

Synthesis and Swelling Characteristics of Responsive Carboxybetaine Gel

Nazia Tarannum, Meenakshi Singh

Department of Chemistry, MMV, Banaras Hindu University, Varanasi-221005, India

Received 1 May 2010; accepted 11 January 2011

DOI 10.1002/app.34159

Published online 20 April 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A polyiminium gel, Dimedone-[N, N' melaminium] butyrocarylate copolymer, comprising of zwitterionic carboxybetaine repeat units was synthesized via a catalyst free facile polycondensation approach. The polymer was studied for its photoluminescence, thermal, and swelling behavior. Swelling behavior was investigated in different solvent mixtures as well as in pure solvents. The extent of swelling was dictated by solvent composition, such as dielectric constant, pH, ionic strength, and other variables for instance, temperature and crosslinking

density. Gel was soluble in alkali and could be regenerated on treatment with an acid. This pH responsive behavior could find various industrial applications, especially in wastewater treatment. A preliminary study on sorption of dyes was also carried out. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 241–248, 2011

Key words: polycarboxybetaine; swelling; responsive gel; zwitterionic; crosslinker

INTRODUCTION

A gel is a crosslinked polymer network immersed in a fluid. It is an important state of matter found in a wide variety of biomedical and chemical systems. Phase equilibria of gels have been extensively studied theoretically and experimentally.^{1,2} The conformation of macroionic gels is strongly affected by the electrostatic attraction between macroions and their counterions and by the repulsive interactions between a macroion and other macroions and between similarly charged ionic groups on a polymer.

The specific properties of polyelectrolyte gels are related to the ionic nature of the chains and have been under intensive investigation.^{3–5} Polyzwitterions are polyampholytes in the isoelectric state with two charges of opposite signs located on a monomer unit. They are now recognized as well defined classes of polymeric materials showing a broad spectrum of specific and unique properties in solution and in the bulk, arising from the highly dipolar character of their functional unit (dipole moment values in the range 20–30 D).^{6–9} The antipolyelectrolytic behavior, the absence of counterion condensation and the negligible Donnan effect in polyzwitterionic solutions, and gels characterize them as

polyampholytes in the isoelectric state. A subgroup of zwitterionic polymers is the carboxybetaine polyelectrolytes, bearing carboxylate as the anionic moiety, was reviewed by many authors.^{10–12} The biomimetic nature of the zwitterionic structure of carboxybetaines has recently been applied for wide range of biomedical applications. The poly(carboxybetaine methacrylate) was grafted on gold surface, which resisted protein adsorption and was capable of immobilizing certain biological ligands. The biocompatibility of carboxybetaine layer was approved by a number of publications recently.^{13–20} Studies of polycarboxybetaine properties, such as charge interactions, solubility investigation, viscosity measurements, pH and electrolyte responsiveness, thermal analysis, X-ray studies, potentiometric titrations, laser light scattering, etc.^{10,21–27} have revealed their unique and specific properties making them a suitable candidate for technological applications including biomedical devices and other applications requiring biocompatible materials. The ability of charged gels to transition, in response to an environmental trigger, from a collapsed to swollen configuration or *vice versa* may be utilized for various technological applications. Swelling of polyelectrolyte gels can be induced through such stimuli as changes in pH, salinity, ionic strength, etc. For example, gels have been widely examined as drug delivery agents, where the swelling trigger leads to the release of pharmaceuticals entrapped in the collapsed gel. But successful utilization of charged gel requires understanding and control of the swelling transition mechanism.

Correspondence to: M. Singh (meenakshi_s4@rediffmail.com).

Contract grant sponsor: Department of Science and Technology; contract grant number: SR/S2/CMP-65/2007.

Flory-Rhener theory explains the swelling characteristics of ionic gels.²⁸ Peppas and Merrill²⁹ customized the theory to go well with crosslinked gels. Polymer-solvent mixing free energy is the driving force for swelling of a polymer network bearing fixed charges assisted by the translational entropy of mobile ions whose distribution is governed by Donnan equilibrium theory.³⁰ At equilibrium, the mixing and ionic contributions to swelling keep in balance with the elastic response of the polymer network, which opposes swelling.³¹ Manning theory³² suggests that ionic polymers cannot sustain a charge density exceeding a critical value. With univalent charges, it leads to a maximum charge density in aqueous solution at 25°C, corresponding to 1 ionic charge per 7.14 Å (the Bjerrum length) of the fully extended chain. With a shorter distance between fixed charges, the counterions condense on them, preventing any further increase of charge density. Tamura et al.³³ studied the swelling behavior of charged polymeric gels in water/organic solvent mixtures. The dielectric constant and composition of solvent was found to coordinate the swelling behavior.

Keeping abreast of such superior properties of zwitterionic polyampholytic gels compared with those of the pristine polyelectrolytes, and the specific utility in removing toxic heavy metal ions and organic compounds from sewage and industrial wastewater, we were interested to prepare a series of novel carboxybetaine polymeric gel and examine their stimuli responsive behavior in various media with varying pH, temperature, ionic strength, etc.

EXPERIMENTAL

Materials

The reagents melamine (pure), dimedone (pure), and γ -butyrolactone were procured from Loba Chemie Di(ethylene glycol diacrylate) (DEGDA) was from Sigma Aldrich Co. Other chemicals were of analytical grade.

