*Macromolecules* **1996,** *29,* 179−184

# Model Mono-, Di-, and Tri-$\omega$-Functionalized Three-Arm Star Polybutadienes. Association Behavior in Dilute Solution by Dynamic Light Scattering and Viscometry

**Marinos Pitsikalis*,[†] and Nikos Hadjichristidis***

*Department of Chemistry, University of Athens, Panepistimiopolis, Zographou,*
*15771 Athens, Greece, and Institute of Electronic Structure and Laser (FORTH),*
*71110 Heraklion, Crete, Greece*

**Jimmy W. Mays**

*Department of Chemistry, University of Alabama at Birmingham,*
*Birmingham, Alabama 35294*

*Received July 12, 1995; Revised Manuscript Received September 22, 1995*[⊗]

ABSTRACT: The dilute solution properties of three-arm star polybutadienes with one, two, and three dimethylamino or sulfobetaine end groups were studied in tetrahydrofuran (THF) and cyclohexane by dynamic light scattering and viscometry. The polymers were prepared by anionic polymerization techniques using [3-(dimethylamino)propyl]lithium or *sec*-BuLi as initiator and methyltrichlorosilane as linking agent. The dimethylamino groups were converted to highly polar sulfozwitterion groups by reaction with cyclopropanesultone. In the case of the amine-capped polybutadienes, the hydrodynamic behavior in cyclohexane and THF was almost the same, meaning the absence of any appreciable association in cyclohexane. For the zwitterionic polymers, the hydrodynamic, $R_H$, and viscometric radii, $R_v$, in cyclohexane are larger than those for the corresponding amine-capped samples, showing the existence of aggregation. The difference decreases as the number of functional groups increases, which is in agreement with previous static methods results. The micelles formed by the monofunctional species behave hydrodynamically as star polymers with functionality equal to $2N_w$, where $N_w$ is the weight-average degree of association. The $R_v/R_H$ ratio is lower than unity (0.51−0.89), meaning that during the flow in the viscometer there is some disassociation of the aggregates.

## Introduction

Physicochemical properties of ionomers are of ever increasing experimental and theoretical interest. The incorporation of a small amount of ionic groups into a polymer chain changes or improves many of the properties of the resulting materials.[1−4] Their unique behavior results from the fact that ionic groups associate in media of low dielectric constant.[5−9] The specific advantages of ionic interactions have been exploited in a large range of applications including adhesives, lubricants, pharmaceutical and photographic technologies, oil recovery, and magnetic recording and imaging systems.

Two broad classes of ionomers, i.e., random ionomers and telechelic ionomers, can be distinguished. In the first type, a small amount of ionic groups is randomly distributed along the macromolecular chain, whereas in the second type, the polymers have the ionic groups at the chain ends. Although the random ionomers have been extensively studied,[10−13] telechelic ionomers provide the least complicated systems for the correlation between molecular structure and physical properties.[14−17]

A wide variety of methods have been used to produce end-functionalized polymers.[18−22] The development of anionic polymerization offers the most important tool for the synthesis of linear[23−28] and star-shaped[29−31] functionalized polymers with low polydispersity, predicted molecular weights, and controlled placement of the functional groups along the macromolecular chain.

In the literature, many examples of linear telechelic polymers have appeared and their association behavior has been studied.[32] Functionalized star polymers have rarely been used for similar studies, although there are synthetic methods for their preparation. These samples provide the means by which the influence of the different architectures on the association behavior can be studied.

In a previous paper,[33] the synthesis and the association behavior of three-arm polybutadiene stars with one, two, and three dimethylamine or zwitterion end groups were described. Low-angle laser light scattering (LALLS) and membrane osmometry (MO) were used for the study of association in cyclohexane.

In this paper, dynamic light scattering (DLS) and viscosity measurements were performed in order to gain a better understanding on different aspects such as the association process (intermolecular or intramolecular), size, stability, and hydrodynamic behavior of the micelles.

## Experimental Section

Anionic polymerization techniques were used for the preparation of the $\omega$-functionalized polymers under high-vacuum conditions.[34,35] The introduction of the dimethylamine end group was conducted by using [3-(dimethylamino)propyl]lithium as initiator.[36−38] The synthetic procedure followed was similar to that used for the preparation of the $A_2B$ star polymers.[39] In the first step, a benzene solution of the living arm B was added to a large excess of methyltrichlorosilane followed by removal of the excess silane. The chlorosilane-capped arm $CH_3SiBCl_2$ was then reacted with a small excess of a benzene solution of the other arm A, for the preparation of the final product $A_2B$, where A and B are non- or $\omega$-functionalized polybutadienes. More details about the synthesis and the characterization of these narrow molecular weight distribution samples are given elsewhere.[33]

Translational diffusion coefficients were obtained by dynamic light scattering using a Brookhaven BI200SM goni-

---

[†] Present address: Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL 35294.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

