Permeation of Carbon Dioxide in a Thermotropic Liquid-Crystalline Polyester

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SYNOPSIS

The transport properties of a thermotropic liquid crystalline polyester have been analyzed using carbon dioxide as permeant. Carbon dioxide, in the analyzed range of temperature and pressure, gives some information on the phase organization of the system. The structural model compatible with the transport behavior assumes the presence of a disordered phase within the well-ordered liquid crystalline domains. The same structural model was previously suggested on the basis of the transport behavior of methylene chloride vapors in nematic and smectic liquid-crystalline polymers.

INTRODUCTION

The permeation of gases and vapors through polymeric films is an important phenomenon having many different technological applications. However, the study of the transport properties is also an interesting analytical tool useful to obtain structural information. The information is complementary to other experimental techniques, as X-ray diffraction, optical and electron microscopy, and thermal analysis. In fact, as widely reported for the semicrystalline polymers,[1–3] the transport properties are particularly suitable to investigate the microstructural organization of the permeable phase. The molecules of the diffusant can be considered as probes which "see" the organization of the phase where they diffuse. In a semicrystalline polymer, the permeable phase is the amorphous component, and therefore the obtained information mainly regards the microstructure of this component.

Recently we extended this approach to liquid-crystalline polymers. For these systems it is still under discussion if the liquid-crystalline phase is homogeneous or if, within the ordered liquid-crystalline domains, a less ordered or a truly amorphous component is present. We analyzed the transport properties of a nematic main-chain liquid-crystalline polyester, using methylene chloride as permeant.[4] The obtained results give some evidences of the presence of a disordered phase, behaving as permeable component; this component is characterized by specific thermodynamic transport parameters as sorption and diffusion, in strict analogy with the behavior generally shown by the amorphous phase in semicrystalline polymers. Using the same vapor as penetrant, more recently similar evidence was given by the transport properties of a smectic side-chain liquid-crystalline system.[5]

In the present paper we report results regarding the sorption and diffusion of carbon dioxide in the nematic system previously analyzed.[4] The analysis was carried out in a temperature range encompassing the glass transition, and regards two samples differing in the isotropization enthalpy, and therefore in the order degree. The aim was to obtain a more detailed picture of the transport phenomenon and in particular of the transport mode. In fact, the use of noninteracting gases gives information on the structural organization in a scale comparable to the size of the penetrating molecule; it is also a simpler approach in order to investigate the influence of the temperature on the transport properties and to determine some important thermodynamic parameter, like the activation energy of the diffusion and sorption phenomena.

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EXPERIMENTAL

The measurements of gas transport were performed using an equipment described by Koros et al.,[6] and based on the detection of the gas pressure as function of time; the pressure decay gives the quantitative measurement of the gas transferred from the gas phase to the sample, and therefore sorption and diffusion coefficients can be calculated. The pressure transducers had a sensitivity of ± 100 Pa. Measurements were performed in the temperature range 10–60°C.

Dynamic-mechanical relaxation spectra were detected in monoaxial stretching at a frequency of 110 Hz using a Rheovibron viscoelastometer of Toyo Instruments; the temperature range was -100 to 160°C.

MATERIALS

The analyzed polymer has the formula

$$\left[-OOC-(CH_2)_{10}-COO-\left\langle\bigcirc\right\rangle-C(CH_3)=CH-\left\langle\bigcirc\right\rangle- \right]$$
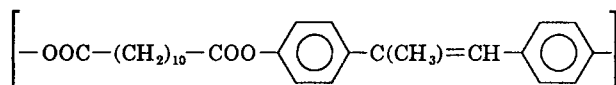
Its liquid-crystal and solid state behavior has been previously described.[7,8] It was prepared by polycondensation in a two-phase (chloroform/water) liquid system. Some variations of the preparation procedure were made,[4] and samples having different isotropization enthalpy were obtained, mainly as a consequence of a different molecular weight distribution. In the present paper two samples are considered, indicated as B(i) and D(i), according to the previous paper.[4] The films used for the analysis of mechanical and transport properties were obtained by pressure molding and rapid quenching to 0°C. The molding temperature was 240°C, which is higher than the isotropization temperature (in the range 205–220°C, depending on the sample). As a consequence of the quenching conditions samples having low crystallinity were expected; however, the shape of the calorimetric curve is affected by crystallization and solid–solid transitions induced by the thermal scanning, and a reliable evaluation of the crystalline content is difficult. As previously reported,[4] the overestimated crystallinity of B(i) is 50%, whereas a relative comparison with D(i) indicates that in this sample the crystallinity is lower by a factor 2. On the other hand, the isotropization enthalpy can be well evaluated, and the obtained values are 17.6 and 10.7 J/g for sample B(i) and D(i), respectively.

