Mechanism of Orientation of Aromatic Molecules by Stretched Polyethylene

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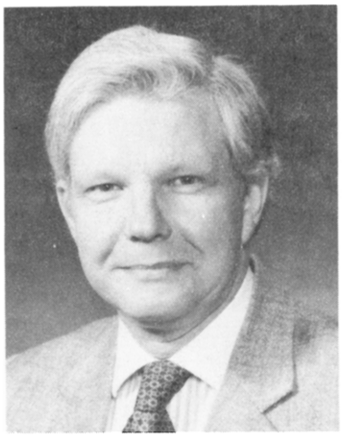
Contents

Overview

A definitive picture is presented of the orientational processes acting on fused-ring aromatic solutes dissolved in polyethylene. Molecules are present only in the amorphous phase or in adsorbed states on the surfaces of polymer crystallites. For certain molecules it has been demonstrated that compound crystals of polyethylene and the aromatic solute are the stable state. However, this state cannot be achieved in practice for molecules diffused into an already crystalline polymer because of the prohibitively slow rate of diffusion of large molecules into polymer crystals. At temperatures above the glass transition (or β-relaxation) molecules in the amorphous phase are unoriented, but molecules adsorbed onto crystal surfaces are oriented. The mechanism of orientation is essentially controlled by epitaxial matching of certain polyethylene crystal planes with those of the crystals of the solute molecules. Several orientational processes may be occurring at a given time dependent on the crystal planes found at the surface of a polymer crystallite; some may orient the molecules in the direction of stretch, and others normal to it. As the polymer passes into the glassy state (i.e., below the β-relaxation temperature), the molecules dissolved in the amorphous phase become partially oriented. For orientation to occur the amorphous phase itself must be oriented, i.e., it must be the interfibrillar amorphous state. At even lower temperatures, below the γ-relaxation (ca. -120 °C), further partial orientation occurs as local mode motions of the polymer chain cease. For many solute molecules a second type of motion ceases at even lower temperatures (ca. -150 °C) in which the molecules are not subject to any orientational effects. These molecules are probably present in the unoriented intrafibrillar amorphous phase. It is suggested that these orientational processes in the glassy state are determined by individual solvation effects and interactions such as have been modeled by other researchers.



Prof. P. J. Phillips has a Ph.D. in physical chemistry from the University of Liverpool and has held academic appointments at the University of London, the State University of New York at Buffalo, and the University of Utah before joining The University of Tennessee in 1984. His areas of specialization are the crystallization and morphology of polymers and their influence on electrical and mechanical behavior. He has published over 100 refereed articles in his area of specialty and is a Fellow of the American Physical Society.

Introduction

It is now two decades since stretched polyethylene was first used as a substrate for the orientation of organic molecules.[1,2] The objective of researchers was always to study the molecules: originally it was the elucidation of their electronic structure through the use of ultraviolet and visible spectroscopy.[3] More recently, the approach has been applied to studies using infrared spectroscopy[4,5] and polarized fluorescence spectroscopy.[6] A major survey of this particular aspect of the literature will not be carried out here; several recent reviews are already available.[7-9] Data have been analyzed by several approaches, that of Thulstrup, Eggers, and Michl,[1,3,10,11] the TEM method, being probably the most appropriate. The TEM model makes no assumptions concerning the nature of the solute orientation, and the analysis results in a determination of the orientation factors of all three major molecular axes. Studies have demonstrated clearly that molecules with the greatest aspect ratios are best oriented by the stretched polymer. These molecules tend to be composed of several linearly fused rings (e.g., anthracene) or are linear polyphenyls (e.g., terphenyl). The orientations are most clearly summarized through the use of the orientation triangle (Figure 1).

In this triangle are plotted the orientation factors, K_z and K_y, characteristic respectively of the long axis of the solute molecule and its in-plane axis. The z-axis

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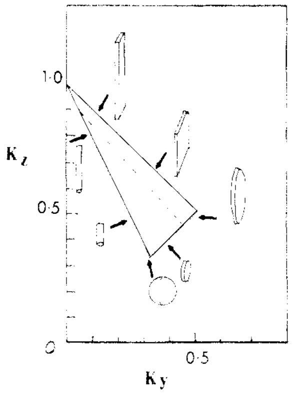

Figure 1. The orientation triangle (after Thulstrup and Michl (Thulstrup, E. W.; Michl, J. *J. Phys. Chem.* **1980**, *84*, 82)).

is the direction of stretching of the polymer film, and the orientation factors are defined as the average cosine squared of the misorientation angle, in the usual fashion. The orientation factors are obtained from the dichroic ratio (d_f) as $d_f/(d_f + 2)$, the ratios being obtained as the intensity of any chosen absorption peak parallel to the stretch direction divided by the intensity perpendicular to the stretch direction. Since only two of the orientation factors are independent, there is no need to determine the third one typical of the out-of-plane molecular axis.

The bottom vertex of the triangle corresponds to totally random orientation ($K_x = K_y = K_z = {}^1/_3$) whereas the top vertex corresponds to perfect uniaxial orientation ($K_z = 1$; $K_x = K_y = 0$). In practice, most molecules fall within a smaller triangle corresponding to the lower part of the drawn triangle but bounded by a line joining $K_z = 0.9$ on the left side to $K_y = 0.45$ on the shortest side (dashed line in Figure 1). No molecules are found close to the top right line of the triangle since it corresponds to $K_x = 0$. Orientation factors tend to be dependent on the extent of orientation of the polymeric substrate and so any orientation triangle has been regarded as specific only to the polymer used and to its orientation or degree of stretching. Popov's extension of the method[12] introduces an additional parameter that factors out the orientation of the polymeric substrate. His model involves assumptions regarding symmetrical distributions that have not been tested; it also introduces an additional degree of complexity to the analyses. It has been used[13] in the analysis of polarized emission studies.

The mechanism of orientation has received much less attention than the utilization of the technique. There is no doubt that both oriented and unoriented solute molecules are present in the stretched film. Yogev and co-workers[2,14-16] proposed the first model to explain the orientation effect. It assumed that the unoriented molecules were present in the amorphous phase and that the oriented molecules were located in the crystalline phase. This model was based on the physically unrealistic picture of crystalline polymers as paracrystalline systems.[17,18] At the time Yogev's model was proposed many new ideas were current in polymer physics, and it was not until later that the paracrystalline model was discounted. In any case, it was proposed for highly crystalline systems and not for low-crystallinity systems such as the low-density polyethylene used for stretched sheets. On empirical grounds it could have been predicted that the activation energy for diffusion of large thick molecules, such as anthracene, into a polymer crystal had to be very high and certainly in excess of 100 kcal/mol. An alternative approach was that of Konwerska-Hrabowska,[19-22] who proposed that the oriented molecules were located on the surfaces of the polyethylene crystallites. The first thorough attempt to list all possible sites where molecules might be located on the basis of current knowledge of the morphology of semicrystalline polymers was made by Jang, Phillips, and Thulstrup.[23]

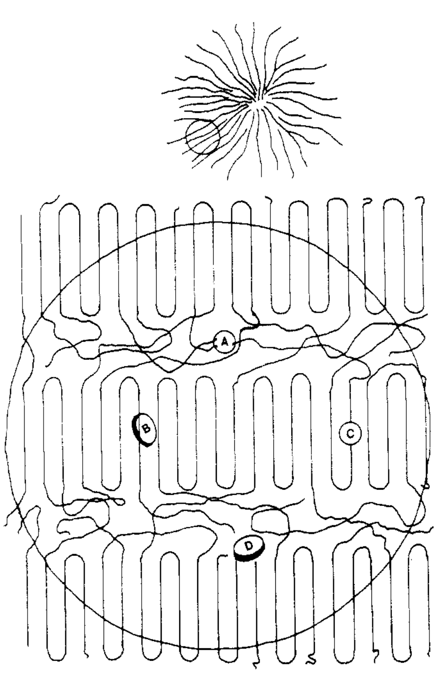

Figure 2. Schematic representation of spherulitic structure together with the location of potential adsorption sites (A, the amorphous phase; B, crystal interior; C, lateral surfaces; D, folded-chain surfaces) (reprinted from *Chem. Phys. Lett.* **1982**, *93*, 66; copyright 1982 Elsevier Science Publishers B.V.).

