We have now studied the IPS chain conformation in a wide range of crystallization temperatures.[1-3] So far all the results and interpretations are fairly consistent and demonstrate the existence of several molecular shapes, the presence of which is mainly controlled by the chain mobility in the original amorphous melt or solution.

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Registry No. IPS, 25086-18-4; neutron, 12586-31-1.

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Photoresponsive Polymers. 5.[1] Reversible Solubility Change of Polystyrene Having Azobenzene Pendant Groups

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ABSTRACT: The solubility in cyclohexane of polystyrene with a small amount of azobenzene pendant groups (~5 mol % of monomer units) was found to change upon irradiation with light of specific wavelength: ultraviolet light (410 > λ > 350 nm) caused precipitation of the polymer, while visible light (λ > 470 nm) resolubilized it. The change of solubility was induced by the photoisomerization of the azobenzene chromophores from the trans to the cis form. Molecular weight distribution measurements of the precipitate and the soluble polymer revealed that the molecular weight of the precipitate ($M_w = 5.4 \times 10^4$, $M_w/M_n = 1.22$) was twice that of the soluble polymer. The dynamics of the precipitation was also studied by a laser photolysis measurement combined with a light scattering detection method.

Introduction

When photoisomerizable chromophores are incorporated into the backbone of polymer chains or into the pendant groups, photoisomerization of the chromophores may affect the physical properties of the polymers and the polymer solutions, especially if isomerization involves appreciable change of a polarity[2] or a geometrical structure. We have recently reported that polymers with spirobenzopyran pendant groups or azobenzene chromophores in the polymer backbone are capable of transforming light energy into reversible alterations of solution viscosity, conductivity, and pH.[1,3-5] Changes of dipole moments of pendant spirobenzopyran groups upon photoirradiation altered the balance of intrachain interaction, resulting in the expansion/contraction of the polymer chains. Geometrical structural changes of the azobenzene residues incorporated in the polymer backbone also caused a conformational change of the polymer chain, affecting solution viscosity, conductivity, and pH. Flash photolysis measurement combined with a light scattering detection method has revealed the relaxation process of unfolding of the above polymer chains.[6]

In this article, we report a reversible solubility change of polystyrene in cyclohexane. Polystyrene with a small amount of azobenzene pendant groups became insoluble in cyclohexane upon irradiation with ultraviolet light, while low molecular weight azobenzene itself did not show any solubility change on photoirradiation. On visible light irradiation, the polymer again became soluble. The dynamics of formation of the precipitation was also studied by a laser photolysis measurement combined with a light scattering detection method.

Experimental Section

Azobenzene chromophores were incorporated into the pendant groups of polystyrene by copolymerization of styrene with 4-(methacryloylamino)azobenzene. Copolymers obtained with a conversion of less than 10% were used for the experiments. 4-(Methacryloylamino)azobenzene was synthesized by the reaction of 4-aminoazobenzene with methacryloyl chloride.[7] The melting point was 150 °C. The azobenzene content of the copolymers was determined by elemental analysis.

Irradiation was carried out with a 1-kW high-pressure mercury lamp and the wavelength was selected with the aid of Toshiba cutoff filters. The laser light scattering measurement apparatus is similar to that described before.[6] The second harmonics of a ruby laser (347 nm) were used as exciting light. An Ar ion laser of 3 W (Spectra-Physics Model 165-07) was used for a scattering light source.

Absorption spectra of the polymer were measured with a Cary 118 spectrophotometer. Polymer precipitation upon irradiation was detected by the decrease of transmittance at 650 nm with a spectrophotometer (Shimadzu UV-200 S). The temperature of the cell was controlled with a temperature-controlled circulating bath (Neslab LT-50). The sample temperature was monitored by a digital thermometer (Doric 410 A), controlled to within ±0.5 °C.

Molecular weight distributions of the polymers were measured by gel permeation chromatography (GPC) with a Toyo Soda H 801 high-speed liquid chromatograph. Molecular weights of the polystyrene with a small amount of azobenzene pendant groups

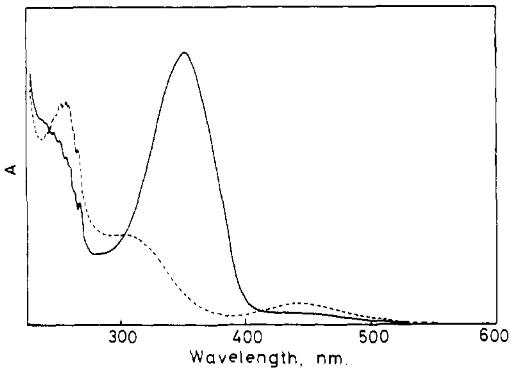

Figure 1. Absorption spectra of polystyrene having azobenzene pendant groups (4.8 mol % of monomer units, PS-A-4.8) in cyclohexane: (—) in the dark before irradiation; (---) after irradiation with ultraviolet light (410 > λ > 350 nm).

were estimated by comparison with polystyrene standard samples.

