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Micellar behavior of a well-defined dendritic polymer $(PS_2PI)_3$: the effects of architecture and solvent selectivity

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Abstract

The micelles formed when a dendritic polymer of polystyrene (PS) and polyisoprene (PI), having the overall structure $(PS_2PI)_3$, were examined in two solvents, dimethylformamide (DMF) and dimethylacetamide (DMA). Both solvents are good solvents for polystyrene and non-solvents for polyisoprene. The aggregation behavior was studied by a combination of static and dynamic light scattering and viscometry. In both systems star-like micelles were formed which followed the hard sphere model. The aggregation number was much lower for the micelles formed in DMA. The polymer–solvent interaction parameters indicate that the interactions are stronger between both PS-DMA and PI-DMA than for either polymer block with DMF. The effects of solvent selectivity are exacerbated by the structure of the polymer. With each polymer molecule contributing six soluble arms to the micelle, in the better solvent (DMA) increased repulsive interactions between the extended polystyrene lead to lower aggregation numbers.

Keywords: Dendritic polymers; Macromolecular architecture; Micellization; DMA; DMF; Light scattering; Viscometry

1. Introduction

Many studies of the micelle behavior of high molecular weight block copolymers in selective solvents have been published over the last years in light of the intellectual and commercial interest in such systems [1–11]. The development of controlled polymerisation systems, capable of the synthesis of well-defined block copolymers and the improvement of analytical techniques have furthered the understanding of the nature of the multimolecular micelles with regard to the effects of composition, chemical nature, temperature, pH, and concentration.

Relatively recently, advances have been made as to the effects of architecture on the structure of micelles with the synthesis of miktoarm star and other well-defined branched copolymers which have allowed factors such as the inclusion of many junction points on the core-corona interface to be examined [12–17]. Generally, an increase in the number of soluble blocks present on a molecule leads to a decrease in the aggregation number, steric factors being important. More recently, studies have been directed to the solution properties of arborescent, dendritic-like and linear-dendritic hybrid copolymers due to the specific highly branched structure of these molecules [18–21]. The formation of unimolecular micelles in such systems is highly probable, due to the presence of a large number of soluble blocks, leading to compartmentalized nano-assemblies, whose structure in solution does not depend on concentration.

The work reported in this paper concerns the micellar properties of a well-defined dendritic copolymer of the

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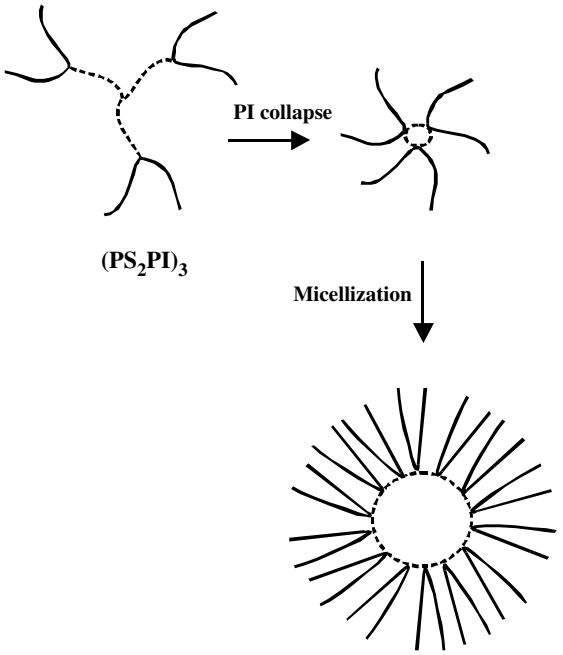

Chart 1. Illustration of the formation of micelles from $(PS_2PI)_3$ in solvents selective for PS.

type $(PS_2PI)_3$ (Chart 1), synthesized by anionic polymerisation high vacuum techniques. In this model system the effects of copolymer architecture and solvent selectivity towards the different blocks are investigated by means of static (LALLS) and dynamic lights scattering (DLS) and viscometry.

