

# Synthesis and Characterization of Zwitterionic Organogels Based on Schiff Base Chemistry

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**ABSTRACT:** Poly(sulfobetaine)s and poly(carboxybetaine)s have been extensively studied for their zwitterionic and biocompatible nature. The specific features that make such zwitterionic structures technologically important are their chemical structure, a straight forward synthetic route, high ionic contents with interesting dilute solution, and solid state properties. The objective of this work is to synthesize novel zwitterionic polymers having gel characteristics. Here, *p*-phenylene diamine/melamine react as nucleophiles with glutaraldehyde to produce poly(schiff base)s. In the subsequent step, the poly(sulfobetaine)s and poly(carboxybetaine)s were produced on treatment with 1,3-propane sultone/ $\gamma$ -butyrolactone. Hence, a catalyst free facile approach to novel zwitterionic polymers was

obtained. The polymers were characterized by elemental analyses, FTIR, XRD analyses, SEM, pH metric titrations, conductometric titrations, and thermal analyses (TGA/DTA). The polymeric samples carry the gel characteristics, showing lamellar structure with porous network. XRD pattern shows Bragg peaks indicative of superstructures. Thermal analysis indicates the Hoffman elimination of  $\beta$  hydrogen and subsequent release of sulfopropyl/carboxybutyl group. One of the gel polymers shows fluorescence also. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2821–2832, 2010

**Key words:** zwitterionic; sulfobetaine; carboxybetaine; polyimine; gel

## INTRODUCTION

Zwitterionic polymers comprising of iminium centers extend the range of properties of those having imine groups as well as those of having charged groups along the chain. Imines play significant role in biological reactions as well as in industrial and technological applications, for instance, the amino acid alanine is being made from pyruvic acid by using imines via reductive aminations,<sup>1</sup> the toxin used by an orbweaver spider to paralyze its prey, an important intermediate in the glycolysis reactions where aldolase catalyzes the conversion of D-glucose to pyruvate molecules. Besides such biochemical significant role, polyimines also known as polyschiff bases, bear good engineering properties too, such as electronic, optoelectronic, nonlinear optical, or liquid crystalline behavior, high thermal stability as well as mechanical strength and moreover, some of them show mesophases on heating.<sup>2–13</sup> In view of such appealing characteristics, the synthesis of novel polymers were attempted through Schiff base chemistry with added advantage of zwitterionic centers being provided by

zwitterionizing the imine centers to fabricate polyelectrolytes of iminosulfobetaine and iminocarboxybetaine, having gel characteristics. Hitherto, the polybetaines consisting of iminium centers have not been reported as per our survey of the literature. Hence, a novel attempt has been made here keeping abreast of the relevance of Schiff base chemistry and the search for nitrogen rich polymers in material science, melamine and/or phenylene diamine, the low cost industrial chemicals were reacted with dialdehydes, in a one-pot polycondensation approach. Since its discovery in 1864 by Hugo Schiff,<sup>14</sup> this classical reaction has been a versatile tool in organic synthesis. The mechanism leading to the Schiff base is well understood. The dynamic nature of the imine bond formation has been also helpful in the build up of complex molecular architectures, such as macrocyclic ligands<sup>15</sup> and interlocked molecules.<sup>16</sup>

Polycarboxybetaines and polysulfobetaines show good biocompatibility,<sup>17–20</sup> antibacterial properties and their utility for building bioinert coatings.<sup>21–24</sup> It is worth mentioning that the structure of sulfobetaine is similar to taurine, present in high concentration in animals and in trace concentration in plants.<sup>25</sup> Further glycine betaine, an analog of carboxybetaine is one of the solutes vital to the osmotic regulation of living organisms.<sup>26</sup> Such structural similarities led us to more in-depth exploration in this area.

Hence, high-mechanical strength and good thermal stability of imines, the zwitterionic and biomimetic nature of poly(sulfobetaine)s and poly(carboxybetaine)s

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may prove these novel materials good candidate for industrial/technological applications. Furthermore, with the advantage of gel characteristics and aforementioned unique properties, a facile catalyst-free approach through Schiff base chemistry, such polymeric zwitterionic gels may have many potential biomedical applications ranging from tissue engineering to drug delivery.

## EXPERIMENTAL SECTION

### Materials

*p*-Phenylene diamine (98% pure), glutaraldehyde (98% pure),  $\gamma$ -butyrolactone (98% pure) were purchased from Spectrochem. Melamine (97%), dimethylsulfoxide (97%), dimethylformamide and polyethylene glycol (PEG) (97%) MW = 400 g were procured from Loba Chemie. 1,3 Propane sultone was from Sigma Aldrich (99% Pure). *N,N*-methylene bisacrylamide was purchased from Ottokemi (99% Pure).

### Synthesis

#### Poly(*N*-phenylene *N'*imino pentyl)imminium propane sulfonate

Equimolar solutions of *p*-phenylene diamine [0.54 g (5 mmol) in 20 mL DMF] and glutaraldehyde [0.47 mL (5 mmol) in 20 mL DMF] were prepared separately. The solutions were mixed and refluxed at 80°C for 1 h. Colour of the mixture changed to black. 1,3-Propane sultone [1.32 mL (15 mmol) in 10 mL DMF] was added to the above mixture and refluxed at 70°C for 3 h. The reaction is exothermic. Resulting product, black gel like material (yield 85%) was washed several times with hot water and dried *in vacuo* at room temperature. Analysis (%): C = 54.14, H = 6.12, N = 9.52. The indicated structure confirms the theoretical percentages (C = 54.35, H = 5.18, N = 10.10);  $n = 27$  estimated by conductometric titrations of charged groups, where molecular weight of a monomer is 294 g with the formula  $C_{14}H_{18}N_2SO_3$ . The corresponding structure is shown in Figure 1(a).

#### Poly(*N*-phenylene *N'*imino pentyl)imminium butane carboxylate

A solution of *p*-phenylene diamine [0.54 g (5 mmol) in 20 mL DMF] was added to a 20 mL solution of glutaraldehyde [0.50 mL (5 mmol) in 20 mL DMF] and the reaction mixture was heated at 45°C for 3 h. The color of the reaction mixture changed to maroon color. The reaction mixture was subsequently treated with  $\gamma$ -butyrolactone (1.22 mL in 5 mL DMF) at 60°C for 1 h. The product, black gel (yield 90%), was washed several times with water and then dried *in vacuo* at room temperature. Analysis (%): C = 67.00, H = 6.21, N = 11.09. The indicated structure confirms the theoretical percentages (C = 68.00, H = 6.72, N = 11.76);  $n = 22$  estimated by conductometric titrations of charged groups, where

molecular weight of a monomer is 476 g with the formula  $C_{27}H_{32}N_4O_4$  including end group. The corresponding structure is shown in Figure 1(a).

