Hydrodynamic Properties of A₈B₈ Type Miktoarm (Vergina) Stars

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ABSTRACT: The dilute solution properties of three (PS)₈(PI)₈ miktoarm (Vergina) stars were investigated by viscometry and dynamic light scattering in toluene and tetrahydrofuran (THF) (common good solvents), cyclohexane at 34.5°C (theta solvent for PS and good for PI) and dioxane at 34°C (theta solvent for PI and good for PS). Experimental intrinsic viscosity [η] and hydrodynamic radii, Rₕ, values in all solvents were larger for the miktoarm stars in comparison to the calculated ones using a simple model which describes the size of the copolymers as a weighted average of the sizes of the homopolymer stars with the same total molecular weight and number of arms as the copolymer. This expansion is discussed on the basis of the increased number of heterocontacts, the topological constrains imposed by the common junction point in this highly branched miktoarm architecture and the asymmetry in molecular weights of the different kinds of arms. The conformation adopted in dilute solutions can explain, to some extent, the morphological results obtained on the same materials. The ratios of viscometric to hydrodynamic radii are consistent with previous investigations on linear and star polymers and in accord with the hard sphere model. © 1999 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 37: 1329–1335, 1999

Keywords: miktoarm stars; hydrodynamic properties; molecular expansion; heterocontacts

INTRODUCTION

The synthesis and bulk properties of miktoarm stars, starlike molecules with arms of different chemistry, have received much attention recently.¹⁻²² The experimental results indicate that dramatic differences in morphology and phase behavior emerge with respect to linear block copolymers. This is presumably due to the constraints imposed on the immiscible blocks.

On the other hand, the solution properties of these macromolecules has received less attention.²,¹²,⁻²³⁻²⁵ Theoretical studies concerning the conformation of these complex copolymers in dilute solutions where the materials are molecularly dissolved (common good or selective theta solvents for one component of the molecule), do exist.²⁵⁻²⁷ Their main concern is to estimate the increase in molecular dimensions brought about in miktoarm stars because of the increased number of heterocontacts between chemically different segments, an increase that results from the macromolecular architecture itself.

Theory²⁵⁻²⁷ predicts that the relative molecular dimensions increase in the order A₂B<A₂B₂<A₃B₃<A₆B₆ irrespective of the selectivity of the solvent when the overall dimensions are compared with the dimensions of the parts of the
miktoarm star that includes all arms with the same chemical composition. In other words, molecular dimensions increase as the number of arms of the two constituents increases and when equality in the number of arms of each component increases (e.g., \(A_2B_2>A_3B\) and \(A_3B_3>A_2B_4\)). Previous experimental studies on \(A_2B\), \(A_2B_2\), and \(A_3B\) stars have shown this expansion predicted by theory.\(^2\),\(^27\)

In this study, we report viscometric and dynamic light scattering results on three \(A_8B_8\) miktoarm (Vergina) stars, where A is PS and B is PI, in solvents good for both parts of the copolymers (toluene and THF) and in selective theta solvents for one part of the copolymer which is good for the other (cyclohexane and dioxane). In this case, eight arms of each kind are brought together into close contact. Due to the presence of one common junction point, more heterocontacts between different segments than in the structures previously investigated, are likely to occur. This is expected to cause a relatively larger increase in the molecular dimensions. By determining the hydrodynamic properties of these miktoarm stars, we can estimate their overall dimensions. We believe that this kind of experiment, apart from giving us a better understanding of the solution behavior of complex macromolecules at the molecular level and providing means for testing theoretical predictions, can also help in the understanding of the bulk properties of these model compounds since these properties are greatly affected by the molecular state in solution.\(^2\),\(^8\)

**EXPERIMENTAL**

The three \(S_8I_8\) miktoarm stars under study were synthesized by anionic polymerization under high vacuum conditions using controlled chlorosilane linking chemistry. Thorough molecular characterization proved that these materials are model compounds exhibiting high degree of molecular, compositional, and architectural homogeneity. Details on the synthesis and the molecular characterization of these macromolecules have been given in a previous publication.\(^9\) The molecular characteristics of the samples are given in Table I.