DYNAMIC-MECHANICAL ANALYSIS

In Figure 1 the dynamic relaxation spectra for sample B(i) and D(i) are shown. The storage modulus E' and the loss factor[9] tan δ are reported as functions of the temperature. Two transitions are visible in the temperature range -100 to 80°C; the tan δ band related to the transition at lower temperature (-40°C) has the same intensity in the two samples and does not affect the trend of the storage modulus, which presents a constant derivative over all the range -100 to about 40°C. A relaxation mode involving local movements of short sequences must be therefore suggested, and this aspect will be considered in a following paper. The second transition, with a maximum in the range 40–60°C, has a different intensity in the two samples and drastically affects the modulus as shown by the relevant change of derivative.

This trend allows us to assume that this is the glass transition of the system, according to the calorimetric measurements. The different intensity of the tan δ bands and the different values of the modulus for $T > T_g$ are related to the different degree
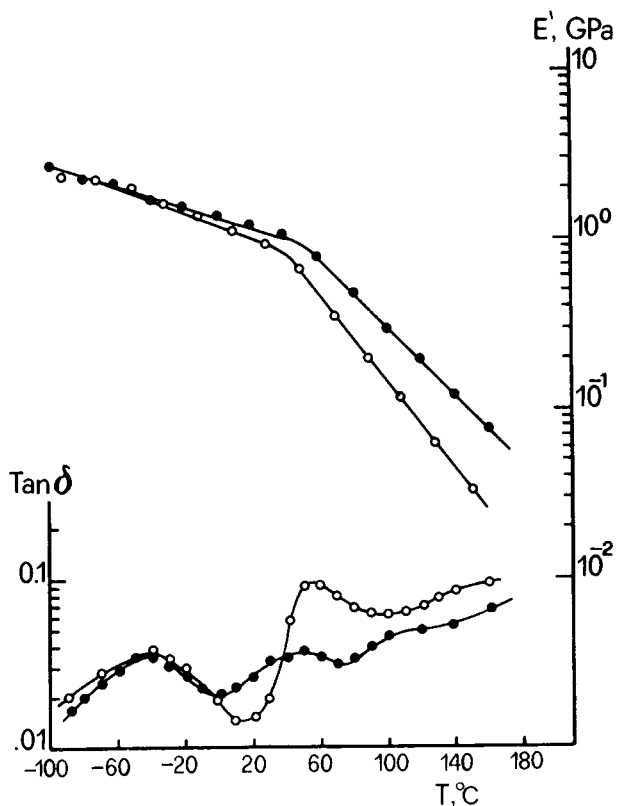
Figure 1 Dynamic-mechanical relaxation spectra. The storage modulus E' and the loss factor tan are reported versus the temperature: ($\bullet$) sample B(i); ($\bigcirc$) sample D(i).

of order, higher in sample B(i), which in fact shows a less intense tan δ band and higher storage modulus. The amplitude of the band gives the amplitude of the transition range that is extended from 10 to about 80°C, with some slight difference in the two samples. At higher temperatures, tan δ shows a positive derivative, indicating that other relaxation mechanisms become active and remain active over all the temperature range; in this range the calorimetric analysis shows a sequence of two solid–solid transitions that, as reported,[7,8] can be attributed to polymorphism phenomena, followed at about 180°C by the melting. The observed behavior can be therefore related to the molecular movements involved in the structural transitions.

TRANSPORT PROPERTIES

The experimental approach used in this work allows to obtain the diffusion coefficient and the solubility of a gas in a solid as a function of temperature and gas pressure. At any temperature and pressure, the function $(P_0 - P_t)/(P_0 - P_{eq})$ can be detected as a function of time; P_0 is the initial pressure of the test gas before sorption starts, while P_{eq} and P_t are the pressures at equilibrium and time t, respectively. The ratio between cell and sample volumes is high enough to ensure that the decrease of the acting pressure P_0 is too small to play an appreciable role on the transport parameters. $(P_0 - P_t)/(P_0 - P_{eq})$ is numerically equal to C_t/C_{eq}, where C_t and C_{eq} are the concentrations of gas in the polymer at time t and at the equilibrium. If the diffusion behavior is ruled by Fick's law, the initial stage of the diffusion phenomenon can be represented by the equation

$$C_t/C_{eq} = 4/d \ (\bar{D}t/\pi)^{1/2}$$

where d is the sample thickness, t the time, and $\bar{D}$ the diffusion coefficient.[1] Therefore, $(P_0 - P_{eq})$ gives C_{eq}, while $\bar{D}$ can be obtained from the slope of the plot C_t/C_{eq} versus $\sqrt{t}$ in the linear range.