#### Poly(*N*-melamine *N'*imino pentyl)imminium propane sulfonate

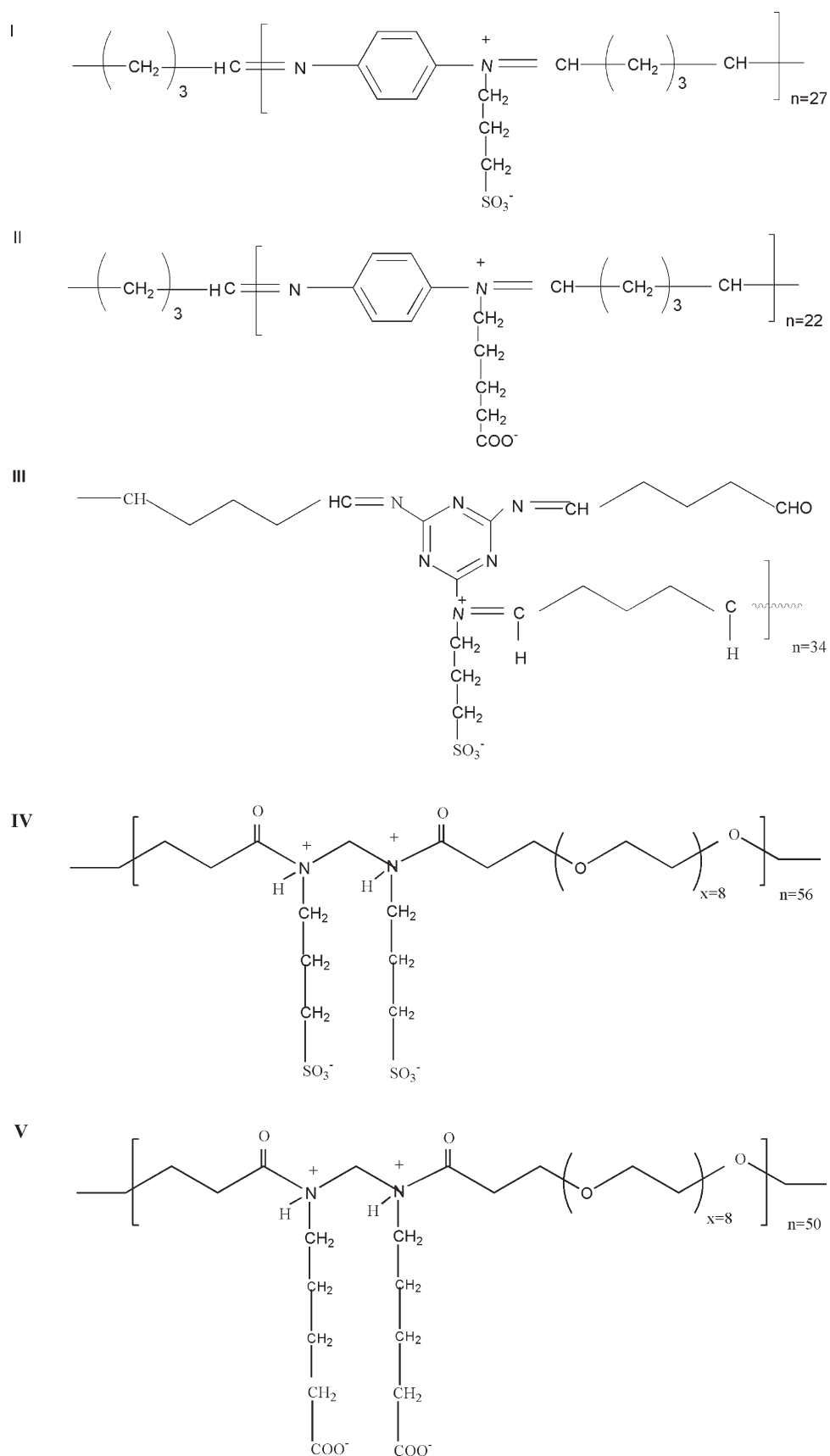
A solution of melamine [0.50 g (4 mmol) in 25 mL DMSO] was added to solution of glutaraldehyde [0.51 mL (6 mmol) in 25 mL DMSO] and the mixture was stirred and heated at 60°C for 3 h. The colorless reaction mixture was treated with 1,3-propane sultone [0.90 mL (10 mmol) in 10 mL DMSO] at 60°C for 1 h. The reaction mixture was kept at room temperature for 2 days. The product, yellowish gel (yield 70%), was washed several times with water and then dried *in vacuo* at room temperature. Analysis (%): C = 48.86, H = 5.73, N = 17.21. The indicated structure confirms the theoretical percentages (C = 49.91, H = 6.61, N = 17.86);  $n = 34$  estimated by conductometric titrations of charged groups, where molecular weight of a monomer is 478 g with the formula  $C_{21}H_{30}N_6O_5S$  including end group. The corresponding structure is shown in Figure 1(a).

#### Polyethyleneglycol-[*N,N'*-methylene bisacrylamide ammonium propane sulfonate] copolymer

A solution of *N,N'*-methylene bisacrylamide [0.77 g (5 mmol) in 30 mL water] was added to a solution of PEG (400) [2.10 mL (5 mmol)] and the reaction mixture was heated with stirring at 60°C for 2 h. The colorless reaction mixture was kept overnight and treated with 1,3-propane sultone [0.90 mL (10 mmol)]. The reaction mixture was again stirred at 60°C for 6 h and kept at room temperature for 48 h. The product, colorless gel (yield 80%), was washed with water repeatedly and dried *in vacuo* at room temperature. Analysis (%): C = 44.10, H = 7.11, N = 3.37. The indicated structure confirms the theoretical percentages (C = 45.81, H = 7.39, N = 3.45);  $n = 56$  estimated by conductometric titrations of charged groups, where molecular weight of a monomer is 768 g with the formula  $C_{29}H_{56}N_2S_2O_{17}$ . The corresponding structure is shown in Figure 1(b).

#### Polyethyleneglycol-[*N,N'*-methylene bisacrylamide ammonium butane carboxylate] copolymer

A solution of *N,N'*-methylene bisacrylamide [3.08 g (20 mmol) in 30 mL water] was added to a PEG(400) solution [8.0 mL (20 mmol)] and the reaction mixture was heated with stirring at 60°C for 2 h. The colorless reaction mixture was kept overnight and treated with  $\gamma$ -butyrolactone [3.50 mL (40 mmol)]. The reaction mixture was again stirred at 60°C for 6 h and kept at room temperature for 48 h. The product, colorless gel (yield 80%), was washed with water repeatedly and dried *in vacuo* at room



**Figure 1** Structures of Polymers: (a) Polyiminobetaines I, II, III, and (b) Polyamidobetaines IV and V.

TABLE I  
Solubility of Polymers in Various solvents

Solvent	I	II	III	IV	V
Distilled water	×	×	×	×	×
DMF	×	×	×	×	×
DMSO	×	×	×	×	×
Benzene	×	×	×	×	×
Chloroform	×	×	×	×	×
Acetone	×	×	×	×	×
THF	×	×	×	×	×
CH <sub>3</sub> OH	×	×	×	×	×
Acetone (30%) + CH <sub>3</sub> OH (20%)	×	×	×	△	×
CCl <sub>4</sub>	×	×	×	×	×
CHCl <sub>3</sub> (50%) + CH <sub>3</sub> OH (50%)	×	×	×	△	×
1,2 dichloroethane	×	-	-	-	-
CS <sub>2</sub>	×	×	×	×	×
Triethylamine	×	×	×	×	×
Acetonitrile	×	≠	△	≠	×
Dioxan	×	≠	×	≠	×
Chloroacetic acid	×	-	-	-	-
Benzyl Alcohol	×	-	-	-	-
0.1N HCl	≠	≠	≠	×	×
0.1N NaOH	×	×	×	×	×
Toluene	×	×	×	×	×

× - Insoluble.

