network is given

$$\Delta G_{1e} = \partial \Delta G_e / \partial n_1 \tag{44}$$

where n_1 is the mole fraction of solvent and can be calculated with aid of the substitution

$$v_2^{-1} = 1 + n_1 V_1 \tag{45}$$

where V_1 is the molar volume of the solvent.

$$\frac{\partial \Delta G_e}{\partial n_1} = \rho RT V_1 v_2^{1/3} M_c^{-1} \left[1 - \frac{2}{N} v_2^{-2/3} + \frac{1}{N^2} v_2^{2/3}\right] \times \left[1 - \frac{3}{N} v_2^{-2/3} + \frac{3}{N^2} v_2^{-4/3} - \frac{1}{N^3} v_2^{-2}\right]^{-1} \tag{46}$$

The total free energy of the system is the sum of eq 46 and 40. At equilibrium $\Delta G = 0$, this condition yields the following equation relating v_2, M_c, and N

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + \rho V_1 v_2^{1/3} M_c^{-1} \left[1 + \frac{2}{N} v_2^{-2/3} + \frac{1}{N^2} v_2^{2/3}\right] \times \left[1 - \frac{3}{N} v_2^{-2/3} + \frac{3}{N^2} v_2^{-4/3} - \frac{1}{N^3} v_2^{-2}\right]^{-1} = 0 \tag{47}$$

The deviations from the Gaussian theory can best be seen by expanding in powers of N^{-1}. This task is straightforward yielding

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + \rho V_1 v_2^{1/3} M_c^{-1} + N^{-1} \rho V_1 v_2^{-1/3} M_c^{-1} + O(N^{-2}) = 0 \tag{48}$$

The term proportional to N^{-1} is the first correction to the statistical theory. Further corrections can easily be obtained but are probably unjustified since the Flory–Huggins equation describing the polymer–solvent interactions only contains terms to order N^{-1}. Equation 48 is currently being used to interpret data on coal swelling.[7]

VI. Discussion

The purpose of this paper has been to show that the modified Gaussian model can be used to incorporate non-Gaussian effects into the theory of rubber elasticity in a mathematically tractable way. The modified Gaussian treatment of the freely jointed chain gives a simpler functional form for the chain entropy than the conventional treatment. This allows the calculation of the network entropy analytically to all orders in N^{-1} as in eq 33. The calculations in this paper have followed the approach of the simple statistical theory in which the contributions of individual independent chains are summed. It should be possible to apply the ideas sketched in section II to an entire network. This should avoid the problem of fluctuations and allow a more accurate treatment of the network.

The modified Gaussian model of the wormlike chain has not been considered in this paper because the equation determining the parameter β is trancendental and hence not analytically invertible. This problem might be avoided in an application of the modified technique to the entire network. These problems are being investigated.

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The Intramolecular Scattering Function of Model Branched Polymers

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ABSTRACT: A light-scattering study of the intramolecular scattering function of a regular star-branched and a comb polymer is described. Angular and wavelength dependence of scattering was used to cover a wide range of μ values. The random-coil model for these branched polymers satisfactorily describes the observed scattering functions.

When light is scattered from one macromolecule in dilute solution, different parts of the light beam may have traveled slightly different distances when they hit the light detector. As a result destructive interference can occur, and the intensity of the scattered light will vary depending on the size of the scattering molecule and the magnitude of the scattering vector $|\mathbf{h}|$.

$$|\mathbf{h}| = \frac{4\pi}{\lambda'} \sin\frac{\theta}{2} \tag{1}$$

where λ' is the wavelength in the medium and θ the scattering angle.

At zero scattering angle there is no interference. The variation of the ratio of the scattered light intensity, I, to the extrapolated zero angle scattered light intensity, $I_{\theta=0}$, is called the intramolecular particle scattering function, $P(\mu)$, where $\mu = h^2\langle S^2\rangle_z$ and $\langle S^2\rangle_z$ is the z-average mean-square radius of gyration.

$$P(\mu) = (I/I_{\theta=0})_{c=0} \tag{2}$$

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From the initial slope of the intramolecular scattering function the mean-square radius of gyration of any shape of macromolecule in solution can be obtained since

$$\lim_{\mu \to 0} P(\mu) = 1 - \frac{\mu}{3} \tag{3}$$

The exact form of the intramolecular scattering function over the whole range of μ depends on the shape of the macromolecule. From the matching of the experimental values of $P(\mu)$ with those calculated for a particular shape, e.g., sphere, rod, platelet, or random coil, one can draw conclusions as to the shape of the macromolecule in solution.

