# Small-angle neutron scattering from polystyrene–DVB networks containing a delta fraction of deuterated polystyrene: Evidence for aggregation during polymerization

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Homopolymer polystyrene–divinylbenzene, PS–DVB, networks were made by free radical chemistry u.v. photopolymerization techniques, and characterized by small-angle neutron scattering (SANS). The networks contained a delta fraction of chains labelled with deuterium. Two different series of samples were made: Method A in which the insertion was made centrally or at the end of the polymerization; Method B in which the delta fraction of deuterated primary chains was inserted at the beginning of the polymerization. Method B samples yielded a molecular weight of about 70,000 g/mole and a radius of gyration of about 120 Å, values in the range expected for single primary chains. Method A samples, however, gave molecular weights of 1–2 million and radii of gyration ranging from 350 to 400 Å. Intrinsic viscosity and gel permeation chromatography (g.p.c.) studies on parallel fractions yielded weight-average molecular weights near 72,000 g/mole for most of the polymerization. These results strongly suggest the existence of aggregation of primary chains synthesized in the same conversion period within the network. A new method of characterizing crosslinking between network chains is proposed, since these experiments count the probability of a chain crosslinking with a chain polymerized immediately before in time.

(Keywords: small-angle neutron scattering; polystyrene–divinyl benzene networks; delta fraction; deuterated polystyrene; aggregation; polymerization)

## INTRODUCTION

Before the introduction of small-angle neutron scattering (SANS), polymer chain conformation studies were restricted to light scattering and small-angle X-ray (SAXS) instrumentation, usually conducted in dilute solution. Under Flory $\theta$-conditions[1], most polymer chains were shown to be random coils. While scientists of that day theorized that the conformation of polymer chains in an amorphous bulk polymer were similar to that which existed under Flory $\theta$-conditions, there was only limited direct experimental evidence in support of this theory[2]. In recent years, SANS has been shown to be an appropriate technique for directly studying the chain conformation and dynamics of flexible polymer molecules in the bulk state[3-6]. Generally, SANS data has been consistent with the existence of random coils in the bulk state[3,7], although several workers[8-13] have shown that on extension, the chain ends appear to deform more than the central section, leading to non-Gaussian statistics.

Here a series of polystyrene–divinyl benzene networks were prepared by free radical polymerization. The ordinary hydrogen-bearing styrene monomer was removed at one point, and 5–20% of deuterated monomer, called a delta fraction, was inserted. On polymerization, then, a

portion of the network consisted of deuterated primary chains. These materials, when examined by SANS, yielded molecular weights many times the known molecular weight of individual primary chains.

From an experimental point of view, the problem was to characterize the exact state of aggregation. From the theoretical point of view, the problem was to develop and examine suitable models of the actual aggregation mechanism. It will be shown below that this state of aggregation is caused, in part, by a just-polymerizing chain having a higher than statistical probability of crosslinking with a chain polymerized in the immediate past, rather than with chains polymerized much earlier in time. This unusual result has to do with the pendant vinyl groups on the already polymerized chains. As the reaction proceeds, these are gradually consumed, leaving the chain unable to crosslink with a chain forming much later in time. Thus, a method of distinguishing a network formed during polymerization from one that is formed after polymerization by vulcanization (e.g. sulphur reacted with rubber) is proposed. This paper will compare various models with the experimental data, and outline how the above conclusion was reached.

## THEORY

The principles of neutron scattering theory as applied to

the solution of polymer problems have been described in a number of papers and review articles[3-15].

The coherent intensity in a SANS experiment is described by the scattering cross-section $d\Sigma/d\Omega$, which is the probability that a neutron will be scattered into a solid angle, $\Omega$, per unit volume of the sample. The quantity $d\Sigma/d\Omega$ expresses the neutron scattering power of a sample and is the counterpart of the Rayleigh ratio, $R(\theta)$, used in light-scattering.

For homopolymer blends consisting of deuterated (labelled) polymer molecules randomly dispersed or dissolved in a protonated polymer matrix, small-angle neutron scattering in the Guinier region arises from the contrast between the labelled (deuterated) and the protonated species. The scattering cross-section can be expressed

$$\left[\frac{d\Sigma}{d\Omega}(K)\right]^{-1} = \frac{1}{C_N M_w}[S(K)]^{-1} \qquad (1)$$

The quantity $M_w$ represents the weight-average molecular weight of the deuterated polymer, and $C_N$ is a calibration constant given by

$$C_N = \frac{(a_H - a_D)^2 N_A \rho (1-X)X}{m_D{}^2} \qquad (2)$$

where $a_H$ and $a_D$ are the scattering lengths of normal (protonated) and deuterated (labelled) monomer structural units, $\rho$ is the density of the polymer, $X$ is the mole fraction of labelled chains, $m_D$ is the mass of the deuterated monomer structural unit and $N_A$ is the Avogadro's number.

The quantity $S(K)$ is the single chain form factor [identical with the $P(\theta)$ function used in light scattering], which describes the conformation of an individual labelled chain. This molecular structure factor becomes independent of particle shape as the angle of scatter $\theta$ approaches zero, and under these limiting conditions (Guinier region $K^2 R_g^2 < 1$) becomes a measure of the radius of gyration, $R_g$.

