Overlap Concentration of an Aqueous Poly(N-vinylcaprolactam) Solution in the Dynamic and Static States

Masoumeh Foroutan,[1] Sepideh Khoee,[2] Mona Zarrabi[1]

[1]*Department of Physical Chemistry, Faculty of Chemistry, College of Science, University of Tehran, Tehran, Iran*
[2]*Department of Polymer Chemistry, Faculty of Chemistry, College of Science, University of Tehran, Tehran, Iran*

ABSTRACT: The overlap concentration of poly(N-vinylcaprolactam)s (PVCLs) of low molecular weights was studied with dynamic and static methods (with viscosity and refractive-index measurements) at three temperatures (25, 30, and 35°C). This concentration, determined by viscometry, was lower than the overlap concentration determined by refractometry. Also, the influence of the temperature and molecular weight on the viscosity and refractive index was investigated, and the opposite effect of the temperature on the viscosity and refractive index of PVCL solutions was observed. The experimental overlap concentration values were compared with those calculated with the Rao, Huggins, and Fuoss equations. The results showed that the Huggins equation is the best equation to describe the dilute solution properties of this polymer. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 597–601, 2008

Key words: molding; phase behavior; refractive index; viscosity; water-soluble polymers

INTRODUCTION

Recently, much attention has been focused on smart polymers,[1,2] which are able to respond to environmental changes, such as changes in the pH and temperature. Poly(N-vinylcaprolactam) (PVCL) is an example of a smart polymer[3] that shows a dissolution/precipitation transition in water at temperatures near physiological temperatures (32–34°C).

Because the hydrolysis of the amide group of PVCL will not produce small amide compounds, PVCL is suitable for biomedical applications. It has been demonstrated that the behavior of PVCL is also sensitive to changes in the polymer concentration, molecular weight of the polymer, and composition of the solution.[4,5] PVCL can be used as a matrix to produce solid pharmaceutical and cosmetic preparations with controlled release of active ingredients.[6] PVCL can also be used as the additive in oil-in-water nanoemulsions for the thickening of the composition.[7] Some properties of PVCL have been determined, such as the phase diagram,[8,9] critical aggregation, and light scattering of copolymers based on PVCL.[10] Recently, many copolymers based on PVCL have been synthesized, such as poly (N-vinylcaprolactam-co-vinyl acetate)[11] and poly (N-vinylcaprolactam-g-tetrahydrofuran),[12] which is a thermoresponsive copolymer. In this work, the overlap concentration of PVCL solutions is studied as another interesting property of this valuable polymer. Experimental and theoretical studies concerning the overlap concentration, which was observed by Simha and Zakin[13] and made concrete by de Gennes,[14] and separating dilute solutions from semidilute solutions have been reported in the literature.[15,16]

SOME EQUATIONS FOR THE VISCOSITY OF POLYMER SOLUTIONS

There are several equations to determine the intrinsic viscosity ([η]) of polymer solutions, such as the Rao,[17] Huggins,[18] and Fuoss equations,[19] which are briefly reviewed here.

Rao equation

The Rao equation is as follows:

$$\frac{1}{2(\eta_r^{0.5} - 1)} = \frac{1}{[\eta]C} - \frac{(a-1)}{2.5} \tag{1}$$

where η_r is the relative viscosity, C is the concentration, and a is a constant for a given polymer–solvent system.

Correspondence to: M. Foroutan (foroutan@khayam.ut.ac.ir).

TABLE I
Conditions for the Synthesis of the Polymer

Polymer	Monomer feed concentration		Time (h)
	Monomer (g)	AIBN (g)	
A	38.00	0.01	6.00
B	48.29	0.20	18.00

Huggins equation

The Huggins equation, the most common equation, is defined as follows:

$$\eta_{\text{red}} = \frac{\eta_{\text{sp}}}{C} = [\eta] + K_H[\eta]^2 C \qquad (2)$$

where η_{red} and η_{sp} are the reduced and specific viscosities, respectively, and K_H is the Huggins constant, which is an indication of polymer–solvent affinity. It has been shown that even in dilute solutions of a polymer, aggregation can be expected. Therefore, the application of Huggins equation is limited to concentrations lower than the overlap concentration.

