Table I
Longitudinal and Transverse Bond Polarizabilities[a]

bond	b_l	b_t
C—C[b]	1.88	0.020
C—C[c]	2.25	0.48
C—N	1.59	0.89
C=N	2.46	0.91
C—O	1.34	0.75
C—S	3.93	2.20
C—H	0.79	0.58

[a] Reference 9; units are Å^3 (10^{-24} cm^3). [b] Aliphatic carbon atoms. [c] Aromatic carbon atoms.

third is the bond polarizability method of Denbigh,[9] in which both $\bar{\alpha}$ and the polarizability components are obtained by vectorial additions of longitudinal b_l and transverse b_t components of the polarizabilities of the bonds. The equations are

$$\alpha_{xx} = \sum_i (b_{li} \sin^2 \phi_i \cos^2 \theta_i + b_{ti} \sin^2 \theta_i + b_{ti} \cos^2 \phi_i \cos^2 \theta_i) \quad (3)$$

$$\alpha_{yy} = \sum_i (b_{li} \sin^2 \phi_i \sin^2 \theta_i + b_{ti} \cos^2 \theta_i + b_{ti} \cos^2 \phi_i \sin^2 \theta_i) \quad (4)$$

$$\alpha_{zz} = \sum_i (b_{li} \cos^2 \phi_i + b_{ti} \sin^2 \phi_i) \quad (5)$$

where ϕ_i is the angle between bond i and the z axis and θ_i is the angle between the x axis and the projection of bond i onto the xy plane.[9] The polarizabilities for C–C and C–H bonds are already available in the literature,[9] whereas for C–N, C=N, C–O, and C–S bonds, they were calculated from standard equations.[9] For single bonds not involving H these are $b_l = 0.600 + 0.098r^6$ (where the bond length r is in Å) and $b_t/b_l = 0.56$. For double bonds $b_l = 0.600 + 0.385r^6$ and $b_t/b_l = 0.37$. These values are summarized in Table I.

The quantum mechanical method[6] applied to the (H terminated) *cis*-PBO repeat unit gave $\alpha_{xx} = 4.69$, $\alpha_{yy} = 0.11$, and $\alpha_{zz} = 27.69$ and thus $\bar{\alpha} = 10.83$ Å^3. This value of $\bar{\alpha}$ is almost the same as the experimental value of benzene,[6,12] whereas the structure of the repeat unit suggests it should be 2–3 times this value. Similar studies[13] of other, simpler molecules have also given serious underestimates of $\bar{\alpha}$, and this method was therefore not considered further.

The atomic additivity scheme[8] gives the value of $\bar{\alpha}$ listed in the second column of Table II; the separate components are unfortunately beyond the scope of this method. The bond additivity scheme[9] gave the values of $\bar{\alpha}$ listed in the following column, and these are seen to be in good agreement with those based on atomic additivities. The PBT chain is predicted to have a larger value of $\bar{\alpha}$ than the two PBO chains, since the C–S bond is much more polarizable than the C–O bond (as is shown by the data in Table I). The corresponding values of the polarizability components are given in the next three columns. They were used to calculate values of the anisotropic ratio δ; the results are given in the last column of the table and should be directly applicable to the interpretation of flow birefringence data.[5] The only relevant experimental value of δ is that obtained from light scattering measurements carried out on some solutions of *trans*-PBT in methanesulfonic acid.[5] Interpretation of these results in the very rough approximation that the chains have cylindrical symmetry gives $\delta = 0.5$.[5] It is gratifying that the experimental and theoretical results are in at least qualitative agreement, particularly since the experimental situation is almost certainly complicated by significant protonation of the PBT chains.

Table II
Calculated Average Polarizabilities, Polarizability Components, and Anisotropic Ratios for the Polymer Repeat Units[a]

polymer	atomic additivity value[b] of $\bar{\alpha}$	bond additivity method[c]				
		$\bar{\alpha}$	α_{xx}	α_{yy}	α_{zz}	δ
cis-PBO	25.0	26.9	31.0	15.8	33.7	0.30
trans-PBO	25.0	26.9	31.2	15.8	33.6	0.30
trans-PBT	30.0	34.2	37.5	23.3	41.7	0.23

[a] Units are Å^3 (10^{-24} cm^3). [b] Reference 8. [c] Reference 9.

