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Segmental Orientation and Chain Relaxation of Polymers by Fourier Transform Infrared Dichroism

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Fourier transform infrared dichroism has been used to investigate molecular orientation in polymeric materials. It is first applied to characterize network behavior in some elastomeric systems such as model networks of poly(dimethylsiloxane). The strain dependence of segmental orientation is analyzed through networks of known degree of cross-linking and experimental results are compared with calculation predictions based on the rotational isomeric state formalism. Infrared dichroism spectroscopy has also been used to analyze orientational relaxation in binary blends of long and short polystyrene chains.The effect of short deuterated chains (M_W = 3000 to 72000) on the orientational relaxation of long entangled chains (Mw = 2 000 000) is examined in the bidisperse melts uniaxially deformed above the glass transition temperature. While the long chain relaxation is found to be dependent on the short-chain concentration, the local orientational order of the latter is molecular weight dependent in agreement with the classical relaxation theories.

Introduction

Mechanical properties of polymers are strongly influenced by molecular orientation occurring during stretching or during various forming-processes. Measurement of this orientation is of particular importance for both a better molecular understanding of the mechanisms involved in polymer deformation and for a better understanding of the molecular relaxation processes.

The directions of chain segments are isotropically distributed in an undistorted material. When the material is macroscopically distorted, the orientation of segments becomes anisotropic. The state of anisotropy in strained polymers may accurately be characterized by various spectroscopic techniques such as polarized fluorescence, deuterium NMR and vibrational spectroscopy, including polarized Raman spectroscopy and infrared dichroism1). These techniques directly probe the orientational behavior of polymer chains at a molecular level, in contrast to the macroscopic information provided by most other characterization techniques.

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The specificity of infrared absorption bands to particular chemical functional groups makes infrared dichroism especially attractive for a detailed study of submolecular-level orientations of materials such as polymers$^{2,3)}$.

In this paper, two different applications of infrared dichroism by using Fourier transform infrared spectroscopy are illustrated.

Molecular orientation in some elastomeric systems, more precisely in model networks of poly(dimethylsiloxane) (PDMS), will be examined first. The strain dependence of segmental orientation are analyzed through networks of known degree of cross-linking. Some new results are shown on filled PDMS networks.

The second part is devoted to an analysis of orientational relaxation in binary blends of long and short polystyrene chains. The influence of the short-chain concentration on the long-chain relaxation will be discussed. In addition, the relaxation behaviour of the short chains is presented.

Polarized infrared spectroscopy

The absorption of infrared radiation is caused by the interaction of the electric field vector of the incident light with the electric dipole-transition moment associated with a particular molecular vibration :

Segmental orientation in a material submitted to uniaxial elongation may be conveniently described by the second Legendre polynomial $<P_2(\cos\theta)>$:

$$<P_2 (\cos \theta) > = \frac{1}{2} (3 <\cos^2\theta> -1)$$

where θ is the angle between the macroscopic reference axis (usually taken as the direction of strain) and the local chain axis or any directional vector characteristic of a given chain segment (Fig.1).

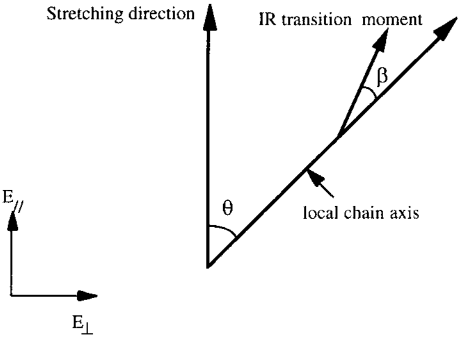

Fig.1. Positions of local chain axis and transition moment with respect to the stretching direction.

The angular brackets indicate an average over all molecular chains and over all possible configurations of these chains.

The relevant parameters commonly used to characterize the degree of optical anisotropy in stretched polymers are the dichroic ratio R ($R= A_{//} / A_{\perp}$) or the dichroic difference ΔA ($\Delta A = A_{//} - A_{\perp}$). $A_{//}$ and $A_{\perp}$ are the absorbances of the investigated band, measured with radiation polarized parallel and perpendicular to the stretching direction, respectively.

