Studies on Miscibility of Polyacrylamide/Polyethylene Glycol Blends

T. M. Mruthyunjaya Swamy, Siddaramaiah

Department of Polymer Science and Technology, Sri Jayachamarajendra College of Engineering, Mysore 570 006, India

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ABSTRACT: Miscibility studies have been conducted on solutions of blends of polyacrylamide (PAAm) and polyethylene glycol (PEG) over an extended range of concentrations in water. The ultrasonic velocity, viscosity, density, and refractive index of the blends have been measured for different compositions viz., 0/100, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/30, 90/10, and 100/0 of PAAm/PEG blends at 30°C. The interaction parameters such as μ and α have been evaluated using the viscosity data to probe the miscibility. The obtained results have been confirmed by the ultrasonic velocity, density, and refractive index. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2048–2053, 2007

Key words: polymer blends; viscosity; ultrasonic velocity; refractive index; miscibility

INTRODUCTION

Most of the polymer blends are immiscible in nature. However, physical mixing of two or more polymers yields polymer blends. In recent years, there has been a great deal of interest in the studies of these polymer systems. The resulting blend systems often exhibit properties that are superior to any one of the component polymers.[1] However, the manifestation of superior properties depends upon the miscibility of homopolymers at the molecular scale. The miscibility results in altogether different morphology of the blends range from single-phase system to two-phase or multiphase systems. Different techniques have been used to evaluate the compatibility of polymer blends. These techniques have involved thermal and mechanical methods[2,3]; nuclear magnetic resonance (NMR) studies[4]; scattering techniques, such as the light scattering technique and neutron scattering, which provide valuable information about the thermodynamic behavior of blends[5,6]; calorimetric data for concentrated solutions in low molecular weight solvents[7,8]; measurement of vapor sorption[4] and inverse gas chromatography.[9–11] However, Chee[12] and Sun et al.[13] suggested the viscometric method for the study of polymer–polymer miscibility. Paladhi and Singh[14,15] showed that the variation of ultrasonic velocity and viscosity with blend composition is linear for miscible blends and nonlinear for immiscible blends. Viscometry becomes an attractive method for studying the compatibility of polymers in solution[15–20] due to its simplicity. In the present work, viscosity, ultrasonic velocity, density, and refractive index techniques were used to determine the miscibility of polyacrylamide (PAAm)/polyethylene glycol (PEG)-6000 and PAAm/PEG-4000 blends at 30°C.

The author selected PAAm, as it is used as flocculants, chemical grouts, stock additives for improving dry strength of paper, thickening agent, etc.[21] Similarly, PEGs also have many industrial applications like lubricants, binders, carriers, solvent, and coatings in the cosmetics, pharmaceutical, paper, food, textile, and chemical specialty field.[23]

EXPERIMENTAL

Polyacrylamide (PAAm) was synthesized in the laboratory as the procedure reported elsewhere.[24] Its molecular weight was determined by viscosity method and found to be $\overline{M}_V = 2{,}08{,}000$. PAAm is a white odorless solid, soluble in water and insoluble in methanol, ethanol, acetone, and hexane. PEGs [$\overline{M}_V = 6000$ and $\overline{M}_V = 4000$] were purchased from E. Merck (Mumbai, India). A dilute polymer solution of 2% w/v was prepared for all the methods. Stock solutions of homopolymers and blends of PAAm/PEG-6000 and PAAm/PEG-4000 of different compositions viz., 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, and 90/10 were prepared in water. Viscosity and density measurements at 30°C were made using Ubbelohde suspended level viscometer

Correspondence to: Siddaramaiah (siddaramaiah@yahoo.com).

TABLE I
The Reduced Viscosity Data for PAAm, PEG-6000, and Their 50/50 Blend Composition in Water at 30°C

Concentration (g/dL)	η_{SP}/C (dL/g) PAAm	PEG-6000	PAAm/PEG-6000 (50/50)	PEG-4000	PAAm/PEG-4000 (50/50)
2.00	4.59	0.20	1.63	0.18	1.55
1.80	4.22	0.19	1.54	0.18	1.49
1.60	3.98	0.18	1.46	0.17	1.42
1.40	3.61	0.18	1.40	0.16	1.35
1.20	3.31	0.17	1.33	0.16	1.29
1.00	3.01	0.17	1.27	0.15	1.22
0.80	2.65	0.16	1.19	0.14	1.16
0.60	2.33	0.15	1.12	0.13	1.09
0.40	2.10	0.14	1.05	0.13	1.02
0.20	1.83	0.13	0.98	0.12	0.95

(USLV) and specific gravity bottle, respectively. The required temperature was maintained within ±0.05°C.

