Synthesis of Amphiphilic Block Copolymer of Butadiene and Acrylamide using Telechelic Polybutadiene and V(V) as Redox System

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Block copolymers of butadiene and acrylamide (AAm) were synthesized by radical initiation using the hydroxy terminated polybutadiene (HTPB) and ammonium meta vanadate (AMV) macroredox initiator pair in heterogeneous medium, in the presence of sulphuric acid/methanol at 35°C in air and in nitrogen. The homopolymer of AAm was not formed under these reaction conditions. The yield of block copolymer decreased on dilution with methanol. No copolymerization was observed in other solvents, namely DMF, DMSO, CHCl₃, and toluene. Formation of block copolymers was confirmed by IR and NMR spectroscopy. Self-assembly of amphiphilic block copolymers was evidenced by swelling, solubility and viscosity measurements.

Keywords butadiene-AAm block copolymer, amphiphilic block copolymer, polybutadiene, macroredox polymerization, self-assembly

Introduction

Block copolymers prove to be efficient compatibilizers for blending immiscible polymers to produce materials with desirable properties (1–7). Block or random copolymers of non polar monomers with polar monomers are of special interest for polymer chemists and polymer engineers because of their excellent dyeing properties, good permeability of gaseous materials, and novel weather-proof functions with high chemical reactivity (8) Mori and Muller (9) included a special section on block copolymer in their review on recent advances in the design and synthesis of novel complex polymers with (meth) acrylic acid segments using various living and controlled polymerization techniques. Cunningham (10) reviewed the reports on the preparation of block copolymers in emulsion or mini emulsion using living radical polymerization.

Special attention is being paid to amphiphilic block copolymers due to the possibility of self-assembly (11–20), feasibility to generate nanostructural materials and numerous applications in controlled drug delivery and smart catalyst separation technology (21–27). They also find applications as stabilizers, emulsifiers, dispersants, foamers, thickeners, membranes (28), in micro encapsulation (29) as well as oil recovery appli-

cations and nanomaterial hybrids (30). Traditional amphiphilic block copolymers containing chemically connected hydrophilic and hydrophobic segments provide a great variety of morphologies both in solid state and in selective solvents (31, 32).

The interaction between amphiphilic polymers and surfactants has also received considerable attention (33). The copolymers of AAm with various hydrophobic comonomers have proved to be of great interest due to their associating behavior in solution (34–46). Amphiphilic block copolymers of AAm and styrene have also been studied (47, 48). Abusharkh and (49, 50) prepared and studied hydrophobically modified water-soluble AAm block copolymers.

Although vanadium (V) has been employed as an effective initiator for grafting of vinyl monomers onto hydrophilic substrate, its use for block copolymerization of hydrophobic monomers was reported for the first time in our previous publication (51). In the present study, block copolymerization of butadiene and AAm is reported in heterogeneous medium using hydroxyl-terminated polybutadiene-V(V) macroredox initiator.

Experimental

Materials

Hydroxy-terminated polybutadiene (HTPB) was a gift from Vikram Sarabhai Space Center, Thiruvananthapuram, India. The number average molecular mass (M_n) of hydroxy-terminated polybutadiene (HTPB), determined by vapor phase osmometry (VPO), was 2450 ± 300. 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 reminder 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. Ammonium meta vanadate (AMV) (Loba Chemie, Bombay, India) of AR grade was used as received. Sulphuric acid, supplied by Qualigens, India, and methanol, petroleum ether (60–80°C) and other solvents of analytical grade obtained from E. Merck, India were used without further purification.

Synthesis of Block Copolymers

A pyrex glass test tube of length 12 cm was used as the reaction vessel. HTPB and AAm were taken in this reaction vessel and kept in a serological bath maintained at the required temperature. AMV was dissolved in the requisite amount of sulphuric acid diluted with methanol, deaerated, and thermostatted separately. It was then added to the reaction vessel quickly, and then oxygen free dry nitrogen gas was bubbled into the reaction mixture. Finally, after a desired time period, the reaction was arrested by adding a known excess of ferrous ammonium sulphate solution so that all the excess of V(V) ions were reduced to V(IV) ions instantaneously. The product obtained was washed thoroughly with 0.1 N sodium hydroxide solutions, then repeatedly with water, and finally with petroleum ether to remove unreacted AAm, HTPB, sulphuric acid and other inorganic materials added to the reaction mixture. The product was dried initially in vacuum, then in air and weighed to a constant weight. The extent of reaction with

HTPB was determined gravimetrically in terms of percentage yield, evaluated using the Equation (1).

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

In order to examine the effect of various parameters, several experiments were performed, varying the examined parameter and maintaining the other ones as constant.

Measurements

The IR (KBr) spectra of the products were recorded on a Perkin-Elmer Model 1430 spectrophotometer.

The NMR spectra were recorded on a Bruker DRX-300 FT-NMR spectrometer in $CDCl_3$ solution.

Viscometric studies were performed at $27°C$ using a Ubbelohde viscometer and chloroform solution. The Huggins' (Equation (2)) and the Kraemer's (Equation (3)) equations were used to determine intrinsic viscosity $[\eta]$, Huggins' constant, k' and Kraemer's constant, k''.

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

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

The morphology of the polymeric material was examined using a LEICA S-430 scanning electron microscope.