For the case of linear monodisperse flexible macromolecules with a random-coil configuration Debye has calculated that the scattering function is given by[1]

$$P(\mu) = \frac{2}{\mu^2}(e^{-\mu} - (1 - \mu)) \tag{4}$$

It took almost 20 years before experimental light-scattering evidence was presented that convincingly showed that eq 4 describes the scattering function with a high degree of accuracy at least under theta conditions and also in good solvents provided values of μ are not too large.[2] The main reason for this time lag between theoretical prediction and experimental verification was the difficulty of obtaining monodisperse linear polymers which have sufficiently high molecular weight and $\langle S^2 \rangle_z$. Indeed, when measurements on polydisperse polymers are made an interference averaged over all sizes present is obtained for each value of μ. From the resulting $P(\mu)$ function no unambiguous conclusions can be drawn with respect to the shape of the macromolecules. Similarly, the intramolecular scattering function will be affected by branching as first shown by Benoit[3] for the case of a regular four-branched star molecule. In general, for a star polymer with p monodisperse branches[4]

$$P(\mu) = \frac{2}{\mu} + \frac{p}{\mu^2}[(p - 3) - 2(p - 2)e^{-\mu/p} + (p - 1)e^{-2\mu/p}] \tag{5}$$

Equation 5 was also derived as the limiting case for a symmetrical comb polymer when λ, the fraction of polymer in the backbone, was set equal to zero.[5] Intramolecular scattering functions for special star polymers were recently calculated.[6]

The most complete theoretical work on the intramolecular scattering functions of comb polymers appeared in 1966.[5] It was preceded by the calculation of the scattering function for a symmetrical comb.[7] In the case of heterogeneous combs, formed by the random incorporation of an average number, f, of monodisperse branches onto a monodisperse backbone, the scattering function is given by

$$P(\mu) = \frac{2}{\mu^2[1 + (1 - \lambda)^2/f]} \Bigg\{ \mu - (1 - e^{-\mu\lambda}) + (1 - e^{-\mu(1-\lambda)/f}) \times \left[f - \frac{2(1 - e^{-\mu\lambda})}{\mu\lambda/f} \right] + (1 - e^{-\mu(1-\lambda)/f})^2 \times \left[\frac{\mu\lambda - (1 - \mathrm{e}^{-\mu\lambda})}{(\mu\lambda/f)^2} \right] \Bigg\} \tag{6}$$

In eq 6 f, μ, and λ are all average values because there is a binomial distribution for the number of branches placed on the backbones. This also causes a distribution around an average molecular weight.[8]

Notice that μ in eq 5 and 6 is defined in terms of $Nb^2/6 = \langle S^2 \rangle_{\text{lin}}$, where N is the total number of segments and b is the segment length. In order to compare polymers with different branching modes on a common basis, the theoretical $P(\mu)$ should be plotted against $g\mu$, so that the tangent at $\mu = 0$ is directly comparable with the experimental radius of gyration in eq 3.

The factor g is the ratio between the mean-square radius of gyration of a branched polymer and of the linear polymer of the same molecular weight.[9] Accordingly,

$$g = \left(\frac{\langle S^2 \rangle_{\text{br}}}{\langle S^2 \rangle_{\text{lin}}} \right)_M \tag{7}$$

This branching factor is calculated from random-walk statistics assuming that the mean-square distance between any two segments i and j of the branched chain is always given by $n_{ij}b^2$, where n_{ij} is the number of segments separating i from j. The same condition underlies also eq 4, 5, and 6. It should be pointed out that eq 4, 5, and 6 are experimentally indistinguishable when $\mu \leq 1.5$. Also, because branched polymers have smaller radii of gyration than linear polymers, their molecular weights have to be higher in order to obtain equally large radii of gyration which permit light-scattering measurements to the same values of μ. In his section on the effect of branching on the particle scattering function Kratochvil remarks:[10] "It is extremely difficult to check the model calculations experimentally, because it is an enormous, if not insoluble, task to synthetize or isolate molecules with a strictly controlled architecture, monodisperse with respect to both molecular weight and structure."

