Diamagnetic susceptibility of liquid crystalline copolyesters: study of molecular relaxation

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SYNOPSIS

The diamagnetic susceptibility of a series of random copolyesters, P(HB/HN), of 4–hydroxybenzoic acid (HBA) with 2–hydroxy–6–naphtoic acid (HNA) has been investigated, both, as a function of composition and temperature. It is shown that the molecular susceptibility of the uniaxially oriented samples linearly decreases with HB content. Results are discussed in terms of the increase in magnetic anisotropy occurring with the introduction of the HN groups. Furthermore, the temperature dependence of the specific susceptibility has been investigated. The diamagnetic susceptibility of these copolymers rises at the beginning of the solid–liquid crystalline transition. Above this temperature, the specific susceptibility exhibits a conspicuous time dependent behaviour which is a function of the temperature at the mesophase. After long storage times at the mesophase, and upon cooling at room temperature, the susceptibility shows values which approach those of a macroscopically isotropic state, i.e. a state with no overall preferred orientation. X–ray diffraction measurements confirm a relaxation mechanism of the molecular orientation occurring at temperatures above the melting point. A similar relaxation process is observed for samples with an initial planar orientation.

Keywords: Diamagnetic susceptibility, molecular relaxation, liquid crystalline copolyesters, orientation.

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INTRODUCTION

Much research activity has been directed in recent years towards the relationship between structure and properties of copolyesters from 4–hydroxybenzoic acid (HBA) and 2–hydroxy–6–naphtoic acid (HNA) [1-3]. The morphology and microstructure of these systems has been investigated by transmission electron microscopy (TEM) [4-6], scanning electron microscopy (SEM) [6-8], small angle X–ray scattering (SAXS) [6,9] and wide angle X–ray diffraction (WAXS) [9-14]. The transition from the solid state to a liquid crystalline phase has been characterized by differential scanning calorimetry (DSC) [10,15,16]. A detailed description of the nature of the melt, as containing smectic–type regions within a nematic matrix, has also been recently reported [17]. Diamagnetic susceptibility, which is sensitive to variations in intermolecular interactions occurring in polymers [18-24], has been shown to be a convenient method to investigate the changes involved in phase transitions [25,26].

The present paper is concerned with the diamagnetic susceptibility study of the phase transition, from the solid state to the liquid crystalline phase, of the above mentioned copolyesters. Diamagnetic susceptibility, χ, is proportional to changes in the precession of the electrons around the nuclei under the influence of a magnetic field. Thus, χ depends primarily on the electronic configuration of each atom and its interaction with the adjacent ones [26]. For uniaxially oriented systems, the average susceptibility is proportional to the trace of the magnetic susceptibility tensor. The present work also examines the variation of the anisotropy of the magnetic susceptibility as a function of comonomer composition and temperature. In aromatic systems the observed strong anisometry has been attributed to the fact that π–electrons in a benzene ring are delocalized and form "ring–currents" [27]. Magnetic anisotropy has been frequently used, in the field of liquid crystals, as a convenient method to describe the degree of order of a mesophase. In the simplest case, which is a nematic phase with uniaxial orientation, magnetic anisotropy is proportional to an order parameter [28]. This parameter is related to the overall molecular orientation.

Finally it is worth pointing out that the study of diamagnetism offers the advantage, in contrast to other techniques (birefringence), to be capable of describing states of orientation of optically opaque materials.

EXPERIMENTAL

A series of commercial copolymers of HBA/HNA with molar ratios 30/70, 58/42 and 75/25 from Hoechst Celanese Corporation, received in the form of extruded cylindric bars and in the form of pellets were investigated. The cylindric bars show uniaxial orientation. The material in the form of pellets was compression moulded (25kN) for 5 minutes at $\sim 20°C$ above its melting point and subsequently quenched. In this way, 0.25 mm thick films with planar orientation were obtained. The microcrystals are disoriented in the plane of the film with the molecular axis parallel to the film surface, as revealed by wide angle X–ray diffraction. The PHN homopolymer was kindly supplied by Prof. Kricheldorf (University of Hamburg) in powder form. PHN was studied in its slab–like morphology. Details of the synthesis and characterization of PHN are given elsewhere [29].