Product Fractionation

The reactants were scaled up by ten times for the typical set to prepare a sample for fractionation. HTPB (10 g, 0.185 mol), AAm (4.43 g, 0.0625 mol), AMV (0.584 g, 5 mmol), 50 mL of H_2SO_4 and 50 mL of methanol were used and the reaction was arrested after 1 h by the addition of excess of ferrous ammonium sulphate. The crude product (Sample I) obtained was washed thoroughly with water and aqueous NaOH repeatedly and finally with water. The resulting product was extracted subsequently with petroleum ether first, and then with toluene, with each for 48 h. The solutions and residues were separated. The solvents were removed by vacuum evaporation and the fractions were weighed till constant weight. A similar procedure was repeated under a nitrogen atmosphere also to prepare Sample II.

The samples (0.05 g) were cut from the fraction insoluble in toluene and were immersed in 50 mL of various solvents for 48 h to attain equilibrium swelling. The swollen samples were then taken out from the solvent bath, pressed gently between filter papers to remove the excess of solvent, and weighed immediately. The swelling coefficient of the crosslinked product (Q) was calculated by Equation (4) (52):

$$Q = \frac{m - m_0}{m_0} \times \frac{1}{d} \qquad (4)$$

where m, is the weight of swollen polymer and m_0 that of polymer taken initially and 'd' is the density of the solvent used. The characteristic parameters for the solvents were obtained from the literature (53).

Results and Discussion

Most of the reports using V^{5+} as an oxidant in redox systems in homopolymerization or graft copolymerization reactions are available for homogenous aqueous reaction medium in the presence of mineral acids. However, polymerization of AAm could not be initiated with the HTPB-V (V) macroredox pair in aqueous medium, since HTPB is hydrophobic in nature. The effort to carry out polymerization in emulsion using a cationic surfactant also proved to be futile. For this purpose, 1 g (18.5 mmol) HTPB, 0.443 g (6.25 mmol) AAm, 0.0584 g (0.5 mmol) of AMV, 5 mL H_2O, 5 mL H_2SO_4 were magnetically stirred with 0.05 g of CTAB. The polymer formed (yield $\sim$ 10%) was precipitated by the addition of acetone, however, it was completely soluble in petroleum ether (sample III) suggesting low reactivity of the system.

In methanolic sulphuric acid medium, the HTPB-V (V) macroredox pair showed a very high reactivity for initiating polymerization of AAm, providing an 86.6% product in 4 h at 35°C.

HO CH_2-HC=CH_2-(-CH_2-HC=CH-CH_2-)m-CH_2-HC=CH-CH_2OH

(HTPB)

H_2C=CHCONH$_2$ $V^{5+}\big/ H_2SO_4\big/ CH_3OH$

(AAm)

-(CH-CH_2-)n-CH-HC=CH-CH_2-(-CH_2-HC=CH-CH_2-)m-CH_2-HC=CH-CH-
| | |
CONH$_2$ OH   (Block Copolymer)   OH

The reaction time affected the yield. However, the reaction was sufficiently fast and 5 h polymerization time was sufficient (Figure 1). To minimize the possible side reactions and to keep DP low for facile characterization of the resulting block copolymers, 1 h polymerization time was found to be suitable for further studies. The theoretical

Figure 1. Effect of time on % yield of block copolymer.

molecular mass ($M_{n, th}$) were calculated with the help of Equation (5) (54) under the assumption that the entire HTPB molecules initiated the polymerization and no termination by coupling occurred.

$$M_{n,th} = \frac{[M_o]}{[I_o]} \times (M_{w,AM}) \times (\text{Conversion}) + M_{n,HTPB} \tag{5}$$

where $[M_o]$ and $[I_o]$ are the initial molar concentration of monomer (AAm) and initiator (HTPB), respectively and $M_{w, Am}$ and $M_{n, HTPB}$ are the molecular masses of monomer and HTPB, respectively and the results obtained are depicted in Figure 2.

Effect of Temperature

The polymerization was studied in the temperature range 30–60°C. The product yield increased with the increase in temperature (Figure 3). AAm did not polymerize by AMV alone. However, on excluding AAm from the reaction mixture HTPB yielded 10% and 40% of insoluble crosslinked product at 35 and 60°C, respectively. Hence, further studies were carried out at 35°C. The concentration of the reactants in the standard set were 18.5 mmol HTPB, 6.25 mmol AAm, 0.5 mmol AMV, 5 mL H_2SO_4 5 mL CH_3OH and the temperature was 35° C. The effect of various parameters was observed by variation of a particular constituent keeping others constant and the results are presented in Figures 3–7.

Effect of Methanol

In this heterogeneous copolymerization system, methanol was used as a diluent for concentrated sulphuric acid. Methanol was used in the volume range of 1.25–10 mL. With the use of a lesser amount of methanol, the reaction mixture charred. In the limiting range (2.5–7.5 mL), the product insoluble in petroleum ether was obtained and the yield of the product decreased with an increase in the amount of methanol (Figure 4). However, a further increase in volume of methanol yielded a product soluble in petroleum ether. It is suggested that in the optimum concentration range of methanol, macroradical cage phenomenon may be predominant, i.e., encagement of the macroradi-
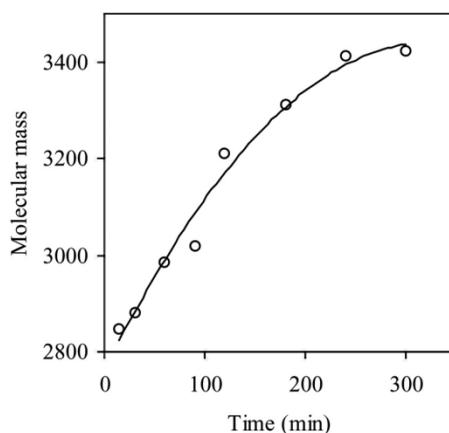
Figure 2. Effect of time on molecular mass.
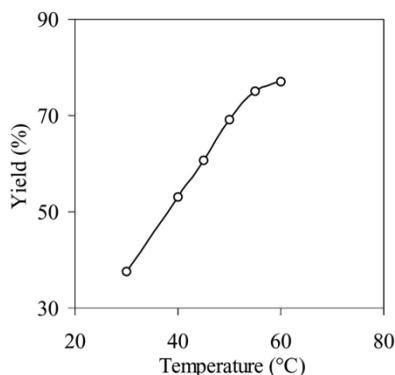
Figure 3. Effect of temperature on % yield of block copolymer.