0024-9297/96/2229-0179$12.00/0

ometer, a ca. 28 mW Ar$^+$ laser operating at 488 nm, and a BI2030AT correlator with 72 channels. Cyclohexane and THF at 25 ± 0.1 °C were used as the solvents. Correlation functions were analyzed to the second order by the method of cumulants.[40] The measurements were conducted to an angle of 45° for the amine-capped star polymers, whereas for the zwitterion-capped samples measurements were taken at 45, 90, and 135°. For the latter case, a small angular dependence of $\Gamma/q^2$ was observed. Second moments, $\mu_2/\Gamma^2$, were lower than 0.1 for the amine-capped samples, whereas for the corresponding zwitterionic polymers, they were larger than 0.2 in almost all cases.

The translational diffusion coefficients at infinite dilution $D_0$ were obtained from the $D_{\rm app}$ vs $c$ plots with extrapolation to zero concentration using the equation

$$D_{\rm app} = D_0(1 + K_{\rm d}c) \tag{1}$$

where $K_{\rm d}$ is a coefficient given by the equation

$$K_{\rm d} = 2A_2M - K_{\rm f} - u_2 \tag{2}$$

where $A_2$ is the second virial coefficient, $M$ the molecular weight, $K_{\rm f}$ a friction term (the coefficient in the concentration dependence of the friction coefficient), and $u_2$ the partial specific volume of the polymer in the solution.

The diffusion coefficient $D_0$ was used to calculate the hydrodynamic radius by the Stokes–Einstein equation:

$$R_{\rm H} = kT/6\pi\eta_{\rm s}D_0 \tag{3}$$

where $k$ is the Boltzmann constant, $T$ the absolute temperature, and $\eta_{\rm s}$ the solvent viscosity.

A common experimental method for characterizing branching architecture is the $h$ parameter, which is defined as the ratio of the hydrodynamic radius of a branched polymer, $(R_{\rm H})_{\rm br}$, to the hydrodynamic radius of a linear polymer, $(R_{\rm H})_{\rm l}$ having the same molecular weight:

$$h = (R_{\rm H})_{\rm br}/(R_{\rm H})_{\rm l} \tag{4}$$

The $h$ value for three-arm stars is equal to 0.97.[42]

Viscometric data were analyzed using the Huggins equation

$$\eta_{\rm sp}/c = [\eta] + K_{\rm H}[\eta]^2c + ... \tag{5}$$

and the Kraemer equation

$$\ln \eta_{\rm r}/c = [\eta] + K_{\rm K}[\eta]^2c + ... \tag{6}$$

where the relative viscosity $\eta_{\rm r}$ is the ratio of solution to solvent flow times, $\eta_{\rm sp}$ is the specific viscosity ($\eta_{\rm sp} = \eta_{\rm r} - 1$), $[\eta]$ is the intrinsic viscosity, and $K_{\rm H}$ and $K_{\rm K}$ are the Huggins and Kraemer constants, respectively. For the cases where the $K_{\rm H}$ values are higher than 0.5, the two methods fail to give the same $[\eta]$.[41] In these cases, the results from the Huggins plot were used. All the measurements were carried out at 25 °C using Cannon-Ubbelohde dilution viscometers with a Scott-Gerate automatic flow timer. Cyclohexane and THF were used as the solvents with flow times greater than 190 s. The viscometric radius $R_{\rm v}$ was calculated using the equation

$$R_{\rm v} = (3/10\pi N_{\rm A})^{1/3}([\eta]M_{\rm w})^{1/3} \tag{7}$$

where $N_{\rm A}$ is the Avogadro number and $M_{\rm w}$ the weight-average molecular weight.