Fuoss equation

The Fuoss equation is frequently used to determine $[\eta]$ and has the following expression:

$$\frac{\eta_{\text{sp}}}{C} = \frac{[\eta]}{(1 + DC^{0.5})} \qquad (3)$$

where D is a constant.

EXPERIMENTAL

Materials

N-Vinylcaprolactam (VCL; Aldrich; 98% (Milwaukee, WI)) was recrystallized from benzene, and 2,2′-azo-isobutyronitrile (AIBN) from Fluka (Geel, Germany) was used as the initiator. The salts (sodium chloride,
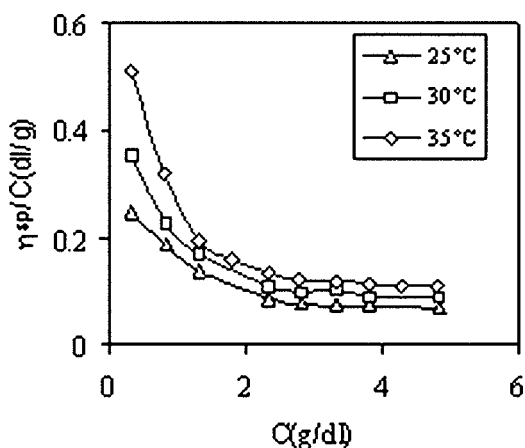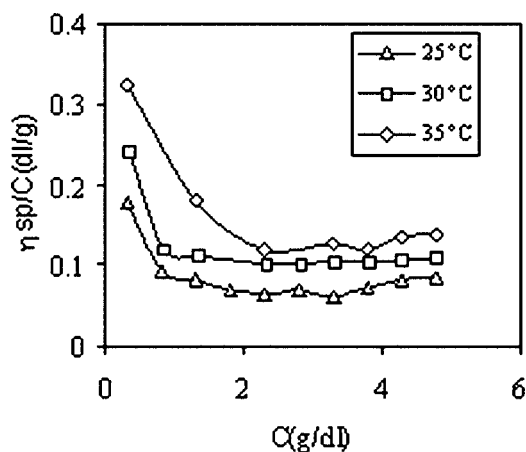

Figure 2 Reduced viscosity (η_{sp}/C) of an aqueous solution of polymer B versus the concentration (C) at different temperatures.

ammonium hydrogen phosphate, potassium hydrogen phosphate, and sodium carbonate) were superpure reagents and were obtained from Merck (Darmatadt, Germany).

Synthesis of linear PVCL

Full details of the synthesis of the polymers have been reported previously.[3,9] PVCL was synthesized as follows. To a dried two-necked flask, 38 g of VCL was added. Toluene was added through a septum under a nitrogen atmosphere. When the monomer was dissolved, 0.01 g of AIBN was added to initiate the polymerization, and the reaction mixture was heated to 60–65°C. The polymerization proceeded under a nitrogen atmosphere for 6 h. The product was recovered by precipitation in diethyl ether, dried *in vacuo* at 40°C for 8 h, and cooled to room temperature.

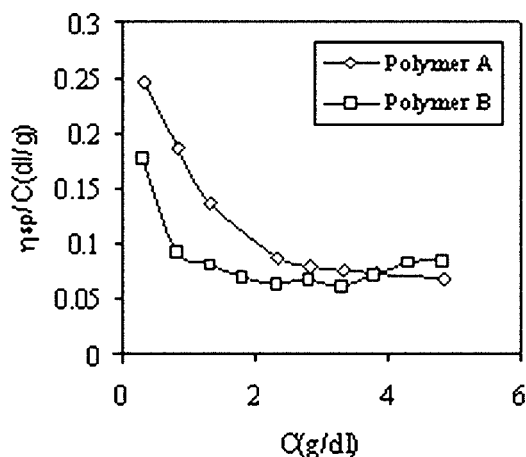To obtain two PVCL samples with different molar masses, VCL was polymerized in toluene with differ-

Figure 1 Reduced viscosity (η_{sp}/C) of an aqueous solution of polymer A versus the concentration (C) at different temperatures.