cals which may be imbricated in a viscous environment favorable to propagation reactions and unfavorable to termination reactions (55). However, an increase in the volume of methanol resulted in a less viscous medium and predominating termination reactions, along with a lesser number of AAm units incorporated in the obtained block copolymer. The latter procedure also produced a copolymer completely soluble in petroleum ether. On using solvents other than methanol, namely, DMF, toluene, DMSO, $CHCl_3$ no solid product could be precipitated. Toluene and $CHCl_3$ yielded a homogenous reaction mixture.

Skaria et al. (56) have also found that polyacrylamide, obtained by suspension polymerization using V(V)-chelated copolymers in combination with cyclohexanone as redox reagent, had a higher molecular mass than that prepared by V(V) ion-cyclohexanone redox initiator pair in homogeneous solution.

Effect of V^{5+} Concentration

With the increase in V^{5+} concentration in the $0.25-1.0$ mmol range (Figure 5), the yield of the block copolymers increased up to a limit and then became constant. This is in accord-
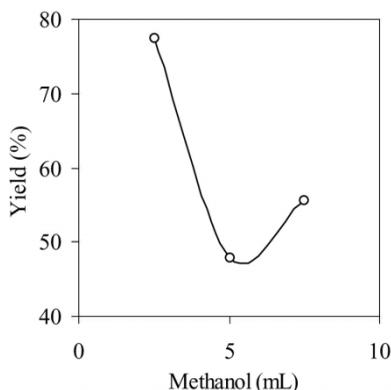
Figure 4. Effect of volume of methanol on % yield of block copolymer.
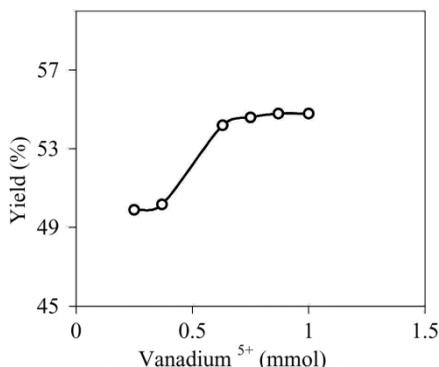
Figure 5. Effect of concentration of V^{5+} on % yield of block copolymer.

ance with the accepted view attributing the termination of copolymerization by the reaction of V^{5+} ions with growing polymer chains.

Effect of Sulfuric Acid Concentration

The product insoluble in petroleum ether was obtained in the limiting range 5–10 mL of H_2SO_4 and the yield of product increased with the increasing amount of sulfuric acid (series a, Figure 6). When the amount of sulfuric acid was further increased, charring of the reaction mixture was observed as a consequence of auto acceleration. However, with a greater quantity of AAm (19.2 mmol) used, higher amounts of sulfuric acid could be used (Series b, Figure 6). The increased amount of sulfuric acid may shift the following equilibrium towards the right hand side to produce a greater quantity of sulphate complexes (Equation (6)).

$$VO_2^+ + HSO_4^- \rightleftharpoons VO_2SO_4^- + H^+ \tag{6}$$
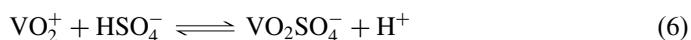
It is known that the bisulphate complexes of V^{5+} are more effective as initiators and less effective as (51). Hence, it is expected that with increasing the sulphuric acid concen-
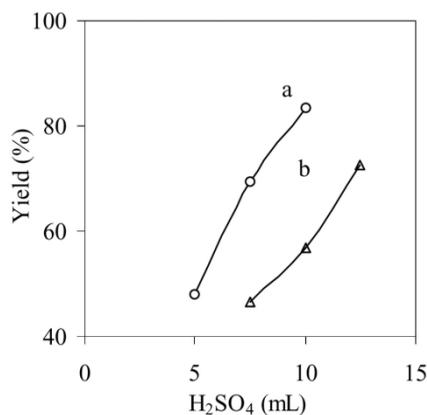
Figure 6. Effect of volume of sulfuric acid on % yield of block copolymer.
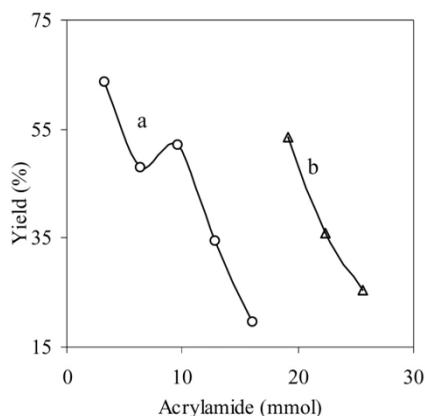
Figure 7. Effect of monomer concentration on % yield of block copolymer.

tration, more of the $VO_2SO_4^-$ species are generated which can initiate a larger number of chains, and at the same time, these species may not be so effective to terminate the growing chains.

