Aggregate Formation in Poly(ethylene oxide) Solutions

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ABSTRACT: Static light scattering and viscosity measurements were performed on different molecular weight poly (ethylene oxide) to see the formation of aggregates in its dilute solutions. Viscosity measurements were carried out for PEO samples in water and methanol at 20–45°C and in chloroform at 20–30°C. Using Huggin's equation, the viscosity plots showed distinct upward curvature indicating the presence of aggregates in both PEO/H_2O and PEO/CH_3OH solutions The [η] values for PEO/H_2O and PEO/CH_3OH system were 2–4 times as large as observed for other linear flexible polymers in good solvents thus showing extensive coil swelling/aggregation. This is also apparent from the exponent *a* values of the Mark–Houwink–Sakurada equation. Light Scattering results using Zimm method showed that aggregation occurred in low molecular weight samples; however, in higher molecular weight samples there was a little evidence for aggregation both in water and methanol. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2578–2583, 2006

Key words: poly(ethylene oxide); aggregate formation; light scattering; viscosity; solution properties; water soluble polymers

INTRODUCTION

Solution properties and behavior of poly(ethylene oxide) (PEO) has been the subject of many studies because PEO is very important polymer due to its solubility in both aqueous as well as organic solvents. At room temperature, aqueous solutions of PEO are transparent. However, the concept of solubility of PEO in water and polar organic solvents is the object of some controversies. Indeed, while it is sometimes considered as molecularly dispersed,[1–3] light scattering or viscosity experiments often reveal the presence of large aggregates.[4–8] Polik and Burchard[4] have shown that the aggregation in aqueous solutions of low molecular weight PEO samples increases markedly upon heating but decreases above 60°C. Devanand et al.[9] were able to prepare aggregate-free solutions and have observed some extraordinary properties for PEO/H_2O system. The exponent obtained from power law relations of both static and dynamic single chain parameters are representative of asymptotically good solvents. The local structure of the solvent and site-specific interaction are shown not to affect power law exponents as expected. The actual value of A_2 (second Virial Coefficient), R_g (Radius of Gyration) and R_H (Hydrodynamic radius) are much larger than are typically found for linear flexible polymer in good solvent. The enormously high value for the ratios $P = R_g/R_H$, and $x = S/R_H$ (where S is coil "equivalent" hard sphere radius) for PEO/H_2O good solvent system have been partially explained by enhanced partial draining in coil exclusively swollen by the effect of excluded volume.

In contrast to the above findings, Polik and Burchard[4] have shown that aggregates of high and low density coexist with molecularly dispersed PEO. The high-density particles are probably spherulites and the low-density aggregates are noncrystalline micro gel particles. On heating the spherulites melt causing the weight fraction of micro gel to increase. The decrease of A_2 is consistent with the concept of hydrodynamic interaction, that is, the increase in the order of water molecules in the neighborhood of PEO. The [η] of aqueous PEO is only slightly influenced by the presence of globular aggregates. Duval and Sarazin[10] have claimed that aggregate formation in PEO solutions in methanol depend upon history of the samples and the sensitivity of the technique, but again their study is limited to the low molecular weight samples ($M_w = 6500$).

All of the above-mentioned work reveal that there is complete contradiction regarding the formation of aggregates in PEO solutions. That may be attributed to the fact that these studies were limited to only one solvent (mostly, methanol) and at room temperature. We feel that to clarify the situation the work in only one solvent and one temperature is not enough. In the present study we have performed the work in three different solvents, i.e., methanol, water, and chloroform and over a wide range of temperature and wide range of molecular weight.
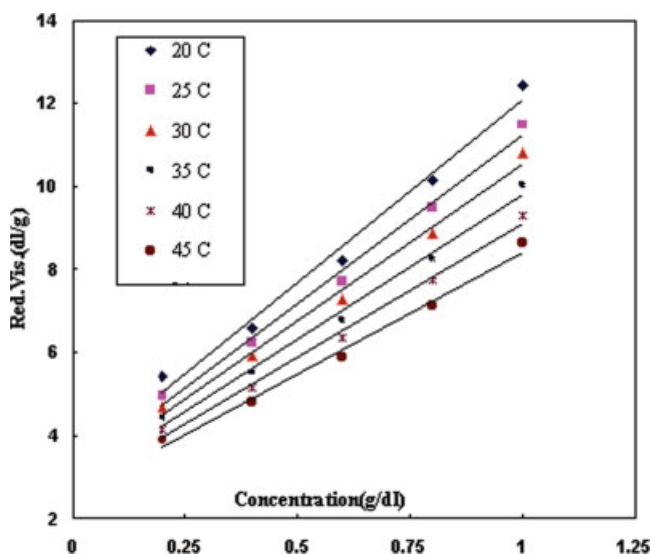
Figure 1 Plot of reduced viscosity versus concentration for PEO–water system (PEO Mw = 600,000). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

