Oxygen Barrier Properties of Copolyesters Containing a Mesogenic Monomer

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ABSTRACT: Thermal properties and solid-state structure of copolyesters based on smectic poly(diethylene glycol 4,4′-bibenzoate) (PDEGBB) and non-liquid crystalline poly(diethylene glycol isophthalate) (PDEGI) were characterized previously. The present study examined the oxygen transport properties and free volume characteristics of quenched films with 10−50 mol % isophthalate. Isophthalate was not accommodated in the smectic lattice; as a result, copolymerization effectively disrupted the LC character. The estimated smectic volume fraction of PDEGBB was 0.84. Copolymerization with 10 and 20 mol % isophthalate decreased the smectic fraction to 0.59 and 0.16, respectively. The copolymer with 30 mol % isophthalate did not exhibit any LC character. Decreasing density and increasing free volume hole size accompanied the loss of LC features. Oxygen permeability also increased due to increases in both solubility and diffusivity. Oxygen solubility of LC glasses conformed to a two-phase model consisting of a less permeable smectic lattice phase and permeable interlamellar and interdomain amorphous phase. The calculated solubility of the smectic lattice was about $^1/_3$ that of the amorphous phase. A simple model for sorption and diffusion, which considered free volume holes arranged on a cubic lattice, was successfully tested against experimental measurements. Taking hole size from PALS and lattice spacing from the activation energy for diffusion, the model gave good correlations with oxygen solubility, fractional free volume (FFV), and specific volume.

Introduction

There exists a growing demand for high barrier packaging materials. As compared to most thermoplastics, aromatic liquid crystalline polymers (LCPs) stand out because of remarkably low gas permeability.[1−5] The complex phase transitions and morphologies typical of LCPs present a challenge to understanding and modeling the chemical and structural origins of low gas permeability in LCPs. The challenge was recently addressed in a study of smectic poly(diethylene glycol 4,4′-bibenzoate) (PDEGBB).[6] In the solid state, PDEGBB can be systematically varied from an LC glass to a crystallized LC glass. A hierarchical structural model for smectic PDEGBB was proposed on the basis of the combined results of atomic force microscopy (AFM) and wide-angle X-ray diffraction (WAXD) in which mesogens organized into smectic layers, stacks of layers formed wavy lamellae, and assembles of lamellae defined domains. The structural model provided the basis for understanding the excellent oxygen barrier of PDEGBB and revealed a liquid crystalline state intermediate between the permeable amorphous glass and the impermeable 3-dimensional crystal.

Copolymerization is widely used to extend the structure−property spectrum of polymers in general.[7] Efforts to copolymerize a mesogenic monomer with a nonmesogenic monomer have focused primarily on reducing the melting temperature in order to facilitate processing.[8,9] It can be anticipated that copolymerization with a nonmesogenic monomer will compromise the outstanding barrier properties of LCPs to some extent. However, this aspect has not been examined.

It is appropriate to extend the previous study of smectic PDEGBB to examine the gas permeability of its copolymers that incorporate a nonmesogenic monomer. Isophthalate is chosen for this purpose because the nonlinear comonomer effectively disrupts the LC order of PDEGBB.[8,9] Indeed, copolymers with 30% isophthalate or more are amorphous. The thermal properties and solid-state structure of PDEGBB, poly(diethylene glycol isophthalate) (PDEGI), and copolymers with up to 50 mol % isophthalate are described in a companion paper.[10] The present study presents the oxygen barrier properties of this family of polyesters and proposes structural models based on findings in the companion study.

Materials and Methods

Poly(diethylene glycol 4,4′-bibenzoate) (PDEGBB), its copolymers with 10, 20, 30, 40, and 50 mol % isophthalate, and poly(diethylene glycol isophthalate) (PDEGI) were provided by KoSa (Spartanburg, SC) in the form of extruded pellets. The copolymers are identified as PDEGBB-*x*I, where *x* is the mole percent isophthalate. The synthesis and characterization are described in the companion paper.[10]

Pellets were compression molded into films 180−200 μm thick as described previously.[10] The films were quenched from the isotropic melt into iced water. Because of the extremely rapid isotropic to liquid crystalline transition, PDEGBB and PDEGBB-10I could not be quenched to the completely amorphous state. Quenched films of copolymers with more than 30 mol % isophthalate were amorphous.

Density was measured at 23 and 6.7 °C with a density gradient column constructed from an aqueous solution of calcium nitrate in accordance with ASTM-D 1505 method B. The column was calibrated with glass floats of known density. Small pieces of film (~25 mm^2) were placed in the column and allowed to equilibrate for 30 min before measurements were taken. The accuracy was ± 0.0009 g cm^{-3}.

Positron annihilation lifetime spectroscopy (PALS) was performed using a conventional fast−fast coincidence system. The instrumentation and procedures for data analysis were described previously.[11]

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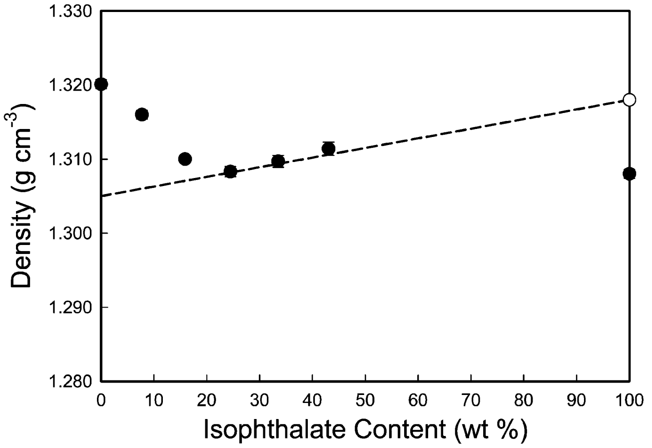

Figure 1. Relationship between density and isophthalate content as weight percent.