For the determination of magnetic susceptibility the Faraday method was used. The uniaxially oriented samples were sectioned in order to obtain cylinders of 8 mm height and 4 mm diameter. The films with planar orientation were cut into disks of 4 mm diameter and then piled up to a height of 8 mm in quartz containers. The samples were, then, suspended by a quartz wire from the beam of a S3D–V Sartorius microbalance and placed between the constant gradient pole pieces of a BM6–Bruker electromagnet. Samples of 100–200 mg give rise to forces of the order of 10^{-5} N depending on the magnetic field. The force could be read to 10^{-9} N in the microbalance. Each sample was measured at two different magnetic inductions, B (0.729 T and 1.015 T for a pole gap of 40 mm) in order to correct for effects due to ferromagnetic impurities. For this purpose, the corrected value of χ was derived from a $\chi \sim B^{-1}$ plot by extrapolating to B→ ∞. The accuracy

in a series of measurements, when varying the temperature for a given sample, is better than 0.1% at low temperatures and it decreases to about 0.5% at 291°C due to a higher instability of the measuring system. As regards the comparison of χ between different copolymers the accuracy of the method is better than 1%. The susceptibility was measured, in the interval from room temperature to 20–50°C above the melting point of the sample, using a micro–oven with a temperature control better than 0.5°C. The samples were kept in a nitrogen atmosphere during the measurement of χ.

RESULTS AND DISCUSSION

Influence of comonomer composition: magnetic anisotropy

The diamagnetic molecular susceptibility, χ_M, of the uniaxially oriented samples of the series P(HB/HN) was investigated at room temperature. The values of χ_M per average repeating unit of the three random copolyesters measured with the chain axis parallel, $\chi_{\parallel}$, and perpendicular, $\chi_{\perp}$, to the direction of the applied field are included in Table I. The average molecular susceptibility, $\overline{\chi}$, corresponding to a system with no overall preferred orientation, was calculated for each copolyester using the expression:

$$\overline{\chi} = \frac{1}{3}(2\chi_{\perp} + \chi_{\parallel}) \tag{1}$$

The experimental $\overline{\chi}$ value for the powder sample of the PHN homopolymer was also measured and is included in Table I. Table I also collects the values of the molecular susceptibility per repeating unit calculated according to the semi–empirical atom and bonding increment system (ABIS) [30]. The method yields values of $\chi_M{}^{HB} = -0.866 \times 10^{-9}$ m^{3}mol^{-1} and $\chi_M{}^{HN} = -1.332 \times 10^{-9}$ m^{3}mol^{-1}. The calculated susceptibility values for the average repeating unit of each copolymer with a given molar fraction, ϕ, of HB units have been obtained from the additivity of the susceptibility increments:

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$$\chi_M = \chi_M{}^{HB}\phi + \chi_M{}^{HN}(1-\phi) \tag{2}$$

where ϕ and $1-\phi$ are, respectively, the molar fractions of HB and HN . Figure 1 represents the values of $\chi_\perp$, $\chi_\parallel$, $\overline{\chi}$ and χ_{calc} as a function of comonomer composition. Results show that the diamagnetic susceptibility values ($\chi_\perp$, $\chi_\parallel$, $\overline{\chi}$) linearly diminish with increasing HB content. The experimental $\overline{\chi}$ values are lower than the calculated ones (solid line). This is most probable due to the contribution of intermolecular interactions in the solid state which are not taken into account in the ABIS method. One also sees that $\chi_\perp$ values are higher than the $\chi_\parallel$ values. This result is a consequence of the delocalization of the π electrons in the aromatic planes, which produces an enhancement of diamagnetism in the direction perpendicular to the chain axis. In addition, the degree of electron delocalization increases with HN content leading to the observed gradual increase of χ_M.

