Synthesis and Molecular Weight and Structural Determinations of (Polyvinylpyrrolidone)-oxime-silico-benzoyl Glycine Copolymer with IR and NMR Spectroscopy

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ABSTRACT: Polyvinylpyrrolidone (PVP)-oximate-silico-benzoyl glycine (POSBG) copolymer has been prepared taking PVP and benzoyl glycine with tetraethylorthosilicate as binder. Average viscosity molecular weights ($\overline{M}_v$) each of PVP-oxime and POSBG were determined with dilute aqueous solutions. For molecular weights primarily a calibration curve between intrinsic viscosities [η] and different molecular weights of polyvinyl alcohol (marker) has been obtained to determine $\overline{M}_v$ of oxime as 42,042 g mol^{-1}. Similarly the $\overline{M}_v$ of POSBG as 80,297.13 g mol^{-1} was determined with [η] of lysozyme (molecular weight = 24,000 g mol^{-1}) egg albumin (40,000 g mol^{-1}) and BSA (65,000 g mol^{-1}). For structural illustration, IR spectra of PVP-oxime and copolymer were recorded in Nujol, which do not depict band frequency of —OH group of binder. The 1602, 1688, 1182, and 1127 cm^{-1} stretching vibration frequencies noted in spectra infer presence of —C=N, —C=O, —Si—O—Si—, and —Si—O—C— groups, respectively, in POSBG. Structures of PVP-oxime unit of POSBG are supported with Proton NMR. The work is aimed to develop new valuable biosensor and conducting copolymer molecule to serve as useful biochip and a biocompatible template. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3261–3268, 2007

Key words: average viscosity molecular weight; PVP-oxime; silicic acid; benzoyal glycine; glycine copolymer; NMR; stretching vibration frequencies

INTRODUCTION

Currently, composites, copolymers, and allied formulations of several polymeric units with effective binding sites are in focus for developing smart materials with vivid physicochemical properties. In general, the polymeric materials are made up of either polymerization of homomeric units like ethylene in case of polyethylene or heteromeric in case of nylon 66 or Bakelite made up of phenol and formaldehyde.

Such materials have restricted physicochemical properties[1,4] but because of technological innovations and fast and multipurpose approaches in materials sciences and technology, it has become necessary to develop the materials with wide range of applications as per green chemistry approach. The materials that are of multipurpose uses do have several heteromeric units along with certain metallic atoms where latter do introduce specify features in the materials that make them responsible to perform variety of functions like binding, interstices, and conducting signals behaving as biosensor.

Similarly, metal based copolymers assumed to have controlled conducting properties are in high demands for defense purposes, X-ray diffraction, and X-phosphorescence spectra. The ordinary copolymers lack sensing properties but metal-based copolymers like ours are assumed very significant as biosensor and implants uses. Preparation of polymer materials[1] with several chemical moieties has been fascinating for nanotechnological innovations,[2] especially weakly conducting synthetic biopolymers because of their tremendous applications in biochips, biophysics, and drug delivery systems. However, the polymer composites have been an asset for multipurpose uses[3,4] but most of them are nondegradable materials and nonstructural compounds without any specific trends of their physicochemical properties.

Thus, a preparation of the copolymers with various applications in several fields have been urgent need of the hour; thus, in present work, the copolymer of polyvinylpyrrolidone (PVP)-oxime and benzoyl glycine assisted by silicic acid is prepared and structurally characterized with IR and NMR spectroscopy. The copolymer is supposed to be biocompatible[5] as it

has amino acid in its structural framework, and it is also a conducting material owing to silicon. A concept of developing silicon based electronic copolymer has never been reported before. Silicon, a good prospective element, introduces unique applicability in photoconducting cells, photovoltaic cells, and IR detectors. The preparation of oxime from PVP, benzoyl glycine, and adjoining them with binder (silicic acid) and formation of copolymer is fundamentally a new concept to prepare the bindlex on the pattern of preparations based on condensation reactions.

Such compounds are of current industrial interest and can open new channel in the fields of nanotechnology,[6] as a biosensor[7] in the field of science, technology, and semiconductors. The structural elucidation of such compounds has become an informatory approach for assessing the feasibility of their structure for structure-based applications like synthesis etc. Such work might boost up the semiconductor and defense sciences for coded messages, optics,[8] etc, and facilitate the other allied sciences[9–11] emerging for specific applications in conducting materials. These have been the grounds to choose the present studies for developing the copolymer materials with silicon as hub of molecule that introduces the conducting properties.

Our work would definitely be a step forward in materials science with regard to the innovative applications of PVP-oximate-silico-benzoyl glycine (POSBG) copolymer in bioscience, catalyst, pharmaceutical science, surfactants, and thixotropic materials. The POSBG molecule may behave as first tier dendrimer because the benzoyl glycine and the PVP units are attached to the Si atom in a regular manner.

