Determination of Scaling Properties of Randomly Branched Polycyanurates by Combined SEC/LALLS/VISC

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ABSTRACT: Size exclusion chromatography coupled with refractive index, light scattering, and viscosity detectors and viscometry are employed to study the scaling behavior of trifunctional randomly branched polycyanurates. An exponent $\tau = 2.22 \pm 0.02$, which is close to the prediction of three-dimensional percolation theory, was found for the molecular weight distribution $w(M) \sim M^{1-\tau}\, f(M/M^*)$, where $f(M/M^*)$ is a cutoff function and M^* is the cutoff molecular weight. The exponent $a = 0.34 \pm 0.02$ in the relationship $[\eta] \sim M^a$ for *fractionated* polymers gives a fractal dimension $D = 2.24 \pm 0.03$ which agrees well with $D = 2.21 \pm 0.04$ derived from $b = 0.20 \pm 0.03$ in $\langle [\eta] \rangle \sim M_w^b$ for *unfractionated* polymers according to a theory of Daoud, Family, and Jannink. Both values remain within the theoretically predicted limits of $D = 2.5$ for the unswollen state and $D = 2.0$ for the fully swollen state. These findings lead to the conclusion that the polycyanurates with their complex chemical structure when synthesized in bulk can swell only slightly in the good solvent THF. Furthermore, the exponent $c = 0.66 \pm 0.05$ in the relationship $A_2 \sim M_w^{-c}$ for the second virial coefficient was found to satisfy the relationship $a + c = 1$. The resulting constant value of $MA_2/[\eta] = 2.14 \pm 0.06$ for the randomly branched polycyanurates is higher than the value of 1.1 for linear chains, which implies a constant ratio Ψ_b/Φ_b for *fractionated* polymers, whereas the molecular weight dependence $\Psi_b/\Phi_b \sim M_w^{0.14}$ found for *unfractionated* polymers is caused by the differently weighted averages of M, A_2, and $[\eta]$. The physical meaning of the ratio Ψ_b/Φ_b is discussed.

Introduction

Because of the rapid development of equipment and computers, multiple detection in size exclusion chromatography (SEC) has now become a valuable tool for measuring the molecular weight distribution of polymers. In this way, by simultaneous recording of the refractive index (RI) and the intensity of scattered light at a certain small angle (LALLS), the molecular weight distribution of a polymer can be directly calculated without any further calibration with standards by use of the common light scattering (LS) equation[1,2]

$$M = [(Kc/R_\theta) - 2A_2c]^{-1} \tag{1}$$

In this equation K is the common optical contrast factor which contains the refractive index increment dn/dc of the sample, R_θ is the absolute scattering intensity at a certain small scattering angle ($\theta = 6$–$7°$), A_2 is the second virial coefficient, and c is the concentration as measured by the RI detector. The scattering angle of 6–7° chosen in this study is sufficiently small so that the influence of the particle scattering factor can be neglected.

On the other hand, the molecular weight can be obtained from online viscometry (VISC) with the aid of the universal calibration

$$f(v_e) = [\eta]M \tag{2}$$

suggested by Grubisic et al.,[3] where v_e is the elution volume. The calibration curve $f(v_e)$ can be determined with common standard polymers of low polydispersity, e.g., polystyrene with different molecular weights and intrinsic viscosities. The molecular weight of an unknown sample can then be calculated by dividing the known value $f(v_e)$ at a certain elution volume v_e by the intrinsic viscosity, which can be obtained from the recorded specific viscosity $\eta_{sp} = (\eta - \eta_0)/\eta_0$ in combination with the RI signal via

$$\eta_{sp}/c = (\eta - \eta_0)/\eta_0 c = [\eta](1 + k_H[\eta]c) \tag{3}$$

The concentrations of the fractions passing the detector are small enough so that the influence of the concentration-dependent part on the right-hand side of eq 3 can be neglected. (Here, k_H is the Huggins constant.)