2. Experimental

2.1. Synthesis of the dendritic polymer $(PS_2PI)_3$

The dendritic polymer, $(PS_2PI)_3$ was prepared using high vacuum anionic polymerisation techniques [22]. The detailed synthesis has been published elsewhere [23]. Briefly, a stoichiometric equivalent of polystyryllithium was added slowly to a solution of 4-(chlorodimethylsilyl)styrene (CDMSS) in benzene, preferentially reacting at the chlorosilane site and forming a macromonomer. A second equivalent of polystyryllithium was then reacted with the styrenic double bond of CDMSS and isoprene polymerised from the resulting living styrenic site. Trichloromethylsilane was used as a linking agent to react with three equivalents of the living polyisoprenyllithium thus forming a second generation dendritic polymer.

2.2. Preparation of solutions

Dimethylformamide (DMF) was dried over 4 Å molecular sieves and fractionally distilled just prior to use. Dimethylacetamide (DMA) was also fractionally distilled after drying over calcium hydride for at least 24 h and THF was similarly distilled from sodium. Stock solutions were prepared by the accurate weighing of the sample and solution, heated at 60 °C overnight in order to ensure complete dissolution and stirred occasionally to remove non-equilibrium structures. The solutions were then allowed to stand at room temperature for 24 h to ascertain the continuing solubility of the polymers and reweighed before dilution and measurement in order to obtain an accurate concentration. Prior to light scattering measurements, the solutions were filtered using 0.45 μm nylon filters.

2.3. Measurements

A Chromatix KMX-6 low-angle laser light scattering photometer (LALLS) equipped with a 2 mW He–Ne laser ($\lambda = 633$ nm) was used to obtain values for the apparent weight–average molecular weight, M_w, and the second virial coefficient, A_2. Measurements were performed at 30 °C. M_w and A_2 were calculated from the concentration dependence of the reduced scattering intensity.

DLS experiments were performed at 30 °C using a Series 4700 Malvern system comprising of a PCS5101 goniometer with a PCS stepper motor controller, a Cyonics variable power Ar^+ laser, operating at a wavelength of 488 nm and 10 mW power, a PCS8 temperature control unit, and a RR98 pump/filtering unit. A 192 channel correlator was used for the accumulation of data and the correlation functions were analyzed using CONTIN software. Angular dependence of the correlation function was initially checked, and subsequent data collected at 90°. The apparent translational diffusion coefficient at zero concentration and zero angle $D_{0,app}$ was calculated for each system, using Eq. (1)

$$D_{app} = D_{0,app}(1 + k_D c + \cdots) \quad (1)$$

where D_{app} is the apparent diffusion coefficient at each concentration at zero angle and k_D is the coefficient of the concentration dependence of D_{app}. Apparent hydrodynamic radii, R_h, were determined using Eq. (2)

$$R_h = \frac{k_B T}{6\pi\eta_s D_{0,app}} \quad (2)$$

where k_B is the Boltzmann constant, T the absolute temperature, and η_s the viscosity of the solvent.

Viscometry was performed using a Cannon–Ubbelohde dilution viscometer in a temperature controlled water bath (±0.01 °C temperature variation). The flow times for the solvent and solutions were measured with a Schott-Geräte AVS410 automatic flow timer. In all instances, the flow times were sufficiently long as to

avoid having to apply kinetic energy corrections. The Huggins (Eq. (3)) and Kraemer (Eq. (4)) were used to calculate the intrinsic viscosity $[\eta]$ of each system

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c + \cdots \quad (3)$$

$$\frac{\ln \eta_r}{c} = [\eta] + k_K[\eta]^2 c + \cdots \quad (4)$$

where η_{sp} is the specific viscosity and η_r is the relative viscosity and k_H and k_K are the Huggins and Kraemer coefficients respectively. Viscometric radii, R_v, were calculated from Eq. (5)

$$R_v = (3/10\pi N_A)^{\frac{1}{3}}([\eta]M_w)^{\frac{1}{3}} \quad (5)$$

N_A being Avagadro's number and M_w, the weight average molecular mass of the micelle as determined by static light scattering. Details are given elsewhere [13].