Results and Discussion

Photoisomerization. Azobenzene is known to be isomerized from the trans to the cis form by irradiation with ultraviolet light ($\lambda \sim$ 320 nm).[8] Intense absorption at 320 nm due to π–π^* transition decreases, while absorption at 430 nm due to n–π^* transition increases.

A similar spectrum change was observed for the polystyrene having azobenzene pendant groups as shown in Figure 1. On irradiation of a cyclohexane solution of the polymer with ultraviolet light (410 > λ > 350 nm), the intense absorption at 353 nm decreased, while the absorptions at 440 and 255 nm increased. The absorption band at 350 nm is ascribable to the π–π^* transition of the trans form of the pendant azobenzene residues and the band at 440 nm to the n–π^* transition of the cis form. The conversion of the 350-nm band to the 440-nm band and the appearance of isosbestic points at 243 and 412 nm are clear evidence of the isomerization of the pendant azobenzene residues.

The cis content, $1 - (\epsilon_c/\epsilon_t)y$, in the photostationary state under ultraviolet irradiation (410 > λ > 350 nm) was estimated to be 0.88, where ϵ_c, ϵ_t, and y are extinction coefficients of the cis and trans forms at 353 nm and the cis content. The high conversion from the trans to the cis form in comparison with the azobenzene incorporated in the polymer backbone, ca. 0.6,[4] suggests a higher local mobility of pendant groups.

The absorption around 250 nm has a fine vibrational structure, which is ascribable to polystyrene residues. The fine vibrational structure is believed to shift depending on the conformation of the polymer chain, and the change was successfully applied in measuring a conformational change of styrene–maleic anhydride copolymers.[9] Although the polystyrene having azobenzene pendant groups also showed vibrational structural change upon ultraviolet irradiation as shown in Figure 1, it is not appropriate to discuss the conformational change in further detail because of superposition of the absorption of azobenzene chromophores.

Solubility Change. Polystyrene with a small amount of azobenzene pendant groups (less than 10 mol % of monomer units) is soluble in cyclohexane at room temperature and the solution is transparent, having no absorption and scattering of light at wavelengths longer than 600 nm. On ultraviolet irradiation of a cyclohexane solution containing the styrene copolymer (410 > λ > 350 nm), the solution became turbid. Prolonged irradiation caused precipitation of the polymer. The cloudy solution generated by ultraviolet irradiation became transparent when it was allowed to stand for several hours with stirring at 25 °C in the dark.

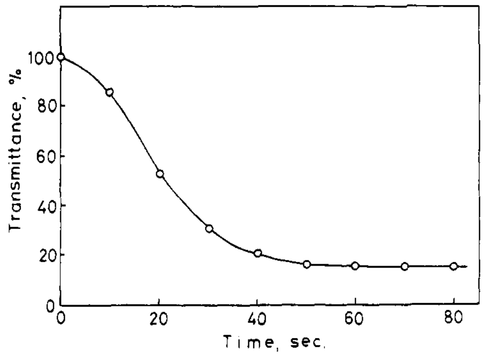

Figure 2. Change of transmittance at 650 nm upon ultraviolet irradiation (410 > λ > 350 nm) of a cyclohexane solution containing PS-A-6.1 at 30 °C. Concentration of the polymer was 0.090 g/dL.

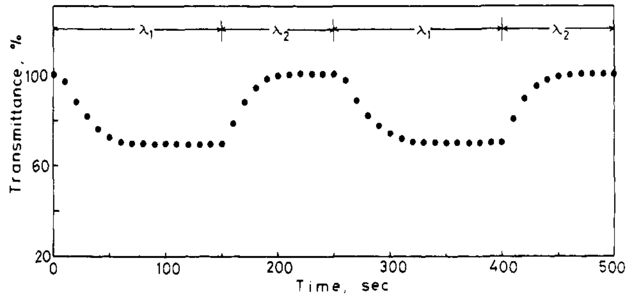

Figure 3. Changes of transmittance at 650 nm of a cyclohexane solution containing PS-A-6.1 on alternate irradiation with ultraviolet (410 > λ_1 > 350 nm) and visible (λ_2 > 470 nm) light at 30 °C. Concentration of the polymer was 0.046 g/dL.