Intrinsic viscosities have been measured in toluene at 35°C (common good solvent), cyclohexane at 34.5°C (theta solvent for linear PS), and dioxane at 34°C (theta solvent for linear PI). Toluene and cyclohexane were refluxed over \(\text{CaH}_2\) for 24 h and were fractionally distilled prior to use. Dioxane was refluxed over sodium and was also fractionally distilled just prior to use. Cannon-Ubbelohde dilution viscometers were used thermostated at the measurement temperature with a precision of \(\pm 0.02^\circ\text{C}\). Solvent and solution flow times were measured by a Scott-Gerate AVS 410 automatic flow timer. Measurements were made on at least five concentrations and data were analyzed by both Huggins and Kraemer equations in order to extract the intrinsic viscosity \([\eta]\) and the Huggins, \(k_H\) and Kraemer coefficient, \(k_K\), respectively. Viscometric radii, \(R_v\), were calculated from

\[
R_v = \frac{3}{10} \pi N_A \left(\frac{M_w[\eta]}{M_w}\right)^{1/3}
\]

(1)

Dynamic light scattering experiments were carried out on a Brookhaven system composed of a BI200SM goniometer, a 264 channel BI2030AT correlator, and a 35 mW He–Ne laser. THF, refluxed over \(\text{Na}\) and distilled just prior to use, was used as the common good solvent due to the higher refractive index contrast for both PS and PI homopolymers in this solvent. Experiments were also conducted in cyclohexane and dioxane at the respective theta temperatures of linear PS and PI. Autocorrelation functions were analyzed to second order by the method of cumulants. Apparent diffusion coefficients at zero concentration, \(D_0\), were obtained using the equation

\[
D = D_0 (1 + k_D c)
\]

(2)
where $D$ is the diffusion coefficient at each concentration, $k_D$ the coefficient in the concentration dependence of $D$ and $c$ the concentration. From the calculated $D_0$ values the hydrodynamic radii, $R_h$, were calculated by

$$R_h = k_B T/6 \pi \eta_0 D_0$$  \hfill (3)

**RESULTS AND DISCUSSION**

**Intrinsic Viscosity Measurements**

As was mentioned in the introduction, repulsive interactions due to incompatibility between A and B segments, in the miktoarm stars, lead to expansion of the overall dimensions of the molecule. We relate the overall dimensions to the dimensions of the corresponding parts of the copolymer. For a linear diblock copolymer under theta conditions we can write:

$$\langle S^2 \rangle_{\text{copol}} = \langle S^2 \rangle_A + \langle S^2 \rangle_B$$ \hfill (4)

where $\langle S^2 \rangle_{\text{copol}}$ is the mean square radius of gyration of the copolymer and $\langle S^2 \rangle_A$, $\langle S^2 \rangle_B$ for the A and B parts, provided that there are no specific interactions between the two segments. When the dimensions of the molecule are small, as in our case, direct measurement of $\langle S^2 \rangle$ requires sophisticated instrumentation and appropriate labeling of one part of the molecule (i.e., neutron scattering facilities and deuterated samples). In this case, the dimensions of one kind of the chemically different arms could be determined and a more direct comparison with theoretical predictions can be made. However, it is easier to perform intrinsic viscosity measurements. Thus, $\langle S^2 \rangle$ can be replaced by $(K/\Phi)^{2/3}M$ where $K$ is the Mark-Houwink-Sakurada coefficient and $\Phi$ the Flory constant, and eq.(4) can be written as \hfill (5)

$$[\eta]_{\text{copol}} = (w_A[\eta]_A^{2/3} + w_B[\eta]_B^{2/3})^{3/2}$$

where $[\eta]_A$, $[\eta]_B$ are the intrinsic viscosities of homopolymers A and B which have the same molecular weight and architecture as the copolymer and $w_A$, $w_B$ are the weight fractions of each component. Finding a common theta solvent in order to test the validity of eq. (5) is very difficult. Equation (5) can be applied to the good solvent conditions if $\Phi$ does not differ for the two components, as is the case for PS and PI. It can also be used for star polymers if the appropriate MHS coefficients for the homostars are used. In an alternative way, if data for the corresponding homopolymer stars are not available, the values of $[\eta]$ for stars can be calculated from the linear homopolymer data using the appropriate values of $g'$, where

$$g' = [\eta]_{\text{star}}/[\eta]_{\text{linear}}$$ \hfill (6)