After rearranging, equation (1) becomes:

$$\left[\frac{d\Sigma}{d\Omega}(K)\right]^{-1} = \frac{1}{C_N M_w}\left(1 + \frac{K^2 R_g^2}{3}\right) \qquad (3)$$

The quantity $K$ equals $4\pi \lambda^{-1} \sin(\theta/2)$, where $\lambda$ is the neutron wavelength and $\theta$ is the angle of scatter. Thus, the Z-average mean square radius of gyration, $R_g^2$, and the polymer molecular weight, $M_w$, may be obtained from the slope and intercept respectively of a Zimm plot of $[d\Sigma/d\Omega]^{-1}$ vs. $K^2$. The values of $M_w$ and $R_g$ were evaluated after appropriate subtraction of the scattering from an unlabelled polymer matrix (blank) from the samples containing different fractions of labelled molecules.

In the above derivation it was assumed that the labelled molecules are fully deuterated. Thus, considering the structural units of the hydrogenated and deuterated polystyrene as $C_8H_8$ and $C_8D_8$, respectively, $a_H = 2.328$ $10^{-12}$ cm, and $a_D = 10.656\ 10^{-12}$ cm. Thus, the difference in scattering lengths between hydrogenated and deuterated monomer repeat units (mers), $(a_H - a_D)$ is $8.328$ $10^{-12}$ cm. Equation (3) is applicable to miscible homopolymer blends in which the molecular size distributions of the labelled and unlabelled polymer molecules are identical. If the size distributions are different, the SANS

scattered intensity contains information of both species, therefore, corrections to the measured values of $R_g$ and $M_w$, are needed. These corrections have been developed by Boué *et al.*[17], and previously used by other authors[14,18].

In the Guinier range, the scattering cross-section under conditions of mismatch in molecular sizes is given by[17]:

$$\left[\frac{d\Sigma}{d\Omega}(K)\right]^{-1} = \frac{1}{C'_N}\left\{\frac{(1-X)}{N_{wD}} + \frac{X}{N_{wH}}\right.$$
$$\left. + \frac{K^2 a^2}{18}\left[\frac{N_{zD}(1-X)}{N_{wD}} + \frac{X N_{zH}}{N_{wH}}\right]\right\}$$

where

$$C'_N = \frac{(a_D - a_H)^2 \rho N_a X(1-X)}{m_D} \qquad (5)$$

and where $a$ represents the length of one mer. The weight average, $N_w$, and the Z-average, $N_z$, degree of polymerization of the labelled (D) and unlabelled (H) polymer chains, are related by:

$$N_{wH} = N_{wD}(1 + \Delta w) \qquad (6)$$

$$N_{zH} = N_{zD}(1 + \Delta Z) \qquad (7)$$

Substituting $N_H$ in terms of $N_D$, $N_z a^2/6$ by $R_g^2$, and $m_D N_{wD}$ by $M_w$, equation (4) becomes:

$$\left[\frac{d\Sigma}{d\Omega}(K)\right]^{-1} = \frac{1}{C_N M_w}\left\{\left[1 - \frac{X\Delta w}{1 + \Delta w}\right] + \frac{K^2 R_g^2}{3}\right.$$
$$\left. \left[1 + \frac{X(\Delta Z - \Delta w)}{1 + \Delta w}\right]\right\} \qquad (8)$$

The correction terms in the square brackets depend on the mismatch in the size distribution. The curve of $[d\Sigma/d\Omega(K)]^{-1}$ vs. $K^2$, yields apparent values of $M_w$ and $R_g^2$. The corrected values may be obtained:

$$M_w = M_{w\ app}\left[1 - \frac{X\Delta w}{1 + \Delta w}\right] \qquad (9)$$

$$R_g^2 = R_{g\ app}^2\left[1 + \frac{X\Delta Z}{1 + (1-X)M_w}\right]^{-1} \qquad (10)$$

It should be pointed out that when the molecular sizes of both species are equal, $\Delta w = \Delta Z = 0$, and equation (8) reduces to equation (3), as expected.

## EXPERIMENTAL

### Synthesis

In the following, the synthesis of the homopolymer PS–DVB networks will be described, including two different methods for inserting a delta fraction of deuterated primary network chains within this network during the polymerization.

*Method A.* This synthesis involves three steps; in each of them a free radical bulk polymerization was performed.

Step I: Polymerization of the first portion, hydrogenated-polystyrene gel. A monomer mixture composed of styrene, benzoin and divinylbenzene was exposed to u.v. light. The initiator concentration was 0.4%

by weight and the crosslinking agent concentration was 1 mole%, both percentages were based on monomer weight. After 12–16 h u.v. exposure the prepolymer was viscous enough to be poured into a mould, its conversion being about 10–15%. Then, the sample was exposed to u.v. light again for approximately 24–30 h in total. The polystyrene network was then sufficiently gelled to be removed from the mould and was dried in a vacuum oven for 24 h at room temperature followed by 48 h at 60°C, to remove remaining unreacted monomer. The final conversion, corresponding to about 60–70% was gravimetrically determined.

Step II: Polymerization of deuterated styrene as the delta fraction. Small samples of the hydrogenated polystyrene networks (60–70% conversion) from step I were swelled with deuterated styrene monomer, divinylbenzene and benzoin mixture to exactly the weight existing before the evaporation of hydrogenated monomer was begun. The swollen gel was placed in a mould and again exposed to u.v. light. After a certain extent of conversion, the polymer gel was again removed from the mould and dried in a vacuum oven. The added conversions ranged from 5 to 20%.

Step III: Polymerization of hydrogenated styrene to complete reaction. The dry network from Step II was reswollen again with protonated styrene, divinylbenzene and benzoin to replace the deuterated monomer removed at the end of the second step. The swollen gel was once more placed in a mould and exposed to u.v. light until completion of the reaction.