Effect of Monomer Concentration

The effect of the monomer concentration was studied in the 3.2–16 mmol range. Upon increasing the amount of AAm the percentage yield of the product decreased (series a, Figure 7). At higher concentration (19.2 mmol) of AAm, the product obtained was a highly viscous rubbery liquid, which was completely soluble in petroleum ether. This is contrary to the general observations that yield of the polymers increases with increasing concentration of monomer. Polymerization of AAm has been extensively studied using several redox systems in an aqueous medium. In most of the cases, yield of the polymer increased linearly with increasing monomer concentration. However, in some cases at a higher concentration of Aam, a deviation from linearity was observed which was attributed to hindrance from increased viscosity of polymer dissolved in reaction medium. Viscosity of the medium rapidly increased with a high extent of conversion, thus causing interference in the normal course of (57). However, in the present study, the system was heterogeneous as HTPB and block copolymer were insoluble in methanolic sulphuric acid, though AMV and AAm were soluble in it. Hence, it was speculated that AAm absorbed the initiator, AMV, thus decreasing the chances of its collision with terminal methylol units of HTPB, which act as the redox initiator pair. In other experimental sets, the concentration of initiator was also increased for higher amounts of AAm, only solid resinous products were obtained. However, with a further increment in the amount of Aam, the product yield decreased again (series b, Figure 7). This confirmed that with an increase in the amount of monomer, an appreciable amount of AMV was absorbed by the monomer and was not available for reaction.

Fractionation of Samples

Due to polymerization in the heterogeneous medium, a broad polydispersity was expected. Hence, the crude product was fractionated by solvent extraction, with the results presented schematically in Scheme 1.
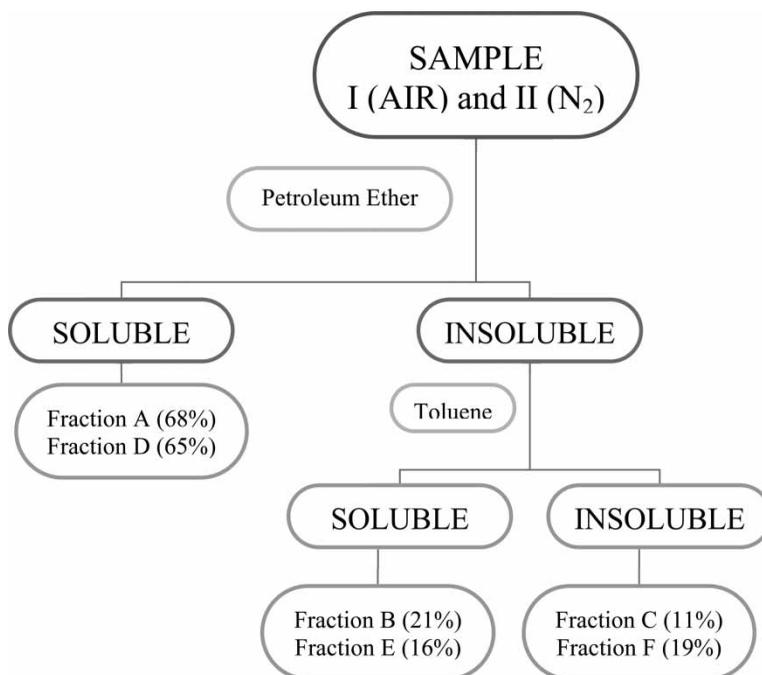
Scheme 1. Fractionation of samples by solvent extraction: fractions A, B and C were obtained from sample I and fractions D, E and F from sample II.

Characterization

Block copolymer formation was confirmed by comparing IR spectra of different samples with those of HTPB and polyacrylamide. The samples were opaque towards IR radiation, probably due to wide molecular mass distribution. Hence, the IR spectra of fractions A, B, and C of the sample prepared in air (sample I) and fractions D and E of the sample prepared in nitrogen atmosphere (sample II) were recorded.

The sample prepared in an aqueous medium (sample III) in the presence of CTAB, completely dissolved in petroleum ether, hence, it could not be fractionated. A strong, broad band with contribution from the NH_2 group of AAm and terminal OH group of HTPB appeared near $3400\,cm^{-1}$. The IR spectra of all samples exhibited broad absorption bands due to ν_{as} C–H and ν_s C–H of HTPB at 2920 and $2850\,cm^{-1}$, respectively, except for the fraction C, where these bands were observed as shoulders on broad band near $3400\,cm^{-1}$. The strong absorption due to in-plane C–H bending of HTPB appeared at $970\,cm^{-1}$ in fraction D and E. In other samples, it appeared as a shoulder on a band in $800–1000\,cm^{-1}$ range. In some fractions, a characteristic peak due to the amide carbonyl group distinctly appeared at $1715\,cm^{-1}$, whereas in others as a shoulder on a broad band in the $1600–1800\,cm^{-1}$ range.

