INFLUENCE OF MORPHOLOGY ON THE TRANSPORT PROPERTIES OF CRYSTALLINE POLYMERS

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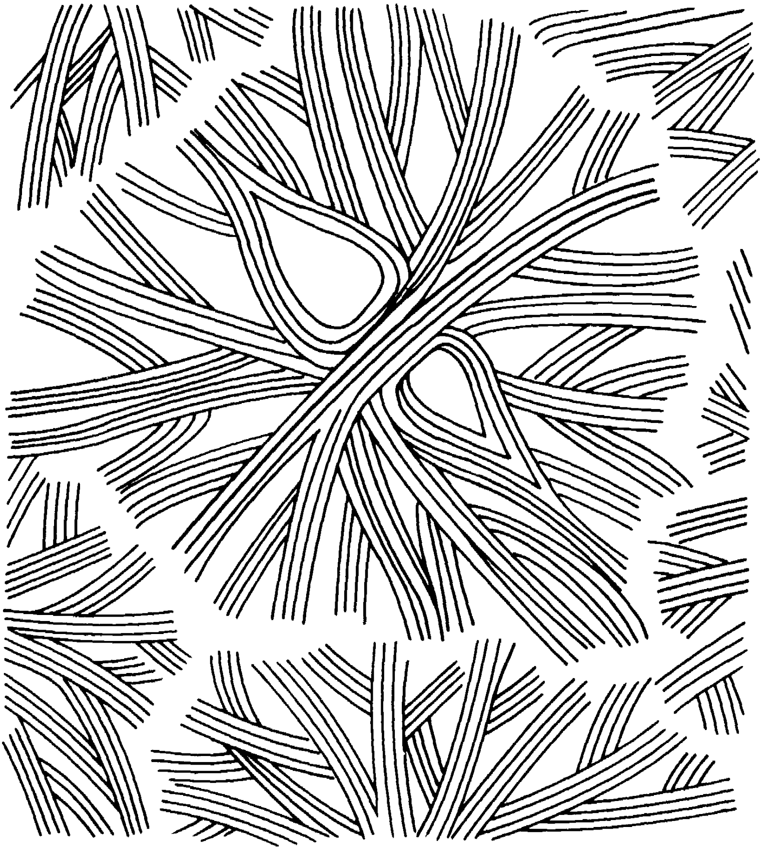
ABSTRACT

The sorption and diffusion of penetrant of low molecular weight proceeds almost exclusively through the amorphous component of the semicrystalline polymer consisting of chain folds, tie molecules and free chain ends. Hence they depend on its transport properties and geometrical distribution which are both modified by mechanical and thermal treatment. The morphological changes induced by such treatment and the ensuing changes of transport properties cannot be described in a satisfactory manner by crystallinity and orientation. That is particularly true for drawn material with fibrous structure exhibiting a high anisotropy of diffusion and a drastic decrease of sorption and diffusion. Both effects are the consequence of the microfibrillar morphology with a large fraction of highly aligned taut tie molecules which by their closer packing eliminate many sorption sites, enormously reduce the diffusivity, and increase its concentration dependence and activation energy. The axial alternation of crystal blocks and amorphous layers making the microfibrils almost impermeable in the longitudinal direction produces the high anisotropy of diffusivity which may be reduced during plastic deformation of the fibrous structure by the increased number of interfibrillar tie molecules. Annealing relaxes the amorphous component by reducing the fraction of taut tie molecules, thus restoring the transport properties to values as observed in undrawn material. Another example of the overwhelming influence of morphology are the hard elastomers where the formation of a great many submicroscopical holes yields permeability increased by many orders of magnitude with no change in crystallinity and only modest increase of crystal orientation.

INTRODUCTION

The material transport through a homogeneous polymer membrane is exclusively diffusive if the driving force as derived from chemical potential of the diffusant is wholly based on a concentration gradient. Under a pressure gradient one has to do also with a hydraulic flow opposed by friction forces of the macromolecules of the membrane. The contribution of hydraulic flow to material transport is substantial in highly swollen membranes and practically disappears at sufficiently low swelling ratio[1]. The situation in porous inhomogeneous membranes, where the transport mainly takes place through the pores, is in many respects similar[2]. With very small pores the hydraulic



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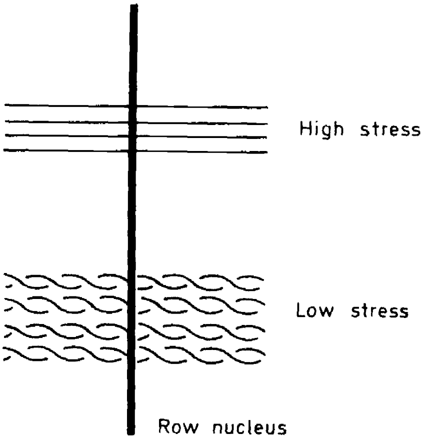

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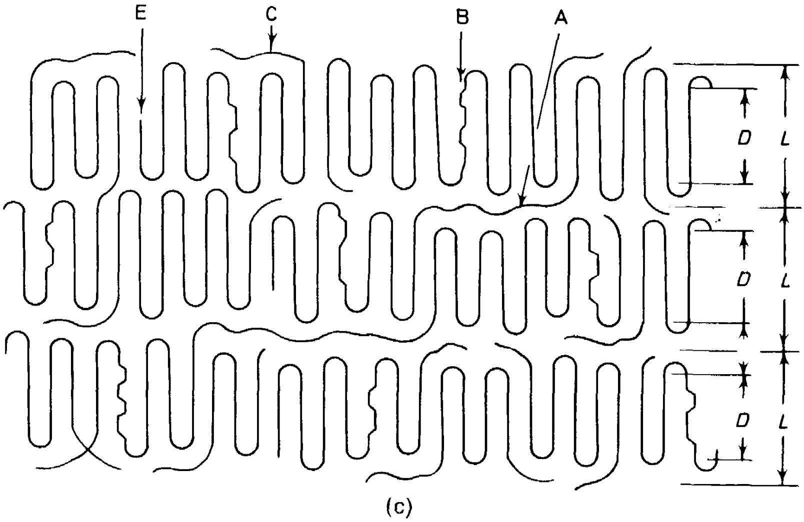


Figure 1. Model of (*a*) spherulitic and (*b*) cylindritic structure with (*c*) stacked lamellae. The amorphous layers of thickness $l = L - D$ contain more or less irregular chain loops, tie molecules (A) and free chain ends (C). The crystal lattice exhibits crystal defect concentration at the boundary between adjacent mosaic blocks (B). A linear vacancy (E) exists at a chain ending inside the crystal lattice.

flow goes to zero and with large pores can be many orders of magnitude larger than the diffusive flow[3].

In that which follows the emphasis will be on diffusive material transport and its dependence on morphology of the semicrystalline membrane. In only one case an inhomogeneous membrane with a great many pores will be considered as an extreme example of the influence of a special morphology on transport properties. In all other cases the membranes considered will be homogeneous and so little swollen by the diffusant that they can be characterized by a sorption (S) and diffusion (D) coefficient generally still dependent on the local volume concentration c of the diffusant. Under such conditions the permeability (P) as the product of S and D is also a function of c.

The diffusive material transport of gases and vapours in a polymer solid (subscript 1) proceed by jumps of the diffusing molecule (subscript 2) from one sorption site to the next one[4]. The formation of the channel through which the jump occurs requires a certain amount of energy, U_D, the activation energy of diffusion

$$U_D = q_2 \, l^* \, E_1 \rho_1. \tag{1}$$

It depends on the effective size or cross section q_2 of the diffusing molecule, on the jump length l^* and on the material properties of the polymer, i.e. on density ρ_1, and the cohesive energy $E_1 = \delta_1{}^2$ which is a function of the density of packing, alignment, mobility, and autoadhesive forces of the macromolecules of the sample. The many ways by which such a channel can be formed are measured by the entropy of diffusion S_D which primarily depends on the volume V_2 of the diffusing molecule and the fractional free volume f of the polymer–diffusant system.

$$f = v_1 f_1 + v_2 f_2 = (1 - c) f_1 + c f_2 \tag{2}$$

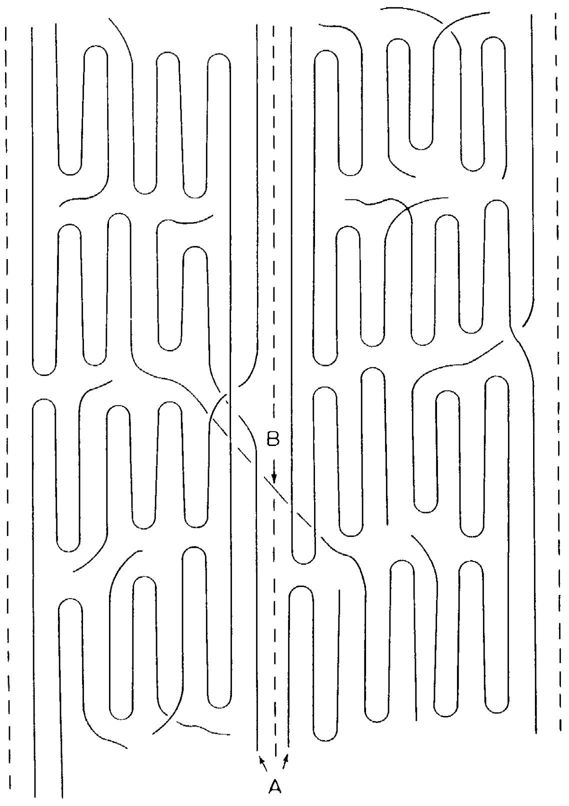
where v_1, v_2 and f_1, f_2 are the volume fractions and fractional free volumes, respectively, of both components.

