Notes

Reevaluation of Light Scattering from Living Polymer Solutions

N. P. Balsara*

Department of Chemical Engineering and Chemistry, Polytechnic University, Six Metrotech Center, Brooklyn, New York 11201

L. J. Fetters

Exxon Research and Engineering Company, Corporate Research Laboratories, 1554 Route 22 East, Annandale, New Jersey 08801-0998

Received November 30, 1998

Revised Manuscript Received April 27, 1999

In a previous paper, we studied light scattering from living solutions of dienyllithium headgroups in benzene.[1] The data indicated the presence of large-scale aggregates. The shape of the aggregates was determined by a combination of static and dynamic light scattering. The dynamic light scattering experiments indicated that the hydrodynamic radius (R_h) of the aggregates was 111 nm. We considered ellipsoids (oblate and prolate ellipsoids) that would give $R_h = 111$ nm, and these structures are summarized in Table 1. We assume that the ellipsoids are obtained by revolving ellipses with semi-axes a and b about the a axis. We used the static light scattering results from the living solutions to distinguish between these possibilities. The static light scattering intensity, I, as a function of scattering vector, Q, is shown in Figure 1. In addition, we show the theoretical scattering curves for dilute suspensions of the ellipsoids given in Table 1. Such a comparison was shown in Figure 8 of ref 1, but the theoretical curves were incorrect, as shown in ref 2. Equation 8 in ref 1 applies to ellipsoids obtained by rotation about the b axis while in the remainder of the text we assume that the rotation is about the a axis. This inconsistency has been corrected and the resulting curves are shown in Figure 1. It is evident in Figure 1 that theoretical curves from prolate ellipsoids with $a = 5$ nm and $b = 608$ nm are closest to the experimental data. The aggregates are thus approximated as thin cylindrical structures with a length of 1200 nm. In ref 1, the cylinder length was estimated to be about 800 nm due to the error. Since the length of the cylinder was not used in subsequent calculations, all of the other conclusions in ref 1 are unaffected by this error.

We noted in ref 1 that "the actual micellar structure is quite likely to be far more intricate than the models that we have considered." In addition, our model does not account for effects such as polydispersity of the aggregates. In recent work, Stellbrink et al.[3−5] have shown that the aggregates involving styrene and butadiene headgroups in living polymer solutions show characteristics of mass fractals. Hence, the lack of quantitative agreement between theory and experiment in Figure 1 is thus not entirely surprising.

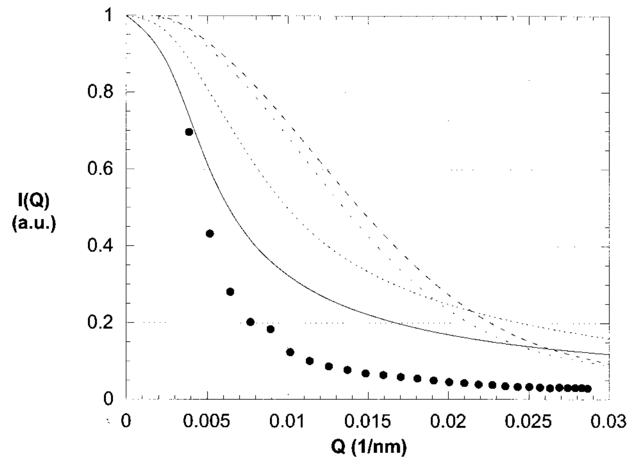

Figure 1. Scattering intensity I vs scattering vector Q from a living polymer solution (symbols) compared with theoretical predictions for a dilute suspension of ellipsoids (curves) described in Table 1. Data were taken from ref 1. Curves are distinguished by the magnitude of the major semi-axis. Oblates: 159 nm (large dashes); 172 nm (small dashes). Prolates: 382 nm (dashes); 608 nm (solid curve). See Table 1 for other dimensions.

Table 1. Dimensions of Ellipsoidal Particles with $R_h = 111.1$ nm (Figure 1)

minor semi-axis (nm)	major semi-axis (prolate)	major semi-axis (oblate)
5	608	172
25	382	159

Bywater[2] ascribed the static light scattering data of the living solution to dust. However, *direct* experimental evidence is given in ref 1 that contradicts that notion. An examination of our[1] Figure 7 shows that the recorded static intensity of the terminated solution is independent of Q over the angular range 35−150°. Conversely, the living parent system shows Q-dependent scattering as exemplified by a strong upturn in the lower Q range. This latter data set arose from the living polymer solution, which supplied the terminated system. Thus, it is clear that for the living solution the Q-dependent intensity is the signature of self-assembled headgroups since it is absent in the terminated counterpart. The foregoing scenario involving the terminated solution was replicated by the dynamic light scattering behavior, Figure 4 of ref 1. It is also worth mentioning that the scattering behavior of the d_6-benzene taken from the reactor (Pyrex cell) prior to the polymerization showed only Q-independent incoherent scattering.

