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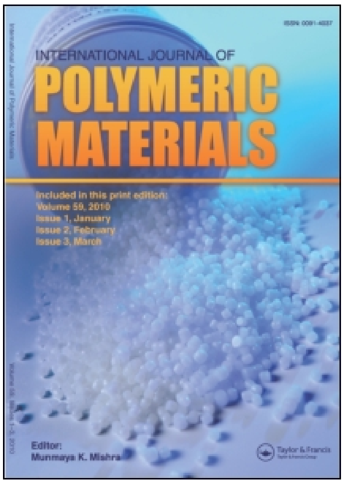

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A. N. Cherkasov[a][b]; J. Kolalk[a]; J. Janáĉek[a]
[a] Institute of Macromolecular Compounds, Academy of Sciences of USSR, [b] Institute of Macromolecular Chemistry Czechoslovak Academy of Sciences, Czechoslovakia

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Correlation Between the Optical and Mechanical Anisotropy of Cast Poly (phenylenesilsesquioxane) Films

Institute of Macromolecular Chemistry
Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia

A. N. CHERKASOV†, J. KOLAŘÍK‡ and J. JANÁČEK

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The spontaneous orientation of ladder poly(phenylenesilsesquioxane macromolecules) on the polymer—solid support interface was investigated by using birefringence and dynamic mechanical measurements. Both methods indicate that the thickness of the anisotropic layer in the cast films (prepared by evaporation of a solution in benzene at 25°C followed by drying at 80°C) attains 60 μm. The results of the birefringence measurements show that the anisotropy is due to the orientation of chains along the interface plane.

INTRODUCTION

The preparation of polymer films by evaporation of a solution on a solid support leads to a spontaneous orientation of macromolecules on the phase boundary.[1-5] The orientation is affected by interface forces; predominantly, however, it is a consequence of the restriction of the space accessible to chain segments situated in the proximity of the contact area. The existing studies of the spontaneous orientation on the phase boundary have been predominantly concentrated on traditional polymers,[2] the oriented layer of which as a rule varies from 0.1 to 10 μm. In accordance with what was expected, it was found that the thickness of the anisotropic layer is the larger the higher the chain rigidity. Ladder siloxane polymers seemed the useful ones for comparing

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† On leave from the Institute of Macromolecular Compounds, Academy of Sciences of USSR, Leningrad, USSR.

‡ To whom the correspondence should be addressed.

data on the thickness of the anisotropic layer obtained by different methods, since for such polymers one may expect the formation of an unusually deep oriented interface layer owing to the chain rigidity. We wanted to compare the data on the thickness of the anisotropic layer obtained by (a) birefringence measurements as a function of the angle between the incident light beam and the direction perpendicular to the film plane, and (b) dynamic mechanical measurements. For this purpose we used poly(phenylsilsesquioxane) (PPSSO) and its copolymer with isobutylsilsesquioxane (PPBSSO), in which the ratio of the phenyl to the isobutyl groups was 3:1.

EXPERIMENTAL

The synthesis of the polymers used has been described earlier.[6] Polymer films were prepared by evaporating 1 % solutions in benzene at room temperature on glass surface. The solvent residue was removed by drying the films at 80°C to constant weight. The dynamic mechanical properties of films were determined by using a Rheovibron DDV-II at a frequency of 110 Hz; the average rate of the temperature increase during the measurements was 1°C/min. The film birefringence as a function of the angle of incidence of a beam of plane-polarized light was measured by using a method described in a preceding paper.[5]

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RESULTS AND DISCUSSION

The results of dynamic mechanical measurements of the polymers investigated are summarized in Figures 1 to 3. The temperature dependence of the modulus E' and of the loss factor $tg\delta$ indicate that the high-temperature dispersion of PPSSO corresponding to the glass transition lies near 250°C and probably has not a multiplet character (cf.[6]). The presence of 25 % isobutyl groups in the copolymer of PPBSO leads to a decrease in the dispersion temperature by 70°C, in accordance with earlier results.[6] PPSSO also exhibits a low-temperature dispersion at c. −150°C (the temperature of the peak of the loss maximum is read off), which after the substitution of the isobutyl groups for the phenyl ones is somewhat shifted towards lower temperatures. Since the loss maxima attributed to the relaxation motion of the phenyl groups of polystyrene are situated[7, 8] near −230°C, it may be assumed that some groups of the main chains may also participate in the low-temperature relaxation of PPSSO and PPBSSO, along with the side groups. According to our experience,[9,10] loss maxima due to the incorporation of low-molecular weights compounds often appear in the temperature range between −100 and 0°C.