The reason for replacing the monomer removed so exactly was to prevent the chain conformation within the already formed material from being disturbed. All the polymerizations were carried out in glass plate moulds with a 1 mm rubbery O-ring, and covered with poly(ethylene terephthalate) (PET) films, to prevent adhesion. The final size of the samples was approximately 1 cm × 1 cm × 1 mm.

*Method B.* This technique is suitable for labelling at the beginning of a polymerization. In a glass vial, deuterated styrene and DVB were polymerized via benzoin and u.v. light. This reaction was stopped before the gel point ($\sim 5$–8% conversion), and the polymer precipitated into methanol. After drying, the branched polydeuterostyrene was dissolved in hydrogenated styrene monomer, DVB and benzoin. The mixture was then poured into the mould and exposed to u.v. light for 36 h. This method permits an exact amount of polydeuterostyrene to be incorporated, and to be characterized before being incorporated into the network. Of course, all samples were also prepared without a deuterated fraction, for purposes of H-PS blank subtractions.

For purposes of molecular weight characterization, polystyrene was also made in the identical fashion as described above, but without any crosslinker.

*Instrumental*

The molecular weights of linear, bulk polystyrene, with its reaction stopped at various levels of conversion were obtained using a Waters Gel Permeation Chromatography instrument calibrated with narrow molecular weight distribution polystyrenes. The intrinsic viscosities were determined on a Ubbelohde-type viscometer using toluene as the solvent. Values of $K = 9.7 \times 10^3$ ml/g and $a = 0.733$ were used for $[\eta] = KM^a$, using toluene at 34°C.

Conversions as a function of time were determined gravimetrically.

The neutron experiments were performed on the 30-m SANS facility[15] at the National Center for Small-Angle Scattering Research (Oak Ridge National Laboratory). The incident neutron radiation had a wavelength of $\lambda = 4.75$ Å, collimated by source slits (1–2 cm diameter) and sample slits (0.5–1.0 cm diameter) separated by a distance of 7.5 m. The area detector ($64 \times 64$ cm$^2$) with 1 cm$^2$ element size was mounted on rails inside a 20 m vacuum flight path and positioned at sample detector distances (SDD) of 16.02 and 18.5 metres.

## RESULTS

*Instantaneous and cumulative molecular weights*

A linear polystyrene was photopolymerized using styrene and benzoin, but no DVB. *Figure 1* shows the extent of conversion, $p$, as a function of polymerization time. At low conversions the rate of polymerization follows a nearly straight line. However, at about 75% conversion, a rate increase is noted which marks the onset of the Tromsdorff effect (see below).

The variation of molecular weight with conversion was followed by g.p.c. *Table 1* shows the data obtained from this experiment. While there is a slow drift upward in both $M_n$ and $M_w$, the molecular weights stay relatively con-
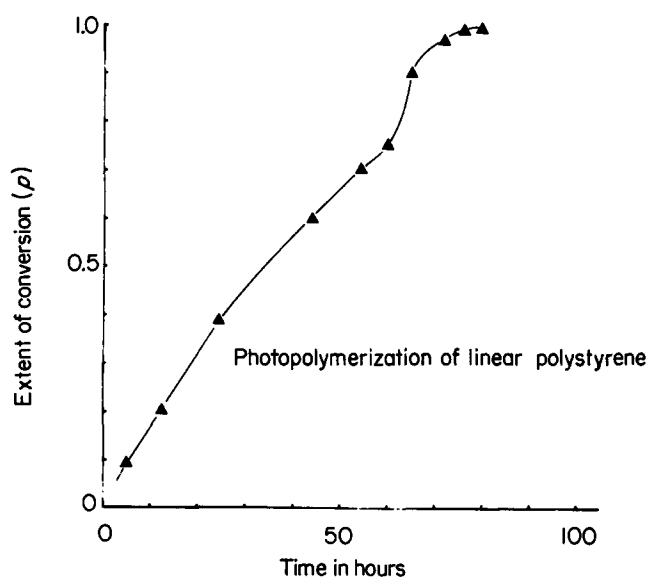


**Figure 1** Kinetics of photopolymerization of polystyrene. Extent of conversion vs. reaction time

**Table 1** Cumulative molecular weights of linear PS by g.p.c.

| Extent of conversion % | $M_n\ 10^{-4}$ (g/mol) | $M_w\ 10^{-4}$ (g/mol) | $D$ ($M_w/M_n$) |
|---|---|---|---|
| 9.51 | 3.9 | 6.1 | 1.57 |
| 20.6 | 3.9 | 6.4 | 1.67 |
| 39.0 | 4.0 | 6.5 | 1.63 |
| 60.0 | 4.1 | 6.5 | 1.61 |
| 70.8 | 4.3 | 7.4 | 1.71 |
| 74.6 | 4.5 | 7.8 | 1.74 |
| 90.7 | 5.5 | 10.0 | 1.85 |
| 96.9 | 5.3 | 19.0 | 3.53 |
| 99.1 | 5.7 | 23.0 | 4.02 |
| 99.3 | 6.6 | 35.0 | 5.24 |

stant until about 75% conversion, above which there is a sharp increase.

*Figure 2* illustrates the variation of the number-average molecular weight, $M_n$, and weight-average molecular weight, $M_w$, with conversion data taken from *Table 1*.