In our case, we use the following relations given in the literature for linear PS and PI in the three solvents used ($[\eta]$ is given in mL/g):

**PS:**
- $[\eta] = 9.96 \times 10^{-9} \ M_w^{0.73}$ in toluene at 35°C\hfill (30)
- $[\eta] = 1.45 \times 10^{-2} \ M_w^{0.51}$ in dioxane at 34°C\hfill (29)

**PI:**
- $[\eta] = 2.05 \times 10^{-2} \ M_w^{0.73}$ in cyclohexane at 34.5°C\hfill (30)
- $[\eta] = 1.16 \times 10^{-1} \ M_w^{0.51}$ in dioxane at 35°C\hfill (29)

**Table II.** Viscometric Results for Vergina Star Copolymers in Toluene at 35°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>$[\eta]$ (mL/g)</th>
<th>$k_H$</th>
<th>$R_v$ (nm)</th>
<th>$[\eta]_{\text{cal}}$</th>
<th>$[\eta]<em>{\text{exp}}$ - $[\eta]</em>{\text{cal}}/[\eta]_{\text{cal}}$ × 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS1</td>
<td>48.3</td>
<td>0.89</td>
<td>13.6</td>
<td>40.7</td>
<td>+18</td>
</tr>
<tr>
<td>VS2</td>
<td>72.4</td>
<td>0.88</td>
<td>20.1</td>
<td>71.1</td>
<td>+2</td>
</tr>
<tr>
<td>VS3</td>
<td>111.9</td>
<td>0.72</td>
<td>25.1</td>
<td>89.3</td>
<td>+25</td>
</tr>
</tbody>
</table>

A$_a$B$_b$ TYPE MIKTOARM (VERGINA) STARS
$g'$ for 16 arm stars was estimated by interpolation of experimental data available for PS, PI, and PBD stars having 3–128 arms in good and theta solvents. The calculated values are $g' = 0.260$ for good solvent conditions and $g' = 0.330$ for theta solvent conditions. In Tables II–IV the experimentally determined parameters for each sample are given together with the calculated values of $[\eta]$.

Experimental values of $[\eta]$ are larger in the common good solvent and decrease in the selective $\theta$-solvents as expected. The larger decreases are seen in dioxane, since in this solvent the PI arms, which make the larger contribution to the overall dimensions, are contracted. The effects of solvent conditions are fully confirmed by the data on VS3. This sample with a large PI fraction (0.59) is minimally contracted in cyclohexane, the $\theta$ solvent for PS but is substantially contracted in dioxane, the $\theta$ solvent for PI. Of course, the percent contraction in the transition from a good to a $\theta$ solvent increases also with molecular weight.

Furthermore, in all cases experimental values of $[\eta]$ are considerably larger than the calculated ones which do not consider repulsion between different chemical segments. The expansion from a simple summation of Gaussian parts as measured by $100 \times (\lbrack \eta \rbrack_{\exp} - \lbrack \eta \rbrack_{\text{cal}})/\lbrack \eta \rbrack_{\text{cal}}$ is largest in the selective $\theta$-solvents. The reason for this is that in a selective $\theta$-solvent the segment concentration is higher and probability of heterocontacts is consequently larger, and promotes repulsive expansion of the whole polymer molecule. Monte Carlo simulations on A$_6$B$_6$ miktoarm stars in good and selective $\theta$ solvents predicted such expansion.