Synthesis

Dimedone-[N, N' melaminium] butyrocarylate copolymer

A solution of melamine [1.26 g (0.01 mol) in 25 mL DMSO] and dimedone [2.10 g (0.015 mol) in 25 mL DMSO] were prepared separately. The solutions were mixed and stirred at 45°C for 48 h. This clear reddish purple reaction mixture was treated with γ -butyrolactone [1.5 mL (0.015 mol) in 10 mL DMSO] and left for 24 h. Again this reaction mixture was subsequently treated with varying amount

TABLE I
Compositional Data of Various Gel Samples

Sample	Crosslinker (%)	Yield (%)	Gelation period
G10	10	0	No gelation
G25	25	10	Gelation (72 h)
G45	45	30	Gelation (48 h)
G65	65	55	Gelation (8 h)
G85	85	75	Gelation (spontaneous)

of DEGDA as crosslinker. Table I describes the ratio of monomers to crosslinker for various gel samples. Anal. Calcd for C₃₁H₅₂N₆O₁₀S₃ (G25): C 48.7%, H 6.8%, N 11.0%. Found: C 48.5%, H 6.8%, N 11.2%. The purity of the sample was checked by TLC in solvent mixture: benzene 14 mL: acetic acid: 1 mL. The corresponding structure is shown in Figure 1.

Swelling measurements

Samples of known weight were immersed in excess of solvent and kept in a sealed container which were placed in temperature-control bath with $\pm 0.5^\circ\text{C}$ accuracy until equilibrium was reached. The samples were removed and blotted dry. The swelling ratio of the copolymer gels was determined gravimetrically. The equilibrium weight of the swollen samples at each temperature was determined. The swelling ratios of the copolymer gels were calculated from the ratio of the weight of the equilibrated gel to the dry weight,

$$\text{Swelling.Ratio} = w_s - w_d/w_d \times 100$$

where w_s = Weight of the swollen gel, w_d = Weight of the dry gel sample.

Equipments

Elemental analyses were performed with CE 400 CHN Analyzer. The FTIR of the samples was recorded with JASCO FT/IR 5300 in KBr from 400 to 4000 cm^{-1} . Thermogravimetric analyses (TGA/DTA) were performed using Perkin-Elmer Diamond TG/DTA at 10.00°C/min. Scanning electron microscopy was performed by FESEM Quanta 200F at 5 KV in low vacuum. Potentiometric titrations were carried out on Systronics μpH system. Conductometric titrations

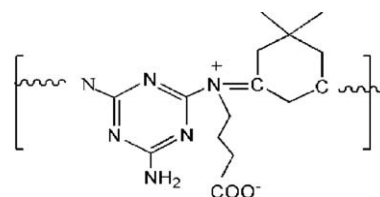


Figure 1 Structure of the polycarboxybetaine.

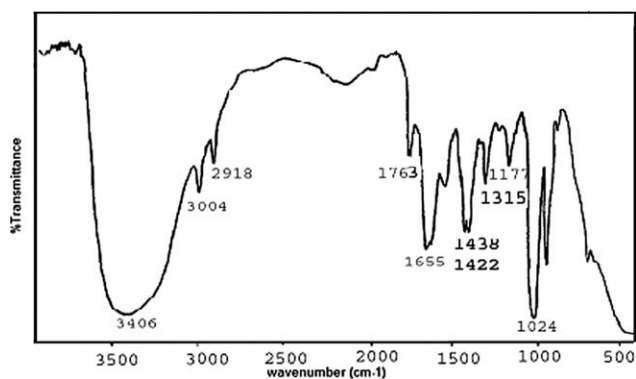


Figure 2 FTIR of the polycarboxybetaine G25.

were carried on CM 180 conductivitymeter. The absorption spectrum was recorded on Varian Cary50 Bio UV-visible spectrophotometer. The photoluminescence studies were performed using 266 nm excitation wavelength from a Nd:YAG laser (Inndas, Spitlight 600, Germany). The fluorescence spectra were recorded in the 400–900 nm region using fluorescence spectrometer (QE6500, Ocea-Optics) and Horibu Fluoromax 4 spectrophotometer. Swelling studies were performed on high precision water bath (error $\pm 0.5^\circ\text{C}$).

RESULTS AND DISCUSSION

Melamine, a nitrogen rich, triazine derivative (2,4,6-triamino-s-triazine) was condensed with a diketone, 5,5-dimethyl-1,3-cyclohexanedione (dimedone) via the nucleophilic addition–elimination reaction. The electronegative substituent can participate in delocalization of the imine double bond and raises the energy of the LUMO, making it less susceptible to nucleophilic attack. Here, the aromatic group from the melamine facilitates the delocalization of the probable charge centers on the C atom of imine groups.³⁴ The resulting polyimine was treated with γ -butyrolactone followed by DEGDA as a cross-linker in varying ratio. The extent of gelation as well as the time period needed for gelation depends on the amount of crosslinker, as shown in Table I, signifying the major role of crosslinking chemistry in the formation of gel.

The infrared spectrum of the copolymer is shown in Figure 2. The absorption due to imine group appears at 1552 cm^{-1} and those for carboxylate group are at 1655 (asym) and 1315 (sym) cm^{-1} . The other characteristic absorptions are 3004 (asym $\nu\text{-CH}_2$), 2918 (sym $\nu\text{-CH}_2$), 1763 ($\nu\text{-COO}$), 1435 ($\nu\text{-}\alpha\text{CH}_2$ bending), 1177 ($\nu\text{-C-C}$ bending), and 1024 ($\nu\text{-CO}$) cm^{-1} . The hygroscopic nature of the polymer was evinced by broad absorptions around 3406 cm^{-1} . The N–H stretch of amine at one end of the melamine is overlapped by broad OH peak.