This contribution is a review of the studies that have been carried out since then, with the aim of elucidating the environments encountered by the solutes, their dependence on temperature, and, of course, the anisotropic nature and orienting abilities of those environments. The review will concentrate on systems containing three linearly fused rings, with particular emphasis on acridine. A definitive picture can now be drawn of the mechanisms operating in the orientation of such molecules by oriented polyethylene. It can also be demonstrated that apparently minor changes in geometrical symmetry and atomic nature can have major influences on the processes, beyond those of simple aspect ratio effects.

Polymer Structure

Prior to deformation, polyethylenes exhibit a spherulitic structure.[24,25] The crystals are in the form of radial arrays (Figure 2) that impinge to produce an overall appearance of polyhedra. Spherulites contain the crystalline lamellae separated by amorphous layers of approximately constant thickness so that on the scale of 500–1000 Å they appear as a stacked sequence (Figure 2). In high-density polyethylene the crystalline fraction or crystallinity is 60–80% of the whole, whereas in low-density polyethylene it comprises ca. 50% of the

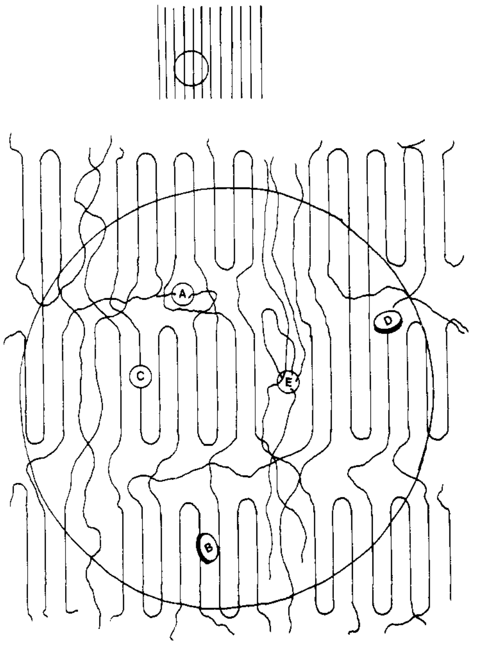

Figure 3. Schematic representation of fibrillar structure together with the location of potential adsorption sites (A, B, C, and D as in Figure 2; E, interfibrillar amorphous phase) (reprinted from *Chem. Phys. Lett.* **1982**, *93*, 66; copyright 1982 Elsevier Science Publishers B.V.).

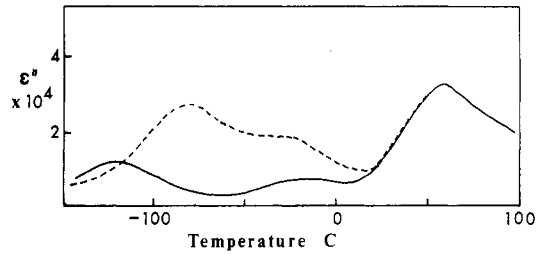

Figure 4. Dielectric loss as a function of temperature at 10 Hz for unstretched LDPE (—) and containing 0.17% acridine (---).

material. Growth within an individual lamellar crystal is such that the polymer chains fold back on one another but also emerge from the crystal, cross the amorphous phase, and enter another crystal, thus producing tie chains which are responsible for the occurrence of elasticity in what would otherwise be a viscous slurry. The crystal growth plane is known to be (110) in single crystals but can also be (100) if the crystals are truncated. In the bulk it is possible for both to occur; however, the orientation of the unit cell is such that the (100) planes always form the external long faces of the lamellae. The fold plane is approximately (001) but has an uneven surface because of the presence of folds, loops, and tie chains. The end of the lamella may have either (110) or (010) exposed planes.[26]

The possible locations for solute molecules in an undeformed system are therefore (a) the amorphous interlamellar space, (b) within the crystal, (c) the fold surfaces, (d) the (100) lateral crystal surfaces, and (e) (110) or (010) crystal surfaces at the ends of the lamellae.

When a crystalline polymer film is subjected to tensile deformation, the spherulitic structure is destroyed during the yielding or necking process. The deformation process is complex and the detailed mechanisms are only partially understood. In general, the polymer chains become partially oriented in the direction of the applied stress. The general phenomenology is well established,[27-29] a microfibrillar structure being generated. Much of the understanding of this structure is based on indirect methods such as wide-angle and small-angle X-ray scattering studies of bulk materials together with electron microscopic studies of thin films. Only recently has it become possible to observe directly the deformation processes and the final structure using electron microscopy of etched bulk specimens.[30] The schematic representation of Figure 3 is generally accepted as broadly true. In addition to the sites possible in the undeformed state, there is now an additional site. This is the interfibrillar amorphous phase which contains partially oriented chains. An unsolved problem lies in the specification of the crystal surfaces in the microfibrillar structure. The slip planes should be the fold planes in any polymer crystal and so should correspond to the growth planes. In single crystals it is established that the (110) planes serve as slip planes, but in the bulk polymer there is evidence for both (100) and (110) planes being active slip planes.[31-34] The slip planes should become the exposed crystal faces of the microfibrils.

The possible locations for solute molecules are therefore (a) the amorphous intrafibrillar space, (b) the partially oriented amorphous interfibrillar space, (c) within the crystal, (d) the fold surfaces, and (e) lateral crystal surfaces which may be (110) or (100) or both.

The Crystalline Phase

Should the solute molecules enter the crystals in a random manner their presence would alter the heat of fusion of the crystals, modify the melting point, alter the unit cell parameters, and, possibly also, influence the breadth of individual X-ray diffraction peaks (line broadening). None of these effects could be observed when molecules were present in amounts up to 5% by weight.[22] If the molecules were able to enter the crystal and locate themselves in a nonrandom manner, then a new crystal structure would result that could be easily detected. This effect does not occur when the molecules are added to an already crystallized film either through vapor deposition or through soaking the film in a chloroform solution. In some cases this effect can be produced by blending in the molten state followed by slow cooling (see later).

One of the most sensitive tests of the presence of dipoles in a polyethylene crystal is to study the α-relaxation process using dielectric spectroscopy.[35,36] Many studies have used partial oxidation or chlorination as a means of placing dipoles in the chain; however, the inserted groupings, although reflecting chain motions, do influence the behavior. Some studies[37,38] that used less disruptive carbonyl groups or relied on adventitious groupings have also been conducted. The α-relaxation process occurs within the crystalline phase and is now believed to involve the motion of a single twist or wave (soliton) along the polymer chain.[39] It is also known to be sensitive to orientation.[40] The presence of polar molecules in the crystalline phase would modify significantly the intensity of this relaxation process and perhaps also its temperature location and its activation energy. Many polar organic solutes have now been investigated and found to have no influence on the process.[23,38,41] Typical dielectric loss curves are pres-

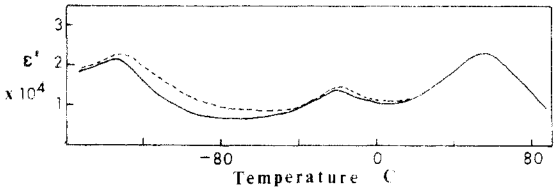

Figure 5. Dielectric loss as a function of temperature of 10 Hz for LDPE stretched 500% (—) and containing 0.18% acridine (- - -).

ented in Figures 4 and 5 for acridine in polyethylene film (stretched and unstretched). Curves for the polyethylene alone[42] are presented in those same figures for comparative purposes. The α-relaxation process is the highest temperature process occurring and is located in the vicinity of 60 °C. Although the magnitude and location of the process are changed by orientation, the presence of acridine does not have any discernible influence on the process in oriented or unoriented specimens. Activation energies of the process, obtained through a study of the frequency dependence of the temperature location, show a similar lack of change.[38,41,42] It can therefore be clearly stated that there is not a single piece of direct evidence that supports the presence of solute molecules in the crystalline phase.