EXPERIMENTAL TECHNIQUES

PVP (Merck), glycine (AR, Merck), tetraethylorthosilicate (TEOS) (Merck, USA), and Benzoyl chloride (AR, Merck) were used as received. Preparation of copolymer was made in four-step process. *Step 1*, first PVP-oxime (II) was prepared by conducting a reaction of PVP (I) with hydroxylamine hydrochloride (III) in 1 : 1 ratio, w/w, in alkaline medium by adding aqueous 5 mL of 1N NaOH. These contents were taken in 250-mL-capacity RB flask and stirred with electric shaker for 15–20 min; during this a white precipitate of PVP-oxime was formed.[12] It was filtered through Whatman filter paper no. 41 with vacuum pump followed with washing several times with 30% aqueous ethanol solutions. The substance was vacuum dried by keeping it in vacuum chamber for 24 h. *Step 1*, second, benzoyl derivative of glycine was prepared where chloride (Cl⁻) atom of benzoyl chloride reacts with amino (—NH₂) functional group of glycine that protects the —NH₂ group exposing the —COO⁻

group to react with the binder, $Si(OH)_4$. Their specific amounts were taken for reaction, as 5 g of glycine was dissolved in 100 mL of 10% aqueous sodium hydrogen carbonate ($NaHCO_3$) solution followed by adding 10 g of benzoyl chloride. This mixture was shaken vigorously in a stoppered flask for 10 min and refluxed for 10 min. It involves evolution of the CO_2 in the reaction mixture; thus, the stopper was removed time to time to ease out its pressure.

Initially the reaction mixture gives an odor of the benzoyl chloride, which ceases with time, indicating the completion of the reaction for benzoyl glycine compound. Afterwards the latter was acidified with dil HCl to form insoluble compound, which filtered off. The residue, the desired product, was washed several times and recrystallized, with absolute alcohol and the melting point of the dried sample was determined and found to be 187°C. The sample was dried in P_2O_5 filled vacuum desiccator. The presence of the nitrogen was confirmed with lassaigne's test and of —COO— with $NaHCO_3$ wet test, respectively, and also with CHN analyzer, the compound is referred to as benzoyl glycine in the text.

Preparation of silicic acid

Third, the TEOS [IV] was hydrolyzed on basis of sol-gel technique[8,9] by taking 85% ethanolic solution of TEOS in 1 : 2 ratio, v/v, in 250-mL RB flask. The 1 mL of ethanolic TEOS solution was dissolved in 4 mL of 1N KOH in 1 : 4 ratio, v/v, to hydrolyze the TEOS into silicic acid [V]. These contents in RB flask were refluxed for 15 min using water condenser of 25 in. long; thereafter, the mixture was air cooled for half an hour. On cooling, a whitish solid precipitate was formed, which was filtered, washed, and dried as of PVP-oxime to get the pure form of the silicic acid.

Step 2, Finally the POSBG [VI] was prepared with the PVP-oxime [II], benzoyl glycine, and silicic acid [V] by admixing together in 1 : 1 : 1 ratio, w/w, in a 500-mL RB flask and subjected for condensation for about 2.30 h, resulting into the POSBG. The latter was filtered off and washed several times with aqueous ethanol, and the yield of the POSBG was found 7.5 g, i.e., 80.6%.

RESULTS AND DISCUSSION

The data for the average viscosity molecular weight determination were obtained with dilute solutions of the POSBG and are given in Tables II and III. The FTIR spectra of PVP-oxime, BDG, and POSBG were recorded in the form of a thin film within a KBr disc using a Nicolet Protégé-460 Spectrometer and are depicted in Figures 1–3, respectively. The NMR spectrum is shown in Figure 4, the reduced viscosities and densities are plotted in Figure 5(a,b). The vibration frequencies for

TABLE I
Viscosities, Intrinsic Viscosities [η], and Densities (ρ) of the PVP-Oxime and POSBG in Aqueous Solutions at 298.15 K

	PVP		POSBG				PVP-oxime		
c%	ρ	η	[η]	ρ	η	[η]	ρ	η	[η]
0.01	0.99962	0.89754	0.74509	0.99891	0.91288	2.46705	0.99923	0.92790	4.15355
0.04	0.99966	0.90335	0.34942	0.99941	0.94766	1.59272	0.99928	1.00161	3.10669
0.07	0.99971	0.90917	0.29290	0.99992	0.95624	1.04771	0.99933	1.00184	1.77889
0.10	0.99976	0.91498	0.27029	1.00042	0.99245	1.13987	0.99938	1.01971	1.44590
0.14	0.99982	0.92273	0.25522	1.00109	1.07231	1.45449	0.99944	1.01998	1.03493

Units: ρ [10^3 kg m^{-3}], η [0.1 kg m^{-1} s^{-1}], [η] [dL kg^{-1}].

