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Polymerization of Acrylamide Initiated by Hydroxy Terminated Polybutadiene-ceric Ammonium Nitrate Redox System

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Amphiphilic copolymer of acrylamide (AAm) and butadiene was synthesized by radical initiation using the hydroxy terminated polybutadiene (HTPB) and ceric ammonium nitrate (CAN) macroredox initiator in heterogenous medium in the presence of nitric acid at 35°C in air. The resulting product was characterized by IR, NMR, viscosity and swelling measurements. Imidization of some AAm units was inferred from NMR spectroscopy and swelling measurement. The product adsorbed Ni(II) and Fe(II) ions from aqueous solution and selectively released Ni(II) only. The release pattern for hydrophilic dye was similar to the usual fractional release behavior of drug release observed for hydrogel systems.

Keywords: Amphiphilic copolymer, polybutadiene-polyacrylamide, imidization, macroredox polymerization, dye release

1. Introduction

The synthesis of macromolecules composed of more than one monomeric repeating unit has been explored as a means of controlling the properties of the resulting materials. In this respect, it is useful to distinguish several ways in which different monomer units might be incorporated in a polymeric material. Block copolymers are among the newer creations of modern chemistry, which provides one of the most exciting classes of materials, both in terms of intellectual stimulation and practical utility. Block copolymers are of particular practical significance and considerable technical importance because their special chemical structure yields unusual physical properties (1).

The ability of block copolymers to organize as micelles or other complex aggregate in selective solvents, above a certain critical micelle concentration (cmc) has been studied for the last several decades (2). In particular, block copolymers with hydrophilic and hydrophobic segments, i.e., "amphiphilic block copolymer" (abc) have been a rich field of research because of their structural diversity in solvents selective for one block (3). Amphiphilic block copolymers form various supramolecular structures such as spherical and cylindrical micelles, vesicles and other complex aggregates in solution (4–6). The reason behind the keen interest in self-association of amphiphilic block copolymers has been their potential application in different fields such as vicosifiers for enhanced oil recovery, surface-active polymers for personal care products, and biocompatible materials in the biomedical field (7–12).

Polymeric micelles, first proposed as a drug delivery system in 1984 (13), are still the object of growing scientific attention in controlled drug delivery, which offers a potential advantage over conventional drug therapy, to maintain the drug in the desired therapeutic range with a single dose. Other advantages include localized delivery of the drug to a particular region in the body, which lowers the systemic drug level. Pharmaceutical research on polymeric micelles has been mainly focused on block copolymers generally having hydrophilic–hydrophobic diblock structure (14). Therefore, to develop a novel method for preparation of amphiphilic copolymers is very important both in theory and in practice. Poly(ethylene glycol) (PEG) (15), poly(lactic acid) (16, 17), poly(β-benzyl-asparatate) (18) are frequently used as the hydrophilic block. The copolymers of acrylamide (AAm) with various hydrophobic comonomers have proved to be of great interest due to their associating behavior in solution (19–28). Block copolymers of butadiene have been synthesized with some other monomers (29–35), but to the best of our knowledge,

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block copolymerization of acrylamide with butadiene has not been reported, except in our latest reports (36, 37).

Ce(IV), alone or in conjunction with suitable organic reducing agents, forms a very effective redox system for initiation of vinyl polymerization (38–47). Ce(IV) has been mostly used as an oxidant in redox systems for homopolymerization (48–51) and graft copolymerization (52–57) of acrylamide. Some reports are also available for block copolymerization of acrylamide with Ce(IV) as an oxidant (58–60). Though Ce(IV) is usually being used in aqueous medium, it efficiently initiated heterogeneous polymerization of butadiene and styrene (61). However, to the best of our knowledge, no report is available on copolymerization of butadiene and acrylamide by radical initiation with Ce(IV). The present study reports the heterogeneous polymerization of acrylamide with hydroxyl terminated polybutadiene-Ce(IV) macroredox initiator in nitric acid medium.

2. Experimental

2.1. *Materials*

Hydroxy-terminated polybutadiene (HTPB) was a gift from Vikram Sarabhai Space Center, Thiruvananthapuram, India. The number average molecular mass (M_n) of HTPB determined by vapor phase osmometry (VPO) was 2450 ± 300 and polydispersity was 2 ± 0.5. Functionality distribution, f_n given as M_n/M_{eq}, where M_{eq} is the equivalent mass (average mass of the molecule per one hydroxyl group), determined by liquid chromatography (LC) using chloroform-ethanol as eluent on silica gel was 1.95–2.0. The microstructure determined by ^{1}H-NMR was 50-55% trans–1,4- and 18–22% 1,2-units and remainder cis-1,4-units for polybutadiene. HTPB was purified by washing with methanol a number of times, residual methanol was then removed under reduced pressure. Acrylamide (AAm) from (Sisco Research Laboratories Pvt. Ltd., Bombay, India) was recrystallized twice from methanol and dried under vacuum. Ceric ammonium nitrate (CAN), nickel sulphate, ferrous ammonium sulphate (FAS) were from CDH, Bombay, India and methyl orange was supplied by BDH, England. Nitric Acid was supplied by Qualigens, India. Chloroform, benzene and other solvents were obtained from E. Merck, India. All these reagents and solvents were of analytical reagent grade and were used as received.

