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Association of Amino-Terminated Polystyrenes. 3. Trifunctional Star Polymers

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ABSTRACT: Amino-terminated three-armed polystyrene stars of narrow molecular weight distribution were prepared by anionic polymerization. The association of these star polymers with a low molecular weight dinitrophenol compound was studied by means of light scattering and ultraviolet−visible spectroscopy in the good solvent 1,4-dioxane and in the Θ solvent diethyl malonate. The concentration dependence of the scattered intensity was used to derive the increase in weight average molecular weights of the associates $M_w(c)$ where a correction was applied that allowed the separation of the influence of repulsion forces. The experimental molecular weights were found to be smaller than predicted by the Flory−Stockmayer branching theory. Deviations are stronger for star polymers of low molecular weight, which is explained by intramolecular complex formation. No substantial difference was detected between the association in good and Θ solvents. Gel formation did not occur, and reasons are discussed.

1. Introduction

In this paper we present light scattering (LS) results from an associating star branched polymer system in solution. The motivation for this study is the investigation of structure formation from well-defined macromolecular architectures as unimeric building blocks. These interact via spectroscopically detectable complex formation. In associating systems molecular weight may increase continuously with concentration. Association may lead to the formation of micelles, helical structures, or reversible networks to mention a few examples. The mechanism of complex formation is often complicated, and reproducible characterization of associating products is usually difficult.[1] For these reasons we prepared trifunctional star branched macromolecules of narrow molecular weight distribution with a tertiary amino group at the end of each arm. These polymers show no self-assembling as previously shown for linear monofunctional and telechelic polystyrenes.[2] Association is induced by adding a bifunctional dinitrophenol compound of low molecular weight, as was found by Worsfold.[3] The equilibrium constant of the 1:1 complex and the extent of formed complexes could be determined by ultraviolet−visible (UV−vis) spectroscopy. Association in solutions ranging from dilute to concentrated was investigated by means of light scattering.

Table 1. Molecular Characteristics of Three-Arm Star Polymers and Linear Precursor Polymers TRI1L, TRI2L, and TRI3L

sample	M_w[c]	M_N[d]	M_w/M_N[e]	A_2[f]	R_h[g]	k_D[h]	g_h
TRI1L[a]	9.8	9.5	1.1				
TRI1[a]	31.0	9.7	1.1	5.4	4.3	4.4	
TRI1[a]	29.0			6.3	4.0	5.6	0.954
TRI2L[a]	33.0	30.0	1.07				
TRI2[a]	105.0	32.0	1.1	4.3	8.1	17.3	
TRI2[b]	107.0			4.2	8.1	17.0	0.957
TRI3L[a]	78.0	80.0	1.09				
TRI3[a]	242.0	78.0	1.1	3.2	13.1	41.0	
TRI3[b]	238.0			3.8	13.0	45.0	0.949

[a] In solvent 1,4 dioxane. [b] In toluene. [c] M_w in 10^3 g/mol. [d] M_N number average molecular weight per amino group (arm) from end-group analysis by UV−vis spectroscopy. [e] M_w/M_n from SEC. [f] A_2 in 10^{-4} (mol mL)/g^2. [g] R_h in nm. [h] k_D in mL/g.

2. Experimental Section

Experimental details are given in refs 2, 4, and 5 and references therein. Trifunctional star polymers were prepared by anionic polymerization as follows.[2,4] Polymerization of a linear prepolymer was initiated by [3-(dimethylamino)propyl]lithium. A sample of this prepolymer was removed from the reactor in order to determine the molecular weight distribution of the arm (Table 1). The molecular weight distribution of the linear precursor polymer was examined by size exclusion chromatography[2] (SEC) prior to addition of the linking reagent. The living carbanionic chains were then coupled with tris(allyloxy)-1,3,5-triazine to form three-arm star molecules.[4] The desired star polymers were separated from unreacted linear chains by fractional precipitation.[4]