The cumulative average molecular weights were converted to instantaneous weight-average molecular weights, $M_w^p$, by the equation[19,20]:

$$M_w^p = M_w^{0-p} + p\frac{dM_w^{0-p}}{dp} \qquad (11)$$

where $0-p$ is the interval of conversion at which the instantaneous molecular weight was estimated, and $M_w^{0-f}$ being the weight-average molecular weight in that interval. *Figure 2* also shows the variation of $M_w^p$ with conversion.

By examining *Figures 1* and *2* and *Table 1*, it is apparent that early during the polymerization, a relatively slight increase in the molecular weight was occurring. At relatively low conversions, the overall molecular weight distribution is intermediate between two limiting values of $M_w/M_n$: 1.5, expected for a termination by coupling; and 2.0, expected for a termination by disproportionation or

chain transfer or a combination of the two. For free-radical polymerized polystyrene, coupling:disproportionation ratios somewhat higher than 10:1 are common[21]. The dispersion values, $D$ from *Table 1* are in the range of 1.6 up to about 70–75% conversion indicating only modest chain transfer and that 4:1 coupling/disproportionation (or transfer) holds in the present instance. At higher conversions, the dispersion value increases to values greater than five. During this stage, increases in the rate of polymerization:rate of termination ratio that accompany the Trommsdorff effect lead to a large increase in the molecular weight of the polymers being formed as the polymerization proceeds[1].

Since molecular weights in the midrange of composition are of greatest interest for the present study, intrinsic viscosity measurements were also made on two syntheses, 61% and 74% conversion, see *Figure 2*. The cumulative viscosity-average molecular weights, $M_v$, were analysed to obtain the corresponding instantaneous molecular weight between 61 and 74 per cent conversions by assuming for purposes of calculation that $M_v \simeq M_w$ the relationship between $M_w$ and its fractions may be written:

$$M_w = \sum_{i=1}^{\infty} w_i M_i \bigg/ \sum_{i=1}^{\infty} w_i \qquad (12)$$

$$M_w = \sum_{i=1}^{j} w_i M_i + \sum_{i=j}^{k} w_i M_i + \sum_{i=k}^{1} w_i M_i + \ldots \bigg/ \sum_{i=1}^{\infty} w_i \qquad (13)$$

where $w_i$ is the weight fraction of any particular portion having a molecular weight $M_i$. For example, the instantaneous value at 61% conversion represents the entire conversion up to that point.

The main point of these characterization experiments, however, was to provide a basis with which to analyse the molecular weights obtained by neutron scattering.

### SANS measurements

Several samples with delta fractions of deuterated polymer between 2% and 20% were prepared, see *Table 2*. These delta fractions were placed initially in the polymerization, in the upper midrange, and as the final portion.

SANS measurements were made on each of the samples, as well as their appropriate blanks, the latter yielding values of incoherent scattering required for subtraction from the data of the samples of interest.

*Figure 3* illustrates the results of the SANS experiment, on Sample No. 1, which contained 2% of deuterated PS introduced at the beginning of the polymerization, Me-
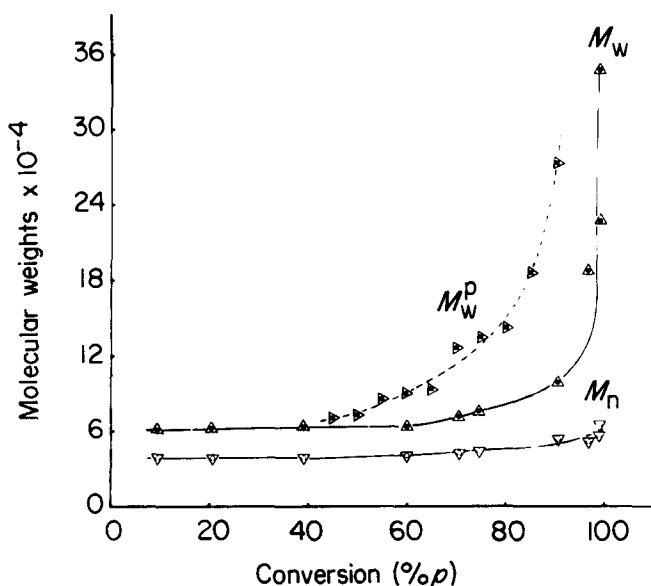


**Figure 2** Variation of molecular weights with conversion. Number-average molecular weight, $M_w$, $\triangledown$; weight-average molecular weight, $M_w$, $\triangle$; instantaneous weight-average molecular weight, $Mp_w$ $\triangleright$

**Table 2** Characterization of polystyrene networks via SANS measurements (values uncorrected for molecular weight mismatches)

| Sample No. | D-PS mole % | Conversion position of delta fraction | $R_g$ [c] (Å) | $M_w$ (g/mol) | Method |
|---|---|---|---|---|---|
| 1 | 2.0 | Initial | 121 | $0.70 \times 10^5$ | B[a] |
| 2 | 20.1 | Final | 350 | $8.0 \times 10^5$ | A[a] |
| 3 | 5.38 | After 75% | 406 | $2.35 \times 10^6$ | A[b] |
| 4 | 10.2 | After 75% | 352 | $1.18 \times 10^6$ | A[b] |
| 5 | 13.9 | After 75% | 337 | $0.85 \times 10^6$ | A[b] |
| 6 | 10.0 | After 60% | 378 | $1.05 \times 10^6$ | A[b] |
| 7 | 13.9 | After 60% | 393 | $0.80 \times 10^6$ | A[b] |

