

Effect of the composition of methanol–water mixtures on tacticity of poly(*N*-ethylacrylamide) gel

Chandra Sekhar Biswas, Elvan Sulu, Baki Hazer

Department of Chemistry, Bülent Ecevit University, Zonguldak 67100, Turkey

Correspondence to: B. Hazer (E-mails: bkhazer@beun.edu.tr or bhazer2@yahoo.com)

ABSTRACT: Two series of macroporous poly(*N*-ethylacrylamide) (PNEAM) gels are synthesized in different composition of methanol–water mixtures ($x_m = 0, 0.06, 0.13, 0.21, 0.31,$ and 0.43 ; where x_m = mole fraction of methanol) in presence as well as in the absence of $0.1M$ Y(OTf)₃ Lewis acid as additive. The gels synthesized in the absence of Lewis acid are atactic and in the presence of the same are isotactic. Synthesis of the corresponding linear PNEAM homopolymers shows that, the isotacticity (meso dyad, %) of the resulted polymers increases for the gels prepared in the presence of Lewis acid (LA) and remains constant for the gel prepared in the absence of LA, respectively, with the increase in the concentration of the synthesis solvent methanol. SEM micrographs reveal that, the hydrogels synthesized in the presence of LA are more porous than the gels prepared in the absence of LA. Swelling ratio of all the hydrogels decreases with the increase in the temperature and LA gels show higher swelling ratio values than non LA gels (NLA). Deswelling rate of the hydrogels prepared in methanol–water mixture in presence of LA is faster than the hydrogels prepared in absence of LA. Moreover, reswelling rate increases with increase in the isotacticity of the PNEAM segment in the gel. All these results have been explained on the basis of the formation of highly porous hydrogels with higher isotactic PNEAM chain segment in the presence of LA in methanol–water mixtures. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41668.

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INTRODUCTION

Poly(*N*-isopropylacrylamide) (PNIPAM) is most extensively studied thermoresponsive polymer.^{1–3} Its homopolymers and gels show volume phase transition at around 33°C.⁴ Introduction of stereoregularity in PNIPAM significantly affected its lower critical solution temperatures (LCST),^{5–7} swelling properties,^{6,7} solubility,⁸ glass transition temperature,⁹ etc.

Poly(*N*-ethylacrylamide) (PNEAM) has ethyl group as *N*-substituents instead of isopropyl group in PNIPAM. Its linear homopolymers and hydrogels undergo volume phase transition (LCST) in water at much higher temperature as compared to PNIPAM, i.e., at around 73 and 62°C, respectively.¹⁰ The presence of electrolytes in the solution also influences its LCST value.^{10,11} Similarly, LCST of PNEAM also affected by its molecular weight.¹⁰ There are reports of LCST measurement of PNEAM hydrogel and homopolymers,¹⁰ swelling properties measurement of crosslinked PNEAM,¹¹ studies of physicochemical measurements of microgels,¹² and its application in lignin separation.¹³ Several efforts has also been given to synthesize and study of the properties including LCST of the copolymers PNEAM with vinyl ferrocene,¹⁴ styrene,¹⁵ poly(*N*-alkylacrylamide),^{16,17} poly(*N,N*-dimethylacrylamide), and

poly(*N,N*-diethylacrylamide).¹⁸ Moreover, emulsion polymerization of *N*-Ethylacrylamide in supercritical carbon dioxide,¹⁹ and temperature-induced self-assembly of triple-responsive triblock copolymers of PNEAM poly(*N*-*n*-propylacrylamide) and poly(methoxydiethylene glycol acrylate) in aqueous solutions²⁰ was reported. Very recently Hirano *et al.* studied the effect of composition and stereoregularity on phase transition temperature of aqueous *N*-ethylacrylamide/*N*-*n*-propylacrylamide solutions.²¹ One of our previous groups reported the synthesis and study of the properties of PNIPAM gels synthesized in different compositions of methanol–water mixtures in the absence²² and presence⁷ of Y(OTf)₃ LA. Very recently we have reported the swelling properties of stereoregular PNEAM hydrogels synthesized in 1 : 1 methanol–water mixtures in presence of different concentrations of Y(OTf)₃ LA.²³

So far, to our knowledge, there was no report about the synthesis and characterization of stereoregular PNEAM gels in different compositions of methanol–water mixture in absence as well as in the presence of Y(OTf)₃ as additives. In this article, we report the synthesis of two series of PNEAM gels (atactic and isotactic) in different compositions of methanol–water mixtures,

Table I. Synthesis of Poly(*N*-ethylacrylamide) Gels in the Different Composition of Methanol–Water Mixture in the Absence of $Y(OTf)_3$ Lewis Acid^a

	X_0	$X_{0.06}$	Run ID			
			$X_{0.13}$	$X_{0.21}$	$X_{0.31}$	$X_{0.43}$
MeOH (mL)	0	0.25	0.5	0.75	1.0	0.75
Water (mL)	1.0	0.75	0.5	0.25	0	0.25
Solution of TEMED (107 mmol/dm ³) in water (mL)	0.5	0.5	0.5	0.5	0.5	0
Solution of TEMED (107 mmol/dm ³) in methanol (mL)	0	0	0	0	0	0.5
Conversion (%) ^b	98	98	93	88	86	61
Swelling ratio (W_s/W_d) at 20°C ^c	12.8	13.4	14.8	16.7	17.2	18.0
Swelling ratio (W_s/W_d) at 40°C ^c	2.5	2.7	2.4	2.4	2.5	2.3

^a NEAM = 160 mg, BIS = 8 mg, APS = 0.5 mL of aqueous solution of concentration 42 mmol/dm³, Polymerization temperature = 5°C, polymerization time = 12 h; appearance of all the gels are transparent.

^b Determined gravimetrically after drying under vacuum at 50°C for 72 h after dialysis

^c W_s = Weight of the swelled gel at a specified temperature after 24 h swelling, W_d = weight of the dry gel.

both in the absence and in the presence of 0.1M LA. Then, their properties like stereoregularity, morphology, swelling properties are studied and the results of atactic and isotactic gels are compared with each other.

EXPERIMENTAL

Materials

N-ethylacrylamide (NEAM, Aldrich) was purified by passing through neutral alumina column. *N,N*'-methylenebisacrylamide (BIS, Aldrich), ammonium persulfate (APS, Aldrich), *N,N,N',N'*-tetramethylethylenediamine (TEMED, Aldrich) and Yttrium tri-fluoro-methanesulfonate [$Y(OTf)_3$, Aldrich] were used as received. Methanol (Marck) was dried and distilled over ignited calcium oxide. Deionized water was prepared by redistillation of distilled water.

Synthesis of PNEAM Hydrogels

Three stock solutions were prepared: (i) solution of TEMED in water of 107 mmol/dm³ concentration; (ii) solution of TEMED in methanol of 107 mmol/dm³ concentration; and (iii) solution of APS in water of 42 mmol/dm³ concentration. At first, required amount (as specified in Table I) of NEAM, BIS, $Y(OTf)_3$, TEMED solution and solvents were taken in small glass tubes (8 mm Internal Diameter × 100 mm Length) fitted with rubber septum. Both the pregel mixture and the APS stock solution in water were purged with argon gas for 30 min. These two mixtures were dip into an isothermal bath maintained at $5 \pm 0.1^\circ\text{C}$ under argon atmosphere for 30 min. Then, the argon purged APS stock solution was added to the pregel mixture through rubber septum by a degassed syringe and mixed immediately by tilting the reaction tubes up and down and allowed to react at 5°C for 12 h. The prepared gels were cut into small disk types of pieces having ~3 mm thickness × 8 mm internal diameter and dialyzed in deionized water to remove the unreacted chemicals for 7 days with changing the water twice in a day. After the dialysis, the gels were dried under vacuum at 50°C for 72 h. The conversion (%) was determined gravimetrically.

Synthesis of Linear PNEAM Homopolymers

The PNEAM homopolymers were synthesized in the absence of crosslinker. Other reaction conditions are similar like the gel synthesis described above. The polymerization was stopped by freezing the reaction mixture at liquid N₂ temperature. The resulted polymerization mixture was purified from unreacted monomer and LA by using dialysis membrane. The polymers were dried under vacuum at 50°C for 72 h. Polymer yield was determined gravimetrically.

