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Orientation in Uniaxially Stretched Plasticized Atactic Polystyrene

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Summary

Fourier transform infrared spectroscopy and birefringence measurements have been used to study the changes in molecular orientation which occur on drawing of plasticized as compared to pure polystyrene (PS) at a temperature T = Tg + Cte. No influence of plasticizers on orientation can be detected whatever the interactions between small molecules and PS chains are. Comparison with previous results obtained on PS-poly(vinylmethyl ether) compatible blends confirms the importance of the macromolecular nature of the second component to enhance the friction coefficient leading to higher level of chain orientation.

Introduction

In previous studies (LEFEBVRE et al. 1984; FAIVRE et al. 1985) we pointed out that atactic polystyrene (PS) chain orientation is strongly enhanced in the compatible blends of this polymer with poly(2,6-dimethyl 1,4-phenylene oxide) (PPO) or polyvinyl methyl ether (PVME). Furthermore the two polymer chains orient in a different way in spite of the compatible nature of the blend. PPO chains acquire a strong orientation while PVME chains remain almost unoriented. Although PPO and PVME chains behave differently, PS chains behaviour is similar in the two types of blends and was interpreted in terms of an hindrance of relaxation of PS chains induced by a modification of friction coefficients due to the molecular interactions which are at the origin of compatibility (FAIVRE et al. 1985). Indeed, compatibility is due to strong molecular interactions. For instance, in the case of PS-PVME blends, LU et al. (1983) pointed out the influence of compatibility on the CH out-of-plane vibration of the ring (700 cm^{-1}) in PS and the COC vibration (1100 cm^{-1}) of PVME. A strong interaction between these groups induces compatibility for this pair of polymers. Therefore, relaxation of the two polymer chains is hindered as an increase of the friction coefficient between species would do. As final orientation is mainly governed by chain relaxation, an increase in orientation should be observed for both polymers in the blends when compared with the pure components. Experimentally the time range which is covered in the experimental conditions only allows to detect changes in PS orientation (FAIVRE et al. 1985).

It is interesting to compare the behaviour of PS chains when the second component is a small molecule possessing similar chemical groups to PVME and leading to the same kind of interaction. The present work deals with the influence of dimethyl ethers of triethylene glycol and tetraethylene glycol on orientation of uniaxially stretched PS using Fourier transform infrared spectroscopy and birefringence measurements. For comparison, results obtained with two others plasticizers (butyl stearate and decaline) are also presented.

Experimental

The polymer used was an atactic polystyrene (Mn = 150000; Mw = 254000) from CdF-Chimie C°. The plasticizers were commercial products. Films of pure and plasticized PS were obtained by casting solutions of polymer and plasticizer in chloroform on a glass plate. After air drying, the films were treated for 24 h at 70°C under vacuum in order to remove any residual solvent. Solvent loss is easily monitored using the 1218 cm^{-1} $CHCl_3$ absorption band. A loss of plasticizer was observed during heating and the plasticizer concentration after treatment was estimated using proton NMR spectroscopy. NMR spectra were performed in CCl_4 solution on a EM 360 Varian NMR spectrometer.

The glass transition temperature of the different samples was measured using a Du Pont 1090 thermal analyser. The heating rate was 20° C/min with a sample size ca. 10 mg. 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 polarization of the infrared beam was obtained by the use of a SPECAC gold wire grid polarizer. Birefringence was measured on an Olympus polarizing microscope with a Berek compensator. A large number of measurements was made in order to obtain statistically meaning-full results.

Stretching experiments were performed at constant strain rates and a temperature T = Tg + 11.5°C on an apparatus developed in our laboratory (FAJOLLE et al. 1983). Two strain rates $\dot{\varepsilon}$ = 0.026 s-1 and $\dot{\varepsilon}$ = 0.115 s^{-1} have been used.

Results and discussion

Four plasticizers have been used in this study at a content up to 6 %: decaline, triethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether and butyl stearate. The transition temperatures of the different samples are given in table 1.