PVP-oxime (Fig. 1) was noted and it confirms the presence of —C=N stretching at 1643.17 cm^{-1} and —C—N stretching at −1469.28 cm^{-1} (s), the —C—H strec at 2989.22 cm^{-1} (b) confirms the polyvinyl side chain. The strec at 3400 cm^{-1} infer the presence of the —OH attached to N atom, which is attached with the C of the pyrrolodine ring.

The vibration frequencies for BDG were noted at 3341.73 cm^{-1} (s) for —N—H strec, at 1687.81 and 1602 cm^{-1} for —C=O, 1454 and 1421 cm^{-1} for —C—N strec, 1325 cm^{-1} for —OH deformation, and 707 cm^{-1} for —(CH$_2$)n, respectively. The presence of the nitrogen atom was confirmed by wet laissganes test, and the copolymer was found water soluble. The vibration frequencies for POSBG confirm the —C—H strec at 2924.28 cm^{-1} for side chain, at 1688.96 cm^{-1} for —C=O strec, at 1602–1582 cm^{-1} for —C=N strec, 1454 cm^{-1} for —C—N strec, at 1182 and 1127 cm^{-1} for —Si—O—Si strec, and —Si—O—R (R = ethoxy alkyl group) asymmetric stretching respectively. H^{1}NMR spectra of PVP-oxime was monitored in deuterium on DPX-dix 300 MHZ Bruker Avance spectrometer using TMS as an internal reference. The proton assignment and H^{1}NMR spectra are given in Figure 4 where H$_{(a)}$ proton signal of hydroxyl group attached to nitrogen appears downfield at 4.64 ppm. The proton of H$_{(b)}$ and H$_{(c)}$ signals as multiplet at 1.16–2.45 ppm which get merged into each other. The proton of H$_{(d)}$ and H$_{(e)}$ signals as triplet at 3.32–3.64 ppm and get merged into each other. It infers preparation of PVP-oxime.

Molecular weight determination

Viscometeric measurements[13] on PVP-oxime and POSBG were made at 298.15 K for molecular weights determination. The 0.005 to 0.050% solutions, at an interval of 0.005%, the PVP-oxime, and POSBG, w/v, were prepared separately for viscous flow time for 10.1 mL each of solution and solvent, respectively, with Survismeter[14] of capillary of 0.5 mm internal diameter. The η values were calculated, with $\eta/\eta_0 = \eta_r = (t/t_0)$ $(\rho/\rho_0$ relation); the η and η_0 functions represent the viscosities, t and t_0 flow times, and ρ and ρ_0 densities of solution and water, respectively, and the η_r parameter represents the values of relative viscosities. Triple dis-

tilled, deionized, and degassed water, of $1 \times 10^{-6}\Omega^{-1}$ cm^{-1} conductivity, was used as reference solvent and for solution preparation, respectively.

The B/t kinetic correction and Survismeter constant (k) were used.[15] The densities were measured with 20×10^{-3} dm^3 bicapillary pycnometer,[16] with 0.01 mg Dhona balance model 100 DS. Prior to weighing, the solutions were thermostated for about 30 min in water bath, and the pycnometer was absolutely dried with tissue paper. The densities (ρ) were calculated with $\rho = ((w - w_0)/(w_0 - w_e))\rho_0 + 0.0012 (1 - (w - w_0/w_0 - w_e))$ equation, the ρ_0 is density of water, $0.0012 (1 - (w - w_0/w_0 - w_e))$ buoyancy correction[17] in weights in air; the w_e, w_0, and w are weights of empty pycnometer, solvent, and solution filled, respectively. The molecular weights can be obtained with end group analysis and osmometry but the intrinsic viscosities [η] are assumed an effective technique for their determination. The PVP-oxime and POSBG were found soluble in water; thus, the η_r values were measured for 0.005 to 0.050 g per 100 mL at 298.15 K. The [η] values derived from the η_r values were fitted to Mark–Houwink equation for the $\overline{M}_v$ values.[4] The η_{sp} denotes specific viscosities that are calculated from a $\eta_{sp} = (\eta_r - 1)$ relation, and the reduced viscosity $(\eta_{red} = \eta_{sp}/c)$ values compute the [η] values with equation given as under.

$$\eta_{red} = \eta_{sp}/c = [\eta] + Dc \qquad (1)$$

TABLE II
Densities and Viscosities of the Markers Use for Molecular Weight Determination of POSBG