The molecular weights and their corresponding intrinsic viscosities can then be used to establish a Kuhn–Mark–Houwink relationship for *fractionated* samples

$$[\eta] = KM^a \tag{4}$$

The constant K and exponent a give valuable information on the structure of the polymer in solution.

From a practical point of view, the precision of the calculated molecular weight distribution and the Kuhn–Mark–Houwink relationship strongly depend on the precision of the universal calibration curve $f(v_e)$. In fact, an examination of the universal calibration curve published by Grubisic et al.[3] reveals typical errors in the range of ±25%. A simultaneous detection of concentration (RI), molecular weight (LALLS), and viscosity (VISC) should therefore improve the accuracy of the calculations, especially for polymers with a broad molecular weight distribution.

In previous papers[4,5] polycyanurates (the polycyclotrimerization products of difunctional aromatic cyanates; see Figure 1) were shown to serve as models for trifunctional randomly branched polymers. Their very broad molecular weight distributions are well suited for applying the SEC/LALLS/VISC technique. In the following we report for this material the scaling behavior of (i) the molecular weight distribution and (ii) the intrinsic viscosity and the second virial coefficient obtained by combined SEC/LALLS/VISC, static light scattering, and viscometry. The exponents demonstrate self-similarity and are used to calculate the fractal dimension in solution of both the whole sample with its broad molecular weight distribution and the fractionated, "uniformly branched" clusters. The results are compared with theoretical predictions.

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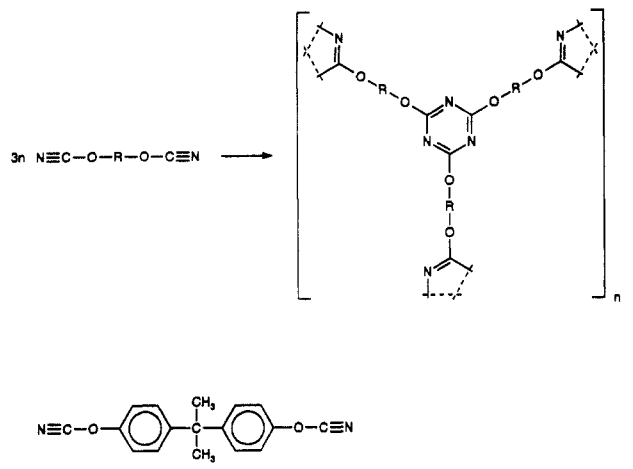

Figure 1. Scheme of the polycyclotrimerization of dicyanates and the structure of the used monomer 2,2-bis(4-cyanatophenyl)-propane (dicyanate of Bisphenol A, DCBA).

Experimental Section

Materials. The dicyanate monomer used for the synthesis of the polycyanurate polymers, 2,2-bis(4-cyanatophenyl)propane (dicyanate of Bisphenol A, DCBA), was synthesized by the cyanobromide method.[6] Resins were prepared in bulk at 463 K in a stirred 100-mL flask which was heated on an oil bath. The reaction was stopped by cooling the flask with liquid nitrogen after reaching a highly viscous state.

Size Exclusion Chromatography. Common PL gel columns (10^4 and 10^6 Å, Polymer Laboratories, Amherst, MA) were chosen for the size exclusion chromatography with tetrahydrofuran (THF) as solvent and eluent in all cases. The fractions were first detected by low-angle light scattering with a Chromatix KMX-6 instrument (Milton and Roy, Germany). This detector was followed by a refractive index detector which recorded the concentration of the fractions. Finally, the viscosity was measured by a capillary viscometer. The RI detector and viscometer were incorporated in a single unit supplied by Knauer Scientific Instruments, Berlin. The applied flow rate was 30 mL/h, the injection volume was 0.1 mL, and the injection concentration was 10 mg/mL. The separation was proved to be independent of the injection concentration down to 1 mg/mL but the signal became unsatisfactorily noisy at low concentrations. The signals from the detectors coupled in series are shifted by small volumes which were calculated from the flow rate and finally calibrated with a standard polystyrene sample. No correction for peak broadening was applied, since this effect is only important for narrowly distributed polymers. Indeed, comparison of the weight fraction distributions from a broad linear PMMA and a PMMA/EGDMA microgel determined by this SEC/LALLS/VISC method with those from dynamic light scattering revealed no significant differences.[10]