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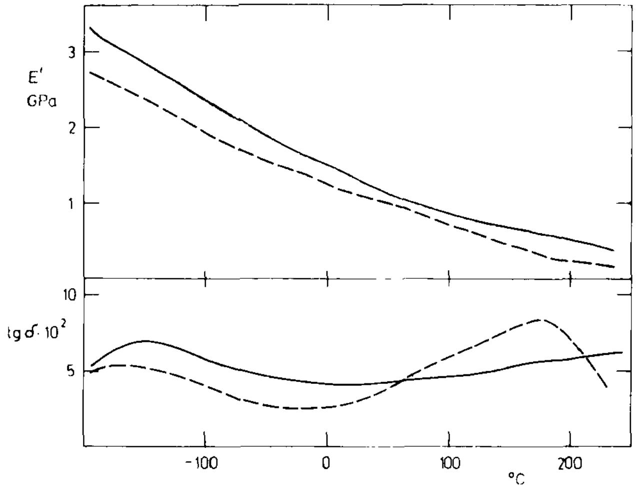

FIGURE 1 The temperature dependence of the storage modulus and loss factor of poly(phenylsilsesquioxane) (full) and of the copolymer phenylenesilsesquioxane—isobutylsilsesquioxane (3:1) (broken).

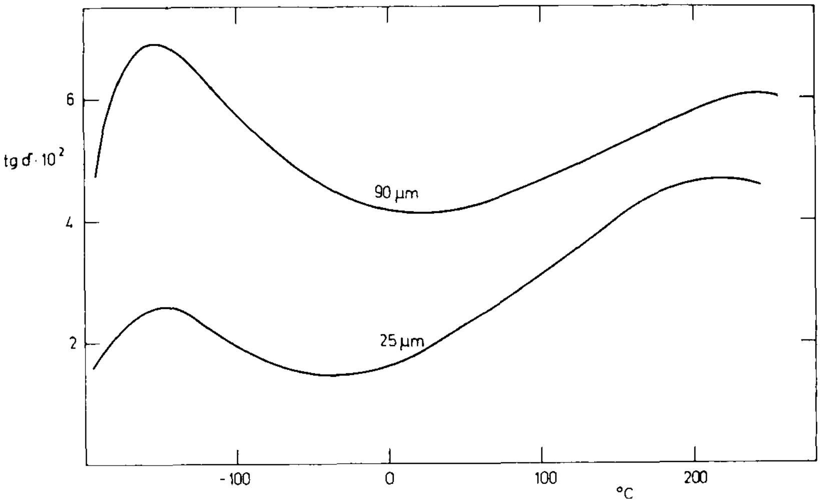

FIGURE 2 Effect of film thickness on the temperature dependence of the loss factor of poly(phenylsilsesquioxane).

It is therefore possible that the small loss maxima observed earlier[6] were a consequence of the presence of residues of solvents or of other low-molecular weight compounds.

The effect of film thickness on molecular mobility was investigated by means of the loss factor, because this quantity does not depend on the accuracy of determination of the size of the sample. Measurements carried out within a broad range of temperatures show (Figures 2 and 3) that with increasing thickness the level of the loss factor also increases without any changes in the temperature position of the loss maxima. The increase in the loss factor of PPSSO with film thickness is also corroborated by measurements carried out at 25°C (Figure 4). The results indicate that the orientation of chains along the interface leads to a decrease in the energy losses (probably owing to the more compact order), but that the molecular motion sets in at the same temperature as in an unoriented layer.

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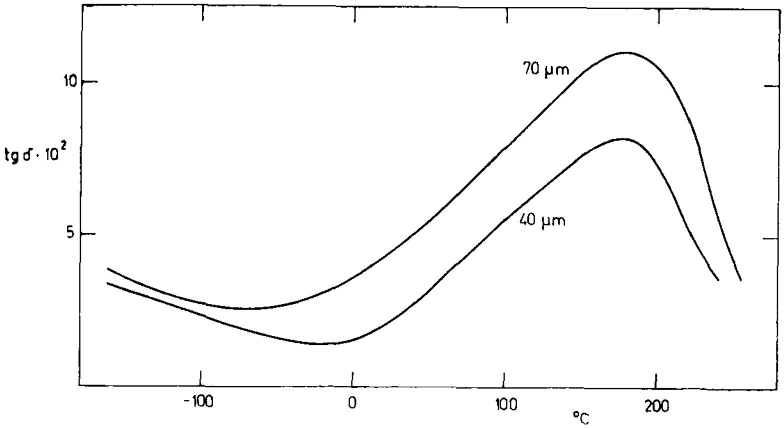

FIGURE 3 Effect of film thickness on the temperature dependence of the loss factor of the copolymer phenylsilsesquioxane—isobutylsilsesquioxane (3:1).