EXPERIMENTAL

Viscosity

Viscosity measurements were carried out for PEO samples in triply distilled water and methanol at 20–45°C and in chloroform at 20–30°C. For the flow time measurements we used a viscometer of the Ubbelhode type. Measurements were carried out at polymer concentration in the range from 0.2 to 1.0 g/dL in water and methanol and from 0.12 to 0.6 g/dL in chloroform. The flow time of each solution was measured to a precision of ±0.1 s and each solution was maintained at constant temperature within ±0.01°C during the measurements. The obtained data for η_{sp} and η_{red} for each solution series were treated by Huggins plots to evaluate intrinsic viscosity $[\eta]$.

Static light scattering

Light scattering is a standard technique to extract information about the size and structure as well as equilibrium polymer–polymer coil interactions of flexible, linear polymer chain in dilute solution. In this study, light scattering measurements were made by using Brookhaven Instruments Light Scattering photometer. The light source was a 60-mW He–Ne laser. All stock solutions were prepared gravimetrically and a concentration series was prepared (concentrations were same as described in the viscosity measurements) by diluting stock solution. To remove dust these solutions were pressed through a filter of defined pore size into the measuring cell beginning with the pure solvent as the blank followed by
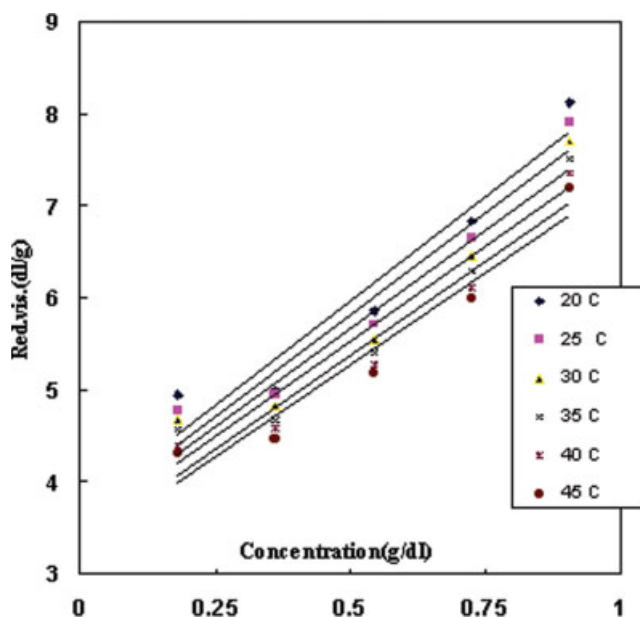
the polymer solution in order of increasing concentration.