Figure 2 shows as an example the traces of the refractive index (RI), scattered light (LALLS), and viscosity (VISC) as a function of the elution volume for a DCBA polycyanurate with $M_w = 4.7 \times 10^6$. From the RI signal the concentrations of the individual fractions at certain elution volumes were calculated with $dn/dc = 0.1854$ in THF at a wavelength of $\lambda = 633$ nm in vacuum. Combination with the LS signal allowed the determination of the molar mass for the fractions according to eq 1. For each sample a second virial coefficient was used which was measured separately by static light scattering.

Viscosity. Viscosity measurements of the unfractionated samples were carried out in THF at 20 °C with an automated Ubbelohde viscometer (Schott). Huggins constants in the range 0.5–0.7 were measured for all samples. By use of these constants in the analysis of the viscosity signal of the SEC traces, the concentration-dependent term in eq 3 was found to be negligibly small. Indeed, the concentrations of the polymer, after separation into fractions, are very small.

Light Scattering. Static light scattering experiments were performed with a computer-driven goniometer equipped with an ALV-3000 structurator/correlator (ALV-Langen, Germany).

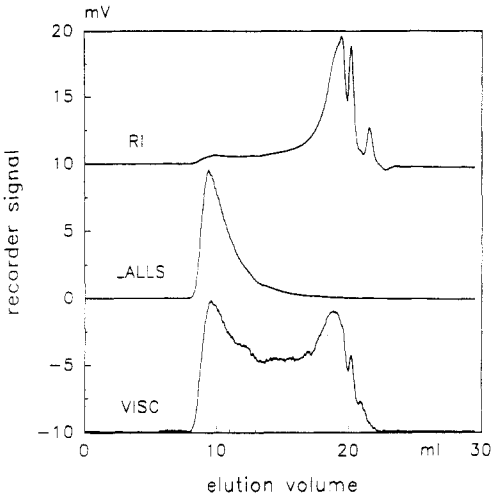

Figure 2. Recorded SEC signals of the refractive index (RI), low-angle laser light scattering (LALLS), and viscosity (VISC) detectors for a polycyanurate with $M_w = 4.7 \times 10^6$ and $[\eta] = 18$ cm³/g.

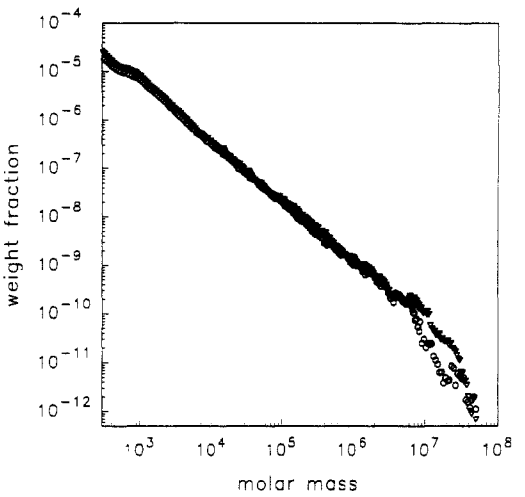

Figure 3. Double-logarithmic plot of the weight fraction molecular weight distribution of polycyanurates with $M_w = 4.7 \times 10^6$ (▽) and $M_w = 4.2 \times 10^5$ (○) as calculated from the RI and LALLS signals.

The red line of a krypton ion laser (Model 2000, Spectra Physics) was used as the light source. The solutions were filtered through 5-μm Millipore filters directly into the LS cells.