The precipitation of the polymer upon irradiation with ultraviolet light was followed by measuring transmittance at 650 nm, where azobenzene has no absorption. Figure 2 shows that the transmittance decreased under irradiation with ultraviolet light and reached a plateau value in 50 s. Initially, the decrease of transmittance was very slow, and then it decreased quickly. After removal of the light, the transmittance returned to the initial value in several hours. The decrease of the turbidity in the dark is partly ascribable to the formation of large precipitated particles.

Relative to the dark reaction, visible irradiation (λ > 470 nm), which causes the isomerization of azobenzene groups from the cis to the trans form, accelerated the slow recovery of the transmittance. Figure 3 shows the decrease of transmittance at 650 nm of a polymer solution by ultraviolet irradiation (410 > λ > 350 nm) and the recovery with visible light (λ > 470 nm). The transmittance returned to the initial transparent state in 30 s, though the thermal recovery takes several hours in the dark.

Because of scattering of light by the precipitate, it was impossible to compare quantitatively the precipitation process and the absorption spectral change due to the isomerization in the same system. The photoinduced spectral change in a diluted condition (Figure 1), however, unambiguously indicates that the precipitation was caused by the isomerization of the azobenzene pendant groups. Important physical property changes of azobenzene associated with the isomerizations are (1) a geometrical structural change and (2) an increase in the dipole moment. The dipole moment increases from 0.5 to 3.1 D by the isomerization from the trans to the cis form.[10] These property changes, however, do not affect the solubility of azobenzene itself in cyclohexane. Precipitation of azobenzene was not observed under ultraviolet irradiation even in a saturated cyclohexane solution of azobenzene.

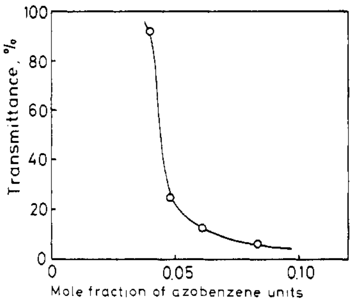

Figure 4. Dependence of transmittance at 650 nm in the photostationary state under ultraviolet irradiation (410 > λ > 350 nm) of polystyrene having azobenzene groups on the content of azobenzene units at 30 °C. Concentration of the polymer was 0.090 g/dL.

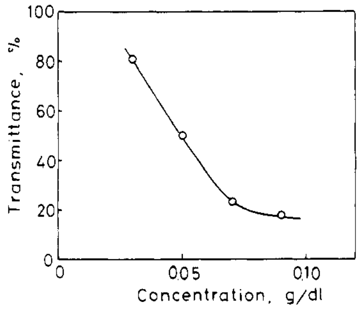

Figure 5. Concentration dependence of transmittance at 650 nm in the photostationary state under ultraviolet irradiation (410 > λ > 350 nm) of PS-A-6.1 at 30 °C.

Thus both the solvation of polystyrene in cyclohexane and the physical property changes of the pendant groups contribute to the precipitation of the polymer.

Cyclohexane is a Θ solvent for polystyrene (at 34 °C).[11] The dipole moment and geometrical structural changes of the pendant groups by ultraviolet irradiation are considered to alter the balance of polymer–solvent and polymer–polymer interactions. The introduction of the nonpolar trans form of azobenzene into polystyrene pendant groups scarcely affects the polymer–solvent interaction in cyclohexane, while the polar cis form tends to decrease the polymer–solvent interaction. Therefore, upon ultraviolet irradiation, the polymer–solvent interaction decreases considerably until the polymer precipitates.

Figure 4 shows the amount of precipitate at constant polymer concentration (0.09 g/dL) on the azobenzene content. Transmittance in the photostationary state under ultraviolet irradiation (410 > λ > 350 nm) sharply decreased when the azobenzene content exceeded 5 mol % of monomer units. The change of transmittance at rather low contents of azobenzene units indicates that isomerization of a few mole percent of azobenzene units in the polymer chain is enough to cause a solubility change of the polymer. Intra- or intermolecular dipole–dipole interaction between the *cis*-azobenzene units is considered to make an insignificant contribution to the property change below 5 mol % of the azobenzene units. The decrease of polymer–solvent interaction due to the appearance of polar structures in the pendant groups possibly plays a dominant role in the property change. When the content of azobenzene units was less than 2 mol %, precipitation was hardly observed even in the polymer solution containing about 0.2 g/dL. This result supports the above argument that the interpolymer dipole–dipole interaction is not the primary cause of the precipitation.