The Amorphous Phase

Solute molecules present in the amorphous phase will show temperature-dependent behavior since the amorphous phase can be rubbery or glassy, dependent on the temperature. The glass transition temperature of polyethylene is approximately −40 °C[43,44] and is reflected in the β-relaxation process, which because of frequency effects is usually observed about 20 °C higher than the figure quoted. There is an additional transition at a much lower temperature (ca. −120 °C), which corresponds to the freezing out of local mode motions of the polyethylene chains, giving rise to the γ-relaxation. All of these relaxation regions can be seen in Figures 4 and 5. It is therefore necessary to investigate the behavior of solute molecules in three temperature regions: (a) above the β-relaxation region, (b) the β-relaxation region and the temperature range between the β- and γ-relaxation regions, and (c) the γ-relaxation region and below.

The most convenient temperature to use in the study of the rubbery amorphous region is ambient temperature. An ideal material to use for this region would be totally noncrystalline and capable of retaining all of its orientation. Lightly cross-linked low-density polyethylene retains a crystallinity level close to that of the non-cross-linked material and so is inappropriate.[44,45] Copolymers of ethylene containing moderate amounts of propylene are noncrystalline and can be cross-linked by conventional methods. Such a material (Vistalon 404, Exxon) was prepared by using 2% by weight of dicumyl peroxide and a curing temperature of 200 °C in a compression mold. The curing time was such as to ensure 99.9% decomposition of the cross-linking agent. An extraction was then carried out with refluxing xylene for 48 h to remove non-cross-linked molecules (18.7% by weight). The resultant gel film was dried and mounted in a straining frame, and the infrared dichroism of the 1368-cm^{-1} band of polyethylene was studied for elongations of up to 600% (Figure 6). A small but definite increase occurred, as expected (ca. 1.4 at 540% elongation). Its stress–strain behavior was also studied in an independent experiment to determine the amount of permanent set, which corresponded to 8%. Hence it was clear that the polymer was behaving like a rubber and that the amount of creep occurring was acceptable. Acridine was then added to the film and the infrared dichroism of the 956-cm^{-1} band (characteristic of the long axis) was studied for concentrations up to 2% by weight and elongations up to 600% nominal (540% allowing for permanent set). Data obtained are shown in Figures 6 and 7, where it can be seen that the dichroic ratio remained at 1.0 throughout. It is therefore clear that oriented amorphous polymer chains do not cause orientation of acridine molecules dissolved in the amorphous phase while it is in the rubbery state. Although the chains in a cross-linked copolymer are not identical with those in low-density polyethylene, the mole fraction of propylene present was not high and for the levels of acridine considered, would not have interfered with polyethylene–acridine interactions. Hence it is reasonable to assume that the behavior of the copolymer is a good indicator of the behavior of oriented amorphous polyethylene.

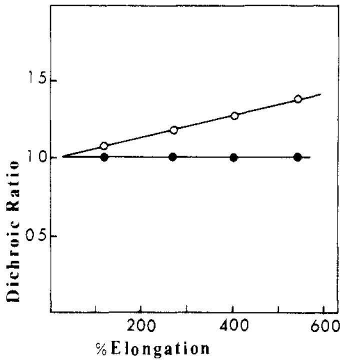

Figure 6. Infrared dichroic ratios as a function of elongation of cross-linked ethylene–propylene rubber for the 1368-cm^{-1} band of polyethylene (○) and the 956-cm^{-1} band of acridine (●).

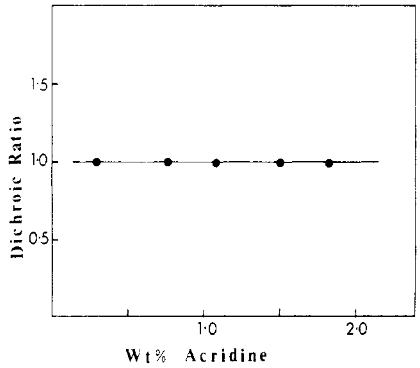

Figure 7. Infrared dichroic ratio of the 956-cm^{-1} band of acridine dissolved in 540% elongated cross-linked ethylene–propylene rubber as a function of acridine concentration.

Infrared dichroism studies have not been carried out as a function of temperature; however, dielectric relaxation data can be processed to give equivalent information. Both the β- and α-relaxation regions are sensitive to orientation, and it is possible to resolve the regions into the contributions from the polymer and the solute molecules, respectively. The number of solute molecules active in each process can be calculated from

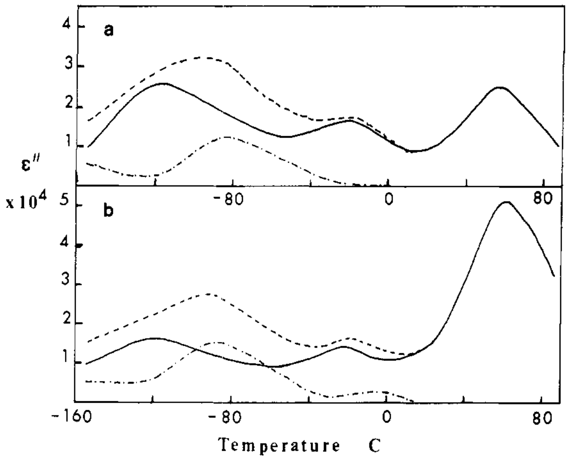

Figure 8. Dielectric loss of extruded rod polyethylene at 10 Hz as a function of temperature with the electric field (a) perpendicular to and (b) parallel to the extrusion direction ((—) polymer; (---) polymer + 0.18% acridine; (-·-) difference curve giving loss from acridine alone).

the Onsager equation if the magnitude of the dielectric process ($\Delta\epsilon'$) is known. The Onsager equation[46] is

$$N\mu^2 = \frac{3kT}{4\pi}\left(\frac{2\epsilon_r + \epsilon_u}{3\epsilon_r}\right)\left(\frac{3}{\epsilon_u + 2}\right)^2(\Delta\epsilon') \qquad (1)$$

where μ is the dipole moment in vacuo, ϵ_r is the relaxed value of the dielectric constant, and ϵ_u is the unrelaxed value (both are close to 2).

The value of $\Delta\epsilon'$ can be obtained by integrating a plot of the dielectric loss (ϵ'') against reciprocal absolute temperature and use of the Williams equation.[47]

$$\epsilon_r - \epsilon_u = \Delta\epsilon' = \frac{2\Delta E}{\pi R}\int_0^\infty \epsilon''\, d(1/T) \qquad (2)$$

ΔE is the activation energy of the process which is obtained from an Arrhenius plot of the frequency dependence of the temperature of the loss maximum. This equation assumes that the distribution of relaxation times remains invariant with temperature.