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Density Difference Determinations of Ordinary and Freeze-Dried Polystyrenes in Bulk in the Analytical Ultracentrifuge

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I. Introduction

The possibility that isolated chains of synthetic high polymers may undergo an abrupt change in molecular dimensions (collapse) when the solvent becomes poorer, as a result of either lowering the temperature or addition of nonsolvent, has long been considered.[1,2] Recently, several papers have appeared dealing with the theoretical[3–8] or experimental[9,10] aspects of the problem. On the other hand, it has long been known from electron microscopy experiments[11–14] that isolated macromolecules of glassy polymers in a vacuum are in a nearly spherical, compact form. Richardson[13] in particular has found that if the substrate was plain mica, agglomerates of macromolecules in compact form were obtained (Figure 1a). In fact

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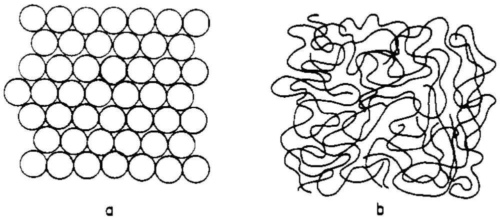

Figure 1. (a) Schematic representation of a conformation made up of collapsed chains, forming a structure of aggregated spheroids. Such a structure has already been obtained by Richardson.[13] (b) Usual structure of amorphous polymers, where Gaussian chains form a continuous network of entangled macromolecules.

Richardson did obtain microquantities of a new structure for bulk polystyrene, constituted by an aggregation of compact macromolecules of nearly spherical shape with little or no mutual interpenetration, as is clear from Figure 5 of ref 13. Ordinary amorphous polystyrene is formed by a network of entangled macromolecules (Figure 1b) obeying Gaussian statistics.

In this paper we report on preliminary results which convey the possibility that a "caviar-like" structure of polystyrene has now been obtained in finite amounts, although several other explanations may account for our results (see section III).

II. Experimental Section

A dilute solution (volume 100 mL, concentration 0.5 mg/mL) of a Waters standard polystyrene of molecular weight 50 000 in cyclohexane was cooled to 7.5 °C, a temperature at which no phase separation occurs for the molecular weight and concentration considered. The concentration was so chosen as to ensure good separation in the mean of individual macromolecules. The solution was then abruptly immersed into liquid nitrogen so that in about 1 min the entire solution was solidified. It was hoped that in this way the isolated macromolecules were "frozen" in positions far apart from each other. The solid solution was then freeze-dried at −20 °C, using a Lauda Cryomat. After total sublimation of the solvent the remaining polymer was collected at the bottom of the flask and stored at −18 °C until use. If the isolated polystyrene macromolecules under vacuum at the temperature of freeze-drying are in a collapsed, compact form, it is expected that the collected product should have a structure of noninterpenetrating compact spheroids. Such a structure may have a density somewhat different from that of ordinary amorphous polystyrene. Therefore the density of the freeze-dried product (FPS) was studied by analytical ultracentrifugation in a density gradient generated by a nonsolvent mixture, using the original polystyrene (OPS) as a probe. The nonsolvent mixture was a mixture of ethanol with lithium iodide. The suspensions to be studied were made as follows: for FPS, ethanol was poured into the storage flask and shaken. The suspension thus formed was allowed to rest for 0.5 h to permit the heavier particles to settle. The remaining homogeneous-looking suspension was then separated for use; for OPS, 40 mg of the standard Waters sample used for the freeze-drying was mixed with 10 mL of ethanol and sonicated until a nearly homogeneous suspension was obtained and then allowed to rest and separated as previously. Sonication of FPS was avoided to prevent possible destruction of an aggregated structure by ultrasons. No attempt was made to measure the diameters of the suspended particles, but they are believed to lie between 0.01 and 0.1 mm. The concentration of the suspended particles was estimated to be about 1 mg/mL. The suspensions were kept in the dark before use (to avoid decomposition of LiI) for 1 month to ensure that if some ethanol swelled the suspended particles, thermodynamic equilibrium was attained.