Figure 5 shows the polymer concentration dependence of the decrease of transmittance under the influence of ultraviolet irradiation (410 > λ > 350 nm). When the azobenzene content was above 4 mol %, the amount of precipitation increased with an increasing concentration of the polystyrene in cyclohexane. The concentration dependence is simply interpreted as resulting from the increase of the insoluble polymers.

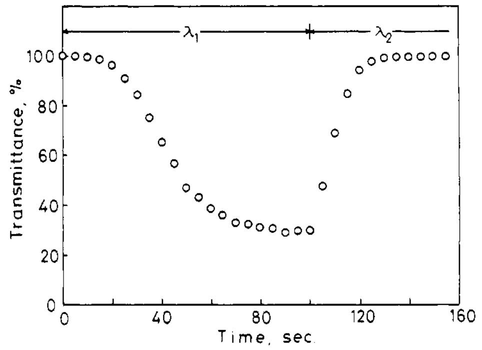

Figure 6. Changes of transmittance at 650 nm of a Decalin solution containing PS-A-6.1 on alternate irradiation with ultraviolet (410 > λ_1 > 350 nm) and visible (λ_2 > 470 nm) light at 30 °C. Concentration of the polymer was 0.21 g/dL.

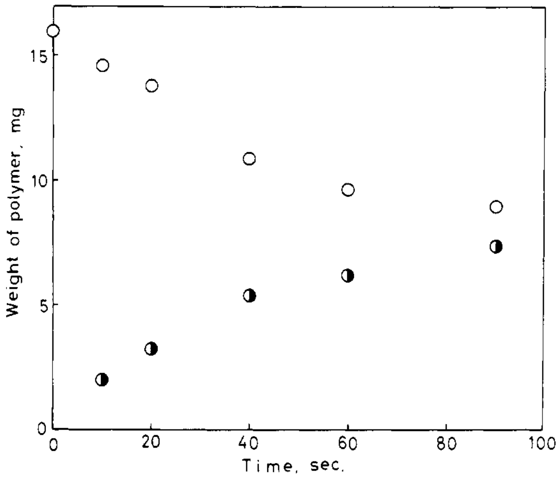

Figure 7. Formation of (◑) insoluble polymers on ultraviolet irradiation (410 > λ > 350 nm) of a cyclohexane solution containing PS-A-4.8 at 30 °C. The insoluble polymers were separated by passing the cyclohexane solution through a 0.2-μm Millipore filter. Concentration of the polymer was 0.080 g/dL.

The precipitation behavior depended on the nature of the solvent. Figure 6 shows the photoresponse of transmittance in Decalin. Decalin is a better solvent for the copolymer compared with cyclohexane. In Decalin an induction period for the precipitation was clearly observed and the polymer quickly became soluble under visible irradiation. This supports the suggestion that the decrease of polymer–solvent interaction due to the appearance of polar pendant groups caused the precipitation and the intra- and intermolecular dipole–dipole interactions between *cis*-azobenzenes was not a primary cause of the precipitation.

Molecular Weight Distributions. In the preceding section, precipitation was followed by the decrease of transmittance at 650 nm. The change of transmittance, however, could not give quantitative information concerning the ratio of insoluble and soluble polymers. The amount of insoluble polymer on ultraviolet irradiation of the cyclohexane solution containing polystyrene having azobenzene pendant groups (4.8 mol % of monomer units, PS-A-4.8) was measured by gravimetry, as shown in Figure 7. Half of the styrene copolymer became insoluble under the influence of ultraviolet irradiation (410 > λ > 350 nm). Because of experimental error, evidence for an induction

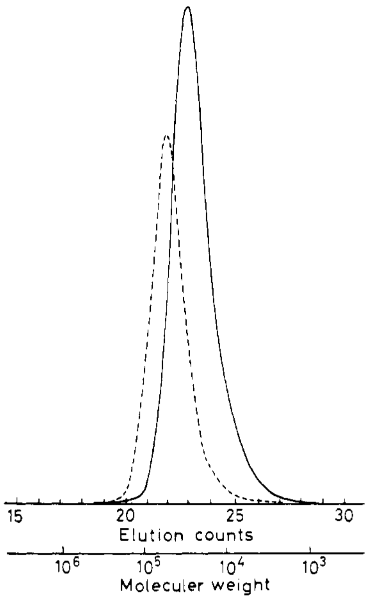

Figure 8. Molecular weight distributions of PS-A-4.8: (---) insoluble polymers in cyclohexane under ultraviolet irradiation (410 > λ > 350 nm); (—) soluble polymers.

period for the precipitation was not obtained by this method.