One hence has for the diffusion coefficient at constant pressure

$$\begin{aligned} D &= \mathrm{D}^* \exp(-F_D/kT) = \mathrm{D}^* \exp(S_D/k - U_D/kT) \\ &= \mathrm{A} \exp(-\mathrm{B}V_2/f - U_D/kT). \end{aligned} \tag{3}$$

D*, A, and B are general constants which in first approximation are independent of material.

Such a description works well in a homogeneous material as for instance the purely amorphous polymer solid, either rubber or glass, but needs substantial modification in the case of crystalline polymer, which is a two-component solid with complicated morphology. In undeformed material the crystals are very thin lamellae, about 100 Å thick with lateral dimensions some orders of magnitude larger. Stacks of parallel lamellae are the main constituent



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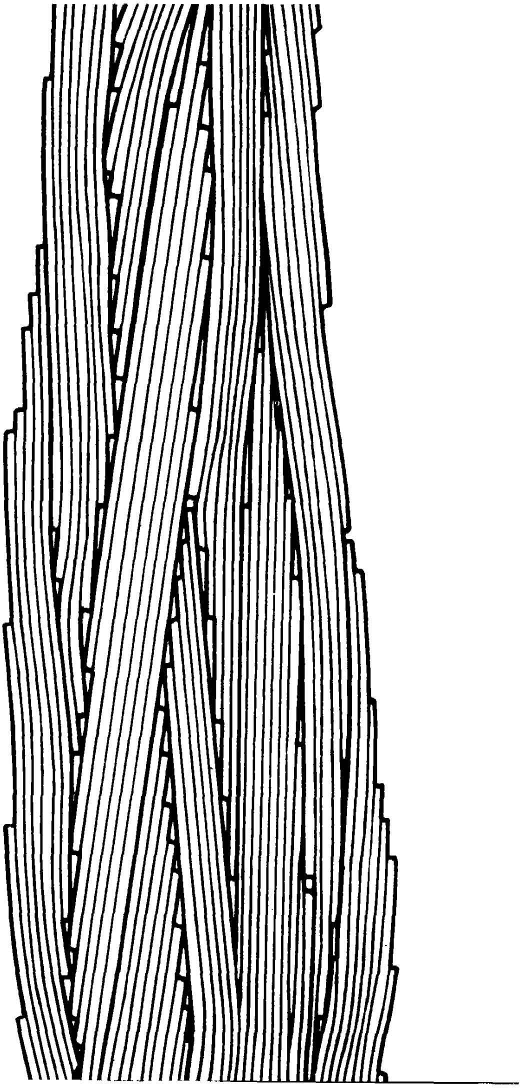

(b)

Figure 2. Microfibrillar model of fibrous structure: (*a*) fine structure of the microfibril with a great many intrafibrillar (A) and a few interfibrillar (B) taut tie molecules; (*b*) bundling of parallel microfibrils into fibrils with a great many lattice defects on the outer boundaries.

of spherulites and cylindrites which originate from point and row nuclei, respectively (*Figure 1*) and of the columnar structure originating from a planar arrangement of nuclei[5]. A particularly important case of highly oriented cylindrites is that of hard elastomers[3]. In a highly drawn sample the basic element is the microfibril composed of regularly alternating crystalline blocks and amorphous layers[6] (*Figure 2*).

The channel formation is obviously easier and hence U_D smaller in loosely packed amorphous than in the highly aligned and dense crystalline phase. A very similar consideration applies to the entropy of channel formation which is much higher in the former than in the latter case. The difference between F_{Dc} and F_{Da} is indeed so large that for all practical purposes in a two-component system of crystals (subscript c) and amorphous phase (subscript a) the transport through the former can be safely neglected and all the observed sorption, diffusion and permeability correlated with the properties and distribution of the latter component.

The so much less permeable crystalline phase mainly plays the role of an impermeable obstacle which lengthens the diffusion path as reflected in the tortuosity factor, $\tau < 1$, and reduces the area accessible to the penetrant but

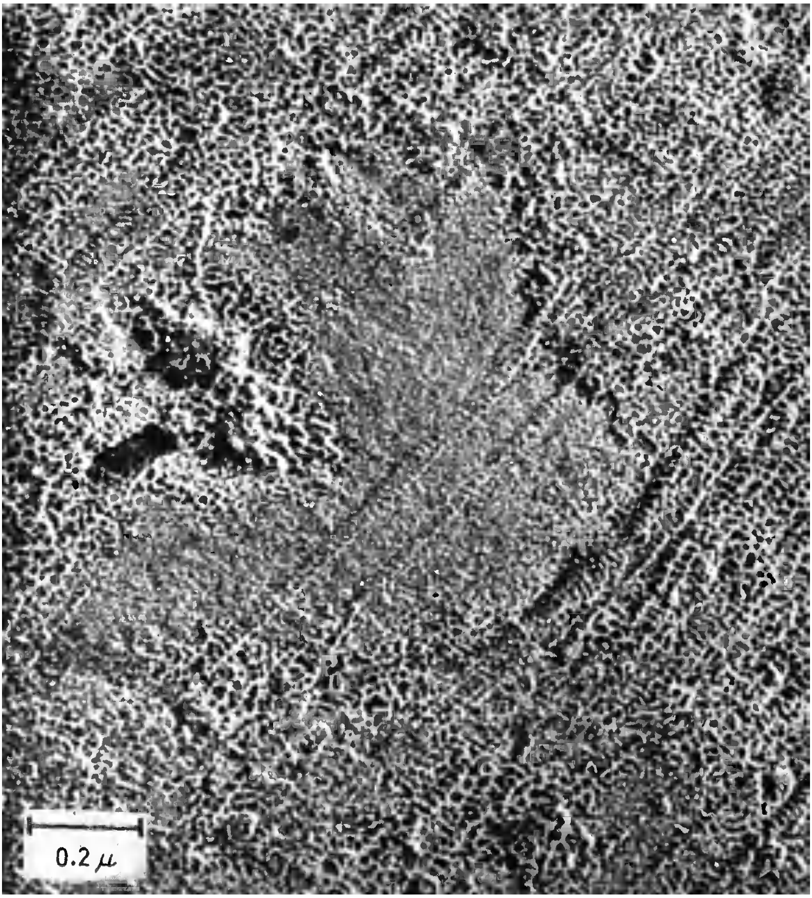

Figure 3. Electron micrograph of iodine stained microfibrils obtained by plastic deformation of multilater polyethylene crystals. The dark areas represent crystals alternating in axial direction of the microfibril with the less-stained amorphous layers. After Peterlin, Ingram and Kiho[7].

does not contribute measurably to the measured sorption and diffusion of the sample. That does not mean that diffusion and sorption do not obtain in it. As a consequence of the fact that the crystalline lamellae and blocks of the polymer are so extremely thin, about 100 Å, they are easily permeated by the diffusant in a short time as can be derived from the corresponding time lag $l^2/6D$ being about 1 s even for $D \sim 10^{-13}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. Hence under the normal conditions of a permeability experiment the crystals exhibit equilibrium sorption corresponding to the local chemical potential of the diffusant in the adjacent amorphous regions.