3. Results and discussion

3.1. Hydrodynamic properties of $(PS_2PI)_3$ in THF

The characterization data for $(PS_2PI)_3$ and its component arms have been listed in Table 1 along with results from DLS and viscosity measurements in THF, a common good solvent for the two components.

The values obtained from viscosity measurements reflect that THF is a good solvent for both polystyrene (PS) and polyisoprene (PI). The Huggins coefficient, k_H is close to the limit for flexible polymer chains in a good solvent (0.3) [24]. The DLS results are in reasonable agreement with those obtained from viscometry giving $R_v/R_h = 1.1$, the theoretical value for R_v/R_h being 1 at the hard sphere limit [24,25]. Values of the ratio ranging between 1.05 and 1.15 have been reported for linear and branched flexible polymers [24,25].

Table 1
Molecular characteristics of $(PS_2PI)_3$ dendritic copolymer in THF at 30 °C

M_w[a] $(PS_2PI)_3$ (g/mol)$\times 10^{-5}$	1.19
M_n[b] PS arm (g/mol)$\times 10^{-4}$	1.71
M_n[b] PI arm (g/mol)$\times 10^{-3}$	5.5
M_w/M_n[b] $(PS_2PI)_3$	1.05
wt.% PS[c]	79
$D_{0,app}$[d] (cm^2/s)$\times 10^7$	5.30
k_D[d] (ml/g)	27
R_h[d] (nm)	9.0
$[\eta]$[e] (dl/g)	0.51
k_H[e]	0.32
R_v[e] (nm)	10.0
R_v/R_h	1.1

[a] By LALLS in THF at 25 °C.
[b] By SEC in THF at 25 °C using PS and PI standards.
[c] By ^{1}H-NMR in $CDCl_3$ at 30 °C.
[d] By DLS in THF at 30 °C.
[e] By viscometry in THF at 30 °C.

Table 2
Properties of $(PS_2PI)_3$ micelles in DMA and DMF at 30 °C

Parameter	Solvent	
	DMA	DMF
dn/dc[a] (cm^3/g)	0.126	0.132
$M_{w,app}$[b] (g/mol)$\times 10^{-6}$	2.79	9.43
A_2[b] (mol cm^3/g^2)$\times 10^5$	3.92	1.98
$N_{w,agg,app}$[b]	22	76
$D_{0,app}$[c] (cm^2/s)$\times 10^7$	1.41	1.15
k_D[c] (ml/g)	6	10
R_h[c] (nm)	18.8	24.0
$[\eta]$[d] (dl/g)	0.158	0.098
k_H[d]	0.93	0.87
R_v[d] (nm)	19.0	24.4
R_v/R_h	1.01	1.02
R_c (nm)	6.4	9.6
A (nm^2)	23	15

[a] The specific refractive index was obtained from differential refractometry at 30 °C using a Chromatix KMX-16 refractometer operating at a wavelength of 633 nm.
[b] By LALLS.
[c] By DLS.
[d] By viscometry.

3.2. Micellization of $(PS_2PI)_3$ in DMA and DMF

Both DMA and DMF are considered to be good solvents for the polystyrene and non-solvents for polyisoprene. The appearance of the $(PS_2PI)_3$ solutions in both DMA and DMA indicated the formation of large, multimolecular micelle structures, the solutions having a slight blue tint. However, as can be seen from the results in Table 2, the aggregation characteristics of $(PS_2PI)_3$ in DMA and DMF are quite different.