The precipitate and the soluble part were compared concerning (i) the content of azobenzene pendant groups and (ii) the molecular weight distribution. The content of azobenzene pendant groups was measured by elemental analysis as well as by absorption spectra. The copolymer composition can be estimated from the absorption intensities at 353 nm due to $\pi-\pi^*$ absorption of azobenzene and at 243 nm due to the phenyl groups of polystyrene. No significant difference in the content of azobenzene in the precipitate and the soluble part was observed.

A remarkable difference, on the other hand, was observed in the molecular weight distributions of the precipitate and the soluble part. Figure 8 shows the molecular weight distributions of the precipitated polymer (higher molecular weight) and of the soluble polymer in cyclohexane after ultraviolet irradiation. The molecular weight of the soluble polymer ($M_w = 2.9 \times 10^4$, $M_w/M_n = 1.28$) was about half that of the insoluble polymer ($M_w = 5.4 \times 10^4$, $M_w/M_n = 1.22$) and M_w/M_n decreased from 1.6 in the original polymer to 1.2 in the insoluble polymer.

The fractionation, accompanied by a decrease of M_w/M_n, suggests that the precipitation behavior observed in this system is similar to the fractional precipitation of a polymer from a solution by addition of a miscible nonsolvent. Fractionation by solubility is usually achieved by varying the nature of the solvent/nonsolvent mixture and the larger molecules precipitate first. A similar change occurs due to the isomerization of the pendant azobenzene groups during ultraviolet irradiation, since cyclohexane is a rather poor solvent for polystyrene with *cis*-azobenzene pendant groups. The fractionation was mainly controlled by the molecular weight and not by the content of the azobenzene groups.

Figure 9 shows the photoirradiation time dependence of molecular weight distributions of the precipitated polymers. The polymer precipitated in the initial 10 s had the largest molecular weight ($M_w = 7.1 \times 10^4$) and the smallest M_w/M_n (1.21). In the later period, the smaller molecular weight polymers successively precipitated. The molecular weight of the polymer precipitated in the final 30 s was estimated to have a M_w of 3.8×10^4. The successive precipitation of polymers having different molecular weights agrees with the assumption that the separation is mainly controlled by the molecular weight.

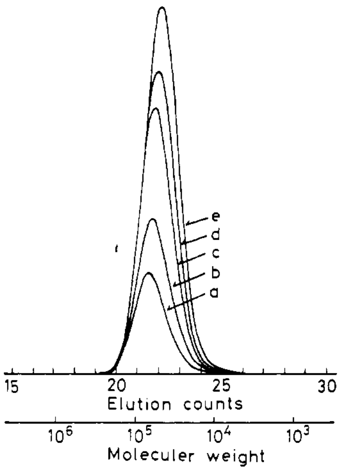

Figure 9. Irradiation time dependence of molecular weight distributions of insoluble PS-A-4.8 in cyclohexane at 30 °C. Irradiation times were (a) 10, (b) 20, (c) 40, (d) 60, and (e) 90 s. Concentration of the polymer was 0.080 g/dL.

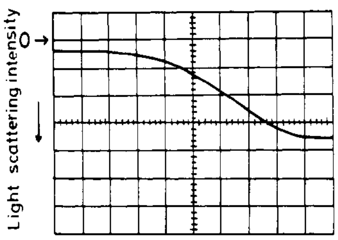

Figure 10. Precipitation of PS-A-4.8 in cyclohexane at 25 °C. Oscillogram illustrates changes of the light scattering intensity after the 20-ns laser pulse (347 nm). 200 ms/div.

The fluctuation of azobenzene content is considered to be negligible in the copolymers of high molecular weight prepared at low conversion.[12] No difference in the chemical compositions among polymers precipitated in the first and last periods ruled out the possibility that polymers containing higher azobenzene contents precipitated first.

Light Scattering Measurement. The time dependence of light scattering intensity monitored at 90° of the incident CW Ar ion laser after excitation with a single laser pulse gives information concerning the conformational change of the polymer[6] as well as the precipitation process. Figure 10 shows an oscilloscope trace showing the light scattering intensity at 514 nm after the 20-ns ruby laser pulse (347 nm). In the first 400 ms the intensity did not show any change; it then increased gradually and finally reached a maximum at 1.4 s after the pulse. The isomerization from the trans to the cis form of pendant azobenzene groups could be followed by monitoring the increase of the absorption due to the cis form (420 nm). The absorption at 420 nm increased within 50 ns after the pulse and did not show any further change. This indicates that the isomerization of the pendant groups is complete in 50 ns.