The image is shown in Figure 3. Surface morphology of the gel G85 was investigated by scanning electron microscopy (SEM) technique that showed grooved structure with large pores Figure 3a. The pore size estimated from SEM image was $3.57\text{ }\mu\text{m}$. Figure 3b is the image showing the gel like morphology of the crosslinked polymer after synthesis taken by a digital camera.

The thermogravimetric (TG) curve (Fig. 4) shows a gradual decrease in the weight with temperature up to $\sim 400^\circ\text{C}$. A broad endothermic region in the temperature range $100\text{--}400^\circ\text{C}$ is due to the degradation of solvent entrapped in the pores of gel. The gel has lost 20% weight up to 200°C and 50% weight is lost at $\sim 395^\circ\text{C}$. In DTA curve a small endothermic peak was observed at 436°C with $\Delta H = 301\text{ J/g}$ representing change in functional group orientations involving a heat change. The gel is completely decomposed at temperatures $>450^\circ\text{C}$.

The absorption spectrum of the G85 gel sample showed peak at 265 nm. The absorption may be due to $n\rightarrow\pi^*$ transition of the chromophores (C=O, C=N, and COO) in the polymeric chain. The fluorescence spectrum of the G85 gel was observed at $\lambda_{\text{ex}} = 266\text{ nm}$

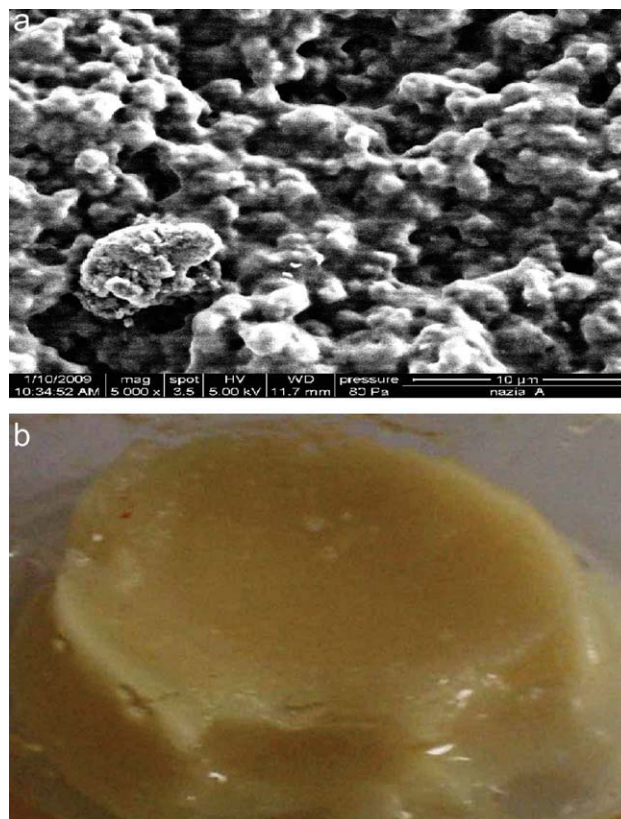


Figure 3 (a) SEM-EDAX of G85 showing the pore size $3.57\text{ }\mu\text{m}$. (b) The gel like morphology of G85. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com)].

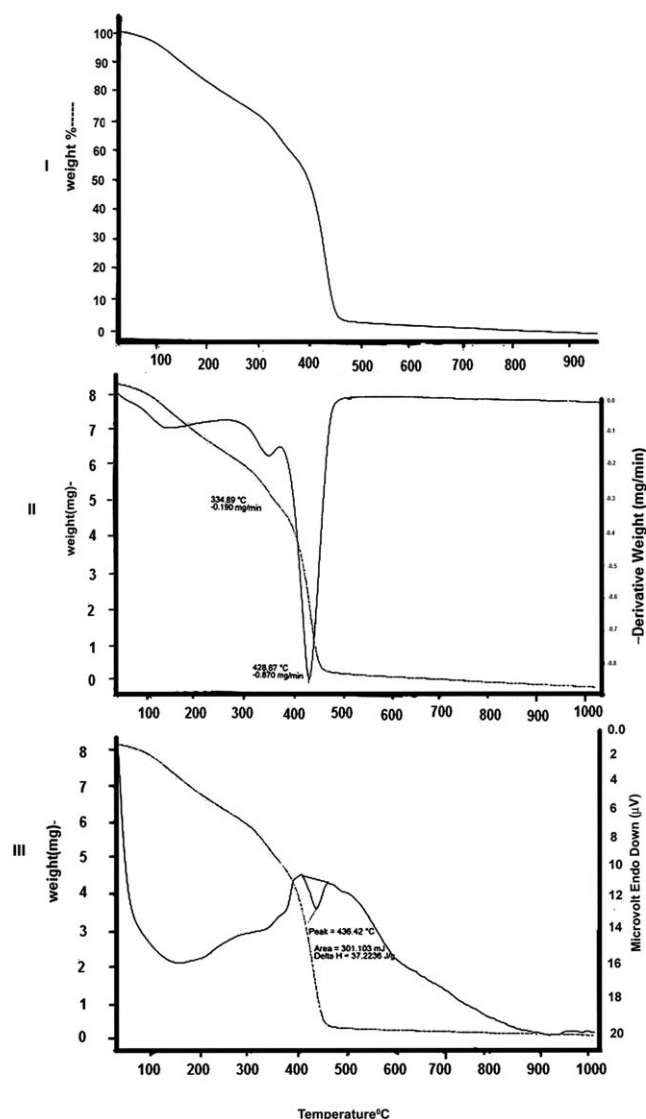


Figure 4 Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) showing the stability of the polymer upto 450°C.

and emission was obtained at $\lambda_{em} = 540$ nm as shown in Fig. 5.