[a] measured at SDD 16.02 metres
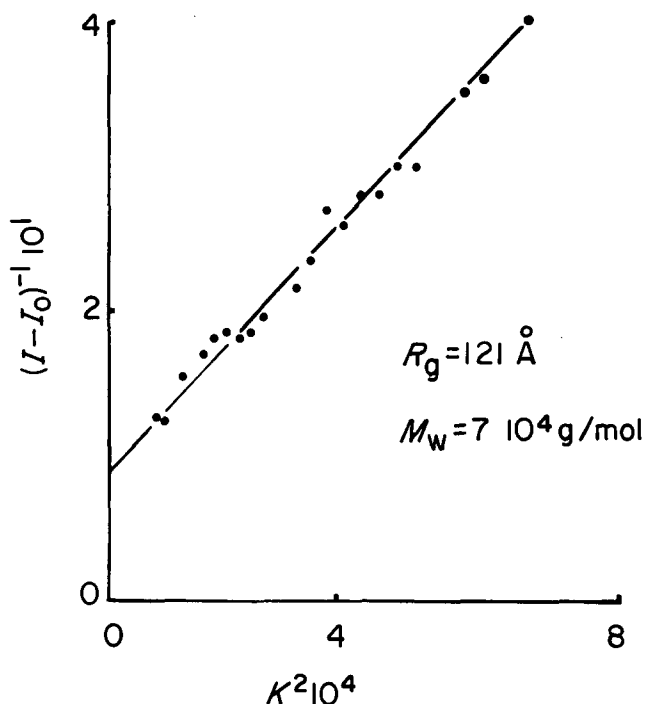[b] measured at SDD 18.5 metres
[c] Z-average data

**Figure 3** Small-angle neutron scattering from Sample 1, method B. Delta fraction is 2% added at the beginning of the polymerization
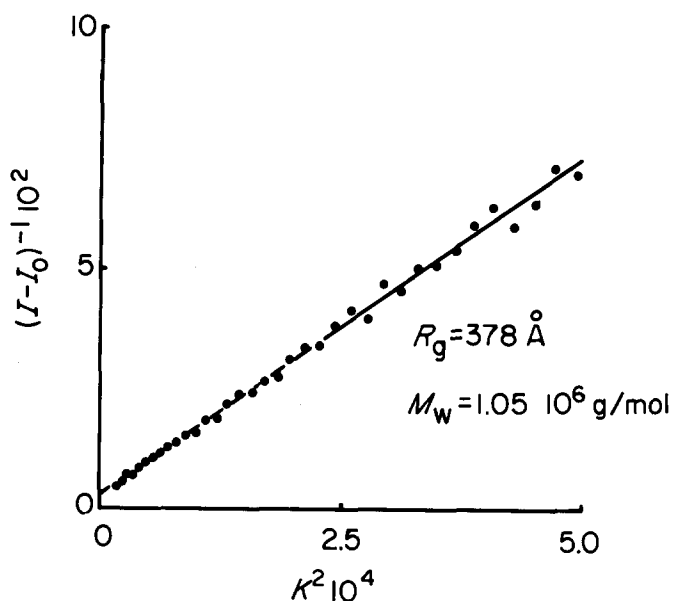


**Figure 4** Small-angle neutron scattering from Sample 6. Delta fraction is 10%, method A after 60% conversion

thod B. Using equation (3), the slope of a plot of $(I - I_0)^{-1}$ [proportional to $(d\Sigma/d\Omega)^{-1}$] vs. $K^2$ yielded the radius of gyration, $R_g$. The intercept, again using equation (3), yielded $M_w$. Values are shown in *Table 2*.

*Figure 4* shows the equivalent data for Sample No. 6, which has a value of $R_g = 378$ Å and $M_w = 1.05 \times 10^6$ g/mole. As a simple experimental finding, the molecular weight of Sample No. 6 is an order of magnitude higher than that of Sample No. 1.

The several values of $R_g$ and $M_w$ determined by SANS for the various delta fractions are shown in *Table 2*. It can be observed immediately that the samples prepared by Method A have molecular weights several times higher than expected from the corresponding values in *Figure 1*.

Interestingly, the molecular weights in *Table 2* increase inversely with the size of the delta fraction.

## DISCUSSION

### Effect of synthetic method

Data in *Figure 2* reveal that the instantaneous weight-average molecular weights of the polystyrene fractions of interest are in the range of 70 000 to over 300 000 g/mole, depending on conversion. By contrast, the SANS results are much higher, strongly suggestive of primary chain aggregation. Viscosity-average molecular weights of $3 \times 10^5$ g/mole obtained for polystyrene synthesized without a crosslinking agent and for a polystyrene–acrylic acid anhydride network after hydrolysis (decrosslinked), were previously observed[22]. This is in good agreement with the present work; indeed, the same basic recipe was used. These results indicate that the original polymerization kinetics were not significantly affected by the presence of the crosslinking agent, except to introduce crosslinks. Thus, the instantaneous molecular weights of the linear polystyrene fractions should be similar to those of the delta fractions synthesized within the network.

It must be pointed out that ordinary, protonated polystyrene and deuterated polystyrene are miscible in all proportions. Using simple blending procedures, Wignall et al.[8] and Cotton et al.[23] both obtained the expected molecular weights and radii of gyration for this system. This data was recently reviewed by Sperling[24].

The present experiments differ from those of Wignall et al.[8] and Cotton et al.[23] by two steps: (1) polymerization of the deuterated fraction *in situ*, and (2) crosslinking simultaneously with polymerization.