The exponential dependence of the diffusion coefficient on F_D, i.e. the fractional free volume and the activation energy of the polymer, makes the diffusive transport phenomena an extremely sensitive tool for the investigation of the packing of macromolecules in the amorphous phase and its changes under the influence of mechanical and/or thermal treatment. Even the significantly smaller effects in sorption which seem to be linearly dependent on f have found a wide application in staining of polymer samples for microscopical investigation. The stain mainly concentrates in the amorphous regions and makes them less permeable to the electron beam than the practically unstained or at least much less stained crystals. With the highly volatile iodine the situation is reversed because in the extremely thin sample needed for transmission electron microscopy the evaporation from the amorphous regions in the high vacuum of the electron microscope is so much faster than that from the crystals that the latter turn out to be more stained than the former[7] (*Figure 3*).

TWO COMPONENT MODEL

In crystalline polymers with a neat separation of the crystalline and amorphous phase one is tempted to describe the physical properties by two parameters, the crystallinity α and chain orientation. It turns out that the chain orientation in the crystalline phase, ϕ_c, can differ quite appreciably from that in amorphous phase, ϕ_a. Therefore, both quantitities have to be considered in the description of the solid polymer.

From the density ρ of the bulk sample, which is markedly smaller than that of the perfect crystal (ρ_c), one deduces a finite crystallinity

$$\alpha = \alpha_v = (\rho - \rho_a)/(\rho_c - \rho_a) \tag{4}$$

which is the volume fraction of the ideally crystalline component imbedded in an ideally amorphous matrix. Here ρ_a is the density of the perfectly relaxed supercooled melt. Neither the crystals are perfect nor is the amorphous component, consisting of chain folds, free chain ends, tie molecules connecting adjacent lamellae or subsequent crystal blocks and rejected impurities equal in density to that of a completely relaxed supercooled melt. Hence α_v is more a useful crystallinity index than the exact crystalline fraction of the sample.

If the sample is unoriented and sufficiently well relaxed one can represent the sorption by

$$S = \alpha S_c + (1 - \alpha)S_a \sim (1 - \alpha)S_a \tag{5}$$

and the diffusion coefficient

$$D = \tau D_a \tag{6}$$

yielding the permeability

$$P = SD \risingdotseq (1 - \alpha)\, \tau P_a \tag{7}$$

under complete neglect of diffusion through the crystalline component. Such a simplified description requires perfect isotropy of sufficiently large volume elements and homogeneity of the amorphous component throughout the sample. Both conditions are fairly well met in a crystalline membrane with perfectly relaxed microspherulitic structure as can be obtained by slow cooling or by quenching from the melt and subsequent annealing.

A rather satisfactory description of the tortuosity factor is given by the empirical expression[8]

$$\tau = (1 - \alpha)^m \tag{8}$$

with a constant m depending on the geometry of amorphous and crystalline phase. In the validity range of equation (7) the permeability of a crystalline polymer turns out to be

$$P = (1 - \alpha)^{m+1}\, P_a \tag{9}$$

It may represent well the situation in many polymer systems as long as the morphology remains the same[9]. The power m can be calculated for simple geometries of amorphous and crystalline phase. The calculated values, situated between 0.3 and 1.9, correlate well with experimental data.

Most commercial films obtained by extrusion or blowing exhibit a small but finite chain orientation in the crystalline and amorphous component and some anisotropy of morphology which yield an anisotropy of mechanical and transport properties[10]. The situation is still more extreme in plastically deformed material as for instance in man-made fibres which are produced by cold drawing of fibres as spun. In such a case besides a high anisotropy as a consequence of geometrical anisotropy of sample morphology, also a drastic reduction of transport properties obtains which cannot be described by equations (4) and (5). One is instead faced with an extreme modification of transport coefficients, S_a and D_a, of the amorphous phase depending on the details of plastic deformation, the temperature of drawing and subsequent thermal treatment[11–20].

The effects are so enormous that they cannot be overlooked. They reflect substantial changes of chain packing and alignment produced by mechanical treatment. Vice versa the change of transport properties can be used as an excellent and extremely sensitive method for the study of micromorphology of the amorphous component. This turns out to be quite an advantage because in contrast to the situation with the crystalline phase which can be so thoroughly investigated by x-rays there are so few suitable methods available for the investigation of subtler aspects of the amorphous phase. Moreover, the same details of the amorphous phase which affect the transport properties turn out to be also decisive for the mechanical properties of the crystalline polymer solid. Therefore, a better knowledge of sorption and diffusion of structural polymers can be of substantial help in their engineering applications.

One is often tempted to correlate the transport phenomena with the orientational factor ϕ which considers the orientation of the crystalline (ϕ_c) and amorphous (ϕ_a) component

$$\phi = (3 < \cos^2 \theta > - 1)/2 = \alpha\phi_c + (1 - \alpha)\, \phi_a \tag{10}$$

where θ is the angle between chain direction and a symmetry axis of the sample. The latter direction is that of drawing in drawn samples and that of flow in extruded material. Both values ϕ_c and ϕ_a can be derived from infrared dichroism[21] or x-ray scattering and optical birefringence[22]. As will be shown in that which follows, ϕ is a very poor parameter for the description of transport properties. A little better is ϕ_a, the orientation factor of the amorphous component, which is closely correlated with mechanical[23] and transport properties of drawn samples[18] as long as their basic morphology is not changed by thermal or mechanical treatment. One has indeed the quite general fact that crystallinity and chain orientation are the proper parameters for the description of transport properties of oriented crystalline polymer solids only in the case that morphology is known and remains constant. With other words *one must first know the membrane morphology and determine the dependence of transport on* α *and* f_a *characteristic for that morphology.*

UNORIENTED POLYMER WITH MICROSPHERULITIC MORPHOLOGY

On solidification from fully relaxed melt the randomly oriented and distributed primary nuclei yield a random distribution of stacks of parallel lemellae. If space permits they may grow by noncrystallographic branching into well developed spherulites with the stacks radiating from the central primary nucleus. This is indeed the case with slowly cooled melt. The low supercooling produces a small number of homogeneous nuclei so that the spherulites can grow to large size if the melt can be kept sufficiently free of heterogeneous nuclei. By rapid cooling (quenching) or by introduction of heterogeneous nuclei one starts crystallization at so many points that merely the embryonic stages of spherulites can develop, i.e. stacks of parallel lamellae. In spite of the large difference of supercrystalline morphology between these two extremes the basic mechanism of crystallization is the same and so is the dense packing of parallel lamellae into stacks. Therefore, all such samples can be called *spherulitic* although no well-developed spherulites are detectable in a very rapidly quenched sample. The true differences are not so much in the morphology but in finer details. There are more interlamellae tie molecules in the quenched sample and more rejected impurities on the outer boundary of spherulites in the slowly cooled sample. Moreover, the crystalline and amorphous components are closer to thermodynamic equilibrium and ideal density with a smaller content of defects in the latter than in the fromer case. But the growth of large spherulites may also yield a great many holes in the boundaries between adjacent spherulites, as is the case with polypropylene[24]. Such holes significantly modify the material transport and seriously distort the crystallinity determination from density data.

The amorphous component is primarily located in the surface layers of lamellae in which the macromolecules fold back in a more or less regular manner. Stacks of parallel lamellae indeed represent in the direction normal to the lamellae a fairly regular alternation of crystalline and amorphous layers which can be very well investigated by small-angle x-ray scattering. The rest of the contribution to the amorphous component $1 - \alpha_v$, i.e. to the density defect, originates in crystal defects and in the rejected material on the outer boundaries of stacked lamellae, spherulites and cylindrites.

In the former case one suspects some concentration of crystal defects on the boundaries between the mosaic blocks of the lamella which are so much displaced to each other that the crystal-lattice coherence as measured by the radial width of the wide-angle x-ray diffraction maxima is interrupted[25]. Moreover, very precise polyethylene lattice measurements have shown that as a consequence of the stresses connected with chain folds the lateral unit-cell dimensions are larger in thinner than in thicker crystals or in oligomers which crystallize without folding[26].

The packing of crystal lamellae very strongly interferes with transport properties[27, 28]. The sorption in the amorphous layers is mainly affected by the many constraints imposed on chain folds and tie molecules which also influence the mechanical properties. One has less unperturbed sorption sites per unit volume of amorphous component than in a supercooled melt. The diffusion, however, is affected not only by such constraints which increase the free energy of diffusion but also by the lengthening of the diffusion paths as a consequence of the geometry of lamella packing. The diffusive transport proceeds only through the thin amorphous layers between the lamellae and the amorphous boundaries between the randomly oriented stacks of lamellae and between the spherulites. Therefore, the diffusion paths are substantially longer and the tortuosity factor smaller than in the case of random distribution of spherical crystals in an amorphous matrix.