Figure 3 Representation of the reduced viscosity (η_{sp}/C) of polymers A and B versus the concentration (C) at 25°C.

TABLE II
Calculated [η] Values Obtained by Different Equations for Polymers A and B

Temperature (°C)	Polymer	[η] (dL/g)			Parameter		
		Rao equation	Fuoss equation	Huggins equation	K_H	D	a
25	A	53.622	0.167	0.211	−0.550	0.087	2.921
	B	6.321	0.019	0.263	−0.877	−0.361	2.826
30	A	10.958	0.068	0.274	−0.635	−0.077	2.897
	B	10.200	0.062	0.168	−0.619	−0.143	2.912
35	A	46.597	0.126	0.364	−0.527	0.094	2.853
	B	3.759	0.064	0.115	−0.499	−0.163	3.121

ent ratios of VCL to the initiator at different times at 65°C. Table I shows the polymerization conditions for the synthesis of polymers A and B with average molecular weights of 1150 and 1500 g/mol, respectively.

The molecular weight was determined by GPC (1100 series vacuum degasser, Agilent (Ilfov, Romania)); its standard calibration samples had average molecular weights between 120 and 1,000,000 g/mol.

Viscosity and refractive-index measurements

Viscosity measurements of the PVCL solutions were carried out at 25, 30, and 35°C with an Oswald viscometer (Germany). Refractive-index measurements of the PVCL solutions were carried out with a refractometer (RE 50, Mettler–Toledo, Switzerland). The polymer solutions were kept in a constant-temperature bath for about 10 min before the viscosity and refractometry measurements at different temperatures (25, 30, and 35°C) for temperature equilibrium.

RESULTS AND DISCUSSION

Viscosity and refractive-index values of aqueous solutions of polymers A and B, according to the Synthesis of Linear PVCL section, were measured at 25, 30, and 35°C. Because PVCL solutions show a dissolution/precipitation transition in water at temperatures close to 35–40°C, the presented data have been
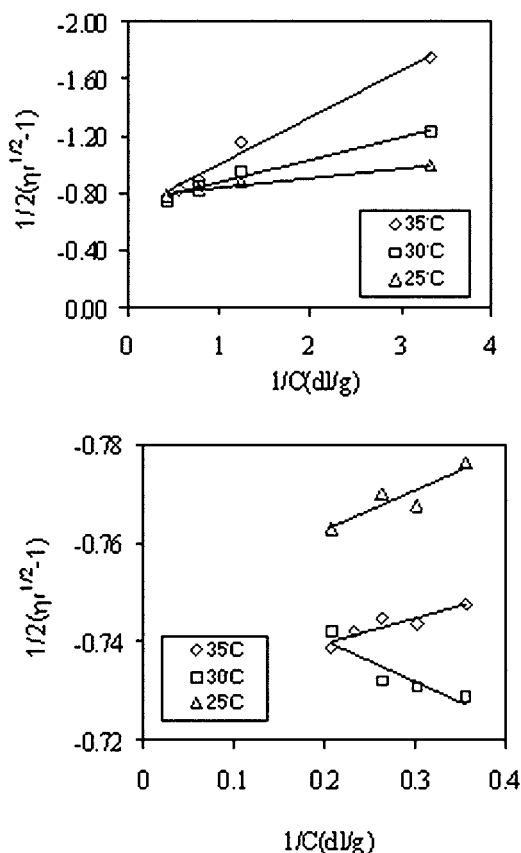

