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Analysis

Infra-Red Dichroism Investigation of Molecular Viscoelasticity Using Isotopically Labelled Block Copolymers

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Summary

Infra-red dichroism has been used to measure the orientation of the different sequences of isotopically labelled block copolymers. We have determined the orientation from dichroic ratios of two bands of deuterated polystyrene, and compared in block copolymers the orientation of the central part of the chain with that of the ends. The relaxation of the ends is more rapid than that of the center, which exhibits a "plateau".

Introduction

Recently, there has been increased interest in viscoelastic properties of polymer melts, both experimentally and theoretically through the approaches of De Gennes (1), Edwards and Doi (2) to chain relaxation.

Although theories can be tested through the behavior of macroscopic parameters such as stress or elastic modulus, the observation of microscopic quantities has proved to be useful for the study of viscoelastic phenomena, on a molecular level. Spectroscopic techniques like small angle neutron scattering (s.a.n.s), fluorescence polarization (f.p.) and infrared dichroism (i.r.d.) are particularly well suited, especially when largely deformed polymer chains are concerned (3).

S.a.n.s. measurements provide information on the structure of chains at various spatial scales, whereas f.p. or i.r.d. lead to the determination of the chain segment orientation. For f.p. measurements, it is necessary to use a fluorescent molecule like anthracene, as a label. The experimentally measured orientation function deals with the orientation of the part of the chain which is directly connected to the fluorescent molecule, i.e. the central part of the chain or the end of the chain. The main advantage of this technique is its very high sensitivity. One can study the behavior of labelled chains at a concentration of 1 wt % in a matrix of unlabelled chains, and thus investigate the effect of the molecular weight of either the labelled chains or the chains of the matrix. In contrast i.r.d. does not require any labelling of the polymer chains. The orientation function measured by i.r.d. is an average, over all the chains of the sample, of the orientation of all the chain segments. In order to look at the orientation of particular species, it is tempting to use deuterium isotopic substitution to label the chains under interest. Indeed, frequency shifts are expected in the infrared spectra between hydrogenated and deuterated species. Preliminary experiments performed in our laboratory have shown that, due to the sensitivity of the i.r. technique, a concentration of deuterated species higher than 10 wt % is required. This eliminates any possibility of studying the effect of the molecular weight of the labelled chains or of the polymer matrix without disturbing the overall

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properties of the material. By using isotopically labelled block copolymers, one should be able to identify the behaviour of the different sequences and to compare the relaxation of the whole chain with that of the ends or the central part of the chain.

The first part of this work is devoted to the determination of the second moment of the orientation function for perdeuterated polystyrene chains from i.r.d. measurements. The second part deals with the study of the orientation of two isotopically labelled block copolymers, from which we extract the orientation of the middle and of the chain ends.

Experimental

Perdeuterated polystyrene, poly(d_8 styrene), noted PSD (Polymer Laboratory, $\overline{M}_w$: 205,000, $M_w/M_n < 1.14$) and normal polystyrene, noted PSH, (supplied by E.A.H.P. (Ecole d'Application des Hauts Polymères, 6 rue Boussingault, 67000 Strasbourg, France), $\overline{M}_w = 181{,}000$, $M_w/M_n = 1.11$) have been used in the first part of our work. In addition two block copolymers were prepared by anionic polymerization by one of us (L.J.F) :

- a diblock copolymer Poly(d_8-Styrene-b Styrene) having a total molecular weight $\overline{M}_w = 184{,}000$, $M_w/M_n < 1.05$ and a d_8 sequence molecular weight $\overline{M}_w = 27{,}000$, $M_w/M_n < 1.03$
- a triblock copolymer Poly(Styrene b-d_8 Styrene-b styrene) with a total molecular weight $\overline{M}_w = 188{,}000$, $M_w/M_n < 1.05$, and a central d_8 sequence of a molecular weight of 30,000 ($M_w/M_n < 1.03$),

The polymer films were obtained by casting a 6 % freshly distillated benzene solution of each polymer on a glass plate, followed by drying at room temperature. 2 cms large strips were annealed under vaccum for 48 hours at 140°C in order to remove any trace of solvent and internal stress.

