Gas sorption in side-chain liquid crystalline polymers

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The sorption properties of CO_2 in several side-chain liquid crystalline polymers (side-chain LCPs) with various mesophases have been investigated. The equilibrium concentrations of the sorbed CO_2 were measured over a wide temperature range, covering the whole of the phase states of the side-chain LCPs. The concentrations have been found to depend strongly on the phase state of the polymers. They increase significantly at the various phase transitions, i.e. crystalline to smectic, smectic to nematic, and liquid crystalline (smectic or nematic) to isotropic. A correlation between the solubility changes and the enthalpies of the transitions has been established.

(Keywords: gas sorption; liquid crystalline polymer; biphasic region)

INTRODUCTION

The sorption of gases and vapours in conventional semicrystalline polymers is generally accepted to occur exclusively in the amorphous regions. The crystalline regions act as impermeable barriers due to the tight packing of the polymer chains. The sorption values of diffusing molecules in these materials can therefore be treated by using a simple biphasic model[1–3]. Based on this model, gas solubility in polymers is directly proportional to the amorphous fraction, and decreases with increasing crystallinity of the polymers.

The chain packing of the liquid crystalline (LC) phase is much 'looser' than that of conventional crystallites. In contrast to the fully ordered structure of the latter, only a two-dimensional, positional order is possible for the most ordered smectic phases[4,5]. The density of the LC phase is thus only slightly higher than that of an isotropic liquid, but is nevertheless much less than that of a crystalline solid[6,7]. Studies of gas sorption and transport properties in LC materials have recently been carried out by several groups[8–13]. Kajiyama *et al.*[8] first measured the sorption and transport properties of gases in blended membranes composed of a monomeric liquid crystal (MLC) and poly(vinyl chloride) (PVC). They found an abrupt increase in the solubility and permeability coefficients as the phase changes from the crystalline to the LC state. However, no significant change in either of these parameters was observed at the transition of the LC to the isotropic state. In the case of liquid crystalline polymers (LCPs), Chiou and Paul[9] reported that glassy main-chain LCPs have a rather low gas permeability, which originates mainly from low gas solubility in the polymers. Comparable results were observed by Vittoria *et al.*[10] for a glassy side-chain LCP: these authors suggested that the LC phase is impermeable to gas penetrants and a biphasic model can therefore be applied. Reinecke and Finkelmann[11] measured the transport properties of organic gases in a series of side-chain LC elastomers. Different activation energies of permeation and heats of solution were observed for the different phase states. In our previous work[12,13], we have found that the gas permeability of side-chain LCPs is quite low, being comparable to that of low-density polyethylene. All of these studies suggest that the LC order has an important role to play in reducing the gas solubility and gas permeability of the polymers.

Gas sorption and transport properties are expected to exhibit discontinuous behaviour at an isotropization transition, as a result of the characteristics of the first-order transformation. We have demonstrated this discontinuous behaviour by measuring the distinct sorption properties of CO_2 in the LC and isotropic phases of a MLC[14]. Following the study of this behaviour for a MLC, it is of interest to investigate the sorption properties of a side-chain LCP. The results could be helpful in further understanding the influence of LC order on gas sorption. Accordingly, in this present work we have synthesized several side-chain LCPs with different LC phases, and the gas sorption properties of these polymers in the different phase states have been characterized and discussed.

EXPERIMENTAL

Materials

The experimental methods used for synthesis of the polymers were identical to those reported in our previous papers[12,13]. The synthetic route used for the preparation of the side-chain liquid crystalline polysiloxanes (PS1–PS4) is outlined in *Scheme 1.* The polymers were prepared by a hydrosilylation reaction between an appropriate olefinic monomer