The response of G25, G45, G65, G85 gel samples were examined toward swelling in different media. Table II shows the extent of swelling in some of the solvents where the swelling was comparatively more appreciable. As it can be discerned from the Table II, the sample G25 showed highest swelling in chloroform:methanol (2 : 1) and the extent of swelling decreased as the concentration of crosslinker in the feed mixture was increased. But the situation was reversed in ethanol:water (1 : 1) and also in the alkali NaOH (N/10). As observed by Hiroki et al.,³⁵ in the study of the effect of alcohol on swelling, the crosslinking increases the hydrophobicity, breaking the clustering tendency of ethanol and/or water, thus increasing the interaction between the polymer chain

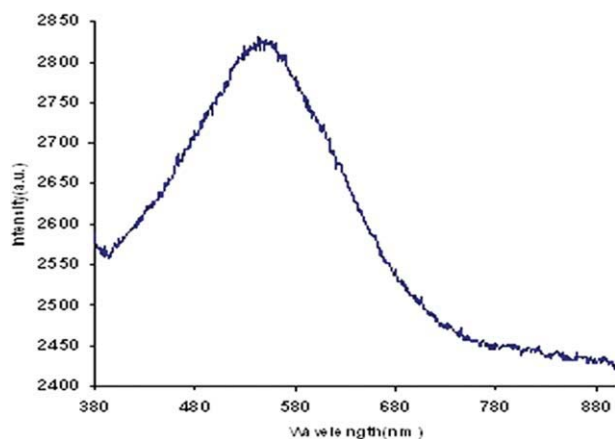


Figure 5 Fluorescence spectrum of the polyzwitterion at $\lambda_{ex} = 266$ nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

and solvent molecules. Hence, as the crosslinking increased from G25 to G85, the swelling also shows a rise from 35 to 200%. But in NaOH (N/10), the gel shows swelling to a larger extent in comparison to alcohol-based solvent compositions and ultimately the gel dissolves completely in alkali. In G25 to G85, as the ratio of carboxybetaine to crosslinker falls down, it takes longer to dissolve in NaOH. The electrostatic interactions between the opposite charges present on the polymer chain keep them in gel state. But in NaOH, Na^+/OH^- ions shield the respective charge centers and break the interionic interaction to dissolve them.²⁴ As the ratio of neutral crosslinks was increased, it took longer for alkali to dissolve them.

G85 was found to be most suitable for further exploration in a few more solvents, viz. 1,4-dioxane, chloroform, acetonitrile, dimethylsulfoxide (DMSO), ethanol:water (1 : 1), chloroform:methanol (2 : 1), and an alkali, i.e., NaOH (N/10) as well as an acid (N/10 HCl). Figure 6 shows the swelling response in these solvents. Being a highly polar system the gel (G85) shows the respective response as the dielectric constants of the media varies. Figure 6 shows lesser

TABLE II
Swelling Response of Gel Samples in Various Solvent Mixtures at Room Temperature

Sample	Swelling (%)					
	Ethanol: Water (1:1)		Chloroform: Methanol (2:1)		NaOH (N/10)	
	1h	24h	1h	24h	1h	24h
G25	15	15	192	192	40 ^a	Soluble in 5h
G45	15	15	83	83	42 ^a	Soluble in 8h
G65	15	15	65	65	48 ^a	Soluble in 26h
G85	40	40	41	41	90 ^a	Soluble in 48h

^a Translucent

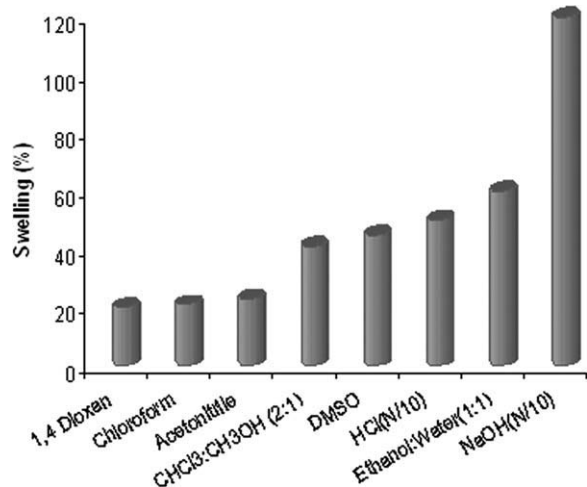


Figure 6 Swelling response of G85 in various solvents in 48 h.

swelling in the media with lower ϵ , i.e., dioxane and chloroform but acetonitrile and DMSO with intermediate range ϵ , show more swelling. However, in the alkali (N/10 NaOH, pH = 12), the charged centers are shielded by respective Na^+ / OH^- ions, breaking the interionic interaction, thus allowing more and more solvent molecules to enter into the polymeric network, making them more swollen.

In Figure 7, the effect of temperature on swelling in NaOH (N/10) is shown. With the temperature, the extent of swelling also rises and it takes lesser time to attain equilibrium. The maximum swelling is observed at 45°C, on still higher temperature (60°C), the gel disrupts and dissolves in alkaline solution in only 15 min.