[g-%]	$\rho \pm 10^{-2}$ [kg m^{-3}]	$\eta \pm 10^{-5}$ [0.1 kg m^{-1} s^{-1}]
BSA		
0.001	0.99641 ± 6.2284	0.7895 ± 6.6435
0.0014	0.99622 ± 6.2291	0.7992 ± 6.6425
0.0018	0.99619 ± 6.2276	0.8085 ± 6.6576
Egg albumin		
0.001	0.99625 ± 6.2286	0.7614 ± 6.6548
0.0014	0.99623 ± 6.2298	0.7769 ± 6.6572
0.0018	0.99623 ± 6.2286	0.7917 ± 6.6613
Lysozyme		
0.001	0.99634 ± 6.2282	0.8039 ± 6.6448
0.0014	0.99621 ± 6.2290	0.8041 ± 6.6637
0.0018	0.99607 ± 6.2292	0.8065 ± 6.6645

TABLE III
Regression Constants for Viscosity of the Markers

Protein	ρ° [10^3 kg m^{-3}]	S_d [10^3 kg^2 m^{-3} mol^{-1}]	$[\eta]$ [10^3 dL kg^{-1}]	D [10^3 kg mol^{-1}]^2
BSA	0.9964	−0.2764	−32.58	22606
Egg albumin	0.9963	−0.022	−96.005	51987
Lysozyme	0.9967	−0.3383	8.45	−1698.1

The η_{sp}/c versus c values were plotted and the values of $[\eta] = \eta_{sp}/c_{rc.0}$; the c is composition in g/100 mL; and the D denotes slope values. Solutions of different compositions of polyvinyl alcohol (PVOH) of 45,000, 500,000, 65,000, and 70,000 g mol^{-1} molecular weights were prepared for viscosities to derive $[\eta]$ values for calibration curve.

The PVOH is feebly hydrolyzed and develops hydrogen bonding with water; thereby its aqueous solutions behave as standard for $[\eta]$ values for PVP-oxime. Thus, the $[\eta]$ values were determined for PVP-oxime and fitted on the predetermined calibration curve, and it gave 40,042 g mol^{-1} molecular weight of PVP-oxime.

Gel permeation chromatography

The gel permeation chromatography for PVOH was run in 45-cm-long with 3-cm-inner-diameter borosil glass column with packing of fine glass wool at its lower end and silica (SiO$_2$) gel slurry in water as stationary phase. The Gel phase was maintained completely wet. First, the 0.005 to 0.150 g per 100 mL of each sample of PVOH of known molecular weights was run at 1 mL min^{-1}, followed by elution with water. The η_r values for each elution volume (V_e) was measured for $[\eta]$ and plotted against V_e for constants "k" and "a" as follows:

$$\text{Log}[\eta] = \log K + a \log M$$
$$\text{(Mark Houwink equation)}, \quad (2)$$