Since the value of $\Delta\epsilon'$ is a direct result of orientation, a value of the dielectric dichroism, D_ϵ, can be constructed that would be the equivalent of the dichroism value obtained by other techniques. As the dipole moments of the molecules concerned are normal to their long axes, the ratio of $\Delta\epsilon'_\parallel/\Delta\epsilon'_\perp$ is equivalent to the dichroic ratio of an absorption corresponding to an in-plane vibration normal to the long axis.

In order to obtain such data, however, it is necessary to study the dielectric behavior for the field direction both parallel and perpendicular to the deformation direction. For stretched sheets only the experiment with the field normal to the orientation direction is feasible. In order to obtain the appropriate data, extruded rods of polyethylene were produced[42] using the technique originally developed by Boyd and Yemni[48] and then sectioned with a diamond saw to generate both radial disk cross sections and axial rectangular sections. When placed between the electrodes of a parallel-plate cell, the disk specimen has the electric field in the orientation direction, whereas the rectangular specimen has the field normal to the orientation direction. Typical curves are presented in Figure 8 for acridine and in Figure 9 for 9-bromoanthracene, a molecule that does not orient well in dichroic studies.

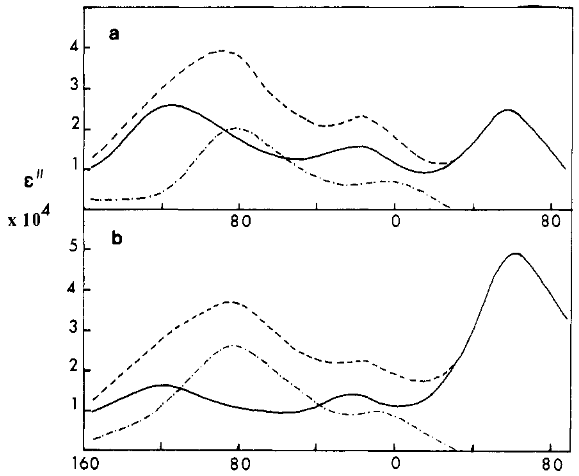

Figure 9. Dielectric loss of extruded rod polyethylene at 10 Hz as a function of temperature with the electric field (a) perpendicular to and (b) parallel to the extrusion direction ((—) polymer; (---) polymer + 0.19% 9-bromoanthracene; (-·-) difference curve giving loss from 9-bromoanthracene alone).

Values obtained for D_ϵ were as follows: acridine (β, 0.27; γ, 1.32), 9-bromoanthracene (β, 0.89; γ, 0.78). These values indicate that the two molecules are partially oriented in the glassy state but quite differently. Acridine tends to have its dipoles partially aligned in the direction of stretch, whereas 9-bromoanthracene has its dipoles partially aligned normal to the direction to stretch. With the notation of Thulstrup et al.[3] the data were converted into incremental values of K_y (medium axis) (i) for acridine (0.388 in the β-region and 0.398 in the γ-region) and (ii) for 9-bromoanthracene (0.308 in the β-region and 0.281 in the γ-region). If the Fraser–Beer[49] assumption of equivalence of K_x and K_y is made, then values of K_z (i.e., the long axis) can be obtained. These incremental values are (i) acridine, 0.224 in the β-region and 0.204 in the γ-region; (ii) 9-bromoanthracene, 0.384 in the β-region and 0.438 in the γ-region.

Hence as temperature is decreased, it is to be anticipated that some degree of orientation will be developed as the β- and γ-regions are traversed (i.e., in the glassy state). The values of K associated with traversals will be slightly different from that of a random distribution, but may vary to either side, dependent on the details of the chemical structure. Clearly, there are no major differences in gross structure between acridine and 9-bromoanthracene. The bromine atom produces a geometrical asymmetry, but sterically its diameter is smaller than the thickness of the rings. On geometrical grounds it would have been predicted that the acridine would be more likely to orient along the stretching direction, but the opposite occurs. It seems likely therefore that interactions between the nitrogen atom and the polyethylene chain are repulsive in nature. Models of the interaction of hydrocarbon chains with fused-ring systems have been few and have generally set the molecules with their π systems interacting with the polyethylene chains.[50–52] This approach is probably appropriate for amorphous-phase interactions; however, it should be recognized that the orientation of amorphous chains in oriented polyethylene is not great. The use of currently available models effectively considers only the interaction of solute molecules with short sections of trans chains. It may be more appropriate

TABLE I. Activation Energies of the β- and γ-Relaxation Processes (kcal/mol)

process and specimen	unoriented	stretched sheet (450%)	parallel[a]	perpendicular[b]
(a) β-process				
polyethylene	76.3	57.2	60.2	67.1
acridine				
subtracted	85.7	81.9	92.9	46.4
raw peak	45.1	38.3	39.1	34.9
9-bromoanthracene				
subtracted	91.2		89.4	103.3
raw peak	58.0		56.0	60.1
(b) γ-process				
polyethylene	9.5	15.0	12.1	14.1
acridine				
subtracted	15.2	14.0	14.6	15.8
raw peak	13.9	15.3	16.2	14.6
9-bromoanthracene				
subtracted	25.2		25.0	28.1
raw peak	25.6		29.2	24.8

[a] Parallel to extrusion direction. [b] Perpendicular to extrusion direction. (Reprinted from *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 1333; copyright 1989 John Wiley & Sons, Inc.)

for more disordered systems to be considered in which gauche orientations are included. Apparently, in the cases of acridine and 9-bromoanthracene, the polyethylene molecules avoid the polar atoms in the generation of specific complexed states in the partially oriented glassy amorphous phase. It is suggested, on the basis of orientation behavior, that the oriented molecules active in the β- and γ-processes are located in the interfibrillar amorphous phase. This is probably a fairly small amount of the total volume, but it cannot be estimated at the present time.

The use of dielectric studies also permits the determination of the activation energy of reorientation for the molecules active in the β- and γ-processes. These data are summarized in Table I, where it can be seen that the activation energies for reorientation of the solute molecules are generally larger than those of the polyethylene chain itself. The molecules are, of course, reorienting by a cooperative process involving the motions of the surrounding polyethylene chains. In the γ-process the molecule is confined to a small space by the polyethylene chains and is incapable of large-scale motions. The solute molecules are probably residing in adventitious pockets of excess free volume and the likely motion involves a spinning mode about the long axis. There is a remarkable correspondence between the relative activation energies of acridine and 9-bromoanthracene with the relative dynamic radii of the molecules for such a process (2.6 and 4.3 Å). For acridine the activation energies in oriented states are close to those of polyethylene, suggesting that the magnitudes of the motions of the polymer and acridine are on a similar scale and that adequate room for motion of the solute molecule is available. However, in the case of 9-bromoanthracene, the activation energy is close to double that of the polymer, suggesting that displacements of the polymer chain do not provide adequate room for motions of the solute molecule and that a much greater degree of cooperation is required.

Looking at the values for the β-process, one can see that the activation energies for acridine and 9-bromoanthracene vary in different ways with orientation. The 9-bromoanthracene, which showed a preference for orientation in the extrusion direction, shows a slightly higher activation energy for reorientation normal to that direction. Acridine shows a significantly lower activation energy for its preferred orientation direction.