Both the ionic centers of the carboxybetaine gel are in ionized form at pI, and thus, are under electrostatic interaction with each other, which get disrupted on addition of NaOH. On raising the temperature from 30 to 45°C, the swelling increases from ~ 75 to 220%. But on enhancing the temperature even further, the gel starts dissolving in the alkali. At 50°C, it takes only ~ 30 min to dissolve completely but at 60°C, it dissolves in 15 min only.

Solution of the gel in N/10 NaOH was titrated with N/10 HCl; on addition of N/10 HCl, the gel was regenerated and characterized by IR spectroscopy. The process was repeated again and again, i.e., the regenerated gel redissolved in NaOH and regenerated again on addition of HCl. The quaternary imminium and carboxyl groups are under coulombic interaction with each other thus forming gel morphology. In HCl, the imminium as well as carboxyl groups are protonated completely. As they get protonated, they are discharged, thus breaking their interionic coulombic interaction to extend the chain and also breaking interchain interaction, which might

have been formed, hence extending the polymeric chain in HCl or at low pH illustrating high swellability with translucent character. However, in alkaline medium, as we add NaOH to the system, the Na^+ and OH^- ions shielded the respective carboxyl and ammonium charge centers to break their interactions, solubilizing the gel at high pH also. This pH responsive behavior could be exploited for various applications. To name a few, wastewater treatment, especially in removing the toxic materials from the affluent of textile industry or other technical/industrial applications.

In the conductivity titration curve of polymer G85 three regions were observed (Fig. 8). In the first region, the conductivity of the solution decreased with neutralization of excessive H^+ or OH^- ions that were present due to preacidification or prealkalization. In the second region, ionization of acidic or basic groups in the polymer caused an increase in conductivity, and hence, the slope of curve conductivity versus volume of titrant. In the third region,

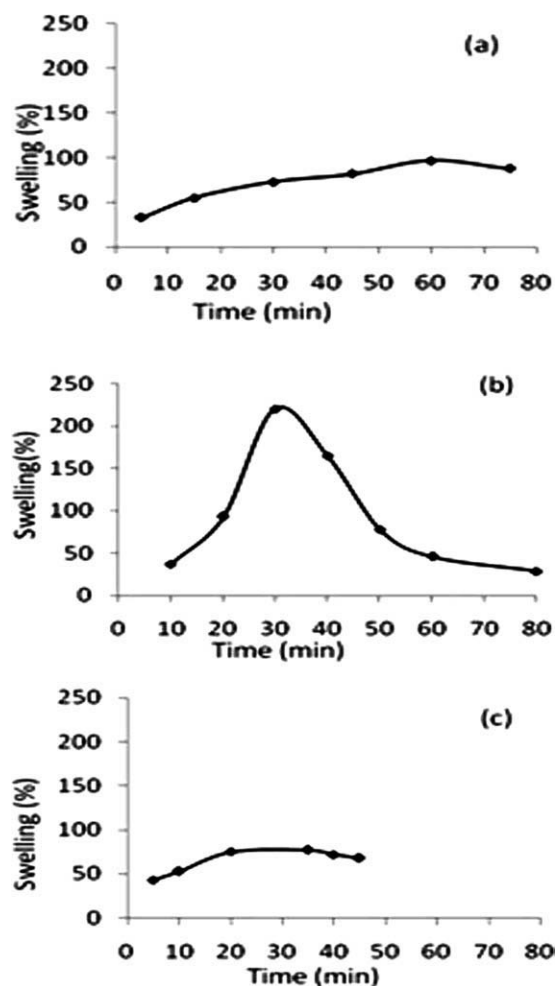


Figure 7 Swelling response of the G85 in NaOH (N/10) at (a) 40°C, (b) 45°C, and (c) 50°C [standard deviation = ± 0.33].

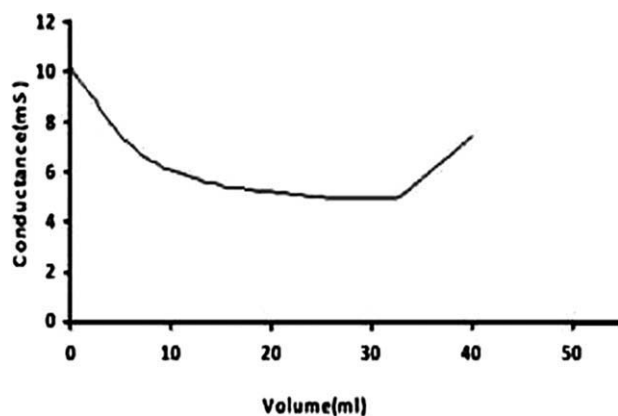


Figure 8 Conductometric curve of G85 dissolved in N/10 NaOH and titrated against N/10 HCl.

the slope was equal to the theoretical conductivity of the titrant. At higher volume of HCl (titrant), it was observed that white film like material deposited at the base which is the regenerated polymer. Potentiometric titrations were carried out by pretreating the gel with NaOH and titrating with HCl and *vice versa*, i.e., by treating the gel with HCl and titrating with NaOH respectively. In both the cases, sigmoid curve was obtained with pI value 7.3 (Fig. 8).

