From a Dissolved Polystyrene Coil to an Intramolecularly-Hyper-Cross-Linked “Nanosponge”

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ABSTRACT: Linear polystyrene of $M_w = 330\ 000$ and $M_w/M_n = 1.04$ in which 50% and 100% of the phenyl residues were chloromethylated were heated in a 0.5 g/L ethylene dichloride solution in the presence of $SnCl_4$ to convert them into an intramolecularly hyper-cross-linked soluble material. The spherical macromolecular species obtained exhibit low density and high surface area (up to 1000 m^2/g) and swell strongly in all nonsolvents for linear polystyrene. Solutions in good polystyrene solvents exhibit low viscosity and reduced partial specific volume, but exceedingly high diffusion and sedimentation constants. According to size exclusion chromatography, dynamic light scattering, low angle X-ray scattering and electron microscopy, the diameter of the hyper-cross-linked species is estimated as about 12 nm in the dry state and about 17 nm in solution. In tetrahydrofuran, they associate reversibly, probably forming clusters consisting of 13 regularly packed particles. Because of the partial association, molecular weight measurements (using elastic light scattering and ultracentrifugation techniques) produce values slightly exceeding the 350 000−370 000 expected for the isolated particle.

Introduction

Among the numerous naturally occurring and synthetic macromolecular species, only four basic types can be distinguished when considering the overall shape of individual species in a dilute solution. These types are dense globular macromolecules, rigid rodlike molecules, flexible and voluminous coils, and highly branched (hyperbranched) macromolecules and dendrimers. Many other variants of macromolecules have been synthesized. Their overall shape, however, represents combinations of the above four basic types, e.g. a globule with one or several long coiled chains grafted onto its surface.

It is the aim of the present paper to introduce a novel macromolecules species, the nanosponge, which differs fundamentally from the above four basic types with respect to its topology, as well as its behavior both in the dry state and in solution. The synthetic path to the nanosponge consists of intramolecularly introducing a large number of rigid spacers (i.e. cross-links) between different repeating units of a single linear polystyrene chain taken in the form of a coil in a diluted solution. A similar, but intermolecular, cross-linking in a more concentrated solution, where the polymeric coils entangle and interpenetrate, converts the solution into a swollen gel of hyper-cross-linked polystyrene, representing a novel type of polymeric network.[1] The feasibility of an extensive intramolecular cross-linking was exemplified in a previous paper[2] by reacting a diluted linear polystyrene solution of a high molecular weight in a thermodynamically good solvent, ethylene dichloride, with monochlorodimethyl ether as a bifunctional cross-linking agent.

In general, intramolecularly cross-linked macromolecules or microgels were prepared by an aqueous microemulsion copolymerization of mono- and bifunctional comonomers using appropriate stabilizer systems.[3−5] This procedure resulted in nearly homogeneous spherical species resembling the structure of networks of conventional gel-type styrene−divinylbenzene (DVB) copolymers.[6] Microgels that have a rather dense center and open up continuously toward the outer regions were produced by a copolymerization procedure in a homogeneous solution in an organic media below a certain critical concentration of the comonomers.[7]

Another approach to producing cross-linked molecular species, the introduction of intramolecular cross-links into dissolved macromolecules, has been examined by several groups, as well. Allen et al.[8] reacted a partially chloromethylated polystyrene with butylamine and then introduced cross-links by involving secondary amino groups thus formed in the reaction with hexamethylene diisocyanate. A reasonable reduction of the radius of gyration of the coil (to about 0.5 for a cross-linking degree of 2.5%) in solution was registered by Allen and associates.[9,10] On the other hand, Antonietti et al.,[11] on cross-linking directly polystyrene coils with *p*-bis(chloromethyl)benzene under Friedel−Crafts conditions, observed a surprisingly small change in the dimension of the coiled species.

Our experiments differ fundamentally from those previously published in that the extent of cross-linking, examined thus far, has been relatively small (usually less than 10%) and our aim has been to involve every phenyl group of the initial polystyrene coil into an intramolecular cross-link. The products of such extensive cross-linking are conformationally rigid. Due to the rigidity, the hyper-cross-linked nanosponges differ from the flexible intramolecularly cross-linked microgels as dramatically as the hyper-cross-linked polystyrene network[1] differs from conventional styrene−DVB copolymers.