The ultrasonic interferometric technique was used to measure ultrasonic velocities of different blend compositions viz., 0/100, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, and 90/10 at 30°C. The temperature was maintained by circulating water from a thermostat with a thermal stability of ± 0.05°C through the double-walled jacket of the experimental cell. The experimental frequency was 2 MHz and the velocity measurements were accurate to better than ± 0.05%.

The refractive indices of blend solutions with different compositions—0/100, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, and 90/10—were measured directly with an Abbe's refractometer with thermostated water circulated system at 30°C. The accuracy of the refractive index measurement is ± 0.02%.

RESULTS AND DISCUSSION

Reduced viscosity measurement studies

The measured values of reduced viscosity data for PAAm, PEG-6000, PEG-4000, PAAm/PEG-6000 (50/50), and PAAm/PEG-4000 (50/50) at 30°C are presented in Table I. Figures 1 and 2 show the Huggins plots of reduced viscosity versus concentration for the pure components and their blends at 30°C. For both the blends, the weight fractions of both the components were maintained at 1.0. For comparison, the

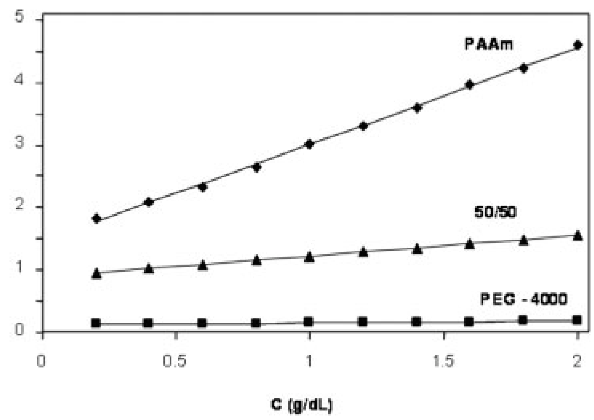

Figure 2 Huggins plot for 1% w/v PAAm/PEG-4000 blend in water at 30°C.

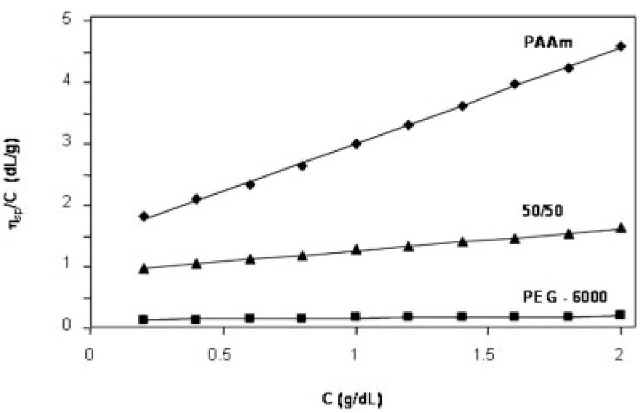

Figure 1 Huggins plot for 1% w/v PAAm/PEG-6000 blend in water at 30°C.

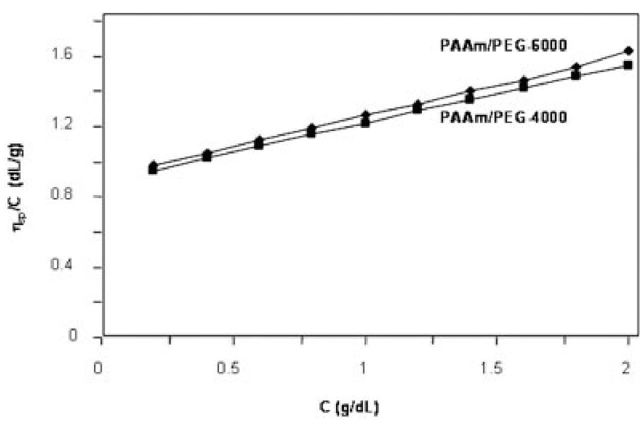

Figure 3 Effect of reduced viscosity for 50/50 wt %, 2% w/v PAAm/PEG blends in water at 30°C.