The long induction period of 400 ms observed in the light scattering intensity suggests that it takes some time for the polymer to precipitate from cyclohexane. The period is much longer than the time observed in the conformational change of polyamides having azobenzene groups in the main chain.[6] The S shape of the light scattering intensity time dependence suggests that the precipitation is a cooperative phenomenon. A similar cooperative phenomenon has been reported in the radiation-induced coagulation of proteins.[13]

In this study, we have presented a new example, solubility, of physical properties of polymers that can be controlled reversibly by selection of the irradiating wavelength. We can expect to control reversibly many other aspects of the properties of polymers by using photoresponsive polymers.

Registry No. PS-A, 35176-66-0.

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Analysis and Dilute Solution Properties of 12- and 18-Arm-Star Polystyrenes[†]

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ABSTRACT: The homogeneity of samples of 12-arm- and 18-arm-star polystyrenes was investigated by ultracentrifugation sedimentation in a Θ solvent and with gel permeation chromatography combined with low-angle laser light scattering. The former method permits the detection of star polymers with different numbers of arms in a sample, and the latter allows the determination of the number of arms in the stars. Light scattering studies revealed that the star polymer coils are expanded from the random walk size in a Θ solvent for the linear polymer. The strong upward curvature at $\mu > 4$ in the reciprocal scattering curve of the stars in a good solvent suggests that the average segment density distribution in the stars is more uniform than predicted by the random walk model. Sedimentation velocity and intrinsic viscosity measurements indicate that these highly branched polymers behave hydrodynamically almost like hard spheres in dilute solution.

Introduction

Star polymers are ideally suited for the study of the relation between the segment density in polymer coils and the physical properties of the polymers, because they allow the segment density to be changed without a concomitant change in the molecular weight of the polymer.[1,2] Initially, only stars with three, four, or six equal arms could be synthesized by the rigorous method of linking monodisperse living anionic polymers with multifunctional chlorosilanes.[3] Star polymers with more than six arms were prepared by coupling living polymers through divinylbenzene nodules. This method does not allow one to predict accurately the number of arms of the stars, nor does it yield polymers with a uniform number of arms.[4] Recently, it has become possible to prepare 8-, 12-,[5] and 18-arm[6] stars by an extension of the chlorosilane method. However, as the number of arms increases, it becomes increasingly more difficult to ascertain the monodispersity in molecular weight and number of arms of the star polymers.

A careful analysis of two very high molecular weight samples of polystyrene with 12 and 18 arms, respectively, has been made in an attempt to identify the homogeneity in architecture and molecular weight of the samples. Light scattering experiments in a Θ solvent and in a good solvent have been made in order to probe the segment density distribution in the stars, at least at long segment–segment distances. Comparisons are made with the random flight model. Data on the intrinsic viscosities and sedimentation velocity coefficients are also included. The hydrodynamic properties of the stars are compared with their static dimensions in solution.

Experimental Section

The synthesis of the 12- and 18-arm polystyrenes was performed along the lines described for 12-arm polyisoprenes[5] and 18-arm polyisoprenes.[6] First a narrow molecular weight linear polystyrene was prepared by anionic polymerization techniques with *sec*-BuLi as the initiator. A small fraction was removed and terminated with degassed MeOH. It is the reference "arm" material. The living polystyryllithium was capped with a few units of butadiene prior to reaction with the multifunctional chlorosilane compound. The 12-arm star was prepared by linking of the arms with $Si[CH_2CH_2SiCl_3]_4$ and the 18-arm star was obtained with $[CH_2Si(CH_2CH_2SiCl_3)_3]_2$. About 50% excess living polymer was used in order to force the linking reaction to completion. The linking reaction was monitored by comparison of the high molecular weight "star" peak and the low molecular weight "arm" peak of GPC traces. The excess living polymer was terminated with degassed methanol. The polymers were extensively fractionated in order to remove the excess arm material. The 18-arm star, 18-PS1, was used as such. The 12-arm star, 12-PS1, was analyzed but was also subjected to an additional four-step fractionation at very high dilution in a mixture of benzene and methanol. This yielded two relatively pure fractions 12-PS1B1A and 12-PS1C, which were further studied.

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