Oxygen flux $J(t)$ at 0% relative humidity and 1 atm pressure was measured with a MOCON OX-TRAN 2/20. The instrument was calibrated with NIST-certified Mylar film of known oxygen transport characteristics. The temperature in the diffusion cell was varied from 10 to 40 °C with an accuracy of ±0.1 °C. The transport measurements below 10 °C were conducted in a remote cell with the temperature controlled by a thermal bath using ethanol as coolant. Specimens were carefully conditioned as described previously[12] in order to obtain the non-steady-state oxygen flux from which the diffusivity D was determined. To obtain the diffusivity D and to accurately determine the permeability P, the data were fit to the solution of Fick's second law with appropriate boundary conditions

$$J(t) = \frac{Pp}{l}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(-\frac{D\pi^2 n^2 t}{l^2}\right)\right] \qquad (1)$$

As indicated previously,[12] the error in determining the two fitting parameters, P/l and D/l^2, was estimated not to exceed 2%. Therefore, the accuracy of P and D was determined mainly by the accuracy of the average thickness measurement. The average thickness l of each specimen was determined as $l = W(A\rho)^{-1}$, where W is the specimen weight, A is the specimen area, and ρ is the density. All the specimens were stored in the freezer, and all the analyses were accomplished within 4 weeks of preparation in order to avoid possible aging effects.

Results and Discussion

Density and Free Volume Hole Size. The relationship between density at 23 °C and composition as weight fraction isophthalate is shown in Figure 1. A decrease in density accompanied the loss in LC character as the isophthalate content increased from PDEGBB to PEDGBB-30I. The density of non-LC glasses, PDEGBB-30I, PDEGBB-40I, and PEDGBB-50I, defined a linear dependence on composition. The linear relationship did not extend to the measured density of PDEGI, which was in the rubbery state at 23 °C. Using the density of the glass at 6.7 °C of 1.3241 g cm^{-3} (Table 1) and a thermal expansion coefficient for the glass of $e_g = 2.3 \times 10^{-4}$ cm^3 g^{-1} C^{-1},[13] the density of glassy PDEGI at 23 °C was estimated to be 1.318 g cm^{-3}. This point is included in Figure 1 where it lies on the additivity relationship defined by the non-LC glassy copolymers. Extrapolation gave the amorphous density of PDEGBB as 1.305 g cm^{-3}, which is significantly lower than the density of smectic PDEGBB, 1.320 g cm^{-3}. Similarly, the amorphous density of PDEGBB-10I and PDEGBB-20I by extrapolation was 1.306 and 1.307 g cm^{-3}, respectively.

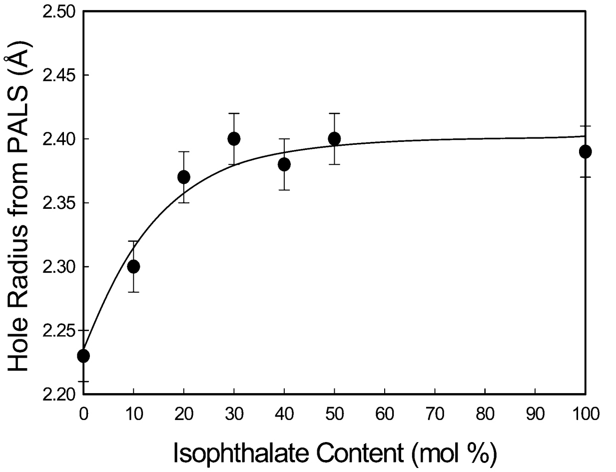

Figure 2. Relationship between free volume hole radius from PALS and isophthalate content as mole percent.

Loss in LC order was accompanied by a significant increase in the free volume hole radius as determined by PALS (Figure 2). The hole radius increased from 2.23 Å for PDEGBB to 2.40 Å for PDEGBB-30I, paralleling the loss in LC character. Further increase in isophthalate content did not significantly affect the hole radius (Table 1). Smaller free volume hole size has been reported for other LCPs[14,15] and seems to be characteristic of the LC state in polymers. Relatively denser molecular packing of LC glasses due to smaller hole size and possible smaller hole density was manifest as higher density.

Oxygen Transport Properties. Typical experimental curves in Figure 3 describe the oxygen flux $J(t)$ through PDEGBB, PDEGI, and PDEGBB-I copolymers at 23 °C. The flux curves were normalized to a film thickness of 200 μm in order to facilitate comparisons among specimens that varied somewhat in thickness. Careful conditioning and appropriate choice of specimen thickness resulted in excellent resolution of the various features of the time dependence. The initial increase in oxygen flux reflected non-steady-state diffusion. This part of the curve was controlled mainly by the diffusivity D. As the permeant concentration in the specimen

Table 1. Physical Properties of PDEGBB-I Copolymers

samples	DSC T_g (°C)	density (g cm^{-3}) 23 °C	density (g cm^{-3}) 6.7 °C	P^a [cm^3 (STP) cm m^{-2} atm^{-1} day^{-1}]	D^a (10^{-13} m^2 s^{-1})	S^a [cm^3 (STP) cm^{-3} atm^{-1}]	S^b [cm^3 (STP) cm^{-3} atm^{-1}]	free vol hole radius (Å)
PDEGBB	42	1.3201	1.3269	0.0318 ± 0.0004	2.6 ± 0.1	0.0142 ± 0.0002	0.0142 ± 0.0002	2.23
PDEGBB-10I	39	1.3160	1.3239	0.0479 ± 0.0008	2.7 ± 0.1	0.0202 ± 0.0004	0.0212 ± 0.0003	2.30
PDEGBB-20I	36	1.3095	1.3160	0.095 ± 0.002	3.5 ± 0.1	0.0314 ± 0.0007	0.0328 ± 0.0004	2.37
PDEGBB-30I	34	1.3083	1.3142	0.110 ± 0.002	3.6 ± 0.1	0.0354 ± 0.0011	0.0372 ± 0.0006	2.40
PDEGBB-40I	32	1.3097	1.3150	0.114 ± 0.002	3.8 ± 0.1	0.0350 ± 0.0006	0.0391 ± 0.0003	2.38
PDEGBB-50I	28	1.3114	1.3168	0.118 ± 0.003	3.9 ± 0.1	0.0351 ± 0.0007	0.0405 ± 0.0004	2.40
PDEGI	16	1.3089	1.3241	0.145 ± 0.012	4.4 ± 0.2	0.0381 ± 0.0018	0.0396 ± 0.0011	2.39

[a] Tested at 23 °C. [b] Tested at $T_g - 18$ °C.