The second moment of the orientation function is related to the dichroic ratio R by this expression :

$$<P_2 (\cos \theta)> = \frac{2}{(3\cos^2 \beta - 1)} \times \frac{(R-1)}{(R+2)} = F(\beta) \frac{(R-1)}{(R+2)}$$

where $F(\beta)$ only depends on the angle β between the transition moment vector of the vibrational mode considered and the local chain axis of the polymer. This angle β can usually be obtained from theoretical considerations arising from group theory .

Model networks of poly(dimethylsiloxane)

The infrared dichroism technique was first applied to characterize molecular orientation in elastomeric networks, which exhibit stable elastic properties if flexible chains are permanently linked together during the cross-linking process.

Strain dependence of the segmental orientation

The use of model networks leads to a better understanding of the properties of elastomeric materials at a molecular level. In this work, model networks of poly(dimethylsiloxane) were obtained by end-linking functionally terminated precursor chains of a given molecular weight to a multifunctional cross-linking agent.

The resulting networks are characterized by constant junction functionality and known molecular weight distribution Mc between cross-links[4,5].

We have investigated the dichroic behavior of the band located at 2500 cm^{-1} ascribed to the overtone of the symmetrical bending vibration of the methyl group located at 1260 cm^{-1}. The transition moment associated with both vibrational modes lies along the CH_3-Si bond which is a symmetry axis of the methyl group.

As expected, since the transition moment associated with the investigated band is nearly perpendicular to the chain axis, this band exhibits a perpendicular dichroism : R is less than 1 and decreases as the deformation increases.

Determination of the orientation function requires the definition of the angle β between the transition moment of the investigated band and a directional vector characteristic of a given chain segment. For the particular case of PDMS chains, the chosen directional vector is that joining two successive oxygen atoms. The angle β is expected to equate to 90°. However, a near-infrared investigation suggests that this value is questionable. More probably, this mode is coupled with other vibrations leading to a lower value of the angle β.

In Fig. 2, values of the orientation function derived from the dichroic ratios are represented against what is called the strain function (α^2 - α^{-1}) which reflects the effect of the macroscopic deformation on orientation. The results, related to networks prepared with four different precursor chains, show that, for a given extension ratio, α, the orientation increases with increasing cross-linking density.

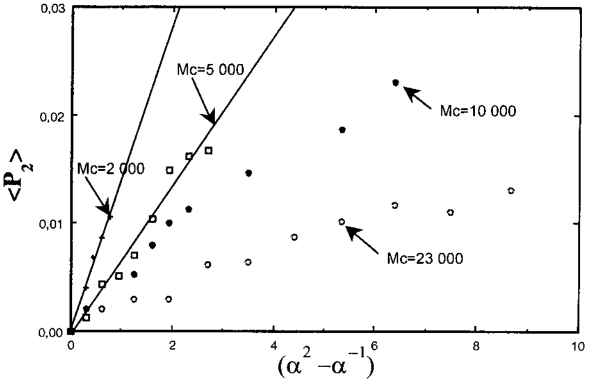

Fig.2. Dependence of the orientation function on deformation.

One practical problem in the case of infrared dichroism measurements arises from the requirement that band absorbance should be sufficiently low to permit a precise use of the Beer-Lambert law. This implies the use of thin films often less than 100 microns thick. This problem can be overcome by using near-infrared spectroscopy which probes overtones and combination bands6). Effectively, the reduced intensity of the near-infrared absorptions makes a wide area of the spectrum available for evaluation of the dichroic effects. NIR spectroscopy give similar information, provided that a correct assignments of the bands is available7). Moreover, one unique advantage of this technique is to allow the analmysus of vibrational modes probably less coupled than in the mid-infrared mode8).

Another problem often met in linear dichroism is the lack of sensitivity in the determination of small dichroic effects. This could be the case for films under low deformation or in polymers exhibiting slight orientation. For these cases, the dichroic differences are small and the dichroic ratios R are close to unity. A polarization modulation approach can be used to measure small dichroic effects with high sensitivity9).