The number average molecular weight (M_n) and polydispersity index (M_w/M_n) of the resulted polymers were determined by Viscotek GPCmax VE-2001 Chromatography in DMF at 50°C with flow rate of 1 mL/min on two polystyrene gel columns connected in series to Viscotek Gradient Pump and a Viscotek RI detector (VE3580). The columns were calibrated against seven polystyrene standard samples.

¹H NMR spectra of the resulted polymers were recorded at 80°C on a Bruker 400 MHz NMR in DMSO-*d*₆ and are reported in parts per million (δ) from residual solvent peak. The diad tacticity of polymer samples were calculated from the methylene proton peaks of the polymers as reported earlier in Ref. [21].

Surface Morphology

Gels were swollen in deionized water at 20°C for 24 h to reach the equilibrium swelling condition. These equilibrium swollen gels were freeze-dried under vacuum to remove water completely. The surface morphology of the freeze-dried samples were analysed by FEI-SEM Quanta 200F (Philips) at an accelerated voltage of 5 kV.

Swelling Ratio at Different Temperatures

Swelling ratio of the different gels at 20, 30, 40, 50, 60, 70, 75, 80, 83, 85, and 90°C temperatures were measured gravimetrically. The preweighed dried gels were immersed in deionized water for 24 h at the desired temperatures to get the equilibrium swollen gels. These equilibrium swollen gels were then taken out and the surface water was soaked with moistened

Table II. Synthesis of Poly(*N*-ethylacrylamide) Gels in the Presence of 0.1M Y(OTf)₃ Lewis Acid in Different Composition of Methanol-Water Mixture^a

	Run ID					
	X ₀	X _{0.06LA}	X _{0.13LA}	X _{0.21LA}	X _{0.31LA}	X _{0.43LA}
MeOH (mL)	0.5	0.25	0.50	0.75	1.0	0.75
Water (mL)	1.0	0.75	0.50	0.25	0	0.25
Solution of TEMED (107 mmol/dm ³) in water (mL)	0.5	0.5	0.5	0.5	0.5	0
Solution of TEMED (107 mmol/dm ³) in methanol (mL)	0	0	0	0	0	0.5
Conversion (%) ^b	96	98	97	90	86	80
Swelling ratio (W _s /W _d) at 20°C ^c	13.1	13.5	14.9	17.7	18.8	19.3
Swelling ratio (W _s /W _d) at 85°C ^c	2.3	2.5	2.4	2.2	2.8	3.0

^a NEAM = 160 mg; BIS = 8 mg; Y(OTf)₃ = 108 mg, APS = 0.5 mL of aqueous solution of concentration 42 mmol/dm³; Polymerization temperature = 5°C, polymerization time = 12 h; all the gels are transparent in nature.

^b Determined gravimetrically after drying under vacuum at 50°C for 72 h after dialysis

^c W_s = Weight of the swelled gel at a specified temperature after 24 h swelling, W_d = weight of the dry gel.

filter paper and weights were taken. The swelling ratio (W_s/W_d) was calculated as the ratio of the weight of the equilibrium swollen gel (W_s) to that of the dried gel (W_d). At each temperature, at least three samples were used and the average of values of three samples was taken into account.

Deswelling Kinetics at 85°C

Deswelling kinetics of the equilibrium swollen gels in water at 85°C were measured gravimetrically. The preweighed equilibrium swollen gels at 20°C after 24 h were immersed quickly in the water at 85°C. With the definite time intervals, the gels were taken out, the surface water was soaked with moistened filter paper and weights were taken. After that, the gels were quickly immersed back in the water at 85°C. Water retention (%) was calculated as the weight percentage of the water retained (W_t - W_d) by the swollen gel (W_t) at any definite time interval (t) with respect to that (W_s - W_d) by the equilibrium swollen hydrogel (W_s) at 20°C. For each measurement, at least three samples were used and the average of values of three samples was taken for consideration.

Reswelling Kinetics at 20°C

Reswelling kinetics in water at 20°C of the equilibrium swollen gels was obtained after immersing in water at 85°C for 24 h were measured gravimetrically. The preweighed equilibrium swollen gels at 85°C were immersed quickly in the water at 20°C. With the definite time interval, the gels were taken out and the surface water was soaked with moistened filter paper and weights were taken and then the gels were quickly immersed back in the water at 20°C. Water uptake (%) was calculated as the weight percentage of water absorbed (W_t - W_d) by the swollen hydrogel at any definite time interval (W_t) with respect to that (W_s - W_d) by the equilibrium swollen hydrogel (W_s) at 20°C. For each measurement, at least three samples were used and the average of the values of three samples was taken for consideration.

RESULT AND DISCUSSION

Synthesis of PNEAM Hydrogels in the Absence of LA

The preparation conditions and the characterization of PNEAM hydrogels in different methanol-water mixtures in absence of

LA are summarized in Table I. All the gels are transparent in nature. That is, no phase separation occurs during synthesis of the gels. Yields of the polymer gels were in between 61 to 98% and yields gradually decreased with increase in the methanol fraction in the synthesis solvent. The gradual decrease in the yield with increase in the x_m value clearly indicates the lack of crosslinking points during gelation. We have also tried, to synthesize the gel with x_m > 0.43, but no gels were formed in that region. This happens because, solubility of the initiator APS is very low in methanol, so at methanol-rich solvent it is unable to initiate the reaction owing to its poor solubility. The gel used in run X₀ and X_{0.31} are used from our previous work (Colloid and Polymer Science, DOI: 10.1007/s00396-014-3399-1).

Synthesis of PNEAM Hydrogels in Presence of LA

The preparation conditions and the characterization of PNEAM hydrogels in different methanol-water mixtures in presence of 0.1M LA are summarized in Table II. Here, all the gels are transparent in nature like the gels synthesized in absence of LA. This again confirmed the absence of any phase separation during the synthesis of the gels. Yields of the polymer gels were in between 80 to 98% and higher yields are observed for the gels synthesized in the solvent mixtures having lesser methanol fraction. Here again no gel was formed at x_m > 0.43. The gel used in run X_{0.31LA} was used in our previous work (Colloid and Polymer Science, DOI: 10.1007/s00396-014-3399-1).

To get the idea about the effect of solvent composition on the tacticity of the PNEAM chain segment in the formed gels in the presence of 0.1M LA, we have prepared the linear PNEAM homopolymers (run X_{0LA'} - X_{0.43LA'}, Table III) in the absence of crosslinker BIS keeping other experimental conditions same as mentioned in Table II for runs X_{0LA} - X_{0.43LA}. Conversions were in between 72 and 98%. Conversion decreased with increase in the methanol fraction in the synthesis solvent like the gels. The number average molecular weight (M_n) of the homopolymers showed no particular trend and varied in between 1.28 × 10⁵ and 4.38 × 10⁵ g mol⁻¹ (Table III and Figure 1). Polydispersities (M_w/M_n) are also wayward (1.49–1.99, Table III). This is understandable as the

Table III. Synthesis of Poly(*N*-ethylacrylamide) Homopolymers in the Presence of 0.1M Y(OTf)₃ Lewis Acid in Different Composition of Methanol-Water Mixture^a

	Run ID					
	X _{0LA'}	X _{0.06LA'}	X _{0.13LA'}	X _{0.21LA'}	X _{0.31LA'}	X _{0.43LA'}
MeOH (mL)	0	0.25	0.5	0.75	1.0	0.75
Water (mL)	1.0	0.75	0.5	0.25	0	0.25
Solution of TEMED (107 mmol/dm ³) in water (mL)	0.5	0.5	0.5	0.5	0.5	0
Solution of TEMED (107 mmol/dm ³) in methanol (mL)	0	0	0	0	0	0.5
Conversion (%) ^b	98	96	90	87	83	72
M _n (gmol ⁻¹)(x 10 ⁻⁵) ^c	4.38	3.59	2.79	1.54	3.18	1.28
PDI (M _w /M _n) ^c	1.71	1.49	1.62	1.99	1.53	1.98
Isotacticity (±1)% ^d	57	58	60	62	64	70

^a NEAM = 160 mg, Y(OTf)₃ = 108 mg, APS = 0.5 mL of aqueous solution of concentration 42 mmol/dm³, polymerization temperature = 5°C, polymerization time = 12 h.