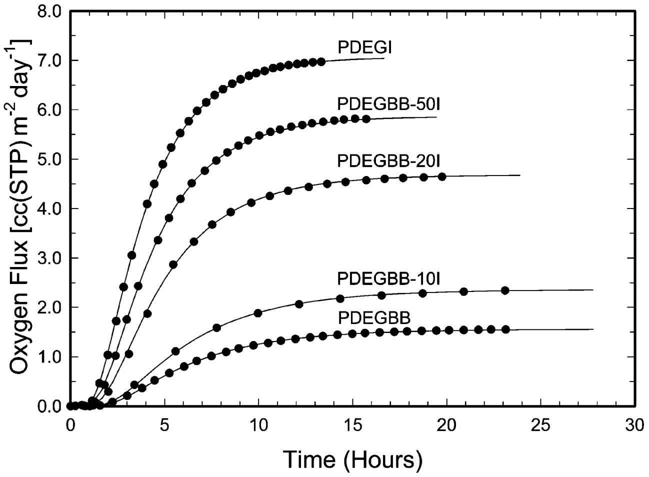

Figure 3. Experimental $J(t)$ data for PDEGBB, PDEGI, and their copolymers tested at 23 °C and the fit to eq 1.

reached a constant distribution, the flux reached the steady-state value J_0. This value, normalized to the film thickness l and the permeant gas pressure p, defined the permeability $P = J_0lp^{-1}$.

Comparison of flux curves indicated that incorporation of isophthalate affected both the non-steady-state and steady-state parts of the flux curve. The non-steady-state region sharpened slightly (faster diffusion), and the steady-state flux increased significantly (higher permeability). The fit to the solution of Fick's second law (eq 1) is included with the experimental points in Figure 3. The fit was equally good for all the experiments in the study. The two fitting parameters, P/l and D/l^2, were used to obtain diffusivity D and to accurately determine the permeability P. Solubility S was calculated from the relationship $S = PD^{-1}$.

The effect of comonomer composition on the oxygen barrier properties at 23 °C is shown in Figure 4. The results are compiled in Table 1. Oxygen permeability of PDEGBB was more than 1 order of magnitude lower than that of amorphous poly(ethylene terephthalate) (PET).[6] As incorporation of isophthalate reduced LC order, P increased considerably from 0.0318 for PDEGBB to 0.110 cm^3 (STP) cm m^{-2} day^{-1} atm^{-1} for PDEGBB-30I. Higher permeability was due to increases in both D and S, with S increasing more than D. This is consistent with literature reports[1-3] that very low gas solubility largely accounts for the exceptionally low gas permeability of LCPs compared to non-LC polymers. The P, D, and S values for non-LC glasses, PDEGBB-30I, PDEGBB-40I, and PDEGBB-50I, were virtually constant, independent of isophthalate content. At 23 °C, PDEGI was in the rubbery state, which accounted for higher P, D, and S values compared to the glassy copolymers.

Oxygen Sorption and Excess Free Volume. Interpretation of the transport parameters obtained at 23 °C was complicated by the proximity of the test temperature T_{test} to the polymer T_g, where major changes in the mechanism of gas transport occur. To understand the effect of glass transition, transport parameters were determined over a temperature range that encompassed the T_g. In Figure 5, the solubility is plotted relative to the glass transition temperature ($T_g - T_{test}$) over a large temperature range. The plot includes data obtained at 23 °C for numerous aromatic copolyesters taken from previous publications[16,17] and extends the analysis through the glass transition, into the rubbery amorphous region, using results for PDEGBB-30I, PDEGBB-40I, and PDEGBB-50I tested at 23 °C and results for PDEGI tested from −11 to 40 °C.

In the glassy state, oxygen sorption at low pressure is the process of filling holes of excess free volume,[18] as reflected by the right branch in Figure 5. The amount of excess hole free volume decreases as the temperature