After several trials, it was found that the proper weight composition of the nonsolvent mixture which would match the density of the suspended particles was 0.639:0.361 ethanol/LiI. Unfortunately, since lithium iodide is very hygroscopic, an unknown amount of water was absorbed when lithium iodide was weighed and added to the ethanol suspension. The extent of this hydration was not realized at the time of the first experiments. Later Karl Fischer determinations of water content in probe mixtures showed that the water content could be as high as 7% by weight. Therefore, the nonsolvent mixture used to generate the density gradient was a ternary ethanol–water–LiI mixture rather than a binary ethanol–LiI mixture. At any rate, this fact does not change the qualitative results which are reported below but introduces only some uncertainty in the precise calculations of the density gradient generated in the ultracentrifuge. The suspensions were centrifuged with a Beckman Model E analytical ultracentrifuge and a 12-mm cell with sapphire windows and schlieren optics. The temperature was held at 25 °C and the speed of rotation was 44 770 rpm.

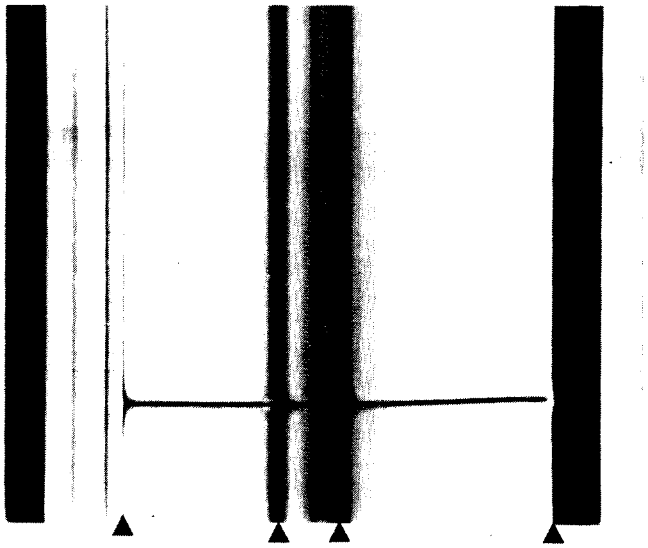

Figure 2. Ultracentrifugation pattern obtained when a suspension in a nonsolvent mixture of ordinary polystyrene is mixed with a suspension of freeze-dried polystyrene. Two main strips are apparent. A fainter strip is also apparent. This fainter strip does not seem significant. The arrows at the lower part of the photograph show the positions, from left to right, of, respectively, the meniscus, the first strip, the second strip, and the bottom of the cell.

III. Results and Discussion

Suspensions of OPS and FPS and mixtures of these suspensions were centrifuged until equilibrium of the density gradient was attained. This required nearly 30 h. For the separate suspensions, only one black strip was apparent on the screen. This black strip corresponded to the position where the suspended particles gathered in the density gradient. The black strips were in fact formed by a series of more or less evanescent interference fringes, appearing and disappearing around some mean position. Due to their weight, it is safe to say that all suspended particles gathered at the same distance from the center of rotation (when macromolecules in solution are centrifuged in a density gradient, they form a nearly Gaussian distribution around some mean value). The evanescent interference fringes, not apparent on the photograph (see Figure 2), are presumably due to the upward and downward Brownian motion of the suspended particles in the plane parallel to the axis of rotation where they are located. When the OPS and FPS suspensions were mixed and centrifuged, two distinct black strips appeared on the screen (Figure 2). The mean distance between the centers of the strips was 0.166 cm. Using a relationship previously derived for the compositional density gradient in the ultracentrifuge[15] and neglecting the gradient due to compression, we find that this distance corresponds to about 0.03 g·cm^{-3} in density difference, OPS being the denser polymer.

We now want to examine the various possibilities which could produce two separate bands when suspensions of OPS and FPS are mixed.