^b Determined gravimetrically after drying under vacuum at 50°C for 72 h after dialysis

^c Determined by SEC in DMF with flow rate of 1 mL/min at 50°C

^d Determined by ¹H NMR in DMSO-d₆ at 80°C.

polymerizations are conventional free radical in nature, so there is no control over molecular weight and polydispersities. The homopolymer used in run X_{0.31LA'} was used in our previous work (Colloid and Polymer Science, DOI: 10.1007/s00396-014-3399-1).

In Figure 2 we have shown ¹H NMR of four homopolymers (X_{0.06LA'}, X_{0.13LA'}, X_{0.21LA'}, and X_{0.43LA'}) for the tacticity determination. From the figure it is clear that, isotacticity gradually increased with the increase in the mole fraction of methanol in the presence of Lewis acids.

In Figure 3, the comparative data of isotacticities with mole fraction of methanol used in the synthesis solvent of the homopolymer synthesized in the absence as well as in the presence of LA are shown. From the figure it is evident that, the isotactic-

ities of the polymers prepared in the presence of LA were gradually increased with increase in the methanol fraction in the synthesis solvent (Table III), whereas those prepared in absence of LA are remained constant. So, methanol played an important role to increase the isotacticity in the presence of LA. But, in the absence of LA, it hardly contributes to the isotacticities. Similar types of results were also observed in case of PNIPAM.⁷

From the Table I we see that, swelling ratio value at 20°C of the gel prepared at pure water (12.8) in absence of LA (X₀) is smaller than the gel prepared x_m = 0.06 (13.4) (run X_{0.06}). This is due to the formation of porous gel [Figure 4(a,b)] in methanol-water mixture, because, PNEAM chain segment slightly present in aggregated state in the mixed solvent due to different kind of interaction of polymer and solvents as compared to pure water and also due to the faster decomposition of APS initiator in the mixed solvent.²⁴ This eventually leads to increase in the porosity [Figure 4(c-e)] and water uptake tendency of the gel. That is why, swelling ratio at 20°C gradually increased with further increase in the x_m value from 0.13 (14.8) to 0.43 (18.0) via 0.21 (16.7) and 0.31 (17.2). Similar type of observation was also observed in our previous work.²³

Swelling ratios (W_s/W_d) of the hydrogels at 85°C are almost equal for all the samples and come in between 2 and 3. This is due to the complete collapse of the coiled conformation of the PNEAM chain segment into its globular form above its LCST.

From the Table II we see that, swelling ratio value at 20°C of the gel prepared at x_m = 0, in presence of 0.1M LA (13.1, run X_{0LA}, Table II) is smaller than the gel prepared at x_m = 0.06 (14.0, run X_{0.06LA}, Table II). This is due to the formation of highly porous crosslinked gel [Figure 5(a-f)] in methanol-water mixture in presence of 0.1M LA. Moreover, here with increase in methanol content in the synthesis solvent medium, isotacticity (% of meso dyad) increased. As we have seen in our previous work, with increase in the isotacticity of PNEAM,

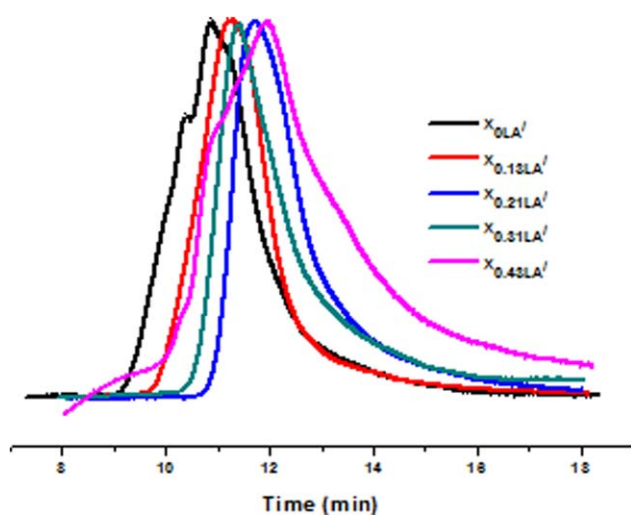


Figure 1. GPC chromatogram of PNEAM homopolymers prepared in presence of 0.1M Lewis acid in different mole fractions of methanol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

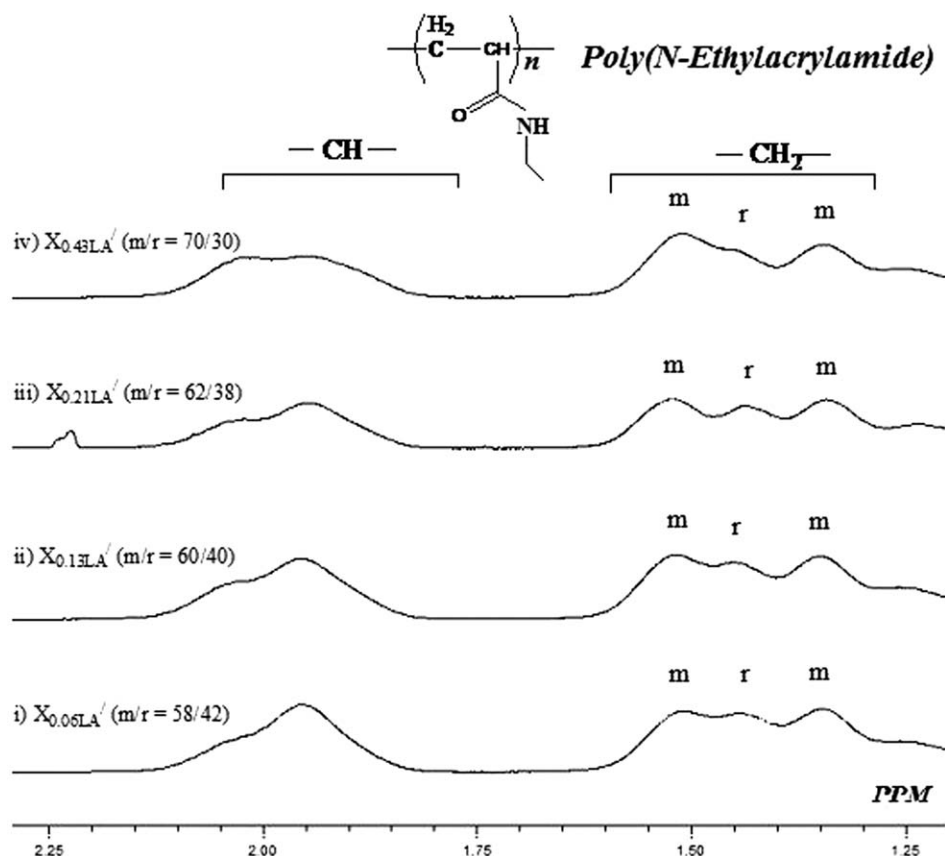


Figure 2. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, 80°C) spectra of the linear poly(N-EAM) homopolymers prepared in 0.06 mol fraction of methanol (run $X_{0.06LA}$), in 0.13 mol fraction of methanol (run $X_{0.13LA}$), in 0.21 mol fraction of methanol (run $X_{0.21LA}$), and in 0.43 mol fraction of methanol (run $X_{0.43LA}$) in presence of 0.1M $\text{Y}(\text{OTf})_3$ Lewis acid.

hydrophilicity increased,²³ so water uptake tendency or swelling ratio gradually increased with increase in the x_m value in the synthesis solvent and maximum value observed at $x_m = 0.43$ (19.3, run $X_{0.43LA}$, Table II).