As indicated above, these syntheses were similar to those which had been previously physically and mechanically studied in this laboratory. One difference should be noted, however: when a new supply of monomer was added in the three-step preparation of the delta-fraction containing materials, a full supply of initiator was added. The effect of this change, however, should be to lower the molecular weights in the delta fractions, not raise them.

*Table 3* shows the state of aggregation varying from a low of about 1 molecule per aggregate for a delta fraction of 20.0% to a high of 27 molecules per aggregate for a delta fraction of 5.38%. Unexpectedly, the aggregation number varies inversely with delta fraction size. Although a straight line is not obtained, a plot of aggregation number vs. delta fraction size (not shown) yields a rough estimate of about 30–35 polymer molecules per aggregate for an infinitesimal delta fraction. The reason for this dependence is unknown.

Other authors[18,29,30] use the term 'clustering' instead of 'aggregation' to describe anomalously high SANS molecular weights resulting from partial segregation of the labelled linear chains from the hydrogenated linear polymer matrix and the consequent formation of clusters (occurring for example in semicrystalline polymers when the D and H molecules have different melting points which give rise to differential crystallization rates and hence a non-random distribution of molecules. While the results in each case are similar (higher molecular weights than expected), the mechanisms of formation of such molecular entities are different and so is the terminology used.

The aggregation of chains formed during a given

**Table 3** State of aggregation as a function of delta fraction size

| Sample No. | Delta fraction size, % | $M_W 10^{-5}$ SANS[a] | $M_W^p 10^{-5}$ g.p.c.[b] | $N$ Aggregation number | $N$ mismatch corrected |
|---|---|---|---|---|---|
| 2 | 20.1 | 8.0 | 17.0 | (1)[c] | (1) |
| 5 | 13.9 | 8.5 | 2.78 | 3 | 4 |
| 7 | 13.9 | 8.0 | 0.82 | 10 | 11 |
| 4 | 10.2 | 11.8 | 0.98 | 12 | 15 |
| 6 | 10.0 | 10.5 | 0.78 | 13 | 16 |
| 3 | 5.38 | 23.5 | 0.88 | 27 | 34 |

[a] From *Table 2*
[b] From *Table 1* (or *Figure 2*), instantaneous molecular weights
[c] This sample was affected by the Trommsdorff effect, and its molecular weight is known with less certainty than the other samples

**Table 4.** Comparisons of weight-average radii of gyration, $R_g^W$, from $R_g^z$ and $M_W$

| Sample No. | $R_g^W$ From $M_W$[a] | $R_g^W$ From $R_g^z$[b] |
|---|---|---|
| 1 | 73[c] | 101 |
| 2 | 246 | 295 |
| 3 | 421 | 342 |
| 4 | 299 | 296 |
| 5 | 253 | 284 |
| 6 | 282 | 318 |
| 7 | 246 | 330 |

[a] $R_g^W = 0.275 M_W^{0.5}$; data from **Table 2**
[b] $R_g^W = (1.7/2.4)^{0.5} R_g^z$; the ratio 1.7/2.4 originates from the known molecular weight distribution, $M_n : M_W : M_z = 1:1.7:2.4$, see *Table 1*
[c] All values in Angstroms

interval of conversion has long been suspected[25–37], and some data, particularly electron microscopy and mechanical studies, have supported this hypothesis[27,28]. However, quantitative verification has never been made.

There are several possible mechanisms which can possibly explain the data. These will now be explored.

### Ultra high molecular weights

The chains in the delta-fractions might not be aggregated at all, but rather might be of very high molecular weights. This could arise, for instance, if it turned out that the method of synthesis of the delta-fraction-bearing samples and the samples used to characterize the molecular weights (*Table 1*) were indeed significantly different. The only known difference in the synthesis was the addition of somewhat more initiator in preparing the delta-fractions, which should lower the molecular weights rather than raise them. Therefore, this possibility is set aside.

### Chain transfer during network formation

The aggregate might be shaped like a random coil, with one chain picking up where another leaves off. The total effect would be close to one giant Gaussian coil.

This type of aggregate might occur if there were considerable chain transfer in the system with the chains held in place by crosslinks. However, this is not the case. Chain transfer exists as a termination mechanism in the range of 20–40%, based (a) on analysis of the molecular distribution which is in the range of $M_w/M_n = 1.6$–1.7, and (b) on a direct counting of the polymerization efficiency from the known amount of initiator and final number of

chains produced. If all of the initiator is consumed during the reaction, about 1.2–1.3 chains are formed per initiator molecule. For chain transfer to explain the findings, an efficiency in the range of 10–20 would be expected.

### Non-statistical gelation

While the exact 'aggregation' mechanism is unknown, some speculation is warranted. After initial network formation, the density of the polymer chains and/or crosslinks might vary statistically from region to region. Those submicroscopic volumes with lower average polymer density would have, at any instant of time, a higher monomer concentration. Hence, these regions will have a higher than average rate of polymerization, leading to a form of aggregation. The situation is aggravated if the mechanisms of Bobalek *et al.*[26] and Labana *et al.*[34] apply during the actual formation of the gel. This mechanism, which postulates the early formation of microgels floating in a soluble monomer–polymer mix, leads to a decidedly non-random distribution of polymer at the point of gelation.

Hence, the remaining monomer will be non-randomly distributed, and will polymerize in a non-random mode.

Labana *et al.*[37] suggest that crosslinked polymers can polymerize into a 'gel ball' structure, where the gel ball is tightly crosslinked within itself, but only loosely crosslinked to other parts of the network. They point out that under certain polymerization conditions, excessive intramolecular reactions within the gel balls exhausts the amount of available double bonds, causing a deficiency in crosslink density in the regions between the gel balls.