To explore the effect of pH in detail, the swelling of G85 gel in water at different pH was studied. The pH effect was studied in two regions, in pH <7 and pH >7 as shown in Figure 9. As the carboxyl groups were protonated more and more, the swellability decreases, it is observed to be more at pH 6, lesser at pH 5, and least swelling at pH 4. But in pH >7, it is maximum at pH 11, when carboxyl groups are supposed to be completely stripped off all the protons and ionizes completely to show more hydrophilicity. The optimum pH at which the gel attains maximum swelling is 12. The pI of the gel (estimated by potentiometric titration) is 7.3. The zwitterionic species shows least solubility at its pI. The aqueous solution of zwitterionic polymer chains exists as a combination of interchain aggregates as well as individual chains. The addition of NaOH or any electrolyte leads to a higher ionic strength, weaker electrostatic attraction, breaking interchain and intrachain associations. However, it also decreases both electrostatic repulsion and solvation and makes the polymer chains more hydrophobic. The hydrophobic attraction results in intrachain contraction and interchain aggregation.

To further explore the behavior of this alkali soluble/swellable carboxybetaine gel, the effect of ionic strength in qualitative aspects were examined (Fig. 10). Three salts with common anion, Cl^- were chosen for this study. In the presence of any salt or say due to enhanced ionic strength, the swellability falls down. The charged centers were shielded by respective ions of opposite charge of the salt thus ren-

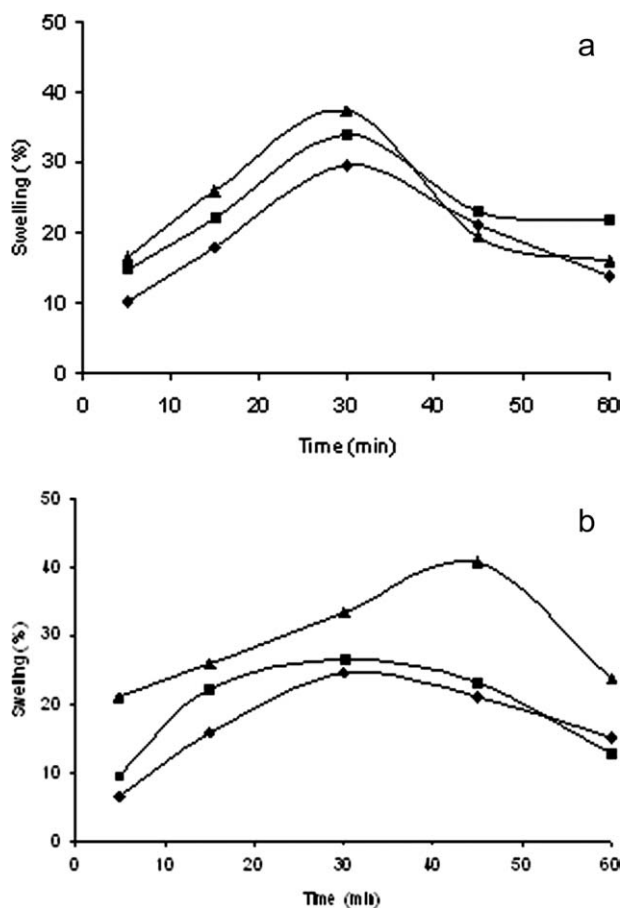


Figure 9 (a) Swelling response of G85 in NaOH (N/10) at pH 4 (◆), pH 5 (■) and pH 6 (▲) [standard deviation = ± 0.25]; (b) Swelling response of G85 in NaOH (N/10) at pH 8.5 (◆), pH 10 (■) and pH 11 (▲) [standard deviation = ± 0.25].

dering the gel with lesser charge density, permitting lesser solvent/water molecules to enter into the gel network. The extent of swelling is dictated by the composition of swelling medium. The addition of KCl into the solution further dissociates the interchain

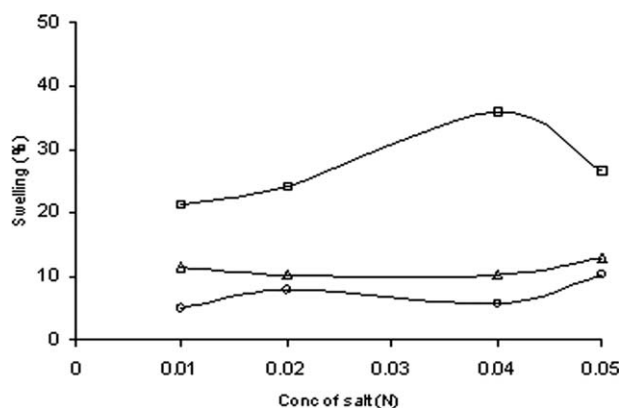


Figure 10 Swelling response of G85 in NaCl (Δ), KCl (\circ), and MgCl_2 (\square) at room temperature.