**Chart 1**

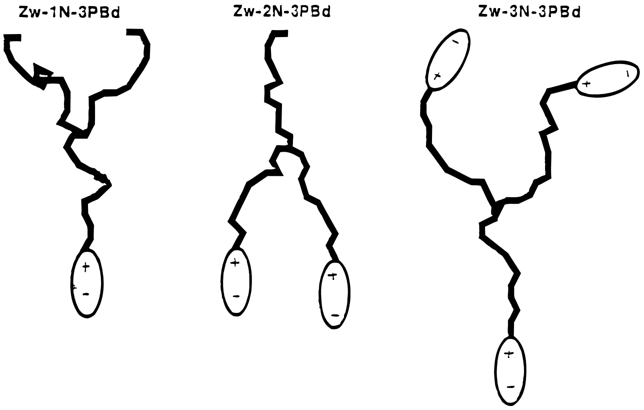

**Table 1. DLS Data for the Amine-Capped Stars in Cyclohexane**

| sample | $M_{\rm w} \times 10^{-3}$ [a] | $D_0 \times 10^7$ (cm$^2$/s) | $K_{\rm d}$ (mL/g) | $R_{\rm H}$ (nm) | $h$ |
|---|---|---|---|---|---|
| 1N-3PBd8 | 25.8 | 5.11 | 12.4 | 4.8 | 0.98 |
| 1N-3PBd15 | 47.9 | 3.51 | 29.8 | 6.9 | 0.97 |
| 1N-3PBd20 | 51.2 | 3.38 | 35.5 | 7.2 | 0.99 |
| 1N-3PBd30 | 111 | 1.99 | 64.9 | 12.2 | 1.07 |
| 1N-3PBd40 | 150 | 1.69 | 99.0 | 14.4 | 1.07 |
| 2N-3PBd8 | 24.4 | 5.52 | 19.0 | 4.4 | 0.93 |
| 2N-3PBd15 | 46.5 | 3.58 | 22.6 | 6.8 | 0.97 |
| 2N-3PBd30 | 62.4 | 2.97 | 37.6 | 8.2 | 1.00 |
| 2N-3PBd40 | 99.0 | 2.19 | 51.4 | 11.1 | 1.04 |
| 3N-3PBd15 | 33.7 | 3.54 | 33.1 | 6.6 | 1.14 |
| 3N-3PBd25 | 67.4 | 2.59 | 55.6 | 9.4 | 1.09 |
| 3N-3PBd40 | 93.1 | 2.25 | 67.2 | 10.8 | 1.05 |

[a] By LALLS in THF.[33]

The ratio of the intrinsic viscosity of a branched polymer, $[\eta]_{\rm br}$, to the intrinsic viscosity of a linear polymer having the same molecular weight, $[\eta]_{\rm l}$, is denoted as g′:

$$g' = [\eta]_{\rm br}/[\eta]_{\rm l} \tag{8}$$

The $g'$ value for three-arm stars is equal to $0.83_3$.[42]

## Results and Discussion

The same three series of polymers with one, two, and three functional end groups were used in this, as in the previous, study.[33] Samples with one dimethylamine group are referred to as 1N-3PBd, where the type (amine) and the number of functional groups (one) and also the number of arms of the star polymers (three) are declared. Using this terminology, 2N-3PBd and 3N-3PBd are samples with two and three dimethylamine end groups, respectively. For the corresponding zwitterion-capped polymers, the symbol Zw is used. The three series are designated as Zw-1N-3PBd, Zw-2N-3PBd, and Zw-3N-3PBd, respectively (Chart 1). The following numbers differentiate samples of the same series.

The presence of the polar dimethylamine group in the initiator increases the 1,2 content from 7–10% for the unfunctionalized to 12–32% for the $\omega$-functionalized arms.

Table 1 summarizes the results obtained by dynamic light scattering for the amine-capped star polymers. $D_0$ values decrease, $R_{\rm H}$ values increase, and $K_{\rm d}$ values increase with increasing molecular weight for each series of samples. It is evident that in most cases the $h$ parameter is greater than 0.97, the corresponding value for three-arm stars. This behavior can be attributed to different reasons: (a) Dynamic light scattering is very sensitive to aggregation, and consequently

**Table 2. DLS Data for Amine-Capped Stars in THF**

| | | cyclohexane | | THF | |
|---|---|---|---|---|---|
| sample | $M_w \times 10^{-3}$ [a] | $R_H$ (nm) | $K_d$ (mL/g) | $R_H$ (nm) | $K_d$ (mL/g) |
| 1N-3PBd30 | 111 | 12.2 | 64.8 | 12.6 | 52.6 |
| 1N-3PBd40 | 150 | 14.4 | 99.0 | 14.6 | 85.4 |
| 2N-3PBd40 | 99.0 | 11.1 | 51.4 | 11.5 | 39.2 |
| 3N-3PBd40 | 93.1 | 10.8 | 62.7 | 11.4 | 48.2 |

[a] By LALLS in THF.[33]

**Table 3. DLS Data for the Zwitterion-Capped Stars in Cyclohexane**

| sample | $D_o \times 10^7$ (cm$^2$/s) | $K_d$ (mL/g) | $R_H$ (nm) | $N_w$[a] |
|---|---|---|---|---|
| Zw-1N-3PBd8 | 1.71 | −17.9 | 15.3 | 9.0 |
| Zw-1N-3PBd15 | 1.06 | 11.7 | 22.8 | 9.2 |
| Zw-1N-3PBd20 | 1.45 | 20.7 | 17.4 | 4.1 |
| Zw-1N-3PBd30 | 0.88 | 95.8 | 27.7 | 2.5 |
| Zw-1N-3PBd40 | 0.90 | 18.1 | 27.0 | 1.5 |
| Zw-2N-3PBd8 | 1.44 | 26.3 | 16.9 | 15.2 |
| Zw-2N-3PBd15 | 1.10 | 66.4 | 22.0 | 3.7 |
| Zw-2N-3PBd30 | 0.91 | 68.9 | 26.7 | 2.8 |
| Zw-2N-3PBd40 | 1.53 | −11.8 | 15.8 | 1.4 |
| Zw-3N-3PBd25 | 2.22 | −109 | 11.0 | 1.4 |
| Zw-3N-3PBd40 | 1.61 | −269 | 15.1 | 1.9 |