The holes on the boundaries between spherulites observable in slowly cooled polypropylene samples with increasing size of spherulites represent short cuts for diffusion[24]. The resulting decrease in density yields an amorphicity $1 - \alpha$ that is so much too high that it may overcompensate the effect of increased diffusivity. A further complication arises from the fact that rapidly cooled polypropylene crystallizes in smectic phase which when heated is transformed into truly crystalline monoclinic phase of higher density without a noticeable change of true amorphicity. Therefore, the sorption remains almost constant upon annealing in spite of the observed increase in density of the sample which according to equation (4) could be interpreted as an increase in apparent crystallinity[29]. Polyethylene, however, without a change in crystal phase exhibits a strict proportionality of sorption and amorphicity as required by equation (5)[30]. As a consequence of crystal phase transition and hole formation during annealing of polypropylene the diffusion constant decreases to a minimum and then increases with decreasing apparent amorphous content. The activation energy for diffusion, however, remains practically constant, which indicates that the mobility of chain segments is not affected by annealing. Therefore, the majority of transport anomalies in polypropylene[24, 30, 31] are either artifacts or a consequence of gross structural defects (holes) which are not considered in the two-component model of crystalline polymers (equations 4–7).

ELASTIC DEFORMATION OF SPHERULITIC MATERIAL

The elastic modulus of the crystals exhibits an enormous anisotropy. In the case of polyethylene, it is 240×10^{10} dyn cm^{-2} ($E_{\parallel}$) in chain direction and 4×10^{10} dyn cm^{-2} ($E_\perp$) in the lateral direction[32]. The elastic modulus of the amorphous component of polyethylene[33] is between 10^9 and 10^{10} dyn cm^{-2} (E_a). This is significantly less than $E_\parallel$ and $E_\perp$ but about 100 times more than the elastic modulus of a rubber in spite of the fact that at room temperature one is far above the glass transition temperature of polyethylene (T_g is either -20 °C or -120 °C) so that one would expect a fully developed rubbery behaviour. The most probable explanation of this effect is the strong constraints on chain sections in the amorphous layers which are at both ends (chain folds and tie molecules) or at least at one end (free chain ends) fixed in the crystal lattice of the lamellae.

As a consequence of this large difference of elastic modulus between the alternating crystalline and amorphous layers, most of elastic deformation occurs in the latter. A shearing deformation does not change the volume of the layer. A tensile force in the direction perpendicular to the lamellae increases the thickness of the amorphous layer and thus decreases its density because the lateral dimensions remain constant. Because the whole increase of specific volume $\varepsilon(1 - 2\mu)/(1 - \alpha)$ shows up in the increase of fractional free volume

$$f = f_0 + \varepsilon(1 - 2\mu)/(1 - \alpha_v) = f_0(1 - \beta) \qquad (5)$$

one expects a corresponding increase of sorption and diffusion coefficient. Here ε is the tensile strain and μ is the Poisson ratio. Experiments on commercial polyethylene films indeed show an increase of S and D with elongation[34] (*Figure 4*). The sorption continues to increase to a rather high ε and approaches a limiting value about 15 or 20 per cent above the sorption in the unstrained state. The diffusion coefficient, however, increases linearly with the strain in an extremely short range of ε, up to $\varepsilon = 0.02$, reaches a maximum about 10 per

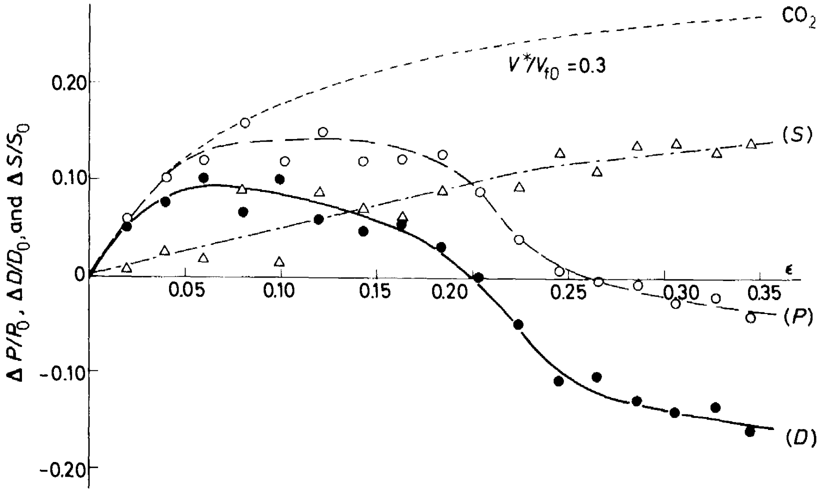

Figure 4. Relative increase of sorption, $\Delta S/S_0$, diffusion coefficient, $\Delta D/D_0$, and permeability, $\Delta P/P_0$, of a commercial polyethylene film as function of recoverable uniaxial strain ε. After Yasuda and Peterlin[34].

cent above the initial value at $\varepsilon = 0.06$ and after that steadily drops. It reaches the initial value at $\varepsilon = 0.20$ and drops to 0.85 of it at $\varepsilon = 0.35$. This behaviour very clearly shows that the pure effect of elastic deformation ends very early, i.e. at the end of the linear range of D which obtains at $\varepsilon = 0.02$. After that the deformation must include a new component which is responsible for the reduced increase and subsequent drop of D below the initial value in the unstrained membrane.

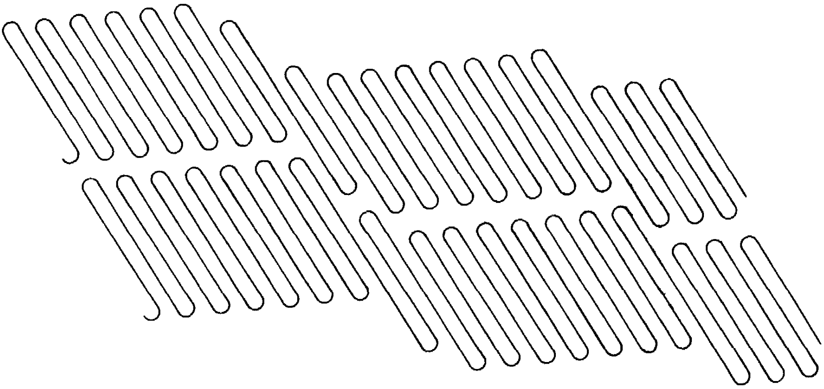

Figure 5. Model of partially recoverable chain slip in a stack of parallel lamellae blocking the diffusive pathways in the amorphous layer.

Such a dependence can be achieved by a decrease of fractional free volume or by longer diffusion path which reduces τ. The steady although sublinear increase of S is an argument against a decrease of f so that one is left with the second possibility as the main aspect of deformation between $\varepsilon = 0.02$ and 0.35 influencing the diffusion but not affecting the sorption. The deformational mode which increases the path length is the shear deformation of lamellae by chain tilt and slip. It is the first step of plastic deformation of single crystals which later tends to lamella fracture and microfibril formation (*Figure 5*). The dislocation of sections of lamellae during this process distorts and even interrupts the coherence of amorphous layers, thus requiring longer diffusion paths, i.e. a reduction of the tortuosity factor without any reduction of fractional free volume. Since a major contribution to deformation is derived from such plastic deformation of lamellae which releases the strain on the amorphous component, and only a rapidly decreasing fraction from the tensile deformation of the amorphous layers, the increase of f slows down as shown by the steadily decreasing slope of $\Delta S/S_0$ as a function of ε. It has to be mentioned that in this initial stage the plastic deformation of lamellae is still to a large extent recoverable. After release of the load the sample does not retract immediately to the initial length but does that almost completely after a sufficiently long period of time.

PLASTIC DEFORMATION OF SPHERULITIC MATERIAL

The transport properties change dramatically with increasing plastic deformation which gradually transforms the crystalline polymer from spherulitic into fibrous morphology. The first stages of plastic deformation involve shear deformation and rotation of stacks of parallel lamellae[22]. Both modes are mainly the consequence of shear deformation of the amorphous layers between lamellae and between stacks of lamellae. Very soon, however, the forces are sufficient for chain tilt and slip within the lamellae[35]. To a large extent these deformations are still recoverable at the temperature of the experiment and hence do not represent truly plastic deformation. But gradually the lamellae are so far deformed by chain slip that a crack develops. The partially unfolded chains bridging the crack lead to successive tearing off of crystal blocks from the lamellae and their incorporation into microfibrils connecting the opposite borders of the crack.