Static and dynamic light scattering were performed simultaneously by using the ALV 3000 correlator spectrometer system.[6] A model 2020 krypton ion laser ($\lambda = 647.1$ nm) and a model 2020 argon ion laser ($\lambda = 488$ nm and sometimes $\lambda = 496.5$ nm), both from Spectra Physics, were used as light sources. Refractive index increments d*n*/d*c* in 1,4-dioxane, toluene, and diethyl malonate were taken from the literature.[2,7] Diethyl malonate (p.A. grade) and 1,4-dioxane (Uvasol, Merck) were purified over an alumina column (mesh 70−230, basic, activity I, Merck) directly before use. Purity of the solvents was analyzed by UV−vis spectroscopy in order to detect water and other impurities which interfere with the acid−base complex formation. Small amounts of water and basic impurities are readily observed, even by the naked eye, when the hydroquinone derivative itself is dissolved in the solvent. The presence of water and basic impurities leads to complex formation which causes a yellowish color due to the absorption maximum λ_{max} of the complex at $\lambda_{max} = 448$ nm in diethyl malonate (DEM). The absence of other impurities that may disturb complex formation is demonstrated by the occurrence of an isosbestic point at $\lambda = 387$ nm in DEM. Values for absorption maxima in solvent 1,4-dioxane are given in ref 2.

3. Results and Discussion

3.1. Amino-Terminated Three-Arm Stars. Three star branched polymers of different molecular weights were prepared. Tris(allyloxy)-1,3,5-triazine was used as linking agent to form the three-arm star polymers. The triazine derivative is a white crystalline solid which is easy to handle and easy to purify by repeated crystallization from *n*-heptane. In THF solution or in mixtures of THF and hydrocarbons the coupling reaction of the polystyryl carbanions is complete. The

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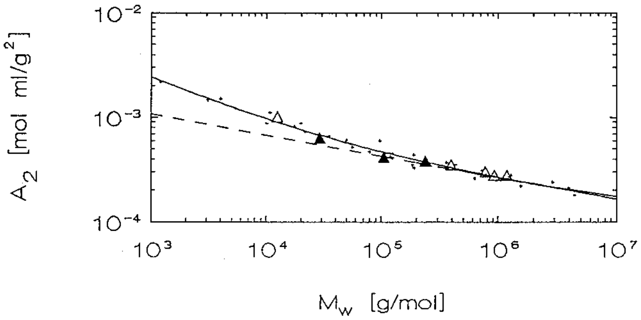

Figure 1. Molecular weight dependence of second virial coefficient A_2 in toluene. Triangles represent three-arm star polystyrenes: (▲) amino-terminated PS; (△) PS stars from refs 14 and 16. The line is a fit to literature data of linear PS in toluene.[2,6,10-13] The dashed line corresponds to[12] $A_2 = 4.36 \times 10^{-3} M_w^{-0.203}$.

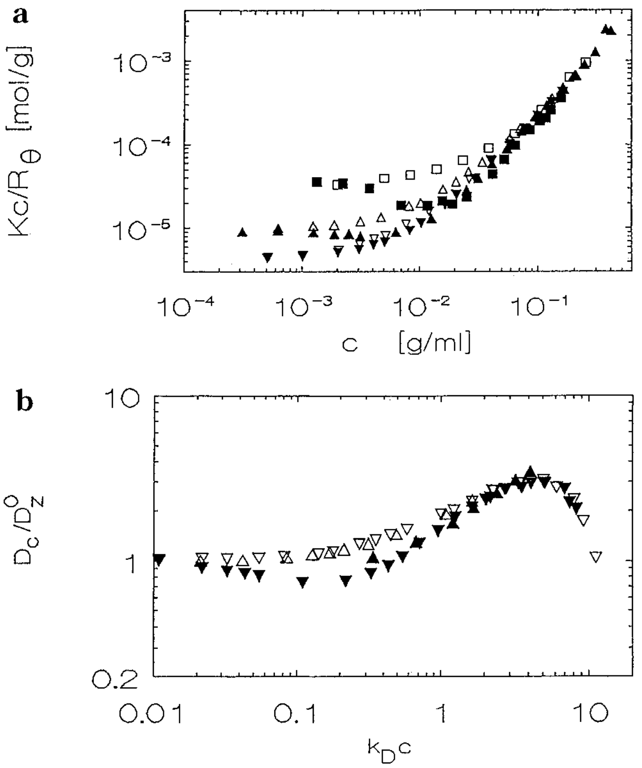

Figure 2. Static (a) and dynamic (b) LS from associating and nonassociating stars: (□) TRI1; (△) TRI2; (▽) TRI3. Filled symbols represent associating solutions with coupler.

formation of a dimer was not observed when a slight excess of carbanionic chains was used.[4] The chlorosilane approach was successfully used in hydrocarbon solvents such as benzene and cyclohexane, but polystyryl carbanions will only form a dimer if the weight average molecular weight M_w of an arm is $M_w \geq 12\,000$ g/mol (ref 16 and references therein). This difficulty can be circumvented when the styryl active center is converted into a dienyl group by adding a small amount of a diene monomer after the styryl prepolymer has been formed. This means purification and handling of an additional (volatile) monomer which can be avoided when the triazine derivative is used. On the other hand the unstable and hygroscopic THF has to be used as solvent in the triazine approach which we considered as less troublesome.