The ^{1}H-NMR spectra of fractions A and D are depicted in Figures 8 and 9, respectively. It was found that when the samples were completely dried, dissolution in chloroform could not be achieved. Thus, the samples used for determination of NMR spectra were not dried in air. The NMR spectrum showed an appreciable amount of solvent, as is evident from the signals observed below 2 ppm. This suggested that due to self-assembly of hydrophobic
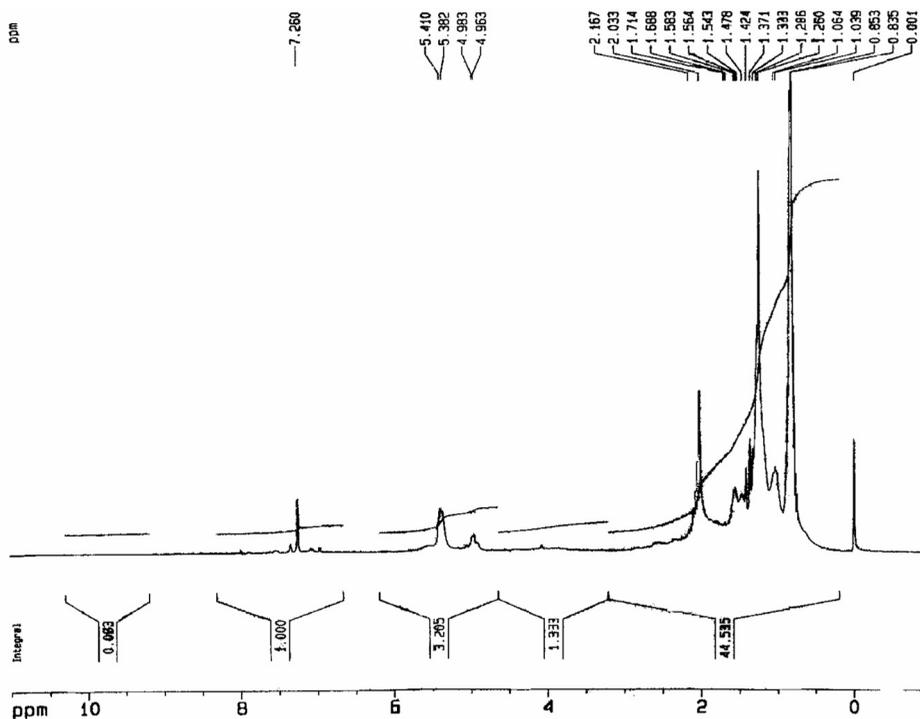
Figure 8. NMR Spectrum of fraction A.

and hydrophilic blocks, the solvent molecules got lodged inside the voids. This was confirmed by weight loss when the block copolymer was dried in an air oven at 60°C for 4 h.

When HTPB, an excess of AAm, and AMV dissolved in methanolic sulphuric acid, were mixed in a beaker and left overnight, a solid product was obtained in the shape of a disc, which was washed thoroughly with water and then kept immersed in water for a few days. The disc swelled greatly with the swollen hydrophilic surface appearing white, whereas the core was dark and rubbery. This observation demonstrated microphase separation due to self-assembly of hydrophobic and hydrophilic blocks and is schematically presented in Figure 10. The polybutadiene blocks associated into an elastomeric core covered by the shell comprising of hydrophilic polyacrylamide blocks. The scanning electron micrograph also showed a uniform texture with fibrilar morphology at the border (Figure 11). Inomata et al. (58) also reported the association behavior and viscoelastic properties of ABA triblock copolymers dissolved in B-selective solvents.