TABLE II
The Interaction Parameters μ and α of 2% w/v PAAm/PEG-6000 and PAAm/PEG-4000 Blends in Water at 30°C

Composition of PAAm/PEG (wt %)	2% w/v PAAm/ PEG-6000		2% w/v PAAm/ PEG-4000	
	μ	α	μ	α
10/90	−0.3990	−5.5686	−0.3914	−6.2604
20/80	−0.3917	−3.4131	−0.3817	−1.2721
30/70	−0.3588	−2.2283	−0.3505	−2.3256
40/60	−0.2888	−1.4672	−0.2999	−1.5628
50/50	−0.2257	−1.0784	−0.2383	−1.1365
60/40	−0.1566	−0.8307	−0.1521	−0.1506
70/30	−0.0905	−0.6805	−0.1197	−0.7241
80/20	+0.0621	−0.4442	−0.0640	−06079
90/10	+0.2247	−0.2473	+0.0498	−0.4520

plots of reduced viscosity as a function of concentration of both blends are shown in Figure 3. As expected the blends of high molecular weight PEG (PEG-6000) showed high reduced viscosity values as compared to corresponding low molecular weight PEG blends with PAAm. The results obtained by the linear least squares treatment of Huggins plot are summarized in Table II. From the table it was noticed that η, *b*, and k_H values of the blends lie between the corresponding values of the homopolymers. The η and *b* values for blends are <1.

To quantify the miscibility of the polymer blends, Chee[12] suggested the general expression for the interaction parameter when the polymers are mixed in weight fractions w_1 and w_2 as

$$\Delta B = \frac{b - \bar{b}}{2w_1w_2} \quad (1)$$

where $\bar{b} = w_1b_{11} + w_2b_{22}$, where b_{11} and b_{22} are the slopes of the viscosity plots for the Components 1 and 2 and is related to Huggins coefficient k_H as

$$b = k_H[\eta]^2 \quad (2)$$

For ternary system, it is also given by

$$b = w_1^2b_{11} + w_2^2b_{22} + 2w_1w_2b_{12} \quad (3)$$

where b_{12} is slope for the blend solution.

TABLE III
Viscometric and Thermodynamic Data for Blends Containing PAAm/PEG

		η (dL/g)	b (dL/g)^2	R^2	k_H
PAAm-PEG 6000	PAAm	3.097	1.459	0.9982	0.152
	PEG-6000	0.100	0.120	0.9999	12.000
	50/50	0.707	0.908	0.9988	1.815
PAAm-PEG 4000	PAAm	3.097	1.459	0.9982	0.152
	PEG-4000	0.070	0.113	0.9802	22.925
	50/50	0.665	0.888	0.9997	2.005

However, Chee's theory fails to account the experimental data when the intrinsic viscosities for the pure components are far apart. In such cases, he defined a more efficient interaction parameter to predict the compatibility,

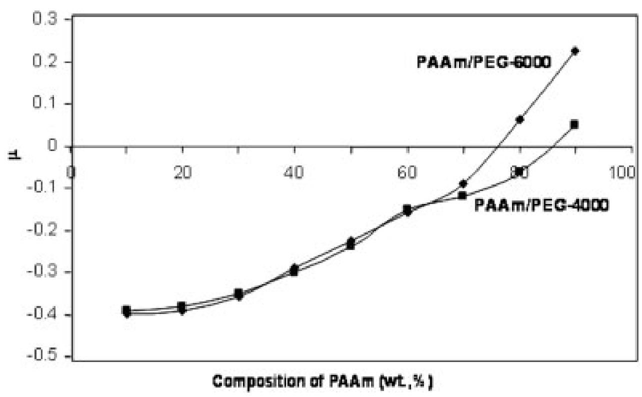

Figure 4 Plot of interaction parameter μ as a function of compositions of PAAm/PEG blends in water at 30°C.