Figure 4 Representation of the Rao equation for polymer A at (a) low and (b) high values of the concentration (C) and at different temperatures.
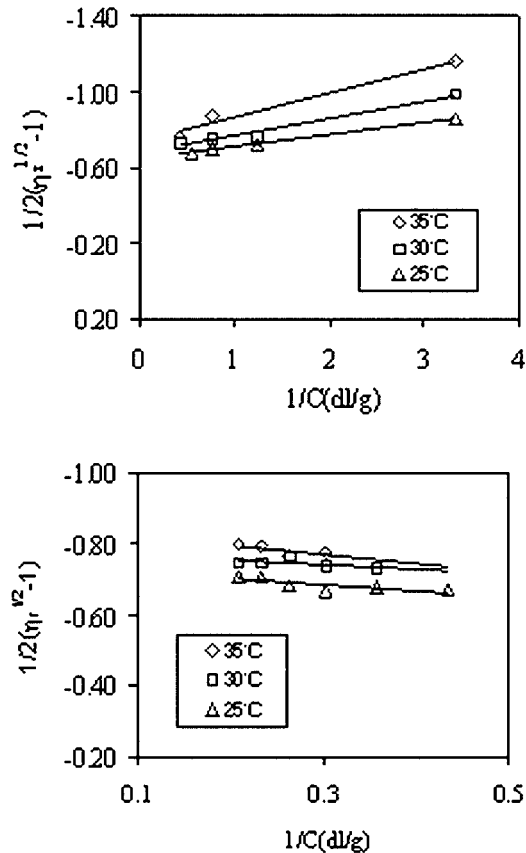
Figure 5 Representation of the Rao equation for polymer B at (a) low and (b) high values of the concentration (C) and at different temperatures.

Experimental and Calculated Overlap Concentrations Obtained by Different Equations for Polymers A and B

Temperature (°C)	Polymer	Overlap concentration (g/dL)			
		Experimental	Rao equation	Fuoss equation	Huggins equation
25	A	1.300	0.004	1.497	1.184
	B	0.900	0.039	1.315	0.950
30	A	1.200	0.022	3.676	0.912
	B	1.000	0.024	4.032	1.488
35	A	0.800	0.005	1.984	0.686
	B	1.800	0.066	3.906	2.173

limited to temperatures lower than 36°C. It has been reported that the cloud point of PVCL depends on the molecular weight of the polymer. For polymers in the range of 5×10^4 to 2×10^5 g/mol, the cloud point slightly increases from 32 to 35–36°C.[9]

Viscosity behavior of aqueous solutions of PVCL

The viscosity behavior of aqueous solutions of polymers A and B at various temperatures on the basis of the concentration is shown in Figures 1 and 2, respectively.

As shown in these figures, the viscosity of the solutions increases with increasing temperature, and similar behavior can be seen with the molecular weight of the polymers increasing. Figure 3 shows that the viscosity of a polymer solution increases with the molecular weight of the polymer increasing.

With the Huggins equation for the dilute regime (with the concentration lower than the overlap concentration), the [η] and K_H values were determined for polymers A and B at different temperatures, and they are tabulated in Table II.

According to the Rao equation, the plot of $1/2(\eta_r^{1/2} - 1)$ versus $1/C$ gives a straight line, and $1/[\eta]$ and constant a can be determined from the slope and intercept of the line, respectively. Various values of concentration parameter a for polymers A and B at different temperatures are given in Table II.
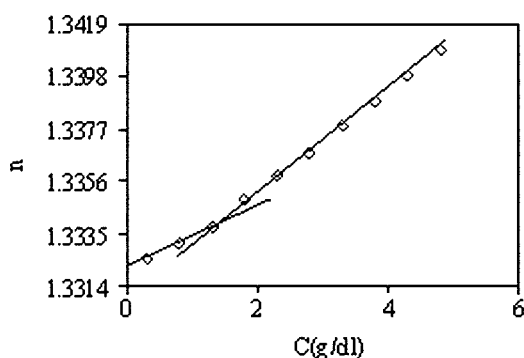
The curves obtained with the viscometric data for polymers A and B in terms of the Rao equation at different temperature are presented in Figures 4 and 5. Because the fitting of the Rao equation to the viscometric data does not lead to a straight line for the whole range of the concentration domain, allowing [η] to be calculated, the viscometric data have been linearized for two concentration ranges, low and high concentrations. We have also used the Fouss equation at low and high concentrations.

