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Kinetic Study of Polymerization of Indole Using UV-Vis Spectroscopy

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The chemical oxidative polymerization of indole (IND) was carried out in 0.5 M H_2SO_4 solution using potassium peroxodisulphate. The rate of polymerization was followed by UV-vis spectroscopy. The absorbance corresponding to the amount of polymer at visible region (λ_{max} = 535 nm) was followed for different concentrations of indole and oxidant at various time intervals of polymerization. Rate of polymerization (R_p) was determined under various conditions. The empirical kinetic was obtained from *ex situ* UV-vis spectroscopy (R_p = k[IND] [PDS]) PDS is peroxodisulfate and the rate constant of poly indole formation was estimated to be 15.26 M^{-1} s^{-1}. The activation energy for polymerization of indole was also estimated. All the results were interpreted based on the mechanism that the polymer chain growth is accomplished by radical cation-monomer reaction pathway.

Key Words: Polyindole, Conductive polymers, Peroxodisulphate.

INTRODUCTION

Study of the polymerization and properties of N-containing heteroaromatic molecules (pyrrole, carbazole, indole and their substituted derivatives) have attracted considerable interest, because, these materials are interesting for electronic devices and sensors applications[1-5].

Among these polymers polyindoles have the advantages of fairly good thermal stability and slow degradation rate in comparison with polypyrrole[6,7]. The chemical and electrochemical syntheses of polyindole have been discussed in detail by several authors[8-18]. The chemical process of formation of polyindole offers high yields and then is suitable for industrial production. Therefore, it seems that the study of the kinetic and mechanism of polyindole formation is noteworthy. Various research groups have studied the mechanism of indole polymerization with wide range of techniques and theoretical calculations[8,19,20]. According to the literature, most likely comply sites were suggested to be 1 and 3 positions[15], 3-6 positions[21], 2-3 positions[19], 3-3, 2-2 couplings[8] and 2-7 coupling[20]. Hence it is very clear that the determination of the coupling sites of indole, the structure of the polymer chain, as well as the mechanism with which polyindole formation (radical cation-radical cation or radical cation-neutral monomer pathway) proceeds are still a matter of discussion[19,20]. On the other hand, our literature survey showed that the kinetic of chemical oxidative polymerization of indole in acidic aqueous solutions have not been studied so far. Kinetic studies can help us to understanding the mechanism of the polymer formation[22]. Several workers have studied the kinetics of polymerization of various monomers by UV-vis spectroscopy[23-27]. In present study the oxidative polymerization of indole using peroxodisulphate (PDS) in 0.5 M sulphuric acid medium was carried out and the kinetic was followed systematically as a function of monomer and oxidant concentrations by UV-vis spectroscopy. Polymeric particles formed at each time interval of reaction progress, were filtered and then dissolved in THF solvent. The more time interval of reaction progress, the more amounts of polymer is obtained and the solution of polymer is more concentrated. UV-Vis spectroscopy technique was used to measure the absorbance of the polymer solutions and establish the reaction order with respect to the peroxodisulphate (oxidizer) and indole (monomer) and also to create the corresponding general kinetic equation.

EXPERIMENTAL

Indole (Merck) was purified by recrystallization from methanol and doubly distilled water. peroxodisulphate (Merck) and other chemicals were used without further purification. All solutions were prepared with doubly distilled water.

The polymerization kinetic was followed by absorption measurements using Shimadzu UV-160A UV-vis spectrophotometer. Before spectroscopic measurements, the base line correction was made suitably using the reactants. In a typical polymerization experiment, an aqueous H_2SO_4 solution of peroxodisulphate was added to indole solution in such a way to keep a definite concentration of indole and peroxodisulphate in the system. The time of addition of the peroxodisulphate to indole solution was noted as starting time of polymerization. After polymerization at different time values, the polymer was separated by filtration. A dark green precipitate was obtained and washed with excess of aqueous H_2SO_4 solution. The filtered polymer was dissolved in THF solvent and used to obtain UV-vis spectra of the polymer solutions.

Monomer and oxidant concentrations were varied, keeping one of them constant to evaluate their respective reaction orders. Peroxodisulphate concentration values was varied from 2×10^{-2}-4×10^{-2} M and the monomer concentration was kept constant at 1×10^{-2} M. In another series of experiments the monomer concentration was varied from 3×10^{-3}-1×10^{-2} M and the peroxodisulphate concentration was kept constant at 3×10^{-2} M. All experiments were performed at 30 ºC unless where cited and the polymerization time was varied from 300-2400 s. The activation parameters were determined from the polymerization rates measured in a temperature range of 14-64 ºC.