Stretching experiments were performed at constant strain rate and at various temperatures above the glass transition temperature (Tg ~ 105°C measured by d.s.c. with a heating rate of 10°C/mn), on a apparatus developped in our laboratory (4).

Infrared spectra were obtained on a Nicolet 7199 Fourier transform infrared spectrometer at a resolution of 2 cm^{-1} with a total of 32 scans. The polarisation of the infrared beam was obtained by use of a SPECAC gold wire grid polarizer, and samples rather than polarizer were rotated 90° in order to obtain the two polarization measurements. Dichroic ratios were calculated from $R = \frac{A_{\parallel}}{A_{\perp}}$ (where $A_{\parallel}$ and $A_{\perp}$ are the measured absorbance for electric vector parallel and perpendicular to the stretching direction respectively).

Results and discussion

1/ Determination of the orientation of perdeuterated chains

Fig. 1 shows the infrared spectra of perdeuterated polystyrene and normal polystyrene. As a relatively small amount of PSD will be used, only strong bands will be considered. Many of these overlap partially with bands of PSH such as those at 1575, 1380, 1330, 840 cm^{-1}. In fact, only the group of bands lying between 2000 and 2300 cm^{-1} is isolated. Bands assignements have been already proposed [5]. The 2100 cm^{-1} and 2195 cm^{-1} bands are attributed to the symmetric and asymmetric stretching vibrations of CD_2 groups respectively, and the band at 2273 cm^{-1} contains stretching vibrations of the aromatic C-D groups.

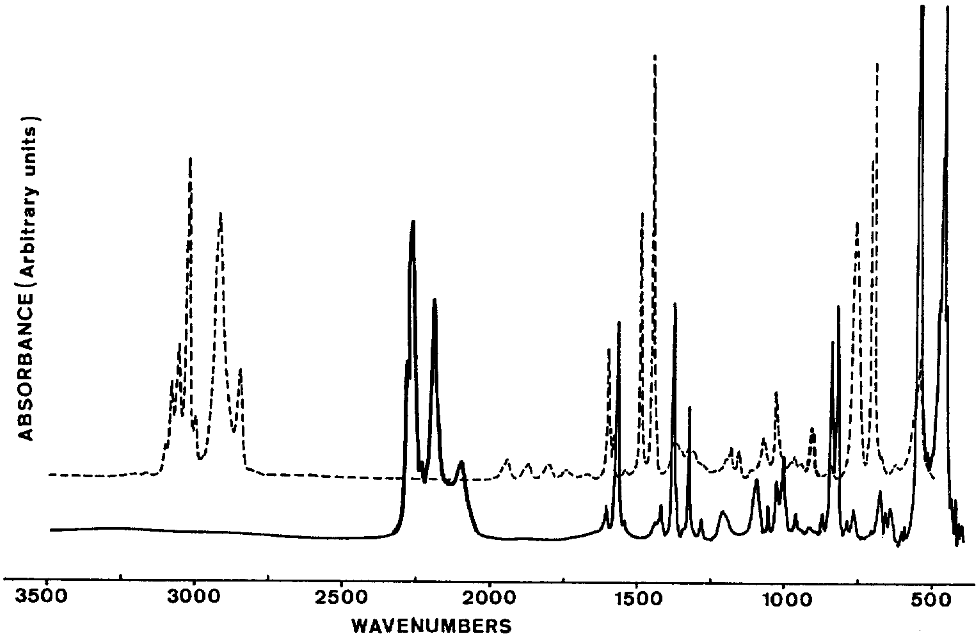

Fig. 1 - Infrared spectra of polystyrene (---) and perdeuterated polystyrene (——)

Dichroic ratios of the 2100, 2195, 2273 cm^{-1} bands have been measured for samples stretched under the following conditions of temperature and strain rate : 121°C, 0.029 s^{-1}; 119°C, 0.029 s^{-1}; 116°C, 0.029 s^{-1}; 113°C, 0.115 s^{-1}. Those perpendicular bands show a dichroic ratio which decreases when the draw ratio increases, or temperature decreases. The most reliable results are obtained from the 2273 and 2195 cm^{-1} bands. These two bands insensitive to the local conformation of the polymer chain, are suitable for dichroism measurements. Unfortunately, the angle between the transition moment and the local chain axis is not known for these vibrations. This impedes the calculation of the quantity $< P_2(\cos \Theta) >$ in which Θ is the angle between the local chain axis and the direction of stretching.