[a] Weight-average degree of association,[33] $N_w = (M_w)_{Zw}/(M_w)_N$.

the above-mentioned results can be seen as evidence of weak association, raised by the tertiary amine groups. (b) For the calculation of the *h* parameters, results from linear polybutadienes possessing low vinyl content (8–10%) were used. Detailed information about polymers having different microstructures is not available in the literature. Nevertheless it is known that dimensions decrease with increasing vinyl content. It is evident that in the case of the three-arm stars with three functional end groups, the influence of the different microstructure is more pronounced. In order to confirm the conclusion that only weak association is promoted by the dimethylamine groups, the $R_H$ values of the higher molecular weight stars were measured in THF. The results, reported in Table 2, show that in THF the dimensions are slightly larger than in cyclohexane. The difference is in the frame of the experimental error but is systematic and can be attributed to the fact that THF is a better solvent than cyclohexane for polybutadiene.[43] These results are in agreement with the LALLS measurements,[33] where the second virial coefficients were lower for cyclohexane than for THF.

For the zwitterion-capped samples, an angular dependence of the $\Gamma/q^2$ values is expected, due to their increased size compared to their precursors. The lower angle of observation, the lower the $\Gamma/q^2$ value. This angular dependence is very small for the lower molecular weight samples and slightly larger for those with the higher molecular weights and reflects the polydispersity in size of the micelles, which is in agreement with the molecular weight polydispersity found by LALLS and MO. A similar conclusion can be drawn by the increased values for $\mu_2/\Gamma^2$ (>0.2). The correlation function shows a deviation from a single-exponential decay but the appearance of two or more exponential decays was never obtained. Although this behavior is not a direct proof, it is consistent with the existence of aggregates with different aggregation numbers in dynamic equilibrium.[44]

The DLS results are presented in Table 3, whereas representative plots for the zwitterion-capped and their amine-capped precursors are given in Figures 1 and 2.

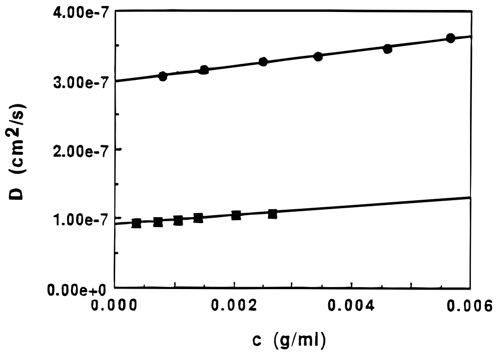

**Figure 1.** Diffusion coefficient versus concentration plots for samples 2N-3PBd30 (●) and Zw-2N-3PBd30 (■) in cyclohexane at 25 °C.

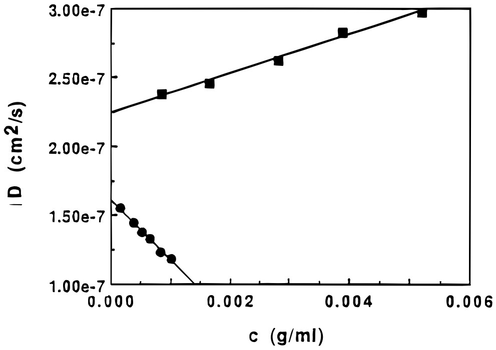

**Figure 2.** Diffusion coefficient versus concentration plots for samples 3N-3PBd40 (■) and Zw-3N-3PB40 (●) in cyclohexane at 25 °C.

The dimensions of the micelles are increased compared with their parent molecules. The $K_d$ values exhibit no regular trend with respect to the molecular weight of the precursor or the aggregates. In some cases, the $K_d$ values are negative, as a consequence of the decreased second virial coefficients (eq 2), due to the association process. Similar results were obtained in other associating systems.[45–46]

Sample Zw-3N-3PBd15, even at the concentration of $8 \times 10^{-4}$ g/mL, forms gel, being impossible to conduct dilute solution measurements on. The samples with three zwitterion end groups present the smaller increase in their dimensions, due to their low degrees of association, whereas their $K_d$ values are strongly negative. This behavior indicates that even though the $N_w$ values (Table 3) are small, the hydrodynamic interactions between the macromolecular chains are very strong and can be seen as evidence of intramolecular association in dilute solution. The above analysis is not straightforward for the samples with two zwitterion groups. In the concentration range used for the measurements, it is clear that intermolecular association does appear, but the possibility for the existence of intramolecular association cannot be ruled out. Apparently, it is easier to find evidence of intramolecular association for samples with higher molecular weights and lower $N_w$ values. The study of these systems is complicated, and quantitative evaluations are not readily made.