Experimental Section

Synthesis of the Intramolecularly Hyper-Cross-Linked Polystyrene. An atactic linear polystyrene standard with the molecular weight of 330 000 Da and narrow molecular weight distribution, $M_w/M_n = 1.04$, was used.

Chloromethylation of the polystyrene was performed in an excess of monochlorodimethyl ether in the presence of zinc dichloride as catalyst. The polymer (1 g) was dissolved in 40 mL of monochlorodimethyl ether, and the solution was slowly

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added to a solution of 1.38 g of $ZnCl_2$ in 40 mL of monochlorodimethyl ether. The mixture was heated to 40 °C for 3 h and then added to 800 mL of methanol. The polymer thus precipitated was washed with several portions of fresh methanol and dried in vacuum. The degree of chloromethylation (13.40% Cl) was 48.4% of theoretical. In another batch, one drop of $SnCl_4$ was added to the above reaction mixture, which resulted in a quantitative (23.34% Cl) chloromethylation of the polymer.

For the intramolecular cross-linking of the chloromethylated polystyrene 1.32 g (0.0086 mol) of the quantitatively chloromethylated polystyrene was dissolved in 2640 mL of dry ethylene dichloride, which was freshly distilled over P_2O_5. To this was added 2.33 mL (0.015 mol) of $SnCl_4$, and the solution was heated to 80 °C. During the first 1.5 h, a pink color of the solution developed which later turned to red and brown. After heating for 10 h, 50 mL of acetone was added to the reaction mixture in order to decompose the colored complex of the catalyst with the polymer. An hour later, the solution was allowed to cool to the ambient temperature and then carefully washed with many portions of distilled water (about 12 L, altogether) until no chlorine ions were detectable in the aqueous phase. The decanted organic solution was finally dried over $CaCl_2$ and kept in the dark before use. To isolate the dry polymer, the above solution was concentrated under reduced pressure to about one-fifth of its original volume, and the polymer was precipitated with methanol, filtered, and dried in vacuum to a constant weight. The final polymer contained 6% residual chlorine.

In another experiment, the polystyrene with 48.4% monomer residues chloromethylated was subjected to intramolecular cross-linking under the above conditions. In this case, the residual chlorine content in the final product was 2%.

Hydrodynamic Properties of Polystyrene Nanosponges. The diffusion and sedimentation rates of the polymers were studied using an analytical ultracentrifuge MOM 3180 (Budapest, Hungary). The experiments were performed at a temperature of 25 ± 0.1 °C.

Diffusion coefficients of both the initial polystyrene and the nanosponges were calculated from the broadening rate of a sharp synthetic boundary formed in the ultracentrifuge cell between solutions of the polymers in tetrahydrofuran and the pure solvent.

Sedimentation coefficients, s_c, were determined at the rotor rotation rate of 10×10^3 to 50×10^3 min^{-1} and the polymer concentration of 2−7 g/L in tetrahydrofuran. By extrapolating the $1/s_c$ values to infinite dilution, the sedimentation constants, S_o, were determined.

The weight-average molecular weight of the polymers in tetrahydrofuran was determined from sedimentation data in accordance with the approach-to-equilibrium of Archibald's method.[12] The rotation rate was selected such that the gradient line crossed the meniscus line at an angle of about 45°. To evaluate the values of M_w, the apparent molecular weights determined for a series of concentrations were extrapolated to infinite dilution.

The second virial coefficient, A_2, was calculated from $1/M_{ap} = 1/M_{sed} + 2A_2C$.

The intrinsic viscosity in tetrahydrofuran, $[\eta]$, mL/g, was determined using a modified Ubbelohde viscometer at 25 ± 0.1 °C by extrapolating specific viscosities in the concentration range, C, of 2−15 g/L to infinite dilution.

Light scattering was measured using the photogoniodiffusometer "Fica" (Paris, France) using vertically polarized light of $\lambda = 564$ nm in the angle interval from 30 to 150° and a temperature of 25 ± 0.1 °C. The polymer solutions in tetrahydrofuran were filtered prior to measurements. The initial concentration of the solutions was 2 g/L. The molecular masses were determined by the Zimm extrapolation method.[13]

Size exclusion chromatography of linear polystyrene and its cross-linking products was carried out at a flow rate of 2 mL/min on a silica gel Diasorb Si 400 column (250 × 16 mm; particle size, 11 μm, mean pore size, 40 nm) which generated 9070 theoretical plates for naphthalene in acetonitrile. The liquid chromatograph used was LC-31, a gift by Bruker (Bremen, Germany). The mobile phase was tetrahydrofuran.