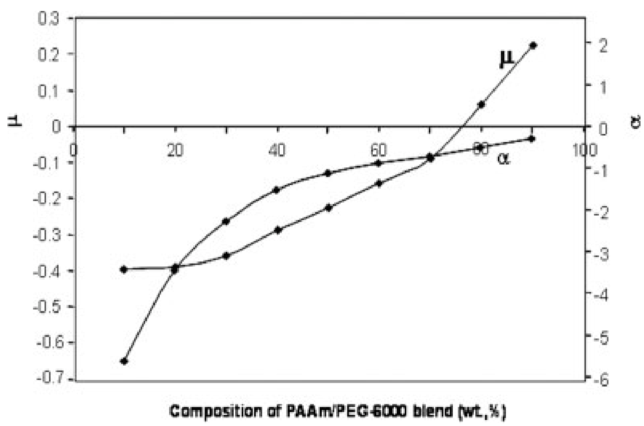

Figure 5 Plot of interaction parameters μ and α as a function of compositions of PAAm/PEG blends in water at 30°C.

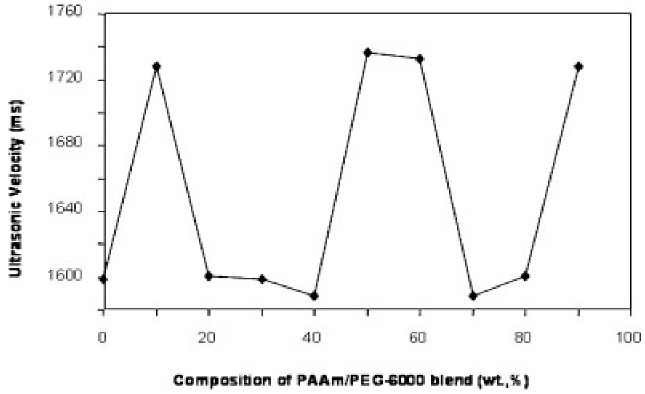

Figure 6 Variation of ultrasonic velocity with composition of PAAm/PEG-6000 blends in water at 30°C.

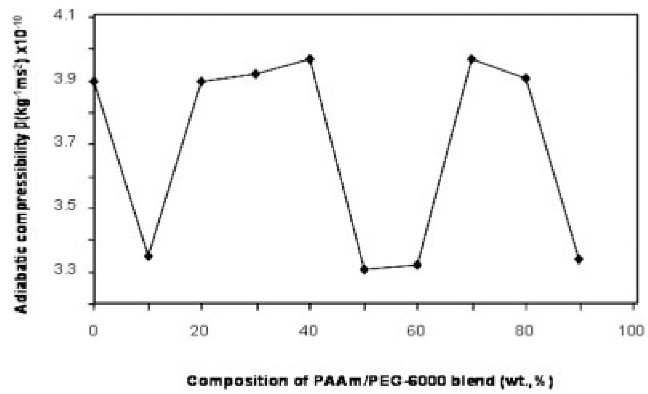

Figure 8 Variation of adiabatic compressibility with composition of PAAm/PEG-6000 blends in water at 30°C.

$$\mu = \frac{\Delta B}{\{[\eta]_2 - [\eta]_1\}^2} \tag{4}$$

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure components solution. The polymer blend is miscible if $\mu \geq 0$ and immiscible when $\mu < 0$.

Recently, Sun et al.[13] suggested a most satisfactory new equation for the determination of polymer miscibility as

$$\alpha = k_m - \frac{k_1[\eta]_1^2 w_1^2 + k_2[\eta]_2^2 w_2^2 + 2\sqrt{k_1 k_2 [\eta]_1 [\eta]_2 w_1 w_2}}{\{[\eta]_1 w_1 - [\eta]_2 w_2\}^2} \tag{5}$$

where k_1, k_2, and k_m are the Huggins constants for individual Components 1, 2, and blend, respectively. The long-range hydrodynamic interactions are considered while deriving the equation. The polymer blend is miscible if $\alpha \geq 0$ and immiscible when $\alpha < 0$.

The computed interaction parameters μ and α for PAAm/PEG-6000 and PAAm/PEG-4000 are presented in Table III. The plots of μ as a function of composition of PAAm content for both PAAm/PEG blends are shown in Figure 4. For comparison, the variation of μ and α with PAAm composition for PAAm/PEG-6000 blend is shown in Figure 5. From these figures, it was noticed that the μ value is positive for higher composition of PAAm in the blend, i.e., beyond the 80% by weight of PAAm.