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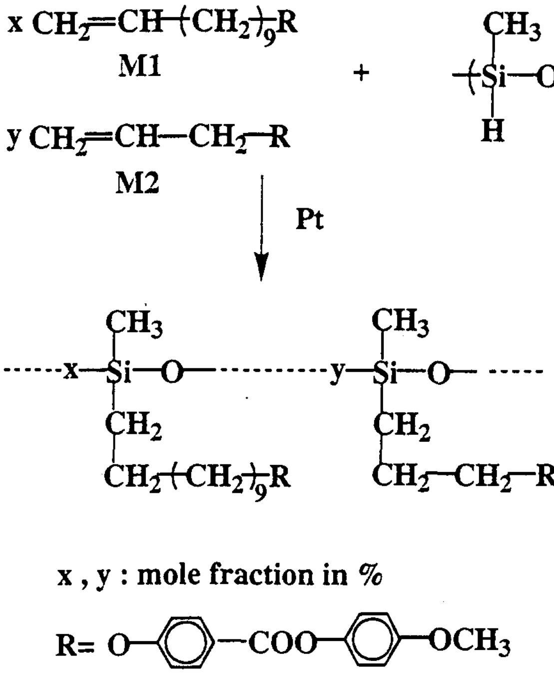
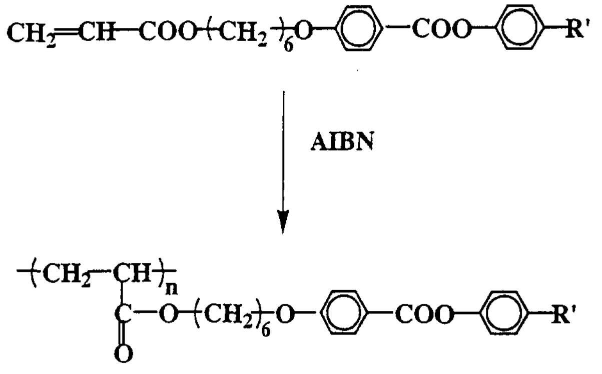


	PS1	PS2	PS3	PS4
x	100	0	70	50
y	0	100	30	50

Scheme 1 Synthesis of side-chain liquid crystalline polysiloxanes

and a poly(methylhydrosiloxane) backbone (Petrarch Systems Inc., $\bar{M}_n = 4500–5000$). The reaction components were dissolved in freshly distilled toluene and refluxed under nitrogen until no Si–H absorption (at 2175 cm^{-1}) (or, at least, only a negligible amount) could be detected by i.r. spectroscopy. The polymers obtained were isolated by precipitation in methanol, purified by several reprecipitations from tetrahydrofuran (THF) solutions in methanol, and finally dried in vacuum.



	PA1	PA2
R'	OCH_3	CN

Sceme 2 Synthesis of side-chain liquid crystalline polyacrylates

Polyacrylate-based side-chain LCPs (PA1 and PA2) were synthesized by the free radical polymerization of the corresponding monomers (see *Scheme 2*). The polymerizations were carried out in chloroform solution at 60°C for 8 h using 2,2'-azobisisobutyronitrile (AIBN) as the initiator, at a concentration of 1.5 mol%, relative to the monomers. The polymers were precipitated in methanol, filtered, purified by several reprecipitations and finally dried in vacuum.

Measurement of molecular weight

The molecular weights of the polymers obtained were determined by gel permeation chromatography (g.p.c.) using an Applied Biosystems (Series 400) instrument equipped with a Viscotek differential refractometer/viscometer detector. The solvent used was tetrahydrofuran, with a flow rate of 1 ml min^{-1}. A calibration plot, constructed with polystyrene standards, was used to determine the molecular weights.

Density measurement

Density measurements on the polymers were performed by the solvent gradient method at 23°C, using aqueous calcium nitrate to set up the density gradient. Glass floats of known densities (factory calibrated to ± 0.001 g cm^{-3}) were used for calibration of the gradient.

Thermal analysis

Thermal analysis was carried out on a Seiko 5200 differential scanning calorimeter. Samples were run at 10°C min^{-1}, with indium used as the calibration standard. A Nikon optical polarizing microscope (Microphot-Fx), equipped with a Mettler FP82 hot stage, was used for locating the thermal transitions and analysing the anisotropic textures.

Solubility measurement

The solubilities of CO_2 in the various side-chain LCPs were determined by a Sartorius electromicrobalance (Model S3D-P), whose sensitivity was 10^{-6} g when sample weights greater than 10 mg were used. The sorption assembly essentially consists of a vacuum and gas supply system, gas storage vessels, and a sorption chamber. The sorption chamber was thermostatted by a mini-oven, which was controlled to ± 0.1°C. The sorption experiment was preceded by placing a known weight of a side-chain LCP sample (60–75 mg) in the sorption chamber and degassing at 130°C under a vacuum of 13.33 Pa (0.1 mmHg) until a constant weight was indicated. The temperature was then reduced to $\sim$40°C and the gas was introduced into the sorption chamber in order to start the sorption measurements. The weight of the sorbing sample immediately increased after introduction of the gas, finally levelling off after a period of time. The weight change was recorded continuously as a function of time by the use of a computer. The sorption temperature was increased when a constant weight was indicated. Temperature ranges, which included all of the various phase transitions of the investigated side-chain LCPs, were covered, in order to obtain the equilibrium concentrations of the gas in the different phase states of the side-chain LCPs.