We have shown that it is possible to synthetize narrow molecular-weight distribution regular four-branched and six-branched star polymers and combs[11-14] with uniform branch structure. Recently, better characterized combs became available.[15,16] A detailed investigation of the scattering function of the largest star and comb polymers is presented here.

Experimental Section

Polymer Samples. The linear polystyrene, PS1000f2, was anionically prepared in benzene solution using *sec*-butyllithium as initiator. Under these conditions a narrow molecular-weight distribution polymer is produced. As a precaution, however, 10% of the high and low molecular weight material was removed by fractional precipitation. From the light-scattering experiments to be described its M_w was found to be 1.79×10^6 in cyclohexane and 1.83×10^6 in toluene in good agreement with earlier determinations.[11]

The synthesis of the six-branched star polyisoprene HSPI9AAA involved the coupling of polyisoprenyllithium with 1,2-bis(trichlorosilyl)ethane.[13] The excess polyisoprene branch material was removed by a triple fractionation from benzene–methanol. The first fraction was retained each time. The molecular weight of the reference branch polymer is 2.88×10^5. For the star polymer $M_w = 1.70 \times 10^6$. The ratio of these two molecular weights yields 5.90 for the number of branches.[13] For a six-branched star $g = (3p - 2)/p^2 = 0.444$.[9]

The comb polymer used in this study, C752, is one sample of a series of comb polymers prepared from one monodisperse backbone polystyrene with $M_w = 8.60 \times 10^5$.[15] An anionically prepared branch polystyrene terminated with a COOK group was coupled with the lightly chloromethylated backbone in benzene/acetonitrile (50/50 v/v) using dicyclohexyl-18-crown-6 as catalyst.[16] The branch polystyrene for C752 has $M_n = 9.8 \times 10^4$. The molecular weight of C752 was $3.7_1 \times 10^6$ in toluene and $3.6_2 \times 10^6$ in cyclohexane. From the latter one obtains $\lambda = 0.2376$ and $f = 28.1$ (theoretical, 30). One calculates $g = 0.300_3$ from[5]

$$g = \lambda + \frac{3(1 - \lambda)^2}{f} + \frac{(1 - \lambda)^3}{f^2} \tag{8}$$

Light Scattering. A Fica 50 photogionometer was used over the angular range from 15 to 150° at 35 °C. Vertically polarized light of 366, 436, and 546 nm was used. With the 366- and 436-nm incident light appropriate filters were located in front of the photomultiplier to remove fluorescent light. Greater instrument stability and reproducibility is obtained with the 436-nm light. For the other wavelengths the high voltage to the photomultiplier is close to the allowed limit causing larger fluctuation in the light intensity readings. Repeat measurements were used to reduce the effect of the fluctuation.

The angular alignment of the instrument was daily checked for each wavelength with an all-glass sealed benzene standard and with the

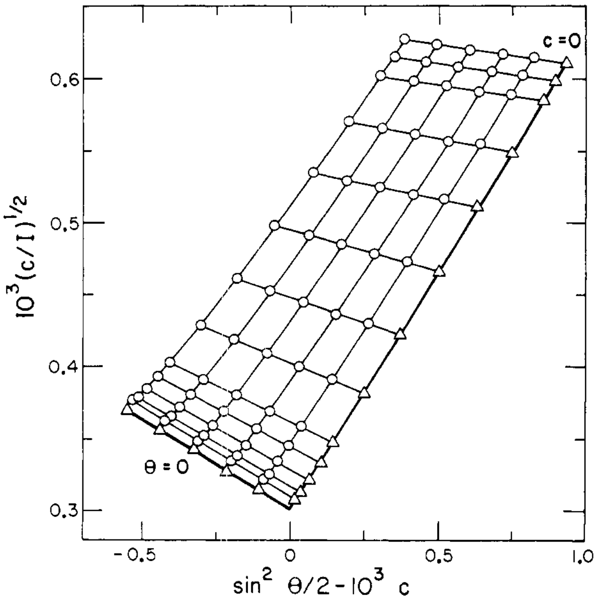

Figure 1. Zimm plot for comb polystyrene C752 in toluene at 35° and 436 nm.

