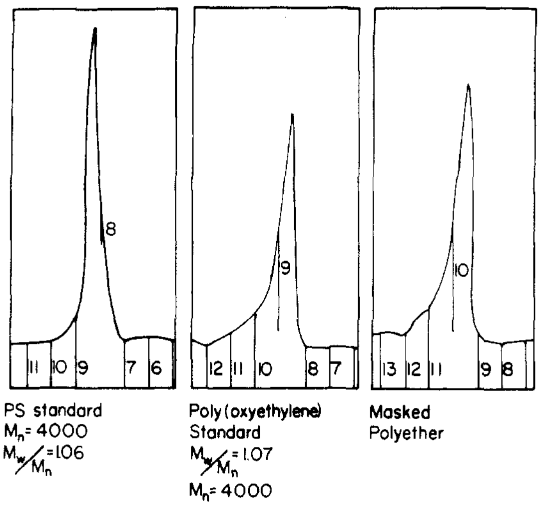

PS standard M_n= 4000 M_w/M_n=1.06

Poly(oxyethylene) Standard M_w/M_n= 1.07 M_n= 4000

Masked Polyether

Figure 10. Gel permeation chromatographs in CH_2Cl_2 at 25 °C: flow rate, 1 mL/min; column, 10^3 Å μStyragel.

with small signals nearby, which could be assigned to end EO units. The "e" methylene carbons attached to ether oxygens appearing between 60.1 and 64.5 ppm also come from the initiator moiety.

Gel permeation chromatographs (GPC) show that **5** has a narrow molecular weight distribution (Figure 10). Also shown in the figure are the GPC curves of a polystyrene standard and a poly(oxyethylene) standard having narrow molecular distributions. It is clearly evident that **5** has a narrow molecular weight distribution. Some absorptive effects are seen in both the poly(oxyethylene) standard and **5**; such effects have been observed before. The number-average molecular weight of **5** given in Figure 10 was calculated by using 300-MHz ^{1}H NMR; sufficient relaxation times were given to obtain a fairly accurate integration.

This research is continuing with the subsequent addition of a pivalolactone segment to form the telechelomer to be followed by step propagation to form highly regular segmented copolymers that should be capable of excellent phase separation.

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Registry No. **1**, 30502-4-1; **2**, 37494-03-4; **3**, 107576-73-8; **4**, 104066-38-8; **5**, 102773-45-5; (EO)(PVL) (block copolymer), 107558-01-0; $Cl(CH_2)_3OH$, 627-30-5; $EtOCH{=}CH_2$, 109-92-2; ethylene oxide, 75-21-8.

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Chain Orientation in Highly Drawn Polystyrene

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A recent small-angle neutron scattering (SANS) study,[1] using substantially monodisperse atactic polystyrene of $M_w = 6 \times 10^5$ doped with 5% deuteriated polymer ($M_w = 5.5 \times 10^5$), has shown that the axial strain represented by the deforming molecular envelope is affine with the applied strain for deformation at 127 °C. Data from this work are replotted in Figure 1 as the spherical harmonic $\langle P_2 \rangle$, which describes the orientation function of vectors orienting affinely with the molecular envelope against the macroscopic draw ratio. These vectors can be identified with network displacement vectors.

The recently developed methods of assessing molecular orientation from wide-angle X-ray scattering (WAXS)[2] can provide a reasonable direct quantitative measure of the orientation of statistical chain segments. Application of this technique to the highly drawn polystyrene produced the slightly surprising result that, even though some of the draw ratios were probably the highest ever obtained with this polymer, the segmental orientation was so low as to be only just detectable. The P_2 coefficients defining the segmental orientation were calculated from the azimuthal distribution of the equatorial scattering maximum at $2\theta = 10°$ (Cu Kα). No correction was made for the intrinsic azimuthal width of this peak, and in view of the low orientations encountered, the errors will be small. The WAXS measurements of segmental orientation are plotted as full circles in Figure 1. Such gradual segmental orientation with strain would be the expected behavior of chains with a large number of links between network points.[3] Curves calculated by using Treloar's approximate expression[4] for chains with 100, 200, and 500 statistical chain segments are also drawn as the broken lines. The behavior can thus be understood if chain lengths between cross-link points are of this order. The degree of polymerization of the molecules, around 5000, is obviously sufficient, although the critical factor is the scale of the effective network. Recent measurements of the entanglement molecular weight using narrow fractions of polystyrene[5] give a value of 18×10^3 or 173 monomer units. It should be noted that in the glassy phase below T_g, noncrystalline polymers show a much more rapid development of orientation with strain especially at low strains (e.g., ref 6).

This experiment demonstrates that even at high levels of chain extension, the degree of segmental orientation may remain low if the effective network length is large. However, the apparent network length depends very significantly on the conditions of deformation as well as the strain.[7]

Note on Calculations of $\langle P_2 \rangle$ from the SANS Data

For each external λ, the SANS λ_N was found from ref 1.

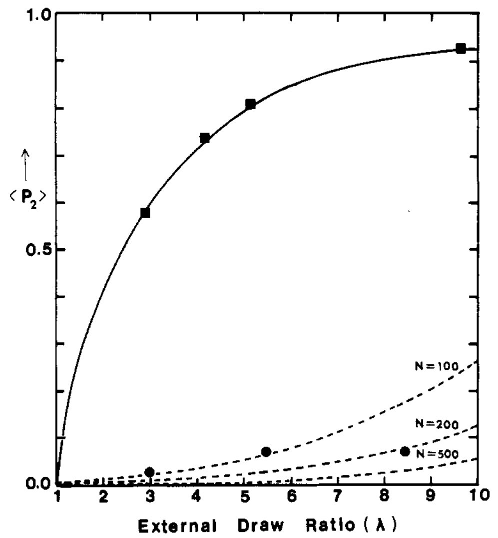

Figure 1. Plots of the spherical harmonic coefficient $\langle P_2 \rangle$ as a function of the external draw ratio, λ, describing the orientation of network displacement vectors derived from SANS measurements of the deformed molecular envelope (continuous curve and square points) and the orientation of the statistical chain segments measured by WAXS (full circles). The dashed curves show the segmental orientation $\langle P_2 \rangle$ calculated for random chains containing different numbers of statistical segments, N.

The probability distribution $N(\theta)$ of the displacement vectors are determined from

$$N(\theta) = K \frac{(\lambda_N)^3}{[\cos^2 \theta + (\lambda_N)^3 \sin^2 \theta]^{3/2}}$$

The $\langle P_2 \rangle$ values were then obtained from the integral

$$\frac{\int_0^{\pi/2} N(\theta) P_2(\cos \theta) \sin \theta \, d\theta}{\int_0^{\pi/2} N(\theta) \sin \theta \, d\theta}$$

and plotted as $f(\lambda)$.

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