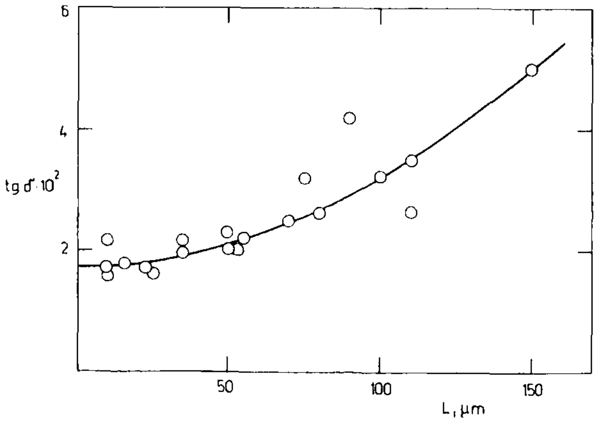

FIGURE 4 Dependence of the loss factor on the film thickness of poly(phenylsilsesquioxane) determined at 25°C.

Owing to the parallel connection, both the oriented and unoriented layer contribute to the final loss factor of the film proportionately to their volume fraction:

$$tg\delta = (H_0/L)\, tg\delta_0 + [(L-H_0)/L]\, tg\delta_p\,, \qquad (1)$$

where H_0 and L respectively are thicknesses of the oriented layer and film and the indices o and p respectively denote the oriented layer and unoriented polymer. For an estimate of H_0, Eq. (1) is suitably rearranged to

$$tg\delta = (tg\delta_0 - tg\delta_p)\,(H_0/L) + tg\delta_p \qquad (2)$$

Since for very thin films $H_0 = L$ and $tg\delta_0 = tg\delta$, we obtain by extrapolating $tg\delta$ for $L \rightarrow O$ a value $tg\delta_0 = 0.017$ (Figure 4). The plot $tg\delta$ against (1/L), Figure 5, allows us to estimate $tg\delta_p = 0.07$ (for 1/L = 0). The broken straight line, which denotes the level of $tg\delta_0$, crosses the experimental dependence plotted according to Eq. (2) for $L = H_0 = 60$ μm. By dividing the slope of the experimentally determined dependence (-3.18 μm) by $tg\delta_0 - tg\delta_p = -0.053$ according to Eq. (2), we also obtain $H_0 = 60$ μm. This value, which is considerably higher than for ordinary polymers,[2] indicates that the spontaneous orientation along the interface plane in PPSSO goes into considerable depth. (It may be expected that H_0 will depend on the type of support and solvent, preparation conditions, additional annealing above the glass transition temperature, etc.) The curves shown in Figures 4 and 5 indicate

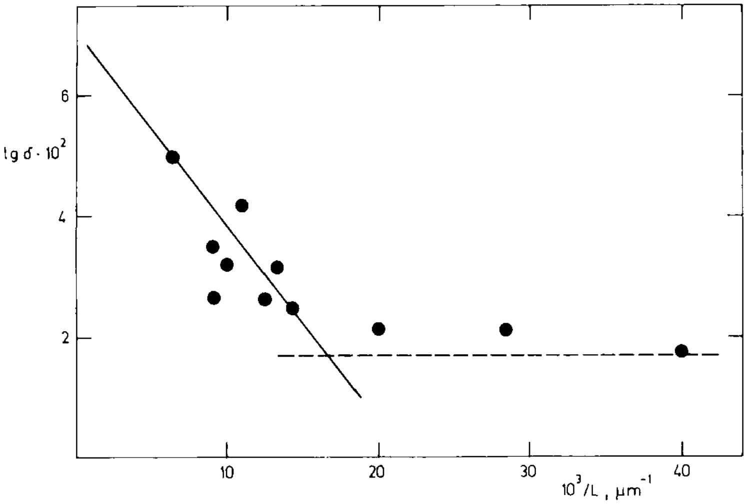

FIGURE 5 Dependence of the loss factor on the inverse film thickness. (For films more than 60 μm thick all experimental data obtained are given; films 50, 35, 25 μm are characterized by a mean loss factor calculated from values given in Fig. 4.)