Results and Discussion

Molecular Weight Distribution. The molecular weight distributions of two polycyanurate samples with $M_w = 4.7 \times 10^6$ and $M_w = 4.2 \times 10^5$ (measured by static light scattering) are shown in Figure 3 in a double-logarithmic plot. Both distributions agree nearly perfectly with each other over almost the whole range. The linear part extends over more than 3 decades in molecular weight and can be described by a power law

$$w(M) \sim M^{1-\tau} f(M/M^*) \quad \text{with } \tau = 2.22 \pm 0.02 \quad (5)$$

The exponent is very close to $\tau = 2.20$ predicted by three-dimensional percolation theory.[7-9] The cutoff function $f(M/M^*)$ with cutoff molecular weight M^* works at the high molecular weight end of the distribution. Unfortunately, this is also the region where the exclusion volume of the SEC columns interferes significantly. This was shown previously by the authors[10] by comparing the SEC size distribution with that obtained from dynamic light scattering applying an inverse Laplace transformation to

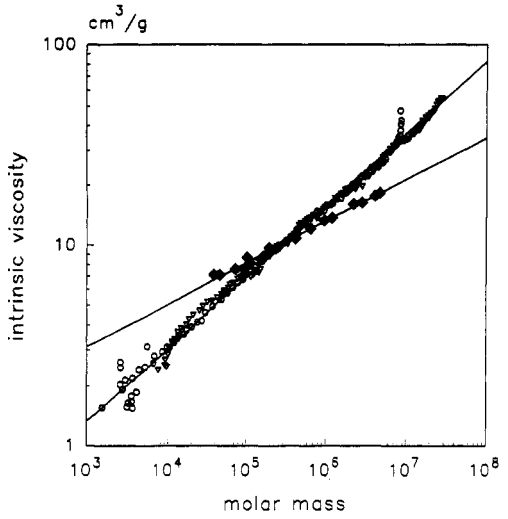

Figure 4. Double-logarithmic plot of intrinsic viscosities versus molar mass for polycyanurates with different mean molecular weights M_w: (♦) unfractionated samples; (○) SEC-fractionated sample with $M_w = 4.7 \times 10^6$; (▽) SEC fractionated sample with $M_w = 4.2 \times 10^5$. The regression lines follow eqs 7 and 8.

the field time correlation function. The values obtained for very high molecular weight are distorted by both the real cutoff of the molecular weight distribution and the separation characteristics of the columns. Therefore, a detailed analysis of the strongly decreasing part of the molecular weight distribution to calculate the cutoff molecular weight was discarded.

In a similar study Schosseler et al.[11] showed that the molecular weight M_{max}, corresponding to the maximum of the LALLS signal (see Figure 2), is proportional to M^* and should scale with M_w as

$$M_w \sim M_{max}^{3-\tau} \tag{6}$$

A previously published[4] analysis of the M_{max} data for polycyanurates over a range of several decades in molecular weight gave $\tau = 2.18 \pm 0.05$, which agrees excellently with the exponent of the molecular weight distribution. Within the limits of experimental error this value coincides with the prediction $\tau = 2.2$ of three-dimensional percolation theory; it does not comply with $\tau = 2.5$ predicted by the Flory–Stockmayer approach.[12-14]

Intrinsic Viscosity. A double-logarithmic plot of the intrinsic viscosities versus the molecular weights of two polycyanurates as obtained by SEC/LALLS/VISC is shown in Figure 4. As expected, both separations yielded the same curves that can be described in their linear part over several decades in molecular weight by a power law relationship

$$[\eta] = K_a M^a \quad \text{with } a = 0.34 \pm 0.02, K_a = 0.12 \pm 0.02 \tag{7}$$

The corresponding dependence on the weight-average molecular weight M_w of the intrinsic viscosity for unfractionated polycyanurate samples is also shown in Figure 4. Regression analysis resulted in a relationship

$$\langle[\eta]\rangle = K_b M_w^b \quad \text{with } b = 0.20 \pm 0.02, K_b = 0.74 \pm 0.12 \tag{8}$$

where the angular brackets denote the weight average of the whole distribution.

