system in which both the side chains and backbones are organized in regular arrays. Rather, the volume ratio of penetrant molecules in the polymer film seems intuitively to be a more suitable quantity for data analysis. The sorption isotherms replotted in terms of volume ratios are shown in Figures 10 and 11 for PTDT and POT, respectively. We note that our data do not conform to Flory's solution theory in which the solubility is expressed as volume fraction of the solvent ($\ln a_1 = \ln v_1 + v_2 + \chi v_2^2$, where a_1 is the activity of the solvent, v_1 and v_2 are the volume fractions of the solvent and polymer, respectively, and χ is the interaction parameter).

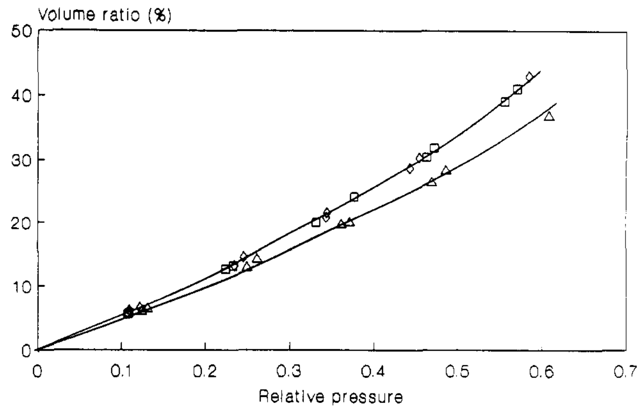

Figure 11. Sorption isotherms, expressed in volume ratios, for POT: (□) 40.1 and (◇) 35.2 °C (top); (△) 30.1 °C (bottom).

As will be seen in later discussions, unoccupied space within each layer or between layers is a probable location for the residence of penetrant molecules. We reason that side-chain order renders a portion of the structure inaccessible to the penetrant and that the smaller amount of hexane vapor imbibed at 30 °C is the direct consequence of less volume available for the penetrant compared to the disordered state at 40 °C. The assumption seems reasonable when one carries out a point-by-point calculation of the ratios of the sorbed amounts represented by the curves in Figures 10 and 11. The ratios are nearly constant for each of the two polymers, namely, 0.75 ± 0.03 for PTDT and 0.84 ± 0.02 for POT. The constancy of the ratios over a wide range of vapor activities lends support to the available-volume concept. Furthermore, since the sorption process is reversible and several sorption–desorption cycles produce the same results, irreversible changes in the structural arrangement which might have been induced by the sorbed hexane molecules must be minimal. In any event, the effect of possibly irreversible structural disruption by hexane can be disregarded if the initial slope of the sorption curve is used for comparison.

The application of the available-volume concept can be further simplified because (1) the polymers have layered structures and (2) the spacing between layers and the *c*-axis spacing of the backbone are essentially the same for PTDT and POT. Consequently, the available volume becomes proportional to the lateral spacing, d, minus the distance of intercalation, x, of the side chains. In the context of sorption studies, the quantity x is defined as the distance to which penetrant is inaccessible. This broader definition takes into account all the geometrical and steric factors which limit the available volume. It is not necessarily identical with the dimension of the crystalline domain.

We further assume that, at temperatures above 35 °C, the disordered state of the side chain removes the constraints imposed by side-chain order so that the available volume is now proportional to d. This assumption can be tested simply by comparing the initial slopes of the sorption curves (Figures 10 and 11) for PTDT and POT at 40 °C. The ratio is 1.45, which is in good agreement with the ratio of d values from X-ray measurements, namely, 1.42.

The ratio of the initial slopes at 30 and 40 °C is $(d - x)/d$. The quantity x is calculated to be 6.7 Å for PTDT and 2.6

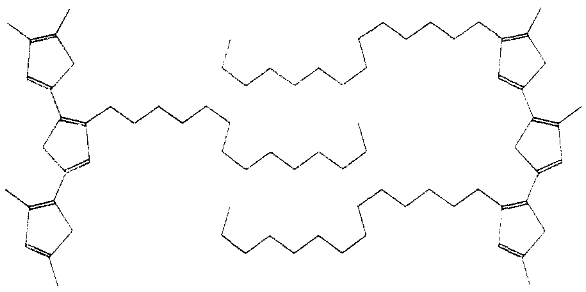

Figure 12. Model for unoriented PTDT.

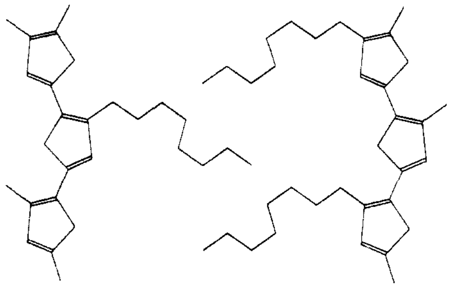

Figure 13. Model for unoriented POT.

Å for POT. The ratio of the solubilities in PTDT and POT at 30 °C should be equal to the ratio of the respective $(d - x)$ values, 1.22. This is indeed the case.