It has also been found that the coil expansion of the A$_6$B$_6$ miktoarm stars is in all cases larger than the expansion found in A$_2$B$_2$ miktoarm stars under comparable conditions. The increased number of arms in the A$_6$B$_6$ miktoarm stars increases the probability of heterocontacts causing the increased coil dimensions.

$k_H$ values are in most cases large and representative of the values reported previously for star polymers. These large values have been correlated with the increased hydrodynamic interactions associated with the branched architecture. The variations of $k_H$ with solvent quality cannot be explained in detail. For all samples $k_H$ decreases in the selectively $\theta$ solvents. Surprisingly, $k_H$ values in cyclohexane and dioxane are similar for all samples. The decrease observed is smaller for VS1 (the symmetric sample having the smaller molecular weight) and larger for VS3 (the asymmetric sample with the largest molecular weight). This may be attributed to core effects that are stronger in the VS1 case. Of course, one must have always in mind that relatively larger experimental errors are associated with this particular parameter.

The finer details of the coil expansion in Tables II–IV are not completely understood at this time. For example, it is not clear why VS2 is systematically less expanded than VS1 except in dioxane,

### Table III. Viscometric Results for the Vergina Star Copolymers in Cyclohexane at 34.5°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lbrack \eta \rbrack$ (mL/g)</th>
<th>$k_H$</th>
<th>$R_v$ (nm) (eq. 1)</th>
<th>$\lbrack \eta \rbrack_{\text{cal}}$</th>
<th>$\lbrack \eta \rbrack_{\exp} - \lbrack \eta \rbrack_{\text{cal}}/\lbrack \eta \rbrack_{\text{cal}} \times 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS1</td>
<td>44.8</td>
<td>0.78</td>
<td>13.3</td>
<td>35.2</td>
<td>+27</td>
</tr>
<tr>
<td>VS2</td>
<td>64.9</td>
<td>0.68</td>
<td>19.4</td>
<td>57.9</td>
<td>+12</td>
</tr>
<tr>
<td>VS3</td>
<td>107.4</td>
<td>0.30</td>
<td>24.8</td>
<td>75.8</td>
<td>+42</td>
</tr>
</tbody>
</table>

### Table IV. Viscometric Results for the Vergina Star Copolymers in Dioxane at 34°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lbrack \eta \rbrack$ (mL/g)</th>
<th>$k_H$</th>
<th>$R_v$ (nm) (eq. 1)</th>
<th>$\lbrack \eta \rbrack_{\text{cal}}$</th>
<th>$\lbrack \eta \rbrack_{\exp} - \lbrack \eta \rbrack_{\text{cal}}/\lbrack \eta \rbrack_{\text{cal}} \times 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS1</td>
<td>32.4</td>
<td>0.74</td>
<td>11.9</td>
<td>25.3</td>
<td>+28</td>
</tr>
<tr>
<td>VS2</td>
<td>50.2</td>
<td>0.67</td>
<td>17.8</td>
<td>40.2</td>
<td>+25</td>
</tr>
<tr>
<td>VS3</td>
<td>65.2</td>
<td>0.38</td>
<td>21.0</td>
<td>45.2</td>
<td>+44</td>
</tr>
</tbody>
</table>
although both polymers have the same composition and VS2 has the larger molecular weight. Core effects may play some role in this case. The larger expansion seen in VS3 may be caused by its larger PI content and/or its larger molecular weight, but more samples are required to disentangle these dependencies.

Intrinsic viscosities have been measured on VS1 in the two selective theta solvents at temperatures below the respective theta temperatures for each component. The results are given in Table V. This sample is symmetric in composition. The molecular dimensions change only slightly with temperature. Even 10° below the homopolymer theta temperatures, the miktoarm star polymer has larger dimensions than calculated. There is no indication of a sudden collapse of the molecules from the theta state.