≠ - Partially soluble.

△ - Partially soluble on heating.

temperature. Analysis (%): C = 45.10, H = 8.28, N = 3.85. The indicated structure confirms the theoretical percentages (C = 45.27, H = 7.25, N = 3.78);  $n = 50$  estimated by conductometric titrations of charged groups, where molecular weight of a monomer is 724 g with the formula C<sub>33</sub>H<sub>60</sub>N<sub>2</sub>O<sub>15</sub>. The corresponding structure is shown in Figure 1(b).

### Characterization

Elemental analyses were performed with CE 400 CHN Analyzer. The FT/IR spectra of the samples were recorded with JASCO FT/IR 5300 in KBr from 400–4000 cm<sup>-1</sup>. Thermogravimetric analyses (TGA/DTA) were performed using Perkin Elmer, Diamond TG/DTA at 10.00°/min. Powder X-ray diffraction studies were done by PW1710 BASED. 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 were carried on CM 180 conductivitymeter. 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, USA) and Horibu Fluoromax 4 spectrophotometer.

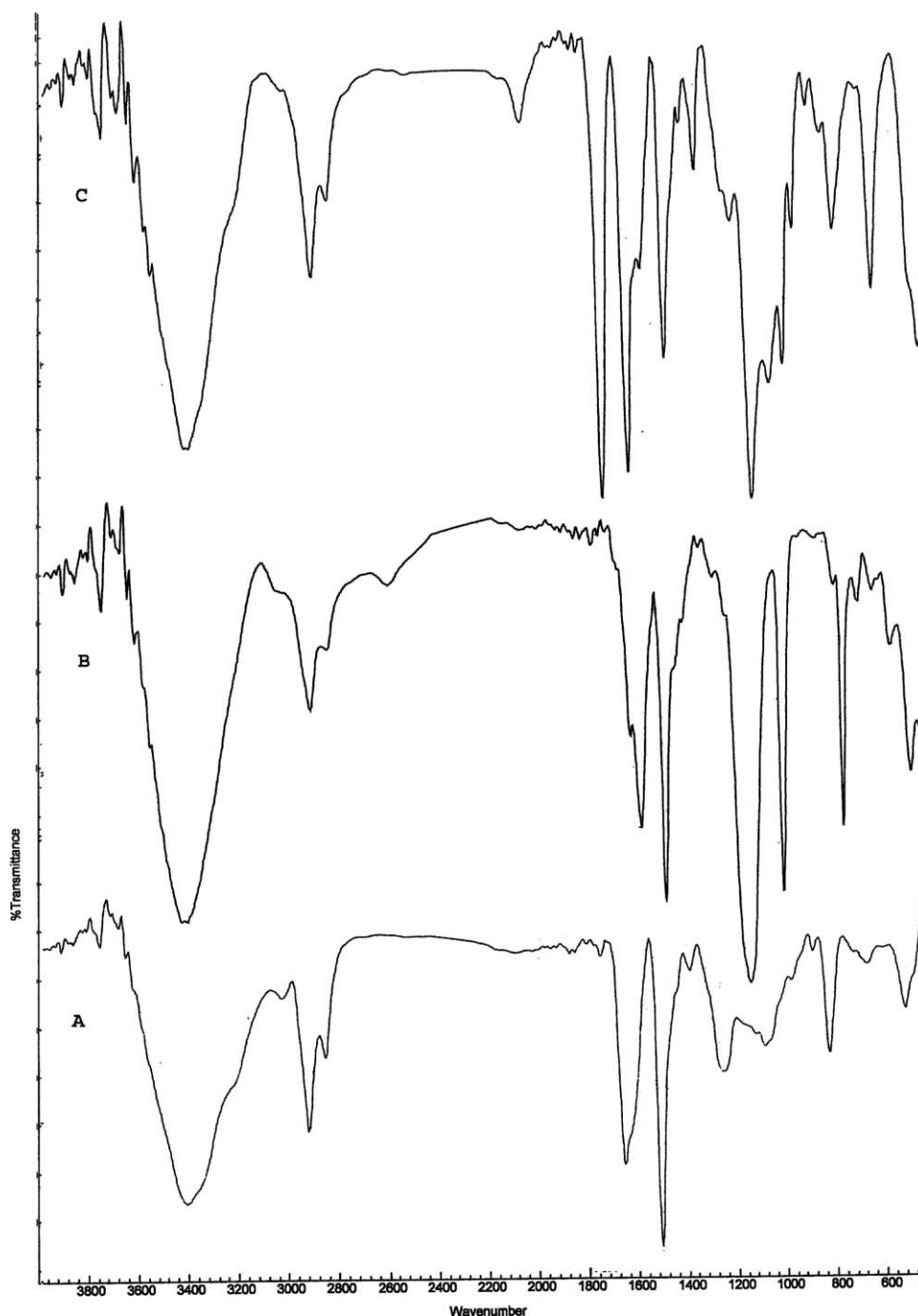
## RESULTS AND DISCUSSION

Poly(sulfobetaine) and poly(carboxybetaine) were synthesized in two stages. In the first stage, the neu-

tral polyimines also known as poly-schiff bases were synthesized. The mechanism leading to Schiff base chemistry is well understood. Imines are nitrogen analogs of carbonyl functional group. Aldehydes and ketones react with primary amines and other ammonia derivatives to form imines, via the nucleophilic addition-elimination reaction. *p*-Phenylene diamine/melamine react as a nucleophile with the glutaraldehyde, a dialdehyde, via the nucleophilic addition elimination. In this mechanism of Schiff base generation, the nonbonded electrons on nitrogen causes water to be eliminated and further subsequent loss of a proton from the resulting protonated imine forms a stable imine. In general, imines are only stable enough to isolate if either the C or N of the imine double bond bears an aromatic substituent and/or nitrogen atom carries an electronegative group. 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. In the polymers I and II SO5, the aromatic group from the *p*-phenylene diamine facilitates the delocalization of the probable charge centers on the C atom of imine groups and in the polymer III, the aromatic ring of melamine facilitates such stabilization.

In the second step, the polyimines were made to react with 1,3-propane sultone, a sulfoalkylating agent. In their reaction with nucleophiles, the imine centers of poly-schiff bases were quaternized resulting in zwitterionic centers along the polymeric chains (Fig. 1). The sulfopropyl groups are introduced by reaction of nucleophiles with commercially available 1,3-propane sultone.<sup>27</sup> The sulfopropyl group has been used extensively to improve the hydrophilicity of a variety of surfactants, dyes, nucleosides, proteins, and polymers.<sup>28–36</sup>  $\gamma$ -Butyrolactone (the carboxy analog of sultone)<sup>37</sup> was used to produce the corresponding carboxybetaine analogs (Fig. 1).