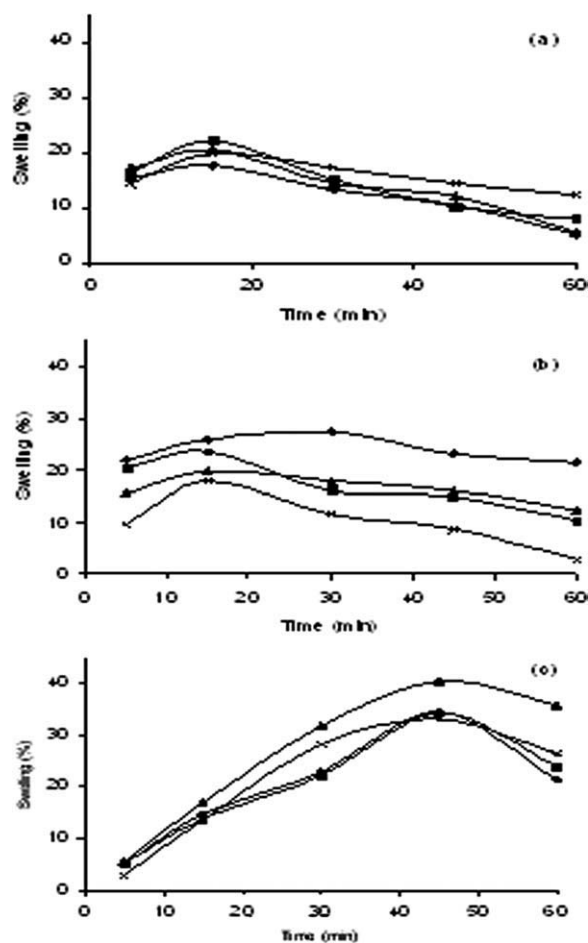


Figure 11 Swelling response of G85 in (a) NaCl, (b) KCl, and (c) MgCl₂ at the concentration 0.01N (◆), 0.02N (■), 0.04N (▲) and 0.05N (x) at room temperature.

association, because of higher ionic strength and weaker electrostatic attraction between = N⁺R₂ and -COO⁻ groups. The electrostatic attraction, induces interchain and intrachain associations, but electrostatic repulsion leads to the solvation of the polymer chains. Therefore, suppressing electrostatic interactions by the addition of electrolyte propagates a change from dissociation-and-extension to aggregation-and-contraction. Addition of KCl or NaCl provides competition for the water molecules hydrating the polybetaines chains. Dehydration of the polybetaine chain results in deswelling. The overall swelling

is the net effect of that due to salt imbibed within the gel (which increases continuously with time) and that because of solvent molecules taken into the gel. The quaternary ammonium/imminium and carboxylate ions are surrounded by a sheath of Cl⁻ and K⁺ ions (in KCl solution), respectively. Hence, zwitterionic character is retained. The possibility of strong intra-chain or interchain interactions is restored, i.e., breakage of such interactions to allow ingress of water is reduced. Disruption and desolvation of the (-NH₂, COO⁻) -solvent weak, noncovalent bonds permits attractive interchain hydrophobic interactions and hydrogen bonding to dominate. Thus, the gel deswells and contracts. Whereas, in the salt solutions of the divalent electrolytes, the swellability enhances in comparison to that in monovalent salt solutions. The divalent cations are more effective in curtailing the charge centers, thus enhancing the water uptake by hydrophilic groups of the polymer chain. The divalent ions facilitated the disruption of crosslinks formed between COO⁻ of one chain with cationic center of another chain by electrostatically binding two of the carboxybetaine groups of a chain simultaneously. This disruption of crosslinks between chains assists in better swelling. Here, three different electrolytes having common anion (Cl⁻), NaCl, KCl, MgCl₂ have been studied. Among them, K⁺ has least charge density and Mg²⁺ has most. The presence of Na⁺ and K⁺ ions deswell the polymeric gel, being incapable of breaking strong attractive forces between the permanent charges of the polymeric backbone. The electrostrictional effect is curtailed encouraging the solvophobicity of the polymeric chain providing pockets to accommodate more and more water molecules. Moreover, the smaller hydration sphere of bigger cations is able to penetrate the gel crosslinks, whereas the smaller ions (Na⁺, K⁺) with larger hydration spheres were unable to penetrate the gel network, thus deswelling the gel. The levelling of the curves in Figure 11 shows that the concentration of 0.01N itself seems to be sufficient to balance the forces responsible for swelling, when the osmotic pressure of the solvent is balanced with the subchain stretching energy within the gel framework.

The swollen G85 sample in NaOH was studied for its deswelling behavior at different temperatures. The swollen sample was taken out of the solvent and

TABLE III
Sorption Parameters Estimated for Various Dyes

S.No.	Dye (λ _{max})	pH	Swelling (%)	Conc. of dye (g/l) before extraction	Conc. of dye (g/l) after extraction	Amount adsorbed (g/l)	Adsorption (%)
1.	Crystal violet (590 nm)	7.50	209	46 × 10 ⁻³	40 × 10 ⁻³	2.70 × 10 ⁻³	13.04
2.	Methylene blue (662 nm)	7.12	70	64 × 10 ⁻³	21 × 10 ⁻³	7.64 × 10 ⁻³	67.18
3.	Phenolphthalein (560 nm)	7.42	530	118 × 10 ⁻³	97 × 10 ⁻³	33.08 × 10 ⁻³	17.79

Contact period of each dye is 60 min.

Amount of dye adsorbed by 10 mg of polymer is reported.

kept at 50°C for 1 h in an oven. The sample showed no change, neither in its morphology nor on the weight of the swollen sample, i.e., it did not deswell at 50°C. On further increasing the temperature to 80°C, for 1h, the gel deswells upto 24%, i.e., the entrapped solvent was evaporated to some extent but the morphology was not altered. At 100°C, 46% weight was lost but the morphology was still intact. But at 120°C, the gel was denatured and became fragile.

The sorption chemistry of gel was studied using the representative of three classes of dye. The dyes used are phenolphthalein, a xanthine dye, crystal violet, a triphenylmethane dye and methylene blue consisting of a phenothiazine ring. The known weight of polymer was added to each dye solution. After mixing dye vigorously in solution of water:ethanol (1 : 1) for desired period, the concentration of the remaining dye was determined. The pH of dye solution was also checked. The sorption of methylene blue was maximum. The dye loading capacity was calculated from the initial and final concentration of dye corresponding to calibration curve. Table III represents the swelling and adsorption capacity of polymer in different dyes. The difference in the extent of adsorption may be due to the ability of the dye to interact with the groups of the polymer, the relative molecular size of the dye and the morphology of the gel (pore size of the gel is fairly large enough to accommodate dye molecules).