From the $\chi_\perp$ and $\chi_\parallel$ values, the magnetic anisotropy $\Delta\chi$ for the three uniaxially oriented copolyesters has been calculated according to the expression:

$$\Delta\chi = \chi_\parallel - \chi_\perp \tag{3}$$

These values, which in our case are positive, are included in Table II. The three extruded samples show a similar level of molecular orientation as revealed by X-ray diffraction. Therefore, the observed increase in $\Delta\chi$ (Table II) can be correlated to the increase of naphtalene units along the chain. This is in accordance with experimental data of Pacault and Lonsdale [30] showing a higher magnetic anisotropy for the aromatic naphthalene group than for the benzene ring. Positive magnetic anisotropy values are characteristic of aromatic polymers, in contrast to polymers like poly(ethylene) [31] and poly(propylene) [32] which show negative $\Delta\chi$ values, as well as lower absolute susceptibility. The magnetic anisotropy of drawn poly(ethylene-terephthalate) and "Kevlar" fibres as a function of draw ratio shows highest values of $\Delta\chi = 0.334$ [33] and 0.596×10^{-9} m^3mol^{-1} [34] respectively. The obtained $\Delta\chi$ results

in the investigated copolyesters together with the values of the theoretical anisotropy of the monomers, point to a low degree of orientation in the starting samples. This result is confirmed by the wide equatorial arcing in the hk0 reflections of X–ray fiber diagrams (see, for example, Fig. 5a).

Temperature dependence

The temperature dependence of the specific susceptibility, $\chi_m = \chi_M/M$ (M = molecular mass of the average repeating unit of the random copolymer), was studied in two samples having different initial orientations: uniaxial orientation and planar orientation. A particular copolyester was selected for each type of orientation.

a) Copolyester 58/42 with uniaxial orientation

The thermal behaviour of magnetic susceptibility was studied for a uniaxially oriented sample of the 58/42 copolyester. In this case the chains are perpendicular to the direction of the applied field. Figure 2 shows the variation of χ_m during heating and cooling from room temperature to a temperature above the solid–mesophase transition ($\sim 250^{\circ}C$). With rising temperature, the magnetic susceptibility slowly increases up to the transition temperature where a step–like increase in χ_m is observed. At $\sim 260^{\circ}C$, χ_m reaches the maximum value of the temperature cycle. If the sample is maintained at $260^{\circ}C$, then the χ_m value decreases as a function of time. At higher temperatures of the melt, there is also a time dependent behaviour of χ_m. Thus, the value of χ_m is always lower at the end of the cooling cycle than the value at the beginning of the experiment. The χ_m value is clearly dependent on the storage time of the sample above the melting temperature. The susceptibility step increase found on heating at the transition temperature can be originated by two factors: either a decrease of intermolecular interactions or a change of the macroscopic molecular orientation. Generally, intermolecular interactions have a much weaker effect upon susceptibility than any orientational factor in aromatic compounds [26]. A decrease of intermolecular interactions could be due to a decrease

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in crystallinity occurring close to the transition or to a lowering of the degree of order at the mesophase. Both arguments should be excluded because, upon cooling into the solid phase (solid symbols in Figure 2), we do not detect a corresponding decrease in χ_m when the crystallization temperature, T_c, is reached. It could be argued that the new solid phase, emerging on slow cooling, might be different from the previous one and/or could have a different degree of crystallinity. Even assuming such possibilities, still no decreasing effect on susceptibility has been observed. Thus, we are bound to conclude that a higher degree of molecular orientation, perpendicular to the direction of the magnetic field, should be achieved at the mesophase transition. This increased orientation is probably a result of a reorganization of the rigid molecules within the more abundant non–crystalline regions, once the constraining effect of the micro–crystals disappears above the melting temperature, T_m. Further X–ray experiments as a function of temperature are needed to confirm this point. Finally, it is worth noting that the influence of the magnetic field which would tend to align the molecules of aromatic polyesters in the parallel direction can also be neglected.

The variation of the temperature has been studied with more detail in Figure 3, which shows the time dependence of χ_m at two different temperatures of the mesophase: 263 and 291°C. It is clear that at both temperatures there is a continuous decrease of the absolute value of the susceptibility, becoming faster the higher the temperature. It means that at the solid–mesophase transition, the thermal disordering effects are still very small but becoming noticeable, for the time scale of our experiments, 10 degrees above that point.