In the second part of the investigation, one of the most versatile and useful strategy for development of novel polymers, the Michael addition, a facile reaction between nucleophiles and activated olefins and alkynes was taken up in which the nucleophile adds across a carbon-carbon multiple bond. The reaction has been used in the synthesis of linear, graft, hyperbranched, dendritic, and network polymers.<sup>38</sup> Although Michael addition is generally considered the addition of enolate nucleophiles to activated olefins, a wide range of functional groups possess sufficient nucleophilicity to perform as Michael donors. Reactions involving nonenolate nucleophiles, such as amines, thiols, and phosphines are typically referred to as Michael-type additions. Michael acceptor possesses an electron withdrawing and resonance stabilizing activating group, which stabilizes the anionic intermediate. Here, the —OH groups of polyethylene glycol (PEG 400) as nucleophile was condensed with



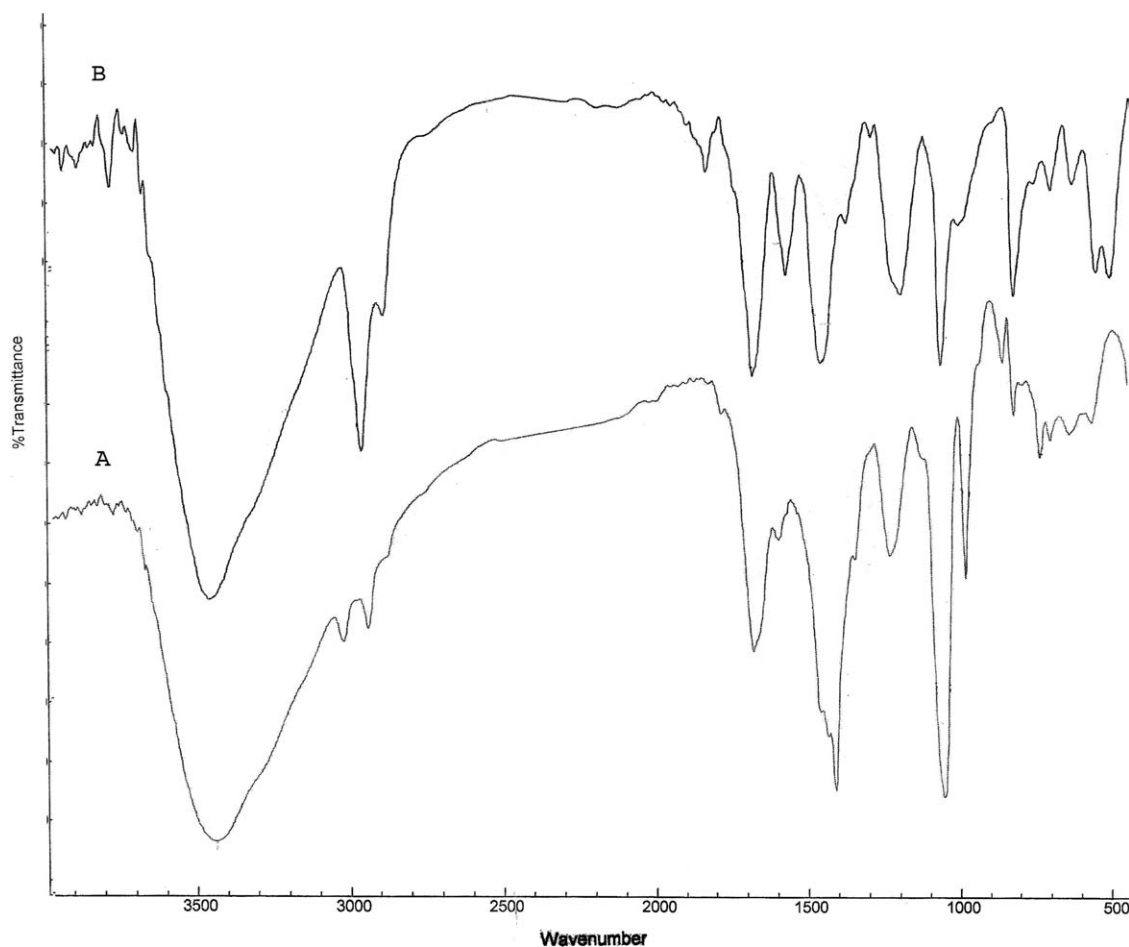
**Figure 2** Infrared spectra of Polymers I and II; (A) polyimine, (B) Polysulfobetaine I, and (C) polycarboxybetaine II.

*N,N'*-bisacrylamide, commonly used as crosslinker,<sup>39</sup> bearing acrylamide group, which behaves as Michael acceptor possessing electron withdrawing activating group. Hence, a catalyst free facile way for synthesis of polyamide chain is reported. As in the case of polyimines mentioned in the above section, the resulting polyamides were reacted with 1,3-propane sultone or  $\gamma$ -butyrolactone in the subsequent step to quaternize the nitrogen centers. Hence, corresponding poly(sulfobetaine) and poly(carboxybetaine) bearing gel charac-

teristics with high flexibility was obtained, via Michael-type addition reaction.

### Solubility

Table I shows the solubility of zwitterionic polymers. The polymers do not show complete solubility in any of the organic solvents. Polymer II showed partial solubility in acetonitrile, dioxane and 0.1N HCl whereas polymer III showed solubility on