Results and Discussion

Synthesis of Polystyrene Nanosponges. In order to facilitate the characterization of products of an extensive intramolecular cross-linking, we used an atactic polystyrene with the molecular weight of 330 000 Da and a narrow molecular weight distribution ($M_w/M_n = 1.04$) as the initial linear polymer.

For cross-links to be formed intramolecularly, i.e. within individual polymeric coils, the initial polymer solution has to be highly diluted, so as to avoid intermolecular cross-linking. For polystyrene with the molecular weight of 330 000 Da dissolved in a thermodynamically good solvent, the critical concentration $c = 1/[\eta]$ is reached below a value of 10 g/L. For a polystyrene chain consisting of 2000 units (molecular weight about 200 000) and having 40 reactive sites, the probability of intramolecular cross-linking at the total polymer concentration of 0.2 g/L was estimated to be 300 times higher than that of intermolecular binding.[8] Moreover, after the first intramolecular cross-links are completed, the coils should contract so that further reactions are even more likely to be intramolecular. The importance of this effect, though difficult to estimate, may be very large. In our cross-linking experiments, the concentration of the initial polymer solution was 0.5 g/L.

Monochlorodimethyl ether, CH_3OCH_2Cl, was first used as the bifunctional cross-linking agent. It substitutes two phenyl groups of polystyrene in the presence of a Friedel−Crafts catalyst to form a diphenylmethane-type bridge between two fragments of the polymer chain. Theoretically, 0.5 mol of the bifunctional reagent is sufficient to bind all phenyl rings of 1.0 mol of polystyrene repeating units, which would correspond to a formal value of 100% cross-linking. Previous experiments, however, showed that, in a reaction mixture which is that much diluted with respect to both the polymer and cross-linking agent, the completion of the cross-linking process requires more than 100 h at 80 °C. Besides, the reaction proved to be very sensitive to impurities present in the solvent, the latter being taken in a large excess.

The above difficulties can be easily overcome if the cross-linking reaction is carried out in two steps. In the first, linear polystyrene is (partially) chloromethylated under well-established conditions to a substitution degree of about 50% (or higher). In the second stage, a diluted solution of the above chloromethylated polymer in ethylene dichloride is heated with the catalyst. In this case, all reaction components, the chloromethyl groups and unsubstituted phenyl rings, are located in the volume of the polymeric coil. In addition to this, tin tetrachloride also has a tendency to coordinate to polystyrene and concentrate within the reacting coil. Therefore, the intramolecular cross-linking requires no more than 10 h at 80 °C. The final reaction mixture remains completely transparent and can be stored before use in the dark. If required, the polymer solution can be concentrated and the polymer precipitated with excess methanol.

When starting with a polymer having a chloromethylation degree of 50%, the cross-linking degree of the final product (sample 1) amounts formally to 100%, though in reality it is smaller, since 2% of chlorine in the product was found to escape the reaction, for one reason or another. In the case of the total chloromethylation of the initial polymer, the chloromethyl groups have no other choice than to react with another chloromethylated styrene residue. This possibility is realized, nevertheless, as the cross-linking reaction takes place readily. Theoretically, each phenyl group should then be involved twice in the formation of cross-bridges, and the final cross-linking density should exceed considerably that of a material cross-linked to 100%. In fact, a residual 6% of chlorine in the product (sample 2) was found to remain unsubstituted under the stated reaction conditions. In any case, the term "hyper-cross-linked" seems to be fully justified for both polymers obtained, though the exact degree of cross-linking will remain unknown. The degree of cross-linking is not really important since it has been repeatedly shown[1] that basic properties of hyper-cross-linked polystyrene do not change noticeably beyond the cross-linking degree of about 60%. Solution properties of the two above batches of intramolecularly hyper-cross-linked polystyrene were also found to be similar, irrespective of the degree of chloromethylation of the initial polymer (50 or 100%).

We assume that the remaining chlorine atoms (2 and 6% in samples 1 and 2, respectively) are mainly located at the surface of rigid polymeric species, where it is more difficult for them to find an intramolecular reaction partner. A similar assumption was also made by Kim and Webster[14] for residual functional groups in hyperbranched polyphenylene macromolecules. If desired, these surface-exposed halogen functions can be chemically modified.