Therefore we have studied the orientation of the blends 85 % PSH, 15 % PSD. Samples were stretched under the following conditions; 121°C, 0.029 s^{-1}; 116°C, 0.029 s^{-1}; 116°C, 0.115 s^{-1}. The orientation of PSH chains was measured using the 906 cm^{-1} absorption band which corresponds to the out-of-plane ν_{17b} mode of the benzene ring, for which the dipole moment makes an angle of the order of 35° with the chain axis [6]. It was impossible to use the 1028 cm^{-1} band, since it is partially overlapped by a PSD band. The orientation of the PSH chains has been calculated using

$$< P_2(\cos \Theta) >_H = \frac{R_o + 2}{R_o - 1} \left(\frac{R - 1}{R + 2}\right)_{906} \quad \text{with } R_o = 2 \,\mathrm{cotg}^2 \alpha$$

and $\alpha = 35°$.

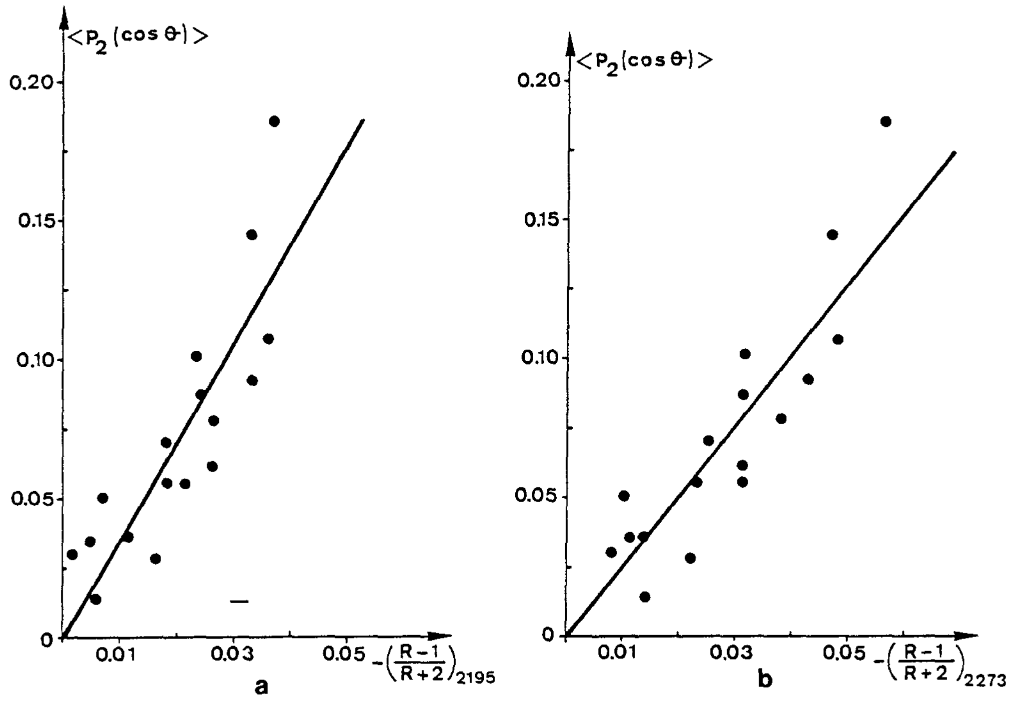

Fig. 2.a - Orientation of polystyrene chains measured with the 906 cm^{-1} band as a function of - (R-1)/(R+2) calculated from the 2195 cm^{-1} band.
b - Orientation of polystyrene chains measured with the 906 cm^{-1} band as a function of - (R-1)/(R+2) calculated from the 2273 cm^{-1} band.