where M is molecular weight; the experimental values of K and a for PVOH were calculated to be 1.987 $\times$ 10^{-4} and 0.7606, respectively, against 2 $\times$ 10^{-4} and 0.76 literature.[4] The column used for gel permeation chromatography was washed several times with ultra pure water, and the PVP-oxime solutions were run through the column at which the PVOH solutions were run; the $[\eta]$ data were determined for each V_e
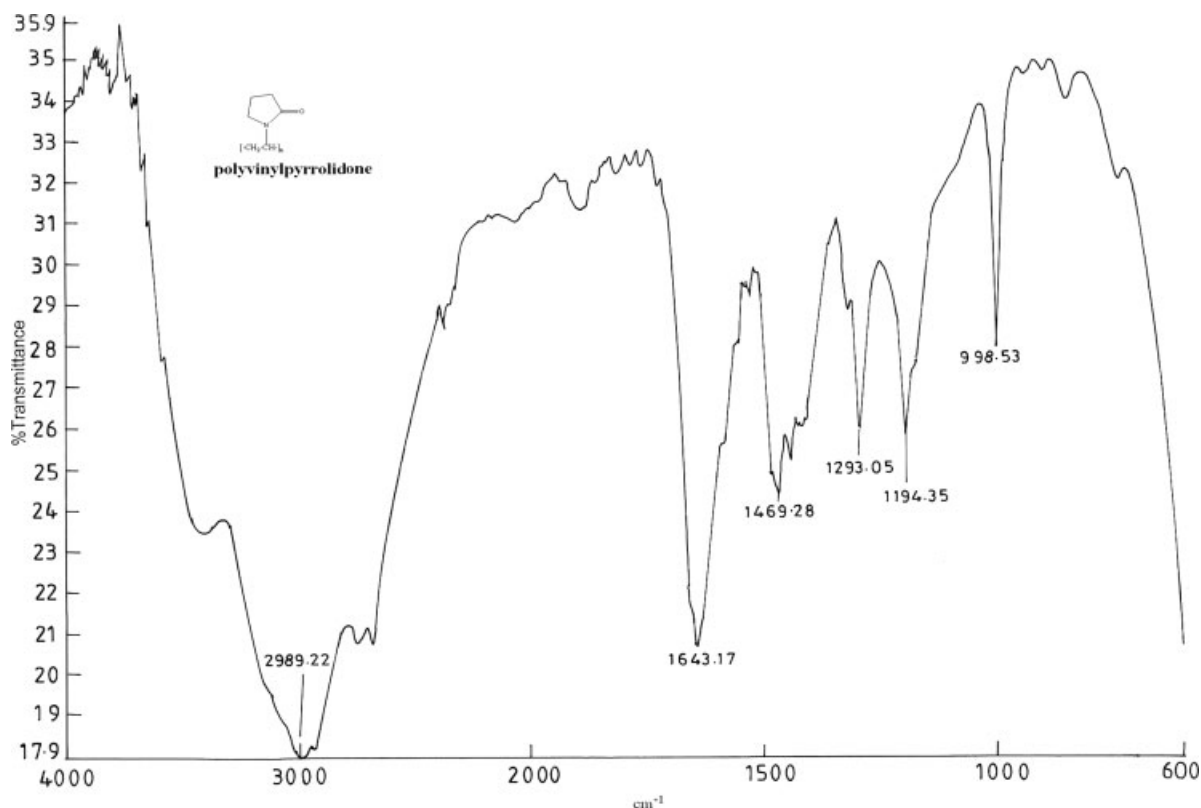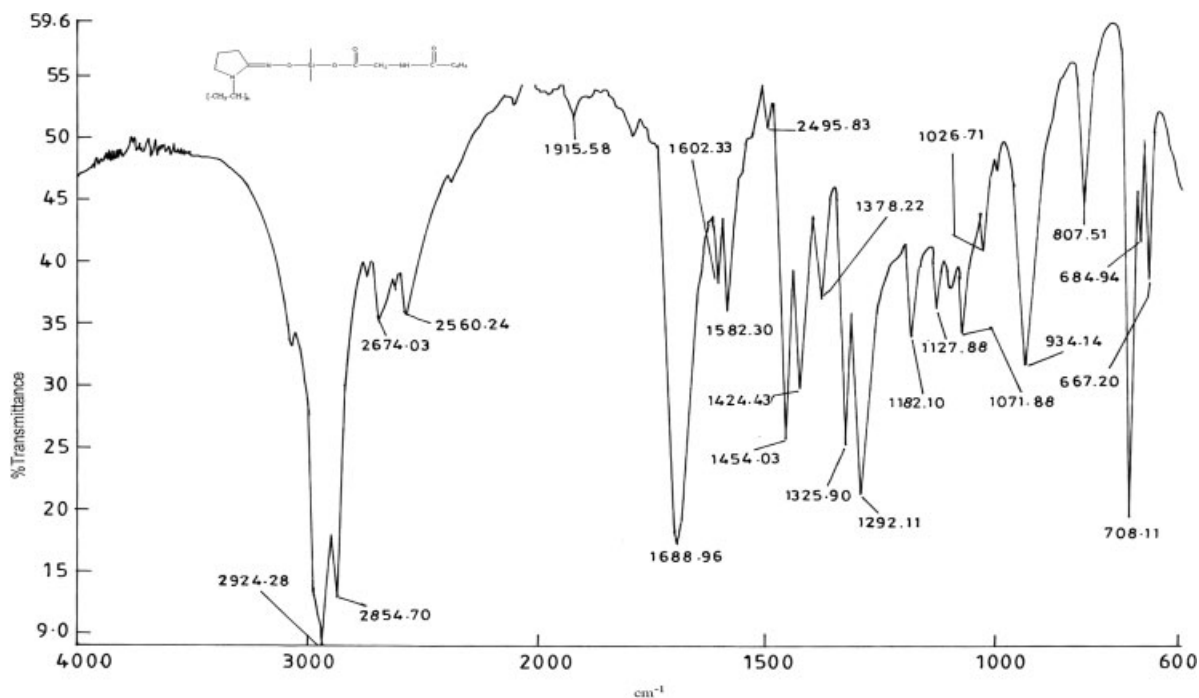