Before the associates were considered, a detailed characterization of the unimeric star molecules was made. The quantities directly obtained by dynamic and static light scattering after extrapolation to zero concentration are the weight average molecular weight M_w, the osmotic second virial coefficient A_2, the *z*-average translational diffusion coefficient $D_z°$, and the k_D parameter which determines the concentration dependence of the diffusion coefficient according to $D_c = D_z°(1 + k_D c)$. A discussion of the radius of gyration is omitted because of the small dimensions and the resulting considerable errors under the experimental conditions. Table 1 lists the molecular characteristics in the good solvents toluene and 1,4-dioxane.

Previously, it was shown for monofunctional and telechelic amino-terminated PS that the presence of this end group does not cause a change in the solution properties when a good solvent is used.[2,5] Figure 1 shows A_2 of the amino-terminated three-arm stars and literature data for untagged three-arm stars. As expected, there is no significant change detectable between amino-terminated and common PS stars. Thus we focus on comparison of star molecules with linear chains. Only dilute solution properties will be reported here. A discussion of semidilute solution behavior was presented elsewhere.[4] A comparison of star molecules with the linear chains of same molecular weight and polydispersity is usually performed in terms of dimensionless ratios g_Q (shrinking factors)

$$g_Q \equiv \frac{Q_{\text{branched}}}{Q_{\text{linear}}} \tag{1}$$

where *Q* is a polymer property. Here we consider g_{A_2} and g_h the ratios based on the osmotic second virial coefficients A_2 and the hydrodynamic radius R_h, respectively. The differences between three-arm stars and linear polymers are not very pronounced, but distinct. Renormalization group (RG) calculations derived $g_{A_2} = 0.968$ and $g_h = 0.957$, independent of molecular weight.[8,9] Figure 1 compares the second virial coefficients of three-arm stars and linear PS in solvent toluene. For the line, which represents linear PS, results from Bantle,[6] Berry,[10] Cowie,[11] Huber,[12] Merkle,[2] and Yamakawa[13] were used. The line merges into the power law behavior of $A_2 = 4.36 \times 10^{-3} M_w^{-0.20}$ [(mol mL)/g^2] for $M_w > 200 \times 10^3$ [g/mol].[12] We calculated the shrinking factor g_{A_2} for the star polymer TRI3 with the highest molecular weight $M_w = 240 \times 10^3$ [g/mol] and found g_{A_2} (TRI3) = 1.08 ± 0.1, which is in agreement with experimental results from three-arm PS stars in the literature[14,16] $g_{A_2} = 1.07 \pm 0.1$. The experimental values are consistently higher than the theoretical prediction[8,15] $g_{A_2} = 0.968$, which was obtained from $g_{A_2} = g_{R_g}{}^{3/2}(\Psi_b{}^*/\Psi_l{}^*)$ with the interpenetration function $\Psi_b{}^* = \{A_2 M_2\}/\{4\pi^{3/2} N_A (R_g{}^2)^{3/2}\} = 0.384$, but the value is still within the limit of experimental errors. Probable reasons for $g_{A_2} > 1$ were discussed previously.[14]

The translational diffusion coefficients of linear PS were found to follow a power law over a wide range of molecular weights[5,12,17] $M_w > 30 \times 10^3$ [g/mol]. This allowed us to calculate the hydrodynamic shrinking factors g_h for all three star polymers in Table 1. These values are in excellent agreement with the semiempirical prediction[8,9] g_h(empirical) = 0.957.