Usually the measured scattering intensities are plotted according to Zimm[11] method. This method of data presentation is based on eq. (1).

$$\frac{K_c}{\Delta R_\theta} = \frac{1}{M_w P_{(\theta)}} + 2A_2 c + 3A_3 c^2 + \cdots \qquad (1)$$

Figure 2 Plot of reduced viscosity versus concentration for PEO–methanol system (PEO Mw = 600,000). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
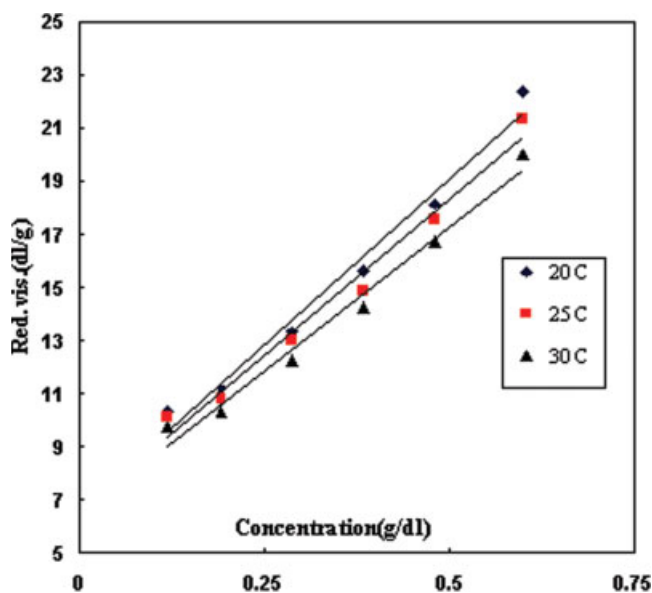

Figure 3 Plot of reduced viscosity versus concentration for PEO–chloroform system (PEO Mw = 600,000). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Values of Intrinsic Viscosity of Poly(ethylene oxide) in Water, Methanol, and Chloroform at Different Temperatures

| | M_w | | | | | |
| | [η] In water (dL/g) | | | [η] In methanol (dL/g) | | [η] In chloroform (dL/g) |
	625,000	896,000	1,038,000	647,000	860,000	647,000
20°C	4.37	–	–	3.7	–	8.01
25°C	4.07	5.21	6.3	3.6	–	7.78
30°C	3.87	4.93	6.05	3.5	4.15	7.72
35°C	3.65	4.5	5.61	3.39	3.95	–
40°C	3.43	4.18	5.29	3.32	3.76	–
45°C	3.22	3.81	4.9	3.16	3.54	–

where c is the polymer concentration in g mL^{-1}, M_w the weight average molecular weight, and A_2 and A_3 the second and third virial coefficients, respectively. K is the optical constant, and R_θ is the Rayleigh ratio of the measured excess of intensity of the solution over that of the solvent (blank), $P_{(\theta)}$ is the particle scattering function, and θ the scattering angle. In the case of vertically polarized incident light, the optical constant K is given by

$$K = \frac{4\pi^2 \times n_o^2 (\frac{\partial n}{\partial c})^2}{\lambda_o^4 \times N_a},$$

where n_o is the refractive index of the solvent, $\partial n / \partial c$ is the specific refractive index increment of the polymer/solvent system measured at dialysis equilibrium, λ_o is the wavelength of the light source in vacuum, and N_a in the Avogadro's number. The measured intensity was then plotted according to the Zimm equation [eq. (2)] given below:

$$\frac{KC}{\Delta R_\theta} = \frac{1}{M_w}\left[1 + \frac{16\pi^2 \langle R_g^2 \rangle \sin^2 \frac{\theta}{2}}{3\lambda^2}\right] + 2Bc + 3Cc^2 + \cdots \quad (2)$$

Here B and C represent the second and third virial coefficients i.e., A_2 and A_3, respectively.

RESULTS AND DISCUSSION

Viscosity measurements

The viscosity measurement results (η_{red}) of the present study in water, methanol, and chloroform were calculated and Huggin's plots of PEO solutions reduced viscosity (dL/g) against PEO concentration (g/dL) are represented in Figures 1–3.

PEO–PEO interactions are clearly evident in the distinct upward curvature of these plots of η_{red} versus concentrations. These plots were fitted according to Huggin's equation given below [eq. (3)]:

$$\eta_{red} = [\eta] + K_H[\eta]^2 c. \quad (3)$$

where η_{red} = reduced viscosity, K_H = Huggins coefficient, and $[\eta]$ = Intrinsic viscosity.