Figure 1 IR spectrum of PVP-oxime IN nujol.
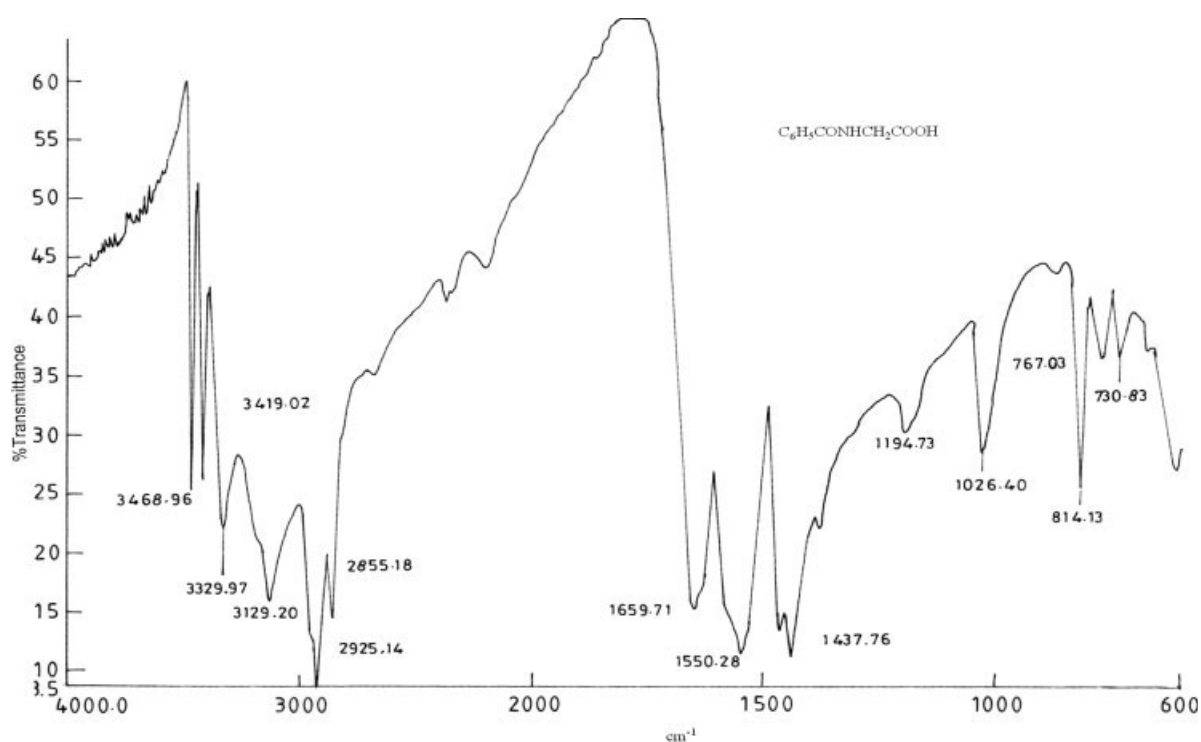
Figure 2 IR spectrum of benzoyl glycine in nujol.

and put on the calibration curve. A perpendicular on its abscissa gave the values 38,721 g mol^{-1} for oxime, the 3.3% lower than those of the estimated with [η] method. The molecular weight of benzoyl glycine, 179 g mol^{-1}, was calculated with its molecular formula; the —COOH group of glycine was protected from polymerization by maintaining slightly acidic