Properties of the Intramolecularly Hyper-Cross-Linked Polystyrene. The intramolecularly hyper-cross-linked polystyrene had an appearance of a slightly yellow powder which was soluble in all solvents of linear polystyrene. The polymer proved to be insoluble in methanol, hexane, and other nonsolvents for polystyrene, though it swelled strongly in these solvents. The bulk volume of the polymeric powder increased in the nonsolvents by a factor of 3, which could be estimated most conveniently in a glass test tube after sedimentation of the polymer in a centrifuge.

In the dry state, the surface area of the polymer powder was found to achieve a value of 680−1000 m^2/g when measured by thermal desorption of argon and calculated using the conventional BET equation. The above value corresponds well to the inner surface area usually measured for a bulk hyper-cross-linked polystyrene.[1] An individual polystyrene macromolecule with $M = 330\,000$ should occupy after cross-linking a volume of a sphere with a diameter of at least 10.4 nm, and the outer surface area of 1 g of such a beaded material would measure less than 600 m^2. The value of 1000 m^2/g found experimentally implies that the inner space of the hyper-cross-linked polystyrene remains accessible to argon, i.e., that the dry nanosponges exhibit some kind of porosity.

Interesting information is obtained when comparing the properties of the initial linear polystyrene with those of hyper-cross-linked nanosponges dissolved in the same solvent, tetrahydrofuran. The difference in the molecular weights of these polymeric species is small since the molecular weight of the initial molecule of 330 000 would rise to 350 000 at a cross-linking degree of 100% due to the $-CH_2-$ bridges introduced (sample 1) and to about 370 000 (sample 2) for a doubled cross-linking density.

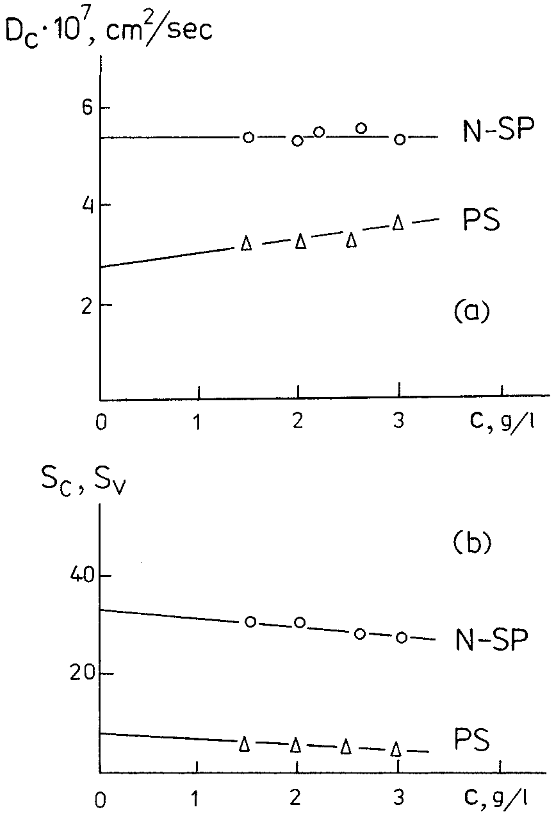

Figure 1. Concentration dependence of diffusion (a) and sedimentation (b) coefficients of the polystyrene 330 000 before (PS) and after the intramolecular cross-linking (N-SP). Solvent: tetrahydrofuran.

It turned out (Figure 1a) that the diffusion coefficient in a concentration gradient for the dense spherical nanosponge (sample 2) exceeded that of the linear coil by a factor of 2, when measured with an ultracentrifuge using a synthetic boundary technique.

In the force field of the ultracentrifuge, the more compact nanosponge naturally moved much faster than the diffused polymeric coil. The sedimentation constants were found to amount to 7.5 and 32.6 s for the linear polystyrene and cross-linked sample 2, respectively (Figure 1b).