6. Conformational Considerations. The question which remains to be answered is the relationship between chain conformation and the extent of side-chain overlap represented by the quantity x. It should be mentioned at this point that the C–C bond emanating from carbon-3 of the thiophene ring makes an angle of 120° with the C3–C4 bond. If the latter bond is parallel to the c-axis of the backbone, then the two opposing R groups in the up-down configuration (Figure 1) will not be parallel to the a-axis; instead, there will diverge and cannot align with each other. Therefore, there must be some distortion in the backbone bond angles so that the C3–C4 bond tilts slightly from the c-axis and the direction of an R group having the all-trans conformation is perpendicular to the c-axis. However, the all-trans conformation of the alkyl chains does not automatically guarantee proper alignment needed for crystallization because the two opposing zigzag chains may be misaligned, that is, not registered correctly. For our unoriented PTDT film, the lateral spacing indeed results in a misalignment of one bond. Therefore, the all-trans conformation for the *entire* alkyl chain cannot be a major contributory factor in side-chain crystallization in the PTDT film we studied. This is not to say that such a conformation is unimportant in films prepared under different conditions.

Since the infrared spectra of the PTDT film indicate bands characteristic of gtg′ and end gauche conformations, we have attempted to determine the influence of these conformations on intercalation. The results become self-explanatory with the aid of Figure 12. In this figure, the bond lengths and bond angles are drawn to scale; the value used for the backbone bond angle may be inaccurate but this has no effect on the calculation. We number the carbons in the tetradecyl group from 1 to 14, with C14 being the methyl group. If a gtg′ kink is introduced at C5, the remainder of the alkyl chain from C8 on is in perfect registration with its counterpart from the opposite direction. However, an end gauche group is required to avoid impingement of the methyl gorup on the other chain. In this diagram, the overlap of 4 C–C bonds presumably gives rise to crystallinity. In terms of impediment to penetrant sorption, the space near the C12–C13 bond is too constricted to accommodate hexane; the proximity of the methyl group to the C7–C8 bond of the neighboring chain may also present some hindrance to hexane sorption. Therefore the restriction to vapor sorption is thought to involve slightly more than five C–C bonds. The projection distance on the a-axis is estimated as 6.3–6.9 Å, in excellent agreement with the x value of 6.7 Å calculated from sorption isotherms.

We do not wish to convey the impression that the diagram represents the only possible conformational arrangement. If the gtg′ kink begins at C3 instead of C5, the sequence available for intercalation is lengthened by two bonds; on the other hand, moving the gtg′ conformation to C7 will cause severe congestion between C7 of one chain and C12 of the next. The gg conformation, which is hinted by a very weak shoulder in the PTDT spectrum, needs to be followed by tgg in order that the remainder of the chain is restored to a direction perpendicular to the c-axis. However, the side chains now have little overlap. Based on these geometrical and spectroscopic considerations, we believe that the two gtg′ conformational alternatives, at C5 and C3, are most attractive than the all-trans or double-gauche arrangements. Of the gtg′ possibilities, the one depicted by Figure 12 has the appealing feature of being compatible with lattice dimension, infrared spectra, and vapor sorption results.

Using the same reasoning as above, we arrived at the conformational arrangement shown in Figure 13 for POT. The arrangement indicates a two-bond overlap which includes the methyl group. Certainly, side-chain crystallinity is not to be expected in this situation; nevertheless, the overlap may already be effective in precluding hexane penetration. The x value of 2.6 Å deduced from vapor sorption studies is in good agreement with the model. However, we are unsure of the role of gg and end gauche conformations if they are indeed present.

7. Sorption of Hexane Liquid. Although a coherent picture of poly(alkylthiophene) structure has emerged from X-ray, infrared spectroscopy, and vapor sorption studies, there is one aspect of the sorption results which deserves additional comment. If increasingly larger quantities of hexane are sorbed by the polymers, the short sequences of overlapped units would eventually dissolve in hexane and/or swelling would enlarge the lateral dimension. To test this thesis, we immersed a PTDT film in liquid hexane at room temperature for 17 h. The approximate weight gain was determined, after pat drying, to be in the neighborhood of 100%. After the film was left to dry at room temperature, X-ray measurement indicated that the spacing d had increased by about 4 Å but b-axis spacing was unchanged. According to our model, the enlarged spacing will decrease the distance of overlap to 2.3–2.8 Å. If this is the case, side-chain crystallinity will vanish. Indeed, the melting endotherm at about 30 °C was no longer observed in the DSC scan.

Finally, a remark on the small heat of fusion value for side-chain melting in PTDT is in order. The experimental value of 6 J/(g of polymer) is translated to a degree of crystallinity for the side chain of about 4% if the heat of fusion for a methylene unit in a perfect crystal, ΔH_u, is taken as 219 J/g.[16] While a low value is not surprising because the film is unoriented and unannealed, the calculation of the degree of crystallinity by using the standard method of comparing experimental ΔH_f with ΔH_u has only limited validity as a result of neglecting the effect of crystallite size and surface energy contribution.

Conclusions

The body of experimental data described above can be summarized as follows.

1. Side-chain melting of poly(3-alkylthiophenes) can be observed in unoriented films when the alkyl groups contain 12 or more carbon atoms.

2. The amount of hexane vapor absorbed by a PTDT film undergoes a large increase when the temperature is raised to above the side-chain melting point. The increased sorption at the higher temperature is ascribed to the disruption of side-chain order. Based on the concept of inaccessible volume, the effective distance of side-chain intercalation is calculated to be 6.7 Å along the *a*-axis. The distance of overlap is about 2.6 Å for POT.

3. Infrared spectroscopic data reveal the presence of gtg′ and end gauche conformations in the PTDT specimen. When the spectroscopic data are taken together with X-ray and vapor sorption results, a model can be constructed which is consistent with all the experimental observations. A similar model for POT has also been constructed.

Acknowledgment. We gratefully acknowledge the support of this investigation by the Neste Co., Finland. Support by the National Science Foundation, Division of Materials Research, Grant 8820046 is also hereby acknowledged. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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