medium to overcome the common ion effect on the proceeding of benzoylation reaction that releases HCl. The $\overline{M}_v$ of copolymer is found to be 80,297.13 g mol^{-1}. The optical densities for very dilute solutions of PVP-oxime and POSBG have shown their uniform distribution. Einstein correlated the η$_{sp}$ values with the shape and size of the corresponding molecules
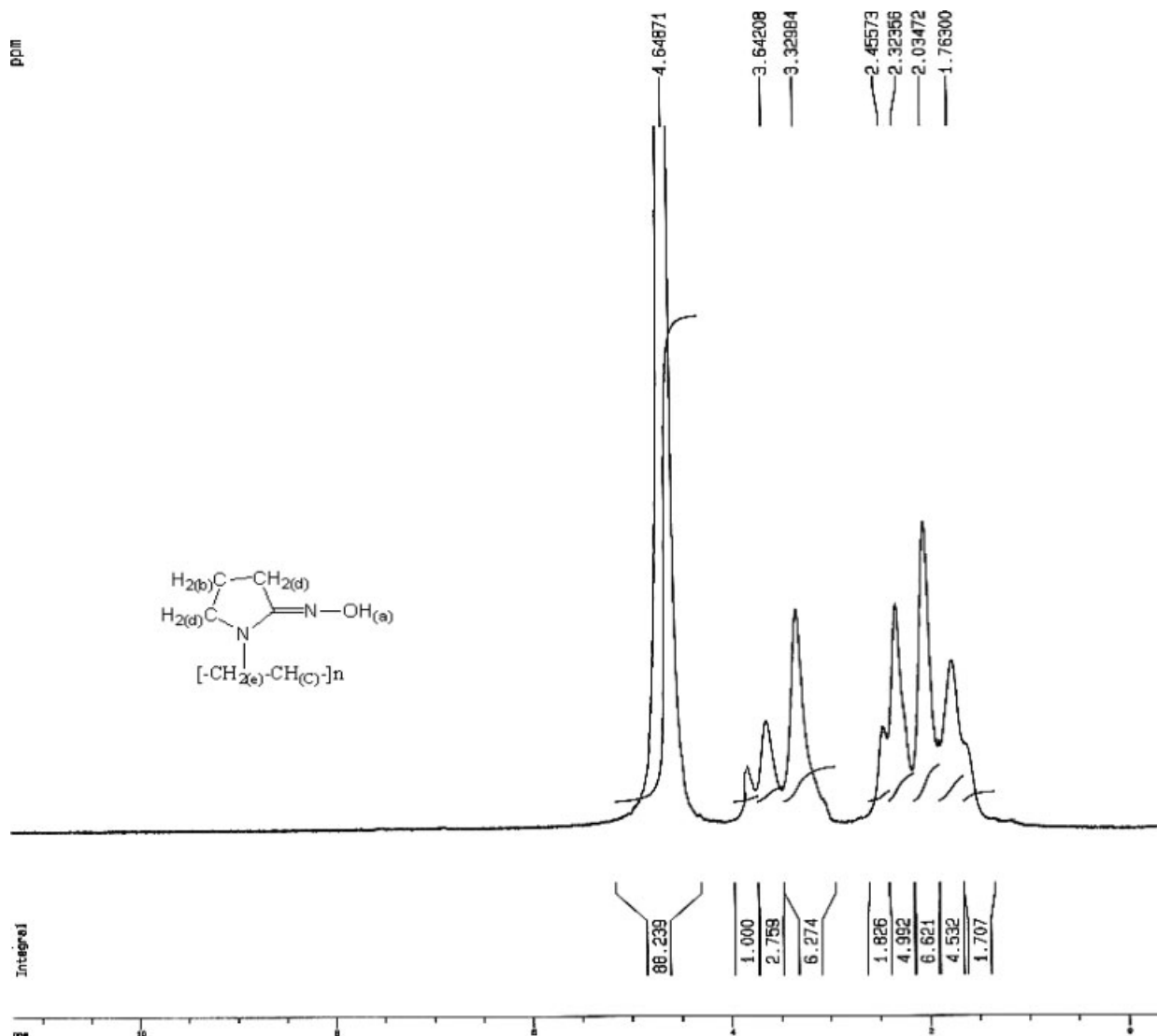