RESULTS AND DISCUSSION

Fig. 1 represents the UV-vis absorption spectra for 1×10^{-5} M indole (a) and its polymer (b) dissolved in THF solvent. It is obvious that UV-vis spectra of indole

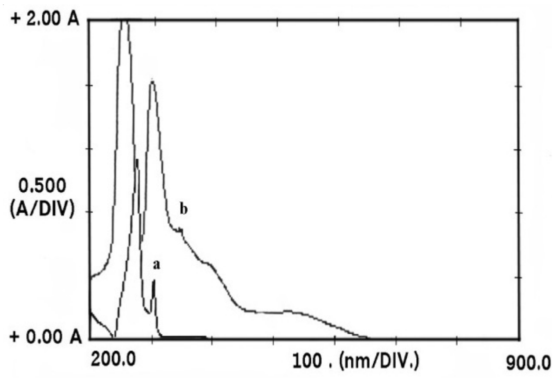


Fig. 1. UV-Vis absorption spectra of (a) indole and (b) its polymer dissolved in THF solvent

shows peaks at 235 and 312 nm without any absorption in the visible region. Then the band at 535 nm observed in the spectrum of polyindole can be used to measure the absorbance of the polymer and follow the kinetics of polymer formation during the course of polymerization.

Fig. 2 represents the UV-vis absorption spectra of the polymer dissolved in THF which has been separated from the reaction mixtures containing various initial concentration of indole and fixed amount of peroxodisulphate at 30 °C. As it is clear, when the time of reaction has progressed, the absorption bands intensity increased and the absorbance at 535 nm increases with increasing the amount of polymer in THF solvent.

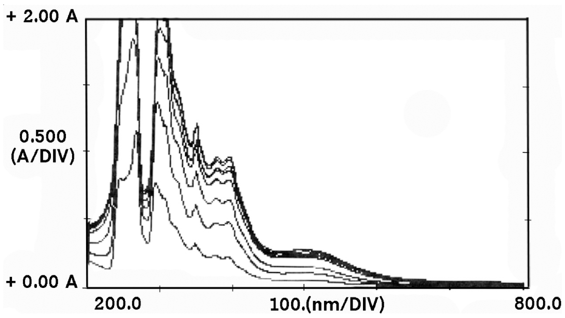


Fig. 2. UV-Vis absorption spectra recorded for various initial concentration of indole (0.010, 0.008, 0.006 and 0.003 M) and initiated by fixed amount of peroxodisulphate (0.03 M) as oxidant at 30 °C

Fig. 3 shows the relationship between the absorbance and the concentration of the polyindole. The absorbance is directly proportional to the amount of polyindole formed during the polymerization reaction. The slope of the line seemed to be dependent on the polymerization conditions, owing probably to the existence of the side reactions. However, changes in the slope would not affect the kinetic study because the rate of polymer formation is directly proportional to the rate of absorbance

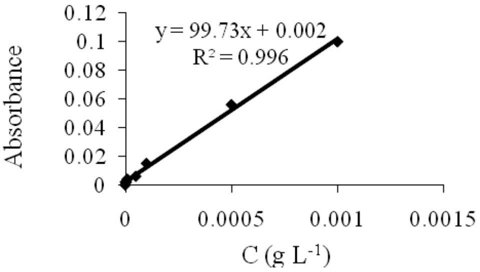
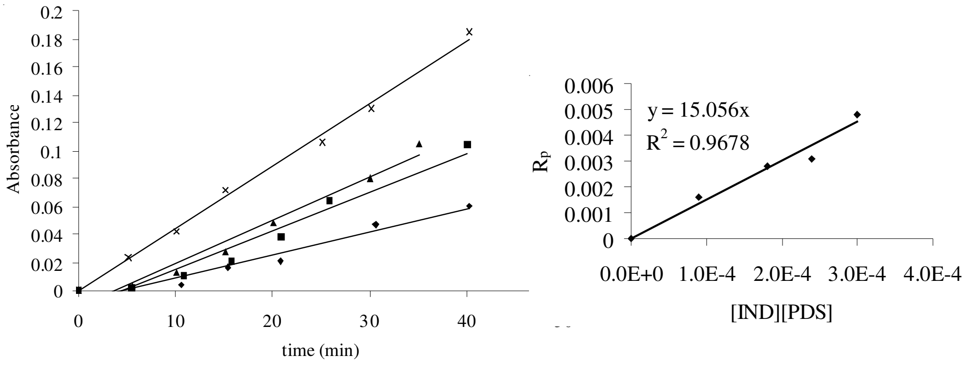