The PEO intrinsic viscosity $[\eta]$ and the Huggin's coefficient K_H are presented in Tables I and II respectively. Huggin's coefficient for PEO in water previously determined by Woodley et al.[2] were with a mean value of 0.26, a value typical for linear flexible polymers in good solvents.[3] The different K_H values for PEO sample in water and methanol as solvents as we determined from the present study may be because of two reasons (i) The Huggin's plots were not linear so there arises a difficulty in its linear fitting. To overcome

TABLE II
Values of Huggin's Coefficients for Poly(ethylene oxide) in Water, Methanol, and Chloroform at Different Temperatures

| | M_w | | | | | | |
| | PEO/H$_2$O | | | PEO/CH$_3$OH | | CHCl$_3$ | |
	625,000	896,000	1038,000	647,000	860,000	1055,000	647,000
20°C	0.15	–	–	0.17	–	–	0.28
25°C	0.17	0.12	0.14	0.18	–	–	0.29
30°C	0.19	0.14	0.14	0.19	0.16	–	0.29
35°C	0.21	0.17	0.16	0.21	0.18	–	–
40°C	0.23	0.20	0.18	0.22	0.21	–	–
45°C	0.26	0.24	0.20	0.25	0.29	–	–

this difficulty we derived the values of $[\eta]$ and K_H from the initial slopes of linear regression plots. The K_H values obtained from this treatment were distinctively in the good solvent range as evident from the Table II, (ii) the curvature found in the Huggin's plots at higher concentrations in water and more in methanol might be attributed to the formation of aggregates in these solvents. The aggregation behavior of PEO in water and methanol and its consequences has been a matter of concern in many studies.[4–8] It is still not clear, however, that whether PEO aggregation is an inherent property of these aqueous and methanolic solutions or not. This discrepancy in solvent quality has also been recorded by differences in the values of the exponent a in the relation between molecular weight (M) and intrinsic viscosity $[\eta]$ i.e., $[\eta] \propto M^a$ and have been ascribed to aggregation of the polymer in water.[12] On the other hand in methanol and chloroform the K_H values are those observed for polymers in good solvents.

PEO intrinsic viscosity i.e., $[\eta]$ values are distinctly larger than the values observed for other linear flexible polymers in good solvents. A rough comparison between PEO and certain other polymers with comparable molecular weight illustrates this point: PEO $[\eta]$ values are about three-fold larger than those for poly α(methyl styrene) (PαMS) in benzene[13] or toluene[14] and about twice as large as those observed for polystyrene in benzene.[15] The extensive swelling was also observed from the value of unusually large radius of gyration (R_g) for PEO. For example R_g values for a representative molecular weight of 500,000 were 452 Å for PEO in water at 30°C[9] while the corresponding values for PαMS in toluene at 25°C were 301.[16] Our values of R_g in water and methanol are unusually large which means there is something like aggregation present in solution. The PEO $[\eta]$ values in CHCl$_3$ are even much larger than those observed in water and in methanol solutions. These values of $[\eta]$ in water are consistent with the earlier determined values.[2] Figure 4 shows plots of log $[\eta]$ versus log M_w in water, respectively, according to
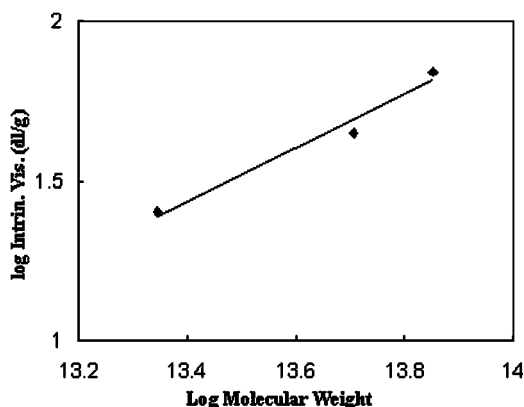
TABLE III
Values of Mark–Houwink–Sakurada k and Exponents a of Poly(ethylene oxide) in Water at Different Temperatures