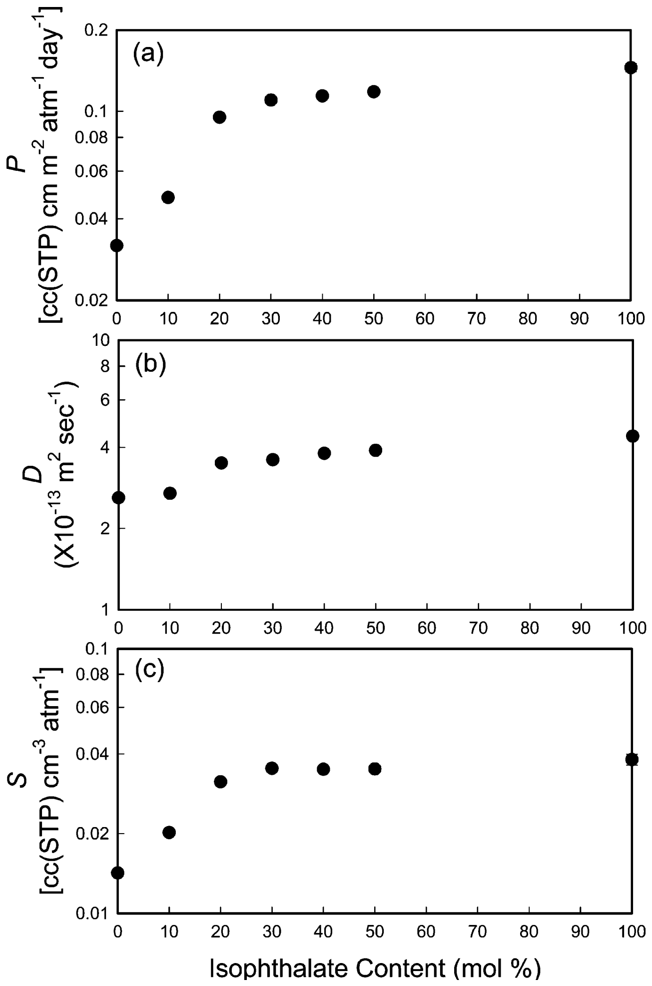

Figure 4. Effect of isophthalate content as mole percent on oxygen transport parameters at 23 °C: (a) permeability, (b) diffusivity, and (c) solubility.

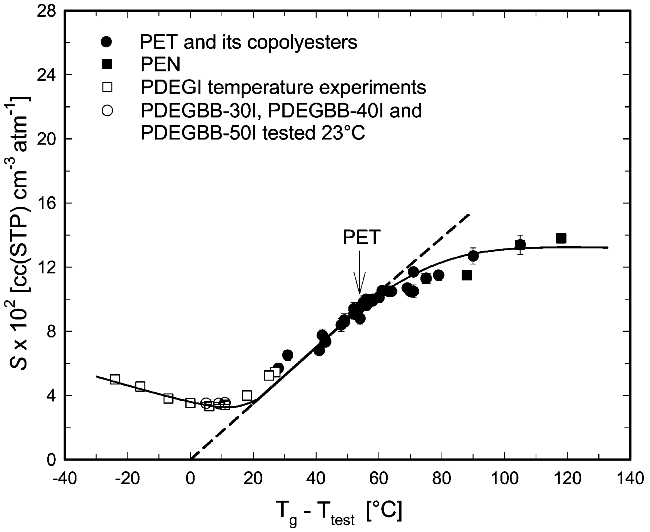

Figure 5. Relationship between S and the difference ($T_g - T_{test}$). Solid symbols taken from refs 16 and 17.

approaches T_g. This appears in Figure 5 as a linear relationship between S and ($T_g - T_{test}$) in the temperature region 20 °C ≤ ($T_g - T_{test}$) ≤ 60 °C. Extrapolation gives zero solubility at $T_{test} = T_g$ where the excess free volume is expected to disappear.[19] The slope gives the density of sorbed oxygen in the free volume holes.[16] Inclusion of data obtained at temperatures other than 23 °C assumes that the density of sorbed oxygen does not change very much over the small temperature range probed. Further from T_g, the decreasing slope of the relationship between S and ($T_g - T_{test}$) for $T_g - T_{test} \geq$ 60 °C suggests that the excess hole free volume approaches a constant value above the second-order transition at T_g − 60 °C.[16,20,21] At temperatures above T_g, Henry's law sorption dominates as reflected by the left branch in Figure 5. The contribution of Henry's law sorption is responsible for deviation from the linear relationship as T_{test} approaches T_g. Significant deviation beginning at about ($T_g - T_{test}$) = 20 °C reveals the considerable breadth of the glass transition region. As T_{test} passes through T_g, S levels off and then increases as the polymer reaches the rubbery state ($T_g - T_{test} <$ 0).

It is now possible to determine the effect of LC order on S by comparing solubilities of an LC glass and a non-LC glass at the same temperature relative to T_g, i.e., the same value of $T_g - T_{test}$, again assuming that the temperature range is small and the density of sorbed oxygen does not change. Oxygen solubility was determined at T_g − 18 °C where T_g was measured from DSC (Table 1). The solubility of oxygen in amorphous PDEGBB-I glasses at $T_g - T_{test}$ = 18 °C was about 0.039 cm^3 (STP) cm^{-3} atm^{-1}. At $T_g - T_{test}$ = 18 °C, PDEGBB had S of 0.0142 cm^3 (STP) cm^{-3} atm^{-1}. The effect of LC order in PDEGBB was to decrease S by a factor of 2.8 compared to a normal glass. Similarly, LC order decreased S by a factor of 1.7 in PDEGBB-10I and by a factor of only 1.1 in PDEGBB-20I.

Two-Phase Model for Oxygen Sorption. Structural models based on two phases[12,22,23] or three phases,[24,25] each phase having a different gas solubility, have been useful for describing gas solubility of crystalline polyesters. It seems reasonable to consider a similar approach to describing gas solubility of LC polyesters. A two-phase structural model for smectic PDEGBB and PDEGBB-I copolymers was proposed previously on the basis of the combined results of atomic force microscopy (AFM) and wide-angle X-ray diffraction (WAXD).[6,10] In this model, the ordered LC phase consists of more or less extended DEGBB chains assembled with the mesogenic bibenzoate groups organized into smectic layers with the spacing of 15.6 Å. Stacks of smectic layers form lamellae. Assemblies of lamellae constitute domains on the micron size scale. The interlamellar regions and the domain boundaries constitute a disordered, amorphous phase.