**Figure 3** Infrared spectra of Polymer III; (A) polyimine, (B) Polysulfobetaine III.

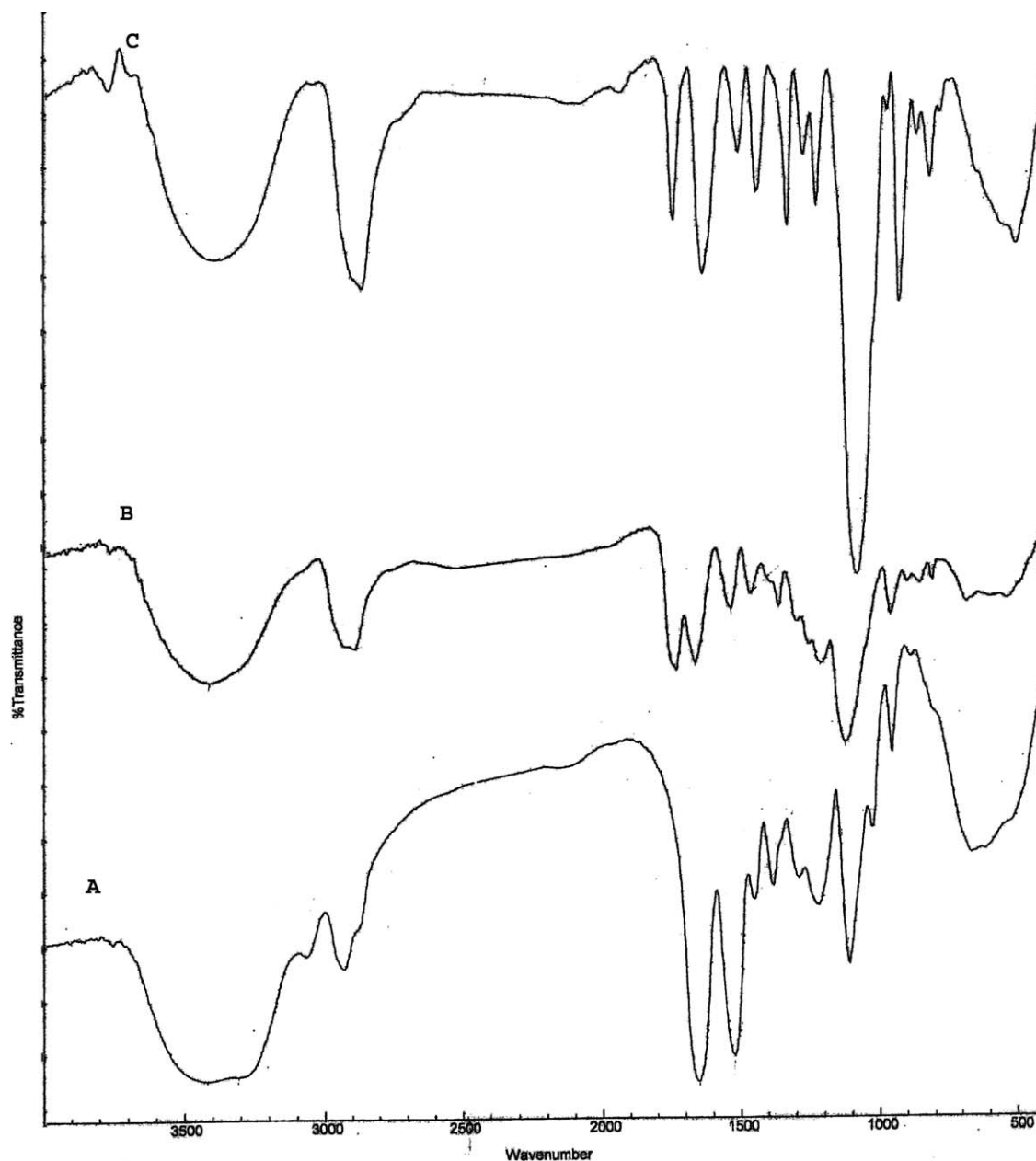
heating in acetonitrile. Polymer IV showed solubility in the mixture of solvents  $\text{CHCl}_3 : \text{CH}_3\text{OH}$  (1 : 1) and in  $\text{CH}_3\text{COCH}_3 : \text{CH}_3\text{OH}$  (3 : 2) on heating. These characteristics of solubility show that polyimine-based polymers are usually insoluble in organic solvents. These solubility restrictions did not allow for either  $^1\text{H-NMR}$  or  $^{13}\text{C-NMR}$  analysis.

### Infrared characterization

The infrared (IR) spectra of polyimine (A), polyiminosulfobetaine (B), and polyiminocarboxybetaine (C) are shown in Figure 2 for samples I and II. Spectra were obtained in KBr media. The absorptions common in all three spectra at  $2925\text{--}2928\text{ cm}^{-1}$  (C=H asymmetric stretch),  $2800\text{--}2858\text{ cm}^{-1}$  (C-H symmetric stretch),  $1500\text{--}1515\text{ cm}^{-1}$  (Ar C-C) are characteristic of polyimine skeleton. The absorption because of C=N (imine) stretch appear at  $1658\text{ cm}^{-1}$ . The absorption band shifts to  $1612\text{ cm}^{-1}$  on quaternization of nitrogen center after treatment with sultone in curve B. The respective absorptions in curve C is observed at  $1661\text{ cm}^{-1}$  with a shoulder at  $1605\text{ cm}^{-1}$  on treatment with  $\gamma$ -butyrolactone. The characteristic absorption for sulfonate groups

in polyiminosulfobetaine (curve B) appear at  $1178\text{ cm}^{-1}$  and  $1038\text{ cm}^{-1}$  both of which are highly intense. The carboxybetaine was characterized by absorptions at  $1167\text{ cm}^{-1}$  (C-CO-C) stretched band with shoulders at  $1093$  and  $1035\text{ cm}^{-1}$  and C=O stretch at  $1767\text{ cm}^{-1}$ . The two bands, a strong asymmetric stretch at  $1661\text{ cm}^{-1}$  and weaker symmetrical stretch at  $1380\text{ cm}^{-1}$  characterizes carboxylate anion (curve C). Out of plane C-H bending was observed in the range  $798\text{--}861\text{ cm}^{-1}$  in all three curves. The hygroscopic nature of these polymeric gels was evident due to broad absorptions near  $\sim 3425\text{ cm}^{-1}$  (free O-H) peak.

The IR spectra of polyimine (A) and polyiminosulfobetaine (B) for sample III are shown in Figure 3. The absorptions at  $2919\text{--}3003\text{ cm}^{-1}$  were because of C-H asymmetric stretch. The absorption at  $1651\text{ cm}^{-1}$  shows C=N stretch of aromatic ring of melamine residues. The sulphonate group was characterized by absorptions at  $1166$  and  $1030\text{ cm}^{-1}$ . The aromatic ring stretching absorptions (C=C, C=N) can be seen in the range  $1340\text{--}1570\text{ cm}^{-1}$  in curves A and B. The peak at  $1423\text{ cm}^{-1}$  corresponds to  $\alpha\text{-CH}_2$  bending vibrations. Samples IV and V were characterized by respective IR absorptions. The spectra of the three analog, polyamido

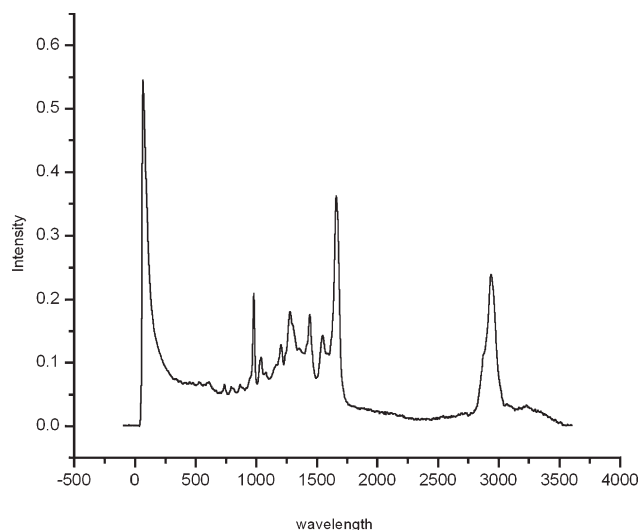


**Figure 4** Infrared spectra of polymers IV and V; (A) polyimine, (B) Polysulfobetaine IV, and (C) polycarboxybetaine V.