TABLE 1

Glass transition temperatures of plasticized PS films and PS-PVME blends

Plasticizer	Percentage of plasticizer	Tg/°C
None		108
Decaline	4.5	82
Triethylene glycol dimethyl ether	2.5	87.5
Tetraethylene glycol dimethyl ether	4.0	88
Butyl stearate	2	97
"	4	87
"	6	77.5
PVME	5	93
"	10	82

The second order moment of the orientation function was calculated from infrared data using the relation (JASSE and KOENIG 1979)

$$< P_2(\cos \Theta) > = \frac{R - 1}{R + 2} \times \frac{R_0 + 2}{R_0 - 1}$$

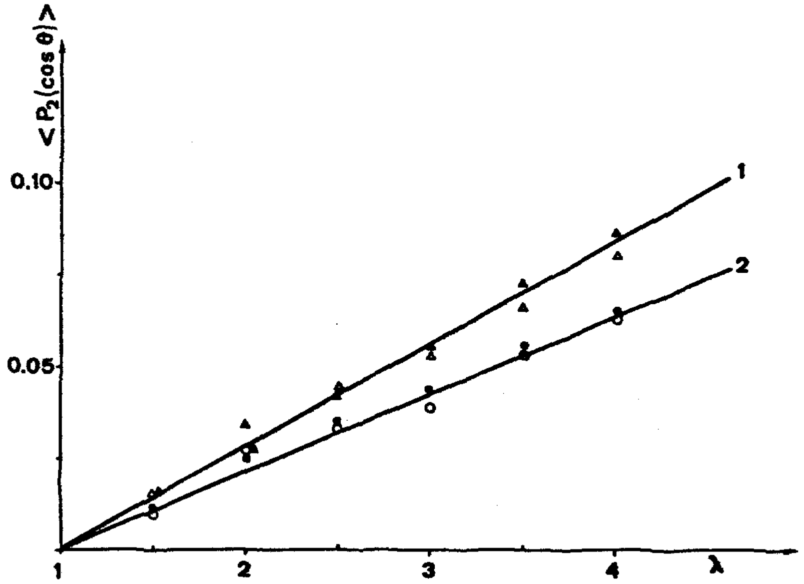

Fig. 1 - Average orientation function < $P_2(\cos \Theta)$ > of polystyrene versus draw ratio λ. Strain rate : (1) $\dot{\varepsilon}$ = 0.115 s^{-1}; (2) $\dot{\varepsilon}$ = 0.026 s^{-1}. T = Tg + 11.5°C. (○, △) infrared; (●, ▲) birefringence.