The apparent weight average molecular mass, $M_{w,app}$, of micelles and their *true* weight average molecular mass are likely to be very similar because dn/dc is high for both the PS and PI components of the dendritic species in DMA and on the other hand molecular, compositional and architectural homogeneity of the dendritic material is low. The same conditions apply for DMF. The second virial coefficient value is very low for both systems, but the A_2 value is especially low in DMF since the thermodynamic quality of this solvent for $(PS_2PI)_3$ is particularly poor. The light scattering plots are shown in Fig. 1. The apparent weight average molecular mass for the micelles formed in DMF is much higher than for that for micelles in DMA, and the apparent weight average aggregation number, $N_{w,agg,app}$ as calculated using Eq. (6), is correspondingly large.

$$N_{w,agg,app} = M_{w,app,micelle}/M_{w,unimer} \quad (6)$$

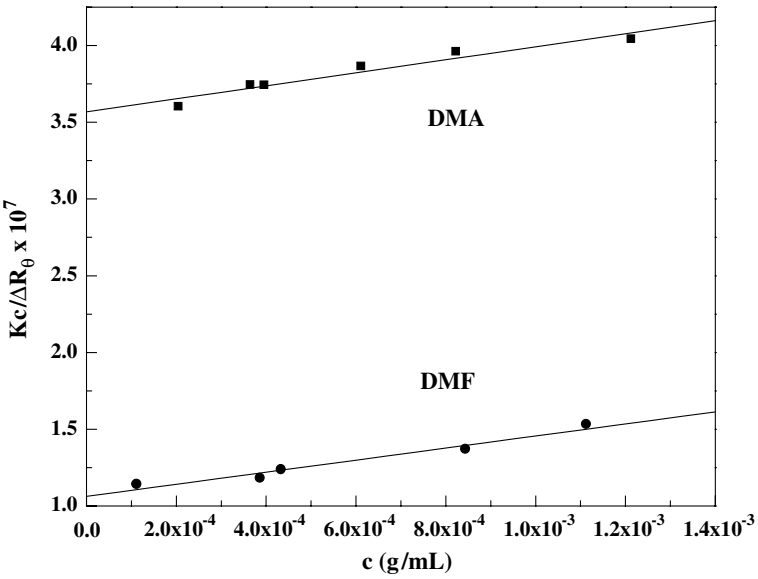

Fig. 1. $Kc/\Delta R_\theta$ vs concentration plots for $(PS_2PI)_3$ micelles in DMA (■) and DMF (●) at 25 °C.

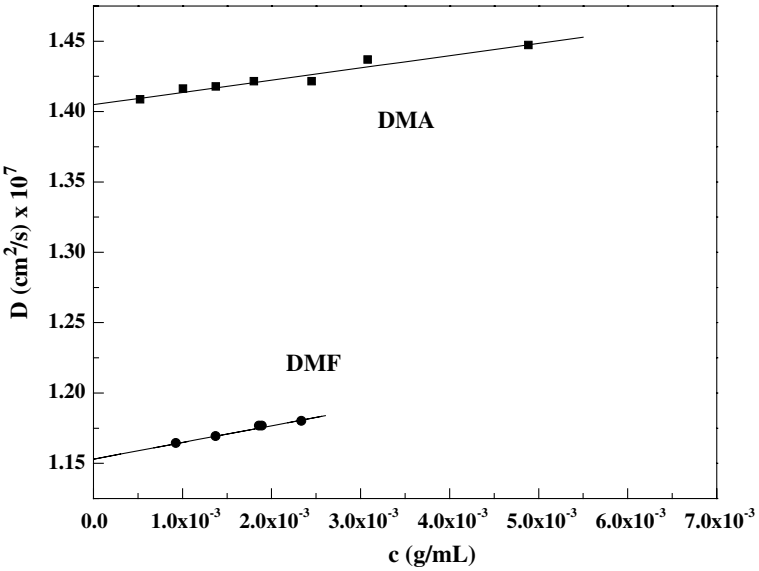

Fig. 2. Diffusion coefficient vs concentration for $(PS_2PI)_3$ micelles in DMA (■) and DMF (●) at 25 °C.