It should also be noted that the temperatures of the subtracted loss peaks of the solute molecules are as much as 25 °C above those of the polymer. They are therefore able to reorient in a fairly free manner only when the polymer is already quite mobile and expansion has occurred, generating additional free volume. It is difficult to explain the data in the absence of specific models. However, the motions involved will be fairly large scale and complex. Rotation about either of the minor axes would be fairly difficult for both molecules. This effect is probably responsible for the high activation energies observed for both molecules. In the situation where the electric field is normal to the extrusion direction, molecules active will have a preferred orientation such that the dipole is in the same direction as the electric field (i.e., the long axis is aligned in the microfibril direction). It seems likely that the motion would incorporate a spin about the long axis as one component. As such, the lower activation energy for spinning about the long axis of acridine, known from the γ-process, probably is responsible for the lower β activation energy observed for relaxation normal to the orientation direction.

At temperatures lower than that of the γ-process, an additional process, the δ-relaxation, has been observed.[38] Occurring well below the region in which local motions of amorphous polyethylene have ceased, the relaxation is probably due to a "particle-in-a-box" type of short-range movement of the solute molecules which occurs without the cooperation of the surrounding immobile polyethylene matrix. This mode shows no dependence on the orientation of the polyethylene sheet.

In summary, therefore, it can be stated that (a) there is no orientation of solute molecules in the amorphous rubbery state up to 600% imposed elongation, (b) molecules become partially oriented as the material passes through the glass transition, and (c) further orientation occurs as local mode motions of the glassy polyethylene matrix cease. Whether or not a particular molecule will tend to orient in the glassy state so that its major axis tends to become parallel or perpendicular to the orientation direction of the polyethylene cannot be predicted on an a priori basis. The effect is determined in a subtle way by the polar and steric effects of heteroatoms present in the solute molecules.

The Crystal Surface

The crystal faces exposed vary according to the crystallization and deformation history of the specimen. In undeformed polyethylene the lateral surfaces available for adsorption are assumed to be primarily (100) planes, the total area for adsorption being quite small since the crystals will be ca. 1000 Å wide and only 100 Å thick. The folded-chain surfaces will therefore be expected to provide surface areas in excess of 10 times that available from the lateral surfaces on which adsorption might be expected to occur. In the deformed state exposed faces are probably (110) and (100). The microfibrils will be ca. 50–500 Å in diameter[53,54] but probably have microfaceted surfaces.

The microfibrils are expected to have large areas of lateral crystal surface available for adsorption which will probably exceed in area the amount of lamellar crystal–amorphous interface present in spherulites. The detailed structures of the lateral surfaces of both lamellar crystals and microfibrils have not yielded to experimental investigations. Slip planes in polyethylene are clearly (110) in single crystals, but (100) may also occur in the bulk. It would be expected that the external surfaces of microfibrils would be slip planes, since the microfibrils are produced by plastic deformation processes. Models of interactions between the polyethylene chains and fused-ring aromatics have invariably considered the extended trans conformation of the polyethylene chain and the flat-on orientation of the aromatic molecule. This is largely because the skeleton of the polyethylene chain and the outer long edges of the molecules are similar in shape and dimension. Such a model has been used recently[52] in modeling adsorption of pyrene on polyethylene crystal faces.

Considerable information does, however, exist on the interactions between crystalline polyethylene films and the crystals of fused-ring aromatic molecules.[54–56] These studies were aimed at obtaining an understanding of the function of crystals of aromatic molecules as nucleating agents in the crystallization of polyolefins. Through studies of orientation of polyethylene films crystallized on various aromatics, including anthracene and *p*-terphenyl, it was demonstrated that nucleation occurs through an epitaxial growth mechanism. In the case of fused-ring aromatic hydrocarbons, it was generally concluded that the polyethylene grows with its (100) face lattice matched to the (001) face of the substrate crystal. All these organic crystals have the same space groups and nearly identical spacings in the (001) plane, which essentially consists of the stacked molecules viewed end-on. In the case of polyphenyls, because of the somewhat longer spacings in the (001) plane, the polyethylene crystallizes using its (110) plane as the contact plane. There is therefore a considerable body of firm evidence on how crystals of polyethylene and aromatic molecules interact. A logical hypothesis would be that aromatic molecules would adsorb on exposed polyethylene faces in crystallographic register using a reverse epitaxy mechanism, if the appropriate faces of the polyethylene crystal were exposed.

On the basis of the data of Wittmann and Lotz it would be predicted that epitaxial growth would occur on (100) planes of polyethylene if they were exposed. In order to test this hypothesis thin films of polyethylene were crystallized on large single crystals of acridine using a method similar to that of Wittmann and Lotz.[55] X-ray studies[58] of film and substrate crystal (Figure 10) confirm that the polyethylene crystallized epitaxially with a (100) contact plane on the top face of the substrate crystal, as expected. The polyethylene reflections correspond to a superposition of two diffraction patterns caused by epitaxial growth along both the [110] and [1$\bar{1}$0] directions of acridine. For this case, the acridine molecules have their long axes perpendicular to the chain axis of the polymer. In this case, because the crystals were a few mils thick, film was found adhering to the sides of the substrate crystal also. X-ray studies of this film showed that it had a (110) contact plane (Figure 11). Again there are two populations of crystals; however, in this case the acridine molecules have their long axes parallel to the chain axis of the polymer. Polyethylene can therefore crystallize on at least two faces of acridine crystals, giving rise to two different epitaxial mechanisms. The films were recovered and all acridine was removed by evacuation. These films were then used as substrates for the vapor deposition of acridine molecules. It was found that acridine crystals deposited with the exact reverse epitaxial relations. It was thought that perhaps other

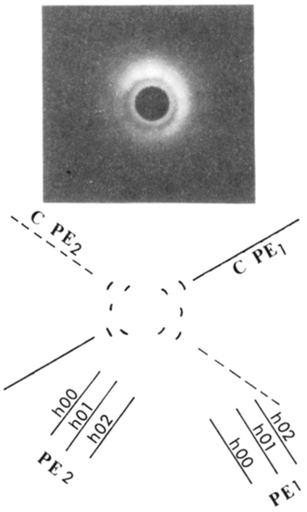

Figure 10. X-ray diffraction pattern of LDPE film epitaxially crystallized on the top of an acridine crystal, showing a (100) contact plane (C is the polymer chain axis).

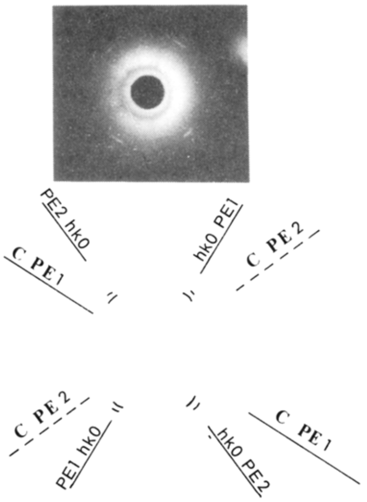

Figure 11. X-ray diffraction pattern of LDPE film epitaxially crystallized on the sides of an acridine crystal, showing a (110) contact plane (C is the polymer chain axis).

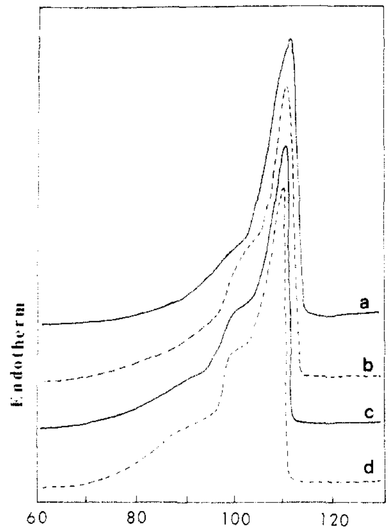

Figure 12. Melting curve of extruded rod LDPE containing acridine ((a) 0%; (b) 1.04%; (c) 2.75%; (d) 3.27%).