If we assume Zimm-type behavior, i.e., strong hydrodynamic interaction, the intrinsic viscosity of the fractionated polymers can be expressed in terms of the radius of gyration R_g through[9,16]

$$[\eta] \sim R_g^d/M \tag{9}$$

where d is the dimension of space. This relationship holds strictly true only for flexible linear chains in the limit of large molar masses and is an intuitive assumption for other molecular architectures. The relationship does not hold for rigid rods. On the other hand, for self-similar objects a mass fractal is defined via[7,9]

$$M \sim R_g^D \tag{10}$$

with an exponent D that defines the fractal dimension. (A system is called self-similar when its description becomes independent of the chosen length scale. Such scaling behavior in turn has its counterpart in power law relationships.[8,15]) Combining eqs 7, 9, and 10, one obtains

$$D = d/(a+1) \tag{11}$$

which for $d = 3$ gives $D = 2.24 \pm 0.03$.

For the exponent b Daoud et al.[16] derived by integration the scaling equation

$$b = (d/D - \tau + 1)/(3 - \tau) \tag{12}$$

or

$$D = d/[(3-\tau)b + \tau - 1] \tag{13}$$

With $b = 0.20 \pm 0.03$ and $d = 3$, one finds $D = 2.21 \pm 0.04$. This value again nicely agrees with $D = 2.24$ found from the fractionated samples and confirms the theory of Daoud et al. Eliminating D/d from eqs 11 and 13, one finds another relationship for τ that is based on exponents for fractionated and unfractionated samples

$$\tau = (2 + a - 3b)/(1 - b) \tag{14}$$

which gives $\tau = 2.18$ with an estimated error of ± 0.035, in good agreement with the values calculated directly from the molecular weight distribution (eq 5) and the maximum of the light scattering curve (eq 6).

In the previous paper[4] we estimated the fractal dimension of the same polycyanurate clusters from the power law relation between the z-average radius of gyration and the weight-average molecular weight

$$M_w \sim \langle R_g^2\rangle_z^{1/2\rho'} = \langle R_g^2\rangle_z^{D(3-\tau)/2} \tag{15}$$

With the experimentally determined exponents $\tau = 2.2$ and $\rho' = 0.52$, we obtained $D = 2.4$, which seems to be at variance with the fractal dimension evaluated from viscosity measurements. However, taking into account the experimental errors for ρ' and τ, with $\tau = 2.18$ and $\rho' = 0.54$ we find from $D = 1/\rho'(3-\tau)$ a value of $D = 2.26$.

In summary, by taking all data obtained from the independent measurements of a, b, τ, and ρ', a fractal dimension of $D = 2.27 \pm 0.09$ is obtained. In no case was a value smaller than 2.18 found. The average value with its band of experimental inaccuracy lies between the theoretical predictions of $D = 2.5$ for the unswollen state and $D = 2.0$ for the fully swollen state and suggests that the polycyanurates with their complex chemical structure can swell only slightly in the good solvent THF after synthesis in bulk.

Second Virial Coefficient. The molecular weight dependence of the second virial coefficient as measured by static light scattering is plotted in Figure 5. A regression

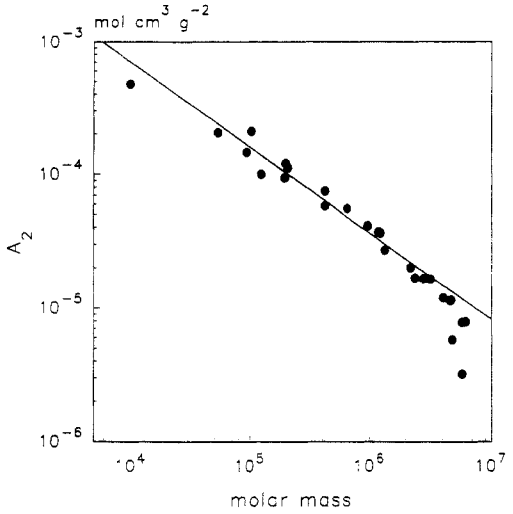

Figure 5. Double-logarithmic plot of the second virial coefficient A_2 versus mean molar mass M_w for polycyanurates as measured by static light scattering. The regression line follows eq 16.