The proportion of butadiene and AAm units in the block copolymer was calculated from the NMR data and is presented in Table 1. The sample of HTPB used has a number average molecular mass of about 2400. From the intensity of the methylene protons on AAm units and butadiene units respectively, the butadiene to AAm ratio in fraction A was calculated to be 1.56 : 1 (61%:39%) and that for fraction D was 2.24 : 1 (69%:31%). The ratio of vinyl protons of butadiene units and methine protons of AAm for fraction A was calculated to be 1.47 : 1 (60%:40%) and for fraction D as 1.66:1 (62%:38%). The close resemblance of the values for fraction A suggested that the double bonds of butadiene were not affected during the polymerization process. But in
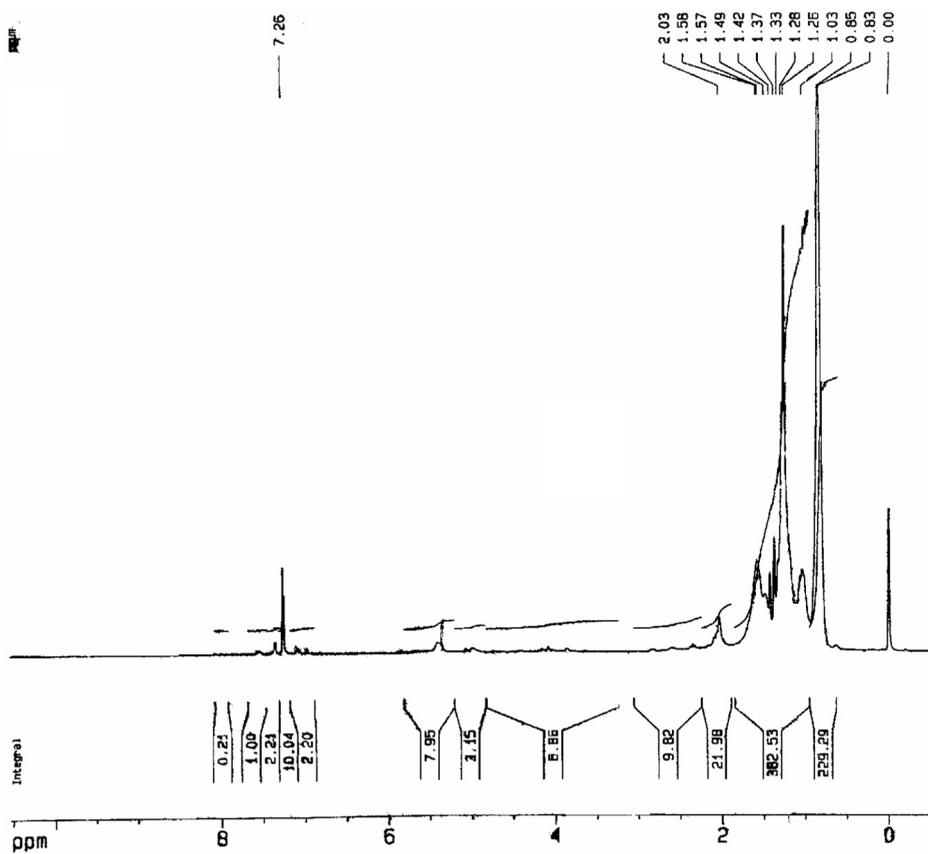
Figure 9. NMR Spectrum of fraction D.
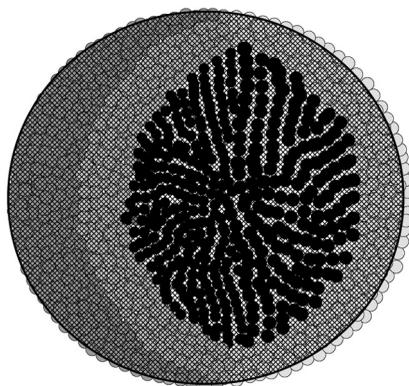
Figure 10. Schematic presentation of micelle formation for butadiene-acrylamide block copolymer in non-polar solvents: gray circles represent polyacrylamide block and dark circles polybutadiene blocks.
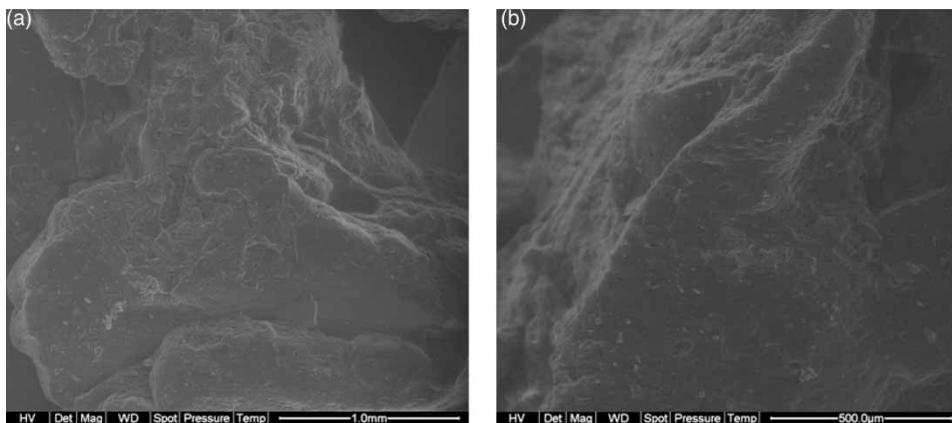
Figure 11. SEM of fraction F Magnification (a) 100 (b) 200.

the case of fraction, the results suggested that there must be some crosslinking through the residual double bonds of the butadiene units.

During preparation of sample 1, HTPB was floating over the solvents (methanol and sulphuric acid), which are polar in nature, hence the terminal methylol groups only must be in contact with AMV. The growing chain bearing radical on the terminal AAm unit must also be attracted towards the solution phase. Therefore, only the AAm monomer molecules must be involved in propagation of the chain. However, when nitrogen gas was bubbled through the reaction mixture during the preparation of sample II, gentle agitation might bring the radical end of the chain in contact with the residual double bonds on the butadiene block, thus causing crosslinking of the chains. The viscosity measurements were carried out in chloroform solutions for fraction soluble in petroleum ether and toluene (fraction A and B), respectively. The results are depicted in Table 2 and Figure 12. The values obtained for Huggins' constant, k′ and Kraemer's constant, k″ are well in agreement with the acceptable value in good solvent and the constants satisfy the condition of Equation (7).

$$k' + k'' = 0.5 \qquad (7)$$

Table 1

NMR spectral data of the acrylamide-butadiene block copolymer

Samples	Protons	Frequency (ppm)	Relative intensity
Fraction A	Methylene (Butadiene units)	2.167–2.033	2.94
	Methylene (Acrylamide units)	2.600–2.326	1.88
	Methine (Acrylamide units)	4.434–3.864	1
	Vinyl (Butadiene units)	5.650–4.920	1.47
Fraction D	Methylene (Butadiene units)	2.173–2.033	3.3
	Methylene (Acrylamide units)	2.839–2.325	1.4
	Methine (Acrylamide units)	4.34–3.864	1
	Vinyl (Butadiene units)	5.684–4.968	1.6

Table 2

Viscosity measurement of acrylamide-butadiene block copolymer

S. No.	Sample	$[\eta]$	k'	k''
1.	Fraction A	0.3257	0.3742	0.1282
2.	Fraction B	0.2898	0.3548	0.1522

It is known that k' for flexible polymers, in good solvents, is often near 0.35. The k' values for the fraction (A) and fraction (B) are indicative of the flexible nature of this polymer. Viscosity was measured for dilute solution in chloroform. Chloroform is a better solvent (δ_s 9.3) for polybutadiene (δ_p 8.6) than for polyacrylamide. Hence, in dilute solution, the amphiphilic block copolymer may self assemble into isolated flower-like micelles as depicted in Figure 10. The butadiene block chains may take the loop conformation with polyacrylamide blocks at both ends, incorporated in the same associated miceller core. Thus, it is inferred that the toluene fraction contained a large number of AAm units, thus making the self-assembly into isolated micelles possible. In dilute solution these spherical micelles may exert less hindrance to the flow. Values for k' and intrinsic viscosity are higher for the petroleum ether fraction than those for the toluene fraction. The higher viscosity and higher k' values indicated lesser flexibility of the petroleum ether fraction, suggesting that this fraction may have shorter blocks of the AAm units. These short terminal PAAm blocks may associate through H-bonding, producing the dendritic structure which accounted for higher viscosity.