3.2. Association in Good Solvent. All experiments were performed in 1,4-dioxane at $T = 20$ °C. The ratio of amino groups and hydroxyl groups was kept constant at 1:1. Parts a and b of Figure 2 show SLS results after extrapolation to zero scattering angle. The filled symbols denote the concentration dependence of the scattering intensity from the polymer with coupler. The open markers correspond to PS in dioxane. Due to the fairly high equilibrium constant of the acid–base process, the complex is fully dissociated only at very low concentrations. The association develops with increasing concentration and results in a higher scattering intensity and lower diffusion coefficients D_c than for the corresponding nonassociating PS's. A further increase in concentration leads to a decrease in the scattering intensity. This decrease is due to repulsive interactions between the particles which reduces the osmotic compressibility. The effect is more pronounced at the higher molecular weights of the star polymer. The different behavior between the associating and nonassociating chains can be explained as follows. The thermodynamically defined overlapping concentrations $c^* = 1/A_2M_w$ are 62, 22, and 13 g/L for the three samples TRI1, TRI2, and TRI3, respectively. In addition, polymers with lower molecular weights contain a higher molar concentration of amino groups. Thus, according to the acid–base equilibrium, at the same mass concentration the small star exhibits a larger fraction of formed complexes than the stars of higher molecular weights. These two effects, a lower coil overlap concentration and a smaller amino group concentration, are responsible for the diminishing differences between solutions of stars with and without coupler if the molecular weight of the primary star increases. At polymer concentrations of $c > 150$ g/L all the samples merge into the same curve. This is in accordance with the concept of semidilute and concentrated polymer solutions, where the scattering depends only on the total polymer concentration. The solution properties are now governed by the correlation length ξ which determines the mesh size of the transient network. If ξ becomes smaller than R_g it makes no difference whether the stars have different molecular weights or whether large associated clusters are formed. Also in DLS the differences disappear between solutions with coupler and without coupler in the high-concentration regime. The diffusion coefficient in that region becomes solely dependent on the hydrodynamic correlation or screening length $\xi_h \sim \xi$, and the same arguments hold as for the scattering intensity. The time correlation function is nearly single exponential for all concentrations. No slow modes were observed in contrast to literature data of linear PS in 1,4-dioxane.[18] The effect of the coupling reagent is recognized by the different slope (first cumulant) in the TCF in the dilute region or by the difference in the ratio of the slopes in the dilute and semidilute regimes, i.e., R_h/ξ_h.

The molecular weights of the associates at a finite concentration c may be estimated from the static scattering intensity.[2,19,20] In nonassociating systems the scattered intensity can be represented by the following series expansion which is truncated after the third term:

$$\frac{Kc}{R_\Theta} \equiv \frac{1}{M_{\mathrm{app}}} = \frac{1}{M_w}[1 + 2X + 3gX^2] \qquad (2)$$

$$X = A_2 M_w c \qquad (3)$$

$$g = \frac{A_3 M_w}{(A_2 M_w)^2} \qquad (4)$$

The other symbols have their usual meaning. In nonassociating systems the molecular weight is easily obtained by extrapolation to zero concentration. In associating systems, however, the molecular weight, and probably also the structure, changes with concentration. Thus M_w has to be replaced by $M_w(c)$. $M_w(c)$ is the weight average molecular weight of an associate that has formed at a finite concentration c. The second virial coefficient A_2 is molecular weight dependent and follows the power law $A_2 = K_{A_2}M_w^{-aA_2}$. In associating systems this relationship has to be replaced by $A_2(c) = K_{A_2}M_w(c)^{-aA_2}$. $A_2(c)$ is the second virial coefficient of an associate with the corresponding molecular weight $M_w(c)$, which implies that A_2 of an associate with $M_w(c)$ is the same as A_2 of a covalently linked polymer with exactly the same molecular weight and architecture. Adequacy of this assumption was shown in several cases.[2,5,19,20] Inserting these expressions in eq 2 the molecular weight $M_w(c)$ at concentration c can then be extracted from the scattered intensity at each concentration c if the exponent a_{A_2} and the g factor are known. A closed expression could be derived if $g = 0.33$ and $a_{A_2} = 0.5$, but for all other pairs a numerical procedure has to be applied to find $M_w(c)$. Both parameters g and a_{A_2} were found to be sensitive to the polymer architecture.[19–21] The exponent a_{A_2} has been determined from different randomly branched systems and varied between 0.5 and 0.8 and g was found as $g \geq 0.33$.[19,20] The g factor, which connects the third and the second virial coefficient, is in discussion of being not only structure but also molecular weight dependent. In the hard sphere limit $g = 0.625$ and calculations using a Gaussian model[23] (soft spheres) result in $g = 0.257$. Renormalization group calculations predict $g = 0.277$ for linear polymers, independent of molecular weight.[9,22] This result was confirmed by LS experiments of linear PS in toluene; i.e. $g = 0.29 \pm 0.02$ was found to be independent of molecular weight[19] for $1 \times 10^5 < M_w < 7 \times 10^6$ [g/mol]. Recent LS experiments of linear polymers in good solvents suggest a molecular weight dependence of g such that the $0.25 < g < 0.5$ with a minimum at $M_w \approx 10^5$ g/mol.[24–26] Presently, it is not clear what the reason is for this discrepancy in the g factor determination but different evaluation techniques are applied. The M dependence of g was obtained from Bawn plots[27] and requires extreme accuracy of measurements, which is difficult to achieve in particular in a region below c^*. Our technique on the other hand is based on eq 2 and allows a fit[4,19] over the whole concentration range up to $c = 2c^*$. Clearly, this fit is robust and does not sensitively depend on small errors in the dilute regime. In fact the height of the maximum in the rearranged eq 2 depends sensitively on g. We, however, found a very satisfactory mastercurve for molecular weights between 1×10^5 and 7×10^6. Similar behavior was found also for branched systems.[28] Thus for the present treatment we assume g to be independent of molecular weight and only sensitive to the structure of the macromolecules. Figure 3 shows the normalized scattered intensity vs the reduced concentration $X = A_2M_wc$ for different branched systems as well as eq 2 with $g = 0.33$ and $g = 0.6$ as limiting cases which demonstrates the value of $g = 0.6$ as being too large. For the calculation of the molecular weights $M_w(c)$ of the associating star molecules from $1/M_{\mathrm{app}}(c)$ we chose the values with $a_{A_2} = 0.5$, $g = 0.33$ as one limit and $a_{A_2} = 0.5$, $g = 0.6$ as the other. The results are shown in Figure 4 where the normalized molecular weights $M_w(c)/M_w(0)$ are plotted against the concentration of amino groups. $M_w(0)$ is the molecular weight at concentration $c = 0$, i.e. no association, and represents the molecular weight of the nonassociated star molecule.