Fig. 3. Calibration line between absorbance at λ = 535 nm and concentration of polyindole

development. Then, the calibration line between absorbance and concentration of polyindole (at λ_{max} = 535 nm) was used further to estimate the amount of polymer formed during the polymerization reaction and hence to evaluate the rate of polymerization, R_p, at various time intervals of the reaction. From the slope of the calibration line, the value of the absorptivity coefficient (a) can be obtained which is 99.74 $cm^2\ g^{-1}$.

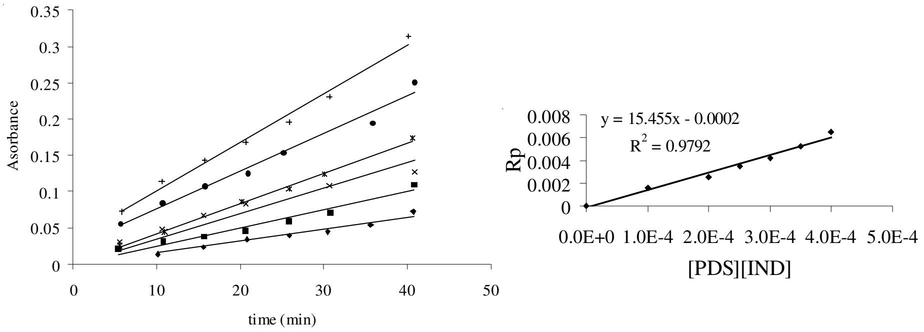
Fig. 4a represents the plot of absorbance of polymer *versus* time of reaction progress for indole polymerization. Absorbance showed a constant trend with time throughout the polymerization process and found to be higher with increasing concentration of indole [indole] at any time interval of polymerization reaction. The R_p values were used to obtain the dependence of indole concentration. The plot of R_p *versus* [IND] (Fig. 4b) was drawn and found to be linear and passing through the origin confirming the first order dependence of R_p on concentration of indole [IND].



(a) (b)

Fig. 4. (a) Time dependence of growth of absorbance at λ = 535 nm. [PDS] = 0.03 M [IND] = (×) 0.01, (▲) 0.008, (■) 0.006 and (◆) 0.003 M. (b) Dependence of rate of polymer formation on concentration of indole

Similarly, by varying the concentration of peroxodisulfate [PDS] for fixed value of concentration of indole [IND], a set of experiments were conducted. On varying the concentration of peroxodisulfate [PDS] by keeping constant the concentration of indole [IND] (Fig. 5), the plot of R_p *versus* [PDS] was straight line with negligible



(a) (b)

Fig. 5. (a) Time dependence of growth of absorbance at λ = 535 nm. [IND] = 0.01 M [PDS] = (+) 0.045, (ˆ) 0.04, (∗) 0.035, (×) 0.03, (■) 0.025 and (◆) 0.02 M. (b) Dependence of rate of polymer formation on concentration of peroxodisulphate

intercept and then R_p has first power dependence on [PDS]. These dependences of R_p on peroxodisulphate and indole concentrations were used to deduce rate expression for the polymerization of indole in aqueous acidic solutions.

$$R_p = k[IND]\,[PDS] \tag{1}$$

The polymerization reaction may proceeds *via* two different paths:

Radical cation-monomer pathway;

$\text{IND} \rightarrow \text{IND}^{+\hat{}} + e$

$\text{IND} + \text{IND}^{+\hat{}} \rightarrow (\text{IND})_2^{+\hat{}}\ (- e - 2H^+) \rightarrow \text{Dimer} \rightarrow \text{Polymer}$

Or radical cation - radical cation pathway;

$\text{IND} \rightarrow \text{IND}^{+\hat{}} + e$

$\text{IND}^{+\hat{}} + \text{IND}^{+\hat{}} \rightarrow (\text{IND})_2^{2+}\ (- 2H^+) \rightarrow \text{Dimer} \rightarrow \text{polymer}$

The observed first order dependence of R_p on indole concentration and the results obtained in the literature[11-14,18-20,23,28] suggest that initiation of polymerization proceeds *via* radical cation-monomer pathway through the 2 and 3 positions coupling (**Scheme-I**).