RESULTS

Characteristics of the side-chain LCPs

The investigated side-chain LCPs exhibit various mesophases with a wide range of isotropization enthalpies. The thermal and physical properties of these polymers are summarized in *Table 1*. PS1 and PS2 are homopolymers with a difference in their flexible spacer length, which causes both these polymers to exhibit quite distinctive thermal properties. *Figure 1* presents the differential scanning calorimetry (d.s.c.) curve of PS1. Due to the long spacer length, a side-chain crystallization takes place below 54°C. Above this temperature PS1 exhibits a smectic phase which undergoes isotropization at ~143°C. In contrast to PS1, PS2 displays both a glass transition and a nematic phase. Both phase transitions are much lower, respectively, than those of PS1. Copolymerization of the side-chain monomers M1 and M2 (see *Scheme 1*), using different molar ratios, could lead to different mesophases and also different thermal transitions. For the polymer with a higher M1 content (PS3), a smectic phase is formed, while the side-chain crystallization disappears and the isotropization enthalpy is much lower than that of PS1. Obviously, the addition of M2 results in a less ordered smectic phase. In the case of PS4, which contains equal amounts of both M1 and M2, a nematic phase is formed. The isotropization enthalpy obtained is larger than that of PS2, reflecting a more ordered nematic phase. The glass transition temperatures of both copolymers are lower than those of both of the homopolymers (PS1 exhibits a side-chain crystallization), while the isotropization temperatures lie between the values of the latter compounds. A similar copolymer behaviour was also observed by Percec and Lee[15], and by Imrie *et al.*[16].

The other series of side-chain LCPs is based on the polyacrylate backbone, i.e. PA1 and PA2. Both polymers have the same spacer length, but possess different mesogenic end groups, namely methoxy and cyano groups. For PA1, which contains methoxy end groups, a smectic and a nematic phase could be obtained. The d.s.c. curve is shown in *Figure 2*. In contrast to PA1, PA2 exhibits only a nematic phase. Both polymers, however, exhibit the same glass transition temperature.

Effect of crystalline–smectic transition

Figure 3 shows the plot of the equilibrium concentration of sorbed CO_2 in the PS1 polymer as a function of temperature. An appreciable increase in gas solubility is

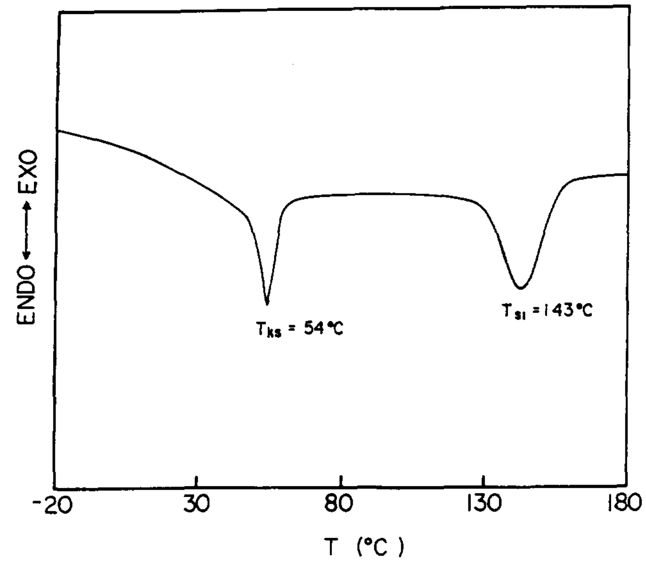


Figure 1 D.s.c. thermogram of the PS1 polymer

Table 1 Thermal and physical properties of the various side-chain liquid crystalline polymers studied in this work

Polymer	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Phase behaviour[a]	Density
PS1	32 700	3.4	K54(5.8)S143(11.7)I	1.140
PS2	22 100	3.0	G15N75(2.1)I	1.244
PS3	29 500	3.2	G0.1S101(6.9)I	1.172
PS4	27 300	3.1	G5N91(2.8)I	1.185
PA1	11 200	2.1	G18S82(2.1)N103(1.2)I	1.221
PA2	14 400	2.4	G18N98(1.9)I	1.213

[a] Temperature in °C: G, glassy; S, smectic; N, nematic; I, isotropic; K, side-chain crystallization. Values in brackets are the enthalpies of the transitions, with units in J g^{-1}