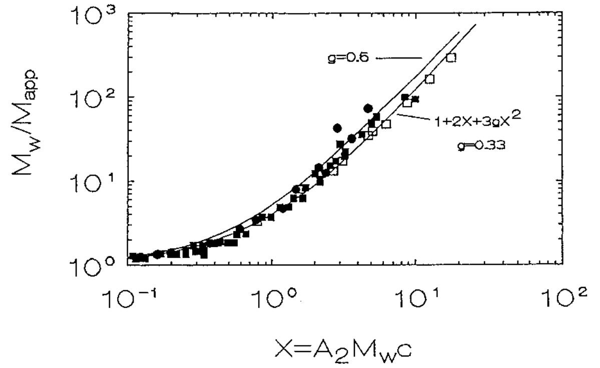

Figure 3. Reduced scattering intensities of three different branched systems with different architectures: (□) cross-linked poly-allylamine;[19,20] (■) randomly branched polycyanurate;[40] (●) starburst polystyrenes.[41] The lines are calculated with eq 2 with $g = 0.6$ (upper curve) and $g = 0.33$ (lower curve), respectively.

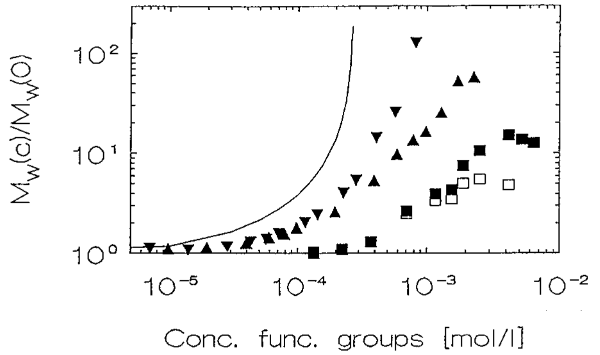

Figure 4. Reduced molecular weights of associates with increasing concentration of functional groups: (■) TRI1; (▲) TRI2; (▼) TRI3 obtained with $g = 0.6$; (□) TRI1 $g = 0.33$. The line is calculated from FS-branching theory with $K_{av} = 30 \times 10^3$ L/mol.