This non-classical mechanism cannot be ruled out on the basis of the present work. Further experiments, now in progress, are designed to evaluate what fraction of the phenomenon, if any, should be assigned to this mechanism.

### Aggregation analysis

Numerical values of $R_g^w$, the weight-average radius of gyration, were estimated from the known molecular weight distribution, and compared with $M_w$ through the relation

$$R_g^w = 0.275 M_w^{0.50} \qquad (14)$$

in *Table 4*. Interestingly, these values are fairly close to one another.

*Table 5* shows the values of $M_w$ and $R_g^w$ after correcting for mismatch in the molecular weights between the labelled polymer and the hydrogenated matrix. When compared with the values of $R_g^z$ and $M_w$ in *Table 2*, the

corrections give rise to increases of 7–10% and 14–22% in $R_g^z$ and $M_w$, respectively.

*Table 6* compares the weight-average radii of gyration $R_g^w$, from mismatch corrected values of $R_g^z$ and $M_w$. It should be noted that all the results in *Table 6* (except for Sample No. 1), are shifted to a larger value by effect of the theoretical corrections.

The two last columns in *Table 6* compare the values of the radii of gyration for the aggregates, $R_g^{agg}$, estimated by using the relation

$$R_g^{agg} = R_g^w N^b \qquad (15)$$

where $R_g^w$ represents the radii of gyration of a primary chain, and $N$ the number of aggregated labelled molecules.

Attention must now be drawn to the approximation inherent in equation (3) caused by the expansion of Debye's equation for $S(K)$ of the random coil[35]. Use of the full equation for $S(K)$ yields a sensitive indication of whether or not the 'aggregate' is really one large random coil. This problem is explored in the Appendix. The conclusion is that the assumption of the random coil does not hold for the aggregated systems.

The values in *Table 6* show that equation (15) with $b$ approximately equal to 0.5 is followed for the aggregates. Interestingly, both the correlation network[29,30] and the random phase[36–39] theories also predict a 0.5 power relationship. The equations in both of these cases, however, were derived to account for the pair interactions among long chain molecules. This is quite different from that of the present experiments, where the chains are chemically bound together. Hence, a quantitative interpretation of the present data will only be possible once a new development in scattering theory of networks becomes available.

The points of contact above statistical are provided by the dangling vinyl groups in the form of chemical crosslinks. Those chains most recently formed by free radical processes will have, on the average, the most dangling vinyl groups available. In the present synthesis, the delta fraction of deuterated material has the greatest probability of being chemically crosslinked to itself.

In *Table 2*, the weight-average molecular weight of Sample No. 1 is listed as 70 000 g/mole and the z-average radius of gyration was found to be 121 Å. This latter is about 30% too high, based on equation (14). A possible

**Table 5** Corrections of $M_w$ (SANS) and $R_g^z$ from mismatch in average degrees of polymerization between the data fraction and the hydrogenated matrix

| Sample No. | $\Delta W^a$ | Correction[b] factor for $R_g^z$ | Correction[c] factor for $M_w$ | $R_g^z$ (Å) corrected | $M_w \times 10^{-5}$ corrected |
|---|---|---|---|---|---|
| 1 | 4.40 | 1.02 | 0.98 | 120 | 0.69 |
| 2 | -0.53 | 0.82 | 1.22 | 387 | 9.76 |
| 3 | -0.84 | 0.78 | 1.28 | 459 | 30.0 |
| 4 | -0.68 | 0.82 | 1.21 | 388 | 14.3 |
| 5 | -0.56 | 0.85 | 1.18 | 366 | 10.0 |
| 6 | -0.64 | 0.85 | 1.17 | 410 | 12.3 |
| 7 | -0.53 | 0.86 | 1.16 | 423 | 9.28 |

[a] $\Delta Z \cong \Delta W = \dfrac{M_{wH}}{M_{wD}} \times \dfrac{m_D}{m_H} - 1$, where $\dfrac{M_D}{m_H} = \dfrac{112}{104}$, the ratio of the mer molecular weights

[b] $1 + \dfrac{X \Delta Z}{1 + (1 - X) \Delta W}$

[c] $1 - \dfrac{X \Delta W}{1 + \Delta W}$

**Table 6** Comparison of weight-average radii of gyration, $R_g^w$, from molecular size mismatch corrected $R_g^z$ and $M_w$

| Sample No. | $R_g^w$ From $M_w^a$ (1) | $R_g^w$ From $R_g^{z\,b}$ (2) | $R_g^{agg} = R_g^{sing} X_N^{b\,d}$ Single chain value from (1) (3) | Single chain value from (2) (4) |
|---|---|---|---|---|
| 1 | 72[c] | 101 | 72 | 101 |
| 2 | 272 | 325 | 72 | 101 |
| 3 | 476 | 386 | 420 | 589 |
| 4 | 328 | 326 | 279 | 391 |
| 5 | 275 | 308 | 144 | 202 |
| 6 | 305 | 345 | 288 | 402 |
| 7 | 265 | 356 | 239 | 335 |