T (°C)	$k \times 10^5$ (dL g^{-1})	a
25	6.103	0.83
30	5.044	0.84
35	8.812	0.80
40	8.424	0.79
45	2.515	0.75

Mark–Houwink–Sakurada (MHS) expression equation, i.e., $[\eta] = kM^a$. This power law expression for poly(ethylene oxide) in water obtained at 25°C is

$$[\eta] = 6.103 \times 10^{-5}M^{0.83} \ (dL/g) \qquad (4)$$

The exponent a value of 0.83 we obtained is slightly higher than the value obtained by Woodley et al. i.e., 0.79. The values of k and in water at other temperatures are given in Table III. The values of the exponents $a = 0.75$–0.83, which we obtained, reflect extensive coil swelling/aggregation due to the excluded volume effects and lead to the conclusion that PEO/H$_2$O system exhibits asymptotic good solvent behavior, already in molecular weight range 10^5–10^6. The values for k and a for PEO/H$_2$O good solvent system are also in accordance with the earlier experimentally determined values for the same system of Woodley et al.[2] for higher molecular weight poly(ethylene oxide), though the exponent a has been found to have a lower value for lower molecular weight poly(ethylene oxide). They have found the values of $k = (1.1 \pm 0.48) \times 10^{-5}$ and $a = 0.791 \pm 0.032$ with $[\eta]$ expressed in mL/mg. for PEO/H$_2$O good solvent system, thus further supporting that there exist aggregation in the PEO/H$_2$O good solvent system.
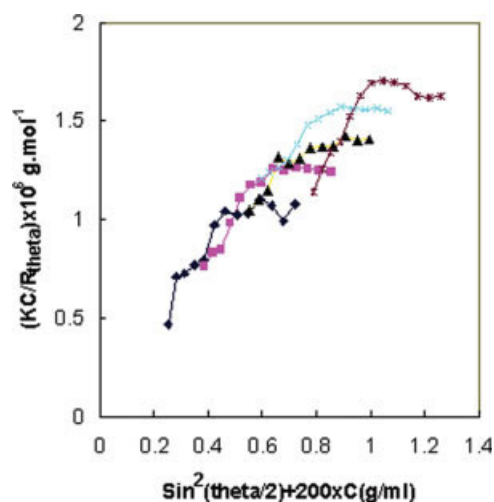

Figure 5 Zimm plot of Poly (Ethylene oxide) in water at 25°C (Sample no. PEO-1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 4 Plot of log intrinsic viscosity versus log Mw for PEO in water at 25°C.

Light scattering measurements

Static light scattering measurements were carried out over wide range of concentration and scattering angles. The data obtained was analyzed using the Zimm plot method. The excess inverse Raleigh ratio $(KC/\Delta R_\theta)$ were plotted against $\sin^2(\theta/2) + KC$. The corresponding Zimm plots for PEO/H$_2$O and PEO/CH$_3$OH are shown in Figures 5–8 (PEO 1 corresponds to $M_w = 100{,}000$ while PEO 10 corresponds to $M_w = 1{,}000{,}000$, only two samples graph are given for comparison of low and high molecular weight samples). From the slope of $(KC/\Delta R_\theta)_{\theta=0}$ versus concentration the molecular weight and second virial coefficient A_2 were determined and from the slope of $(KC/\Delta R_\theta)_{\theta=0}$ versus $\sin^2(\theta/2)$, R_g (Radius of gyration) was calculated. The molecular characteristics so obtained from the Zimm plot are given in Table IV for both solvents—water and methanol.

The molecular weight characteristics obtained in both water and methanol are very nearly similar. The molecular weights of these samples determined using Zimm method does not differ significantly from those of the manufacturer's values. The R_g values were fit to a log–log plot against molecular weight (Fig. 9) and the following relations were established by using a direct power law fit of R_g to M_w.