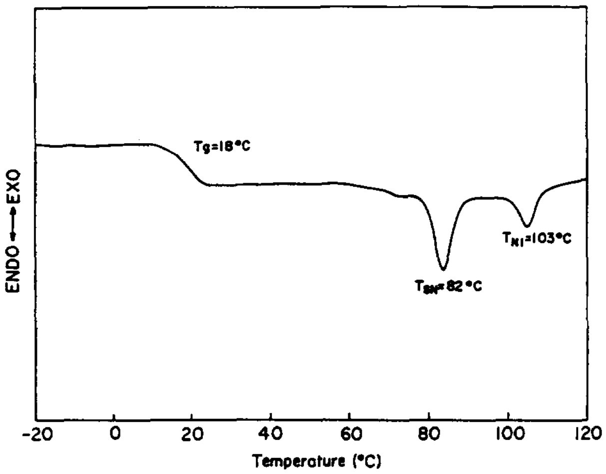


Figure 2 D.s.c. thermogram of the PA1 polymer

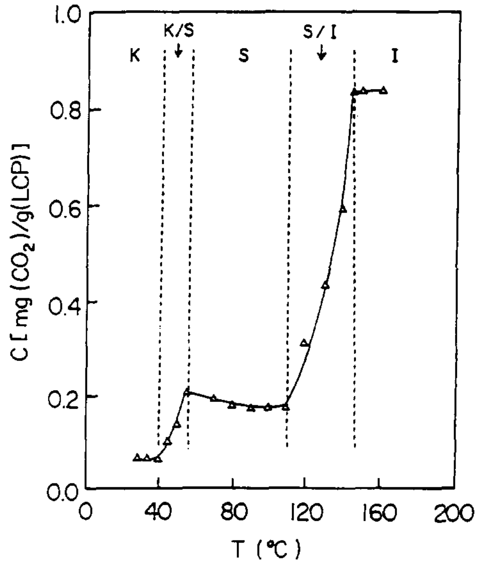


Figure 3 Equilibrium concentrations of CO_2 in the PS1 polymer at 1.2 bar as a function of temperature

found when the phase changes from crystalline to smectic. In the crystalline state, the sorption is supposed to occur exclusively in the more or less coiled backbone regions since the side-chain crystalline regions are impermeable to gas penetrants, as suggested by the conventional biphasic model. Therefore, the solubility increase at the transition implies that gases can be dissolved in the side-chain mesogenic regions, i.e. in the smectic phase. This result suggests that gas sorption in the mesophase state of a side-chain LCP does not follow the simple biphasic model.

Effect of smectic–nematic transition

A nematic phase possesses only orientational order, and is lacking in the positional order of the smectic phase. This less ordered structure results in a slight increase in specific volume and a decrease in molecular cohesion[6]. The difference in gas solubility between the two phases can be seen from the sorption curve for PA1 (*Figure 4*). The gas solubility in the nematic phase is found to be markedly higher than in the smectic phase. This demonstrates that the 'tightness' of the LC phase also influences the sorption of a gas. The more ordered the LC phase, then the lower is the gas solubility.

Effect of liquid crystalline–isotropic transition

Figures 3 and *4* also indicate a significant solubility change at the isotropization transitions. The LC phase is thus implied to decrease the gas solubility. Nevertheless, PS1 appears to show a much larger magnitude of change than PA1. This difference reflects the fact that the solubility change increases with the increasing enthalpy of isotropization transition (see also *Table 1*). Similar tendencies are found with the other side-chain LCPs. *Figure 5* shows the sorption curve of CO_2 in PS3, in which the latter displays a less ordered smectic phase than PS1. The solubility increase at the isotropization transition is shown to be much lower than that of PS1. The sorption behaviour of PA2 is presented in *Figure 6*. A slightly higher solubility change at the nematic–isotropic transition is found (when compared to PA1), due to a somewhat larger isotropization enthalpy for PA2.