[a] $R_g^w = 0.275 M_w^{0.5}$; data from *Table 5*

[b] $R_g^w = (1.7/2.4)^{0.5} R_g^z$; data from *Table 5*

[c] All values in Angstroms

[d] From the relation $R_g^{agg} = R_g^{sing} N^b$ (using values of $R_g^{sing}$ ($R_g$, single chain) equal to 72 Å and 101 Å; the corrected values of $N$, and a value of $b = 0.50$ within experimental error)
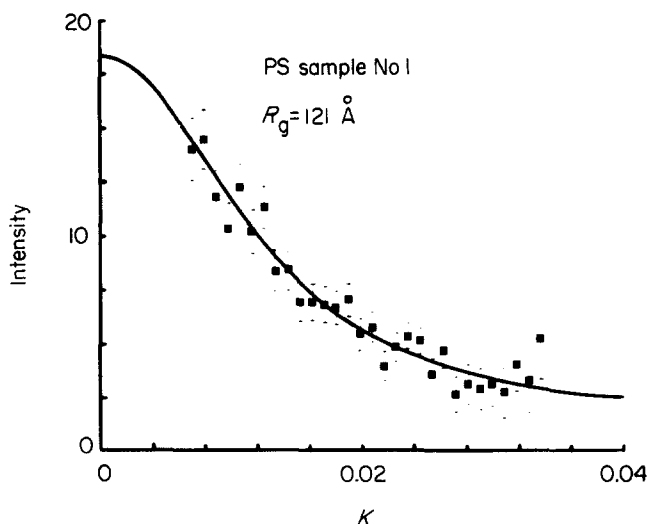
**Figure 5** A Debye plot of scattered intensity *vs. K* for Sample 1, and the theoretical values for a random coil given by equation (16)
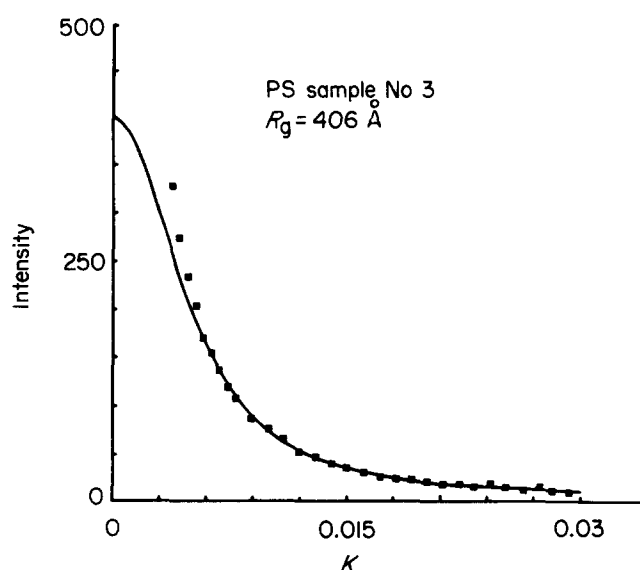


**Figure 6** A Debye plot of scattered intensity *vs. K* for Sample 3, compared with the theoretical values for a random coil given by equation (16). Note the lack of fit below $K = 0.0060$

explanation of the discrepancy is to note that in this case, the polystyrene was dissolved in styrene monomer, which increases its value of $R_g$ because styrene is a good solvent. Subsequent network formation may freeze the chains in the slightly extended conformation. Intrinsic viscosity results in good solvents (similar to styrene) and $\theta$ solvents[31] suggest a value of $\alpha = R_g/R_{g\theta}$ of about 1.15, which can explain about half the difference, and brings the results within experimental error.

Several experiments can be imagined which would lend themselves to obtaining further evidence of the actual aggregation mechanism. One of these is to synthesize a linear delta fraction, rather than a crosslinked one. In that case, the deuterated chains would have (perhaps) less reason to form a correlation network. Other experiments could be based on crosslinking the polymer after formation, rather than during synthesis.

## CONCLUSIONS

Free radical polystyrene chains polymerized in network form are aggregated according to extent of conversion during polymerization. The state of aggregation seems to depend inversely on the size of the delta fraction, aggregation numbers of 1–34 molecules per aggregate being calculated. These aggregates have a size, $R_g$, of 350–400 Å.

The importance of these experiments for future work lies in the development of this new method of characterizing network formation. The present paper, in effect, outlines a quantitative method for estimating the actual crosslinking reaction of instantaneously forming chains with chains synthesized just before vs. chains synthesized much earlier in the polymerization. Thus, this technique offers an opportunity to distinguish the non-random crosslinking reactions of polymers crosslinked during polymerization by multivinyl compounds, vs. polymers crosslinked after polymerization, for example, by vulcanization.

## APPENDIX

As illustrated in the text, the 'aggregated' species fits the general equation $(R_g)_{agg} = 0.275(M_w)_{agg}^{0.5}$, raising some questions as to whether or not the aggregates might really be large molecules. A more sensitive guide as to whether the chains are single structures or aggregates is provided by the Debye form of $S(K)$ for a random coil[35],

$$S(K) = \frac{2}{R_g^4 k^4}\{R_g^2 k^2 - [1 - \exp(-R_g^2 k^2)]\} \qquad (16)$$

Equation (16) was used rather than the Guinier approximation leading to equation (3). The results for Samples 1 and 3 are shown in *Figures 5* and *6*, respectively.

The Debye form of $S(K)$, equation (16), is seen to fit the data of Sample 1 within experimental error. The results for Sample 3 are different, no satisfactory fit below $K = 0.0060$ being obtained. It will be recalled from the text that Sample 1 yielded a molecular weight consistent with g.p.c., while Sample 3 was suspected of being aggregated. From *Figure 6*, it may be concluded that Sample 3 is not a single large molecule, since it is far from being a random coil.

## ACKNOWLEDGEMENT

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