(a) The first possibility is that OPS and FPS have the same structure. The observed difference in density is due to microbubbles of air adhering to the FPS suspended particles. Such microbubbles could not exist for OPS because sonication would quite certainly destroy them. This possibility is remote. The pressure at the location of the FPS strip, the one nearest the meniscus, is about 60 atm. At such a pressure microbubbles should either float or dissolve in the surrounding medium.

(b) The difference in density is due to some cyclohexane remaining in the freeze-dried product. This is quite improbable. The freeze-drying lasted 20 h and after 13 h no more cyclohexane was sublimating, as shown by the constancy in weight of the freeze-drying flask. On the other hand, the product, about 50 mg, was left at -18 °C for several months in a sealed flask of about 1-L capacity. Finally, assuming that some cyclohexane still adhered to the FPS, it should for the most part have dissolved in the ethanol when the FPS was suspended in ethanol. For the same reason, the density cannot be ascribed to swelling of one of the samples by ethanol since, if OPS and FPS had the same structure, they should swell the same way in the identical nonsolvent mixtures. At any rate, the trace of remaining cyclohexane cannot account for the very significant density difference observed.

(c) The surface area may be considerably greater in the FPS suspended particles. If one of the components of the nonsolvent mixture is preferentially adsorbed, this may lead to a density difference with OPS particles. We cannot rule out such a possibility, but it seems likely that, if such a phenomenon occurred, we should have had a continuous distribution of densities (due to the polydispersity of the surface/volume ratio of the FPS suspended particles) or at least not two sharply defined bands.

(d) A more consistent interpretation would be that, due to their different thermal histories, the OPS and FPS samples are in permanent metastable states of different densities. It was shown long ago by dilatometric studies[16] that the density of a glassy polymer depends on its previous thermal history. More recently, it was shown that poly(vinyl chloride) and polystyrene samples having different thermal and solvent vapor exposures show differences in vapor sorption isotherms and, inferentially, have different densities.[17-19] Quite recently, it has been found that freeze-drying has a substantial effect on the differential scanning calorimetry curves of polystyrene and poly(methyl methacrylate).[20] For the above reasons, it is quite possible that the observed density difference merely reflects the different thermal histories of our OPS and FPS samples, both samples having the usual structure of entangled chains.

(e) There remains the possibility that the observed density difference is due to a different bulk structure of the OPS and FPS samples, in which case the FPS sample may have the structure schematically shown in Figure 1a. Such a possibility should not be discarded, particularly if one considers previously obtained electron microscopy results,[11-14] where, clearly, aggregation of macromolecules in a compact form has been observed. The freeze-drying process of the very dilute solution here used seems equivalent to the evaporation process of microbubbles of a poor solvent containing, on the average, a single macromolecule.[13]

Further progress to elucidate the reason for the density difference observed in this work will necessitate the use of various techniques, which may include differential scanning calorimetry (DSC), small-angle neutron scattering (SANS), and electron microscopy.

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Concentration Dependence of Viscoelastic Properties of Concentrated Solutions of Six-Branched Polystyrenes[†]

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The rheological properties of star polymers of styrene,[1-6] butadiene,[7,8] isoprene,[9] and α-methylstyrene[10] have been investigated by various authors. Among these investigations, experimental results obtained for three- and four-branched star polymers[5,8] indicate that the steady-state compliance (J_e°) is inversely proportional to the polymer concentration over a wide range of concentration. This behavior is quite different from those obtained for linear-polymer solutions. The concentration dependence of J_e° measured for four- and six-branched polyisoprenes[9] is very complicated. Recently, the viscoelastic properties of star polybutadienes having three and four branches and their concentrated solutions were measured by Marin et al.[8] However, no work on solutions of six-branched star polymers over such a wide range of concentration has been reported yet.

In the present study, the rheological properties of concentrated solutions of six-branched star polystyrene were measured, and the concentration dependences of the zero-shear viscosity (η_0), steady-state compliance (J_e°), and rubbery plateau compliance (J_{eN}°) were determined. The concentration dependence of these rheological parameters are discussed and compared with those for linear poly-

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[†] Rheological Properties of Anionic Polystyrenes. 8.