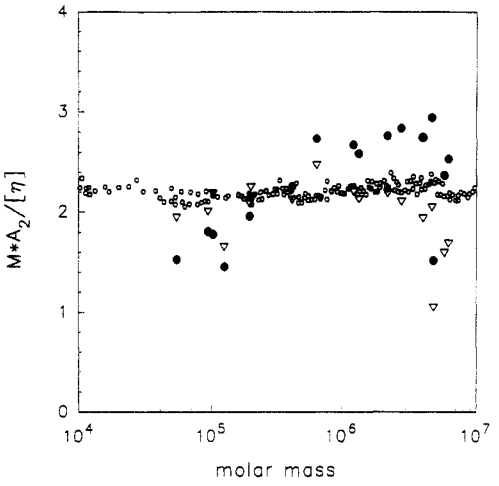

Figure 6. Ratio $MA_2/[\eta]$ as a function of the molar mass for polycyanurates with different mean molecular weights M_w calculated with different combinations of M, A_2, and $[\eta]$: (●) M_w, A_2, and $[\eta]$ for unfractionated samples; (○) M and $[\eta]$ from SEC/LALLS/VISC, A_2 calculated from eq 16; (▽) M and $[\eta]$ from SEC/LALLS/VISC, A_2 from static light scattering of the unfractionated samples.

analysis through the data gives the power law

$$A_2 = K_A M_w^{-c} \quad \text{with } c = 0.66 \pm 0.05,\ K_A = 0.31 \pm 0.14 \quad (16)$$

For $M_w > 3 \times 10^6$ the second virial coefficients seem to decrease faster than for lower molecular weights. The experimental error for these small values of A_2 is very high, but similar behavior was also found for branched epoxies.[26] There may be a reason for this effect which is not yet clear.

We finish the discussion by comparing the molecular weight dependence of the dimensionless ratio $MA_2/[\eta]$ for different combinations of M, A_2, and $[\eta]$. The results are shown in Figure 6. As expected from eqs 7 and 16, the combination of the intrinsic viscosity data for the fractionated samples from SEC/LALLS/VISC with the regression line for the second virial coefficient gives a constant value $MA_2/[\eta] = 2.14 \pm 0.06$ over the whole accessible range of molecular weights. This behavior is, of course, equivalent to the relation $a + c = 1$ of the two power law exponents a for the intrinsic viscosity and c for the second virial coefficient.[27]

On the other hand, the ratio $MA_2/\langle[\eta]\rangle$, where the data of the unfractionated polymers are used for the calculation, increases for increasing molecular weights and, therefore, for increasing polydispersity. This is also reflected by the exponents b and c (eqs 8 and 16), leading to a molecular weight dependence $\Psi_b/\Phi_b \sim M_w^{0.14}$. The sharp decrease for very high molecular weights is due to the very low second virial coefficients with high experimental error as discussed before.[26]

To interpret this result we start with eq 9, valid for nondraining behavior of polymers in dilute solution

$$[\eta] = \Phi_b(R_g^3/M) \quad (17)$$

which has the form of the Fox–Flory relationship but with a prefactor Φ_b for branched systems that differs from the Flory constant Φ for linear polymers.[13] In fact, this prefactor is determined by the hydrodynamic interaction among the segments in a coil[17] and increases with the segment density. In the Debye–Bueche[18] picture this means a reduced solvent penetration through a moving branched core. For the second virial coefficient we may write in a similar manner

$$A_2 = 4\pi^{3/2} N_A (R_g^3/M^2) \Psi_b \quad (18)$$

where N_A is Avogadro's constant and Ψ_b is the segment interpenetration function,[17] which attains a constant value in good solvents. Ψ_b increases with the segment density, as was predicted by theory and shown experimentally.[17,19,23]