2.2. *Block copolymerization of acrylamide*

A pyrex glass test tube of length 12 cm was used as the reaction vessel. HTPB and AAm were taken in this vessel and kept in a serological bath maintained at the required temperature. CAN was dissolved in requisite amount of nitric acid, deaerated and thermostatted separately. It was then added to the reaction vessel as quickly as possible and the reaction mixture was stirred for desired time. Finally, the reaction was arrested by adding a known excess of ferrous ammonium sulphate solution so that all the excess of Ce(IV) ions were reduced to Ce(III) ions instantaneously. The product obtained was washed subsequently with 0.1 N sodium hydroxide solution, water and finally with petroleum ether to remove unreacted materials. The product was dried initially in vacuum and then in air. The extent of reaction with HTPB was determined gravimetrically in terms of percentage yield, evaluated using Equation 1.

$$\text{Yield of the product (\%)} = \frac{\text{Weight of the product}}{(\text{Weight of HTPB} + \text{weight of acrylamide})} \times 100 \quad (1)$$

2.3. *Measurements*

IR spectra were recorded on a Perkin-Elmer Model 1430 spectrophotometer using KBr as dispersant. NMR spectrum was recorded on a Bruker DRX-FTNMR spectrophotometer in $CDCl_3$ solution.

Viscometric studies were performed at 27°C using an Ubbelohde viscometer in chloroform solution. The Huggins (Eq. 2) and the Kraemer's (Eq. 3) equations were used to determine intrinsic viscosity [η], Huggins' (k′) and Kraemer's (k″) constants.

$$\eta_{sp}/C = [\eta] + k'[\eta]^2C \quad (2)$$

$$ln\eta_r/C = [\eta] + k''[\eta]^2C \quad (3)$$

Where [η], η_{sp} and $\eta_r$are intrinsic, specific and relative viscosities, respectively. Results for both the equations were plotted on the same graph. The point of intersection of both the lines at the ordinate was taken as the intrinsic viscosity.

The product samples (0.05 g) were cut and immersed in 20 mL of various solvents for 48 h to attain equilibrium swelling. The swollen samples were taken out from the solvent bath, pressed gently between filter paper to remove the excess of solvent and weighed immediately. The swelling coefficient of the product (Q) was calculated by Equation 4 (62).

$$Q = (m - m_0)/(m_0 \times d) \quad (4)$$

Where m is the weight of the swollen polymer and m_o that of the polymer taken initially and d is the density of the solvent used. The characteristic parameters for the solvents were obtained from the literature (63).

2.4. *Study of dye-release as a model for in vitro drug-release and study of metal-ion extraction*

Dye and metal ion release experiments were conducted by a swelling-controlled release system. For the above studies, samples of the copolymer were immersed in the saturated aqueous solutions of hydrophilic dye (methyl orange, 20% w/v), saturated aqueous solutions of nickel sulphate

(71.4% w/v) and ferrous ammonium sulphate (69.2% w/v) in separate vessels for 48 h, to attain maximum swelling, as well as dye-loading or metal ion absorption. The polymer samples were then removed from respective solutions and were washed with water to remove loosely bound dye or metal ion on the surface. The samples were dried at 35°C in air in a dust free chamber and weighed to a constant weight.

For release study, the loaded polymeric sample was cut into pieces of 50 mg weight, which were immersed in 10 mL of buffer solution of pH 9.2 for dye release and in 0.1 N HNO_3 solutions for metal ion release, respectively at 30°C. After the desired time interval, the polymers were removed from the solutions. The amount of dye released at different time intervals was analyzed colorimetrically by measuring absorbance of supernatant solutions at 423 nm.

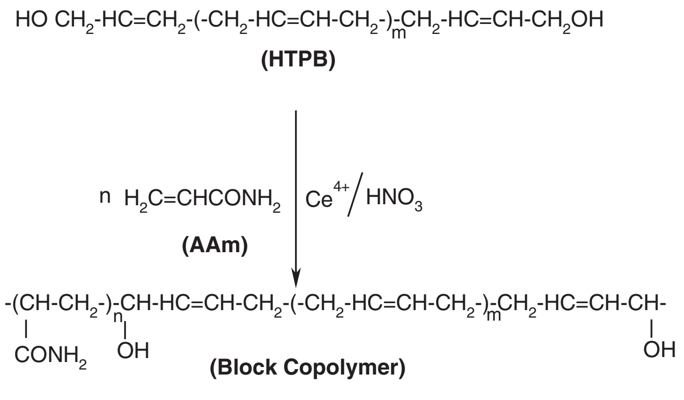
Nickel (II) and iron (II) ions were estimated colorimetrically after complexation with dimethyl glyoxime (DMG) and 1,10-phenanthroline, respectively by the usual methods (64). The fractional release was taken as m_t/m_∞, where the amount of dye or metal ions released at desired time was m_t and after 72 h m_∞.