The sedimentation of nanosponges is further accelerated by the unexpected fact that their partial specific volume is smaller than that of the linear precursor. The corresponding values for tetrahydrofuran solutions are 0.856 and 0.896 cm^3/g, respectively. This cannot be due only to the residual chlorine content, since a similar difference was previously observed[2] for other hyper-cross-linked nanosponges including samples with no residual chlorine. Obviously, 1 g of the linear polymer displaces more solvent from a solution than does 1 g of an intramolecularly cross-linked polymer. In our opinion, this tendency can be explained by the difference in the mobility of structural units of the two species under comparison. Whereas phenyl groups of the linear polystyrene freely vibrate and rotate around the single bond to the carbon−carbon chain, thus requiring a definite additional space, all functional groups in the hyper-cross-linked network are highly restricted from any kind of movement. Here, the amplitude of the hyper-cross-linked polymer's own movements is small, which facilitates a more intensive interaction of the whole network with the solvent molecules.

Intramolecular cross-linking causes a dramatic drop in the intrinsic viscosity of solutions of polystyrene, from

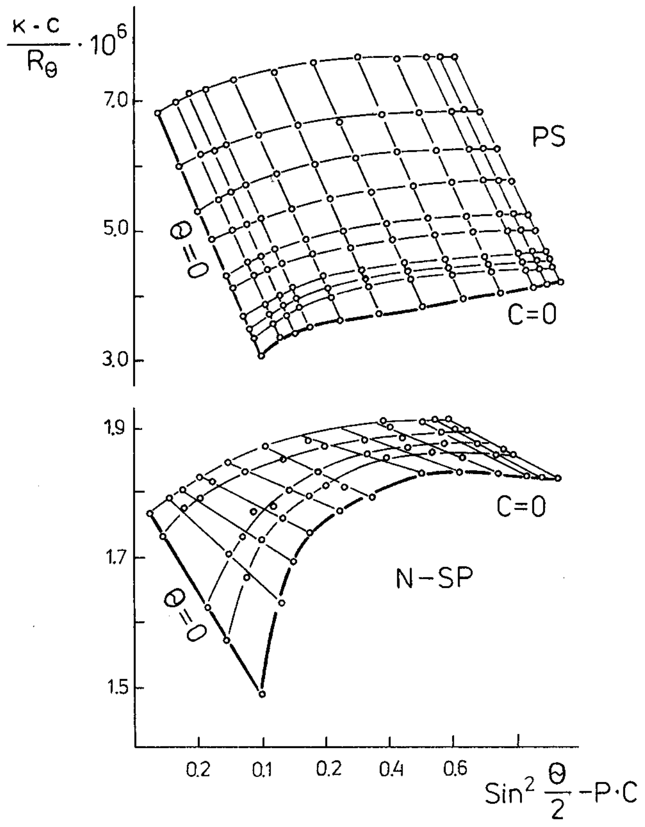

Figure 2. Zimm's diagrams for solutions of the polystyrene 330 000 before (PS) and after the intramolecular cross-linking (N-SP). Solvent: tetrahydrofuran.

0.98 down to 0.10 dL/g. Moreover, the viscosity becomes nearly independent of the concentration of the solution as well as molecular weight of nanosponges (samples with molecular weights of 23, 50, 80, 100, and 320 × 10^3 have been examined,[2,16] all giving minimal intrinsic viscosity in toluene and ethylene dichloride, usually in the range of 0.08−0.10 dL/g). These data indicate that the polymeric species behave in solution like rigid spheres.

In estimating the molecular weight of polymers by Archibald's method, a qualitative difference should be pointed out: whereas for the linear polymer a strong dependence of the apparent molecular weight on the concentration is always registered, this is not the case with the hyper-cross-linked polymer. Accordingly, the second virial coefficients calculated from these dependencies are 7.6×10^{-4} and 1.0×10^{-5} g^2 mol^{-1} cm^3, respectively (as against light scattering values of 5.5×10^{-4} and 4.0×10^{-5}). A low A_2 value is characteristic of rigid spheres.

The molecular weight of sample 2 of 460 × 10^3, obtained from the Archibald method, appears higher than the expected value of 370 × 10^3. This method is especially sensitive to high molecular weight byproducts, which are present in the nanosponge preparations, as will be shown below.

The same sensitivity to larger particles is characteristic of the elastic light scattering technique. Here, a highly distorted Zimm diagram was obtained (Figure 2), which, in terms of Guinier,[15] could approximately be interpreted as scattering from a polymer of the molecular weight of 490 × 10^3 containing an admixture of 0.3% of the polymer with $M = 85 \times 10^6$. By contrast, the initial polystyrene gives a classical Zimm diagram, with a good match of the calculated and expected molecular weights of 330 × 10^3.