The crack is indeed a craze[36] (type II craze) differing from the well known crazes of amorphous glasses[37] (type I crazes) in the properties of micronecks on the boundary between the microfibrils and the lamella. In the latter case the micronecking is activated only under the substantial stress concentration at the sharp tip of the craze but is not more operative as soon as the craze is formed and the stress concentration ceases to obtain. As a consequence of this situation the craze grows laterally as long as the stress at its tip is sufficiently high but does not grow significantly in thickness beyond the value obtained during formation. The type II craze, however, primarily grows in thickness by micronecking which transforms the lamella into microfibrils until the transformation is completed but does not grow substantially in lateral direction. The force required for breaking off of crystal blocks from the lamella is certainly smaller than that for the formation of the first crack which initiated the micronecking and type II crazing.

The microfibril consists of alternating crystal blocks and amorphous layers bridged by a great many taut tie molecules[6, 7]. They are almost fully stretched and closely packed so that in polyethylene they resist attack by fuming nitric acid nearly as well as the chains in the crystal[39]. In polyethylene they may constitute up to 30 per cent of the amorphous layer at a draw ratio $\lambda = 20$[40] in contrast with about one per cent at $\lambda = 1$. The high orientation of such taut chains in amorphous conformation increases the density[41, 42], reduces the heat content[43, 46] and reduces the number of sorption sites for the diffusing molecules[16–19]. But the most drastic effect is the enormous reduction of diffusion coefficient[11–20] and the increase of activation energy of diffusion[13, 16]. Hence the microfibril acts as a structural element almost as impermeable to diffusing molecules as the crystals. In the first stage of plastic deformation with a small volume fraction of microfibrils their influence is still overcompensated by the loosening of the spherulitic structure. The reduced density of amorphous layers under pure shear, the voids and fissures of the still spherulitic matrix indeed slightly increase the permeability in spite of the gradual formation of the almost impermeable microfibrils[14, 15]. But very soon the influence of the latter elements prevails and the sorption and diffusion coefficients drop drastically with increasing draw ratio[14–20].

The equilibrium concentration $c = Sp$ of methylene chloride in undrawn

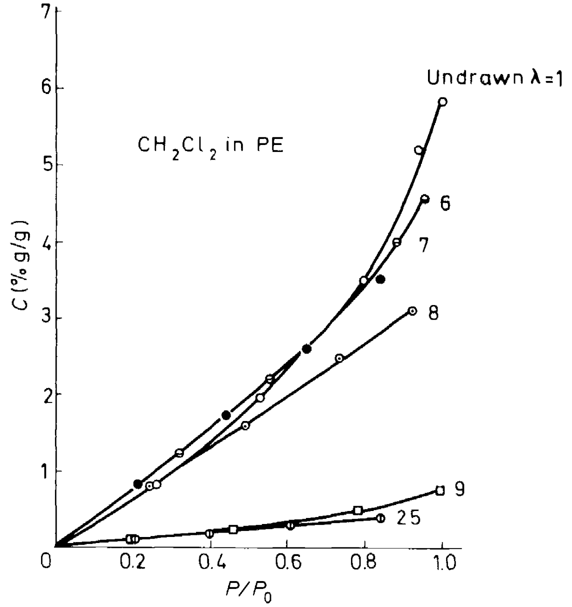

Figure 6. Equilibrium concentration of methylene chloride sorbed at 25°C in undrawn quenched linear polyethylene (Fortiflex A60–500, Celanese Corporation trademark) $\lambda = 1$, and in films drawn at 60°C to draw ratios 6, 7, 8, 9, 25 versus vapour activity p/p_T ($p_T = 412$ torr). After Williams and Peterlin[18].

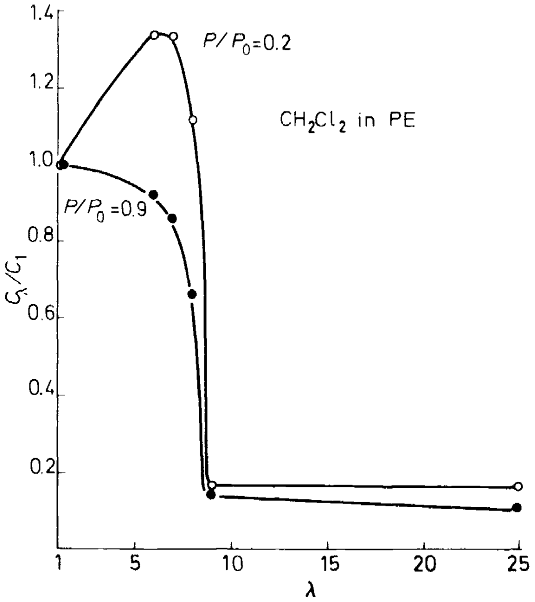

Figure 7. Relative sorption c_λ/c_1 of methylene chloride in polyethylene films versus draw ratio λ at penetrant activities 0.2 and 0.9. After Williams and Peterlin[18].

polyethylene and in samples with draw ratios, 6, 7, 8, 9, and 25 as function of relative pressure (activity) p/p_T of sorbent vapour exhibits strong departures from the linear Henry's law evident with higher penetrant activity[18] (*Figure 6*). The deviations are most conspicuous for the undrawn sample but still detectable even at the largest draw ratio. The isotherms obtained are of the normal mixing rather than hole-filling type. At low activity (0.2) the equilibrium concentration of the sorbate first increases up to $\lambda = 7$ (*Figure* 7) and then drastically drops to a new value which is about 15 per cent of the value of undrawn sample. Drawing beyond $\lambda = 9$ up to $\lambda = 25$ has very little additional effect on sorption. At high activity (0.9), however, the equilibrium sorption steadily decreases without a maximum at low λ and drastically drops to a new low plateau at $\lambda = 9$. This difference in S_λ/S_1 versus λ curves at low and high activity is a consequence of the larger deviation from Henry's law in the undrawn material. These results are very similar to those obtained on water sorption which, however, obey Henry's law in both the undrawn and drawn material[17]. One has the impression that between 8 and 9 the linear polyethylene sample is fully transformed from spherulitic to fibrous structure. The latter does not change appreciably with further drawing.

The data in *Figure* 7 can be interpreted in terms of sorption in the amorphous component if one applies the correction according to equation (5) as a consequence of a slight change of crystallinity. Drawing of quenched polyethylene increases steadily the density[42] and hence according to equation (4) reduces the amorphicity $1 - \alpha$. It indeed drops from 28 to 17 per cent with λ increasing from 1 to 25. Such a correction hardly affects the initial dependence of relative sorption $(S_\lambda/S_1)_a$ on λ and the drastic drop between $\lambda = 8$ and 9 but it makes the final plateau more horizontal. Although the density increases and the amorphous fraction decreases with increasing draw ratio it is clear that considerably more than crystallinity changes are involved in the drastic drop of sorption. According to the microfibrillar model of fibrous structures[45-47] the effect is caused by the complete replacement of the spherulitic by the fibrous structure. The highly strained amorphous layers of the microfibrils with a high content of taut tie molecules offer less sorption sites than the relaxed amorphous layers of stacked lamellae with very few tie molecules. As long as relaxation phenomea can be excluded one finds from the temperature independence of sorption[16] that, within experimental error, there is no change of heat of mixing caused by drawing. That means that the sorption sites are identical in both cases, most likely located in fully relaxed chain loops. But their number is reduced by the presence of so many taut tie molecules and by the more diffuse boundary between amorphous and crystalline regions caused by their extended interpenetration. The latter effect is one of the main causes of the high breadth and poor observability of small angle x-ray[48] and laser-Raman scattering peaks[49] of drawn material.