In order to calculate the orientation of PSD chain we postulate $< P_2(\cos \Theta) >_D = < P_2(\cos \Theta) >_H$. (Both types of chain have approximatively the same length). The quantity $< P_2(\cos \Theta) >_D$ can be expressed as :

$$< P_2(\cos \Theta) >_D = A\left(\frac{R - 1}{R + 2}\right)_{2195}$$

$$< P_2(\cos \Theta) >_D = B\left(\frac{R - 1}{R + 2}\right)_{2273}$$

The constants A and B can be determined by plotting $< P_2(\cos \Theta) >_H$ as a function of $(\frac{R-1}{R+2})_{2115}$ and $(\frac{R-1}{R+2})_{2273}$. (Fig. 2 (a) and (b)). A linear least square regression yields A = - 3.8 and = - 2.7, with an accuracy of about 15 %. The magnitude of theses coefficients indicates that the dichroism of these PSD bands is weaker than for the 906 cm^{-1} PSH band for which the constant is round - 2.

2/ Orientation of the copolymers

In order to study the orientation of the chains in a large time domain, samples were stretched at temperatures varying between 110°C and 135°C and strain rates between 0.115 s^{-1} and 0.008 s^{-1}. The temperatures (T) and strain rates ($\dot{\varepsilon}$) were chosen to obtain the largest variation, at a reference temperature T_o, of the quantity $\dot{\varepsilon}\, a_{T/T_o}$, while minimizing the number of experiments (a_{T/T_o} is the time-temperature shift factor at the temperature T). This procedure is commonly used to obtain a master curve at a temperature T_o from viscoelastic dynamic data [7]. The average orientations of D and H blocks were independently determined as described above and the average orientation of the whole chain was calculated as the weight average of the orientation of each block.

Figure 3 illustrates the behavior of the orientation of the chain and of the D block for the triblock copolymer at 113°C, 0.115 s^{-1} and 128°C, 0.029 s^{-1}. Figure 4 exhibits the different behaviors of the D. blocks in the two copolymers. Within the experimental error, a linear relationship holds between $< P_2(\cos \Theta) >$ and the draw ratio for both types of blocks. Fig. 3 shows that at 113°C, the orientation of the central part of the chain is quite similar to the average orientation, whereas at higher temperature (128°C), the central block has an higher orientation than the average. This effect is more obvious when we compare blocks of the same length but differently located on the chain (Fig. 4). Indeed the difference between the orientation of the central and the end portions of the chain increases with temperature. At 113°C the ends are somewhat less oriented than the central part of the chain whereas at 128°C they are significantly less oriented.

Fig. 5 shows the orientation at $\lambda = 4$ of the deuterated sequences as a function of the parameter log $\dot{\varepsilon}\, a_T$ at a reference temperature of 120°C. The average orientation of the chain has not been represented here for clarity, but it lies between the two curves. The right part of the plot represents the short time behavior of the relaxation, the left part exhibits the behavior at longer times. At short times, the relaxation of orientation is rather independent of the location of the observed sequence on the chain. When we go to larger times, Fig. 5 shows that the orientation of the ends of the chain decreases much more rapidly than that of the central part. The relaxation of the center passes through a plateau, whereas the orientation of the ends decreases continuously.

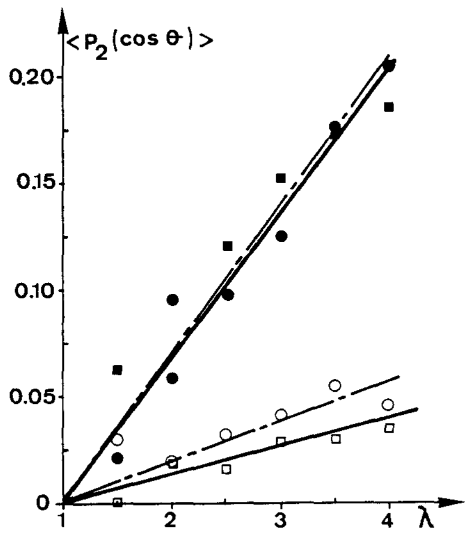

Fig.3 - Orientation of the deuterated block (circles) and average orientation (squares) of the triblock copolymer as a function of the draw ratio.(filled symbols 113°C, 0.115 s^{-1} ; open symbols 128°C, 0.029 s^{-1})