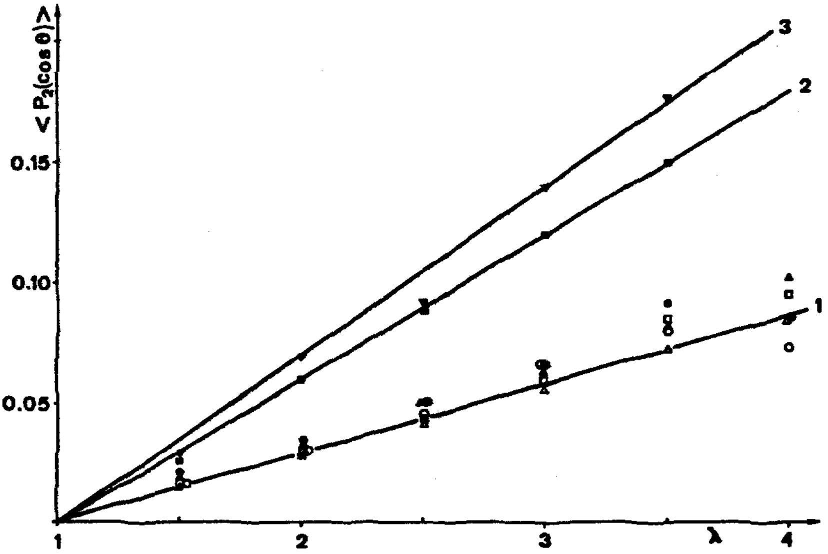

Fig. 2

Average orientation function < $P_2(\cos \Theta)$ > of plasticized polystyrene versus draw ratio λ. Strain rate $\dot{\varepsilon}$ = 0.115 s^{-1}. T = Tg + 11.5°C. (1) Unplasticized PS; (2) PS - PVME 5 % blend; (3) PS-PVME 10 % blend. Plasticized PS : (○) decaline; (●) triethylene glycol dimethyl ether; (▲) tetraethylene glycol dimethyl ether; (□) stearate de butyle 6 %.

Where $R = A_{\parallel}/A_{\perp}$ ($A_{\parallel}$ and $A_{\perp}$ beeing the measured absorbance for electric vector parallel and perpendicular to the stretching direction, respectively) is the dichroic ratio and $R_o = 2 \cot^2 \alpha$, α beeing the angle between the dipole moment vector of the considered vibration and the local chain axis. We used the in plane CH bending mode of the aromatic ring at 1028 cm^{-1} which is not overlapped by plasticizer's absorption bands. For this vibration $\alpha = 90°$.

For any binary blend the relation between birefringence and second order moment of the orientation function of the two components is given by

$$\Delta = f \Delta^o_{PS} < P_2(\cos \Theta)_{PS} > + (1 - f)\Delta^o_{PL} < P_2(\cos \Theta)_{PL} >$$

where f = volume fraction of polystyrene in the blend; Δ^o_{PS}, Δ^o_{PL} = intrinsic birefringence of PS and plasticizer, respectively; $<P_2(\cos \Theta)_{PS}>$, $< P_2(\cos \Theta)_{PL} >$ = second moment of the orientation function of PS and plasticizer, respectively. Studies of the value of Δ^o_{PS} are given by GURNEE (1954), STEIN (1961) and LEFEBVRE et al. (1982). A reasonable value would appear to be about - 0.13. Infrared spectra of oriented blends indicate that no dichroism exists for plasticizer's absorption bands so

$$< P_2(\cos \Theta)_{PL} > = 0 \quad \text{and} \quad \Delta = f \Delta^o_{PS} < P_2(\cos \Theta)_{PS} >$$

As shown in fig. 1, relative to pure PS samples, a good agreement is observed between the two methods of measurement of orientation. As expected, an increase of strain rate results in a higher level of orientation. Fig. 2 illustrates the results obtained with the different blends given in table 1, for a strain rate $\dot{\varepsilon}$: 0.115 s^{-1}. For clarity, the results obtained with the blends containing 2 % and 4 % of butyl stearate are not represented. No influence of plasticizers on PS orientation is detectable while PS orientation is noticeably increased in PS-PVME blends. The use of a lower strain rate $\dot{\varepsilon} = 0.026\ s^{-1}$ leads to lower levels of orientation and similar observations.

These results show that PS orientation is not influenced by the presence of a small molecule when stretching is performed at a temperature T = Tg + Cte, although the glass transition is lowered of about 10 to 26°C. The results would be different if all the samples were stretched at a same temperature T, according to the effect of plasticization.

Among the investigated plasticizers, decaline does not present any specific interactions with PS chains, contrary to dimethyl ethers of triethylene glycol and tetraethylene glycol and to butyl stearate. The fact that all these plasticizers do not lead to any change in the orientation of PS chain, clearly proves that specific interactions of small molecules with PS chains are unable to hinder their relaxation. On the contrary, when specific interactions of PS chains occur with a polymer chain, as in the case of PVME, the PS chain relaxation is hindered in the same way as an increase in friction coefficient would do, resulting in an increase of PS orientation. The above reported experiments point out the importance of the macromolecular nature of the interacting species on orientation in polymer blends.

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