### Dynamic Light Scattering Measurements

Assuming that the ratio $R_h/<S^2>^{1/2}$ is constant for 16-arm stars in good and theta solvents, the hydrodynamic radius of the star copolymer can be estimated from

$$R_{h,copol} = \left( R_{h,A}^2 w_A + R_{h,B}^2 w_B \right)^{1/2} \quad (7)$$

where $R_{h,A}$ and $R_{h,B}$ are the hydrodynamic radii of the 16-arm homopolymer stars with molecular weight equal to the copolymer. $R_{h,A}$ and $R_{h,B}$ are obtained in an analogous way from data on linear homopolymers and the hydrodynamic branching factor $h$,

$$h = R_{h,star}/R_{h,linear} \quad (8)$$

By interpolation of literature data\textsuperscript{33–35} we have $h = 0.687$ for 16-arm stars in good solvents and $h = 0.741$ for theta solvents. We use the following equations for PS and PI in THF and cyclohexane ($R_h$ given in nm):

**PS:**

- in THF at 25°C: $R_h = 1.37 \times 10^{-9} M_w^{0.564}$
- in cyclohexane at 35°C: $R_h = 2.255 \times 10^{-9} M_w^{0.5}$

**PI:**

- in cyclohexane at 25°C: $R_h = 1.23 \times 10^{-9} M_w^{0.584}$

These equations allow for the calculation of $R_h$ for the PS and PI homopolymer stars. Unfortunately, literature data for PI in

### Table V. Viscometric Results for Sample VS1 at Different Temperatures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$[\eta]$ (mL/g)</th>
<th>$k_H$</th>
<th>$R_v$ (nm)</th>
<th>$[\eta]$ (mL/g)</th>
<th>$k_H$</th>
<th>$R_v$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta$-state</td>
<td>44.8</td>
<td>0.78</td>
<td>13.3</td>
<td>32.4</td>
<td>0.74</td>
<td>11.9</td>
</tr>
<tr>
<td>30°C</td>
<td>44.9</td>
<td>0.72</td>
<td>13.3</td>
<td>30.8</td>
<td>0.64</td>
<td>11.7</td>
</tr>
<tr>
<td>25°C</td>
<td>43.5</td>
<td>0.75</td>
<td>13.1</td>
<td>29.4</td>
<td>0.76</td>
<td>11.5</td>
</tr>
<tr>
<td>Calculated</td>
<td>35.2</td>
<td>12.2</td>
<td>25.3</td>
<td>25.3</td>
<td>11.0</td>
<td></td>
</tr>
</tbody>
</table>

### Table VI. Dynamic Light Scattering Results for the Vergina Star Copolymers in THF at 25°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D_v \times 10^7$ (cm$^2$/s)</th>
<th>$k_D$ (mL/g)</th>
<th>$R_h$ (nm)</th>
<th>$R_{h,cal}$ (nm)</th>
<th>$R_{h,exp}$ – $R_{h,cal}/R_{h,cal} \times 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS1</td>
<td>3.19</td>
<td>47</td>
<td>14.8</td>
<td>13.3</td>
<td>+11</td>
</tr>
<tr>
<td>VS2</td>
<td>2.36</td>
<td>68</td>
<td>20.0</td>
<td>20.7</td>
<td>-3</td>
</tr>
<tr>
<td>VS3</td>
<td>1.90</td>
<td>118</td>
<td>24.8</td>
<td>23.9</td>
<td>+4</td>
</tr>
</tbody>
</table>
THF and PS and PI in dioxane are not available. Therefore, comparisons between experimental and calculated values are limited to THF and cyclohexane (in the case of THF the data of PI in cyclohexane are used since both solvents are good for PI). The results obtained in the three solvents are given in Tables VI–VIII.