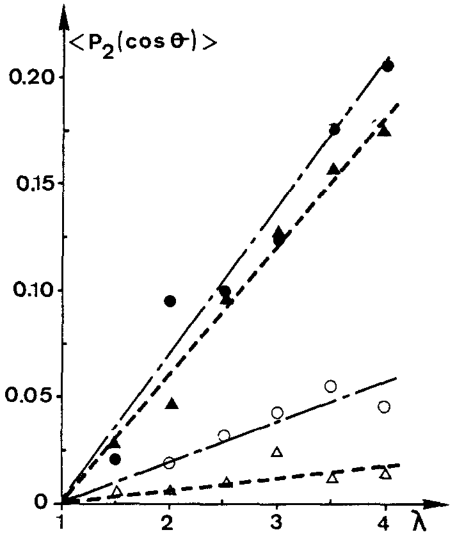

Fig.4 - Orientation of the deuterated blocks (circles : central block; triangles : end block) as a function of the draw ratio (filled symbols 113°C, 0.115 s^{-1}; open symbols 128°C, 0.029 s^{-1})

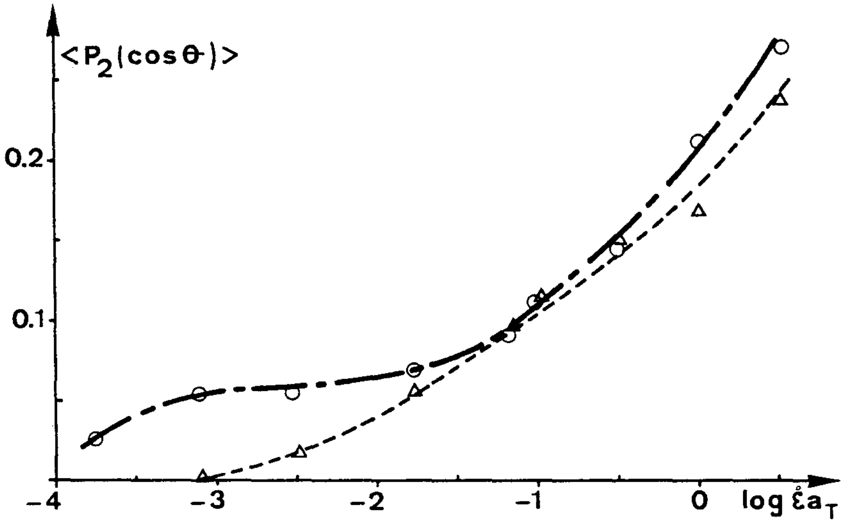

Fig. 5 - Orientation measured at a draw ratio λ = 4, as a function of $\log \dot{\varepsilon}\, a_{T/T_0}$. (T_0 reference temperature = 120°C)

△ deuterated end block, ○ deuterated central block.

Conclusion

The use of infra-red dichroism on isotopically labelled block copolymers is a new and powerfull tool to look at the relaxational behaviour of different parts of polymer chains. This qualitative study points out that a polymer chain does not relaxe uniformly, but that chain ends relaxe more quickly than the central part of the chains. A quantitative study, based on the comparison of these results with theoretical predictions, is in progress in our laboratory.

References

1. De GENNES, P.G., J. Chem. Phys., 55, 572 (1971)
2. DOI, M., EDWARDS, S.F., J. Chem. Soc., Faraday Trans. 2, 74, 1789, 1802, 1818 (1978)
3. MONNERIE, L., Faraday Symp. Chem. Soc., 18, (1983)
4. FAJOLLE R., TASSIN, J.F., SERGOT, P., PAMBRUN, C., MONNERIE, L., Polymer, 24, 379 (1983)
5. MROSS, W.D., ZUNDEL, G., Spectrochimica Acta, 26A, 1113 (1970)
6. JASSE, B., KOENIG J.L., J. Polym. Sci., Polym. Phys., Ed., 17, 799 (1979)
7. FERRY, J.D., in "Viscoelastic properties of polymers", 3 rd Ed. Wiley, 1980, Chap. 11.

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