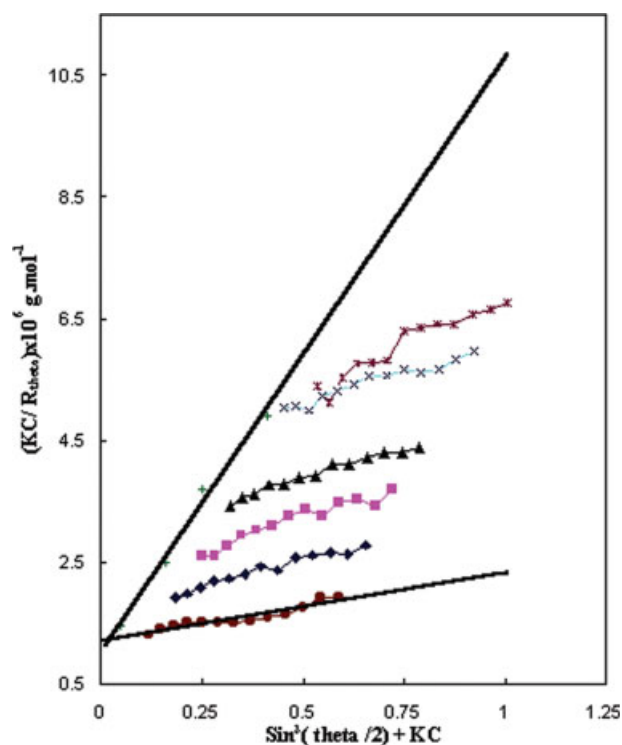$$R_g = 1.2 \times 10^{-3} M^{0.79} \quad \text{(in methanol)} \qquad (5)$$

Figure 7 Zimm plot of Poly (Ethylene oxide) in water at 25°C (Sample no. PEO-10). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$R_g = 9.2 \times 10^{-3} M^{0.65} \quad \text{(in water)} \qquad (6)$$

The values of the exponents a in both the solvents have achieved the asymptotic good solvent limit. Devanand and Selser[9] have obtained the exponent $a = 0.583$ in water and Kinugasa et al.[17] have obtained
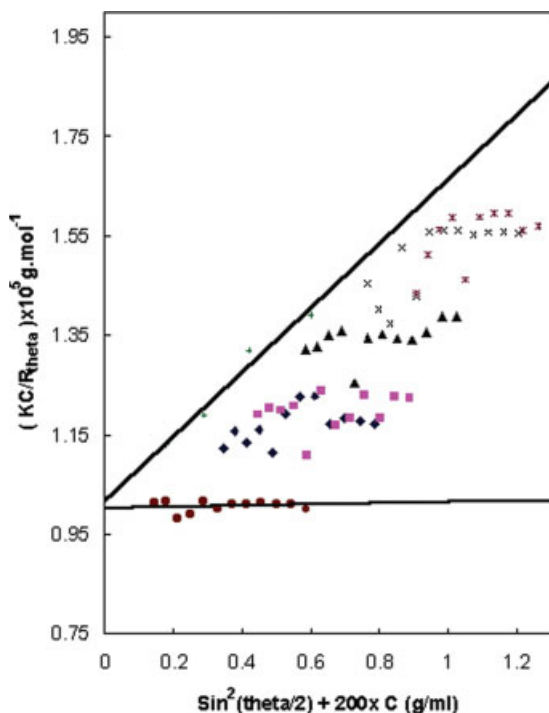

Figure 6 Zimm plot of Poly (Ethylene oxide) in methanol at 25°C (Sample no. PEO-1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 8 Zimm plot of Poly (Ethylene oxide) in methanol at 25°C (Sample no. PEO-10). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
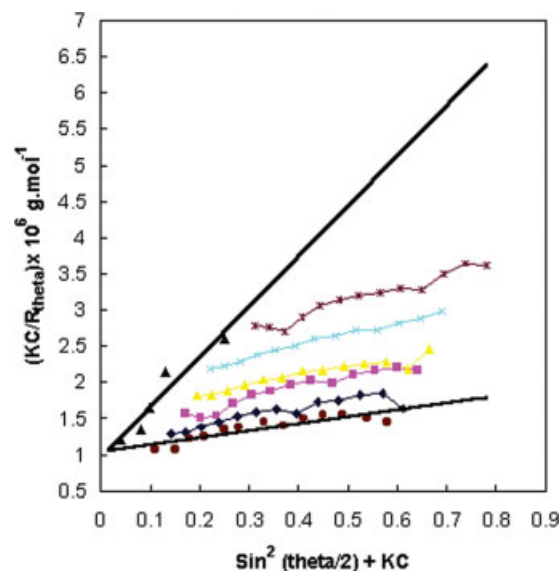
the exponent $a = 0.61$ in the log–log plot of R_g against M_w. The values of these exponents in both water and methanol are in good agreement both with the asymptotic values from Flory's prediction of 3/5.[18]