The main optical component in a polarization-modulation experiment is a photoelastic modulator placed in a linearly polarized beam of light and which can alternate rapidly the state of polarization of the electromagnetic radiation between directions parallel and perpendicular to the stretching axis. This technique allows a direct evaluation of the dichroic difference ΔA in a single measurement. By improving the signal-to-noise ratio, this method is able to detect the onset of orientation and leads to a more precise determination of the dichroic effects[10].

Precise experimental measurements are effectively required to test the limits of the validity of the various theoretical models used to estimate molecular orientation under deformation.

The orientation function which characterizes the segmental orientation in phantom and affine network models under uniaxial extension is given by the following expressions :

$$<P_2>_{phantom} = D_0 (1 - 2 / \phi) (\alpha^2 - \alpha^{-1})$$
$$<P_2>_{affine} = D_0 (\alpha^2 - \alpha^{-1})$$

where α is the extension ratio defined as the ratio of the final length of the sample in the direction of stretch to the initial length before deformation, ϕ is the junction fonctionality and D_0 is the configurational factor[11-13]. This factor, which incorporates the structural features of the network chains, only reflects the "orientability" of the chain segments.

The values of D_0 which are of the order of 1/n (n being the number of bonds in the chain between two junctions) can be evaluated from the rotational isomeric state formalism by using a Monte Carlo chain generation technique[14].

In an affine network, the junction points are assumed to be embedded in the network and transform affinely with macroscopic deformation, while in the phantom network model the junction points fluctuate over time without being hindered by the presence of the neighboring chains[11].

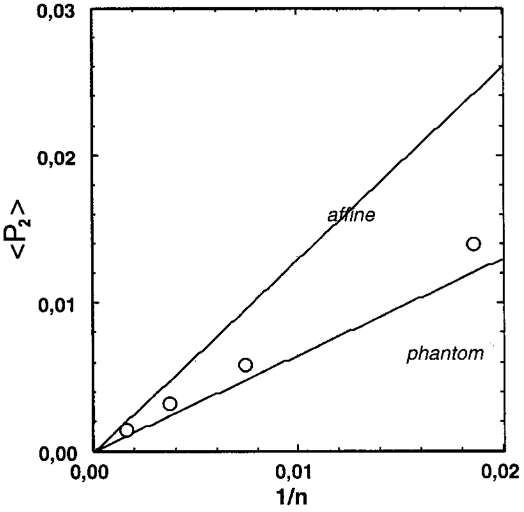

Fig.3. Comparison of the experimentally determined function with theoretical predictions. The abscissa represents the reciprocal of the number of bonds.

The theoretical predictions for affine and phantom networks are shown in Fig. 3 together with the points resulting from FTIR experiments. These points represent the reduced orientations obtained from the slopes of the curves representing <P_2> versus the strain function. The experimental points lie between the predictions of the affine and the phantom network models. This behavior is predicted by the constrained junction model of real networks.

The experimental results for segmental orientation are in close agreement with the phantom network model for the smaller values of M_c. Segmental orientation approaches the affine limit as the network chains get longer[15)].

This behavior is also predicted by the constrained junction theory according to which the fluctuations of chains relative to those of the phantom network decrease with increasing chain length and the network behavior approaches that of the affine network.

Filled poly(dimethylsiloxane) networks :

Incorporation of fillers such as silica in poly(dimethylsiloxane) elastomers is well known to improve the mechanical properties of the final materials. Analysis of the orientational behavior of the filled samples provides an area for understanding the molecular origin of the reinforcement effect[16)].

Stress-strain measurements for the unfilled and filled PDMS networks are represented in Fig. 4 as plots of the true stress (which is the force divided by the deformed area) against the strain function.

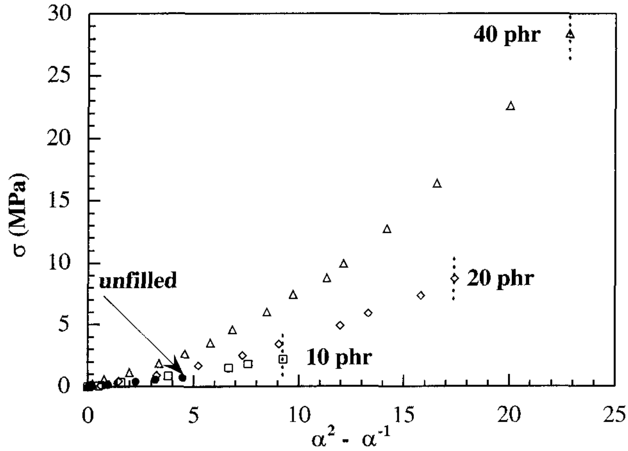

Fig.4. Stress-strain curves at room temperature.