Bywater[2] also impugns the isolation procedure of the terminated solution. In essence his stance is based on the perceived presence of lithium methoxide in the terminated solution and its deleterious influence on the

10.1021/ma981842+ CCC: $18.00
Published on Web 06/25/1999

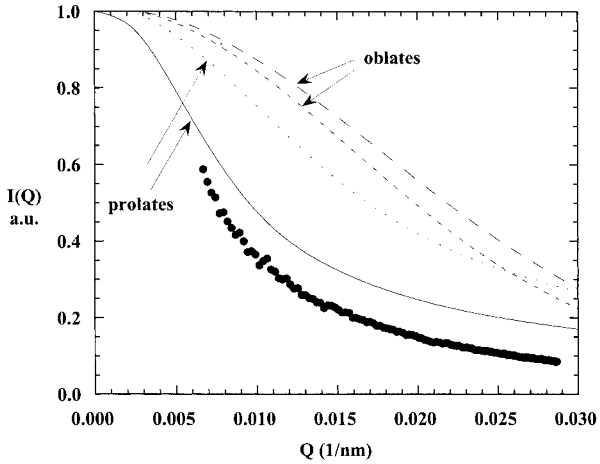

Figure 2. Scattering intensity I vs scattering vector Q from a block copolymer solution (symbols) compared with theoretical predictions for a dilute suspension of ellipsoids (curves) described in Table 2. Data were taken from ref 6. Curves are distinguished by the magnitude of the major semi-axis. Oblates: 104 nm (large dashes); 117 nm (small dashes). Prolates: 220 nm (dashes); 405 nm (solid curve). See Table 2 for other dimensions.

scattering intensity. A reading of our experimental procedure[1] reveals that methanol-d_4 was used for termination. This was done in order to create the necessary difference in densities between the d_6-benzene and the lithium methoxide byproduct. Thus, the terminated system was allowed to remain under vacuum in the reactor for several weeks in order for the methoxide to coagulate and settle. The terminated solution was then captured in a Pyrex cell. While this procedure does not in itself guarantee that particulate matter was wholly absent, the subsequent light scattering evaluations failed to show the scattering anomalies associated with the presence of such material.

Table 2. Dimensions of Ellipsoidal Particles with R_h = 76.4 nm (Figure 2)

minor semi-axis (nm)	major semi-axis (prolate)	major semi-axis (oblate)
4	405	117
25	220	104

The methodology described in the first paragraph of this paper was also used in another study wherein the structure of hydrogen-bonded block copolymer micelles in a selective solvent was studied by light scattering.[6] The results of this study were similar to those obtained from the living solutions.[1] The same error was made in the analysis of the light scattering data in ref 6. We use this opportunity to present the correct analysis of the data presented in ref 6. The value of R_h obtained for the hydrogen-bonded micelles was 76.4 nm, and the dimensions of the prolate and oblate ellipsoids that are consistent with this R_h are given in Table 2. In Figure 2 we show the scattering data given in ref 6 along with the corrected theoretical scattering curves. In this case the best agreement between theory and experiment is obtained for the case of prolate ellipsoids with $a = 4$ nm and $b = 405$ nm. This implies the presence of thin cylindrical micelles with length of 800 nm. In ref 6 the cylinder length was estimated to be 500 nm.

References and Notes

(1) Fetters, L. J.; Balsara, N. P.; Huang, J. S.; Jeon, H. S.; Almdal, K.; Lin, M. Y. *Macromolecules* **1995**, *28*, 4996.
(2) Bywater, S. *Macromolecules* **1998**, *31*, 6010.
(3) Stellbrink, J.; Willner, L.; Jucknischke, O.; Richter, D.; Lindner, P.; Fetters, L. J.; Huang, J. S. *Macromolecules* **1998**, *31*, 4189.
(4) Stellbrink, J.; Willner, L.; Richter, D.; Lindner, P.; Fetters, L. J.; Huang, J. *Macromolecules*, submitted for publication.
(5) Fetters, L. J.; Huang, J. S.; Sung, J.; Willner, L.; Stellbrink, J.; Richter, D.; Lindner, P. In *Applications of Anionic Polymerization Research;* Quirk, R. P., Ed.; ACS Symposium Series 696; American Chemical Society: Washington, DC, 1998, p 36.
(6) Zhao, J. Q.; Pearce, E. M.; Kwei, T. K.; Jeon, H. S.; Kesani, P. K.; Balsara, N. P. *Macromolecules* **1995**, *28*, 1972.

MA981842+