In star polymers it is known that the ratio of the viscometric radius of the star $(R_v)_{star}$ to the viscometric radius of the arm $(R_v)_{arm}$ depends only on the functionality of the star.[47] These ratios are the same for polystyrene, polyisoprene, and polybutadiene stars with the same number of arms. In addition, it is well known that $R_v/R_H$ is close to unity[48–50] and so it can be concluded that the ratio $(R_H)_{star}/(R_H)_{arm}$ should have the

**Table 4. Degrees of Association from DLS for the Zw-1N-3PBd Samples**

| sample | $(R_H)_{Zw}/(R_H)_N$ | $N_{DLS}$ | $N_w{}^a$ |
|---|---|---|---|
| Zw-1N-3PBd8 | 3.19 | 16.5 | 9.0 |
| Zw-1N-3PBd15 | 3.30 | 18.5 | 9.2 |
| Zw-1N-3PBd20 | 2.42 | 6.7 | 4.1 |
| Zw-1N-3PBd30 | 2.27 | 5.4 | 2.5 |
| Zw-1N-3PBd40 | 1.88 | 2.9 | 1.5 |

[a] Weight-average degree of association.[33]

**Table 5. Viscometry of the Amine-Capped Stars in Cyclohexane**

| sample | $[\eta]$ (dL g$^{-1}$) | $K_H$ | $R_v$ (nm) | $R_v/R_H$ | $g'$ |
|---|---|---|---|---|---|
| 1N-3PBd8 | 0.371 | 0.43 | 5.3 | 1.10 | 0.83 |
| 1N-3PBd15 | 0.546 | 0.41 | 7.4 | 1.07 | 0.80 |
| 1N-3PBd20 | 0.599 | 0.41 | 7.8 | 1.08 | 0.85 |
| 1N-3PBd30 | 0.987 | 0.63 | 12.0 | 0.98 | 0.80 |
| 1N-3PBd40 | 1.20 | 0.64 | 14.2 | 0.99 | 0.79 |
| 2N-3PBd8 | 0.348 | 0.34 | 5.0 | 1.14 | 0.86 |
| 2N-3PBd15 | 0.557 | 0.42 | 7.4 | 1.09 | 0.83 |
| 2N-3PBd30 | 0.751 | 0.43 | 9.0 | 1.10 | 0.88 |
| 2N-3PBd40 | 0.989 | 0.58 | 11.6 | 1.04 | 0.87 |
| 3N-3PBd15 | 0.491 | 0.48 | 6.4 | 0.97 | 0.91 |
| 3N-3PBd25 | 0.777 | 0.41 | 9.4 | 1.00 | 0.89 |
| 3N-3PBd40 | 0.969 | 0.41 | 11.3 | 1.05 | 0.89 |

same behavior as the corresponding ratio of the viscometric radii. Considering that the aggregates correspond to star polymers and their precursors to the arms of these stars and using the reported data for the $(R_v)_{star}/(R_v)_{arm}$ ratios for stars with different functionalities, it was possible to calculate the degree of association from dynamic light scattering measurements ($N_{DLS}$). This analysis is valid only in the case of the monofunctional polymers, where there is no possibility of intramolecular association. The results, given in Table 4, show that the $N_{DLS}$ values are almost double those from the $N_w$ values. The conclusions drawn from this analysis are the following: (i) The aggregates formed from the monofunctional star polymers behave hydrodynamically as star polymers with functionality equal to $2N_w$. For example, when the degree of association is equal to 2 ($N_w = 2$), the aggregate behaves as a four-arm star. The zwitterion groups form a polar core with the macromolecular chains anchored at the periphery of this core. It seems that the two unfunctionalized arms of the precursors are responsible for the overall size of the micelles. (ii) Almost the same aggregation behavior was evidenced by LALLS and DLS. So it appears that the aggregates are stable during the DLS measurements and that their lifetime is comparable to the characteristic time of the experiments, $(Dq^2)^{-1} \sim 10^{-3}$ s.

More information about the association process can be extracted from viscosity measurements. The results concerning solutions of the amine polymers in cyclohexane are reported in Table 5. It is evident that by increasing the number of functional groups, the vinyl content and the $g'$ are increasing. This behavior can be attributed to reasons already mentioned for the $h$ parameter and confirms the conclusions drawn from the dynamic light scattering data. Representative diagrams are given in Figure 3. The viscometric radii, calculated from $[\eta]$ and $M_w$ measured in THF by LALLS are in good agreement with the hydrodynamic radii from DLS experiments.