As expected, the reduction of sorption by drawing is enormously enhanced with increasing molar volume of the sorbate. At $p/p_T = 0.82$ the ratio $(S_{10}/S_1)_a$ is $15/86.3 = 0.17$ for methylene chloride ($V = 63.6\,\text{cm}^3\,\text{mol}^{-1}$) and $4.9/125.6 = 0.04$ for tetrachloroethylene ($V = 101.8$)[16]. The full extent of the reduction in solvent sorption of the latter liquid in highly drawn polyethylene was first demonstrated by wide-line n.m.r. measurements[50]. In contrast with undrawn material exhibiting a substantial enhancement of

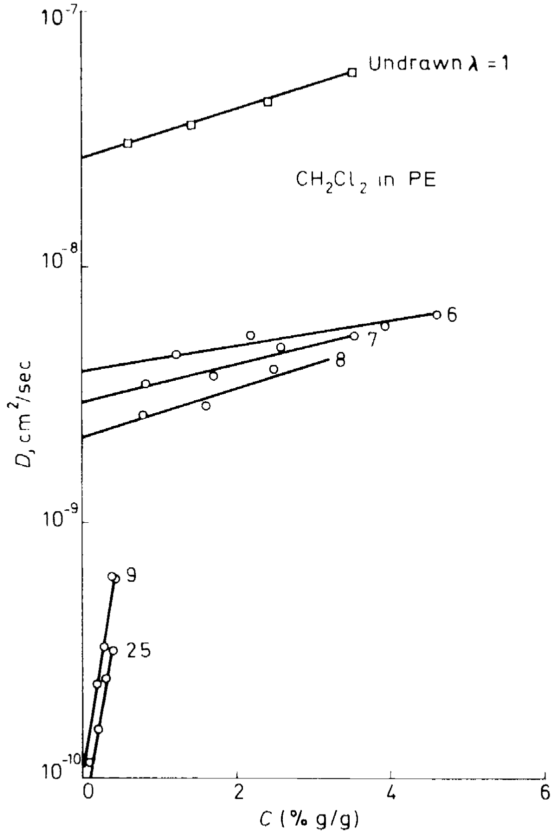

Figure 8. Diffusion coefficient of methylene chloride at 25 °C in undrawn and drawn polyethylene films versus concentration of penetrant. The values are derived from the initial slope of the weight gain versus square root of time. After Williams and Peterlin[18].

chain mobility upon exposure to tetrachloroethylene no such effect could be achieved in drawn material. According to the volume effect of the sorbate (equation 3) one expects a still more drastic reduction of sorption for the large dye molecules. Indeed the earlier dye chemists observed the lack of dyeability of certain fibres which had been cold drawn. They therefore increased the dye concentration in order to obtain the same shades as obtained with the undrawn material.

The effect of drawing on diffusion is still more drastic than on sorption. As seen in *Figure 8* the diffusion coefficient drops by one decade at a draw ratio 6 to 8 and for more than another decade at draw ratio 9 but then remains practically constant up to the maximum draw ratio 25[18]. The concentration dependence changes very little up to $\lambda = 8$ and gets extremely high but constant for λ between 9 and 25. The extrapolation to zero concentration yields D_0 as function of λ as shown in *Figure 9*. The temperature dependence of D_0 at high λ yields an activation energy of 34 kcal mol^{-1} which is more than twice the value 14.4 for undrawn material[16].

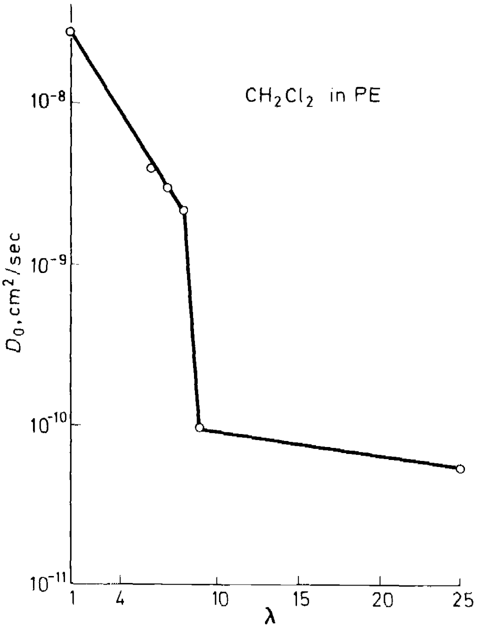

Figure 9. Diffusion coefficients from *Figure 8* extrapolated to zero concentration of penetrant as function of draw ratio. After Williams and Peterlin[18].

The obvious interpretation of these data is by the same morphological terms as in the case of sorption. The gradual formation of the almost impermeable microfibrils reduces the fraction of spherulitic material of almost unchanged or even slightly enhanced permeability. The diffusion takes place primarily through the latter component. Because it is randomly interrupted by bundles of microfibrils the diffusion paths are much longer than in the undrawn material. Hence the initial drop of diffusion coefficient is considered to be due to the decrease of the fraction of highly permeable spherulitic material and the decrease of tortuosity factor τ. Between $\lambda = 8$ and 9 the transformation to the fibrous structure seems to be completed so that the diffusion has to proceed through the so much less permeable microfibrils. Hence the final drop of D is primarily a consequence of the drastic reduction of D_a caused by the large number of taut tie molecules in the amorphous layer.

The general effect of taut tie molecules in the fibril structure on S and D can be best understood in terms of fractional free volume of the amorphous component. From wide-angle x-ray data one has deduced a higher density of the amorphous material in highly drawn polyethylene as compared with that of annealed or undrawn specimens. The corresponding decrease of free volume decreases the number of sites for sorption. In first approximation the relationship between f and S is linear[34]. The influence of f on D_0, however, is exponential as seen in equation (3). By considering the change of f with increased concentration of the sorbate (equation 2) one also deduces the enhanced dependence of D on concentration as observed experimentally. The effect on activation energy of diffusion can be caused by the wider spacing of available

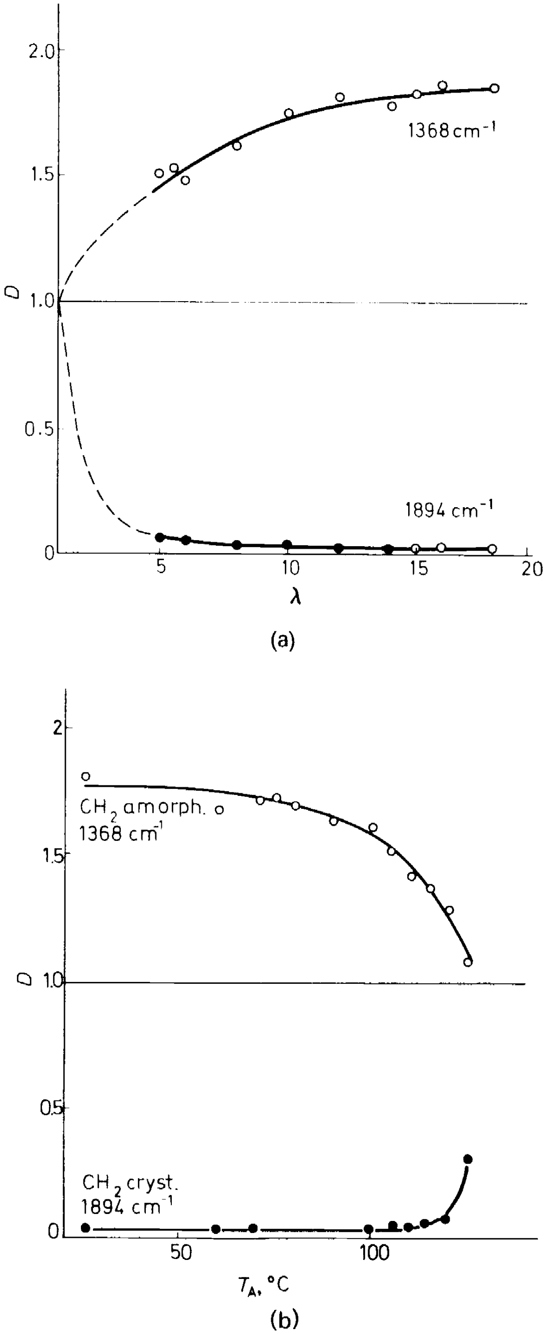

Figure 10. Dichroism for the crystalline based 1894 cm^{-1} and amorphous band 1368 cm^{-1} of linear polyethylene as function of (*a*) draw ratio, (*b*) annealing temperature. The relative orientation functions $\phi/\phi_{\max}$ are linear functions of dichroism. After Glenz and Peterlin[52].

sorption sites, i.e. by an increase of l^*, and by an increase of cohesive energy as a consequence of denser packing of the amorphous chains. The existence of the latter effect is best demonstrated by the decrease of the heat content H_a of the amorphous component[43].

Annealing relaxes the taut tie molecules, restores the density and heat content of the amorphous component to equilibrium values. Hence one expects and indeed observes a recovery of permeability[19, 51]. The sorption and diffusion coefficient approach rapidly the values of the undrawn material. A partial recovery may also obtain by sorption at high sorbate activity[16]. In order to avoid this effect all experiments have to be performed with vapours sufficiently below saturation pressure.