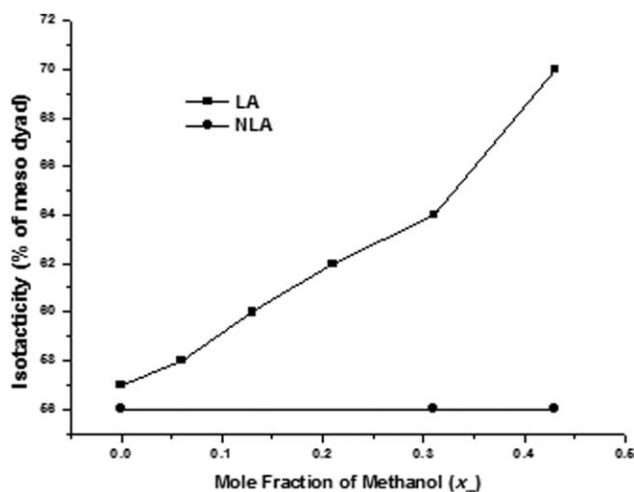


Figure 3. Comparison of isotacticities of the homopolymers synthesized in presence of 0.1M $\text{Y}(\text{OTf})_3$ Lewis acid (LA) and in absence of Lewis acid (NLA) in different mole fraction of methanol.

Swelling ratios (W_s/W_d) of the hydrogels at 85°C are almost same for all the gels and comes in between 2 and 3 due to the complete collapse of the coiled conformation of the PNEAM chain segment into its globular form above its LCST.

Morphology of the Gels Prepared in the Absence of LA

Figure 4 shows the SEM images of all the freeze-dried hydrogels. The magnifications of all the SEM images are $6000\times$. The gel prepared in the run X_0 is nonporous [Figure 4(a)] as evident from the absence of any apparently visible pores due to homogeneous phase polymerization and very slow polymerization in pure water. But the gels synthesized in different methanol–water mixtures shows highly porous nature [Figure 4(b–e)] due to the aggregated PNEAM chain segment in the mixed solvent and faster decomposition of APS initiator in presence of methanol²⁴ as discussed previously. For better clarity of the images a scale bar is shown in the image.

Morphology of the Gels Prepared in the Presence of LA

In the Figure 5, morphologies of the gels synthesized in the presence of 0.1M LA are shown. From the figure it is clear that, all the gels are highly porous in nature as 0.1M LA was used as additives during the synthesis of the gels (Table II). So, the gel synthesis in pure water is also highly porous [Figure 5(a)] unlike the gel synthesized in the absence of LA [Figure 4(a)]. So

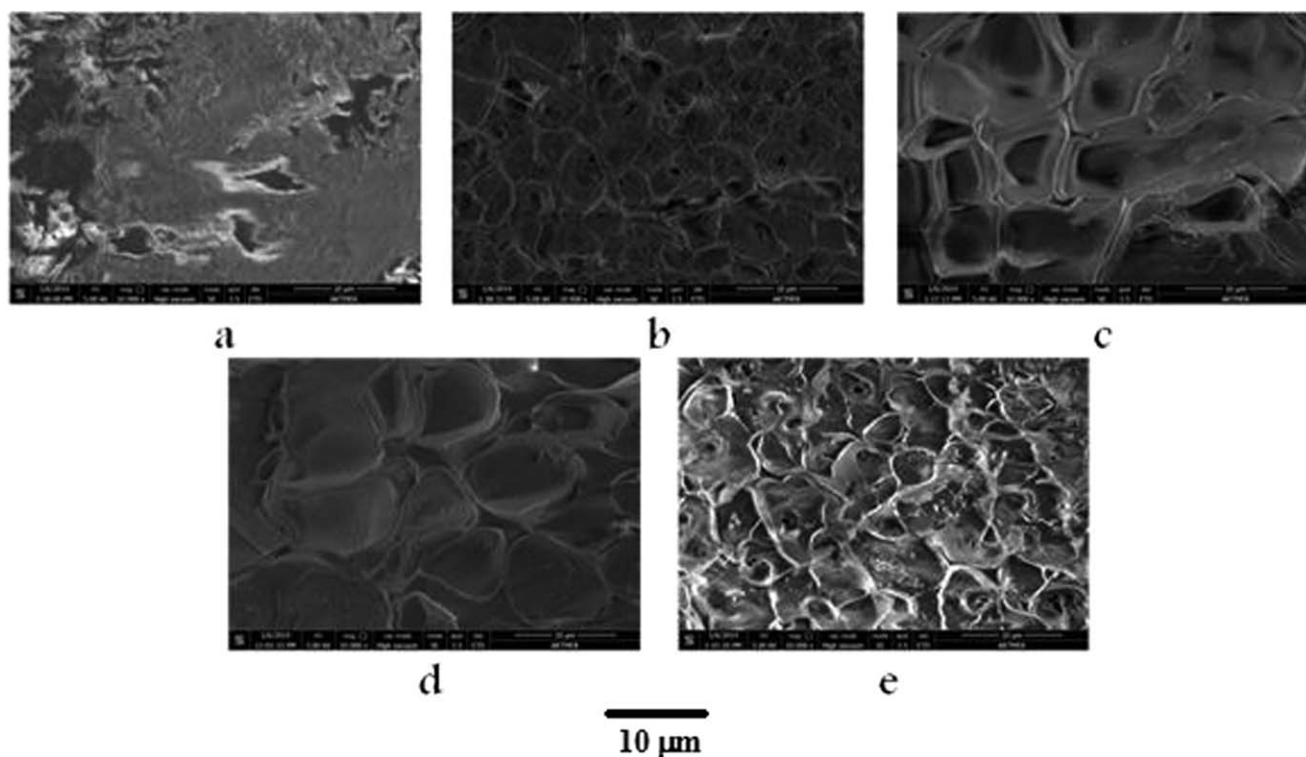


Figure 4. SEM micrographs of the hydrogels prepared (a) in water (run X_0), (b) in 0.06 mol fraction of methanol (run $X_{0.06}$), (c) in 0.13 mol fraction of methanol (run $X_{0.13}$), (d) in 0.21 mol fraction of methanol (run $X_{0.21}$), and (e) in 0.43 mol fraction of methanol (run $X_{0.43}$) in absence of Lewis acid.

LA is a major factor to produce porous gels. This factor plus the presence of methanol–water as mixed synthesis solvents, made the other LA gels highly porous [Figure 5(b–f)] as com-

pared to their corresponding counterparts synthesized in the absence of LA [Figure 4(b–e)]. So, by using LA, highly porous and isotactic gels can be synthesized.