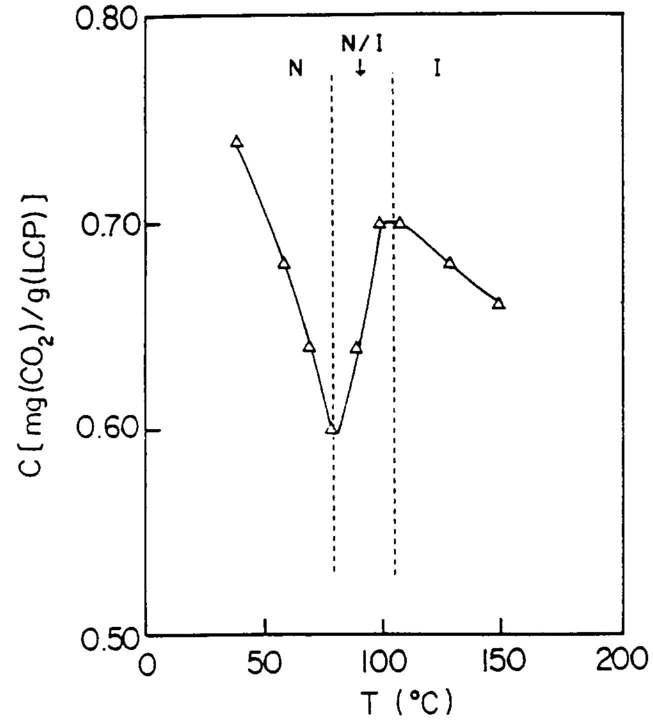


Figure 5 Equilibrium concentrations of CO_2 in the PS3 polymer at 1.2 bar as a function of temperature

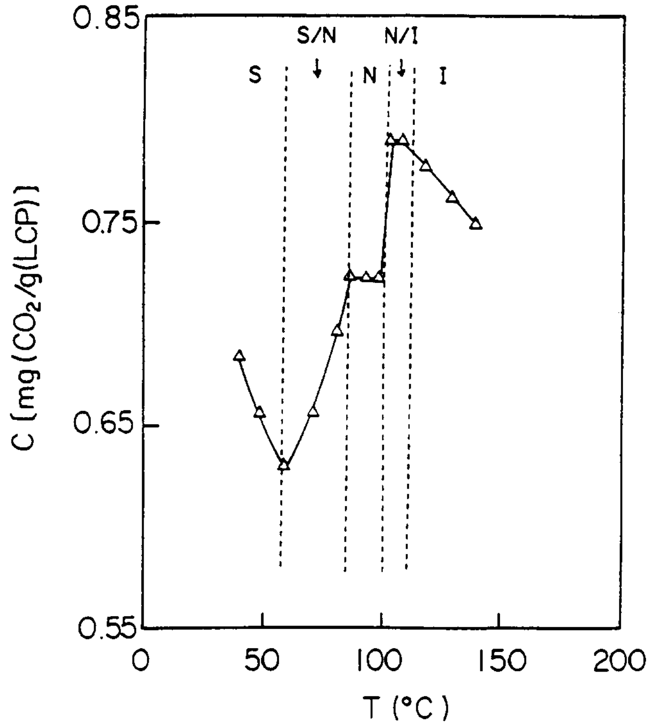


Figure 4 Equilibrium concentrations of CO_2 in the PA1 polymer at 1.2 bar as a function of temperature

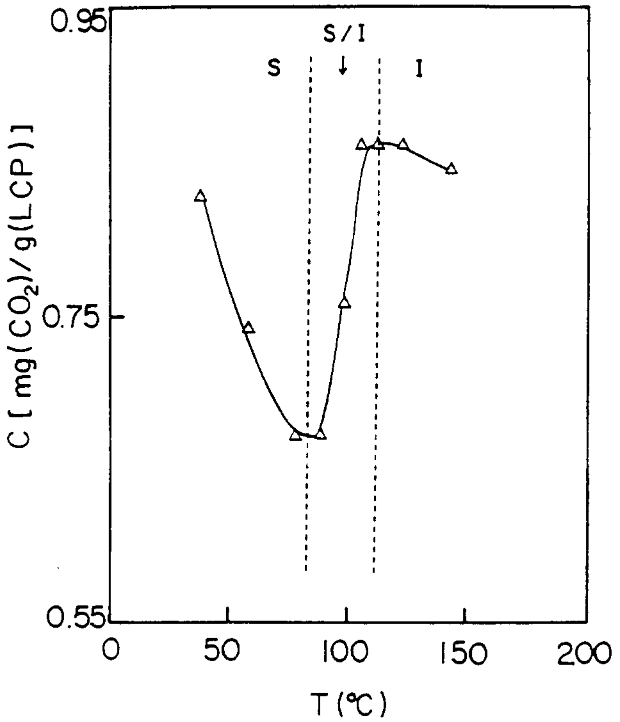


Figure 6 Equilibrium concentrations of CO_2 in the PA2 polymer at 1.2 bar as a function of temperature