The results of DLS experiments, also listed in Table 2, reflect the structure and dimensions of the micelles formed in DMA and DMF. The apparent diffusion coefficient, $D_{0,app}$, is much higher for the unimeric $(PS_2PI)_3$ in THF. It can also be noted that the micelles formed in DMF have a greater hydrodynamic radius than the DMA species which is a reflection on its higher aggregation number as determined by static light scattering. In both solvents, the angular dependence of the diffusion coefficient was found to be negligible and the second moment values μ_2/Γ^2, from cumulant fits to the correlation functions, were very low, less than 0.05 in the majority of the measurements, an indication of the uniformity of the micelles in size. No unimers were observed even when the temperature was raised to 50 °C. The high $M_{w,app}$ compensates for the low A_2 value to give a higher k_D for the micelles formed in DMF compared to the DMA system (Fig. 2).

The results of the viscosity experiments agree well with those of the DLS measurements in that there is

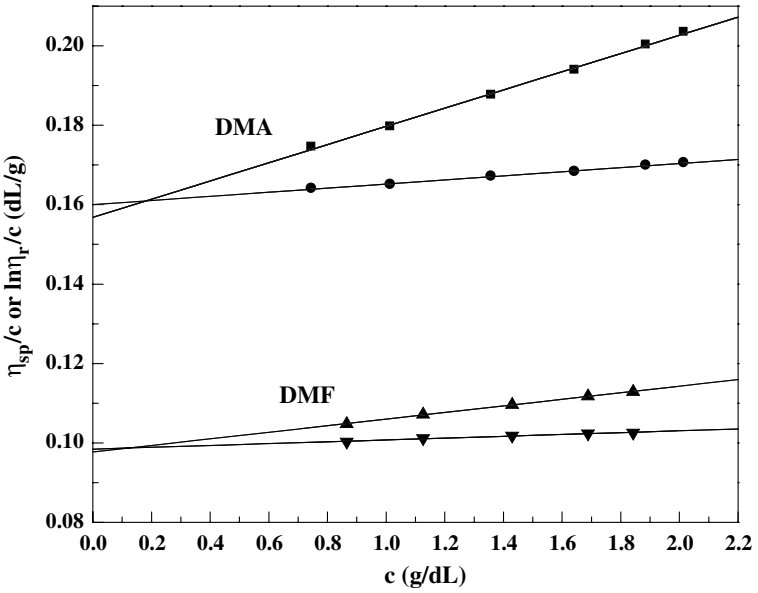

Fig. 3. Huggins (■) and Kraemer (●) plots for $(PS_2PI)_3$ in DMA and Huggins (▲) and Kraemer (▼) plots for $P(S_2I)_3$ in DMF at 25 °C.

negligible difference between R_v and R_h for the micelles formed in the solvents in this study (Fig. 3). A R_v/R_h ratio of around 1 is characteristic of hard sphere behavior [24,25]. This indicates that the micelles are stable and uniform in dimension over the different ranges of concentrations required for the analytical techniques employed, and remain unaffected by the small yet sometimes significant shear forces which can arise from the passage of micelles through the capillary of a viscometer. In both DMA and DMF, the micelles have the characteristics of compact hard spheres, where the PI chains have collapsed, forming a small core, as illustrated in Chart 1. The intrinsic viscosity of the dendritic polymer in both solvents is accordingly low compared with the unimeric species in THF due to the swelling of the whole molecule in the latter good solvent. In both DMA and DMF the Huggins constant has a relatively high value, ($k_H = 0.99$, in theory, for hard spheres [24]) a reflection of the solvents being poor and of increased hydrodynamic segment interactions within the micelles.