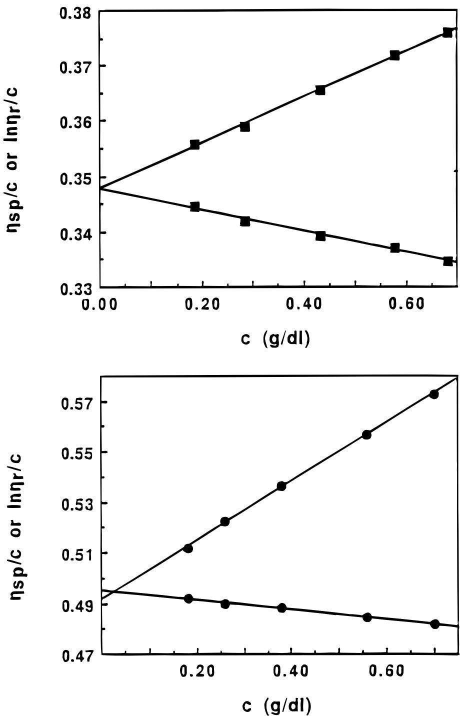

**Figure 3.** $\eta_{sp}/c$ or $\ln \eta_r/c$ vs $c$ for samples 2N-3PBd8 (■) and 3N-3PBd15 (●) in cyclohexane at 25 °C.

**Table 6. Viscometry Results for the Amine-Capped Stars in THF**

| sample | $M_w \times 10^{-3}$ $^a$ | $[\eta]$ (dL g$^{-1}$) | $K_H$ | $R_V$ (nm) | $(R_v)_{THF}/(R_v)_{Cycl}$ |
|---|---|---|---|---|---|
| 1N-3PBd30 | 111 | 1.14 | 0.43 | 12.6 | 1.02 |
| 1N-3PBd40 | 150 | 1.32 | 0.41 | 14.6 | 1.03 |
| 2N-3PBd40 | 99.0 | 0.954 | 0.46 | 11.4 | 0.99 |
| 3N-3PBd40 | 93.1 | 1.05 | 0.43 | 11.6 | 1.02 |

[a] By LALLS in THF.[33]

**Table 7. Viscometry for the Zwitterion-Capped Stars in Cyclohexane**

| sample | $[\eta]$, (dL g$^{-1}$) | $K_H$ | $R_v$ (nm) |
|---|---|---|---|
| Zw-1N-3PBd8 | 0.477 | 0.60 | 12.1 |
| Zw-1N-3PBd15 | 0.820 | 1.11 | 17.9 |
| Zw-1N-3PBd20 | 0.711 | 0.69 | 13.2 |
| Zw-1N-3PBd30 | 1.18 | 0.53 | 17.4 |
| Zw-1N-3PBd40 | 1.44 | 0.51 | 17.2 |
| Zw-2N-3PBd8 | 0.452 | 0.98 | 13.9 |
| Zw-2N-3PBd15 | 0.715 | 0.51 | 12.2 |
| Zw-2N-3PBd30 | 0.926 | 0.57 | 13.5 |
| Zw-2N-3PBd40 | 1.05 | 1.60 | 12.7 |
| Zw-3N-3PBd25 | 0.685 | 5.95 | 9.82 |
| Zw-3N-3PBd40 | 0.804 | 7.82 | 12.8 |

Intrinsic viscosity measurements were also conducted in THF for the high molecular weight polymers. The results are given in Table 6. Similar conclusions with the corresponding DLS measurements can be drawn. The intrinsic viscosities and the viscometric radii are slightly larger from the corresponding values in cyclohexane, in almost all cases, indicating that the amine groups promote only weak association and that THF is a better solvent than cyclohexane for polybutadiene.

The results for the viscosity measurements of the zwitterion-capped stars are presented in Table 7, whereas representative diagrams are given in Figure 4. Interesting conclusions can be extracted from these measurements. In the case of polymers with one and two zwitterion groups, the intrinsic viscosities of the aggregates are larger than those of their precursor molecules and the $K_H$ values are increased.[51,52] The above results support the conclusion that these polymers form

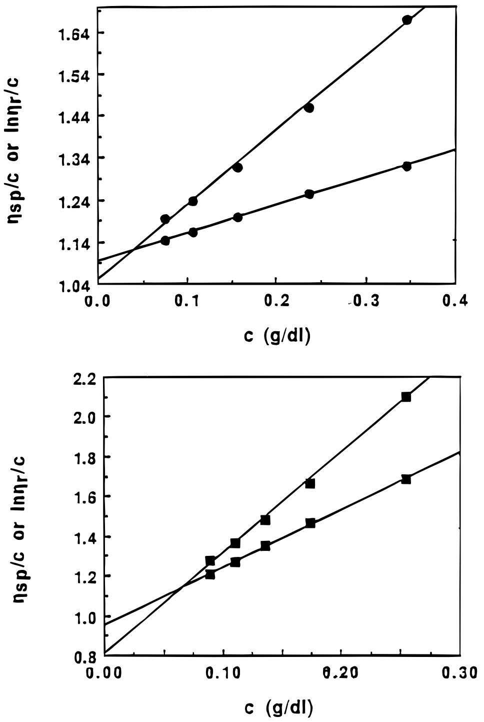

**Figure 4.** $\eta_{sp}/c$ or ln $\eta_r/c$ vs $c$ for samples Zw-2N-3PBd40 (●) and Zw-3N-3PBd40 (■) in cyclohexane at 25 °C.