3. Results and discussion

3.1. *Synthesis of block copolymerization*

A preformed telechelic block of 1,3-butadiene, namely hydroxyl terminated polybutadiene (HTPB), was used in conjunction with CAN to generate the macroredox system for heterogeneous radical polymerization of acrylamide in concentrated nitric acid medium (Scheme 1).

CAN has been effectively used as an initiator in aqueous redox polymerization systems, but in the presence of even a small amount of water polymerization of AAm was not observed by the HTPB-CAN system in a nitric acid medium. This was attributed to the hydrophobic nature, as well as a weaker nucleophilic character of HTPB than that of water (61).



Sch. 1. Polymerization of AAm with HTPB-CAN macroredox system

AAm did not polymerize by CAN/HNO_3 in the absence of HTPB, whereas in the absence of AAm an orange-red colored product was obtained. 11.25% of this product was insoluble in petroleum ether and in other polar, as well as non-polar, solvents. The insoluble fraction resulted from crosslinking between chains of HTPB (61).

A tentative mechanism for copolymerization of styrene initiated by HTPB-CAN was proposed on the basis of differential scanning colorimetric (DSC) analysis of products obtained under various reaction conditions. It was observed that with increasing homogeneity of the reaction mixture, increased amount of crosslinked product was obtained (61). In the present study, HTPB and AAm were not miscible with each other; hence the reaction mixture was heterogeneous throughout the reaction. It was suggested, therefore that in the presence of AAm, the possibility of formation of crosslinks between pure HTPB chains may not be great because the small monomers molecules (AAm) would react with greater velocity.

The effect of various parameters was observed by variation of a particular constituent, keeping other ones constant. The reaction time affected the yield (Fig. 1). However, the reaction was sufficiently fast with no induction time and 5 h polymerization time was sufficient.

3.2. *Effect of temperature*

The polymerization was studied in the 30–60°C temperature range. The product yield increased with the increase in temperature (Fig. 2). In this heterogeneous polymerization system, effective dissipation of reaction heat was not possible. Hence, for better temperature control and to keep crosslinking at a minimum, further studies were carried out at 35°C, since in the absence of a monomer, crosslinking of HTPB was observed to increase with a rise in temperature.

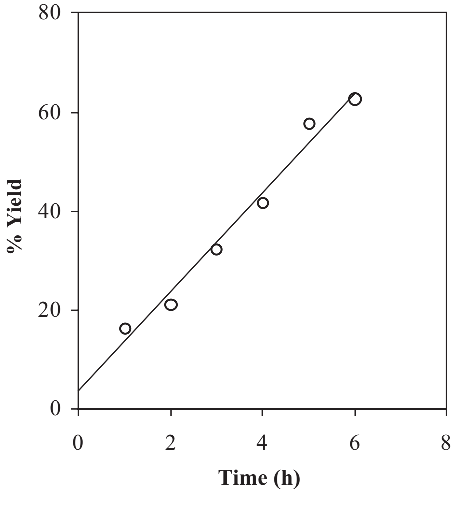


Fig. 1. Effect of time on % yield of block copolymer (Reaction conditions: HTPB, 18.5 mmol; AAm, 6.25 mmol; CAN, 0.183 mmol; HNO_3, 2 mL; Temperature, 35°C).

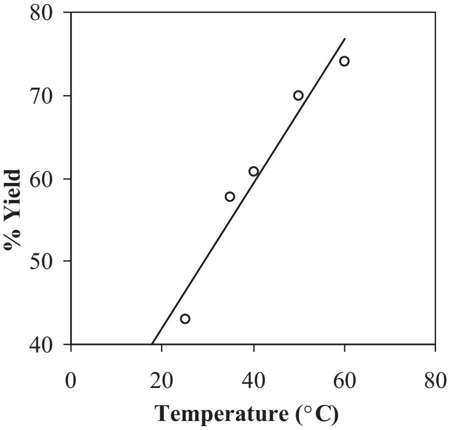


Fig. 2. Effect of temperature on % yield of block copolymer (Reaction conditions: HTPB, 18.5 mmol; AAm, 6.25 mmol; CAN, 0.183 mmol; HNO_3, 2 mL; Reaction time, 5 h.)