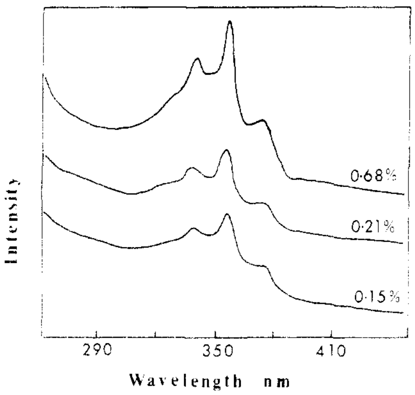

Figure 13. UV spectra of unstretched LDPE as a function of acridine concentration (reprinted from *J. Chem. Phys.* **1985**, *83*, 1948; copyright 1985 American Institute of Physics).

modes of deposition might occur; however, only the exact reverse epitaxy could be detected in each case. Diffraction patterns obtained from acridine crystals so produced were much more uniform and well resolved than those of the original acridine substrate crystal.

So, it has been demonstrated that acridine molecules deposited from the vapor onto polyethylene films will epitaxially crystallize onto the (110) and (100) exposed faces of polyethylene crystals. When crystallization occurs on the (100) faces, the long axis is normal to the chain axis of the polymer, and when crystallization occurs on the (110) faces, the long axis is parallel to the polymer chain. There is evidence from other techniques[59] that oriented microcrystals do exist inside stretched sheets of polyethylene to which acridine has been added either from the vapor or by soaking in chloroform solution. Two examples of this evidence are presented in Figures 12–14. A melting curve for extruded rod polyethylene containing various amounts of acridine is shown in Figure 12, where it can be seen that both the melting point of acridine and its monoclinic–orthorhombic transition can be detected. There is an additional low-temperature shoulder arising from a totally unforeseen occurrence, which will be discussed in the section following this one. In Figures 13 and 14 may be seen ultraviolet spectra of polyethylene containing acridine in unstretched and stretched sheets, respectively. For unstretched sheets, the spectra are clear and well resolved, indicating isolated molecules, whereas for stretched sheets, smearing occurs at concentrations greater than 0.12%, indicating microcrystal formation.

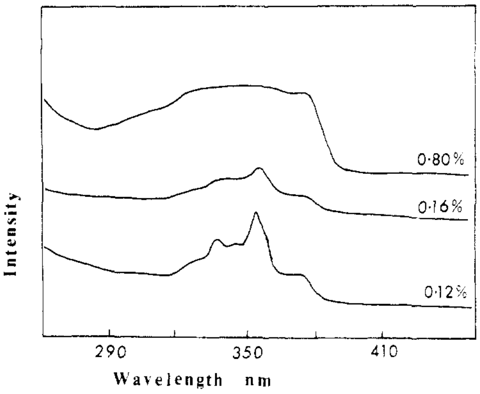

Figure 14. UV spectra of 900% elongated LDPE as a function of acridine concentration (reprinted from *J. Chem. Phys.* **1985**, *83*, 1948; copyright 1985 American Institute of Physics).

There is additional evidence from studies of the intensity of dielectric relaxation peaks[41] that large numbers of molecules previously detectable in the amorphous phase of the unoriented polymer can no longer be detected in the amorphous phase of the oriented polymer. Such an event does not occur for a molecule such as 9-bromoanthracene, which does not orient well or show other evidences of crystallite formation in oriented polyethylene. The magnitude of dielectric loss, $\Delta\epsilon'$, can be used as a measure of this effect. For extruded rods an exact estimate can be made of the amount of immobile material present, whereas in stretched sheets immobility and orientation effects cannot be separated. A measure is to calculate the quantity $(2\Delta\epsilon'_{\perp} + \Delta\epsilon_{\parallel})/3\Delta\epsilon'$, where $\Delta\epsilon_{\perp}$ is the magnitude normal to the orientation direction, $\Delta\epsilon_{\parallel}$ is the magnitude parallel to the orientation direction, $\Delta\epsilon'$ is the magnitude in an unoriented specimen. For acridine the values of the ratio are 0.17 for the β-process and 0.72 for the γ-process. In 9-bromoanthracene the values are 0.91 for the β-process and 0.87 for the γ-process. Since the inherent errors in the use of the integration method are about 10%, it is clear that the data for acridine show that on orientation a major loss of aromatic molecules occurs in the β-process, the relaxation associated with the glassy amorphous state. A lower but noticeable decrease occurs for the γ-process also, but the data changes for 9-bromoanthracene are close to the error involved in both relaxations. When $\Delta\epsilon'$ values are processed to give molecular concentrations using the Onsager equation (eq 1), quantitative estimates of the concentrations of molecules present in the amorphous phase are obtained.[41] The number active in the β-process is invariably 3–4 times that active in the γ-process. It is believed that the immobility is caused by epitaxial crystallization of the solute molecules.

Clearly, epitaxial crystallization is a major orientation mechanism for fused-ring aromatic and polyphenyl molecules. On the basis of acridine data, it is the dominant mechanism if the concentration exceeds 0.1% by weight. For fused-ring molecules, growth on both the (110) and (100) faces is possible. In the case of acridine, and presumably other fused-ring systems, growth on the (110) face orients the long axis of the aromatic molecule into the direction of the polymer chain, but growth on the (100) face orients it normal to the polymer chain. There are, therefore, three populations of aromatic molecules present at ambient temperature in oriented polyethylenes. These are (a) randomly oriented molecules present in the amorphous phase, (b) molecules adsorbed in an epitaxial manner on (110) faces and having orientation identical with that of the polymer chains in the crystals, and (c) molecules adsorbed on the (100) faces in an epitaxial manner and having an orientation normal to that of the molecules in b.

The proportions present in these different sites can be estimated by using a combination of data from dielectric relaxation and infrared dichroism studies, as follows. The fraction of molecules present in the amorphous phase (and hence unoriented) is known from dielectric relaxation studies of extruded rod specimens and can be taken as the sum of those active in both the β- and γ-processes. The remainder (i.e., all of the oriented molecules) are to be found in the form of epitaxially grown microcrystals. It will be assumed that those molecules present in crystals grown on the (110) faces have the same orientation factor as the molecular backbone of the polyethylene crystals and that those present in crystals grown on the (100) faces have a similar value of that orientation factor but normal to the direction of orientation. If it is further assumed that crystal growth is directly proportional to the area of exposed crystal face, then estimates can be made of the proportions present in each crystal orientation.

The volume fractions of molecules to be found in the different specimen locations can be written as

$$V_A + V_{110} + V_{100} = 1$$

where V_A is the fraction present in the amorphous phase and V_{110} and V_{100} are the fractions epitaxially crystallized on the (110) and (100) faces, respectively. Assuming that K_z, the orientation factor of the adsorbed molecules in the direction of stretch, can be written as an average of the orientation factors of the three different locations scaled by their respective volume fractions, the following equation results:

$$K_z = V_{110}K_{110} + V_{100}K_{100} + V_AK_A$$

where K_{110} and K_{100} are the orientation factors in the stretch direction of the molecules epitaxially crystallized on the (110) and (100) faces, respectively, and K_A is that of the molecules in the amorphous phase.

Writing $V_{100} = 1 - V_A - V_{110}$ leads to the equation

$$V_{110} = \frac{K_z - K_{100} - V_A(K_A - K_{100})}{K_{110} - K_{100}}$$

The value of V_A is known from the dielectric experiments and, since the molecules in the amorphous phase are essentially random, K_A can be made equal to $^1/_3$ (1368-cm^{-1} band of polyethylene). The values of K_z and K_{110} can be calculated from the dichroic ratios of adsorptions associated with the solute molecule and the polymer backbone, respectively. The orientation factor of the molecules adsorbed on the (100) face is more difficult to estimate. These molecules will be oriented primarily in a direction normal to the chain axis. The simplest case is to assume that they are normal to the stretch direction, i.e., $K_{100} = 0$. A more general assumption would be that K_{100} is equal to half of $1 - K_{110}$.