In order to describe changes in orientation, the susceptibility data have expressed, in Figure 4, in terms of magnetic anisotropy values. The data are fitted in this figure according to a Kohlrausch–Williams–Watts (KWW) function, which has been frequently used to describe slow relaxation phenomena [35]. The general expression of the KWW law is:

$$\Phi(t) \sim exp\left[-\left(\frac{t}{\tau_{ww}}\right)^\beta\right] \tag{4}$$

where τ_{ww} is a characteristic relaxation time and β is a parameter ranging between 0 and 1 [36]. In our case, $\Phi(t)$ is the diamagnetic anisotropy, β takes a value of 0.82 and the characteristic time strongly depending on temperature ranges from 2.4h at 291°C to 14.2h at 263°. This means that the relaxation process is remarkably slow. Such a relaxation process should be related to the gradual change of orientation of each nematic domain of rigid molecules, as a whole, from the initial common director orientation towards an isotropic distribution of orientation directions. X–ray diffraction photographs, taken at room temperature, for the initial oriented sample before (Fig. 5a) and after (Fig. 5b) having been at 291°C for $\sim$ 400 min confirm a clear change from the uniaxial orientation towards a macroscopically isotropic state. The obtained high β value corresponds to a narrow relaxation time distribution (not far from a Debye behaviour) [37]. It implies a low degree of intermolecular coupling which should be favoured by large relaxing species as the proposed nematic domains.

During molecular relaxation at temperatures above the melting point, the susceptibility values approach that of a sample without an overall preferred orientation. The latter is characterized by decreasing absolute values with respect to the χ_m values measured in the perpendicular direction of the chain axis of uniaxially oriented samples. Once more the difference between the experimental χ value in the macroscopically isotropic state at 291°C (χ_M = -1.01×10^{-9} m^3 mol^{-1}) and that calculated from ABIS (Table I) is larger than the experimental error. On the other hand, the experimental χ value of the sample investigated at 291°C after a long storage time and the $\overline{\chi}$ value of Table I are very close to each other. This means that from the point of view of intermolecular interactions, as revealed by diamagnetic susceptibility, there is a very small difference between the solid state and the liquid crystalline mesophase. This result could be in agreement with the structural model of Blackwell et al. [38] which predicts the occurrence of three–dimensional order by means of just a small shift of each chain from the nematic phase. Recent wide–angle scattering re-

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sults also show the presence in the melt of segregated, layered (smectic–like) regions within a nematic matrix [17]. These regions could be identified as the precursors of non periodic layer crystallites and their presence explains the striking crystallization capability of random copolyesters even under the most severe quenching.

b) Copolyester 75/25 with planar orientation

The specific diamagnetic susceptibility of the 0.25 mm thick films of the 75/25 copolyester was also measured as a function of temperature. In this case the molecular chains are disoriented in planes which are parallel to the magnetic field. At room temperature, the experimental value, $\chi_m = -6.48 \times 10^{-9}$ m^{3}kg^{-1} ($\chi_M = -0.86 \times 10^{-9}$ m^{3}mol^{-1}), was obtained. This value should arise from averaging all the possible values of χ measured in every direction of a plane which contains the magnetic field vector. The χ value obtained when the magnetic field is applied in a direction that forms a ϕ angle with the direction of the molecules (which is the direction of minimum molecular susceptibility $\chi_{\parallel}$) is derived according to:

$$\chi = (cos\psi \; cos\phi) \begin{pmatrix} \chi_{\parallel} & 0 \\ 0 & \chi_{\perp} \end{pmatrix} \begin{pmatrix} cos\psi \\ cos\phi \end{pmatrix} \tag{5}$$

where $\psi = 90 - \phi$.

The matrix product is equal to:

$$\chi = \chi_{\parallel}cos^2\psi + \chi_{\perp}cos^2\phi = \chi_{\parallel} + cos^2\phi(\chi_{\perp} - \chi_{\parallel}) \tag{6}$$

The average of χ over all possible values in a plane is:

$$<\chi> = \chi_{\parallel} + \frac{(\chi_{\perp} - \chi_{\parallel}) \int_0^{2\pi} cos^2\phi d\phi}{\int_0^{2\pi} d\phi} = \chi_{\parallel} + \frac{\chi_{\perp} - \chi_{\parallel}}{2} = \frac{1}{2}(\chi_{\perp} + \chi_{\parallel}) \tag{7}$$

By taking the $\chi_{\perp}$ and $\chi_{\parallel}$ values for the 75/25 composition from Table I, a $<\chi>$ value of -0.88×10^{-9} m^3 mol^{-1} is calculated, which is in reasonable accordance (within 2%) with the experimental value of χ_M.