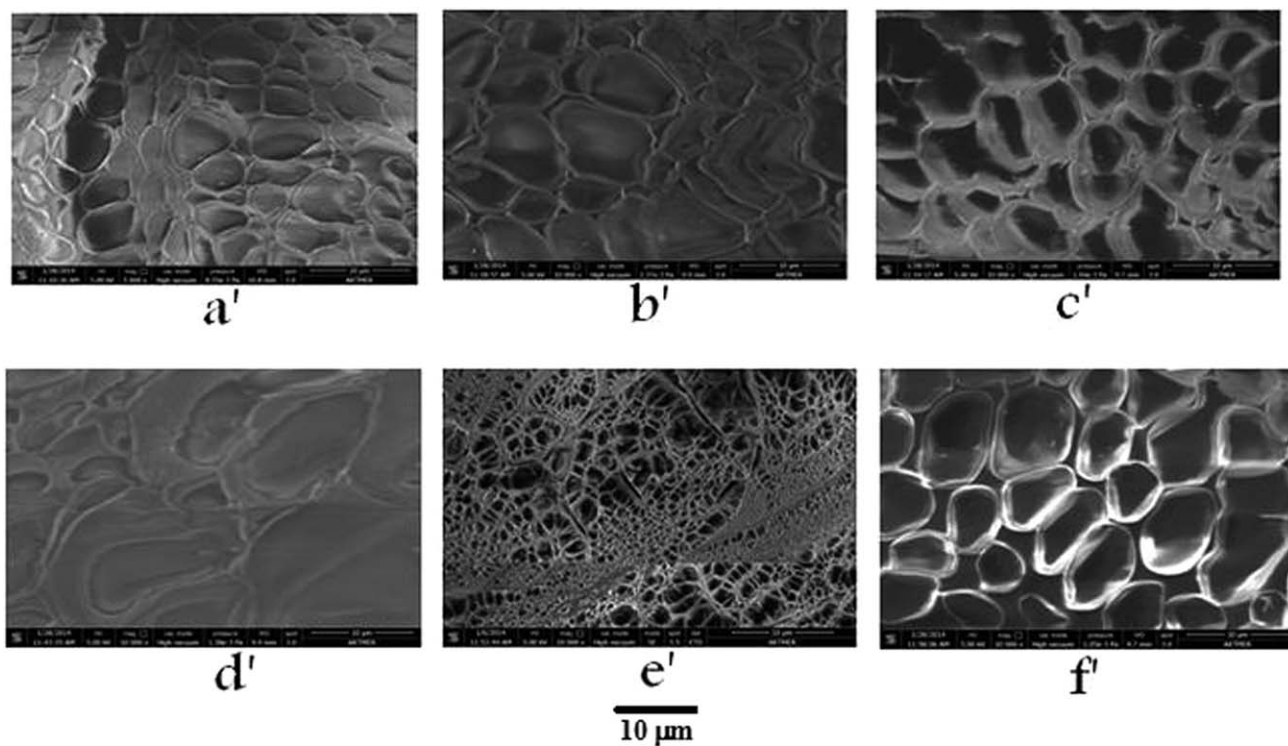


Figure 5. SEM micrographs of the hydrogels prepared (a) in water (run X_{0LA}), (b) in 0.06 mol fraction of methanol (run $X_{0.06LA}$), (c) in 0.13 mol fraction of methanol (run $X_{0.13LA}$), (d) in 0.21 mol fraction of methanol (run $X_{0.21LA}$), and (e) in 0.43 mol fraction of methanol (run $X_{0.43LA}$) in presence of 0.1M Lewis acid.

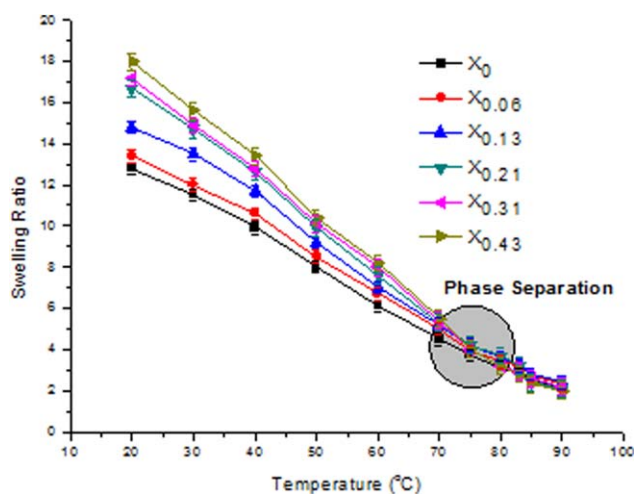


Figure 6. Equilibrium swelling ratios of all PNEAM hydrogels in water at 20, 30, 40, 50, 60, 70, 75, 80, 83, 85, and 90°C temperatures prepared in the absence of Lewis acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Swelling Ratio at Different Temperatures of the Gels Synthesized in Absence of LA

Swelling ratios at different temperatures of all hydrogels prepared in the different methanol–water mixtures in absence of LA are shown in the Figure 6. The equilibrium swelling ratio in water at 20°C of the PNEAM gels follows the order: $X_{0.43} > X_{0.31} > X_{0.21} > X_{0.13} > X_{0.06} > X_0$ as discussed in the synthesis section. In general, for all the gels, swelling ratio values decrease with increase in the temperature because of the release of water owing to the gradual collapse of the PNEAM segment in the gel. All the gels showed phase separation (LCST) at around 75°C as the PNEAM chain segment in all the gels had almost identical isotacticity (Figure 3). In other words, we can say that, LCST of PNEAM gels are independent on the solvent compositions used for the synthesis in the absence of LA.

Swelling Ratio at Different Temperatures of the Gels Synthesized in Presence of LA

Swelling ratio at different temperatures of all the hydrogels prepared in the different methanol–water mixtures in presence of 0.1M LA are shown in the Figure 7. Here, the equilibrium swelling ratio in water at 20°C of the gels follows the order: $X_{0.43LA} > X_{0.31LA} > X_{0.21LA} > X_{0.13LA} > X_{0.06LA} > X_{0LA}$ as discussed in the synthesis section. Like the previous case, here also swelling ratio values decreases with increase temperature because of the release of water owing to the gradual collapse of the PNEAM segment in the gel. The gels prepared at $x_m = 0$ (run X_{0LA}), at $x_m = 0.06$ (run $X_{0.06LA}$), and at $x_m = 0.13$ (run $X_{0.13LA}$) showed phase separation (LCST) at around 70°C (Figure 7). The gels synthesized at higher x_m values in presence of 0.1M LA shows phase separation at around 75–80°C [run $X_{0.21LA}$, $X_{0.31LA}$, and $X_{0.43LA}$ (Figure 7)]. So, LCST of PNEAM gels are increased gradually with the increase in the isotacticity of PNEAM chain segment unlike PNIPAM. Similar types of results for PNEAM homopolymers were observed in our previous work.²³

Comparison of Swelling Ratio of the Gels Prepared in Absence as well as in Presence of LA at Different Temperatures

To understand the effect of LA on the swelling ratio values of the gels, a comparative plot of the swelling ratio of the gels synthesized in absence of LA, and those synthesized in presence of 0.1M LA are shown in Figure 8. From the plot it is clear that the gels prepared in presence of LA have the higher swelling ratio values than the gels prepared in absence of LA in all the temperatures below their LCST throughout all methanol–water compositions used for the synthesis. This is due to the increase in both porosity and hydrophilicity of the gels owing to the presence of higher isotactic PNEAM chain segment in presence of LA. As a result the water uptake tendency of the gels also increases with the increase in the isotacticity. So, it is quite clear that, swelling ratio of the PNEAM gels are affected by both the porosity and isotacticity.

Deswelling Kinetics of the Gels at 85°C Synthesized in Absence of LA

Deswelling rates of all the hydrogels (synthesized in absence of LA) in water at 85°C are shown in the Figure 9. From the figure it is evident that, the synthesis solvent composition has very little effect on the deswelling rate of the gels as very minimum difference observed in the deswelling rates with time. This may be due to the presence of similar hydrophilic PNEAM chain segments in the gels, lesser porosities, and higher solvation of PNEAM chain segment towards the solvent for all the gels. So, percentage of water retention for all the gels with time at 85°C is almost similar. So, it is quite clear that the deswelling rate of PNEAM hydrogels are not affected significantly by the synthesis solvent compositions (here methanol–water).

Deswelling Kinetics of the Gels at 85°C Synthesized in Presence of LA

Deswelling rates of all the hydrogels (synthesized in presence of 0.1M LA) in water at 85°C are shown in the Figure 10. Deswelling rate is fastest for the gel prepared in pure water (run X_{0LA}). This rate gradually decreased with increase in the methanol

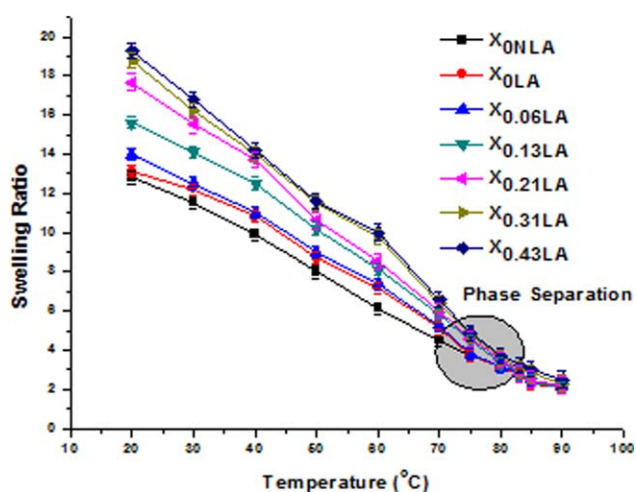


Figure 7. Equilibrium swelling ratios of all PNEAM hydrogels (prepared in the presence of 0.1M Lewis acid) in water at 20, 30, 40, 50, 60, 70, 75, 80, 83, 85, and 90°C temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