For the case in question, namely, acridine in polyethylene, $V_A = 0.56$, $K_z = 0.47$ (956-cm^{-1} band of acridine), and $K_{110} = 0.85$, determined by using the 1894-cm^{-1} band of polyethylene. Using the assumption that $K_{100} = 0$ leads to $V_{110} = 0.33$ and $V_{100} = 0.11$. In other words, assuming that in each case the number of molecules per unit area is the same, 75% of the exposed crystal planes are (110). Assuming $K_{100} = (1 - K_{110})/2$ leads to $V_{110} = 0.31$ and $V_{100} = 0.13$; i.e., 70% of the exposed planes are (110). A third possible approach would be to assume $K_{100} = 1 - K_{110}$, in other words, no contributions to the x direction. This assumption leads to the same results, i.e., 70% is (110). Hence, the range of possible values of V_{110} is fairly short, ranging from 0.31 to 0.33, and the fraction of exposed planes being (110) is 70–75%.

Polymer scientists have never previously been able to obtain a quantitative estimate of the relative amounts of the (110) and (100) slip systems operating during drawing. The ratio obtained will vary with the draw ratio, the rate of drawing, and the temperature of drawing. It is also likely to change with the source of polyethylene and how it was originally crystallized. Variations in orientation function values from several laboratories studying the same solute are likely to be a result of these dependences.

In the case of the unstretched spherulitic polymer, the lateral surfaces of the lamellar crystals have been believed to be (100) but no direct test has been possible. It was demonstrated in the studies referred to above that acridine epitaxially crystallizes on (100) surfaces. However, spectroscopic and thermal analytical studies have clearly demonstrated that acridine is present only in dissolved form in the amorphous phase of the undrawn spherulitic polyethylene. Hence the lateral surfaces cannot be (100) faces. The surfaces may be rough in accord with the ideas of Sadler and Gilmer[60] or may be microfaceted. Short alternating microfacets of (310) and $(3\bar{1}0)$ planes would be a possibility. So two pieces of unexpected information important to polymer physicists have resulted from this study. Indeed, it appears that fused-ring aromatic molecules provide a very sensitive probe of the nature of the exposed crystal surfaces of polymers.

Thermodynamic Aspects of Solute–Polymer Behavior

The initiation of this research was motivated largely with the objectives of confirming the invalidity of the Yogev model[2,14,15] and of uncovering the true orientational mechanisms. To a large extent these objectives have now been achieved. However, another question of major fundamental importance can now be posed. The aromatic molecules are undoubtedly drawn to exposed (110) faces, where they will epitaxially crystallize, even when present in low concentrations. In the absence of orientation the molecules are dissolved in the amorphous phase and show no tendency to crystallize. Does the imposition of orientation reduce the solubility limit of the molecules in the amorphous phase? Apparently not, since the concentration of molecules present in the amorphous phase increases with the overall concentration added in the oriented systems. Why then do the crystals form? One hypothesis would be that they are actually trying to enter the crystals but

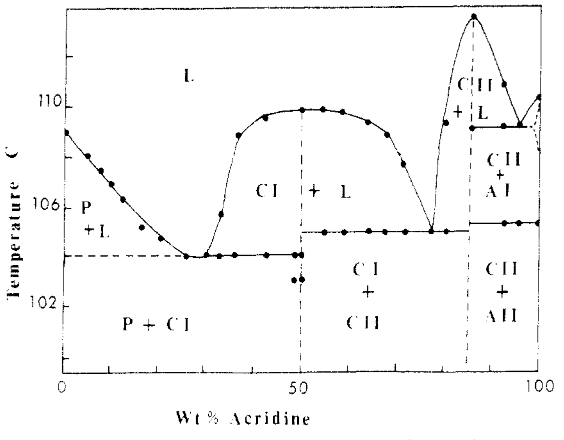

Figure 15. Phase diagram of acridine and low-density polyethylene (P, polymer crystals; L, liquid; CI, compound I; CII, compound II; AI, orthorhombic acridine; AII, monoclinic acridine) (reprinted from *Polymer* **1989**, *30*, 705; copyright 1989 Butterworth Ltd.).

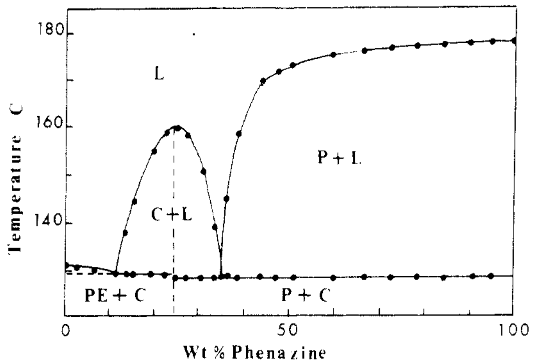

Figure 16. Phase diagram of phenazine and high-density polyethylene (PE, polymer crystals; L, liquid; C, compound; P, phenazine crystals) (reprinted from *Polymer* **1989**, *30*, 705; copyright 1989 Butterworth Ltd.).

cannot do so for diffusional reasons, simply because they are too big and thick to penetrate the crystal. The only reason they might attempt to enter the crystal would be because they could achieve a more stable state through the formation of a compound, such as is commonly encountered as water of crystallization in inorganic salts. No such compounds had been detected for nonpolar polymers, although some special adducts are known for certain polar polymers such as poly(ethylene oxide).

In order to test this possibility the phase diagrams of low-density polyethylene with acridine and of high-density polyethylene with phenazine have been determined.[61] These have been constructed by slow cooling of unoriented melts followed by differential scanning calorimetry carried out at a heating rate of 10 °C/min. The two phase diagrams are shown in Figures 15 and 16. The LDPE–acridine system shows three eutectics and two compounds, whereas the HDPE–phenazine system shows two eutectics and one compound. In the LDPE–acridine system the eutectics occur at 28.5% (104.9 °C), 78% (104.9 °C), and 96% (108.85 °C) acridine by weight. The compounds occur at 50% and 84% acridine. Since the amount of the amorphous phase is not known, the exact compositions of the compounds cannot be quoted. In the HDPE–phenazine system the eutectics occur at 12% (129 °C) and 34% (128.5 °C) phenazine by weight. The compound occurs in the vicinity of 25% phenazine.

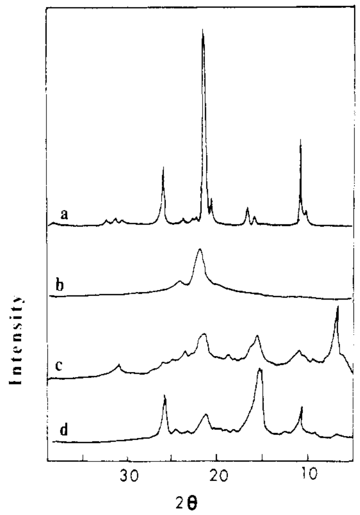

Figure 17. Wide-angle X-ray diffraction patterns of (a) acridine, (b) polyethylene, (c) compound I, and (d) compound II.