Solubility and Swelling Behavior

Equilibrium swelling of the fraction insoluble in toluene was determined in various solvents. A plot of the swelling coefficient Q, against δ_s, the solubility parameter values for various solvents (Figure 13) exhibited a maxima (~ 10.7) corresponding to δ_p, the solubility parameter of the polymer. The swelling coefficient, Q was shown to be related to
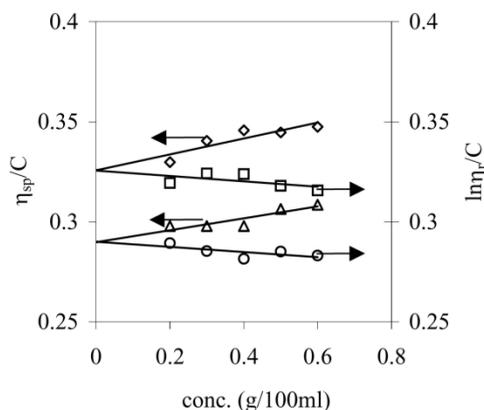
Figure 12. Plot of η_{sp}/C or ln η_r/C vs concentration (C).
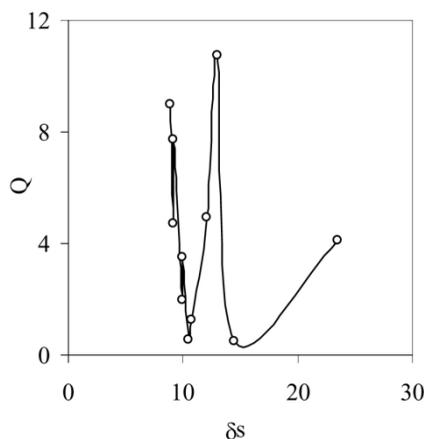
Figure 13. Plot of solubility parameter (δs) vs swelling coefficient (Q).

solubility parameters of polymers (δ_p) and solvent (δ_s) by the Equation (8), where Q_{max} is the maximum swelling observed and ϕ_s is the volume fraction of the solvent.

$$Q = Q_{max} \, e^{-(\delta_s - \delta_p)^2 \phi_s} \tag{8}$$

On plotting $(1/\phi_s) \ln (Q_{max}/Q)^{1/2}$ vs. δ_s, a straight line was obtained which intersected the abscissa at a value corresponding to δ_p, *i.e.*, 10.7 (Figure 14). The value is nearly equal to the arithmetic mean (10.2) of δ_p values for polybutadiene (8.4) and polyacrylamide (≈ 12). δ_p value for polyacrylamide has been calculated from molar attraction constants using Equation (9).

$$\delta = \rho \sum F_i / M_o \tag{9}$$

where ρ is the density of amorphous polymer at the solution temperature, M_o is the formula weight of the repeating unit and $\sum F_i$ is the sum of all molar attraction constants (59(a)). Maximum swelling was observed in DMSO, which has δ_s (13) comparable to the δ_p of polyacrylamide. As compared to the solvents other than DMSO, the
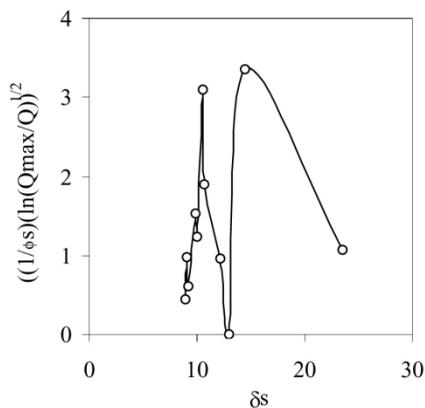
Figure 14. Plot of $[(1/\phi s)(\ln(Qmax/Q)]^{1/2}$ vs δs.

polymer swelled to a higher extent in toluene and benzene, which have δ_s values closer to the δ_p value for polybutadiene. Solubility can be expected if $\delta_p - \delta_s$ is less than about 2 (cal cm^{-1})$^{1/2}$ and there are no strong polar or H-bonding interactions in either the polymer or solvent. DMF also has δ_s value equal to 12.1, but lesser swelling was observed, probably because of higher HBI (59(b)).

The graph between Q and δ_s values (Figure 13) showed a very irregular trend, hence, it was thought that instead of swelling only, dissolution of the polymer was also possible. Therefore, the swollen samples were left in the respective solvents for one month and the remaining portion of the samples were weighed again and the weights so obtained, w_2 are depicted in Table 3. From these values, a significant dissolution of the samples in DMSO, benzene and toluene can be inferred. It can also be concluded that some portion of the sample dissolved within 48 h in DMF accounting for the lower value of Q in this solvent. The higher HBI of DMF might bring about the disentanglement of block copolymer chains through strong interactions with the polyacrylamide block.