3.3. *Effect of concentration of CAN*

The effect of CAN concentration on the yield of copolymer was studied in the 0.09–0.365 mmol range (Fig. 3), and a linear increase in reaction rate was observed, which was quite logical. However, conclusive results could not be obtained on a further increase in CAN concentration, as its solubility was limited in nitric acid.

3.4. *Effect of monomer concentration*

The effect of AAm concentration was studied in the 3.2–19.2 mmol range (Fig. 4). Generally, the increase in monomer concentration results in the enhancement of the rate of polymerization. In the present study, a relatively anomalous effect of increasing monomer concentration was observed. The percentage yield of the product decreased with an increasing quantity of acrylamide. At a higher concentration (19.2 mmol) of acrylamide, the product obtained was a highly viscous rubbery liquid, which was completely soluble in petroleum ether indicating incorporation of a few acrylamide units in the product. It was found that if the concentration of CAN was also doubled, a solid resinous product could be obtained but with a further increase in monomer concentration, the same decreasing trend of percentage yield was observed.

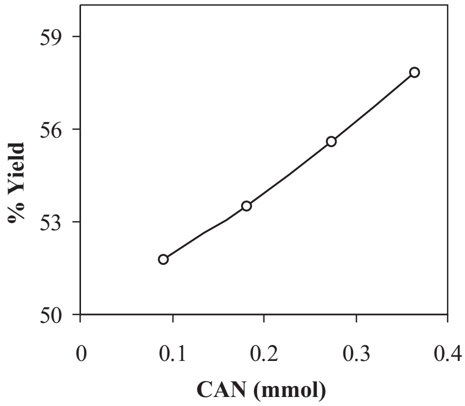


Fig. 3. Effect of concentration of CAN on % yield of block copolymer. (Reaction conditions: HTPB, 18.5 mmol; AAm, 6.25 mmol; HNO_3, 2 mL; Temperature, 35°C; Reaction time, 5 h.)

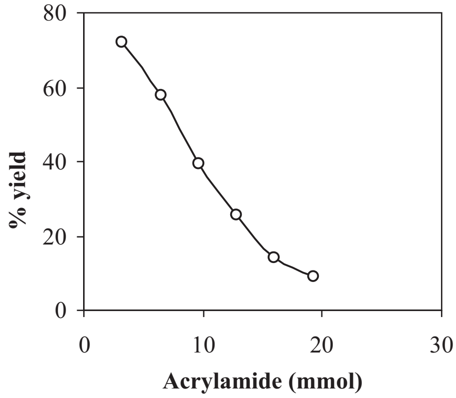


Fig. 4. Effect of monomer concentration on % yield of block copolymer. (Reaction conditions: HTPB, 18.5 mmol; CAN, 0.183 mmol; HNO_3, 2 mL; Temperature, 35°C; Reaction time, 5 h.)

When AAm or PAAm were mixed with the aqueous solution of CAN, a slight fading of yellow color was observed. The colorimetric determination also indicated that if AAm or PAAm was dissolved in the aqueous solution of CAN, its absorbance (at λ_{max} 423 nm) decreased. Thus, adsorption of CAN by AAm or PAAm was suggested. The decrease in absorbance was greater on the addition of AAm than for PAAm. Flocculation was very apparent on the addition of PAAm to a solution of CAN after a few minutes.

It is well known that PAAm is useful as a flocculant in the treatment of industrial waste (65). Sreedhar and Anirudhan (67) synthesized a graft copolymer of acrylamide onto coconut husk, which exhibited a very high absorption potential or Hg (II). Hence, it was inferred that a decrease in the yield of copolymer on increasing the AAm concentration should be due to absorption and/or flocculation of CAN.

Shukla and Mishra (67) studied the aqueous polymerization of acrylamide initiated by an acidic permanganate/thiourea redox system. They attributed the deviation from the linear behavior at high monomer conversion to interference of the polymer dissolved in the medium, as the viscosity increases due to a high extent of conversion. The same authors (68), in their study on aqueous polymerization of acrylamide by acidic thiourea/potassium bromate redox system, observed that with an increasing monomer concentration, the conversion was steady at a lower monomer concentration and became constant at a higher concentration.

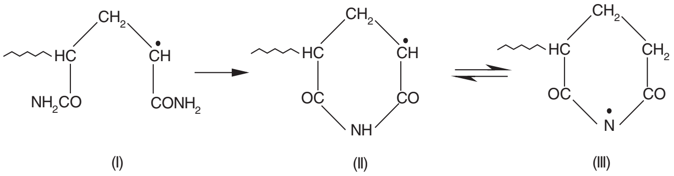
Bajpai and Ahi (69) studied polymerization of acrylamide using a mandelic acid/permanganate redox system in acidic medium and observed that the increase in monomer concentration increased the rate initially, but at higher concentration, the percentage conversion decreased. However, these authors did not present any explanation.