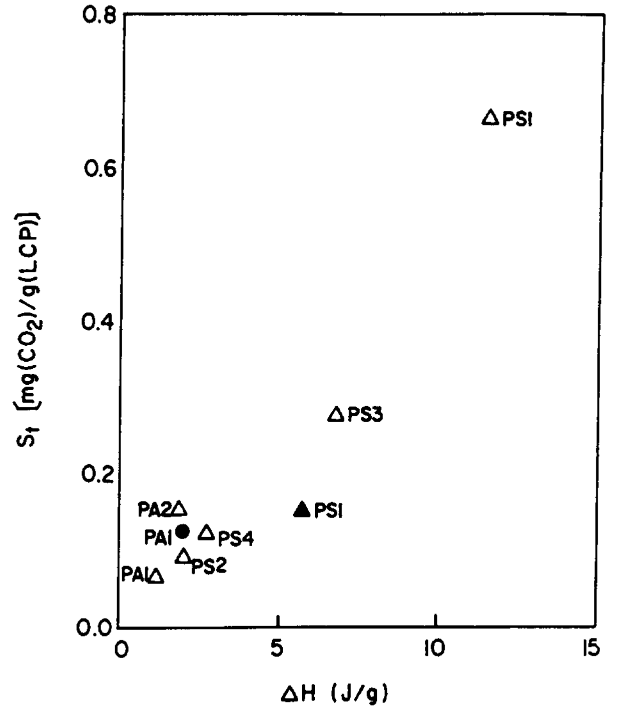


Figure 7 Correlation between transition sorption (S_t) and enthalpies of the transitions: (▲) crystalline–smectic transition; (●) smectic–nematic transition; (△) liquid crystalline–isotropic transition

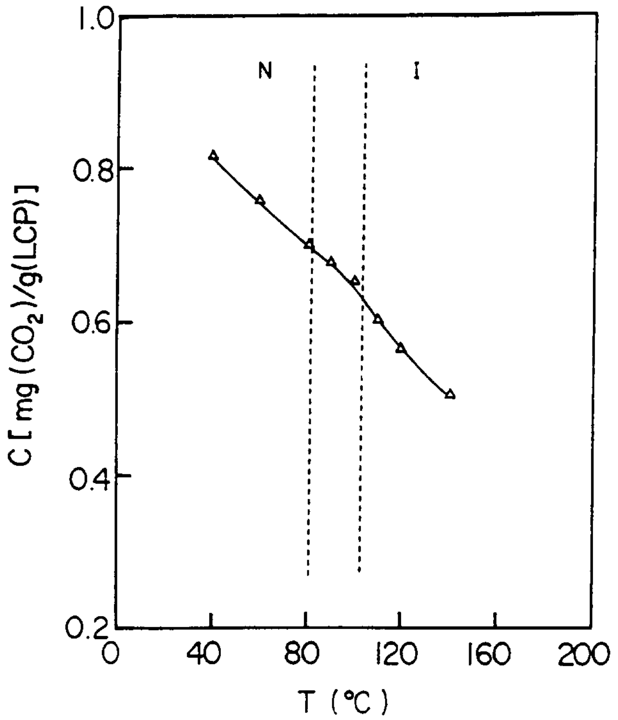


Figure 8 Equilibrium concentrations of CO$_2$ in the PA2 polymer at 1.2 bar as a function of temperature, after sample was degassed at 80°C

From the discontinuous sorption behaviour which occurs at three different types of first-order phase transition, it is clear that gas solubility in the side-chain LCPs is undoubtedly depressed by the crystalline or LC order. The solubility increase which is due to the phase transformation at these first-order transitions can be designated as 'transition sorption', S_t. However, since the gas solubility is affected by the temperature, S_t is difficult to determine exactly. For simplicity, the value for the heat of solution within the biphasic gap was taken as being equal to that measured just before the transition. The relationship between the resulting S_t and the enthalpy of the transition is presented in *Figure 7*. In general, the higher the enthalpy, then the larger is the S_t. This suggests that the depression of gas solubility becomes more pronounced as the transition enthalpy becomes larger.