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Figure 6 shows the χ_m variation with temperature. At temperatures around 220°C there is a change in the slope that could be attributed to a transformation from a pseudohexagonal crystal structure (unit cell angle $\gamma = 120°$)to a quasihexagonal structure (γ angle close but different to $120°$), previously observed by X–ray diffraction measurements [14]. The latter structure is characterized by a more dense packing. At temperatures where the solid–liquid crystalline transition takes place ($\sim 300°$C) an increase in the absolute value of χ_m is observed. This increase of χ_M, similarly to the uniaxial case, denotes the onset of a change in the orientational order of the system. Above the transition temperature, an increase of the specific susceptibility values is observed as a function of time and temperature in the mesophase. Upon cooling to room temperature, the χ_m values are higher than the ones at the beginning of the experiment. X–ray measurements, at temperatures above the solid–liquid crystalline transition, indicate a decrease in the initial planar orientation. Above this temperature the sample tends towards a macroscopically isotropic state again revealing the occurrence of a molecular relaxation mechanism. The χ values at these temperatures approach those of a state without any preferred orientation, which are higher than the $< \chi >$ values of the initial oriented sample. The differences between the value measured upon cooling at room temperature and the $\overline{\chi}$ values of Table I lie within experimental error.

A final comment should be made about the observed lack of orientation capability of the applied magnetic field in our materials at temperatures above the mesophase transition. It is known, from a previous work on the 75/25 P(HB/HN) copolymer [39], the possibility to achieve a high degree of orientation depending on time in the field, field strength, temperature and molecular weight of the sample. In our case, orientation of the magnetic field is clearly hindered by the higher molecular weight of the investigated material (~ 30000) and by the short time (few seconds) that the samples are, during the susceptibility measurements, under the influence of the highest intensity of the magnetic field (~ 1 Tesla). For such short times the thermal disordering effects prevail.

CONCLUSIONS

Magnetic susceptibility is shown to decrease linearly with HB content, both in the parallel and perpendicular direction to the chain axis. Magnetic anisotropy rises with the introduction of HN groups, provoking a higher delocalization within the copolyester chains. For both, uniaxially oriented materials and samples with planar orientation, evidence is provided of a very slow rate molecular relaxation mechanism above the melting temperature which, depending on storage time and temperature at the mesophase, induces a gradual loss of the initial orientation.

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Legends to figures.

Figure 1. Plot of molecular magnetic susceptibility as a function of molar percent of HB groups: $\triangle$, $\chi_{\parallel}$; ∇, $\chi_{\perp}$; $\bigcirc$, $\overline{\chi}$. Calculated values are represented by a solid line.

Figure 2. Variation of specific magnetic susceptibility versus temperature for the 58/42 copolyester. Open symbols: heating; solid symbols: cooling. Upper left corner: schematics of the perpendicular orientation of the molecules in relation to the magnetic field H. (T_m: melting temperature into the mesophase. T_c: crystallization temperature).

Figure 3. Specific susceptibility as a function of storage time for two temperatures of the mesophase: 263 and 291°C.

Figure 4. Diamagnetic anisotropy as a function of reduced storage time t/τ_{ww}. The line corresponds to the KWW law. Same symbols as in Fig. 3.

Figure 5. X–ray diffraction patterns of 58/42 copolyester sample: (a) before and (b) after measuring the magnetic susceptibility as a function of time at 291°C.

Figure 6. Dependence of specific magnetic susceptibility on temperature for the 75/25 copolyester. Open symbols: heating; solid symbols: cooling. Upper left corner: schematics of the planar orientation of the molecules in relation to the applied magnetic field H.

Table I: Magnetic molecular susceptibility per average repeating unit of the random copolyesters P(HB/HN) as a function of composition. The $\overline{\chi}$ value for PHN (0/100) was determined experimentally. The $\overline{\chi}$ values for the copolyesters were derived from equation 1.