Figure 4 includes the theoretical prediction according to the Flory–Stockmayer (FS) theory.[29–31] For an average equilibrium constant $K_{av} = 30 \times 10^3$ [L/mol], measured by UV–vis spectroscopy,[2] the molecular weight should diverge at $c = 2.74 \times 10^{-4}$ [mol/L]. This is the concentration when the extent of reaction α reaches $\alpha_{crit} = (f_p - 1)^{-1/2} = 0.707$, i.e. the condition for gelation according to Flory and Stockmayer. All experimental curves are shifted to higher concentrations. A possible explanation for this behavior is ring closure, which is more probable for shorter chains.[31,32] Percolation theory takes intramolecular reaction into account. However, this branching and gelation theory can make predictions only on scaling behavior and cannot make predictions of prefactors which determine the gel point.[33] Therefore, we used Flory's mean field assumption[30] of an effective extent of reaction α_{eff} as a crude estimate on the amount of functional groups which are involved in the formation of cyclic structures

$$\alpha_{eff} = \alpha(1 - \alpha_r) \qquad (5)$$

α_{eff} is the extent of reaction which should give the measured molecular weight when Stockmayer's formula is used[31] (no ring formation). α is the fraction of total reacted functional groups which was experimentally determined by UV–vis spectroscopy. $\alpha = N_r/N_0$ with N_r the number of reacted functional groups and N_0 the number of all functional groups in the system. α_r is the overall fraction of reacted functional groups which is involved in intramolecular reactions ($\alpha_r = N_{r,r}/N_r$, where $N_{r,r}$ is the number of reacted functional groups in rings). This treatment does not represent the true physical situation because all functional groups are assumed to have the same probability of ring formation, independent of the different sizes of the cluster which at least for linear chains is definitely not correct. Thus we are aware of the approximate character of our estimation of the amount of cyclic structures. Figure 5 shows the fraction of amino groups reacted in rings $\omega_r = N_{r,r}/N_0 = \alpha\alpha_r$ as a function of polymer mass concentration. These data suggest that ring formation is stronger for star polymers of low molecular weights than for larger ones, which is in accordance with the findings with linear polymers.[32]

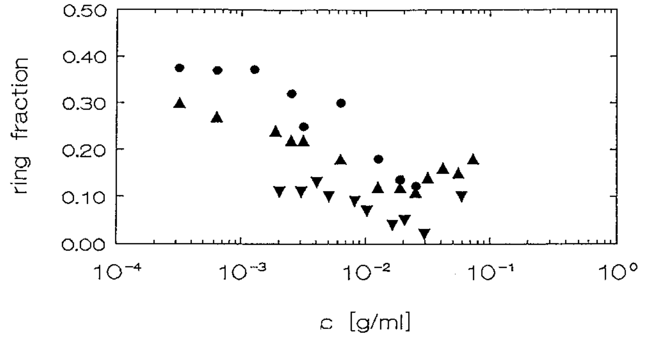

Figure 5. Weight fraction of units which are involved in intramolecular association: (●) bifunctional PS BI2; (▲) TRI2; (▼) TRI3.

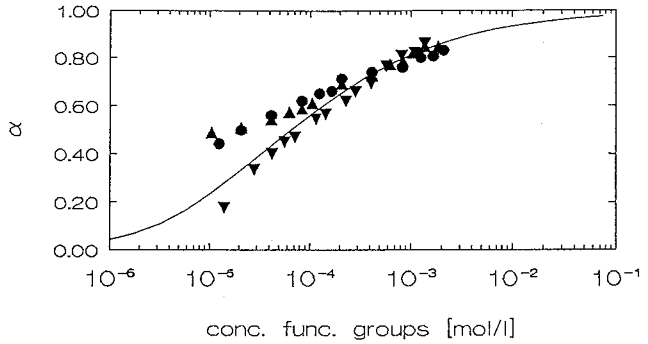

Figure 6. Concentration dependence of the extent of reaction α from UV–vis spectroscopy: (●) bifunctional PS BI2; (▲) TRI2; (▼) TRI3. The line is calculated with equilibrium constant $K_{av} = 30 \times 10^3$ L/mol.