(A), corresponding sulfobetaine (B) and carboxybetaine (C) are shown in Figure 4. The hygroscopic nature of the polymer was evinced by broad absorptions around  $3300\text{--}3400\text{ cm}^{-1}$  which has overlapped the secondary N–H stretch in the region in the curves A, B as well as in C. The asymmetric and symmetric stretches in these curves were observed in the ranges  $2900\text{--}3065\text{ cm}^{-1}$  and  $2875\text{--}2950\text{ cm}^{-1}$ , respectively. The C–N stretch in curve A at  $1384\text{ cm}^{-1}$  has shifted to  $1352\text{ cm}^{-1}$  in B and to  $1353\text{ cm}^{-1}$  in curve C, an evidence of quaternization to respective sulfobetaine and carboxybetaine. The  $>\text{C}=\text{O}$  group from IV and V absorbs at  $\sim 1660\text{ cm}^{-1}$  in A, B and C. The C–O–C stretch is observed at  $\sim 1110\text{ cm}^{-1}$  in curves A and B, but has intensified much in curve C

because of addition of carboxylate ion from carboxybetaine group. A little broader peak in the range  $1000\text{--}1200\text{ cm}^{-1}$  in curve B has overlapped the absorptions of sulfonate group. The absorption of  $\text{CH}_2$  bending is observed at  $\sim 950\text{ cm}^{-1}$  in the curves A, B, and C.

Raman spectrum of III, yellow colored gel was recorded (Figure 5). The C=N stretch was observed at  $1700\text{ cm}^{-1}$  confirming the compound to belong to iminium group. The sharp peak in between  $2900\text{--}3000\text{ cm}^{-1}$  denotes the presence of C–H stretch (two symmetric stretches, C–H are in separate atmospheres; one of glutaraldehyde and another of sulfopropyl chain). The characteristic peak at  $1230\text{ cm}^{-1}$  confirmed the presence of S=O of sulfopropyl group. The

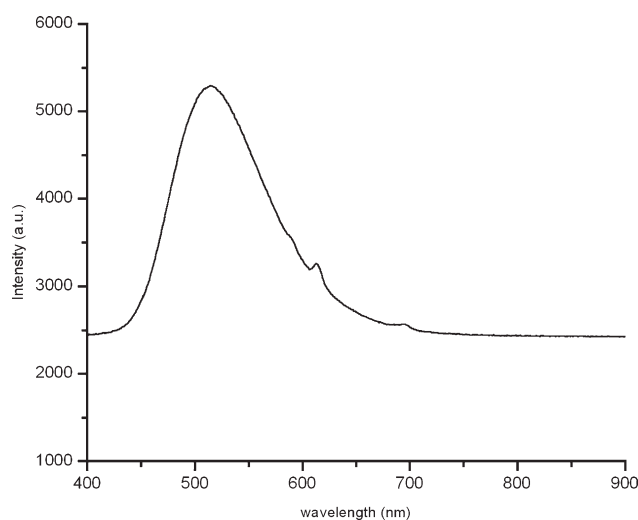


**Figure 5** Raman spectra of polymer III characterizing the presence of basic groups.

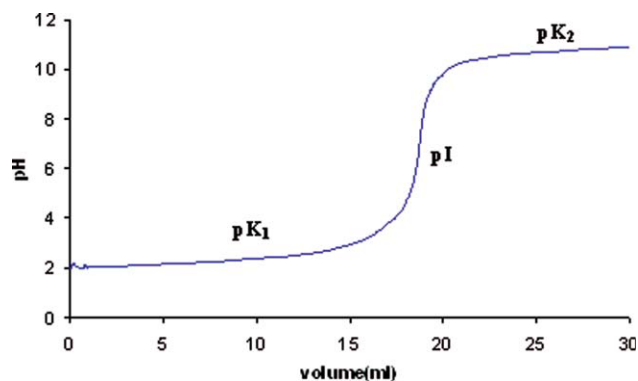
characteristic absorption at  $1031\text{ cm}^{-1}$  confirmed C—H bending. The peaks in between  $980\text{--}1000\text{ cm}^{-1}$  showed ring breathing of aromatic ring of melamine including C=N. Raman spectra of black colored samples (I and II) and other samples could not be recorded.

### Fluorescence spectra

Fluorometric analysis of III showed fluorescence at 525, 625, and 700 nm because of N-substituted aromatic ring, —C=N linkage and  $\text{—SO}_3^-$  groups (Figure 6). I and II are black colored polymers and their fluorescence spectra could not be obtained. Absorption spectra of these samples could not be recorded because of insolubility of the polymers in any solvent.



**Figure 6** Fluorescence spectra of polymer III obtained by exciting it at a wavelength 266 nm.



**Figure 7** Representative plot of potentiometric titration of pretreated polymers I–V with alkali/acid at room temperature. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Potentiometric Titrations

Polysulfobetaine/polycarboxybetaine was pretreated with acid/alkali and titrated against alkali/acid, respectively. Titrations were carried out at room temperature. The representative plot of samples I–V is shown in Figure 7,  $pK_1$  denoted in the curve is the pH at which ionization of acidic moiety takes place whereas  $pK_2$  is the pH at which ionization of basic moiety takes place.  $pI$  is the pH at which the compound is in zwitterionic form, determined by Henderson–Haselbach equation.

$$pI = \frac{pK_1 + pK_2}{2} \quad (1)$$

The respective  $pK_1$ ,  $pK_2$ , and  $pI$  for the polysulfobetaines and polycarboxybetaines are tabulated in the Table II. The  $pI$  data shows that the polymers have net charge zero at a pH just a little shorter than neutrality (6.3–6.9), almost the biological pH which could be useful for various biomedical applications as such polymers have also shown biocompatibility.