Sample	$-\chi_M[10^{-9}\mathrm{m^3mol^{-1}}]$			
	$\chi_\perp$	$\chi_\parallel$	$\overline{\chi}$	χ_{calc}
0/100			1.247	1.332
30/70	1.219	0.939	1.126	1.192
58/42	1.091	0.827	1.003	1.062
75/25	0.993	0.774	0.920	0.982
100/0				0.866

Table II: Magnetic anisotropy per average repeating unit for the copolyesters P(HB/HN).

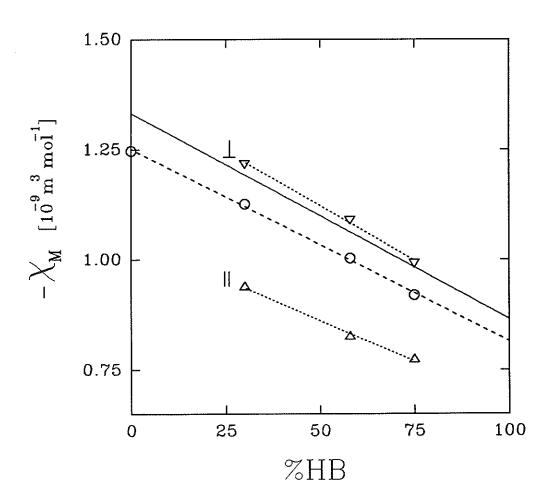| P(HB/HN)	$\Delta\chi[10^{-9}\mathrm{m^3mol^{-1}}]$
30/70	0.280
58/42	0.264
75/25	0.219

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Fig. 1

Fig. 2

Fig. 3

Fig. 4
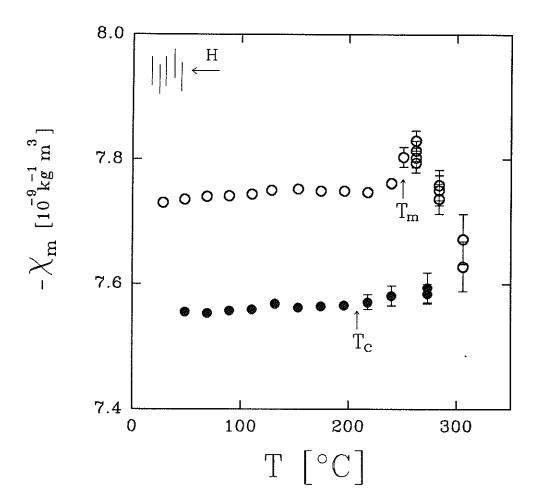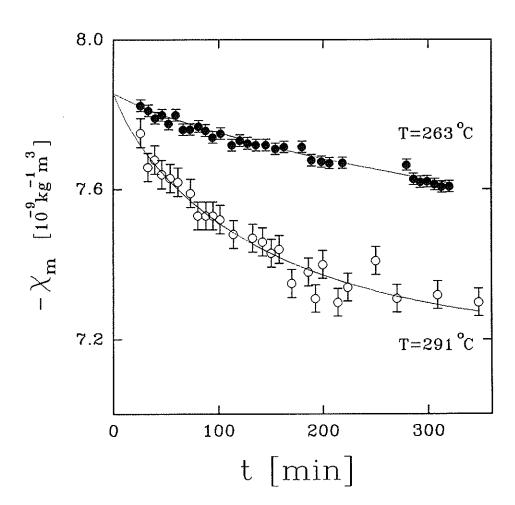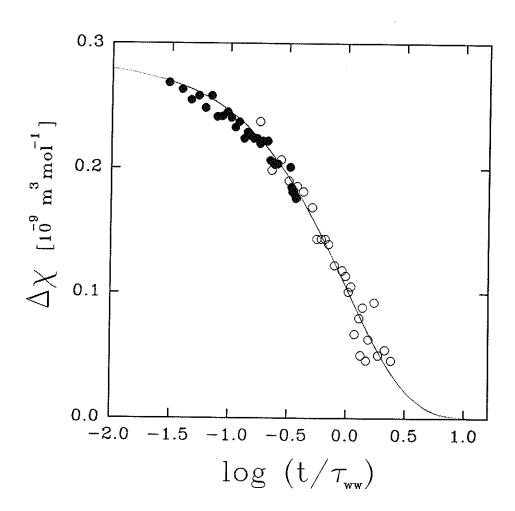
a   b

Fig. 5

Fig. 6