This conclusion is confirmed by the UV–vis data. Figure 6 shows the experimentally determined extent of reaction α as a function of molar concentration of the end groups. The full line is calculated from the law of mass action with an equilibrium constant $K_{av} = 30 \times 10^3$ [L/mol], which was determined by UV–vis spectroscopy for the association of linear PS with the coupler. The two hydroxyl groups of the coupler are not equally reactive but have the values[2] $k_1 = 40 \times 10^3$ [L/mol] and $k_2 = 20 \times 10^3$ [L/mol]. The three amino end groups of the star polymers on the other hand were found to have equal reactivities. The same equilibrium constant $K = 30 \times 10^3$ [L/mol] was determined for solutions of star polymers and monofunctional hydroquinone of different ratios and total concentrations.[2,3] The fact that the extent of reaction of the star polymer TRI2 is higher than predicted by the equilibrium constants can only be explained by intramolecular reaction. The same was found for the association of the telechelic polymers. For comparison the data of the bifunctional PS BI2 with $M_w = 35 \times 10^3$ are included in the figure. It is no surprise that the data points of the telechelic BI2 and three arm star TRI2 collapse. At very low concentrations association of the functional groups within the same macromolecule will be the most probable process. The molecular weight per amino group M_A of BI2 is M_A(BI2) = 17 500, which is just half of that for the star TRI2, M_A(TRI2) = 35 000. According to Jacobson and Stockmayer[32] the ring formation is proportional to $M^{1.5}$, which means a reduction of the ring closure probability by a factor of 0.35 for the star polymer TRI2. This factor cancels out if one considers that there are not two but three amino groups per star molecule.

Ring formation is also concentration dependent. Increasing the concentration results in a higher probability for *inter*molecular reactions which reduces the amount of cycled structures. A behavior like this was observed for the associating telechelic polymers.[2] The same behavior was found also for the stars (see Figures 4 and 5) up to a concentration of 2−3%. Then, however, a steep increase in ring formation occurs. This effect is most pronounced for the smallest star molecule TRI1. The increase in molecular weight $M_w(c)$ with concentration seems to stop at a certain level of association, suggesting the formation of a kind of elementary structure, for instance the formation of microgels with no reactive groups on the periphery.[34] At present we are not able to make more precise comments on the actual size and architecture of these cyclic structures, because all the absolute values of $M_w(c)$ depend on model parameters (g factor, a_{A_2}) used for the evaluation of the molecular weights $M_w(c)$. As seen in Figure 4 the deviations caused by different approximations become important at high concentrations. For this reason we limited the evaluation of $M_w(c)$ to concentrations $c <$ 80 g/L. Although the LS data were sampled over the whole concentration range from dilute through concentrated solutions up to that high concentration, no physical gelation was observed. The system showed viscous flow even at the highest concentrations. A steep increase in ring formation close to the gel point is to be expected, because now the branched cluster has reached such a large dimension that *intra*molecular reactions become far more feasible than reactions between two clusters. Note that because of the branched structure the cluster can only partly interpenetrate, such that for steric reasons a large number of unreacted groups cannot form a complex with a group from another cluster.

On the other hand there are only three reversible bonds per polymer with $\Delta H = -42$ kJ/mol which can open and close. Thus the effect on solution viscosity due to the acid−base complex formation is expected to be weak compared to the major contributions which result from the three-arm star polymers themselves. It has been shown previously by Worsfold[3] that a concentrated solution of monofunctional polystyrenes does not show the 10-fold increase in viscosity as would be expected from the 3.4 power law for a polymer of doubled molecular weight. Recent experiments suggest that for the formation of reversible gels a certain number of neighboring functional groups is necessary which induces a cooperativity.[35]

3.3. Association in Θ Solvent. Diethyl malonate (DEM) is a suitable solvent for both polystyrene and the coupling reagent. DEM is known[36−38] to be a Θ solvent for linear PS at $T = 33 \pm 3$ °C. The Θ temperature for sample TRI2 was determined by SLS ($A_2 = 0$) to $T_\Theta = 40 \pm 0.5$ °C. This high Θ temperature is somewhat unexpected. Branching is known to influence the Θ conditions, but in the opposite direction. Probably the presence of a polar end group in the polymer or undetected impurities in the solvent are responsible for the observed opposite effect.

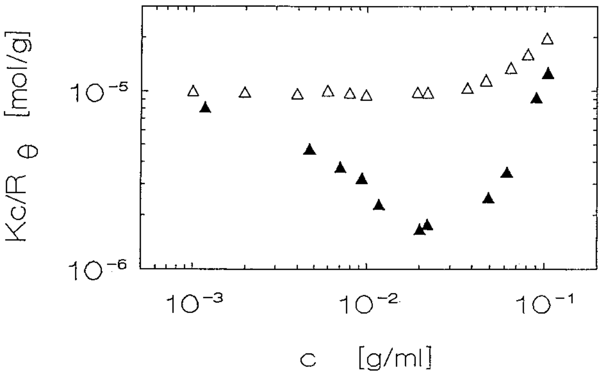

Figure 7. Zero angle SLS from three-arm star TRI2 in DEM at Θ temperature $T = 40$ °C (▲) with and (△) without coupler.