For PAAm/PEG-6000 blend, it is observed from this table that the μ values are negative upto 70/30 composition and positive beyond this value, but the α values are found to be negative over all the composition range. The μ and α values give contradictory information for 80/20 and 90/10 blend compositions. Similarly, for PAAm/PEG-4000 blend, the μ values are negative upto 80/20 composition and then positive beyond this value, whereas α values give contradictory information for only 90/10 blend composition. Hence, it can be stated that the PAAm/PEG-6000 and PAAm/PEG-4000 blends are completely immiscible over all the composition range.

Ultrasonic velocity, density, adiabatic compressibility, and refractive index measurement studies

To confirm the exact nature of the PAAm/PEG-6000 and PAAm/PEG-4000 blends, the measured values

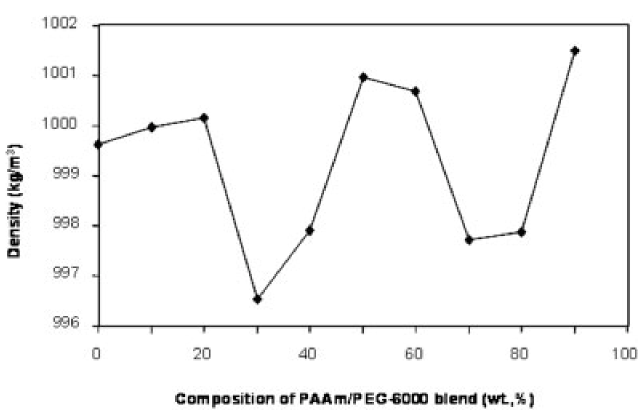

Figure 7 Variation of density with composition of PAAm/PEG-6000 blends in water at 30°C.

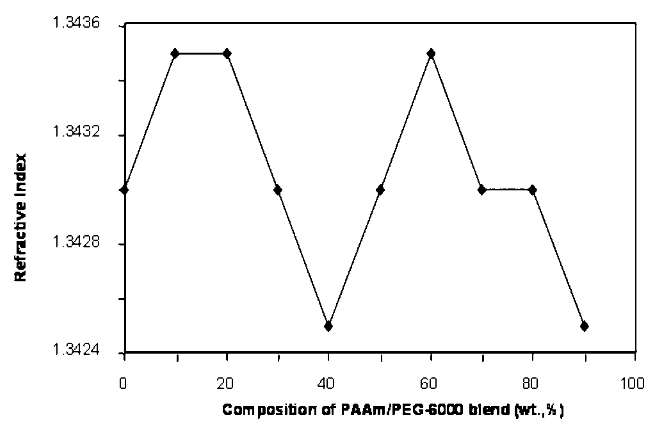

Figure 9 Variation of refractive index with the composition of PAAm/PEG-6000 blends in water at 30°C.

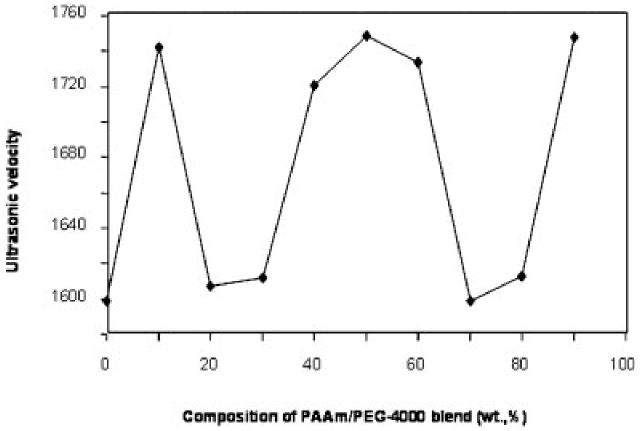

Figure 10 Variation of ultrasonic velocity with the composition of PAAm/PEG-4000 blends in water at 30°C.