The sorption or swelling depends on the chain flexibility of the latter. At T < Tg (glass transition temperature), segmental motion is practically not realized. Therefore, the solvent vapors can penetrate only into voids which exist in a polymer, but closely packed polymers have a small number of voids (60(a)). The measurements were carried out at room temperature (27°C) well above the Tg (− 70°C) of polybutadiene. Thus, it is in a rubber like or flexible state, making the segmental motion possible. The

Table 3

Solubility and swelling behaviour of block copolymer (fraction F of sample II)

Solvents	δ_s [a] (Cal cm^{-1})	HBI[b]	Q	Φ_s	Weight of the sample[c]		
					w_1[d] (g)	w_2[e] (g)	w_r[f] (%)
DMSO	13	5.0	10.72	0.942	0.6396	0.2704	42.3
Toluene	8.9	3.8	8.965	0.895	0.4382	0.2836	64.7
Benzene	9.2	2.2	7.752	0.883	0.3906	0.2006	51.4
DMF	12.1	6.4	4.94	0.847	0.2836	0.1608	56.7
THF	5.3	2.2	4.69	0.852	0.2586	Fragmentation	
Water	23.5	16.2	4.116	0.839	0.2558	0.2614	102.2
Acetone	10.0	5.7	3.52	0.734	0.1888	Major part dissolved	
1,4-Dioxane	9.9	5.7	1.95	0.72	0.1504	0.1442	95.9
Methyl propyl Ketone	8.7		1.27	0.756	0.1384	Major part dissolved	
Pyridine	10.7	8.7	1.24	0.6	0.1108	0.1102	99.5
Acrylonitrile	10.5	4.3	0.556	0.31	0.0724	0.0714	98.6
Methanol	14.5		0.485	0.275	0.0692	0.0658	95.1

[a]Values taken from literature data.[53]
[b]Hydrogen bonding index.[53]
[c]Weight of sample initially taken in every case 0.050 g.
[d]Weight of samples after soaking in the solvent for 48 h.
[e]Weight of the sample after soaking in the solvent for 30 days.
[f]Residual weight after one month $w_r = (w_2/w_1) \times 100$.

mechanism of the swelling process consists in the exchange of places of solvent molecules and units or segments of flexible macromolecules (60(b)).

It is quite interesting that if δ_s and HBI were the only criteria, pyridine should also dissolve appreciable quantity of the block copolymer, which is not the case. However, the ketonic solvents, viz., acetone and methyl propyl ketone appeared to be more efficient solvents for the block copolymer. Swelling was less in these solvents and most of the samples dissolved within one month. The alkyl groups of these solvents may become associated with the polybutadiene block and $-CH_2-CH<$ groups of polyacrylamide blocks. Whereas, the carbonyl groups may form hydrogen bonds with the amide groups of the polycrylamide blocks.

The disentanglement of the polymer chains inferred from the dissolution gave evidence against the interchain crosslinking. In our earlier report on polymerization of styrene in the presence of HTPB-AMV macroredox couple, the resulting block copolymer was found to be lightly crosslinked (51).

Polyacrylmide homopolymers are highly soluble in water and lightly crosslinked samples swell to a great extent in water forming hydrogels. In the present study, the butadiene-AAm block copolymer did not show appreciable swelling in water. However, samples did not exhibit any weight loss in water after one month, rather a little more swelling was observed. It is inferred that hydrophobic polybutadiene block find a hostile environment in water and self-assembly to form a core and the polyacrylamide blocks formed the corona (Figure 15). It is known that for block copolymers, self-assembly results from a competition between different contributions among which are the stretching energy of the neutral chains in the corona (61, 62).

In our earlier studies on block copolymer synthesis of styrene and butadiene using HTPB-ceric sulphate (63), HTPB-ceric ammonium nitrate (64) and HTPB-AMV (51), redox couples crosslinking of block copolymer chains through attack of growing radical on residual double bonds on polybutadiene was inferred. However, in the present study, negligible crosslinking of block copolymer chains is concluded. It is suggested that this may be due to high reactivity of AAm monomer and radical because the Q and e values, which are the measure of resonance stabilization and polar properties respectively, are high for AAm (e = 1.18 and Q = 1.30) (65).
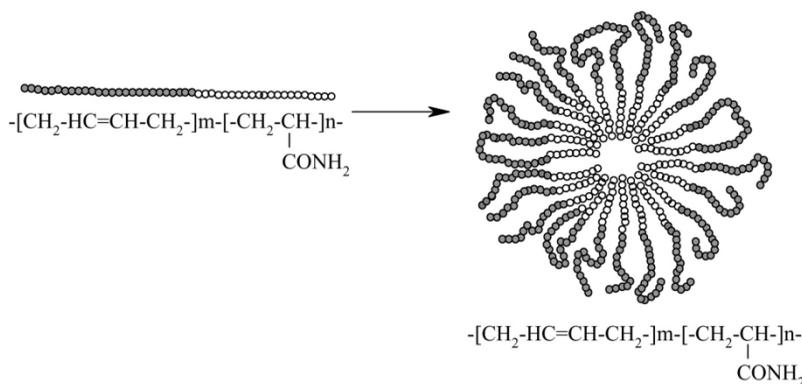
Figure 15. Self assembly of butadiene-acrylamide block copolymer in water.

Conclusions

The amphiphilic block copolymer, comprised of polybutadiene as a hydrophobic block and polyacrylamide as a hydrophilic block, was synthesized conveniently in good yield, using AMV as an initiator. Block copolymer synthesized in air was not crosslinked, whereas that prepared by bubbling of nitrogen gas in the reaction mixture was crosslinked, by reaction of chain end radical with the residual double bonds on the polybutadiene block. The method is useful for synthesis of amphiphilic block copolymer for those applications where strict molecular mass control and narrow molecular mass distribution is not required.

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