From the slopes of the plots of R_p *versus* concentration of indole [IND] and concentration of peroxodisulfate [PDS], the value of k can be calculated and is found to be 15.26 $M^{-1}\ s^{-1}$ at 30 ºC.

The variation of [IND] with time is defined by

$$[IND] = [IND]_0 - n[P] \tag{2}$$

where n = average number of monomer units in the polymer molecules, $[IND]_0$, the initial concentration of indole and [P] = concentration of polymer found at any time of polymerization reaction. Assuming that 2.1 electrons are necessary to oxidize one molecule of indole[11] and then, 1.05 mol of peroxodisulphate are consumed in the oxidation of 1.0 mol of indole, makes to write at any time (t) as

$$[PDS] = \{[PDS]_0 - ([IND]_0 - [IND])\}/1.05 \tag{3}$$

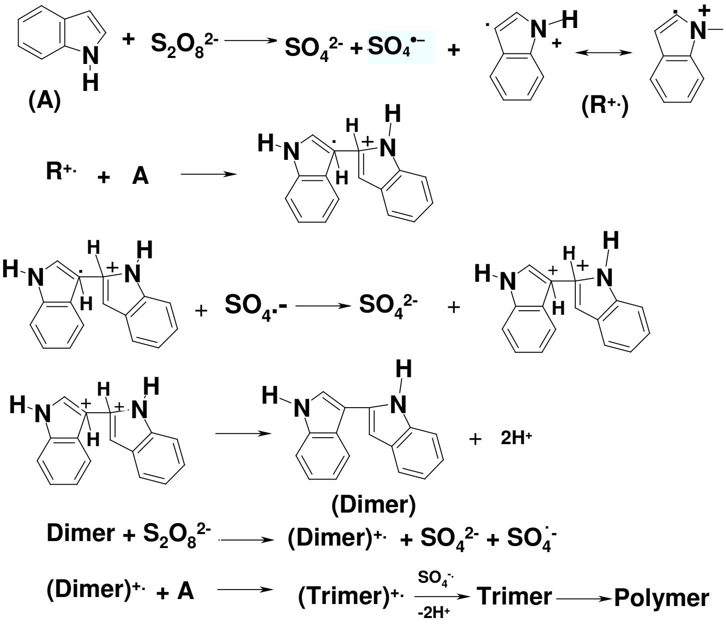
$$[PDS] = [PDS]_0 - ([IND]_0 - [IND]_0 - n[P]) = [PDS]_0 - n[P] \tag{4}$$

$$-d[IND]/dt = R_p = k\{([IND]_0 - n[P])([PDS]_0 - n[P])\} \tag{5}$$

$$R_p = d[P]/dt = k\ \{[IND]_0[PDS]_0 - n[P][IND]_0 - n[P][PDS]_0 + n^2[P]^2\} \quad (6)$$

$$A = \alpha_{535}b[P] \qquad (b = 1\ \text{cm}) \quad (7)$$

$$dA/dt = R_p = k\ \{[IND]_0[PDS]_0 - nA[IND]_0/\alpha - nA[PDS]_0/\alpha + n^2A^2/\alpha^2\} \quad (8)$$



Scheme-I

Using the value of α from the slope of the calibration line and k, n values appearing in eqn. 8 can be estimated to be 5 at the initial stage and 55 at the longer times of the polymerization process. Also by decreasing the monomer concentration with respect to oxidant, n increases (from 22-55) and on the other hand, by increasing the oxidant concentration and keeping constant the concentration of the monomer (n) decreases (from 25-15). Then, it can be concluded that, by decreasing the concentration of the monomer (0.010-0.003 M) and keeping constant the concentration of the oxidant (0.03 M), the rate of radical cation formation (nucleation process) decreases and then the more time is provided for growth of the polymer chains and (n) increases. On the other hand, by increasing the oxidant concentration (0.02-0.04 M) and keeping constant the concentration of the monomer (0.01 M), the rate of radical cation formation (nucleation process) increases and it leads to low molecular weight products. Similar results are obtained when the temperature of the polymerization reaction is increased, so by increasing the temperature from 14 ºC to 64 ºC, n reduces from 50 to 18. Increasing the temperature, increases the rate of radical cation formation (and then the nucleation process) so, there is not enough time to grow the polymer chains. All calculated (n) values are tabulated in Table-1.