In the present study, the polymerization system was heterogeneous as HTPB and copolymer were insoluble in nitric acid, though acrylamide and initiator were soluble. It was expected that HTPB would acquire tight conformation in a polar medium (i.e., concentrated HNO_3 and AAm). Hence, the reaction was studied with THF and methanol as solvents to explore whether the normal trend could be obtained, but even then a slimy product with poor yield resulted. Apparently, acrylamide absorbed the initiator CAN, through the formation of charge transfer complex (70), thus the chances of its collision with terminal methylol units of HTPB to act as the redox initiator were decreased. Similar results were obtained in our study using V(V) instead of CAN (38).

3.5. *Effect of nitric acid concentration*

The product, insoluble in petroleum ether, was obtained when concentrated nitric acid was used in the 1.5–4 mL range (Fig. 5). A further increase in the amount of nitric acid resulted in charring of the reaction mixture. The increment in volume of HNO_3 would result in better solubilization of CAN, as well as AAm, thus facilitating the reaction. Initially, this accounted for the rapid enhancement in the reaction rate. However, with a further increase in volume of HNO_3, the product yield increased less rapidly, probably an effect of dilution, as well as increased termination rate (71).

Acrylamide polymerization has usually been studied extensively in aqueous solution. Acrylamide, as well as polyacrylamide are soluble in water, so the aqueous solution reaction of this monomer is not expected to fall kinetically into the class of heterogeneous polymerization. Nevertheless, Jenkins (72) discussed that the kinetics of AAm polymerization have a marked similarity to those with heterogeneous polymerization, viz., acrylonitrile, vinyl chloride, vinylidene chloride and triflurochloro ethylene although apparently for a different reason. He described that in AAm polymerization, the radicals are in some way "buried", under which conditions they have a lifetime of several hours. This self-burial cannot be considered a result of coiling because the experimental life times are much longer than those, which could reasonably be expected on this basis. At low pH values, slow imidization occurs, so that for long periods the radical has the glutarimide structure (II) rather than the acetamide structure (I). II might well resemble the well-known succinimidyl radical (III) in stability.



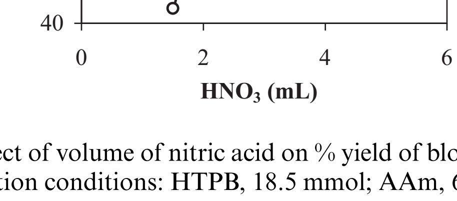


Fig. 5. Effect of volume of nitric acid on % yield of block copolymer (Reaction conditions: HTPB, 18.5 mmol; AAm, 6.25 mmol; CAN, 0.183 mmol; Temperature, 35°C; Reaction time, 5 h).

It was inferred, on the basis of all the kinetic observations, that many, and in some cases, perhaps all of the polymer radicals precipitate from the liquid phase during growth. Considering the behavior of polymer molecules in poor solvent environments, it is assumed that such precipitated radicals will be tightly coiled. Coiling in itself will reduce the reactivity of the radicals since, if the radical end is shielded by the remainder of the molecule, any potential reactant may have to penetrate a diffusion barrier. Though the radical end will not always be in an internal arrangement, but on a statistical basis it will accommodated for a fraction of its time. If the precipitated radical also undergoes coalescence with dead polymer particles, the average reactivity will be further reduced and the relative kinetic importance of coiling and coalescence may vary according to conditions. Coiling would not be expected to be of great significance when the polymer is swollen, but in an unswollen state, it may restrict reactivity significantly (72). Since in this heterogeneous polymerization system, the reaction was carried out in nitric acid medium, few more experiments were performed to develop insight into the inherent mechanism involved. Swelling of samples of copolymer was investigated in nitric acid, as well as in nitric acid solution of AAm. 13.6% Swelling was observed in HNO_3 and 22.4% in acidic solution of AAm in 72 h. Since greater swelling was observed in the AAm solution, it was speculated that with the progress of the reaction, as the concentration of AAm decreased, the copolymer would be less swollen and the radical end may remain occluded in the final product. This speculation found further support by the following observations. In an experimental set, scaled up by 10 times, the reaction was arrested by the addition of FAS solution. The product was washed thoroughly with water and petroleum ether and then left immersed in water for several days. It was found that the coagulated lump set into a very tough and porous mass. The surface layer of the