The resulting two-phase sorption model for LC polymers considers a smectic lattice phase and an interlamellar and interdomain amorphous phase. In contrast to the two-phase model for conventional crystalline polymers, where the ordered phase is considered impermeable, both phases of the LC polymer are permeable to oxygen with the LC phase having lower gas solubility than the amorphous phase.[6] Application of the simple two-phase sorption model requires that oxygen solubility in each of the phases not change as copolymerization with isophthalate reduces the amount of LC character. To justify this assumption, it is noted that the layer spacing in the WAXD pattern of PDEGBB is not affected by copolymerization, suggesting that isophthalate groups are excluded from the smectic layers and copolymerization reduces the amount of smectic phase without altering the basic LC structure. It seems reasonable to assume that gas solubility in the smectic phase is also unaltered. There is no direct experimental evidence to indicate how changing smectic fraction affects the disordered phase. Indeed, it is known that crystallization causes dedensification of the amorphous phase of PET and PEN, leading to increased oxygen solubility in the amorphous phase.[12,24,25] However, crystallization of a BB copolymer closely related to PDEGBB-I does not alter amorphous phase specific volume or oxygen solubility[23] and thereby supports the assumption of constant disordered phase oxygen solubility.

The resulting relationship between solubility and volume fraction smectic phase ϕ_s is

$$S = S_s\phi_s + S_a(1 - \phi_s) \qquad (2)$$

where S_s is the oxygen solubility in the smectic lattice, S_a is the oxygen solubility in the amorphous regions, taken as 0.035 cm^3 (STP) cm^{-3} atm^{-1}, and S is the solubility measured at 23 °C (Table 1). The volume fraction smectic phase can be calculated from density according to

$$\phi_s = \frac{\rho - \rho_a}{\rho_s - \rho_a} \qquad (3)$$

where ρ is the density measured at 23 °C, ρ_s is the density of the smectic lattice, and ρ_a is the amorphous phase density. Although ρ_a can be obtained for each of the LC polymers by extrapolation as shown in Figure 1, ρ_s is not known. However, ρ_s is assumed to be the same for PDEGBB and smectic copolymers based on the constant smectic layer spacing. Also, the density of the LC phase of PDEGBB is reasonably assumed to be intermediate between the extrapolated amorphous phase density of 1.305 g cm^{-3} and the crystal density of 1.371 g cm^{-1}.[6] A value of 1.323 g cm^{-3} was chosen for ρ_s. Although the choice was somewhat arbitrary, it seems reasonable. For comparison, the mesomorphic phase density of cold drawn PET is estimated to be 1.371 g cm^{-3},[26] similarly intermediate between the amorphous phase density of 1.337 g cm^{-3} and the defective crystal phase density of 1.48 g cm^{-3}.[27] Furthermore, from the known layer spacing of 15.6 Å and assuming hexagonal packing of the mesogens, a density of 1.323 g cm^{-3} corresponds to an interchain spacing of about 4.39 Å, in reasonable agreement with the value of 4.33 Å from the broad WAXD reflection.[6]

The smectic volume fraction ϕ_s from eq 3 was 0.84 for PDEGBB. For comparison, a slightly higher value of 0.90−0.95 was obtained for the volume fraction nematic phase in a copolyester of hydroxybenzoic acid (HBA) and 27 mol % 2,6-hydroxynaphthoic acid (HNA).[3,4] From ϕ_s and the measured ΔH_{S-I} of 17 J g^{-1} for PDEGBB,[10] ΔH^{o}_{S-I} for the smectic-to-isotropic transition of PEDGBB was determined to be 20 J g^{-1}. Copolymerization with isophthalate rapidly reduced the volume fraction of smectic phase to 0.59 for PDEGBB-10I and 0.16 for PDEGBB-20I. Detection of the small amount of LC character in quenched PDEGBB-20I film, which was not revealed by wide-angle X-ray diffraction or thermal analysis,[10] illustrated the sensitivity of oxygen transport as a structure probe.

The corresponding oxygen solubility of the smectic lattice S_s from eq 2 is 0.010, 0.012, and 0.012 cm^3 (STP) cm^{-3} atm^{-1} for PDEGBB, PDEGBB-10I, and PDEGBB-20I, respectively. The average value for S_s of 0.011 cm^3 (STP) cm^{-3} atm^{-1} is about $^1/_3$ that of the amorphous phase, 0.035 cm^3 (STP) cm^{-3} atm^{-1}. Lower solubility translates as lower free volume of the smectic phase. Smaller hole size as measured by PALS, and possibly smaller hole density as well, are molecular origins of the densification. Overall, the simple two-phase model provides a consistent and reasonable description of the copolymers in terms of oxygen solubility, density, and fraction of smectic phase.

Oxygen Diffusivity. Although lower gas permeability of LCPs is primarily the result of lower gas solubility, lower diffusivity also contributes (Table 1). To estimate the effect of LC character on D, it is noted that D of the amorphous glassy copolymers is approximately independent of comonomer composition and equal to 3.8×10^{-13} m^2 s^{-1} (Figure 4). Assuming that amorphous glassy PDEGBB has the same D as the copolymers, comparison with D of smectic PDEGBB of 2.6×10^{-13} m^2 s^{-1} indicates that LC order decreased D by a factor of 1.5. This is less than the factor of 2.8 reduction for oxygen solubility.

Diffusivity of gases in polymers typically follows the Arrhenius relationship for an activated process

$$D = D_0 \exp\left[-\frac{E_D}{RT}\right] \tag{4}$$

where D_0 is a preexponential factor and E_D is the activation energy. Permeability embodies the combined contributions of D and S. The temperature dependence of P is empirically analyzed according to

$$P = P_0 \exp\left[-\frac{E_P}{RT}\right] \tag{5}$$

where P_0 is a preexponential factor and E_P is the apparent activation energy for permeation. When plotted as in Figure 6, the temperature dependencies of D and P for PDEGI showed a change in slope in the vicinity of T_g, indicating a change in the diffusion mechanism.