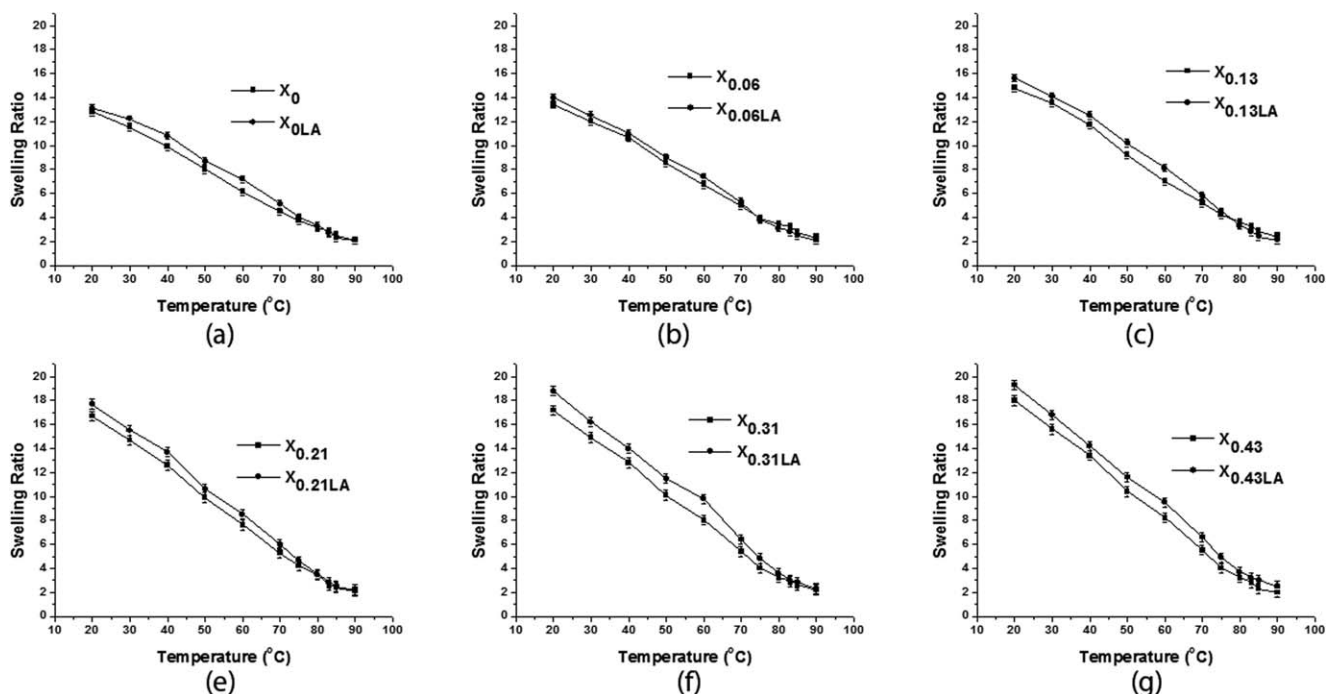


Figure 8. Comparative results of the swelling ratio in water at different temperatures for the gels prepared in different methanol–water mixtures in the absence and presence of 0.1M Lewis acid.

fraction in the synthesis solvent. The slowest deswelling rate is observed with the gel synthesized at $x_m = 0.43$ (run $X_{0.43LA}$). This may be due to the increase in the isotacticity of the PNEAM chain segment with increase in the methanol fraction in the synthesis solvent in the presence 0.1M LA. As the isotacticity of PNEAM chain segments gradually increases, hydrophilicity also increases. So, higher hydrophilic gels do not give up water easily compared to lesser hydrophilic gels. Moreover, here all the gels are highly porous in nature and present in the higher solvated state, so they play almost similar roles in the

deswelling rates. As a result, isotacticity plays the most important role here to determine the fate of deswelling rate. So by tuning the isotacticity, the deswelling rates of PNEAM hydrogels can be changed. Here, the deswelling rates of the hydrogels prepared in presence of 0.1M LA decreased in the order $X_{0LA} > X_{0.06LA} > X_{0.13LA} > X_{0.21LA} > X_{0.31LA} > X_{0.43LA}$.

Comparison of Deswelling Rates of the Gels Prepared in Absence as well as in Presence of LA at 85°C

In Figure 11, the comparative results of the deswelling rates in water at 85°C of the gels prepared in different methanol–water

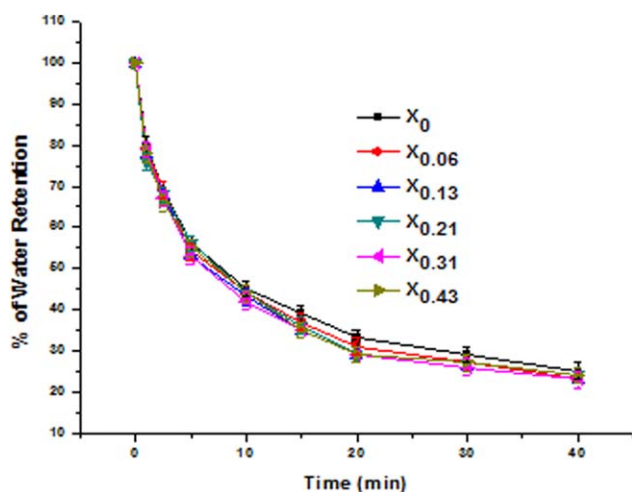


Figure 9. Deswelling kinetics of the PNEAM hydrogels synthesized in 0 (run X_0), 0.06 (run $X_{0.06}$), 0.13 (run $X_{0.13}$), 0.21 (run $X_{0.21}$), 0.31 (run $X_{0.31}$), and 0.43 (run $X_{0.43}$) mole fractions of methanol in absence of Lewis acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

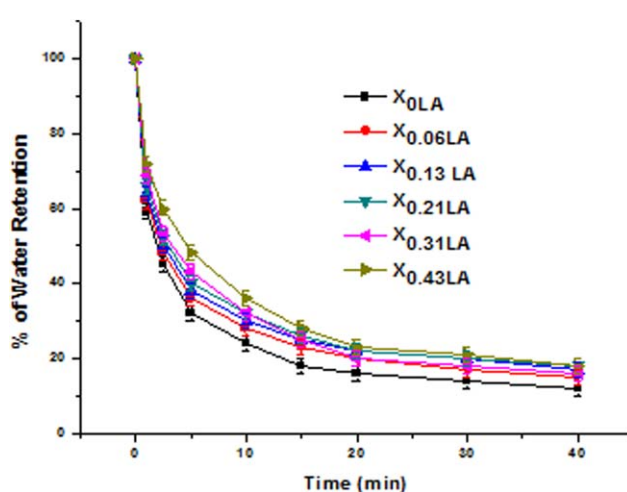


Figure 10. Deswelling kinetics of the PNEAM hydrogels synthesized in 0 (run X_{0LA}), 0.06 (run $X_{0.06LA}$), 0.13 (run $X_{0.13LA}$), 0.21 (run $X_{0.21LA}$), 0.31 (run $X_{0.31LA}$), and 0.43 (run $X_{0.43LA}$) mole fractions of methanol in presence of 0.1M Lewis acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