The obtained [η] values for polymers A and B from the Rao, Fuoss, and Huggins equations are listed in Table II. It has been shown that the calculated overlap concentration (C^*) can be obtained with the following expression:

$$C^* = \frac{0.25}{[\eta]} \qquad (4)$$

where [η] is the intrinsic viscosity obtained from the Huggins, Fuoss, and Rao equations. The experimental and calculated overlap concentrations for polymers A and B are tabulated in Table III.

The agreement between the experimental overlap concentration and the calculated overlap concentration obtained from the Huggins equation is better than that obtained from the Rao and Fuoss equations. If we have a higher molar mass PVCL, we will obtain a lower difference between the overlap concentration values.[18] Because the high-molecular-

Figure 6 Overlap concentration (C) of an aqueous solution of polymer A at 25°C. n: refractive index.
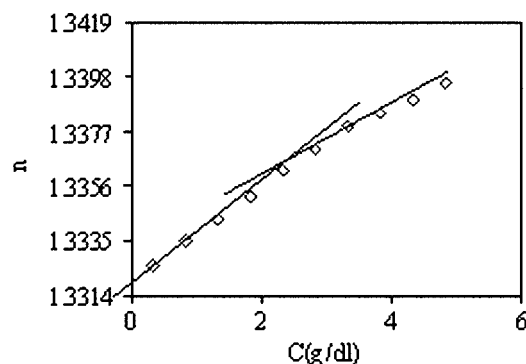

Figure 7 Overlap concentration (C) of an aqueous solution of polymer B at 25°C. n: refractive index.

weight fractions of a polymer in solution are more expanded than the low-molecular-weight fractions, consequently the interpenetration of polymer chains, to which the overlap concentration is attributed, must appear at a lower concentration when the molecular weight increases.

Refractive-index behavior of aqueous solutions of PVCL

The refractive-index behavior of aqueous solutions of polymers A and B at various temperatures (25, 30, and 35°C) has also been determined. The refractive indices decrease with increasing temperature, especially at a higher concentration. Also, it becomes clear that with increasing temperature, the refractive indices shift to lower points. This is different from what is observed for the viscosity behavior of aqueous solutions of polymers A and B. The overlap concentration for polymers A and B at 25°C is shown in Figures 6 and 7.

It is clear that the crossover point, which determines the static overlap concentration, depends on the molecular weight of the polymer. Increasing the molecular weight from polymer A to polymer B shifts the overlap concentrations to higher points. The overlap concentrations obtained by both viscometry and refractometry are listed in Table IV.

The experimental overlap concentration obtained by these methods are not the same because the overlap concentration is sensitive to the applied method, but the results confirm each other.

Figure 8 shows that the overlap concentration obtained from viscometry is lower than the overlap concentration obtained from refractometry. However, this figure shows that the data obtained from viscometry and refractometry exhibit the same behavior.

CONCLUSIONS

The viscosity and refractive-index behavior of aqueous solutions for PVCL polymers at various temperatures (25, 30, and 35°C) over a wide concentration range were determined. The experimental data were plotted in terms of the Huggins, Fuoss, and Rao equations. The $[\eta]$ values calculated by the Huggins equa-
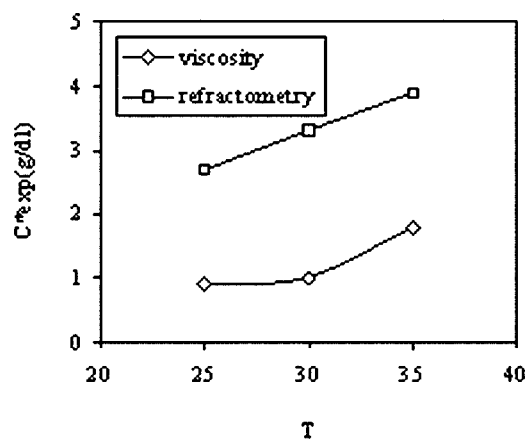