micelles in cyclohexane. Especially for the sample Zw-2N-3PBd40, the increase of the $[\eta]$ is very small whereas the increase in $K_H$ is very large. The high molecular weight of this sample introduces strong excluded volume repulsions which prevent the intermolecular association ($N_w = 1.4$), but the high $K_H$ value implies strong hydrodynamic interactions between the polar groups, indicating the existence of intramolecular association. This behavior is much more intense in the case of star polymers with three zwitterion groups. Their intrinsic viscosities are lower than those of the corresponding amine polymers and the $K_H$ values are extremely high. These results imply that, in the concentration range used for the measurements, the macromolecules change their conformation toward a more compact structure, where the hydrodynamic interactions are very strong. It seems that the intramolecular association dominates in these systems at the very dilute regime. The LALLS[33] and DLS data support the above conclusions.

From the comparative examination of $R_v$ and $R_H$ of the zwitterion-capped star polymers, it is evident that in all cases $R_v < R_H$. The reduction of the $R_v$ values is not so large as to correspond to the nonassociated chains. This result shows that the micelles deaggregate to some extent, due to the shear forces applied in the viscometric tube, although these forces are not very strong. This means that the critical shear rate is very small. Only in the case of the samples with the lower degrees of aggregation is there a rather good agreement between $R_v$ and $R_H$. Similar behavior has been noted in the literature for systems which form micelles.[53] Linear polyisoprenes[16] and polybutadienes[54] with zwitterionic end groups do not give evidence of deaggregation in the viscometric tube, showing that the net forces which lead to the formation of the micelles from the star polymers are not so strong as in the case of linear polymers. The increased steric repulsions due to the unfunctionalized chains is perhaps the reason for this behavior.

## Conclusions

Three-arm polybutadiene stars with one, two, and three dimethylamine and zwitterion end groups were studied by dynamic light scattering and viscometry. The amine-capped polymers do not give evidence of strong association in cyclohexane. In THF their dimensions are slightly increased because of the difference in quality, in the thermodynamic sense, between the two solvents.

The situation is completely different for the zwitterion-capped stars. These samples associate strongly in cyclohexane. The degree of association decreases with increasing molecular weight of the base polymer, due to the excluded volume repulsions. In the case of stars with three functional groups, the degrees of association are very low. Difunctional and especially trifunctional samples form gels at low concentrations (lower than the overlap concentration, $c^*$). Strong evidence supports the conclusion that in very dilute solutions, the polymers, especially those with low degrees of association, tend to interact intramolecularly.

The zwitterion polymers deaggregate to some extent due to the shear forces applied in the viscometer tube, showing that the unfunctionalized arms introduce steric repulsions which make the micelles rather weak.

The samples capped with one zwitterionic group form micelles which behave hydrodynamically as star polymers with functionality equal to $2N_w$.

## References and Notes

(1) Holliday, L., Ed. *Ionic Polymers*; Applied Science Publishers: London, 1975.
(2) MacKnight, W. J.; Earnest, T. R., Jr. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.
(3) Fitzerald, J. J.; Weiss, R. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 99.
(4) Mauritz, K. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 65.
(5) Lundberg, R. D.; Phillips, R. R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1143.
(6) Lantman, C. W.; MacKnight, W. J.; Peiffer, D. G.; Sinha, S. K.; Lundberg, R. D. *Macromolecules* **1987**, *20*, 1096.
(7) Kim, M. W.; Peiffer, D. G. *J. Chem. Phys.* **1985**, *83*, 4159.
(8) Hara, M.; Wu, J. L. *Macromolecules* **1988**, *21*, 402.
(9) Desjardin, A.; van der Ven, T. G. M.; Eisenberg, A. *Macromolecules* **1992**, *25*, 2412.
(10) Wilson, A. D.; Prosser, H. J., Eds. *Developments in Ionic Polymers*; Applied Science Publishers: New York, 1983; Vols. 1, 2.
(11) Eisenberg, A.; King, M. *Ion-Containing Polymers, Physical Properties and Structure*; Academic Press: New York, 1977.
(12) Tant, M. R.; Wilkes, G. L. *J. Macromol. Sci. Rev.* **1988**, *C28*, 1.
(13) Utracki, L. A.; Weiss, R. A., Eds. *Multiphase Polymers: Blends and Ionomers*; ACS Symposium Series 395; American Chemical Society: Washington, DC, 1989.
(14) Broze, G.; Jerome, R.; Teyssie, P. *Macromolecules* **1982**, *15*, 920.
(15) Worsfold, D. J. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2237.
(16) Davidson, N. S.; Fetters, L. J.; Funk, W. G.; Graessley, W. W.; Hadjichristidis, N. *Macromolecules* **1988**, *21*, 112.
(17) Möller, M.; Omeis, J.; Muhlesein, E. In *Reversible Polymeric Gels and Related Systems*; Russo, P. S., Ed.; ACS Symposium Series 350; American Chemical Society: Washington, DC, 1987.
(18) Lenz, R. W. *Organic Chemistry of Synthetic High Polymers*; Interscience: New York, 1967.
(19) Athey, R. D. *Prog. Org. Coat.* **1979**, *7*, 289.
(20) Kennedy, J. P. *Rubber Chem. Technol. (Rubber Rev.)* **1983**, *56*, 639.
(21) Kennedy, J. P.; Ross, L. R.; Lackey, J. E.; Nuyken, O. *Polym. Bull.* **1981**, *4*, 67.