Each curve is labeled with the amount of filler present in the network and the vertical broken lines locate the rupture points. The data clearly indicate that the incorporation of the reinforcing particles significantly increases the modulus and the ultimate properties like the stress at rupture and the maximum extensibility.

Orientational analysis also shows that, at a given extension ratio, the orientation function increases continuously with an increase in the filler fraction (Fig.5).

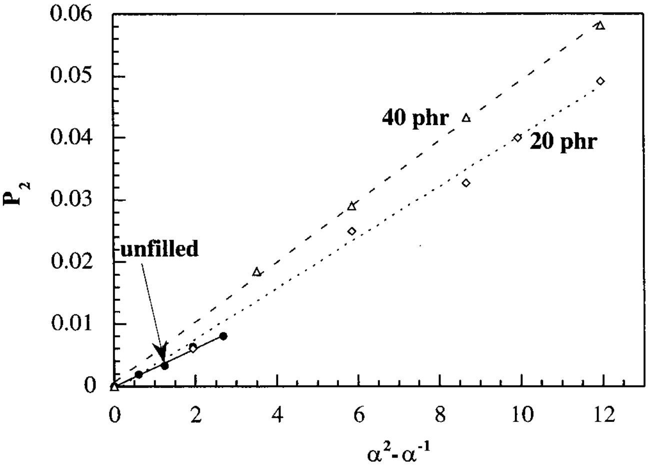

Fig.5. Strain dependence of the orientation function.

The higher molecular order observed by addition of filler is attributed to the fact that particles act as additional cross-links, thus increasing the effective degree of cross-linking.

In the silica/PDMS system, the interaction between the filler and the polymer chains occurs between the silanols present in the surface with the oxygen atoms of the PDMS chains via hydrogen bonding. This number of additional cross-links increases with the amount of filler or with the interface area of the particle polymer/system, thus inducing an increase in orientation.

Analysis of orientational relaxation of long and short chains in binary blends of polystyrene

Infrared dichroism can also probe orientational dynamics and chain relaxation processes following a step strain.

The work presented here has been focused on the orientational relaxation of long and short chains in binary blends of polystyrene. The main objective was to analyze the effect of polydispersity which strongly affects the viscoelastic properties of polymer melts. Analysis of model systems has proved to be a useful approach for investigating this polydispersity effect.

We have investigated binary blends composed of deuterated short chains of molecular weights ranging from three to seventy-two thousand and of fully entangled undeuterated long polystyrene chains of molecular weight 2 millions. By deuterating one type of chain, one is able to characterize with infrared spectroscopy the orientation function of each species owing to the mass dependence of the vibrational frequency. We have examined the influence of both the concentration and the length of the short deuterated chains on the long-chain relaxation. The relaxation behaviour of the short chains is also be presented.

In our experiments, the samples were uniaxially stretched at constant strain rate ($\dot{\varepsilon}$= 0.115 s^{-1}) at temperatures above the glass transition temperature and at a draw ratio α equal to four. The samples were then allowed to relax under constant conditions of length and temperature for a given time t_R, called the relaxation time. They were then quenched rapidly to room temperature in order to freeze the state of orientation, which was subsequently characterized by infrared dichroism (Fig.6). The temperature and relaxation time were varied in order to study the chains in various relaxation states. Analysis of the time-dependence of the orientation state provides an access to the molecular relaxation processes.