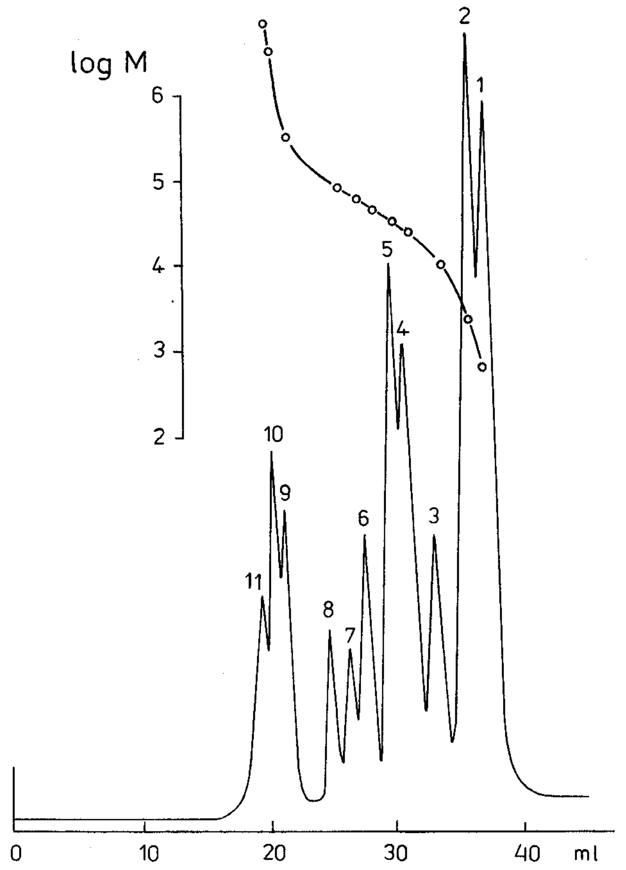

Figure 3. Size exclusion chromatography of 11 polystyrene standards with molecular weights 0.68 (1), 2.45 (2), 10.1 (3), 22 (4), 30.3 (5), 52 (6), 66 (7), 96 (8), 330 (9), 3000 (10), and 7000 (11) kDa, respectively, and the corresponding calibration graph.

To estimate dimensions of molecular species, we applied size exclusion chromatography and dynamic light scattering to the nanosponges in solution and electron microscopy and low-angle X-ray scattering to the dry material. As mentioned above, a fully collapsed cross-linked polystyrene molecule with molecular weight 370 × 10^3 would occupy the volume of a sphere with a diameter of 10.4 nm if it could maintain the density of a conventional polystyrene, 1.04 g/cm^3. Since the hyper-cross-linked polystyrene is a "porous" low-density material (usually 0.69 g/cm^3), the nanosponge possibly should have a diameter of 11.9 nm when in the dry state and 17.2 nm after having increased its volume by a factor of about 3 on swelling with an organic solvent.

When examined by the low-angle X-ray scattering technique in its dry state, the intramolecularly hyper-cross-linked polystyrene, a light powder, scatters X-rays as a material with the fluctuations in its density having a period of about 12 nm. Size exclusion chromatography of cross-linking products, on both analytical and preparative scales, was carried out on a silica gel Diasorb Si 400 column of an acceptable performance and resolution power (see separation of a test mixture of 11 polystyrene standards in Figure 3; sample 9 in this mixture represents the starting material for the subsequent intramolecular cross-linking). As shown in Figure 4, the product of the cross-linking reaction contained two high molecular weight fractions, in addition to the main sharp peak. The elution volume of the latter corresponded to the elution volume of a linear polystyrene standard with a molecular weight of 70 800, which can be taken from the calibration graph presented