(22) Sogah, D. Y.; Webster, O. W. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 927.
(23) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1.
(24) Quirk, R. P.; Yin, J.; Guo, S.-H.; Hu, X. W.; Summers, G.; Kim, J.; Zhu, L.-F.; Schock, L. E. *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 47.
(25) Morton, M.; Fetters, L. J.; Inomata, J.; Rubio, D. C.; Young, R. N. *Rubber Chem. Technol.* **1976**, *49*, 303.
(26) Quirk, R. P.; Chen, W.-C. *Makromol. Chem.* **1982**, *183*, 2071.
(27) Burgess, F. J.; Cunliffe, A. V.; McCallum, J. R.; Richards, D. H. *Polymer* **1977**, *18*, 719, 726, 733.
(28) Veda, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1990**, *23*, 939.
(29) Schulz, D. N.; Halasa, A. F.; Oberster, A. E. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 153.
(30) Schulz, D. N.; Halasa, A. F. *J. Polym. Sci., Part A-1* **1977**, *15*, 2401.
(31) Storey, R. F.; George, S. E.; Nelson, M. E. *Macromolecules* **1991**, *24*, 2920.
(32) Krauss, G.; Gruver, J. T. *Rubber Chem. Technol.* **1969**, *42*, 800.
(33) Pitsikalis, M.; Hadjichristidis, N. *Macromolecules* **1995**, *28*, 3904.
(34) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359.
(35) Roovers, J.; Toporowski, P. *Macromolecules* **1983**, *16*, 843.
(36) Stewart, M. J.; Shepherd, N.; Service, D. *Br. Polym. J.* **1990**, *22*, 319.
(37) Eisenbach, C. D.; Schnecko, H.; Kern, W. *Eur. Polym. J.* **1975**, *11*, 699.
(38) Pispas, S.; Pitsikalis, M.; Hadjichristidis, N.; Dardani, P.; Morandi, F. *Polymer* **1995**, *36*, 3005.
(39) (a) Mays, J. W. *Polym. Bull.* **1990**, *23*, 247. (b) Iatrou, H.; Siakali-Kioulafa, E.; Hadjichristidis, N.; Roovers, J.; Mays, J. W. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(40) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(41) Ibrahim, F.; Elias, H. G. *Makromol. Chem.* **1964**, *76*, 1.
(42) Douglas, J. F.; Roovers, J.; Freed, K. F. *Macromolecules* **1990**, *23*, 4168.
(43) Colby, R. Experimental Tests of Tube Model and Scaling Law Predictions for the Viscoelastic Properties of Polymer Melts and Solutions. Ph.D. Thesis, Northeastern University, Evanston, IL, 1985.
(44) Elias, H. G. *Int. J. Polym. Mater.* **1976**, *4*, 209.
(45) Stock, J.; Burchard, W.; Stadler, R. *Macromolecules* **1992**, *25*, 6885.
(46) Xu, R.; Winnik, M. A.; Hallet, F. R.; Riess, G.; Croucher, M. D. *Macromolecules* **1991**, *24*, 87.
(47) Bauer, B. J.; Fetters, L. J.; Graessley, W. W.; Hadjichristidis, N.; Quack, G. F. *Macromolecules* **1989**, *22*, 2337.
(48) Roovers, J.; Toporowski, P. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1907.
(49) Roovers, J.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1983**, *16*, 214.
(50) Roovers, J.; Martin, J. F. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 2513.
(51) Misra, N.; Mandal, B. M. *Macromolecules* **1984**, *17*, 495.
(52) Bitsch, J. L.; Reiss, G.; Banderet, A. *J. Chim. Phys.-Chim. Biol.* **1970**, *67*, 1977.
(53) Antonietti, M.; Heinz, S.; Schmidt, M.; Rosenauer, C. *Macromolecules* **1994**, *27*, 3276.
(54) Pitsikalis, M.; Siakali-Kioulafa, E.; Hadjichristidis, N. *J. Polym. Sci., Polym. Phys. Ed.*, in press.

MA951001S