TABLE-1
DEPENDENCES OF POLYMER CHAIN LENGTH ON INITIAL CONCENTRATION OF REACTANTS AND TEMPERATURE

[Indole]	[Peroxodisulphate]	Temperature (ºC)	n
0.010	0.030	30	22
0.008			33
0.006			34
0.003			55
0.010	0.020	30	25
	0.025		25
	0.030		22
	0.035		16
	0.040		15
0.007	0.030	14	50
		22	40
		35	28
		43	22
		57	21
		64	18

Accurate theoretical approach based on Hartree-Fock calculations by Talbi *et al.*[19] and spectroscopic studies by Xu *et al.*[13] showed that polymerization of indole goes through formation of bonds between C_2 and another atom, more preferably C_3 and the mechanism is more likely to occur *via* a radical cation-monomer pathway. Combining these results and the observed first power dependence of R_p on indole suggests that initiation of polymerization proceeds according to the steps shown in **Scheme-I**[23].

Effect of temperature on the rate of polymer formation: In general, the rate of polymer formation increases as the temperature is increased. The chemical polymerization of 7×10^{-3} M indole was carried out in presence of 3×10^{-2} M peroxodisulfate in 0.5 M H_2SO_4 aqueous solution at different temperature ranging from 14 ºC to 64 ºC. Fig. 6 presents the Arrhenius plot of logarithmic constant of polymer formation reaction (k) *versus* 1/T which yields a straight line, indicating that the polymerization reaction obeys the Arrhenius equation.

$$\ln k = \ln A - Ea/RT \tag{9}$$

The activation energy (Ea) and preexponential factor (A) can be determined from the slope and intercept of the plot which are 30.113 kJ mol^{-1} and 1813919 M^{-1} s^{-1}, respectively and corresponds to an increase in the rate of reaction by 4.5 % per degree increase in temperature.

It is indicating that by increasing the temperature, more soluble low molecular weight products are produced and then the rate of polymer formation is expected to increase lower than 10 % per degree increase in temperature[22]. Other activation parameters, *i.e.*, activation enthalpy ($\Delta H^{\#}$) and activation entropy ($\Delta S^{\#}$), were determined from slope and intercept of the plot of ln (k/T) against 1/T, (Fig. 7), according to the following equation[28]:

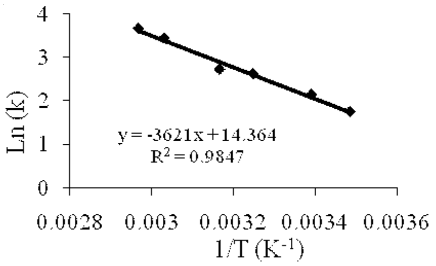


Fig. 6. Plot of ln k against 1/T for chemical polymerization of indole

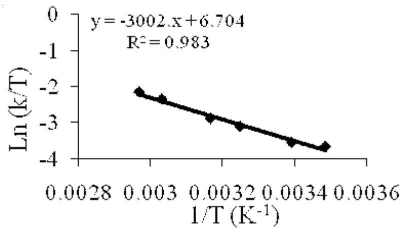


Fig. 7. Plot of ln k/T against 1/T for chemical polymerization of indole

$$\ln (k/T) = -\Delta H^{\#}/T + \Delta S^{\#}/R + \ln (k/h) \qquad (10)$$

where R = gas constant, k = Boltzmann's constant and h = Plank's constant. All the data along with the Gibbs free energy of activation ($\Delta G^{\#}$) calculated at 298 K are listed in Table-2. The negative $\Delta S^{\#}$ can be due to the more solvation of the radical cations than the monomers in aqueous solutions and also that the polymer chain growth involves bimolecular reaction between the radical cations and incoming monomers[28].