Figure 3 IR spectrum of POSBG in nujol.

Figure 4 H^1 NMR spectra of PVP-oxime.

using the v/V data. The v is the volume occupied by all the spheres and V the total volume of solution taken in the Survismeter bulb; thus, the v/V value calculated with η_{sp} values was found as $v/V \leq 2.5$ for the copolymer molecule.

Einstein[12] reported the v/V value < 2.5 for spherical particles and $v/V > 2.5$ for nonspherical. For our copolymer the v/V values derived viscosity data are found $v/V \leq 2.5$, which remain almost constant, supporting the copolymer molecule to be nearly spherical in shape with no change on viscous flow without any preferential orientation.

The $[\eta]$ data were calculated with the following relation:

$$[\eta] \equiv \lim_{c \to 0} \frac{\eta_{sp}}{c} = \lim_{c \to 0} \left(\frac{1}{c} 2.303 \log, \eta \right) \quad (3)$$

where c is % concentration in 100 g of solutions, the plots of η_{sp}/c versus $1/c$ (2.303) log η_r show a linear

line as those of the polymeric molecules. The negative slopes of the $1/c$ (2.303) log η_r versus c data further ensure the similarities of copolymer molecule with those of the polymers in structure and properties. The obtained data estimate a rational relation between volume and molecular weights; thus, monomer of our copolymer molecule along with markers show properties like macromolecules. The intercept of η_{sp}/c versus $1/c$ (2.303) log η_r plot at zero concentration illustrates the degree of rotation around their bonds and configuration around successive carbon atoms along with the PVP-oxime propagating chain. Thus, for very dilute solutions the number of molecules in a prescribed weight of the copolymer molecule is inversely proportional to the molecular weight. It facilitates an evaluation of volume occupied by molecules in a given weight as $v_m = cVM^{1/2}$ relation, the v_m values are the volume occupied by molecules in a given weight. Thus the Mark–Houwink–Sakurada equation
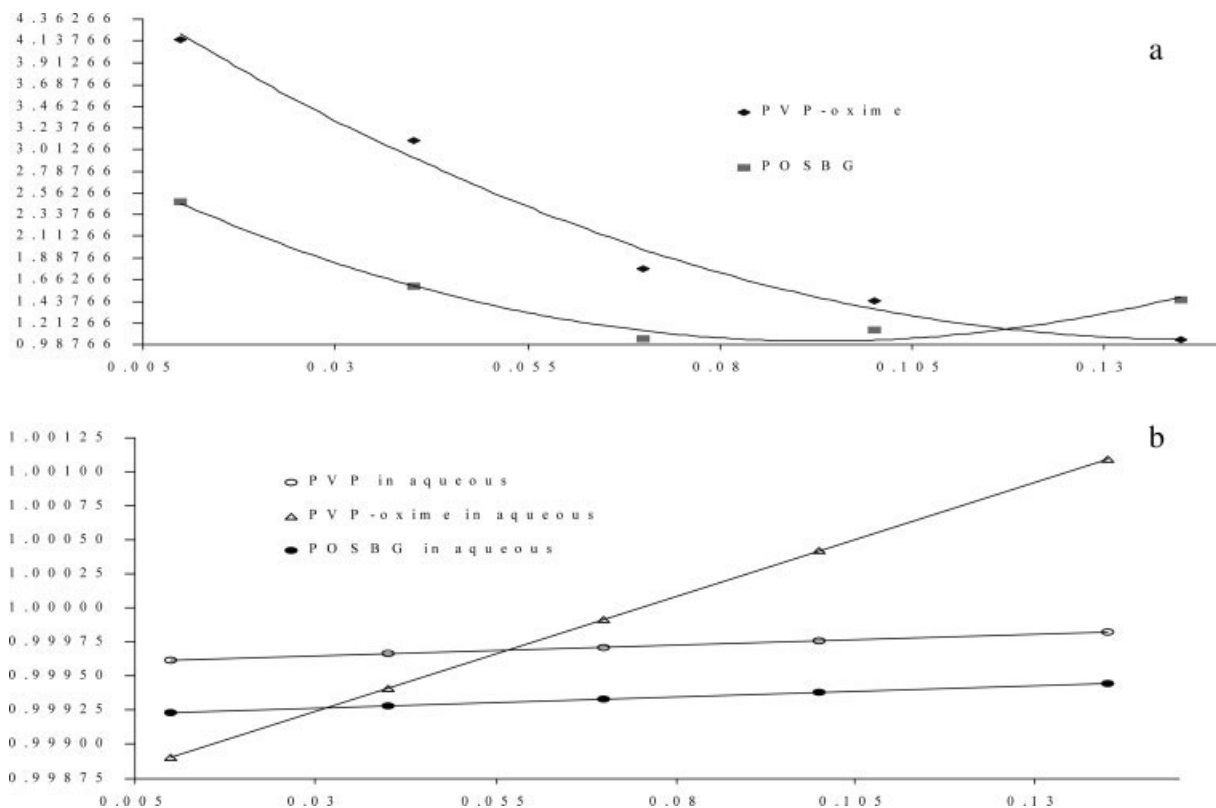
Figure 5 (a) y-axis denotes η_{red} values and x-axis concentrations c in percent for aqueous PVP-oxime and copolymer solutions. (b) y-axis depicts densities and the x-axis, the concentration in percent (bottom). The POSBG denotes copolymer.

is relevant for their molecular weight determination with respect to the viscous flows.

The a and k were found to be 0.2645 and 0.0174, respectively. Reportedly, the a value for very coiled rigidly rod like molecules ranges from 0.5 to 1.7. Flory and Leutner[4] found 2.0×10^{-4} and 0.76 values for k and a, respectively, by taking monodispersive specimens of PVOH with different molecular weight. Densities are noted as PVP-oxime in H_2O > PVP in H_2O > POSBG in H_2O, except densities of PVP-oxime at around lower compositions [Fig. 5(b)]. The ρ of PVP-oxime for lower compositions are lower than those of the PVP alone and POSBG but for higher compositions the increment in densities is higher than those of other compounds (Tables I–III). This infers stronger PVP-oxime intermolecular forces than that of POSBG which infer weaker intermolecular forces for large sized molecule. But the ρ values for PVP-oxime are lower than those of PVP and copolymer in water, which predicts slightly weaker molecular interactions of the oxime, and copolymer with water molecules [Fig. 5(a,b)]. The viscosities of POSBG are higher than those of PVP-oxime at 298.15 K, which illustrate participation of forces, like potential, electronic, and transnational and make POSBG geometry steric. It infers copolymer as more branched with larger frictional forces on viscous flow [Fig. 5(a,b)]. Intrinsic vis-

cosities for PVP-oxime are higher than those of POSBG but the PVP-oxime seems to have maximum reorientation with stronger hydrodynamic forces while the solution of same concentration of copolymer occupies lower hydrodynamic volume. Interestingly, their viscosities with compositions intersect at a common composition point with similar molecular activity; it infers intermolecular interactions with almost similar strength of pairwise interactions. For 0.115% composition both the molecules acquire the same value of hydrodynamic volume and forces (Newtonian forces) but after this composition the PVP-oxime occupies maximum hydrodynamic volume with stronger torque while the copolymer does occupy lower volume.

CONCLUSIONS

The presence of —Si—O—Si— and —Si—O—R frequencies infers binding of electronic site in POSBG copolymer. The absence of frequencies for —OH group confirms the replacement of —OH group. Also the v/V values found almost very slightly lower then 2.5 confirming its shape near to spherical molecule. It shows least activity with composition.

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