Gas diffusion through polymers in the glassy state is generally viewed as taking place by discrete jumps. The jump motion proceeds by formation of a channel between two neighboring holes of static free volume. In contrast, rapid redistribution of free volume in the rubbery state suggests that the diffusing molecule is carried along by density fluctuations in the matrix.[28] Diffusion in the glassy state is typically characterized by lower activation energy.[29-31] The difference is about a factor of 2 for PDEGI with E_D of 39.5 kJ mol^{-1} in the glassy state compared to 68.3 kJ mol^{-1} above T_g (Figure 6). The corresponding values of the prefactor expressed as ln D_0 (D_0 in 10^{-13} m^2 s^{-1}) are 17.2 and 29.2 for oxygen diffusion in glassy and rubbery PDEGI, respectively. The large difference in D_0 is ascribed to significantly lower entropy of activation in the glass compared to that of the rubbery state.[30,31] A plot of ln D_0 vs E_D shows that the so-called linear free energy rule, which is observed for many glassy and rubbery polymers,[32,33] also holds for PDEGBB-I copolymers and other aromatic polyesters (Figure 7). Indeed, the relationship appears to cover a broad range of glassy, crystalline, oriented, and LC polyesters. The slope of 3.2×10^{-4} m^2 mol s^{-1} J^{-1} is consistent with literature reports.[32,33]

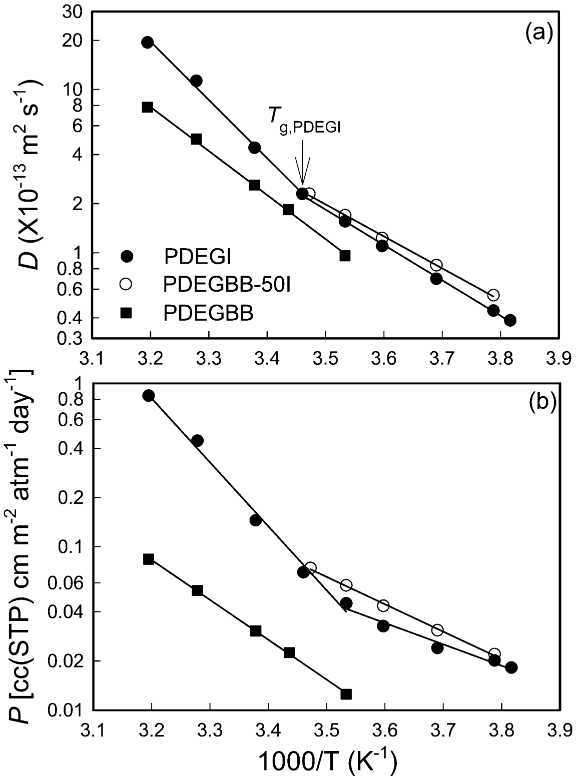

Figure 6. Temperature dependence of P and D for PDEGBB, PDEGBB-50I, and PDEGI.

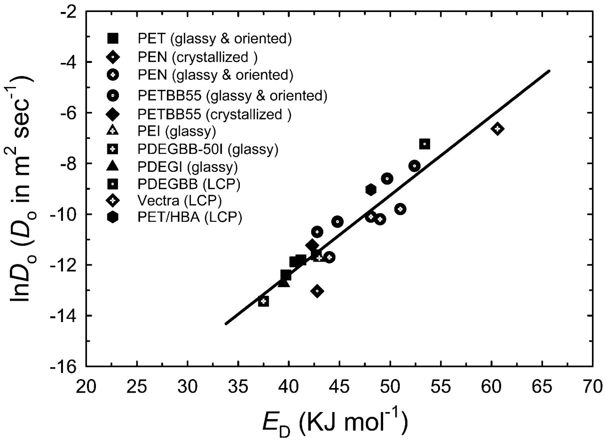

Figure 7. Linear relationship between ln D_0 and E_D including data from the literature for various aromatic polyesters. Data taken from Table 2 and ref 37.

Diffusivity is determined by the frequency ω with which the diffusing molecule makes a successful jump of length α in accordance with[34]

$$D = \frac{1}{6}\alpha^2\omega \tag{6}$$

The jump length can be estimated from E_D according to a mechanistic interpretation for diffusion of simple gases proposed by Meares.[31] The energy to activate a diffusional jump equates to the energy required to break the physical bonds between polymer segments and

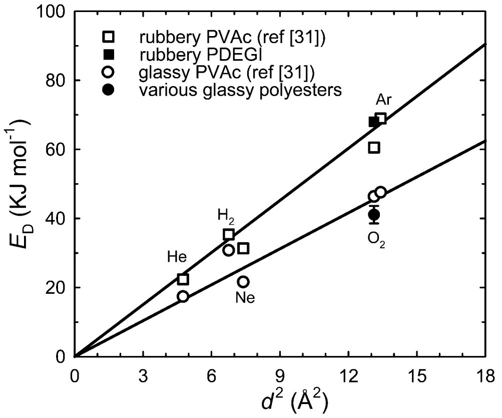

Figure 8. Dependence of E_D on the square of the permeant diameter for simple gases.

create a channel of cross-sectional area $\pi d^2/4$ and length α

$$E_D = \frac{1}{4}\pi d^2 \alpha CED N_A \tag{7}$$

Here E_D is the activation energy for diffusion in J mol^{-1}, d is the collision diameter of the penetrant gas in m, α is the jump length in m, *CED* is the cohesive energy density of the polymer in J m^{-3}, and N_A is the Avogadro number.

Because *CED* and α are not very different for glassy polymers, eq 7 suggests that E_D should be directly proportional to the square of the penetrant diameter. This relationship has been established for diffusion of simple gases through various polymers[35] and is illustrated in Figure 8 with data taken from the literature for poly(vinyl acetate).[31] All the glassy polyesters in Table 2 have about the same value of E_D for oxygen diffusion, and the average value is included in Figure 8. On the basis of the excellent fit with the established relationship, use of equation eq 7 to describe oxygen diffusion in glassy polyesters seems reasonable. The value of E_D for rubbery PDEGI conforms to a similar relationship defined previously for rubbery polymers. It should be emphasized that cases exist where the linear relationship between E_D and the square of the permeant diameter does not hold. Deviation tends to occur if the permeant has a high critical point.[36] Swelling of the polymer by the permeant is thought to be the cause.