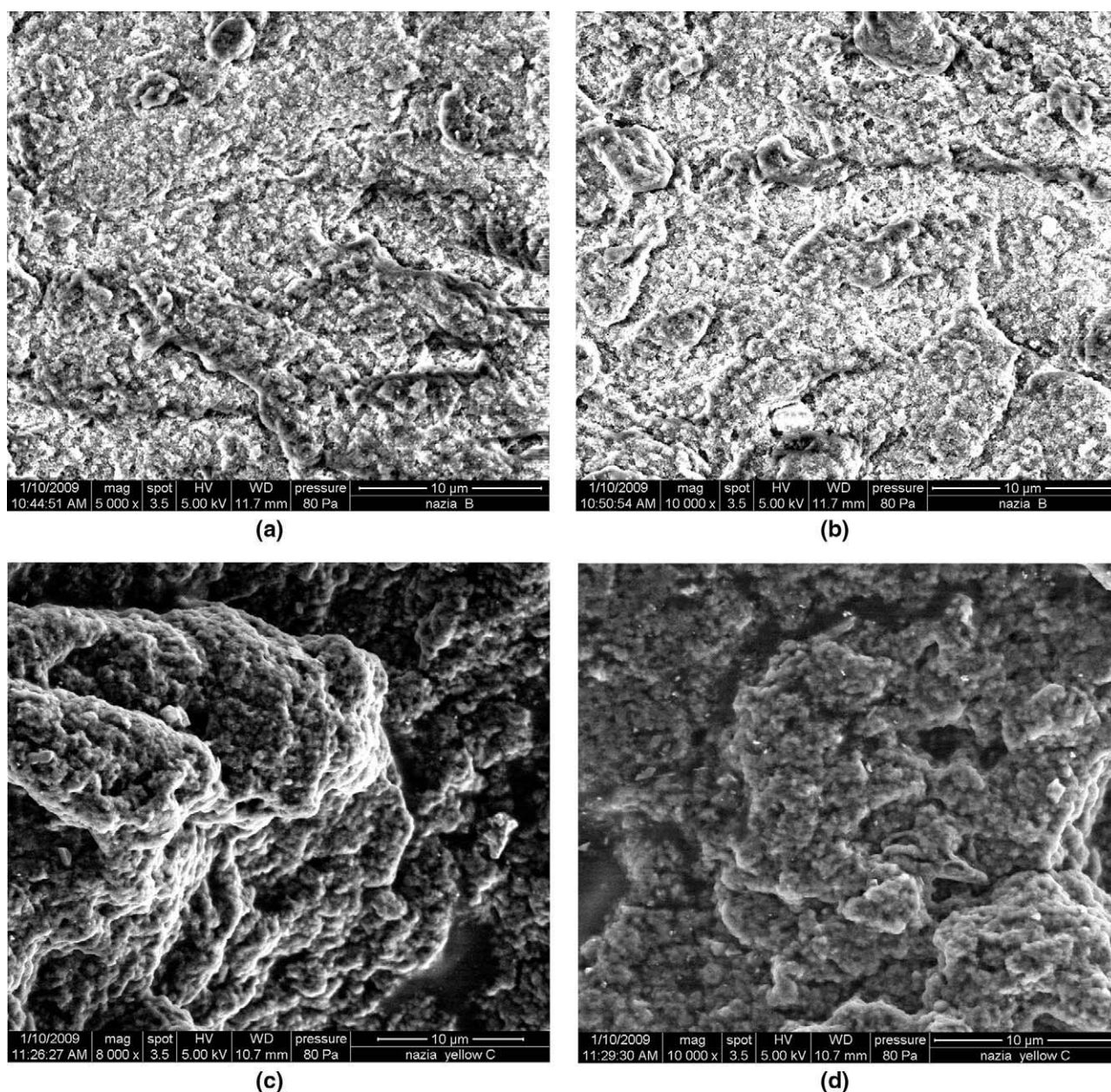
### Surface morphology

Samples were investigated by scanning electron microscopy (SEM) technique to investigate the surface appearance. The SEM images of III show more open/grooved structure but as the image shows, the sample II has comparatively less open structure (Figure 8). On enlarging

**TABLE II**  
 $pK_1$ ,  $pK_2$ , and  $pI$  of Polymers obtained by Potentiometric Titrations

Sample	$pK_1$	$pK_2$	$pI$
I	2.00	10.50	6.45
II	2.00	10.25	6.45
III	2.90	11.35	6.90
IV	2.40	10.25	6.35
V	2.60	10.70	6.60





**Figure 8** (a) SEM images of (a) polymer II at 5000 magnification, (b) polymer II at 10,000 magnification, (c) polymer III at 8000 magnification, (d) polymer III at 10,000 magnification.

the image, the surface showed granular structure. In comparison with III, sample II surface is little less coarse and moreover a smoother surface appears with cracks here and there to channelize the solvent flow (Figure 8). Samples I, IV, and V also showed similar morphology (images are not shown for the sake of brevity).

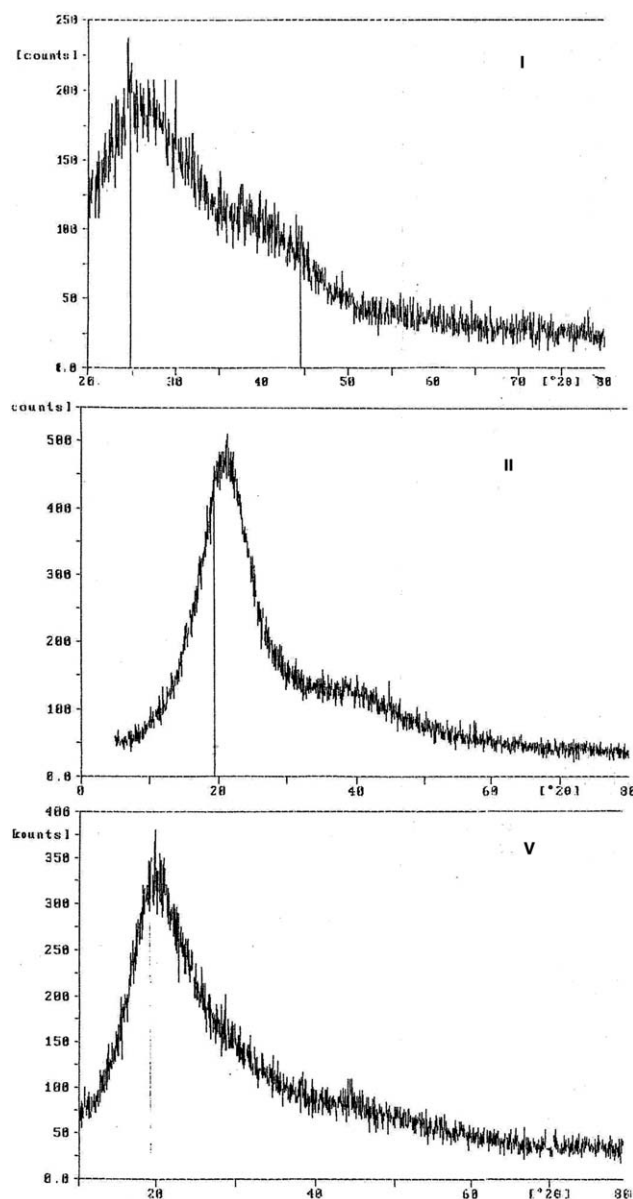
#### X-ray diffraction

The poly(sulfobetaines) and poly(carboxybetaines) were investigated by X-ray powder diffractograms. As in previous studies<sup>40–42</sup> powder diffractograms of the polymers show the noncrystalline nature, but Bragg peaks indicative of superstructures are found in sam-

ples I, II, and V (Figure 9). Similar peaks were also observed in polymers III and IV. The diffraction patterns are characteristic for the geometry adopted by the corresponding polymer.<sup>43</sup> The X-ray powder diffractogram patterns are indicative of a complex lamellar structure as has been proposed by other workers. It is compatible with a lamellar mesophase. The lamellar structures have also been proposed in swelling behavior of polysulfobetaines in presence of salts.<sup>44</sup>

#### Thermal characteristics

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed for the



**Figure 9** X-ray diffraction patterns of polymers I, II, and V showing their noncrystalline nature.

polymers being studied to give an insight into their structure and properties. On studying the thermal degradation patterns (Figure 10), it was observed that the first weight loss is at  $\sim 100^\circ\text{C}$ , which is attributed to dehydration or loss of water molecules which are occluded in the gel network. The gels have the inherent property of holding large amount of solvent/water. On close surveillance of the TG curves, the three samples consisting of iminium centers (I, II, III) were observed to have a larger capacity to hold water, in comparison with the polyamidobetaines (IV and V). At  $\sim 100^\circ\text{C}$ , the two iminosulfobetaines I and II has lost 30 and 50 of their weight as water, respectively. The more hydrophilic nature of iminocarboxybetaine is evident by loss of