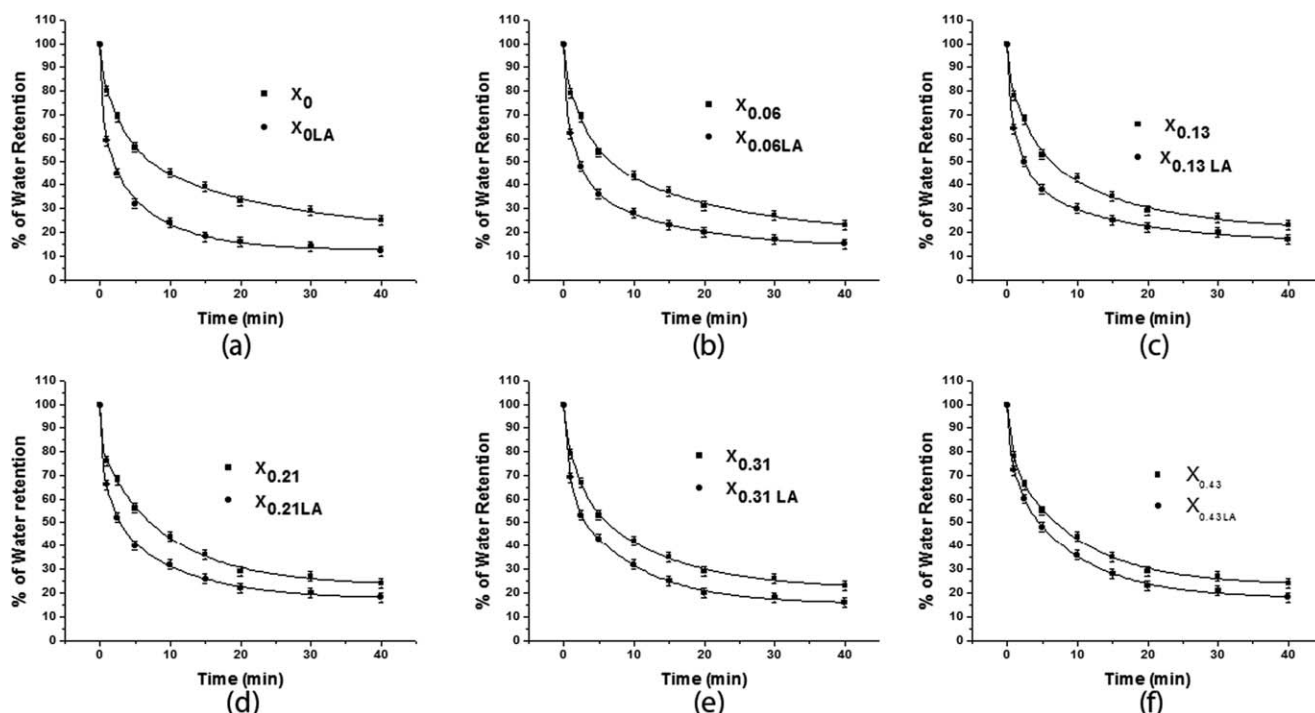


Figure 11. Comparative results of the deswelling rate in water at 85°C for the gels prepared in different methanol–water mixtures in the absence and presence of 0.1M Lewis acid.

mixtures in the absence and presence of 0.1M LA are shown. Here in all the cases, deswelling rate of the gels synthesized in presence of 0.1M LA shows higher deswelling rate than their counterparts synthesized in absence of LA. The gel prepared in pure water in presence of 0.1M LA, shows higher deswelling rate as compared to the gel prepared in absence of Lewis acid [Figure 11(a)]. Here two contradictory factors like (i) isotacticity and (ii) porosity affecting in the deswelling rates. The gel prepared in presence of LA has higher isotacticity value, which increases the hydrophilicity of the gel and hence plays negative role in deswelling rate. On the other hand, the porosity plays positive role in deswelling rate. In this case, in presence of LA, increase in the isotacticity is very small (from 56 to 57) but porosity increased significantly [Figures 4(a) vs. 5(a')]. So porosity factor plays predominant role over isotacticity factor, which reflected in the deswelling rate. With increase in the methanol fraction in the synthesis solvent, the difference in the deswelling rate gradually decreases and the difference is minimum for the gels prepared at maximum x_m value [$x_m = 0.43$, Figure 11(f)]. This is quite understandable. With increase in the methanol fraction the isotacticity of the LA gels increased continuously where as the isotacticity of the non LA gels (NLA) remained constant. The difference is maximum at $x_m = 0.43$ [isotacticity 56 (not shown here) vs. 70 (Table III)]. So, isotacticity expected to play a major role here to decrease the deswelling rate of the LA gels. On the other hand, it is also clear from the SEM images that, LA gels are much more porous compared to NLA, which plays an important role to increase the deswelling rate of the LA gels. So, these two factors tried to counter balance each other and finally the porosity factor managed to keep the edge over isotacticity factor, although the difference in

the deswelling rate decreased to a significant extent at $x_m = 0.43$ [Figure 11(f)]. So, it is clear from the discussion that the deswelling rates of all of the gels prepared in the presence of the LA are faster with respect to those prepared in the absence of the LA.

Reswelling Kinetics of the Gels at 85°C Synthesized in Absence of LA

Reswelling rates of all the gels prepared in absence of LA in different methanol–water mixtures at 20°C are shown in the Figure 12. From the figure it is quite clear that, the synthesis solvent composition has not much effect on the reswelling rate of the gels like deswelling kinetics. All the gels show more or less similar reswelling rates. This is also due to the happening of highly solvated PNEAM chain segment of all the gels in all methanol–water compositions during the synthesis. As a result PNEAM chain segments in all the gels are present in loosely aggregated states and have same chance to play with water. Further, all the gels have almost similar hydrophilicity, so rate of water uptake with time at 20°C should also be similar. Although, porosity of the gels synthesized at higher methanol fraction shows porous nature, but the above factors played predominant role over porosity like the deswelling rate. So, reswelling rates of PNEAM hydrogels too are not affected significantly by the synthesis solvent compositions (here methanol–water) in absence of LA.

Reswelling Kinetics of the Gels Synthesized in Presence of 0.1M LA at 85°C

Reswelling rates of all the hydrogels (synthesized in presence of 0.1M LA) in water at 20°C are shown in the Figure 13. Reswelling rate is slowest for the gel prepared in pure water (run

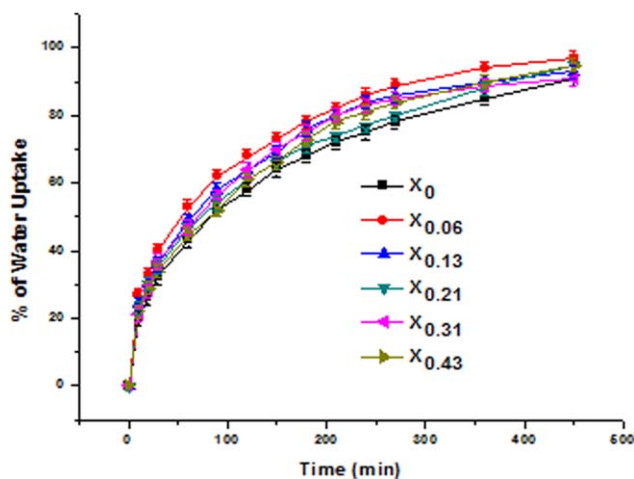


Figure 12. Reswelling kinetics of the PNEAM hydrogels synthesized in 0 (run X_0), 0.06 (run $X_{0.06}$), 0.13 (run $X_{0.13}$), 0.21 (run $X_{0.21}$), 0.31 (run $X_{0.31}$), and 0.43 (run $X_{0.43}$) mole fractions of methanol in absence of Lewis acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

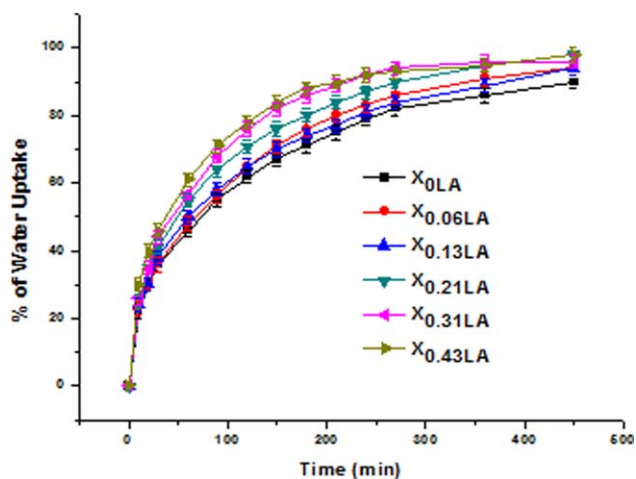


Figure 13. Reswelling kinetics of the PNEAM hydrogels synthesized in 0 (run X_{0LA}), 0.06 (run $X_{0.06LA}$), 0.13 (run $X_{0.13LA}$), 0.21 (run $X_{0.21LA}$), 0.31 (run $X_{0.31LA}$), and 0.43 (run $X_{0.43LA}$) mole fractions of methanol in presence of 0.1M Lewis acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