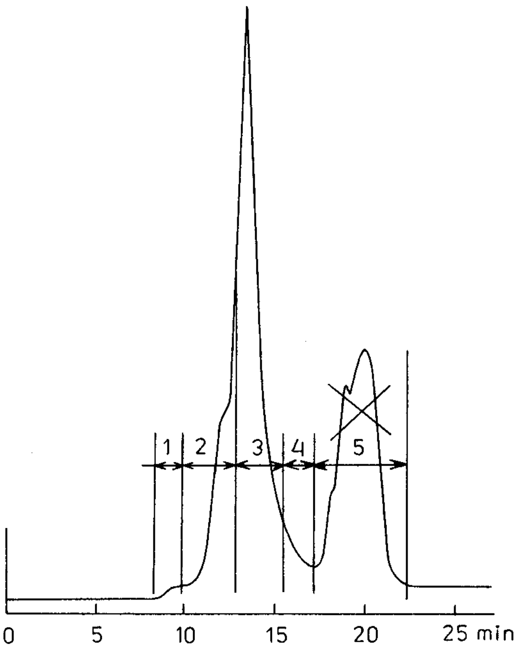

Figure 4. Preparative size exclusion chromatography of the bulk intramolecular cross-linking product. Fractions 1, 2, and 3 correspond to microgels, clusters, and nanosponges, respectively; fraction 5 includes low molecular weight impurities, e.g. tetrahydrofuran peroxides.

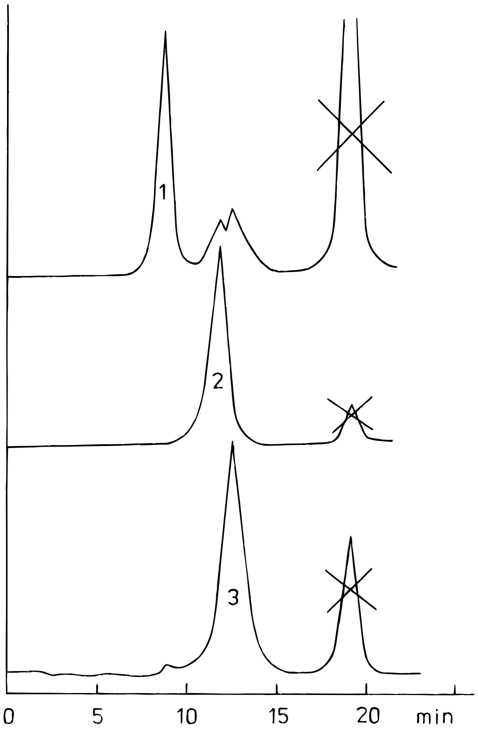

Figure 5. Analytical-scale size exclusion chromatography of fractions 1, 2, and 3 obtained in the preparative fractionation.

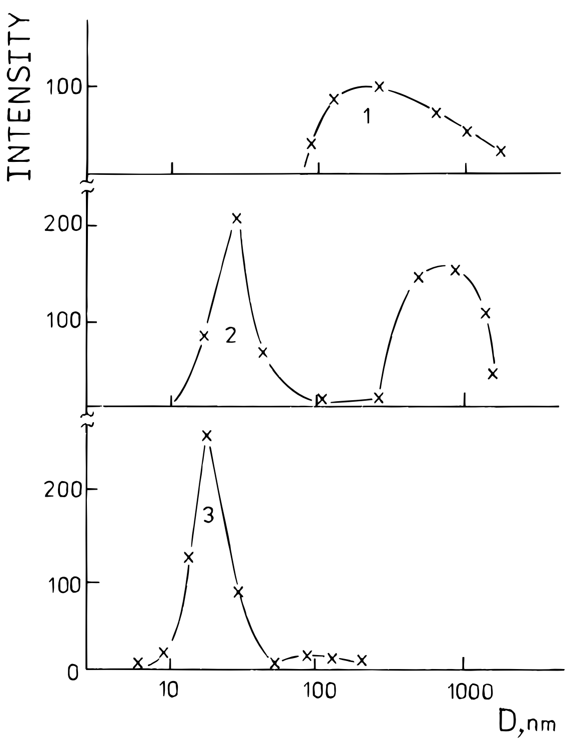

Figure 6. Size distribution of species calculated from dynamic light scattering experiments on fractions 1, 2, and 3.

in Figure 3. The mean gyration radius of a coil of such molecules can be calculated to amount to $2R_g = 18.7$ nm. This value coincides with the expected diameter of a nanosponge particle of 17.2 nm given above.