Figure 8 Variation of the dynamic and static overlap concentrations as a function of temperature (T) for an aqueous solution of polymer B (C^*_{exp} is the experimental overlap concentration).

tion led to overlap concentration values closer to the overlap concentration values experimentally determined than to those calculated in accordance with the other equations. The opposite effect of the temperature in viscometry and refractometry was observed.

References

1. Hoffman, A. S.; Stayton, P. S.; Bulmus, V.; Chen, G.; Chen, J.; Cheung, C. J Biomed Mater Res 2000, 52, 577.
2. Maimstadt, N.; Yager, P.; Stayton A. S. Anal Chem 2003, 75, 2943.
3. Loos, W.; Verbrugghe, S.; Goethals, E.; Filip, E.; Du Prez, F.; Bakeeva, I. V.; Zubov Vitali, P. Macromol Chem Phys 2003, 204, 98.
4. Meeussen, F.; Nies, E.; Berghamans, H.; Verbrugghe, S.; Goethals, E.; Du Prez, F. Polymer 2000, 41, 8597.
5. Kirsh, Y. E. Water Soluble Poly N Vinylamides; Wiley: New York, 1998; Chapter 3.
6. Meffert, H.; Ruchatz, F. U.S. Pat. 6436440 B1, 2001.
7. Hasirci, V.; Vrana, E.; Zorlutuna, P.; Ndreu, A.; Yilgor, P.; Basmanav, F. B.; Aydin, E. J. Biomaterials Sci, Poly Ed 2006, 17, 1241. U.S. Pat. 0035182 A (2002).
8. Yanul, N. A.; Zemljanov, O. Y.; Kalninsh, K. K.; Kirsh, Y. E. Z Fiz Chim 1998, 72, 1037.
9. Meeussen, F.; Nies, E.; Berghmans, H.; Verbrugghe, S.; Goethals, E.; Du Prez, F. Polymer 2000, 41, 8597.
10. Naturalium, R. Ph.D. Dissertation, Deresden University of Technology, 2004.
11. Kirsh, Y. E.; Soos, T. A.; Karaputadze, T. M. Vysokomol Soedin A 1993, 35, 481.
12. Verbrugghe, S.; Du Prez, F.; Bernaerts, K. Macromol Chem Phys 2003, 204, 1217.
13. Simha, R.; Zakin, J. L. J Chem Phys 1960, 33, 1791.
14. de Gennes, P. G. Scaling Concepts in Polymer Physics; Cornell University Press: Ithaca, NY, 1979.
15. Vidakovic, P.; Allain, C.; Rondelez, F. Macromolecules 1982, 15, 157.
16. Nystrom, B. Polym Sci 1982, 8, 333.
17. Rao, M. V. S. Polymer 1993, 34, 592.
18. Zhang, Y. X.; Da, A. H.; Butler, G. B.; Hogen-Esch, T. E. J Polym Sci Part A: Polym Chem 1992, 30, 1383.
19. Fouss, R. M.; Strauss, U. P. Polym Sci 1948, 3, 246.

TABLE IV
Experimental Overlap Concentrations for Polymers A and B Obtained from Viscosity and Refractive Index Measurements

Experimental overlap concentration (g/dL)	Polymer	Temperature (°C)		
		25	30	35
By viscometry	A	1.30	1.20	0.80
	B	0.90	1.00	1.80
By refractometry	A	1.40	1.90	2.90
	B	2.70	3.30	3.90