The crystal structures and the properties of these compound materials have not yet been evaluated. However, high-temperature X-ray diffractometry has been carried out to verify the existence of compounds and eutectics. Since these experiments were carried out at constant temperature and not in a scanning mode (as was the differential scanning calorimetry), a discrepancy between the eutectic temperatures of the phase diagram and the X-ray studies was expected. For compounds I and II the eutectic occurred somewhere between 83 and 95 °C in the X-ray studies. X-ray diffraction scans of acridine, polyethylene, and compounds I and II can be seen in Figure 17. It is clear that the diffraction patterns of the compounds bear little resemblance to those of the pure components.

Surprisingly, therefore, we are led to the conclusion that for the most orientable of fused-ring aromatic molecules, orientability in stretched polyethylene exists only because they *cannot* enter the polyethylene crystals due to kinetic effects. It is possible that the first layer deposited epitaxially on the polyethylene surfaces forms, together with the polyethylene surface, a packing typical of that of a fully formed compound crystal. In terms of the origin of the effect, we have therefore come almost full circle in that the original explanation of Yogev et al.[2,14-16] involving the molecules entering the crystal is, in one sense, correct since it provides the underlying thermodynamic reason for the behavior, but has been circumvented by the kinetics of solid-state diffusion.

Application to Other Solute Molecules

It is believed that the rationale presented above to explain the behavior of acridine in oriented polymers will be applicable generally to fused-ring aromatic hydrocarbons. This is because of the crucial information contained in the nucleation studies of Wittmann and Lotz.[55-57] The crystals of fused-ring aromatics are effectively isomorphous in their (001) planar structures and also in the spacings in their (110) planes. In order to apply the principles deduced above for acridine to other solute molecules, several concerns need to be addressed.

The resultant dichroic ratios will depend on the ability of the solute molecules to epitaxially crystallize on two different planes. It will be recalled that, to a first approximation, epitaxial growth on one set of planes aligns the solute molecule with its long axis normal to the direction of stretch whereas epitaxial growth on the second set of planes aligns the solute molecule into the direction of stretch. For this idealized situation the relative areas of the two sets of polyethylene planes control the measured value of the dichroic ratio. In reality, of course, the molecules need not be perfectly aligned or perfectly misaligned, since they may be inclined at an angle to the edges of their own crystalline unit cells. The crystals of the solute molecules are usually monoclinic whereas the polyethylene crystal is orthorhombic. There are major variations in the monoclinic angle from solute to solute. For instance, in anthracene β is equal to 124.7°, in phenanthrene 97.7°, and in chrysene 116.2°. In these cases identical epitaxial behavior would lead to different dichroic ratios. There also exist situations (e.g., in phenanthrene and pyrene) where the geometry of the molecule makes it likely that crystals having two quite different orientations could grow on a single face of a polyethylene crystal. Naturally, such an occurrence would lead to abnormally low values of the dichroic ratio.

Another interesting example is benzanthracene,[9] which has the additional complication that it is essentially an ell-shaped molecule having arms of different lengths. It can be looked upon as an anthracyl group having one additional off-axis fused ring or as two naphthyl groups fused together in an off-axis manner. It could epitaxially crystallize with either the anthracyl major axis or one of the naphthyl major axes adsorbed on the surface of the polyethylene crystal. In a case like this one, the preferred mode would depend on the lattice match along the molecular axis rather than being simply determined by the inter-ring separations of the molecular crystal. Such considerations would apply to both sets of planes on which epitaxial crystallization is occurring but would be of particular importance to crystallization on the (110) planes, which align the molecules in the direction of applied strain. For the (110) plane the spacing along the molecular axis of polyethylene is 2.55 Å and so the spacing along the molecular axis of the solute crystal must be related to this value. In anthracene it is 11.18 Å and in acridine 13.65 Å, being close to 4 and 5 times the polyethylene chain spacing, respectively. In naphthalene the *c*-axis value is 8.66 Å, whereas 3 times the polyethylene spacing is 7.65 Å. These values lead to lattice mismatches of 7% for acridine, 10% for anthracene, and 14% for naphthalene. The maximum allowable lattice mismatch is about 15%. Since the value of the lattice mismatch tends to reflect the strain energy resulting, it is clear that acridine and anthracene should give stable epitaxial growth. However, naphthalene, being close to the instability limit, might not epitaxially crystallize, thereby leading to a low value of the dichroic ratio. Chrysene, having a *c*-axis spacing of 25.2 Å, gives an almost perfect lattice match of 10 polyethylene spacings, but does not appear on the most recent orientation diagram.[9]

The presence of heteroatoms such as nitrogen, oxygen, or sulfur may also be deleterious to epitaxial growth since interactions between such atoms and the methylene groups of the polymer chain may be repulsive. Such a situation could make the energetics of epitaxial crystallization less favorable than might be assumed on the basis of lattice mismatch alone.

Similar criteria to those discussed above for fused-ring systems would also apply to polyphenyls, since Wittmann and Lotz[55-57] showed clearly that lattice matches can also be achieved for such molecules with polyethylene. However, for these cases, Wittmann and Lotz[55-57] found the lattice match to occur on the (110) faces of polyethylene, not the (100) faces. The tendency for these systems is, therefore, for epitaxial crystallization to be preferred along the (110) face, leading to the much better orientation observed for terphenyl.

One additional complication would be with regard to the molecules dissolved in the amorphous phase. Very little is known about the influence of solute shape on solubility in the amorphous phase. It is known that the ability of a molecule to diffuse into the polymer is very dependent on its size. Long molecules undoubtedly perturb the conformation of the polymer chains from the random state and so might tend to limit the solubility also. Only phase diagrams on the liquid state can resolve this problem. As far as can be ascertained (see earlier), molecules such as acridine are not oriented in the amorphous phase and so do not contribute to the dichroic ratio in any major way. Molecules present in the amorphous phase obviously cannot be epitaxially crystallized, and they contribute to the overall dichroic ratio by limiting the number of oriented species present.

In light of the above discussion, it should be recognized that only careful modeling studies, which incorporate the known crystal structures of the solute molecules, can test the applicability of the rationalization provided in this section. There is a need for a careful review of the behavior of aromatic molecules in epitaxial crystallization, care being taken to identify clearly the orientation of the molecules within the crystals, possible multiple orientations, and the effects of substituents of chemical character different from the methylene groups.

The hypotheses presented here are also applicable to other crystalline polymers used as stretched sheets for spectroscopic studies. Poly(vinyl alcohol) has been used as a polymer that permits the study of aromatic molecules of a more polar nature than those accepted by polyethylene. It is an appropriate choice, despite its affinity for water, since its unit cell is, essentially, that of polyethylene. Being an atactic polymer having small side groups capable of being incorporated into the polyethylene lattice as defects, poly(vinyl alcohol) retains the unit cell structure of polyethylene with slight perturbations. In the absence of any specific deformation studies of poly(vinyl alcohol) that delineate the slip systems and hence the crystal faces exposed by stretching, it is reasonable to assume behavior similar to that of polyethylene.

Other aliphatic polymers having crystal packings similar to that of polyethylene would also be expected to function efficiently as stretched-sheet substrates. The most obvious candidates would be the aliphatic polyamides. Although their structures are often monoclinic or triclinic, the interchain spacings are closely related to those of polyethylene. The major difference lies in the spacing along the molecular axis of the polymer, which is determined by the number of methylene groups separating amide groups. This parameter varies from one polyamide to another but is rarely less than four methylene units long. Some common polyamides have as many as twelve methylene units in sequence, adequate for deposition of most aromatic molecules of interest. Although, the crystallographic details of the drawing might differ from those of polyethylene because of the hydrogen bonding, lattice matches will undoubtedly occur. It appears, therefore, that likely alternative substrates can be chosen with a high chance of success as a result of our understanding of the acridine–polyethylene system.

Registry No. Acridine, 9002-88-4; polyethylene, 260-94-6.

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