Aggregation

Aggregation in low molecular weight poly(ethylene oxide) is still uncertain. From the angular dependence of the scattered light, it has been shown that low molecular weight poly(ethylene oxide) has a pronounced tendency to aggregate.[4,7] In a study on PEO/H$_2$O and PEO/CH$_3$OH by Kinugasa et al. obtained good Zimm plots and in the plots of the angular dependence of $KC/\Delta R_\theta$ against $\sin^2(\theta/2)$. They observe no striking downturn at lower angles indicating that PEO disperse molecularly and particularly no aggregates exist in water. For stock solution preparation we followed the procedure adopted by Kinugasa et al.[17] We kept the solutions at 40–50°C in an oven for over night. But in spite of this treatment we were unable to obtain good Zimm plots like those indicating that some aggregate still exists in the PEO solutions even after heating treatment. For low molecular weight sample we observed a significant downturn at lower angles both in water and methanol as is evident from Figures 5 and 6. Similar behavior was also observed by Polik and Burchard[4] and Zhou and Brown.[10]

For high molecular weight PEO aqueous solutions Devanand and Selser[14] have given evidences that PEO does not necessarily aggregate in water, they obtained good Zimm plots with no downturn at lower angles. To obtain such aggregate free solutions they insisted on taking special care in preparing solutions and used highly purified water. However, Kinugasa et al.[17] showed from their experiments that special care in the preparation of PEO aqueous solutions is not necessary rather than to take special care in the solution preparation described by Devanand and Selser.[13]

CONCLUSIONS

Viscosity studies done on PEO solutions in water and methanol show slight upward curvature especially

TABLE IV
Molecular Characteristics Obtained for Poly(ethylene oxide) in Water and Methanol from Zimm Plots at 25°C

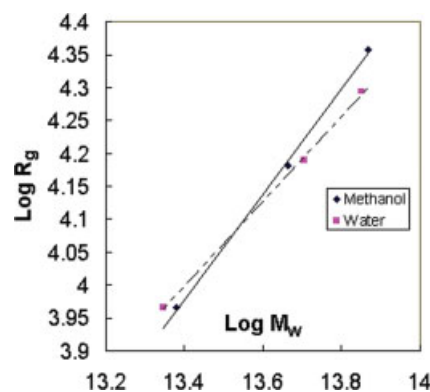| Solvent	M_w (g mol^{-1})	M_w/M_n^b (PDI)	$A_2 \times 10^4$ (mL mol g^{-2})	R_g (nm)
Water	625,000	1.04	6.57	52.75
	896,000	0.99	0.30	66.03
	1,038,000	1.04	9.65	73.28
Methanol	647,000	1.07	8.42	52.76
	860,000	0.96	3.57	65.44
	1,055,000	1.06	7.81	78.06

Figure 9 Log–log plot of PEO radius of gyration versus molecular weight in water and methanol at 25°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

more in methanol, which indicates the presence of aggregates. Due to curvature in the Huggin's plots, the intrinsic viscosity and Huggin's coefficient were determined from the initial slopes of these curved plots. The [η] values for PEO/H$_2$O and PEO/CH$_3$OH system were 2–4 times as large as observed for other linear flexible polymers in good solvents thus showing extensive coil swelling/aggregation. This is also apparent from the exponent a values of the Mark–Houwink–Sakurada equation. Light Scattering studies using Zimm plot method also showed the aggregation phenomenon in these solutions.

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