For samples investigated above the glass transition, C_{eq} at any temperature is a linear function of the gas pressure P, and Henry's law can be applied[10]:

$$C_{eq}(P) = SP$$

where S is the sorption coefficient. For samples in the glassy state, C_{eq} is a more complex function of P and dual mode sorption is generally observed.[10] In our case we do not observe any anomalous behavior, depending on the chosen temperature interval. The coefficient $\bar{D}$ can be dependent on P and

C_{eq}, but with systems following Henry's law, $\bar{D}$ is generally independent on pressure and, at any given pressure, it can be assumed equal to D_0, the thermodynamic diffusion coefficient.[1] The analysis of the transport properties carried out at different temperatures gives the dependence of $\bar{D}$ and S on temperature. In the present study the temperature range, 10–60°C, was indeed chosen on the basis of the thermal and dynamic-mechanical behavior. In fact, this is the range encompassing the glass transition where the molecular mobility is high enough to expect that the solubility of non interacting gases can be ruled by Henry's law.

In Figure 2, C_{eq}, expressed in cm³ (STP) of carbon dioxide per cm³ of bulk polymer, is reported for samples B(i) and D(i) as a function of the pressure at different temperatures. At each temperature C_{eq} is higher in sample D(i) and, with the exclusion of sample B(i) at 10 and 20°C, the solubility is a linear function of the pressure according to Henry's law. At 10 and 20°C the positive deviation from the linear trend observed for sample B(i) indicates that the
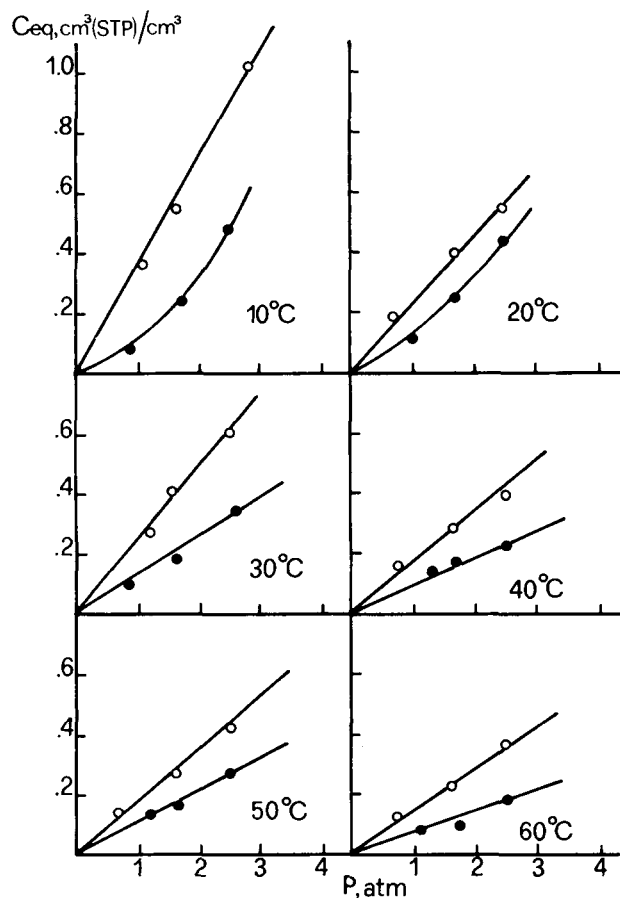
Figure 2 The equilibrium concentration C_{eq} of carbon dioxide in the polymer is reported versus the pressure at different temperatures: (●) sample B(i); (○) sample D(i).
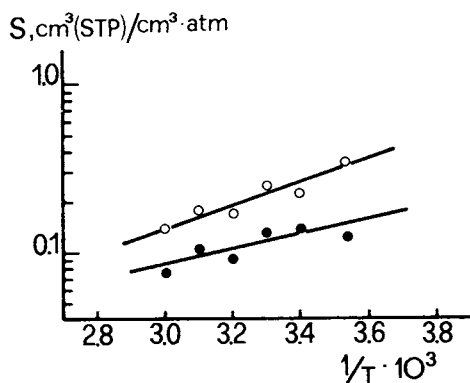
gas behaves as plasticizer; at these temperatures the molecular mobility in the permeable matrix is therefore still low for the CO_2 molecules. From the data in Figure 2 the sorption S can be derived as the slope of C_{eq} versus P; for sample B(i) at 10 and 20°C the sorption was calculated in the range of low pressures, where the trend is linear. In Figure 3 the coefficient S is reported in logarithmic scale as a function of $1/T$. The slope gives the heat of solution[10]; the obtained values are substantially the same in the two samples, in particular, -2.4 and -2.0 kcal/mol for samples D(i) and B(i), respectively.