By repeating many times the size exclusion chromatography of a concentrated nanosponge solution, an attempt was made to obtain the major product (as well as the two byproduct fractions) in the purest possible form. Surprisingly, even after repeated rechromatography, each of the three fractions collected (Figure 5) proved to be "contaminated" in the neighboring fractions, which implies an equilibrium between the individual nanosponges (fraction no. 3), "clusters" (fraction no. 2), and higher associates or microgels (fraction no. 1). When taken separately, clusters in fraction 2 elute with the elution volume of a polymer having a molecular weight of about 158 500 and an average diameter of about 30 nm, though the exact position of the elution peak of this product could not be estimated precisely. The microgel fraction 1, whose content does not exceed a few percent of the total synthesis product, elutes outside the calibration range of the chromatographic column ($M > 7 \times 10^6$). This fraction may include both the products of unavoidable intermolecular cross-linking and the higher associates of nanosponges and/or clusters.

Dynamic light scattering on the effluent fractions (Figure 6) allowed estimation of the diameter of the nanosponges as 17 nm and that of clusters (with the admixture of monomeric nanosponges) as 34 nm. Microgels (fraction 1) were not further examined, whereas the material of fractions 3 and 2, after evaporation of tetrahydrofuran, could be visualized using transmission electron microscopy (Figure 7). Spherical species of about 15−25 nm and about 40−50 nm can be clearly seen representing the individual nanosponges and their regular associates. (Size estimations are very approximate using this technique.)

We introduce the term nanosponge for the first type of species since, on the one hand, it refers to the macromolecular range of sizes of the species, of about several hundreds to several thousands of angstroms. On the other hand, this term implies the low density and porosity of the material, its ability to readily incorporate large amounts of any liquid, and the rigidity of the species, in both its dry and swollen states.

A remarkable property of the hyper-cross-linked polystyrene nanosponges, when dissolved in tetrahydrofuran, is their tendency to reversibly form larger associates, with one specific aggregate being more stable

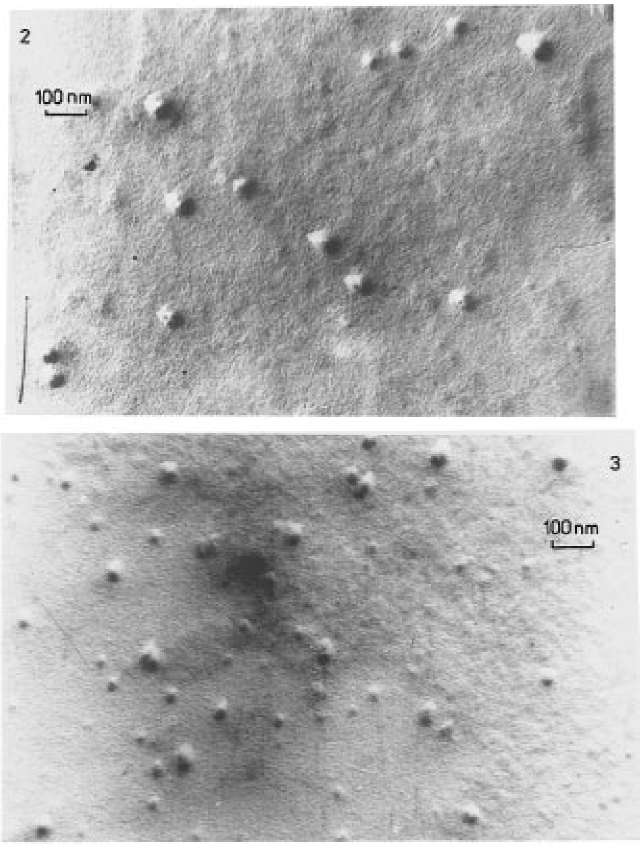

Figure 7. Transmission electron micrographs of the polymeric species in fractions 3 (nanosponge) and 2 (clusters).

than aggregates of larger and smaller size. On the basis of preliminary data, we believe these specific structures to be composed of 13 particles. This figure is confirmed by more accurate molecular weight measurements,[17] thus representing the first example of a regular cluster obtained from a synthetic polymeric species.

Conclusion

The introduction of large amounts of rigid intramolecular bridges into individual polystyrene coils taken in a dilute solution converts the coils into strongly contracted spherical species, nanosponges, whose solutions exhibit low viscosity, high diffusion, and sedimentation rates. Like the bulk hyper-cross-linked polystyrene, the nanosponges display a high inner surface area and they swell strongly in nonsolvents for linear polystyrene.

When dissolved in tetrahydrofuran, provided that the molecular weight distribution of the polystyrene nanosponges is narrow, the individual species tend to reversibly form associates, the most stable of which probably represent clusters consisting of 13 regularly packed individual species.

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