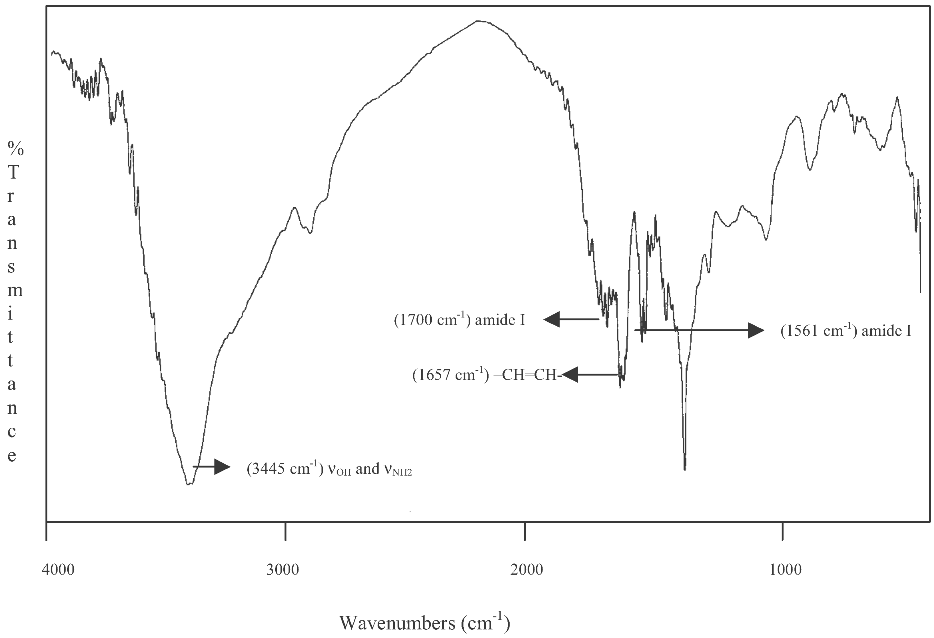


Fig. 6. I R Spectrum of block copolymer.

product appeared white and scaly which could be removed by a spatula; however, the interior was very hard and could not be cut, even with a knife. Although this toughened material could not be characterized due to its intractable nature, it became evident that the occluded radical ends of the copolymer chains continued the reaction slowly and extensive crosslinking and imidization occurred. This partially hydrophilic, porous and tough material can be useful as a material for artificial bone.

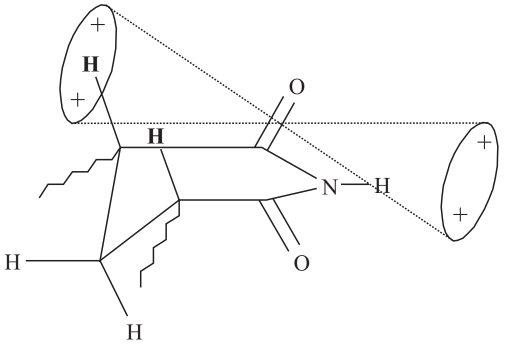
3.6. *Characterization*

Block copolymer formation was confirmed for the sample prepared by a 5 h reaction, where 185 mmol HTPB, 62.5 mmol AAm, 1.83 mmol CAN, 20 mL HNO_3 were used and the temperature was 35°C.

A comparison of the IR spectrum (Fig. 6) of this sample with those of HTPB and PAAm confirmed the copolymer formation. A very intense band, observed at 3445 cm^{-1}, involved ν_{OH} of HTPB and ν_{NH2} of PAAm. This band was narrower than the corresponding bands of HTPB and PAAm suggesting lesser H-bonding interactions. The decreased H-bonding was further indicated by the medium intensity split band at 1561 cm^{-1} due to amide II and a separate band with multiple peaks at 1700 cm^{-1} attributed to amide I which involves a major contribution from $\nu_{C=O}$. For PAAm, a very intense and broad band was observed in the 1550–1700 cm^{-1} region assigned to strongly H-bonded amide I and II bands merged together. The decreased H-bonding interactions certainly reflected the imidization of AAm units. Since upon imidization not only the possible number of hydrogen bonds would decrease, but the proper orientation for interchain H-bonding interactions may also be restricted. Absorption due to –CH=CH– groups of polybutadiene was observed at 1657.7 cm^{-1}.

The ^{1}H-NMR spectrum of polymer sample is depicted in Figure 7. It was found that when the sample was completely dried, it could not be dissolved in chloroform. Hence, the sample used for determination of NMR spectrum was not dried in air. The presence of an appreciable amount of solvent was evident from the signals observed below 2 ppm. NMR signals in the 4.91–4.98 ppm range were attributed to the methine protons of acrylamide and those in the 5.38–5.65 ppm range were due to vinyl protons of butadiene. An additional signal at 4.081 ppm was observed for PBd-b-PAAm in this study.