DISCUSSION

Significance of degassing

The sorption curves presented in *Figures 3–6* were all obtained on samples that had been previously degassed at 130°C, in order to remove any residual solvent in the polymers. The same curves were obtained when the degassing process was carried out at higher temperatures (140–170°C), suggesting that no solvent (or, at least, a negligible amount) was present in the polymers after degassing at 130°C. Removal of the solvent is critical for characterizing the transition sorption behaviour of the side-chain LCPs. *Figure 8* presents the sorption curve of CO$_2$ in PA2, after degassing at 80°C. The gas solubility at the isotropization transition is seen only as a slight change in the slope of the sorption curve. This is quite different from the sorption behaviour shown in *Figure 6* (sample degassed at 130°C). Measurements have shown that there was still ~0.7 wt% residual solvent trapped in the polymer, after degassing of the lower temperature. The inability to detect the transition sorption of the side-chain LCP in this case is obviously due to the presence of unremoved solvent. These results show that a suitable degassing temperature should be used in order to obtain the correct sorption characteristics of the side-chain LCPs.

Biphasic behaviour

The transition sorption behaviour observed in *Figures 3–6* occurs over a wide temperature range; this is different from the behaviour found for monomeric liquid crystals (MLCs)[14], where sharp solubility changes at the transitions are observed. The nature of these broad transition sorptions can be seen more clearly from a plot of gas solubility *versus* time. A typical example is presented in *Figure 9* for the PS1 polymer. Below the isotropization transition (in the smectic phase), a rise in temperature did not cause any obvious solubility change. However, if the temperature rise was within the isotropization transition range, an apparent sorption could occur (e.g. from 110 to 120°C), and a new equilibrium state for the gas solubility could be attained. Similar, successive transition sorptions were observed in the temperature range up to 145°C, while above this temperature, no apparent sorption behaviour occurred. Since the transition sorption originates from the transformation of a smectic phase to an isotropic phase, the equilibrium states within this transition suggest a coexistence of the smectic and isotropic phases. The compositions of the biphasic mixtures vary as the equilibrium states change. In fact, the biphasic behaviour could be observed under a polarizing microscope, where both a dark and a bright LC texture coexisted at temperatures within the biphasic gap. Biphasic behaviour has been reported for both microphase-separated

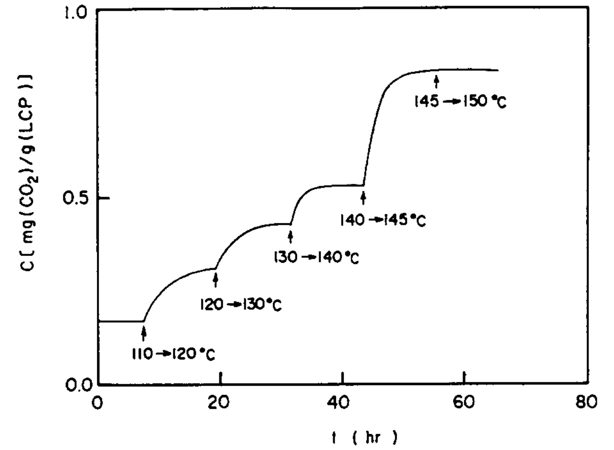


Figure 9 Sorption curve of CO_2 in the PS1 polymer at the isotropization transition. Several equilibrium states with distinct gas solubility values could be obtained at different temperatures, suggesting a coexistence of liquid crystalline and isotropic phases

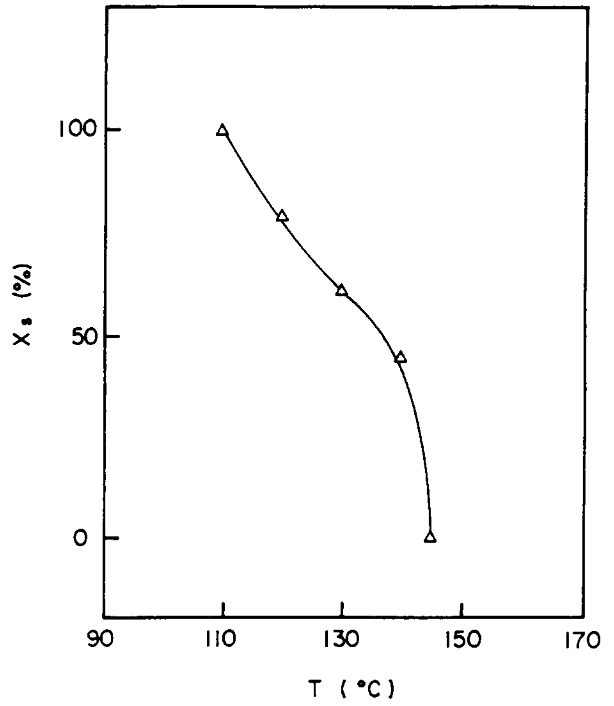


Figure 10 Proportion of smectic phase (X_s) within the biphasic region of the PS1 polymer as a function of temperature

main-chain and side-chain LCPs[17,18]. A distribution in the molecular weights, as well as organization in the chemical structure of the polymers, haa been suggested as being responsible for this behaviour.