appropriate solvent. Both measurements agreed to about 0.25%. From these benzene and solvent measurements alignment correction factors were calculated that were applied to the polymer solutions. These corrections were usually less than 0.5% between 45 and 150°. They are less than 1.5% at 30° and less than 4% at 15°. The 90° angle scattering from a glass standard was measured before and after the measurements on each polymer solution in order to make a correction for the variation in the intensity of the incident light. Such corrections were usually less than 1% over a whole day.

Cylindrical Pyrex cells of 2.5-cm diameter were used. They were provided with exterior ground-glass stoppers. All cells were checked by filling them with distilled benzene but individual cell corrections proved to be within the instrument specifications (0.25%) and were omitted. Polymer solutions were prepared by weighing using CaH_2 dried and fractionally distilled solvents. The solutions were filtered directly into the cells through 0.2-μm Flotronics silver filters. The quality of the filters varied. Only the best batches eliminated dust satisfactorily.

Data Handling. Experimental reciprocal scattering intensities, c/I, were used to construct Zimm plots for measurement in theta solvents. However, $(c/I)^{1/2}$ was used for good solvent systems because it practically linearizes the concentration dependence of the scattered light. An example of a Zimm plot is given in Figure 1. The infinite dilution values $(c/I)_{c=0}{}^{1/2}$ were then extrapolated to zero angle. The extrapolated value was used to determine the molecular weight of the polymer (only from experiments with 436-nm light). The Rayleigh ratio of benzene at 35° was taken as 50.8×10^{-6}.[17] The refractive index increments for polystyrene in cyclohexane and toluene at 35° are 0.181 and 0.114, respectively. For polyisoprene in cyclohexane it is 0.117.

Next, the infinite dilution values $(c/I)_{c=0}{}^{1/2}$ were squared and $(c/I)_{c=0}$ plotted as a function of $\sin^2 (\theta/2)$. in order to better establish the initial slope of this plot $(c/I)_{c=0}$ values were multiplied by $P(\mu)(1 + (\mu/3))$, where μ contains an estimated value of $\langle S^2\rangle_z$. For $P(\mu)$ the theoretical intramolecular scattering function was used. All $(c/I)_{c=0}\cdot P(\mu)(1 + (\mu/3))$ values will fall on a straight line provided the correct $P(\mu)$ function and $\langle S^2\rangle$ values have been used. Even if the $P(\mu)$ function is not correct a linearization over a wider initial range of $\sin^2 (\theta/2)$ will result and allow a better estimate of $\langle S^2\rangle_z$. Moreover, the $\langle S^2\rangle_z$ value obtained from the initial slope of the linearized plot has to be consistent with the $\langle S^2\rangle$ value chosen to calculate the $P(\mu)(1 + (\mu/3))$ correction factor.[18] In this way, the uncertainty in $\langle S^2\rangle_z$ is reduced to less than 5%. For each polymer–solvent system the best $\langle S^2\rangle_z$ values obtained from each wavelength differed by about 3%. The refractive indices of toluene and cyclohexane at 35° were 1.5304 and 1.4361 (366 nm), 1.5093 and 1.4275 (436 nm), and 1.4922 and 1.4201 (546 nm), respectively.[19]

Results and Discussion

In Figure 2 the experimental intramolecular scattering function for a linear polystyrene is compared with Debye's classical eq 4 derived for a random-coil model. The agreement is satisfactory. The small deviation found at the highest angles for each wavelength may be of instrumental origin.[20]