However, this signal was inconspicuous for the sample obtained in a similar study with V(V) as an oxidant in H_2SO_4/methanol medium (38). It is suggested that this signal might be from the methine protons of the imidized



Sch. 2. Schematic presentation of anisotropic sheilding of axial protons of imidized acrylamide units

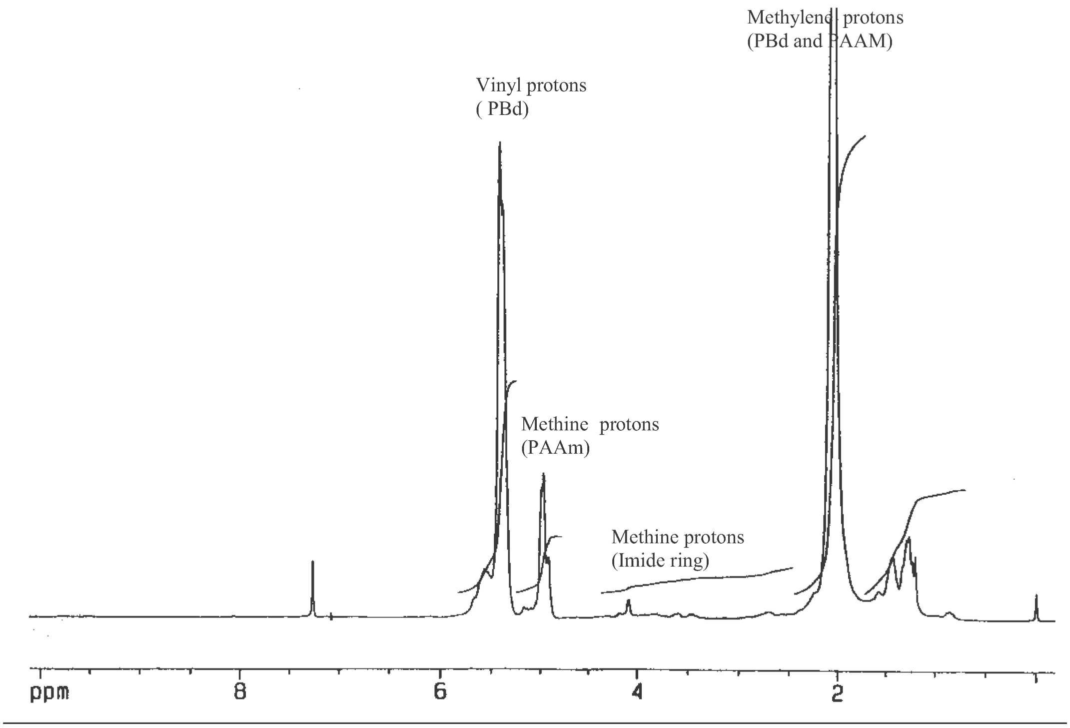


Fig. 7. NMR spectrum of block copolymer.

acrylamide units. These methine protons, indicated in bold letters in structure (Scheme 2), must occupy axial position in the half chair conformation of the cyclic imide unit. Thus, the slight upfield shifting of this signal can be accounted for falling within the anisotropic shielding zone of the carbonyl group.

Pojman and Fortenberry reported imidization and crosslinking during solvent free synthesis of PAAm by frontal polymerization (73). Other authors also reported intramolecular imidization reaction with a concurrent loss of ammonia in both homogeneous and heterogeneous polymerization of AAm (74–75). The proportion of butadiene and acrylamide units present in the copolymer was calculated by comparing the intensity of vinyl protons of butadiene and methine protons of acrylamide and the proportion was found to be 1.37:1 (58%:42%).

The viscosity measurements were carried out in a chloroform solution. The results are depicted in Figure 8. The values for Huggins' and Kraemer's constant (k' and k'') were found to be 0.4061 and 0.1099, respectively. Though the values satisfy the condition $k' + k'' = 0.5$, the value for k' is slightly higher than the usual value for flexible polymers in good solvents, i.e., near 0.35. This observation also in all probability reflected partial imidization of the PAAm, since the rigidity of a chain sharply increases when there is ring formation in the chain (76). It was calculated on the basis of NMR data that approximately 27.4% of amide groups of PAAm underwent imidization. The possibility of interchain crosslinking owing to the imidization of amide groups of different chains also existed. However, it was inferred that only a few units might have joined in this way, because in the previous study on the synthesis of lightly crosslinked butadiene-acrylamide block copolymer (CBC) in presence of *N,N′*- methylene-bis-acrylamide (MBA) (2% weight of AAm) viscosity values of k' and k'' were quite high (1.3278 and 1.4890, respectively) (38). This speculation was further supported by swelling studies.

3.7. *Swelling behavior*

Equilibrium swelling of the polymer sample was determined in some selected solvents. The plot of the swelling

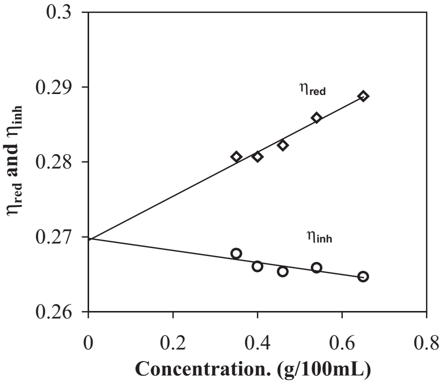


Fig. 8. Plot of ηsp/C and ln ηr/ C vs. concentration (C)