Forming the ratio $MA_2/[\eta]$ at the same molecular weight, one obtains

$$MA_2/[\eta] = 4\pi^{3/2} N_A (\Psi_b/\Phi_b) \quad (19)$$

Thus at first sight one may conclude that the ratio of coil–coil penetration Ψ_b and solvent–coil penetration Φ_b remains invariant of the size of the clusters. In fact, such behavior has been predicted and experimentally found for linear flexible chains when the molecular weight exceeded a certain value, e.g., $M_w > 10^5$ for polystyrene. A ratio of 1.1 ± 0.1 was found.[19] In this limit both functions Ψ and Φ have reached their constant values Ψ^* and Φ^*. These limiting values indicate the beginning of self-similarity with regard to geometric and hydrodynamic scaling.

From eq 18 it is clear that MA_2 defines a thermodynamically equivalent sphere volume[17,19] with a radius $R_{th} = [3/4\pi^{1/2}\Psi_b^*]^{1/3} R_g$. In the same way, the quantity $v_{vis} = 4/3\pi N_A[\eta]/\Phi_b^*$ can be regarded as another volume that is required by the macromolecule, but now defined through the intrinsic viscosity. Therefore, $MA_2/[\eta]$ is the ratio of two differently defined volumes of the macromolecule in the solution that can be used in the same manner as the ρ-parameter[24,25] ($\rho = R_g/R_h$) to detect branching.

It is tempting to interpret the present results in a similar manner and the larger value of Ψ_b/Φ_b as a hindered coil–coil penetration that is stronger than the solvent–coil penetration for such branched clusters. This appears sensible since the solvent molecules are small and basically freely moving. However, this suggestive conclusion would only be strictly correct if the dependence of A_2 on M for the *fractions* was identical with that of A_2 on M_w for the *unfractionated* samples.

Unfortunately, the M dependence of A_2 for fractions is difficult to derive by theory, if only the relationship $A_2 = K_A M_w^{-c}$ is known for unfractionated samples. In principle, the desired relationship for A_2 could be established experimentally by using preparative SEC equipment and collecting a number of fractions which then could be characterized. Such treatment, however, induces inevi-

tably new difficulties. In the Introduction we used the rather vague expression "uniformly branched" clusters and meant clusters of a well-defined hydrodynamic volume. This condition, of course, does not imply monodisperse clusters, since slightly branched clusters of molecular weight smaller than the mean M_{mean} can have the same hydrodynamic volume as densely branched molecules with $M > M_{mean}$. Hence, even in an identical system no absolutely uniform clusters can be measured. This situation becomes far more serious when fractions are collected on a preparative scale and then investigated, because in addition, we have to consider fractions with a significant polydispersity also in the hydrodynamic volume, which, of course, could be estimated by analytic SEC again. One day such troublesome experiments will have to be done, but the required equipment is not available to us.

Thus, the final interpretation of the striking invariance of the ratio $MA_2/[\eta]$ has to be left open until more experimental data become available. To our knowledge the present study is the first one on randomly branched systems where a combination of SEC with LALLS, VISC, and RI detectors is used. In spite of the still remaining incertainties, this type of combined experiments gives valuable insight into further details of the structure of individual clusters. It has been common practice in the past to discuss mainly the relationship between exponents, which could be derived from simple scaling arguments taking into account the effect of polydispersity. In fact, prefactors can in principle not be predicted by such arguments. In the last section of this study we measured ratios of prefactors for "uniform" fractions. Whatever "uniform" may mean in detail, we think the derivation of prefactors is a clear step forward in the direction of a better understanding of branched structures.

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