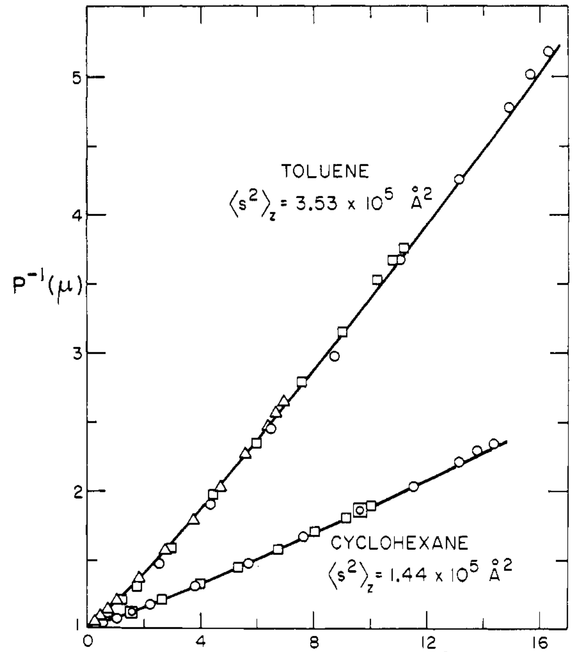

Figure 2. Zero concentration $P^{-1}(\mu)$ for linear polystyrene. The lines are theoretically calculated from eq 4 with the identified radius of gyration. The points are experimental values: (○) data obtained at 366 nm; (□) data at 436 nm; (△) data at 546 nm.

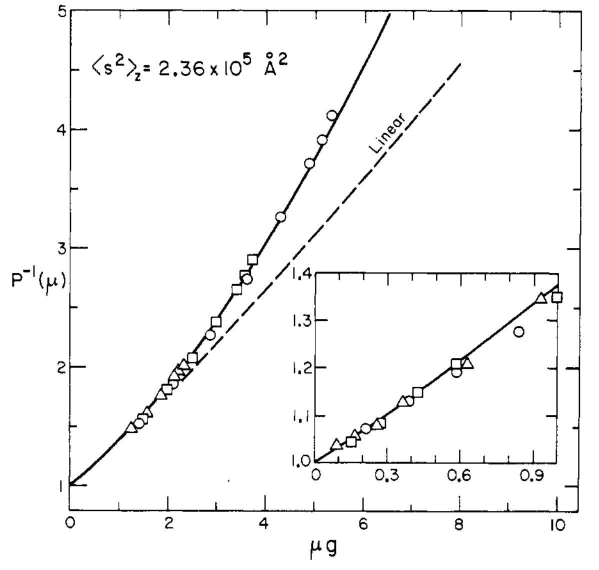

Figure 3. Zero concentration $P^{-1}(\mu)$ function for six-branched polyisoprene in cyclohexane at 35 °C. Line calculated from eq 5. Experimental points as in Figure 2. The insert is an enlargement of the range $0 < \mu g < 1$.

Figure 2 confirms the conclusion drawn from existing experimental evidence that the Debye equation gives a satisfactory description of the intramolecular scattering function under theta conditions.[2,21–24] In good solvents the Debye function was found applicable only when $\mu < 7$[2,23] or when $\mu < 12$.[21,22] The maximum μ value reached in this study is about 9 for PS1000f2 in toluene. Deviations from eq 4 in good solvents at higher μ values have been accounted for by a modification of the mean-square distance between polymer segments with retention of the Gaussian distribution[2,21] or by the introduction of a new segment distribution function which is

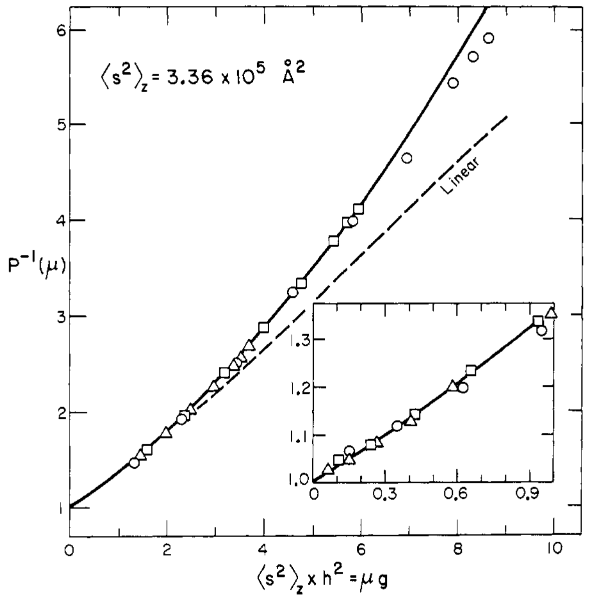

Figure 4. Zero concentration $P^{-1}(\mu)$ function for comb polystyrene C752 in toluene at 35 °C. Line calculated with eq 6. Symbols of experimental points as in Figure 2. The insert shows the range $0 < \mu g < 1$.