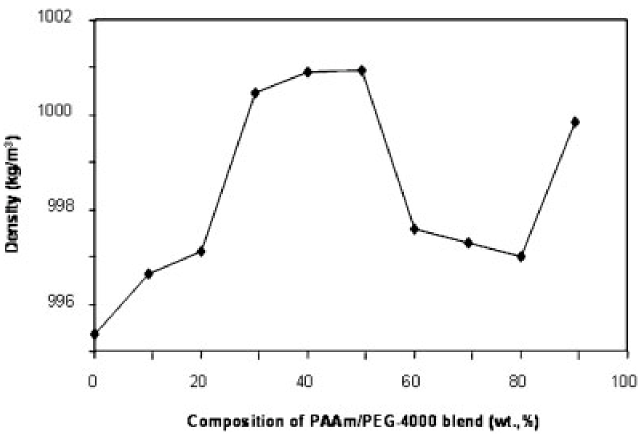

Figure 11 Variation of density with the composition of PAAm/PEG-4000 blends in water at 30°C.

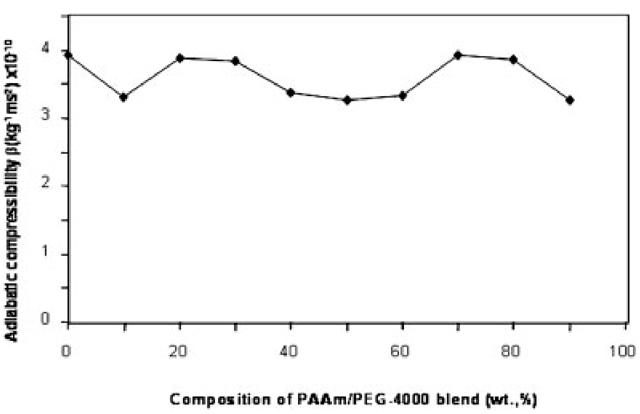

Figure 12 Variation of adiabatic compressibility with the composition of PAAm/PEG-4000 blends in water at 30°C.

of ultrasonic velocity, density, and refractive index are presented in Table III. The variations of ultrasonic velocity, density, adiabatic compressibility (β_{ad}), and refractive index against blend compositions were plotted for PAAm/PEG-6000 and PAAm/PEG-4000

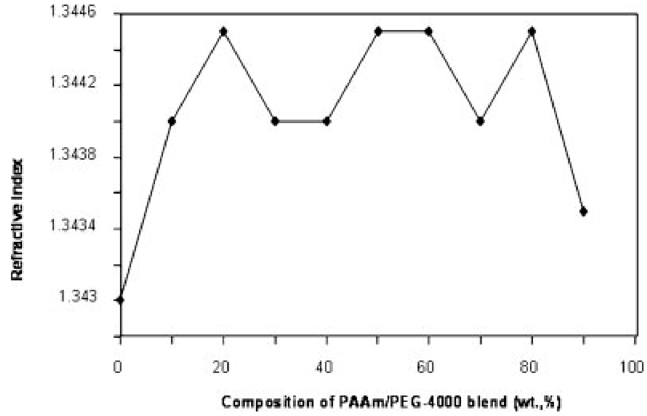

Figure 13 Variation of refractive index with the composition of PAAm/PEG-4000 blends in water at 30°C.

blends in Figures 6–9 and 10–13, respectively. These graphs show only nonlinear regions over all the composition range and it was already established that the variation is linear for miscible and nonlinear for immiscible blends.[15,22] In the present investigation, the nonlinearity in the graphs indicates the immiscibility of both the blends due to the phase separation at 30°C.

The nonlinearity in the graphs may be due to the absence or weak hydrogen-bonding or dipole–dipole interactions between the amide group of PAAm and ether group of PEG in the blend. These observations are in conformity with the α values based on Sun et al. method. Hence, the present investigation indicates that the PAAm/PEG-6000 and PAAm/PEG-4000 blends at 30°C are completely immiscible over the entire composition range.

CONCLUSIONS

Based on viscosity, density, ultrasonic velocity, and refractive index measurements, it can be concluded that both the blends of PAAm/PEG-6000 and PAAm/PEG-4000 are found to be completely immiscible over all the composition range at 30°C. However, on the basis of interaction parameter μ, it can be concluded that both PAAm/PEG blends with 80/20 and 90/10 are miscible in nature, because their μ values are positive.

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