In conclusion, a novel responsive carboxybetaine gel is presented. Its sensitivity toward the composition of swelling medium and its physical parameters could be useful in biomedical devices, in drug delivery, and also in wastewater effluents treatment.

The authors acknowledge Prof.GVS. Sastry (SEM) for kind help.

References

1. Tanaka, T. *Phys Rev Lett* 1978, 40, 820.
2. Ricka, J.; Tanaka, T. *Macromolecules* 1985, 18, 83.
3. Schroder, U. P.; Oppermann, W. In *Physical Properties of Polymeric Gels*; Addad, J. P. C., Ed., Wiley: Chichester, 1996, p 18.
4. Osada, Y.; Gong, J. *Prog Polym Sci* 1993, 18, 187.
5. Lorimer, J. W. D.; Riedel publ. Co: Dordrecht, 1976; p 45.
6. Salamone, J. C.; Volkson, W.; Iseral, S. C.; Olson, A. P.; Raia, D. C. *Polymer* 1977, 18, 1058.
7. Salamone, J. C.; Tsai, C. C.; Watterson, A. C. *J Macromol Sci Chem Ed* 1979, 13, 665.
8. Monroy Sato, V. N.; Salmone, J. C.; Galin, J. C. *Polymer* 1984, 25, 254.
9. Laschewsky, A. *Adv Polym Sci* 1995, 124, 1.
10. Thomas, D. B.; Vasilieva, Y. A.; Armentrout, R. S.; McCormick, C. L. *Macromolecules* 2003, 36, 9710.
11. Lowe, A. B.; McCormick, C. L. *Chem Rev* 2002, 102, 4177.
12. Singh, P. K.; Singh, V. K.; Singh, M. E. *Polymers* 2007, 30, 1.
13. Zhang, Z.; Chao, T.; Liu, L.; Cheng, G.; Ratner, B. D.; Jiang, S. *J Biomater Sci Polym Ed* 2009, 20, 1845.
14. Yang, W.; Zhang, L.; Wang, S.; White, A. D.; Jiang, S. *Biomaterials* 2009, 30, 5617.
15. Cheng, G.; Li, G.; Xue, H.; Chen, S.; Bryers, J. D.; Jiang, S. *Biomaterials* 2009, 30, 5234.
16. Yang, W.; Xue, H.; Li, W.; Zhang, J.; Jiang, S. *Langmuir* 2009, 25, 11911.
17. Emmenegger, CR.; Brynda, E.; Riedel, T.; Sedlakova, Z.; Houska, M.; Bologna, A. A.; *Langmuir* 2009, 25, 6328.
18. Vaisocherova, H.; Zhang, Z.; Yang, W.; Cao, Z.; Cheng, G.; Taylor, A. D.; Piliarik, M.; Homola, J.; Jiang, S. *Biosens Bioelectron* 2009, 24 1924.
19. Fujishita, S.; Inaba, C.; Tada, S.; Gemmei-ide, M.; Kitano, H.; Saruwatari, Y. *Biol Pharma Bull* 2008, 31, 2309.
20. Tada, S.; Inaba, C.; Mizukami, K.; Fujishita, S.; Gemmei-ide M.; Kitano, H.; Mochizuki, A.; Tanaka, M.; Matsunaga, T. *Macromol Biosci* 2009, 9, 63.
21. Bohrisch, J.; Schimmel, T.; Engelhardt, H.; Jaeger, W. *Macromolecules* 2002, 35, 4143.
22. Liaw, D. J.; Huang, C. C.; Lee, W. F.; Borbely, J.; Kang, E. T. *J Polym Sci Polym Chem* 1997, 35, 3527.
23. Fevola, J. M.; Bridges, J. K.; Kellum, G. M.; Hester R. D.; McCormick, C. L. *J Appl Polym Sci* 2004, 94, 24.
24. Niu, A.; Liaw, D. J.; Sang, H. C.; Wu, C. *Macromolecules* 2000, 33, 3492.
25. Lowe, A. B.; Billingham, N. C.; Armes, S. P. *Macromolecules* 1998, 31, 5991.
26. Faversee, P.; Laschewsky, A. *Polymer* 2001, 42, 2755.
27. Noh, J. G.; Sung, Y. J.; Geckler, K. E.; Kudaibergenov, S. E. *Polymer* 2005, 46, 2183.
28. Flory, P. J. *Principles of Polymer Chemistry*. Cornell University Press: New York, 1953.
29. Peppas, N. A.; Merrill, E. W. *J Polym Sci Polym Chem* 1976, 14, 459.
30. Donnan, F. G.; Guggenheim, E. A. *Z. Phys Chem A* 1932, 162, 346.
31. Mark, J. E.; Erman, B. *Rubberlike Elasticity. A Molecular Primer*. Wiley: New York, 1988.
32. Manning, G. S. *J Phys Chem* 1981, 85, 870.
33. Tamura, T.; Kawabata, N.; Satoh, M. *Polym Bull* 2000, 44, 209.
34. Tarannum, N.; Singh, M. *J Appl Polym Sci* 2010, 118, 2821.
35. Hiroki, A.; Maekawa, Y.; Yoshida, M.; Kubota, K.; Katakai, R. *Polymer* 2001, 42, 1863.