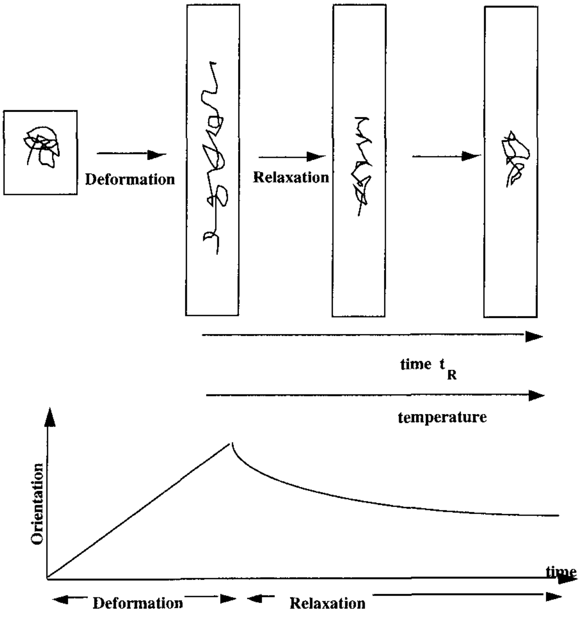

Fig.6. Experimental scheme for the observation of the relaxation processes.

Figure 7 represents the master curve of the orientational relaxation of the pure polymer of molecular weight 2 million. The orientation of the hydrogenated long chains was measured by following the dichroic behavior of the band located at 906 cm^{-1} associated with the out-of-plane vibration of the benzene ring$^{17)}$.

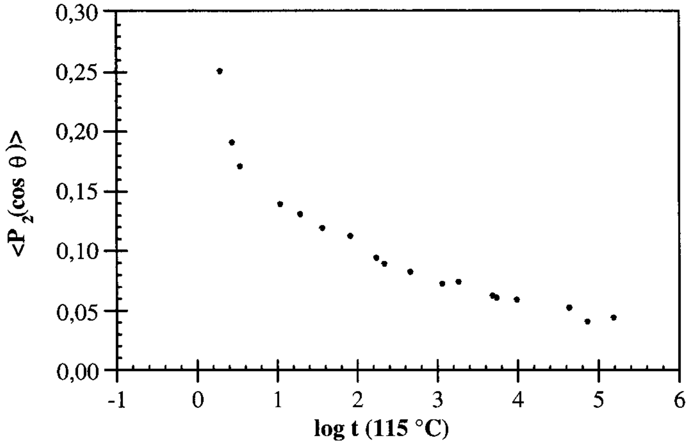

Fig.7. Master curve of the relaxation of orientation of the pure polymer of molecular weight 2 millions at a reference temperature of 115°C.

All the ageing times were calculated at a reference temperature (at 115°C) by applying the time-temperature superposition principle given by the classical WLF equation[18]:

$$\log \frac{t_T}{t_{115}} = \frac{-C_1^{115}\,(T - 115)}{C_2^{115} + T - 115}$$

by using the C_1 and C_2 parameters obtained from our viscoelastics measurements.

At a reference temperature, these parameters are linked to the fractional free volume f_T at this temperature and to the thermal expansion coefficient of the free volume α_f. The relaxation process following a step strain may be briefly described in three stages which constitute the main features of the Doi-Edwards model[19]. Essentially, it has been established that the first relaxation process τ_A which corresponds to a Rouse-like relaxation of chain segments between entanglements is related to the monomeric friction coefficient ζ_0 and to the square of the number of monomers between entanglements N_e. τ_A is given by :

$$\tau_A = \frac{a^2 \zeta_0 N_e^2}{6\pi^2 kT}$$

where a is the monomer length, k the Boltzmann constant and T the absolute temperature.

The second process τ_B which corresponds to a retraction of the deformed chain inside its tube is proportional to the square of the molecular weight of the chain. The next stage τ_C corresponds to the reptation process itself where the entangled chains recover their isotropic configuration at times which scale as the third power of the molecular weight.

This model involves only one adjustable relaxation time, τ_A, for instance, since the others are linked by the following scaling laws :

$\tau_B = 2(N/N_e)^2\, \tau_A$

$\tau_C = 3(N/N_e)\, \tau_B$

where N is the number of monomer units per chain.

From our determination of the monomeric friction coefficient and of the molecular weight between entanglements, we have evaluated the three relaxation times at the reference temperature of 115°C : $\tau_A \approx 16s$; $\tau_B = 4x10^5s$ and $\tau_C = 1.2x10^8s$. Consequently, the time range explored by the experiments allows the observation of the first two steps of the relaxation process of the long polystyrene chains.