If one wishes to correlate these data with orientation one is faced with the substantially different degree of orientation in crystalline and amorphous component[52] (*Figure 10*). The former (ϕ_c) increases very rapidly and reaches very soon, e.g. at $\lambda \sim 5$, a limiting value close to unity. It also decreases very little during annealing particularly if the sample is annealed with fixed ends so that it cannot shrink. One had indeed to anneal very close to the melting point in order to obtain an appreciable disorientation. The amorphous component, however, orients much more slowly and does not reach a saturation value even at $\lambda = 20$. This increase extending beyond $\lambda = 9$ indicates that some changes in amorphous component occur even after the transformation to fibrous structure is completed. They must be connected with the plastic deformation of fibrous structure which is responsible for the drawing between $\lambda = 9$ and 25. Upon annealing the disorientation of amorphous component occurs very rapidly in fairly good correlation with the recovery of sorption and diffusion. But no similarly good correlation exists during drawing where the orientation of amorphous component does not exhibit any such sharp change at λ between 8 and 9 as observed with S and D. One has indeed in this case a complete change in morphology which cannot be adequately described by orientation factors of crystalline and amorphous component. No such morphological change obtains during annealing sufficiently below the melting point, which explains the better correlation between ϕ_a and S and D.

PLASTIC DEFORMATION OF FIBROUS MATERIAL

The material transport data of linear polyethylene between draw ratio 9 and 25 relate to plastically deformed fibrous structure. Such a deformation can only occur by sliding motion of the fibrillar elements of the fibre, i.e. of microfibrils and fibrils[53] (*Figure 11*). The close packing of the extremely long and well aligned microfibrils in a single fibril makes their sliding displacement the more difficult the longer they are. In first approximation the friction coefficient for such a motion is proportional to the surface area, which is the product of thickness d_{mf} and length l_{mf} of the microfibril. The force exerted on the fibril by its neighbours is on the average a shearing force proportional to the skewness of the fibril which in first approximation is proportional to the width d_f of the fibril. The resulting shear deformation is proportional to $d_f/l_{mf} \sim d_f/l_f \sim \lambda^{-3/2}$. It will be large in Nylon 6 where the transformation to fibrous structure is complete at $\lambda^* \sim 3$ yielding a value proportional to

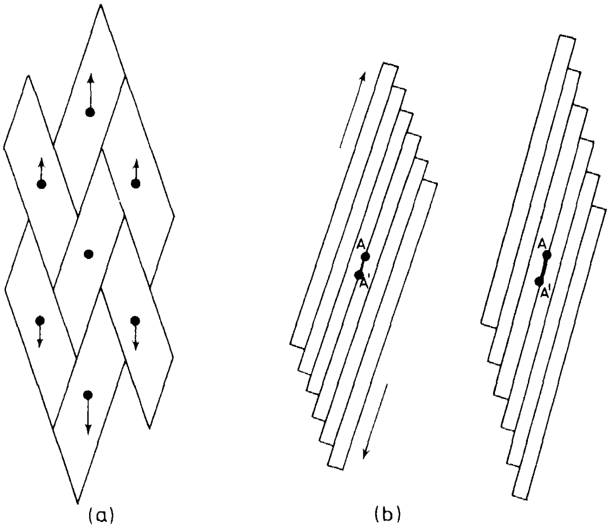

Figure 11. Model of deformation of fibrous structure: (*a*) deformation of fibril displacement (oversimplified: the correct axial ratio of fibrils is between 5 and 30), (*b*) shearing of fibrils by displacement AA' of microfibrils. After Peterlin[53].

1/5 = 0.2 for the ratio d_f/l_f and small in linear polyethylene with $\lambda^* = 9$ yielding the estimate 1/27 = 0.04.

The shear displacement of microfibrils extends enormously the interfibrillar tie molecules even if the resulting shear deformation of the fibril is small (*Figure 12*). With $l_f = 5\,\mu = 50000$ Å, one hundred microfibrils in the fibril and a shear displacement of adjacent microfibrils by 2000 Å the whole length

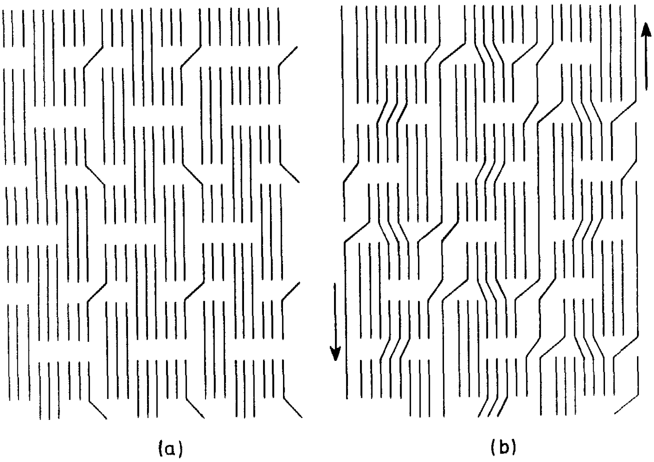

Figure 12. Extension of interfibrillar tie molecules by shear displacement of microfibrils. After Peterlin[53].

of the fibril increases by 20000 Å which is 40 per cent of the initial length. But the extension of each interfibrillar tie molecule by 2000 Å increases their fraction per amorphous layer by a factor of 20 if the long period is 100 Å as is the case with Nylon. In polythylene one expects a much larger $l_f \sim 150000$ so that under the same assumptions the increase of fibril length is only 13 per cent. The increase in fraction of interfibrillar tie molecules per amorphous layer is by a factor ten because the average long period is about 200 Å so that the molecule is now passing through ten such layers instead of one before shear displacement. But if one considers the fact that the shearing stress in polyethylene is about five times smaller than in the case of Nylon, one expects a similar reduction of shear displacement to 400 Å and a multiplication of interfibrillar tie molecules by a factor of two only.

Since the fraction of interfibrillar tie molecules is about one per cent[54] their increase by shear deformation of the fibril is quite substantial for Nylon (20 per cent) and negligible for polyethylene (two per cent) if compared with the intrafibrillar tie molecules (five per cent in Nylon and 15 to 20 per cent in polyethylene)[39, 40]. These extimates agree very well with the observed dependence of diffusion coefficient on draw ratio. In the case of Nylon D_λ continues to drop over the whole draw range up to $\lambda \sim 5$ even after the conversion into fibrous structure which is completed at $\lambda^* \sim 3$[14, 15, 20]. Such a dependence indeed supports the above sketched model of plastic deformation of fibrous structure which in the case of Nylon produces a great many new tie molecules, thus gradually more impeding diffusion. In the case of polyethylene the number of tie molecules increases only marginally thus affecting very little if at all the transport properties.

The observed draw ratio λ_b/λ^* up to fracture is much higher, 1.7 in Nylon and 2.5 in polyethylene, than that of the fibrils which in the above quoted example is about 1.4 in Nylon and 1.03 in polyethylene. Therefore, a large or even the major part of the plastic deformation of fibrous structure occurs by sliding motion of fibrils which very likely does not produce a significant number of new tie molecules. This conclusion is based on the model of formation of fibrous structure which produces an interfibril tie molecule solely from a tie molecule connecting two adjacent stacks of lamellae in the original spherulitic material. Since there are very few such connections one also expects very few tie molecules between adjacent fibrils which can be expanded during sliding displacement of the fibrils. According to this model almost all or at least the major part of the increased fraction of tie molecules which reduces the sorption and diffusion coefficient during deformation of the fibrous structure is formed by the shear deformation of each individual fibril, i.e. by sliding of microfibrils and not by the sliding displacement of the fibrils relative to each other.

ANISOTROPY OF MATERIAL TRANSPORT IN DRAWN POLYMER

Experiments[15, 20] on drawn Nylon 6 have demonstrated that the axial diffusion coefficient $D_{\parallel}$ drops continuously with increasing draw ratio. The usually measured radial diffusion coefficient $D_{\perp}$, however, first increases up to a draw ratio a little below two and then rapidly drops to a fraction of the initial value. But it remains larger than $D_{\parallel}$ although the relative difference $(D_{\perp} - D_{\parallel})/D_{\parallel}$ after the maximum at λ between two and three rapidly drops to about 20 per cent at $\lambda = 5.2$, the highest draw ratio obtainable with the sample (*Figure 13*).

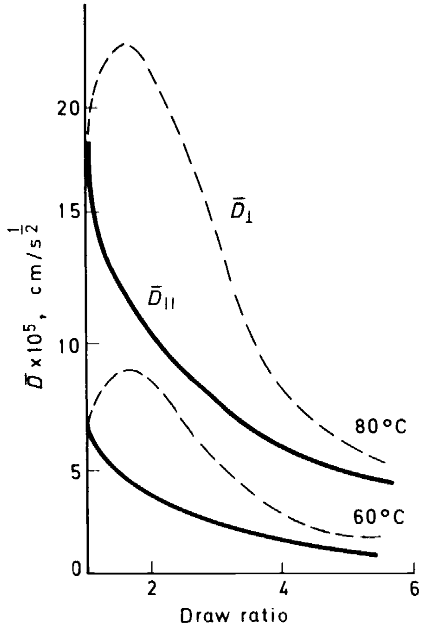

Figure 13. Penetration coefficients $\bar{D}_{\perp}$ and $\bar{D}_{\parallel}$ of Nylon 6 monofilaments drawn at 60 and 80 °C as function of draw ratio λ. The diffusion coefficients D are half the square of $\bar{D}$. After Takagi[15].