In Figure 4 the diffusion behavior of sample D(i) is shown; the diffusion coefficient $\bar{D}$ is reported versus C_{eq} at different temperatures. Similar behavior was observed for sample B(i). It is clear that $\bar{D}$ does not appreciably depend on C_{eq} and therefore extrapolates to the same value for $C_{eq} = 0$.
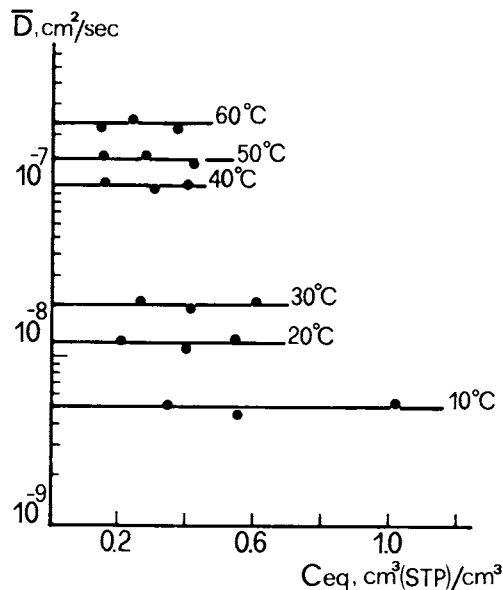
In Figure 5, D_0 values, obtained for samples B(i) and D(i), are reported as a function of $1/T$; a single straight line gives a satisfactory representation of the behavior of both samples. According to the Arrenhius law the slope gives $E_a = 14.7$ kcal/mol as activation energy of the diffusion process.

DISCUSSION

Samples B(i) and D(i) differ for the degree of structural order, as shown by the thermal analysis. The dynamic mechanical relaxation spectra reflect this situation, particularly for the intensity of the glass transition band and for the modulus values in the temperature range $T > T_g$. Considering that the intensity of a given band depends on the amount of material undergoing the transition, it follows that the fraction of the component mobilized at the glass transition is appreciably higher in sample D(i). The
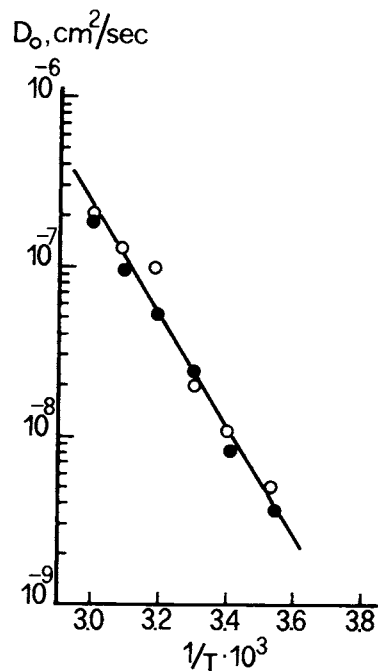
Figure 4 The diffusion coefficient D is reported versus the equilibrium concentration C_{eq} at different temperatures. Data refer to sample D(i).

modulus trend for $T > T_g$ confirms that the fraction of more mobile component, having lower modulus, is higher in sample D(i).

The transport data seem to point in the same direction. As matter of fact, the sorption is higher in sample D(i) at any temperature; the ratio between

Figure 3 The sorption S is reported versus $1/T$: (●) sample B(i); (○) sample D(i).