A particular advantage of the sorption method for observing biphase behaviour is the ability to determine the composition of both phases within the biphasic region. By assuming that the polymer consists of 100% smectic phase at temperatures below the isotropization temperature, the total transition sorption (S_{tt}) (from 110 to 145°C) can represent the sorption value when the proportion of isotropic phase changes from 0% to 100%. Thus, once the intermediate transition sorption value (S_{ti}) within the biphasic region is obtained, the proportion of the isotropic phase can be calculated from the value of S_{ti}/S_{tt}, and the proportion of the smectic phase from $(1-S_{ti}/S_{tt})$. The phase compositions obtained might not be very exact, due to the somewhat approximate estimation of S_{ti} and S_{tt}. The gas sorption method, however, appears to be a convenient way of determining the composition within the biphasic region. *Figure 10* shows the proportion of smectic phase in PS1 as a function of the temperature. The smectic phase decreases most rapidly in the temperature range from 140 to 145°C. This implies that most of the PS1 molecules become isotropic at these temperatures.

Comparison with a monomeric liquid crystal

In order to gain further insight into the influence of LC order on gas sorption, it is helpful to compare the sorption behaviour of a side-chain LCP with that of a corresponding MLC. PS1 is chosen for this comparison, since its side-chain monomer (M1) also displays LC order. The sorption properties of CO_2 in PS1 and M1 are summarized in *Table 2*. The gas solubility in PS1 is found to be much lower than in M1. Two factors could be responsible for this behaviour. One of these arises from the decrease in free volume after polymerization, while the other originates from alternation of the LC phase from nematic to smectic. In the isotropic phase, the gas solubility in PS1 is ~2.9 times lower than in M1, which can be attributed primarily to the reduction in free volume after 'grafting' M1 to the polysiloxane backbone. In contrast, the gas solubility in the smectic phase of PS1 is much lower (by a factor of ~6.2) than in the nematic phase of M1. Obviously, the more ordered LC phase in PS1 has caused a further decrease in the gas solubility.

According to the structural design of side-chain LCPs, flexible spacers are introduced to decouple the motions of the polymer backbone and the anisotropic mesogen. The backbone attempts to form a statistical random coil conformation, while the mesogen seeks to attain orientational order. Nevertheless, this decoupling might be incomplete. Experimental results obtained from the n.m.r. spectra of a deuterated sample have established that the order parameter of the side-chain LCP decreases as follows: from the mesogen to the spacer and then to the main chain[19,20]. Therefore, the LC order might depress the gas solubility not only in the mesogenic regions, but also, to some extent, in the backbone regions. Since the latter is most disordered, it is likely that the sorbed gas is continuously being distributed in the

Table 2 Comparison between the sorption properties of CO_2 in the PS1 polymer and in a monomeric liquid crystal (M1)

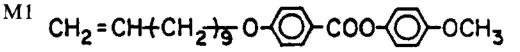
Sample	C_{lc}[a]	C_{iso}[b]	H_i[c]
PS1	0.175	0.839	11.7
M1[d]	1.16	2.42	2.8

[a] Values measured at a temperature just below the isotropization point, with units in mg(CO_2) [g(PS1)]$^{-1}$

[b] Values measured at a temperature just above the isotropization point, with units in mg(CO_2) [g(M1)]$^{-1}$

[c] Isotropization enthalpy, with units in J g^{-1}

[d] M1



Phase behaviour: K70.2N71.8I (data taken from ref. 14) side-chain LCPs, with a concentration gradient which decreases from the backbone to the mesogen.

CONCLUSIONS

We have reported the results of CO_2 sorption in a series of side-chain LCPs. The gas solubility has been shown to exhibit a discontinuous change at several types of first-order phase transition. The magnitude of the change increases with the increasing enthalpies of the transitions. The depression of gas solubility by the liquid crystalline order can therefore be quantitatively determined. When the phase changes from the crystalline to the liquid crystalline state, a significant increase in the gas solubility could be seen. This behaviour proves that gas sorption in the mesophase of side-chain liquid crystalline polymers does not follow a simple biphasic model. From the sorption method, a biphasic region has been found to exist at the first-order phase transitions. The compositions of the phases within the biphasic region can be determined from measurements of the equilibrium gas solubility in the polymers.

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