The jump length α was calculated from eq 7 for PDEGBB, PDEGBB-50I, PDEGI, and for other glassy polyesters including PET, poly(ethylene isophthalate) (PEI), poly(ethylene 2,6-naphthalate) (PEN), and a copolymer of ethylene terephthalate and ethylene 4,4′-bibenzoate (PETBB55).[37] For the calculation, *CED* was obtained from group contributions and the collision diameter of oxygen was taken as 3.47 Å.[38] Similar E_D and *CED* values mean that the diffusional jump length α is about the same for all the glassy polyesters tabulated. Values range from 12.9 to 14.5 Å and are included with the summary of results in Table 2.

Compared to glassy polyesters, E_D for PDEGBB is significantly higher, and the jump length of 18.0 Å is correspondingly higher. Results for other LC aromatic polyesters included in Table 2 suggest that higher E_D, indicative of a longer diffusional jump length, is characteristic of LCPs. It is significant that crystallization of non-LC aromatic polyesters, PETBB55[23] and PEN[24] for example, does not increase E_D compared to the amorphous glass (Table 2). This is because the crystalline phase is impermeable and diffusion only occurs in the amorphous phase according to the simple two-phase model for non-LC crystalline polymers. Thus, E_D is only characteristic of the amorphous phase. In the two-phase LCP model, with high volume fraction of a permeable smectic phase, E_D contains contributions of both phases. A significantly larger E_D value compared to a normal glass reflects participation of the LC phase in the gas transport process. According to eq 6, larger α has the effect of increasing D. The fact that LC character actually decreases D indicates that the jump frequency ω must be much lower in the LC glass than in the amorphous glass.

Diffusional jumping of a gas molecule requires formation of a channel between neighboring holes of static free volume. The frequency of channel formation defines dynamic free volume and derives from accessible conformational changes and segmental motions of the polymer chain. In glassy polymers, it seems reasonable that these thermal rearrangements manifest themselves as sub-T_g relaxation processes. Indeed, a relationship between D and the γ-relaxation, particularly the intensity of the relaxation component associated with gauche conformations of the spacer, was demonstrated previously for PET and copolymers based on PET.[16,17] Motion of gauche conformers appears to be more effective for enabling the jump motion of penetrant molecules between free volume holes.[39] The low gauche fraction of PDEGBB, 0.21 compared to 0.54 for PDEGI, and a small gauche component of the γ-relaxation[10] are qualitatively consistent with low jump frequency.

Lattice Model for Oxygen Transport. A simple lattice hole model, previously demonstrated for glassy

Table 2. Physical Properties of Selected Polyesters

material		density (g cm^{-3})	T_g (°C)	E_D (kJ mol^{-1})	ln D_0[g]	E_P (kJ mol^{-1})	ln P_0[h]	CED (10^8 J m^{-3})	α (Å)	r(PALS) (Å)	FFV from eq 9
glassy polymers	PDEGBB	1.320	42	53.4	22.7	47.5	15.8	5.2	18.0	2.23	0.008
	PDEGBB-50I	1.311	28	37.5	16.5	32.1	10.8	5.1	12.9	2.40	0.023
	PDEGI	1.318[f]	16	39.5	17.2	25.1	7.5	5.1	13.6	2.39	0.023
other glassy polyesters[a]	PEI	1.351	56	43.0	18.2	23.2	7.1	5.5	13.7	2.41	0.023
	PET	1.337	77	39.7	17.5	29.0	10.9	5.4	12.9	2.56	0.028
	PETBB55	1.307	101	42.8	19.2	33.6	13.2	5.3	14.2	2.58	0.029
	PEN	1.328	124	44.0	18.2	29.8	10.2	5.3	14.5	2.59	0.029
crystalline polyesters	PETBB55[b]	1.343		42.3	18.7	35.3	12.9				
	PEN[c]	1.354		42.8	16.9	33.0	10.5				
other LCPs	Vectra[d]	1.405	90	60.6	23.3	40.5	10.1	5.8	18.4		
	PET/HBA[e]	1.390	54	48.1	20.9	43.1	14.2	5.7	14.8		

[a] Reference 37. [b] Reference 23, cold-crystallized at 165 °C for 4.0 h. [c] Reference 24, cold-crystallized at 180 °C for 12.0 h. [d] Reference 1. [e] Reference 2. [f] Estimated (see Figure 1). [g] D_0 in 10^{-13} m^2 s^{-1}. [h] P_0 in cm^3 (STP) cm m^{-2} atm^{-1} day^{-1}.

Table 3. FFV Estimated from Oxygen Solubility, PALS, and Bondi's Group Contribution Method

polymer	density (g cm^{-3})	occupied density $(1.3\nu_w)^{-1}$ (g cm^{-3})	FFV from Bondi group contributions	FFV from oxygen solubility (ref 37, 46)	FFV from PALS eq 9
PDEGBB (LC)	1.320				0.008
PDEGBB-50I (glassy)	1.311	1.384	0.052		0.023
PDEGI (glassy)	1.318	1.389	0.051		0.023
PEI (glassy)	1.351	1.414	0.044	0.027	0.023
PET (glassy)	1.337	1.414	0.054	0.036	0.028
PETBB55 (glassy)	1.307	1.402	0.068	0.040	0.029
PEN (glassy)	1.328	1.422	0.066	0.046	0.029

aromatic polyesters,[37] can test whether the concepts of static and dynamic free volume used to interpret oxygen transport of PDEGBB-I copolymers are reasonable. Spherical holes of excess free volume having radius r are assumed to be arranged on a cubic lattice. This concept is similar to the lattice models used to describe both rubbery and glassy states.[40,41] Sorption is viewed as the process of filling free volume lattice sites, and diffusion is viewed as the process of a gas molecule jumping from one lattice site to a neighboring lattice site.