The initial increase is easily understandable on the basis of the fibre model as shown in *Figure 2* if one considers the initial stages of deformation of spherulitic material up to the complete transformation into fibrous structure. Small-angle x-ray investigation of polypropylene films[55] has shown that the deformation of stacks of lamellae very much depends on lamella orientation. Lamellae parallel to the applied tensile stress are compressed and tend to deform by chain tilt which makes the lamellae thinner. Very little deformation obtains with lamellae at 45° where the applied stress produces shear displacement of the lamellae of the stack without any detectable change of their dimensions. Lamellae perpendicular to the stress are pulled apart and become even physically separated thus creating holes extending in the plane perpendicular to the stress. As a consequence of such deformation one expects a reduction of diffusivity in the axial and some increase in radial direction, in good agreement with experimental data.

In approaching the fully fibrous structure one has to consider the diffusion through the amorphous regions of fibrils and microfibrils. As a consequence of the tendency of lateral fit of the crystal blocks one obtains well coherent amorphous layers extending over the whole cross section of the fibril. The same effect may favour the continuation of the layer also in the transition to the adjacent fibrils. One has in the radial direction a relatively uninterrupted passage through the whole sample ($\tau = 1$) which, however, yields a low $D_\perp$ because the amorphous material with the great many taut tie molecules exhibits a so much reduced permeability. The situation is completely different in the axial direction where the diffusion path is interrupted by crystal blocks. Only very tiny passages are available along the boundary of adjacent microfibrils. How narrow these regions between adjacent crystal blocks are can be concluded from the tendency of the blocks to fit each other laterally. It is indeed almost the same situation as one observes between adjacent mosaic blocks of a folded chain lamellae where the concentration of crystal defects is enough for the interruption of crystal coherency but not for the development of a truly amorphous layer. As a consequence the axial diffusive transport through such passages between crystal blocks of adjacent microfibrils is more hampered than that through amorphous layers in the radial direction, yielding $D_\parallel < D_\perp$.

The production during plastic deformation of fibrous structure of a great many interfibrillar taut tie molecules which are all located in the boundaries between adjacent microfibrils reduces $D_\perp$ more than $D_\parallel$. They mainly increase much more the hindrances to radial diffusion in the amorphous layers by disproportionate increase of the fraction of taut tie molecules than in the axial direction where they act as additional crystal defects. As a consequence $D_\perp$ decreases faster than does $D_\parallel$ so that in the case of Nylon 6 they become almost equal at the maximum draw ratio obtainable.

HARD ELASTOMERS

A very peculiar morphology can be obtained by melt extrusion in a very sharp temperature gradient under high stress[3, 56, 57] or by drawing of liquid swollen spherulitic films[58]. The material consists in the former case of stapled lamellae oriented perpendicular to the machine direction (*Figure 14*). The staple points permit elastic deformation of the free lamella sections between them. Thus extremely large reversible deformations, up to 300 per cent, are possible creating a few hundred Å thick flat holes between stapled lamellae. The material deforms like an accordion. The observed extreme

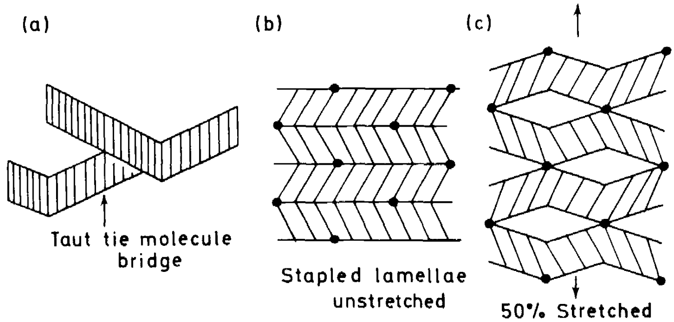

Figure 14. Model of hard elastomer. After Clark[59].

elasticity is of energetic and not of entropic origin as in rubbers. The formation of the great many submicroscopic holes increases the surface area and hence the accessibility of the material to gases and liquids. The consequence of the porous morphology of the stretched sample is a Knudsen-type flow yielding a permeability up to 10^7 times larger than ever observed in a homogeneous polymer membrane.

Morphologically and as far as transport properties are concerned, a fibre as spun with highly oriented cylindrites and an overannealed fibre with conspicuous lamella structure are in many respects very similar to an extruded unstretched ($\lambda = 1$) hard elastomer. Particularly conspicuous is the anisotropy of diffusion, $D_\perp > D_\parallel$, as a consequence of parallel packing of lamellae perpendicular to the machine direction.

The liquid swollen films yield upon drawing a similarly porous material with similar mechanical properties as an extruded hard elastomer but much less chain or lamella orientation. The permeability is inversely proportional to the square root of molecular weight of the diffusing gas or vapour as expected for flow through very narrow pores. The swelling liquid has so much mobilized the amorphous layers that shearing translation and physical separation of lamellae obtains with ease during drawing with less orientation of the crystal lattice as expected in an affine transformation. The forces transmitted through the softened amorphous layers are too small for initiating large-scale plastic deformation or even crack and microfibril formation. As a consequence of the large local variation of deformation caused at this stage by the local variation of lamella orientation, as amply demonstrated with polypropylene at low draw ratio, the drawn material has a more inhomogeneous structure but also a better lateral cohesion.

In both cases the material can be thermoset at any degree of deformation thus preserving the transport characteristics and geometry corresponding to this deformation. It will not return to the original dimensions if not heated above the temperature of thermosetting. Below this temperature it is a highly elastic material with excellent mechanical recovery. Plastic deformation before or after thermosetting, however, partially interrupts the channels in a similar manner as shown in *Figure* 5 and hence reduces the permeability.

These two materials are an excellent example for the demonstration of the importance of morphology and complete failure of the crystallinity and orientation as parameters for the description of transport or mechanical properties. In spite of the difference in crystal orientation they have very much the same macroscopical properties, high rubber-like elasticity and high permeability. The former material has practically the same density, i.e. crystallinity, and orientation of crystalline and amorphous component as a fibre as spun or an annealed drawn fibre without any trace of similarity in elastic and transport properties between them. The same applies to the solvent drawn material which in crystallinity if not in orientation of crystals and amorphous regions is practically identical with a relaxed spherulitic sample.

CONCLUSIONS

The transport properties of a crystalline polymer depend so much on morphology that they cannot be described by the generally used parameters—crystallinity and orientation—in spite of the fact that practically all the sorption and diffusion takes place in the amorphous component and that orientation of the amorphous component very much affects the sorption and diffusion. One has indeed to distinguish three basically different morphological cases: unoriented spherulitic material, fibrous material, hard elastomer.

Unoriented spherulitic material can be fairly well characterized by crystallinity. The presence of the crystals lengthens the diffusion path thus reducing the diffusion coefficient by a tortuosity factor $\tau < 1$ which may be represented by $(1 - \alpha)^m$ with m between 0.3 and 1. Quenched sample may show a smaller S_a and D_a than well annealed material. Crystallinity determination can be difficult if there is more than one crystalline phase present. Any holes make a reasonable description of the system illusory.

Drawn samples with the highly anisotropic morphology exhibit an extreme reduction and some anisotropy of transport properties. As a consequence of the presence of a large fraction of taut tie molecules, the amorphous regions exhibit a drastically lower sorption and diffusion coefficient than the relaxed melt. Upon deformation of the fibrous structure the number of tie molecules increases dramatically in Nylon and only marginally in linear polyethylene. Upon annealing the fraction of taut tie molecules diminishes and so does the reduction of transport properties. In a fully developed fibrous structure a relatively good correlation exists between S, D, P, and amorphous orientation which indeed reflects the fraction of taut tie molecules present. A detailed consideration of the newly formed fibrous and the still remaining plastically deformed spherulitic fractions is needed for the description of samples at low draw ratio.

Hard elastomers exhibiting an almost rubberlike elasticity as a consequence of bending of stapled individual lamellae display an enormous free surface, and a dramatic enhancement of permeability as a consequence of the great many holes formed upon deformation. The Knudsen-type flow yields a current density proportional to the square root of inverse molecular weight of the gas. The transport properties at any stretching can be fixed by thermosetting.

ACKNOWLEDGEMENT

The author thanks the Camille and Henry Dreyfus Foundation for the generous support of this work.

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