TABLE-2
RATE CONSTANT AND ACTIVATION PARAMETERS
FOR THE POLYMERIZATION OF INDOLE

Parameter	
k (M^{-1} s^{-1})	15.26
E_a (kJ mol^{-1})	30.113
A ($M^{-1}s^{-1}$)	1813919
$\Delta H^{\#}$ (J mol^{-1})	3003
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	-142
$\Delta G^{\#}$ (J mol^{-1})	45209

Conclusion

Rate of oxidative polymerization of indole was followed by UV-vis spectroscopy. Present study reveals a kinetic with rate of polymerization showing first order power dependencies on indole and peroxodisulphate. The activation energy and thermodynamical parameters such as activation enthalpy, activation entropy and Gibbs free energy of activation for the polymerization were evaluated. Polymer chain growth was estimated through the modeling of the kinetics of the polymerization progress.

REFERENCES

1. P.S. Abthagir and R. Saraswathi, *Org. Elect.*, **5**, 299 (2004).
2. P.C. Pandey and R. Prakash, *Sens. Actuators B*, **46**, 61 (1998).
3. J.D. Madden, R.A. Cush, T.S. Kanigan, C.J. Brenan and I.W. Hunter, *Synth. Met.*, **105**, 61 (1999).
4. K. D'Almeida, J.C. Bernede, F. Ragot, A. Godoy, F.R. Diaz and S. Lefrant, *J. Appl. Polym. Sci.*, **82**, 2042 (2001).
5. M.R. Nateghi and M. Borhani, *Reac. Func. Polym.*, **67**, 153 (2008).

6. P.S. Abthagir, K. Dhanalakshmi and R. Saraswathi, *Synth. Met*., **93**, 1 (1998).
7. P.S. Abthagir and R. Saraswathi, *Thermochim. Acta*, **424**, 23 (2004).
8. M. Saraji and A. Bagheri, *Synth. Met*., **98**, 57 (1998).
9. J. Xu, G. Nie, S. Zhang, X. Han, J. Hou and S. Pu, *J. Polym. Sci. Polym. Chem*., **43**, 1444 (2005).
10. G. Zotti, S. Zecchin and G. Schiavon, *Chem. Mater*., **6**, 1742 (1994).
11. R.J. Waltman, A.F. Diaz and J. Bargon, *J. Phys. Chem*., **88**, 4343 (1984).
12. H. Talbi, D. Billaud, G. Louarn and A. Pron, *Spectrochim. Acta*, **56A**, 717 (2000).
13. J. Xu, J. Hou, W. Zhou, G. Nie, S. Pu and S. Zhang, *Spectrochim. Acta*, **63A**, 723 (2006).
14. H. Talbi and D. Billaud, *Synth. Met*., **93**, 105 (1998).
15. K.M. Choi, J.H. Jang, H. Rhee and K.H. Kim, *J. Appl. Polym. Sci*., **46**, 1695 (1992).
16. F. Wan, L. Li, X. Wan and G. Xue, *J. Appl. Polym. Sci*., **85**, 814 (2002).
17. D. Sazou, *Synth. Met*., **130**, 45 (2002).
18. R. Holze and C.H. Hamann, *Tetrahedron*, **47**, 737 (1991).
19. H. Talbi, G. Monard, M. Loos and D. Billaud, *J. Molecul. Struct.:Theochem*, **434**, 129 (1998).
20. M. Yurtsever and E. Yurtsever, *Polymer*, **43**, 6019 (2002).
21. F. Koleli, M. Saglam, A. Turut and H. Efeoglu, *Turk. J. Chem*., **18**, 22 (1994).
22. M.R. Nateghi, M. Zahedi, M.H. Mosslemin, S. Hashemian, S. Behzad and A. Minai, *Polymer*, **46**, 11476 (2005).
23. C. Sivakumar, A. Gopalan, T. Vasudevan and T. Wen, *Synth. Met*., **126**, 123 (2002).
24. S. Meenakshisundaram and N. Sarathi, *Int. J. Chem. Kinet*., **39**, 46 (2006).
25. C. Sivakumar, T. Vasudevan and A. Gopalan, *Polymer*, **40**, 7427 (1999).
26. B.J. Johnson and M.S. Park, *J. Electrochem. Soc*., **1277**, 143 (1996).
27. B.A. Deore, I. Yu, J. Woodmass and M.S. Freund, *Macromol. Chem. Phys*., **209**, 1094 (2008).
28. Y. Wei, J. Tian, D. Glahn, B. Wang and D. Chu, *J. Phys. Chem*., **97**, 12842 (1993).

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