By adding 20 weight percent of short deuterated chains of molecular weight 3000, the long-chain orientation in the binary blend is, at a given ageing time and at a same reference temperature, less than that of the pure polymer (Fig.8). This result has to be connected with the fact that chain orientation in the two systems has to be compared in the adequate reference state.

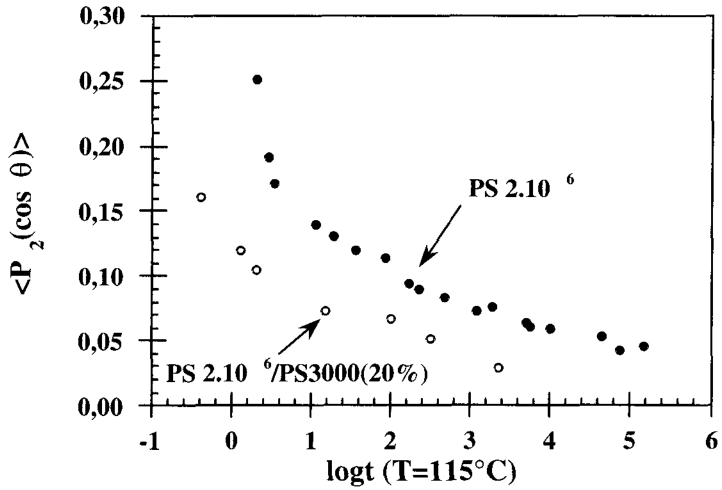

Fig.8. Long-chain relaxation in the pure polymer and in a blend containing 20 wt.-% of short chains (Mw = 3000) at a reference temperature of 115°C.

The presence of short chains modifies the monomeric friction coefficient ζ_0, which has been shown to be a relevant parameter in the relaxation processes. This parameter characterizes the resistance encountered by a monomer unit moving through its environment[18]. The results show that the monomeric friction coefficient is smaller in the binary blend than in the homopolymer. This observed reduction in ζ_0 is only attributed to an increase in the fractional free volume. As it is shown in figure 9, a good rescaling is obtained if the data are compared at a same frictional coefficient. In fact, at temperatures at which the monomeric friction coefficient is the same, we observe a negligible difference between the long-chain relaxation in the pure polymer and that in the blends which contains 20 wt.-% of short chains, even of very low molecular weights. Clearly at this blend ratio, the short chains have a small effect on the long-chain relaxation. By increasing the amount of short chains to 30 %, a decrease in the long-chain orientation is observed compared with that for the undiluted polymer. The level of orientation seems to decrease with the molecular weight of the short species (Fig.10).

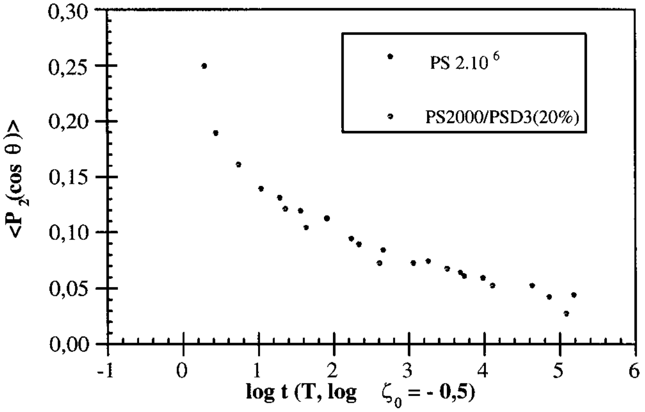

Fig.9. Long-chain relaxation in the pure polymer and in a blend containing 20 wt.-% of short chains (Mw = 3000) at temperatures corresponding to a common value of the monomeric friction coefficient $\log\zeta_0 = -0.5$.