derived from Monte-Carlo calculations of self-avoiding walks on three-dimensional lattices.[22,24]

In Figure 3 the experimental intramolecular scattering function for a six-branched polyisoprene in cyclohexane (good solvent) is compared with the theoretical one according to eq 5 with $\langle S^2\rangle_z = 2.36 \times 10^5$ Å^2. The deviation of $P^{-1}(\mu)$ from that of the linear polymer is about 25% and outside experimental error. If one attempts to match the experimental $p^{-1}(\mu)$ values at high μ values to the scattering function for a linear polymer by increasing $\langle S^2\rangle_z$ a serious disagreement between theory and experiment is found at low μ values.

The mean-square radius of gyration of HSPIiAAA in dioxane (theta solvent) is only about 9.0×10^4 Å^2 [13] and the maximum μ value attainable is about 2. At these low μ values the difference between eq 4 and eq 5 is hardly outside the experimental error. When eq 5 is valid for a six-branched star in a good solvent it should a fortiori also apply under theta conditions. Despite the good fit between the experimental and theoretical intramolecular scattering functions, it seems hardly possible to determine the exact number of branches in a star polymer from its scattering function unless one could reach very high μ values. If this is done by using good solvents deviations from the Gaussian distribution of the distances between segments will become important and invalidate eq 5 as is observed in the case of linear polymers. In a mixture of regular stars containing different degrees of branching polydispersity would also complicate the scattering function.[6]

The $P^{-1}(\mu)$ data for the comb polystyrene C752 are shown in Figure 4. The theoretical scattering function requires the knowledge of the average f and λ which have to be determined from the experimental molecular weights of the comb, backbone, and branches. Fortunately, the theoretical scattering function, eq 6, is not very sensitive to small variations in these parameters. The agreement between the experimental and theoretical scattering function is satisfactory except for the highest μ values. These involve measurements with 366-nm light at the highest angles. The deviation is opposite to that observed with PS1000f2 and may therefore be real. To a first approximation the Gaussian distribution of segments describes also the intramolecular scattering function of this comb polymer. Measurement of $P^{-1}(\mu)$ in cyclohexane at 35° (theta solvent) gave $\langle S^2\rangle_z = 1.16 \times 10^5$ Å^2 and a maximum $\mu \approx 1.90$ (436 nm). At this point the difference between eq 6 (comb) and eq 4 (linear) is about 1.5%. Despite this small difference a plot of $(c/I)_{c=0}P(\mu)(1 + (\mu/3))$ vs. $\sin^2(\theta/2)$ yields a slightly better straight line when $P(\mu)$ of the comb polymer is used than with the scattering function for a linear polymer.

For high molecular weight star-branched polymers with 4 and 6 branches the measured radii of gyration in the theta solvent agree with the one calculated assuming random-flight statistics, i.e., $g_{\text{exp}} = g$.[11-13] For comb polymers, however, at the theta temperature:[14,25]

$$(\langle S^2\rangle_{\text{comb}}/\langle S^2\rangle_{\text{lin}})_{\text{exp}} = g_{\text{exp}} > g \qquad (9)$$

For C752 $g_{\text{exp}} = 0.42$ compared to $g = 0.30$ from eq 8. Increased triple contact interactions have been shown to account for this chain expansion.[25] Despite the special configuration that comb polymers take, the Gaussian distribution describes the initial part of the scattering function satisfactorily.

The other combs of the C7 series, which have smaller branches than C752, have smaller radii of gyration and $P^{-1}(\mu)$ measurements to high μ values are not available. Moreover, their λ is closer to 1 and their intramolecular scattering function according to eq 6 approaches that for linear polymers.

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