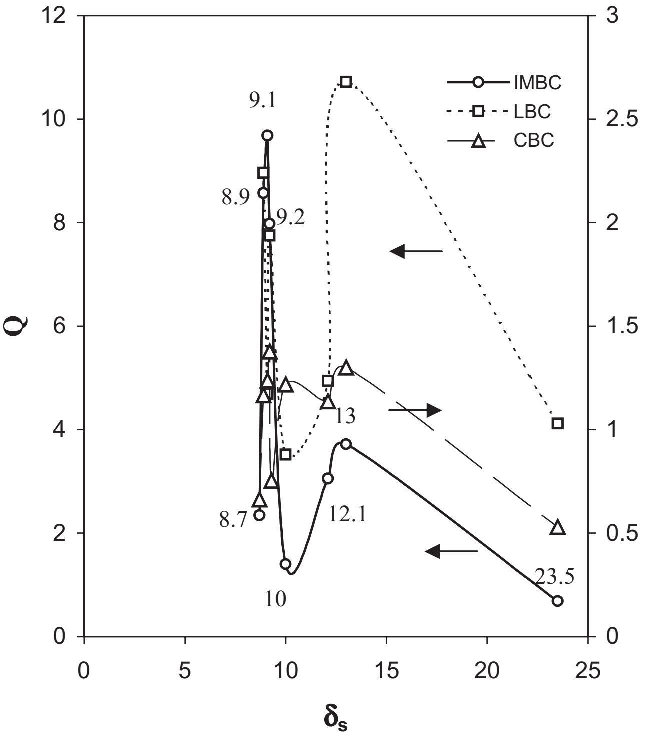


Fig. 9. Plot of solubility parameter (δs) vs. swelling coefficient (Q)

coefficient (Q) against the solubility parameter (δ_S) values of the solvents (Fig. 9) exhibited two maxima at 9.1 and 13, which corresponded to the swelling of polybutadiene and polyacrylamide domains, respectively.

The swelling results for the polybutadiene-polyacrylamide copolymer prepared in this study (IMBC) were compared with those of linear PBd-b-PAAm (LBC) (synthesized by HTPB-V(V) macroredox initiator) (37) and the lightly crosslinked PBd-b-PAAm (CBC) (38) in Figure 9. The order of swelling of these three was found to be LBC $>$ IMBC $\gg$ CBC. This comparison also substantiated the speculation that imidization occurred mostly by intrachain interaction of amide groups.

3.8. *Loading and release of dye and metal ions*

Methyl orange was used as a model hydrophilic organic solute. Nickel sulphate and ferrous ammonium sulphate were chosen as the inorganic salts for the loading and release study. Water was used as a dissolution medium for imbibition of methyl orange and metal ions. 41.8% of methyl orange, 44.08% of nickel sulphate and 39.16% of ferrous ammonium sulphate were loaded in the film. The release pattern for the materials is depicted in Figure 10. About 96.6% and 95.1% of the absorbed methyl orange and nickel sulphate were respectively released in 72 h.The release pattern of these materials were similar to the usual fractional release behavior of drug release observed for hydrogel systems, *i.e.*, the release rate is much faster initially, which gradually slowed down (77). However, almost no release of ferrous ions was observed in the dilute nitric acid medium. Thus, this material adsorbed nickel (II) and iron (II) ions both from their aqueous solutions, but selectively released only nickel (II) ions in dilute HNO_3. Further study on this material regarding its possible use for absorption of metal ions from industrial effluents and subsequent selective release is under way.

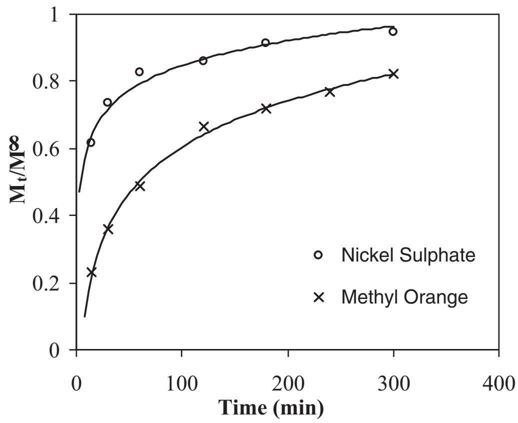


Fig. 10. Plot of fractional release (M_t/M_∞) of dye and metal ion vs. time [M_t and M_∞ are the amount of material released at time 't' and 72 h, respectively)

4. Conclusions

The amphiphilic copolymer, comprised of polybutadiene as a hydrophobic part and polyacrylamide as a hydrophilic part, was synthesized conveniently in good yield using CAN as initiator. The resulting block copolymer was characterized by IR spectral, viscosity and swelling measurements. These block copolymers may be useful for drug delivery and metal ion extraction.

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