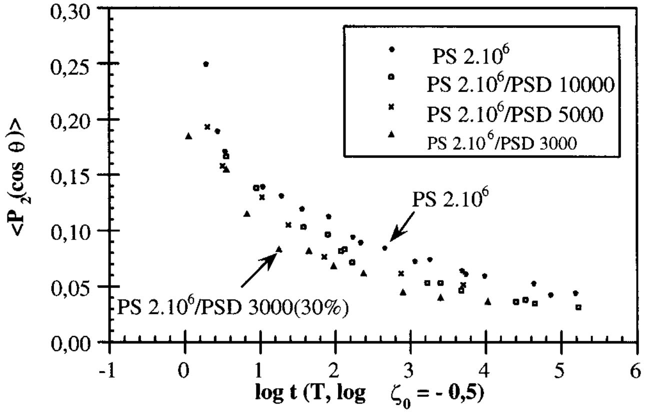

Fig.10. Long-chain relaxation in blends containing 30 wt.-% of short chains

Since all the data were corrected to a common value of the monomeric friction coefficient, the molecular weight between entanglements is solely involved in the first relaxation process. It is generally accepted that unentangled short chains mainly act as diluent species increasing the molecular weight between entanglements according to this relation and thus reducing chain orientation.

A rheological study carried out on the undiluted polymer and on the blend containing 30% of short chains of molecular weight 10000 confirmed a decrease in the plateau modulus which leads to a molecular weight between entanglements in agreement with the predicted relation.

The 2273 cm^{-1} absorption band ascribed to a stretching vibration of the aromatic CD bonds was used to probe the deuterated chain orientation[17,20)].

Figure 11 shows master curves of the orientational relaxation of short deuterated chains of various molecular weights present at 20 % in the matrix of molecular weight 2 millions.

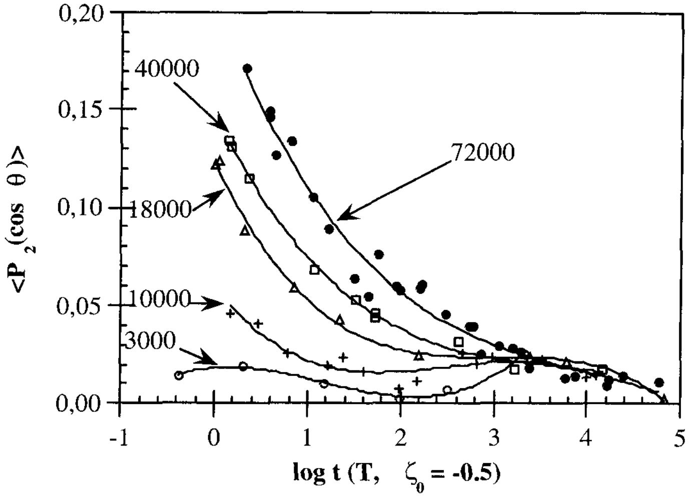

Fig.11. Orientational relaxation of the short deuterated chains blended at 20wt.-% with polystyrene of molecular weight 2 millions.

While the orientation of these deuterated chains shows a strong molecular weight dependence especially at short times, all chains exhibit at long times a residual orientation, which has been attributed to orientational coupling interactions with the long chains of the polymer matrix. Similar orientational correlations have been observed on various systems by 1H NMR spectroscopy studies of stretched elastomers, where even dissolved solvent molecules and free chains were shown to possess a very short-length scale local orientation[21]. This residual orientation was confirmed by the polarization modulation technique which has been shown to be very sensitive to very small anisotropies.

The short chains behave like Rouse chains[22]. They return to an isotropic conformation at times which are proportional to the square of their mass. The Rouse times have been estimated at 115°C from rheological measurements of the same systems. A good agreement with experimental data is obtained.

Conclusion

This paper demonstrates that the infrared dichroism is a powerful tool for probing the chain segment orientation.

A better characterization of segmental orientation can be obtained by combining polarization-modulation with FT-IR spectroscopy. This technique should be exploited more in order to obtain reliable experimental results, thus allowing more extensive comparisons between theory and experiment.

In the case of model networks of PDMS, the strain dependence of segmental orientation follows the predictions of the theoretical models.

In the case of binary blends of high and low molecular weight monodisperse polystyrene, it was shown that the orientational relaxation of the long polystyrene chains in the blends are only weakly affected by the presence of short chains for short chain concentration ranging from 10 to 30 wt.-%. The short chain relaxation was successfully described by the Rouse model.

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