Figure 5 The thermodynamic diffusion coefficient D_0 is reported versus $1/T$: (●) sample B(i); (○) sample D(i).

the sorption observed in sample D(i) and that observed in sample B(i) fluctuates in a narrow range, whose average value is 1.79. The sorption at 10°C, where the deviation from Henry's law is relevant, was excluded. The value 1.79 compares well with the inverse of the ratio between the isotropization enthalpies, which is 1.64. This observation suggests that a linear relationship between sorption and isotropization enthalpy can be found; in particular, the sorption must decrease as the isotropization enthalpy increases. Moreover, we obtain coincident values of D_0 for the two samples and the same dependence on $1/T$, indicating that the permeable component has the same diffusion coefficient and the same activation energy in the two samples. Considering that the diffusion data are very sensitive to the thermodynamic state of the permeable component,[11,12] one can conclude that the permeable component must be substantially the same in the two samples, and therefore must be characterized by the same transport parameters, specific sorption included. This consideration assumes a crucial meaning, in fact it is possible to deduce that the sorption actually observed depends on the fraction of permeable component according to

$$S = \alpha_p S_{sp}$$

where S_{sp} is the specific sorption and α_p the fraction of the permeable component. The ratio between the observed sorptions, or the ratio between the isotropization enthalpies, can be assumed as the ratio between the contents of permeable component in the two samples. The activation energy found for the diffusion process, 14.7 kcal/mol, is typical of an activated process involving cooperative motions of chain sequences to create the sites for the diffusion path.[10] Therefore, the permeable component is characterized by a molecular mobility allowing such cooperative motions. Using methylene chloride as permeant,[4,5] we suggested the hypothesis that the transport occurs in a more mobile and less ordered phase within the liquid-crystalline domains. With this permeant and analyzing different samples with a wider range of isotropization enthalpy, the same correlation between sorption and isotropization enthalpy was found. On the basis of the sorption and diffusion data, similarly to the present paper, we concluded that the permeable component is a less-ordered phase; the higher the fraction of this phase, the higher the sorption and the lower the isotropization enthalpy. A model which assumes the presence of an amorphous phase is not new, and similar conclusions based on different and independent experimental evidences, were reported by different authors.[13-16]

The present results, according to the previous papers,[4,5] show that the analysis of transport properties is very useful in order to give further contributions to the understanding of the phase organization in liquid-crystalline polymers, but a great experimental support is required. In particular it is necessary to extend the analysis to many different systems, changing the experimental conditions and extending the number and the nature of the permeant molecules.

REFERENCES

1. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic, London, 1968.
2. A. Peterlin, *J. Macromol. Sci. Phys.*, **B11**, 57 (1975).
3. L. Araimo, F. de Candia, V. Vittoria, and A. Peterlin, *J. Polym. Sci. Phys.*, **16**, 2087 (1978).
4. F. de Candia, A. Renzulli, V. Vittoria, A. Roviello, and A. Sirigu, *J. Polym. Sci. Phys.*, **28**, 203 (1990).
5. F. de Candia, V. Vittoria, P. L. Magagnini, and B. Bresci, *J. Polym. Sci. Phys.*, to appear.
6. W. J. Koros, D. R. Paul, and A. A. Rocha, *J. Polym. Sci. Phys.*, **14**, 687 (1976).
7. A. Roviello and A. Sirigu, *Makrom. Chemi.*, **181**, 1799 (1980).
8. P. Iannelli, A. Roviello, and A. Sirigu, *Eur. Polym. J.*, **18**, 759 (1982).
9. N. J. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967.
10. C. E. Rogers, in *Polymer Permeability*, J. Cowyn, Ed., Elsevier, Belfast, 1985, Chap. 2.
11. F. de Candia, R. Russo, V. Vittoria, and A. Peterlin, *J. Polym. Sci. Phys.*, **18**, 2083 (1987).
12. H. B. Hopfenberg, *Permeability of Plastic Films and Coatings to Gases, Vapors and Liquids*, Plenum, New York, 1974.
13. R. W. Lenz and J. I. Jin, *Macromolecules*, **14**, 1405 (1981).
14. R. W. Lenz, *Faraday Disc. Chem. Soc.* **79**, 21 (1985).
15. F. Laupretre, C. Noel, W. N. Jenkins, and G. Williams, *Faraday Disc. Chem. Soc.* **79**, 191 (1985).
16. J. S. Moore and S. L. Stupp, *Macromolecules*, **20**, 282 (1987).