The expected dependences for $D_0$ and $k_D$ on molecular weight are observed. $D_0$ decreases and $k_D$ increases with molecular weight in all solvents. It is interesting to note that $R_h$ and $k_D$ values in cyclohexane are only slightly less than in THF. The contraction of the PS fraction therefore causes only small changes in the hydrodynamic volume and the thermodynamic and the hydrodynamic interactions [\[k_D = 2A_2M - k_0 |(4\pi/3)N_A(kD/M)| - v^{36}\] where $A_2$ is the second virial coefficient, $M$ the molecular weight, $v$ the partial molar volume, $N_A$ Avogadro’s number, and $k_0$ is a constant associated with $k_f$, $k_f = k_0N_AV_H/M$, the coefficient in the concentration dependence of the friction coefficient, $f = f_0(1 + kfc)$]. In contrast, $R_h$ in dioxane is substantially lower and $k_D$ are only slightly positive indicating that the thermodynamic term in $k_D$ has decreased. The behavior of $k_D$ for the miktoarm stars must have some relation to the behavior of $k_D$ for the homopolymers. Literature data reveal that $k_D$ for linear PS in cyclohexane is negative but small.\(^{40}\) Unfortunately, such data for linear PI in dioxane are not available. Following this reasoning, one would expect that $k_D$ for the Vergina stars in cyclohexane should be minimally altered compared to its value in THF; whereas in dioxane, $k_D$ should decrease considerably, if the $k_D$ values for linear PI in the same solvent are negative but large. These changes from a common good solvent to selective $\theta$ solvents are parallel to the observations on $[\eta]$.

The differences in experimental and calculated $R_h$ values are expected to be 1/3 of the differences observed in intrinsic viscosity measurements. Consequently the differences in THF, the good solvent, are small and within experimental error (Tables II and VI). In cyclohexane (Tables III and VII), the agreement is qualitatively correct and the experimental results from viscometry are confirmed by dynamic light scattering.

The ratio $R_f/R_h$ in the different solvents are given in Table IX. In all cases, the ratio is close to unity as is common to star branched polymers.\(^{33–35}\)

It should be mentioned that increased lamellae spacing in the bulk of the same samples\(^{41}\) has been observed by transmission electron microscopy and small angle X-ray scattering, in comparison to linear diblocks of the same composition and block lengths. This may be related to the expanded conformation found in the isolated molecule in solution.

## CONCLUSIONS

The analysis of the results from viscometry and dynamic light scattering on three PS\(_8\)PI\(_8\) miktoarm star copolymers in cyclohexane at 34.5°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D_0 \times 10^7$ (cm(^2)/s)</th>
<th>$k_D$ (mL/g)</th>
<th>$R_h$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS1</td>
<td>2.10</td>
<td>41</td>
<td>14.0</td>
</tr>
<tr>
<td>VS2</td>
<td>1.53</td>
<td>66</td>
<td>19.3</td>
</tr>
<tr>
<td>VS3</td>
<td>1.22</td>
<td>102</td>
<td>24.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D_0 \times 10^7$ (cm(^2)/s)</th>
<th>$k_D$ (mL/g)</th>
<th>$R_h$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS1</td>
<td>1.75</td>
<td>15</td>
<td>12.7</td>
</tr>
<tr>
<td>VS2</td>
<td>1.27</td>
<td>35</td>
<td>17.5</td>
</tr>
<tr>
<td>VS3</td>
<td>1.11</td>
<td>27</td>
<td>19.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_f/R_h$ good</th>
<th>$R_f/R_h$ cyclohexane</th>
<th>$R_f/R_h$ dioxane</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS1</td>
<td>0.92</td>
<td>0.95</td>
<td>0.94</td>
</tr>
<tr>
<td>VS2</td>
<td>1.00</td>
<td>1.00</td>
<td>1.02</td>
</tr>
<tr>
<td>VS3</td>
<td>1.01</td>
<td>1.02</td>
<td>1.06</td>
</tr>
</tbody>
</table>
toarm (Vergina) stars strongly suggests that expansion of the molecular dimensions occurs in comparison to homopolymer stars of the same molecular weight and number of arms. The phenomenon is observed both in good and selectively theta solvents and it is more pronounced in the latter case. These 16-armed star copolymers are found to have a compact structure in dilute solutions.

REFERENCES AND NOTES