The lattice jump length α is related to the hole density N_0 as

$$\alpha = \frac{1}{\sqrt[3]{N_0}} \tag{8}$$

Taking the jump length for an amorphous glassy polyester as 13.6 Å (Table 2), a hole density of 4.0×10^{20} cm^{-3} is obtained from eq 8. Various PALS studies, considering either an average hole size[42−44] or a distribution of hole sizes,[45] independently yield the same value for the free volume hole density ($N_0 \cong 4.0 \times 10^{20}$ cm^{-3}) for a wide range of polymers. In addition, the fractional free volume (FFV) can be calculated from the hole density (4.0×10^{20} cm^{-3}) and the hole size r from PALS according to

$$\mathrm{FFV} = \frac{4}{3}\pi r^3 N_0 \tag{9}$$

Values of FFV from eq 9 are in the range 0.02−0.03, except for the much lower value of 0.008 obtained for smectic PDEGBB (Table 3). Additional values of FFV from oxygen solubility are included.[37,46] Slightly lower FFV obtained with PALS suggests that o-positron particles probe less of the free volume than oxygen molecules.

For comparison, FFV of glassy polymers was also calculated by the group contribution method of Bondi,[47] according to

$$\mathrm{FFV} = \frac{\nu - 1.3\nu_w}{\nu_w} \tag{10}$$

where ν_w is the core specific volume from group contributions. The specific volume ν is taken from experimental measurements. The results are compared in Table 3. For glassy polymers, FFV from Bondi's method is about a factor of 2 higher than FFV from PALS; however, the trends with chemical structure are generally the same.

Extending the lattice model to an LC glass, the larger jump length of 18.0 Å for PDEGBB results in a hole density of 1.7×10^{20} cm^{-3} based on eq 8, which is significantly lower than the hole density of 4.0×10^{20} cm^{-3} obtained for an amorphous glass. Smaller hole density in LCPs compared to amorphous glasses has been reported in the literature.[14,15] Taking the hole density of 1.7×10^{20} cm^{-3} and the hole size of 2.23 Å from PALS for PDEGBB (Table 2), the FFV is calculated to be 0.008 from eq 9, which is about $^1/_3$ the FFV calculated for an amorphous glass of 0.023. The FFV can also be obtained from oxygen solubility, $S = \beta\nu FFV$, where β is the slope of the solubility vs specific volume relationship for glassy polyesters and reflects the density of sorbed oxygen in excess free volume holes.[16,46] The FFV ratio from oxygen solubility, using $S = 0.0142$ for smectic PDEGBB and $S = 0.039$ cm^3 (STP) cm^{-3} atm^{-1} for amorphous PDEGBB, is also about $^1/_3$, which suggests that oxygen solubility depends primarily on the amount of excess hole free volume.

The lower FFV of the LC glass compared to that of the amorphous glass is manifest as lower specific volume. It is possible to estimate the difference in specific volume taking into account only differences in free volume hole size r and hole density N_0

$$\frac{\nu_1 - \nu_2}{\nu_1} = 1 - \left[\frac{1 - \frac{4\pi}{3} r_1^{\,3} N_{01}}{1 - \frac{4\pi}{3} r_2^{\,3} N_{02}}\right] \tag{11}$$

where the subscripts 1 and 2 refer to glassy amorphous and glassy smectic PDEGBB, respectively. Assuming that glassy amorphous PDEGBB would have the same hole size as amorphous PDEGBB-I copolymers of 2.40 Å, the decrease in specific volume due to LC order calculated from eq 11 is 1.5%. This is close to the value of 1.1% calculated directly from the density of glassy smectic PDEGBB of 1.320 g cm^{-3} and the extrapolated density of glassy amorphous PDEGBB of 1.305 g cm^{-3} from Figure 1. Considering the simplicity of the lattice model, which incorporates only α from E_D and hole radius from PALS, the model describes free volume concepts of oxygen transport in aromatic polyesters surprisingly well, as demonstrated in comparisons against results obtained independently from gas sorption and specific volume.

Conclusions

Liquid crystallinity is one approach to improving oxygen-barrier properties of polyesters. This study focuses on a series of copolymers based on a mesogenic polymer, poly(diethylene glycol 4,4′-bibenzoate-*co*-isophthalate), and a nonmesogenic polymer, poly(diethylene glycol isophthalate). Because isophthalate is not accommodated in the smectic lattice, copolymerization effectively disrupts the LC character of the polymer, as indicated by thermal analysis and WAXD. A composition of approximately 30 mol % isophthalate separates LC glasses from amorphous ones. Decreasing density and increasing free volume hole size from PALS accompany the loss of LC features.

Significantly lower oxygen permeability of the LC glasses is due to reduced oxygen sorption and, to a lesser extent, to lower oxygen diffusivity. A two-phase structural model consisting of a permeable amorphous phase, which is made up of interlamellar and interdomain regions, and a less permeable smectic phase satisfactorily describes oxygen sorption of LC glasses. Mechanistically, oxygen sorption was viewed as filling of excess free volume holes, in accordance with the general understanding of oxygen sorption in aromatic polyesters. Lower sorption of LC glasses by about one-third was attributed to smaller free volume hole size and lower free volume hole density compared to those of the normal glass.

Oxygen diffusion was viewed as jumping from one free volume hole to another. Lower diffusivity of LC glasses reflected the combined effects of longer jump length, indicated by higher activation energy for diffusion, and lower jump frequency, consistent with dynamic mechanical relaxation behavior. A simple model for sorption and diffusion, which considered free volume holes arranged on a cubic lattice, was successfully tested against experimental measurements. Taking hole size from PALS and lattice spacing from the activation energy for diffusion, the model gave good correlations with measured FFV, free volume hole density, and specific volume.

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