The effect of the architecture on the micellar properties displayed by the systems examined is difficult to ascertain, few systems having been studied in either DMA or DMF although several publications have examined the properties of PS–PI of samples of various architectures in hydrocarbon solvents, primarily *n*-decane [4,7,8]. It has also been found that the aggregation behavior is strongly influenced by the degree of polymerisation (N) of the non-soluble block of a block copolymer but is also dependent on the overall molecular weight of the constituent block copolymer. In the micellization of AB block copolymers, $N_{agg} \approx N_A^{\alpha} N_B^{-\beta}$ where α and β are exponents for the degree of polymerisation of the non-soluble block A and the soluble block B respectively. Theoretically, α is 0.8 for hairy micelles, where the micelle has a large corona relative to the core, $\alpha = 1$ for crew-cut micelles, where the core dimensions are greater than for the corona, and $\alpha = 2$ for amphiphilic micelles where A and B have a characteristically high Flory–Huggins interaction parameter χ [1,10b]. However, the $(PS_2PI)_3$ micelles are not made up of AB diblocks but of dendritic polymer molecules whose architectures are comparable to three AB_2 miktoarm stars joined together at a central junction point at the end of the PI block. The entropic penalties associated with the packing of the additional arms would be expected to give a comparatively low N_{agg} compared to a simple AB diblock and it would be expected that repulsive, steric, forces would increase in the corona from the presence of additional soluble blocks. It is interesting to note that a diblock sample with a total molecular weight of 43,000, almost one third of the dendritic copolymer investigated in this study, and similar composition (81% wt PS) forms micelles in DMF with an aggregation number of 73, almost equal to the one calculated for the dendritic copolymer [9]. The formation of multimolecular instead of unimolecular micelles in both solvents must be a result of the high solvent selectivity for the PS arms as well as to the low density branched structure of the molecule.

The difference in N_{agg} for $(PS_2PI)_3$ in DMF and DMA is obviously related to the interactions between the constituent blocks of the dendritic polymer and the solvent. The behavior is thus dependent on the DMF

and DMA solubility parameters (δ), 24.8 and 22.1 $[Mpa]^{1/2}$ respectively [26]. Since polyisoprene has a solubility parameter of approximately 16 $[Mpa]^{1/2}$, considerably lower than either DMA or DMF, the polyisoprene block is insoluble in these solvents and micellar cores should be essentially free of solvent in both DMA and DMF. The effects exerted by the polystyrene chains in the corona have to be also taken into account in order to explain the differences in N_{agg}. These are also somewhat dependent on the polymer–solvent interactions which are also expected, for similar reasons, to be stronger between DMA and polystyrene ($\delta PS \sim 17$–20 $[Mpa]^{1/2}$) than for DMF. These interactions lead to a greater chain extension and larger repulsive interactions between the chains of the corona in DMA and ultimately to a decrease in the aggregation number in this solvent. The solvent effects are likely to be exacerbated by the architectural constraints arising from the system i.e. the PS corona chains radiating from a single junction point.

For an individual micelle, the dimensions of the core can be calculated from Eq. (7)

$$R_c = (3M_{w,micelle} wt_{PI}/4\pi N_A d_{PI} \varphi_{PI})^{\frac{1}{3}} \quad (7)$$

where $M_{w,micelle}$ is the apparent weight average molecular mass of the micelle as determined by static light scattering, wt_{PI} is the weight percent of PI in the copolymer, N_A Avogadro's number, d_{PI} the density of PI and φ_{PI} is the volume fraction of PI in the core of the micelle ($\varphi_{PI} = 1$ if it assumed that the core is free of solvent as it is probably the case in both solvents).

Also, the area A occupied by each copolymer chain at the core-corona interface, can be calculated using Eq. (8)

$$A = 4\pi R_c^2/N_w \quad (8)$$

The values for the core dimensions and for the area, A, are also listed in Table 2. The results show that the core radius is smaller for the micelle formed in DMA. However, the area occupied by each $(PS_2PI)_3$ unit is significantly larger for the micelle in DMA which indicates that the PS chains are more swollen/extended in this solvent than is the case in DMF.

4. Conclusions

The multimolecular micelles formed by $(PS_2PI)_3$, a second generation dendritic polymer, were found to have quite different characteristics in DMA than for the same polymer in DMF. A much lower degree of aggregation was found for the micelles formed in DMA. In both DMA and DMF the structures formed are stable over a range of concentrations and at elevated temperatures and both species behave as hard spheres. The differences in aggregation number must be due to a combination of the structure of the $(PS_2PI)_3$ and the polymer–solvent interactions, DMA being a better solvent than DMF for polystyrene.

Acknowledgement

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