Immediately below $T = 40$ °C, solutions of star TRI2 with the coupling reagent developed phase separation. In contrast, in solutions of the star polymer TRI2 without coupler phase separation was observed at $T <$ 20 °C. Solutions of telechelic polymers ($M_w < 50 \times 10^3$) with coupler which are only able to form linear and cyclic associates of lower molecular weight than associating star polymers were stable over a wide range of concentration and temperature. Thus this phase separation may be preceded by the formation of large clusters and was indeed monitored by static light scattering, as shown in Figure 7. In order to describe the increase of molecular weight with concentration in DEM we assumed that near Θ temperature conditions ($A_2 \approx 0$) are valid also for the probably branched polymer structures which were formed by the association. The apparent molecular weights $M_{app}(c)$ were corrected only for the third virial coefficient A_3 since near Θ conditions $A_2 \approx 0$ were assumed for all concentrations. The third virial coefficient A_3 for linear polystyrenes in cyclohexane at Θ conditions has been found[39] to be $4 \times 10^{-4} < A_3 < 9 \times 10^{-4}$ [(mol mL^2)/g^3] for $20 \times 10^3 < M_w < 3 \times 10^6$ [g/mol]. The authors suggested that this variance in A_3 with molecular weight is within the limits of experimental errors. Here we assumed that for branched systems A_3 is independent of molecular weight. Further we made the approximation that A_3 of the branched associates is the same as that of the three-arm star polymer. For the star polymer TRI2 $A_3 = 3 \times 10^{-4}$ [(mol mL^2)/g^3] was found from Bawn plots[27] and the scattering intensities were corrected with this value. This procedure is quite crude, but the authors are not aware of any data that describe the molecular weight dependence of A_3 for branched polymers. At present even for linear polymers under Θ conditions it is uncertain whether or not A_3 is molecular weight dependent. The result is shown in Figure 8 together with data obtained from experiments in the good solvent 1,4-dioxane. The agreement may be fortuitous but implies that the solvent quality (excluded volume) has a minor effect on the association. This is in contrast to the micelle formation of monofunctional sulfonated polystyrenes which is significantly influenced by solvent quality.[1,19,20] There, the functional groups are crowded together in the core of a micelle, whereas here, the tertiary amino groups are spread out in the available space and do not interact with each other.

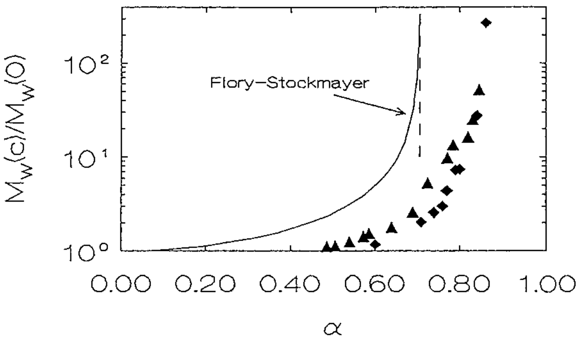

Figure 8. Reduced molecular weights of associates of TRI2 as a function of the extent of reaction α: (▲) in 1,4-dioxane at $T = 20$ °C; (◆) in DEM at $T = 40$ °C. The line represents the FS prediction.

4. Conclusions

As in the case of telechelic linear chains, tertiary amino end groups do not cause a change of the dilute solution behavior of polystyrene stars in the good solvents toluene and 1,4-dioxane.

Ring closure occurs to a considerable extent in the present associating system. As expected, the probability of ring formation for the large molecular weight of the starting three-arm star was found to be smaller than for the low molecular weight. Furthermore, ring formation is more likely for three-arm stars than for telechelic PS of comparable size. The ring formation decreases with growing concentration but increases again when the concentrated solution regime is entered. At very high concentrations the clusters no longer grow. This effect was observed for the smallest star polymer. The same may be true for stars of higher molecular weight, but at concentrations which are too high to estimate the molecular weight $M_w(c)$ properly.

In LS experiments at concentrations $c > 150$ g/L $> c^* = 1/A_2M$ for all polymers only the effects of the transient network are noticeable; i.e. there is no difference between associated and nonassociated three-arm star polymers.

Experiments with the star polymer TRI2 showed that the association process is not affected by the solvent quality as long as the temperature falls not below the Θ temperature of three-arm star TRI2. Shortly below this Θ temperature phase separation occurs for all concentrations of solutions containing the coupling reagent.

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