X_{0LA}). This rate gradually increased with the increase in the x_m value in the synthesis solvent. The fastest reswelling rate observed with the gel synthesized in presence of maximum x_m value (run $X_{0.43LA}$). This may be due to the increase in the hydrophilicity owing to the increase in the isotacticity of the PNEAM chain segment with increase in the x_m value in the synthesis solvent in the presence 0.1M LA. So higher hydrophilic gels can uptake water comparatively easily as compared to lesser hydrophilic gels. Here all the gels are highly porous in nature and present in the higher solvation state during synthesis, so

effect of these two factors on reswelling rate is almost similar for all the gels. So, isotacticity plays the major role to decide the fate of the reswelling rates of the gels. As isotacticity increased continuously with increase in the x_m value in presence of LA, so hydrophilicity also increases at a same rate. As a result, the reswelling rate gradually increases with increase in the x_m value in presence of 0.1M LA. Thus the reswelling rates of the hydrogels prepared in presence of 0.1M LA increased in the following order $X_{0LA} < X_{0.06LA} < X_{0.13LA} < X_{0.21LA} < X_{0.31LA} < X_{0.43LA}$.

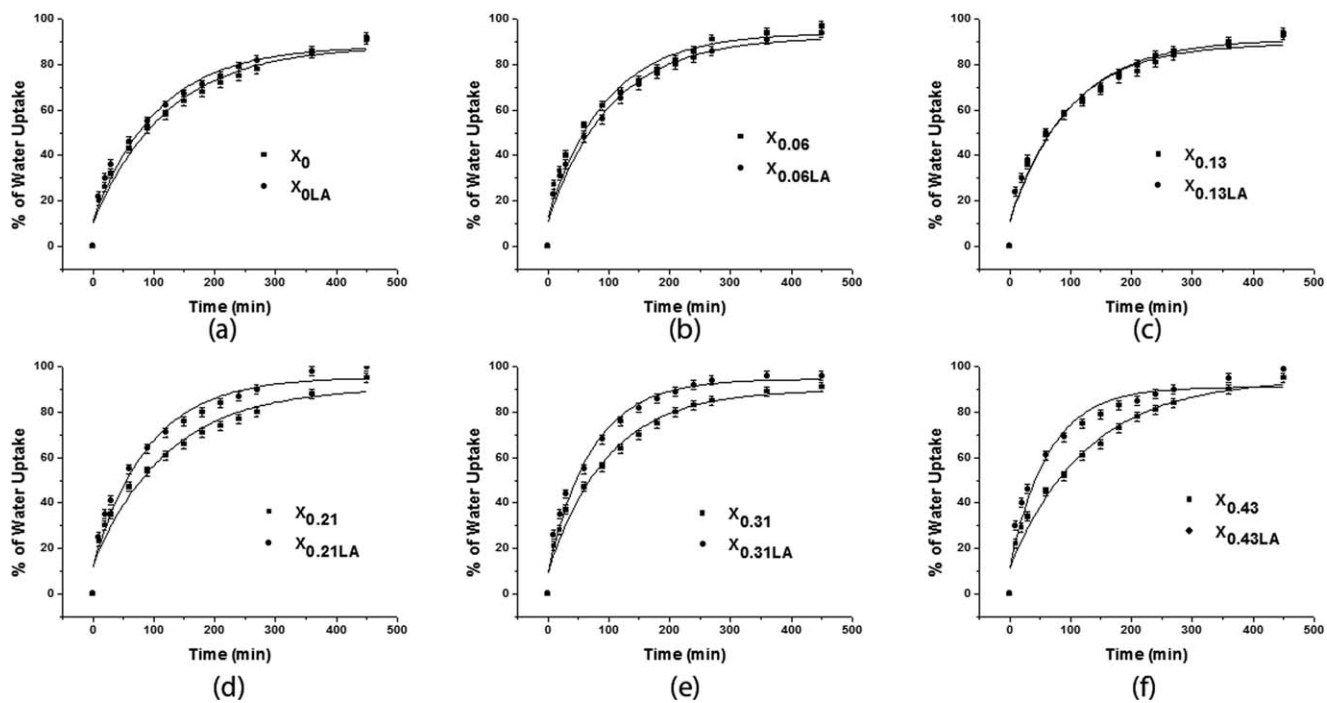


Figure 14. Comparative results of the reswelling rate in water at 20°C for the gels prepared in different methanol–water mixtures in the absence and presence of 0.1M Lewis acid.

Comparison of Reswelling Rates of the Gels Prepared in Absence as well as in Presence of LA at 20°C

In Figure 14, the comparative results of the reswelling rates in water at 20°C for the gels prepared in different x_m values in the absence and presence of 0.1M LA are shown. Here, the reswelling rates of the gels synthesized in presence of 0.1M LA are faster than their counterparts synthesized in absence of LA. The gels prepared at $x_m = 0, 0.06,$ and $0.13,$ in presence of 0.1M LA shows slightly higher reswelling rate as compared to the gel prepared in absence of LA [Figure 14(a–c)]. But, reswelling rates of the gels synthesized with higher x_m value (i.e., $x_m = 0.21, 0.31,$ and 0.43) in presence of 0.1M LA shows much higher reswelling rates as compared to their counterparts synthesized in absence of LA [Figure 14(d–f)]. Here two factors favored the reswelling rates of the LA gels; (i) isotacticity and (ii) porosity. The gels prepared in presence of LA have higher isotacticity values, which increases the hydrophilicity of the gels, and hence helped the gels to uptake water at a faster rate as compared to the NLA. On the other hand, the high porosity also plays an important role to uptake water at a faster rate with time. Here all the LA gels are highly porous, so effect of porosity is more or less similar. So, isotacticity played most important role here to decide the rate of reswelling. Higher is the difference between isotacticities of the gels, higher is the difference in reswelling kinetics. That is why, the difference in reswelling rate is not much prominent in first three cases [Figure 14(a–c)], but started to be prominent after that [Figure 14(d,e)] and most prominent for the gel prepared at $x_m = 0.43,$ in presence of 0.1M LA as compared to its NLA counterpart [Figure 14(f)]. So, it may be concluded that the reswelling rate of PNEAM hydrogels increases with the increase in the isotacticity of the PNEAM chain network.

CONCLUSIONS

Two series of macroporous PNEAM gels were synthesized in different composition of methanol–water mixtures ($x_m = 0, 0.06, 0.13, 0.21, 0.31,$ and 0.43) in presence as well as in the absence of 0.1M LA. The gels synthesized in the absence of LA are atactic and in the presence of the 0.1M LA are isotactic as proved from the NMR of their corresponding homopolymers. Moreover, for the gels prepared in presence of LA, isotacticity gradually increases with the increase in the x_m value. Number average molecular weight and polydispersities of the homopolymers obtained are also broad. SEM micrograph reveals that the hydrogels synthesized in the presence of LA are more porous than the gels prepared in the absence of LA. Swelling ratio of all the hydrogels decreases with the increase in the temperature and LA gels show higher swelling ratio value than NLA. Deswelling rate of the hydrogels prepared in methanol–water mixture in the presence of LA is faster than the hydrogels prepared in the absence of LA. Moreover, deswelling rate decreases with increase in the isotacticity of the PNEAM segment in the gel. The reswelling rate of the LA gels are faster than NLA. Moreover, reswelling rate increases with increase in the isotacticity of the PNEAM segment in the gel. All these results have been explained on the basis of the formation of highly porous hydrogels with higher isotactic PNEAM chain segment in methanol–water mixture in the presence of LA.

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