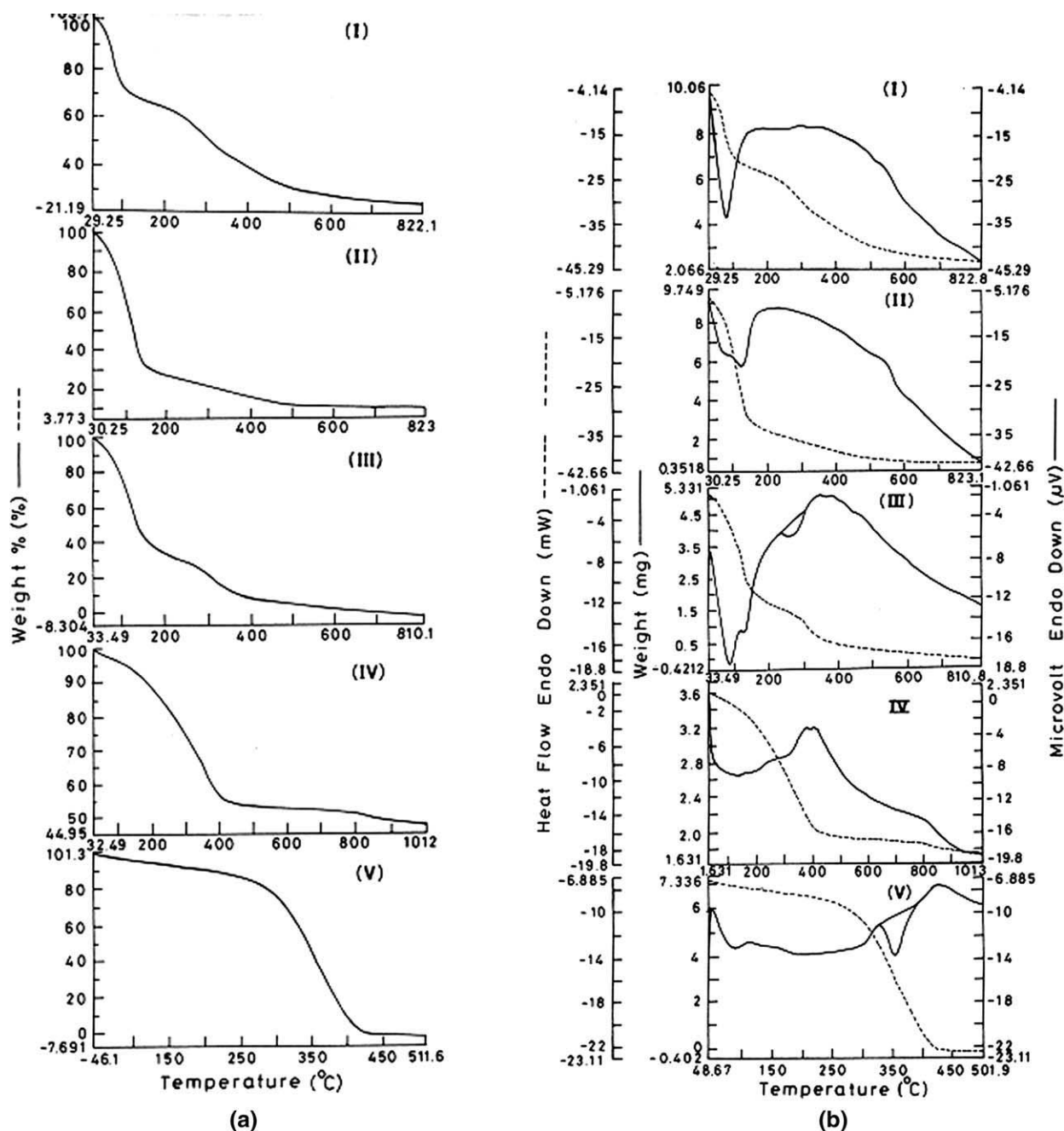
70% water held by it to its original mass and this loss of water is an endothermic process. A sharp peak in I as well as in III at  $100^\circ\text{C}$  clearly indicates their capacity to hold immense quantity of water. The splitting in the dehydration peak in the iminocarboxybetaine sample III shows two different modes of water occlusion. The carboxyl group itself may be responsible for binding water molecules and the other may be the entrapment of polar water molecules between the chains of polymer in the lamellar structure of the polybetaine. On the contrary, the polyamidosulfobetaine (IV) and polyamidocarboxybetaine (V) do not show any weight loss at  $\sim 100^\circ\text{C}$ . On close circumspection of the thermal degradation patterns, the major alterations on temperature enhancement are in the range  $275\text{--}400^\circ\text{C}$ . The sulfobetaine IV at even  $1000^\circ\text{C}$  shows only 50% weight loss indicating the thermal resistance of the residual component and a splitted exothermic peak at  $\sim 400^\circ\text{C}$ . In contrast to the sulfobetaine analog, where an exothermic peak was observed at  $400^\circ\text{C}$ , the carboxybetaine (V) showed the endothermic transition at  $400^\circ\text{C}$ . In the polymer III, an endothermic degradation peak is observed at  $278^\circ\text{C}$  with  $\Delta H = 68.7 \text{ J/g}$ .

Although the exact molecular chain degradation patterns of these polymers are not confirmed, but the most probable mechanism proposed is that the quaternized sulfopropyl iminium centers are lost by Hoffman elimination of  $\beta$  hydrogen<sup>45</sup> and thereby eliminating  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{SO}_3^-$  group leaving behind the neutral polyimine chain, which are quite resistant to thermal degradation, thus leaving behind some residual mass even after  $>800^\circ\text{C}$  also. All the polymers studied here are showing major degradation pattern in the range  $300\text{--}400^\circ\text{C}$ , validating the proposed Hoffman elimination mechanism.

Further, polymer I is being studied for its conductivity behavior in solid state. The polymer itself has shown good prospects and is under further investigation via impedance spectroscopy. Different salts were doped in various ratios to further investigate its application as polymer electrolyte material. Additionally, polymer II also has shown good prospects as imprinted gel to develop the sensitive analytical technique to analyze small clinically relevant molecules with complementary chemistry.

## CONCLUSIONS

In conclusion, we have presented a synthetic protocol for the design and build up of zwitterionic poly (sulfobetaines) and poly(carboxybetaines) organogels based on Schiff base chemistry, a versatile tool in organic synthesis. No catalyst is needed for this synthesis so the materials are not contaminated with inorganic remains or by-products. Moreover, the lamellar structure of the gels with porous network to



**Figure 10** (a) Thermo gravimetric (TG) curves for polymers I-V and (b) Differential thermal analysis (DTA) curves for polymers I-V.

channelize the flow of solvent across them could be used for the development of biomedical devices for drug delivery. Additionally, the fluorescing nature of the polymer (III) is interesting to explore the optoelectronic application.

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