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that the transition between the oriented and unoriented material is not sharp.

Further information about the thickness of the oriented layer was obtained from the dependence of film birefringence on the angle ϕ between the incident beam and the direction perpendicular to the film surface. By using a concept presented in ref.[11], a relationship has been derived[5] between the optical retardation δ and the angle ϕ:

$$\delta = B(1 - cos2\phi). \tag{3}$$

The proportionality constant B is given by:

$$B = \frac{\pi N H_0 (a_{\parallel} - a_{\perp})}{\lambda n^3} \left(\frac{n^2 + 2}{3}\right)^2 S, \tag{4}$$

where N is the number of monomer units in a volume unit, $(a_{\parallel} - a_{\perp})$ is the optical anisotropy of the monomer unit, n is the refractive index, λ is the wavelength of light used, and S is the orientation factor. The value of the factor S depends on the distribution orientation function of monomer units in the direction perpendicular to the plane of support; in the plane parallel to the latter the distribution density of monomer units is the same for all angles, and for $\phi = 0$ the film does not exhibit any birefringence. Figures 6 and 7 show that $(-B)$ increases linearly with the film thickness up to $L = 50$–60 μm and remains virtually unchanged with further increase in the film thickness ($B \lambda 10^2 = -22$ μm). This dependence also shows that the anisotropic surface layer attains a depth $H_0 = 50$–60 μm and that the spontaneous orientation of chains in this layer does not depend to any marked degree on the film thickness L.

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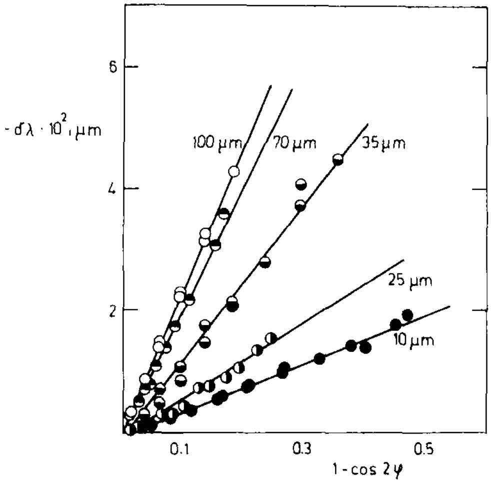

FIGURE 6 Dependence of optical retardation on the angle ϕ (cf. Eq. (3))

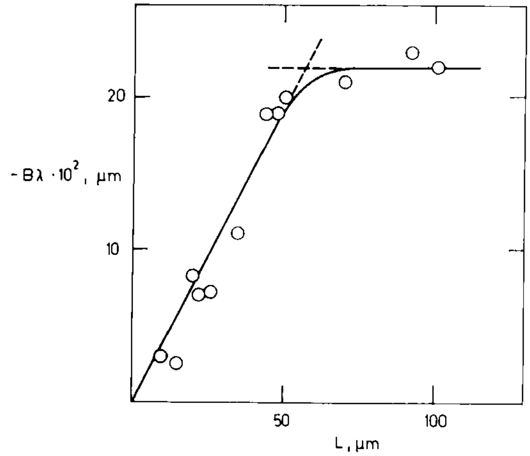

FIGURE 7 Dependence of the constant B from Eq. (4) on the film thickness.

By substituting into Eq. (4) the values[5] $N = 4.57 \times 10^{-3}$ mol/cm^3, $(a_{\parallel} - a_{\perp}) = -2.6 \times 10^{-24}$ cm^3, $n = 1.6$ and $B\lambda\, 10^2 = -22$ μm ($\lambda = 546$ nm), we obtain $SH_0 = -17.5$ μm. As H_0 is approximately 60 μm, the orientation factor S is -0.29. If the chain segments are randomly oriented in planes parallel with the film surface (plane-isotropic order), the factor S assumes its limiting value, i.e. -0.5. The above data confirm the original assumption that in the oriented layer the chains are predominantly situated parallel with the surface of the solid support. If, on the other hand, we use $S = -0.5$ in our calculations, we find that the oriented layer is equivalent to the plane-isotropic layer having the thickness $H_0' = -17.5$ μm$/-0.5 = 35$ μm. Hence, the data obtained allow a conclusion that under the given conditions a c.60 μm thick layer is formed in PPSSO on the phase boundary with a solid support and that in this layer the chain segments are predominantly oriented along the interface plane. One should bear in mind that the thickness and properties of the oriented layer will be affected by the method of film preparation and by the thermal history of the samples.

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