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Synthesis and Characterization of Amphiphilic Block Copolymer by Block Copolymerization of Butadiene and Acrylamide using Macroazoinitiator

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Macroazoinitiator (MAI) was prepared from hydroxyl-terminated polybutadiene (HTPB) and 4,4′-azobis-4-cyanopentanoic acid by direct polycondensation in the presence of 1-methyl-2-chloropyridinium iodide at room temperature. This MAI used for block copolymerization of AAm at 60°C gave the best results in chloroform but the formation of a crosslinked product could not be ruled out in dioxane. It was inferred that for production of a linear block copolymer, homogeneous reaction mixture was required.

The resulting products were characterized by spectral studies IR and NMR, viscosity measurements. Distinct phase segregation of hydrophobic and hydrophilic blocks was evident through DSC analysis.

Keywords: amphiphilic block copolymer; polybutadiene-*block*-polyacrylamide; macroazoinitiator; polycondensation

1 Introduction

Block copolymers are generally prepared in three different ways: (i) The most common method being the living and controlled polymerization, which involves sequential addition of monomers. (ii) The two-step polymerization method involves the separate preparation of different blocks and their subsequent chain coupling reaction. (iii) A mono or multifunctional macroinitiator (comprising of the first monomer) is applied for the polymerization of another monomer (1).

Cationic and anionic techniques require stringent reaction conditions for the synthesis of block copolymers and hence are limited to certain monomers. Therefore, their adoption by industries becomes restricted. Free radical methods are less expensive with wide applications but are accompanied by side reactions and formation of significant amounts of homopolymers. However, block copolymer preparations by free radical techniques may be practical for applications where either strict control over polymer architecture is not required or polymer blends and composites may be used. Among the free radical polymerization methods, block copolymerization through macroinitiators is gaining increasing interest (2–11). Macro(molecular)initiators are precursors for the synthesis of block and graft copolymers (depending on the site of initiation). This technique is advantageous because one component can be fully characterized before the preparation of block copolymers. The selected functional groups of the macromolecule can be activated chemically (12, 13), thermally (14–17), mechanochemically or photochemically (16) to yield active centers that initiate the polymerization of other monomers to produce block and graft copolymers (18).

In an earlier report, we successfully synthesized the MAI, poly(polybutadiene-4, 4′-azobis-4-cyanopentanoate) (PBACP) by direct polycondensation of hydroxy-terminated polybutadiene (HTPB) with 4, 4′-azobis-4-cyanopentanoic acid (ACPA) in the presence of 1-methyl-2-chloropyridinium iodide (MCPI) at room temperature. PBACP effectively initiated the thermal polymerization of styrene (19).

Amphiphilic block copolymers are an interesting class of materials that find a variety of applications (20–26). The literature survey revealed extensive study on homo or graft copolymerization of acrylamide (AAm) in aqueous medium, but there were limited reports on the synthesis of its amphiphilic block copolymers (27–30). The present article report is on the synthesis of block copolymer of 1, 3-butadiene and AAm by thermal polymerization of AAm initiated by PBACP.

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2 Experimental

2.1 Materials

HTPB, a gift from Vikram Sarabhai Space Center, Thiruvananthapuram, India, had a number average molecular mass (M_n) of 2450 ± 300, as determined by vapor phase osmometry (VPO) and had polydispersity 2 ± 0.5. HTPB was purified by washing with methanol several times, the residual methanol was then removed under reduced pressure. AAm from Sisco Research Laboratories Pvt. Ltd. Bombay, India was recrystallized twice from methanol and dried under vacuum. ACPA and MCPI of AR grade obtained from Fluka Chemika, Switzerland and Merck, Germany, respectively were used as received. Triethylamine, dichloromethane, diethyl ether, chloroform, 1, 4-dioxane, methanol and other solvents of analytical grade obtained from E. Merck, India were used without further purification.

2.2 Synthesis of Block Copolymers

The MAI, PBACP was prepared by direct polycondensation of HTPB and ACPA in the presence of MCPI in a dichloromethane solution by the method reported earlier (19). For the synthesis of block copolymer, nitrogen gas was passed for 10 min through the solution of PBACP and AAm placed in a conical flask, which was then tightly stoppered and kept in a constant temperature bath at 60°C for 24 h and was intermittently shaken. The reaction mixture was poured into a large volume of methanol. The product thus precipitated was filtered and dried under reduced pressure. The yields (%) were determined gravimetrically.

2.3 Measurements

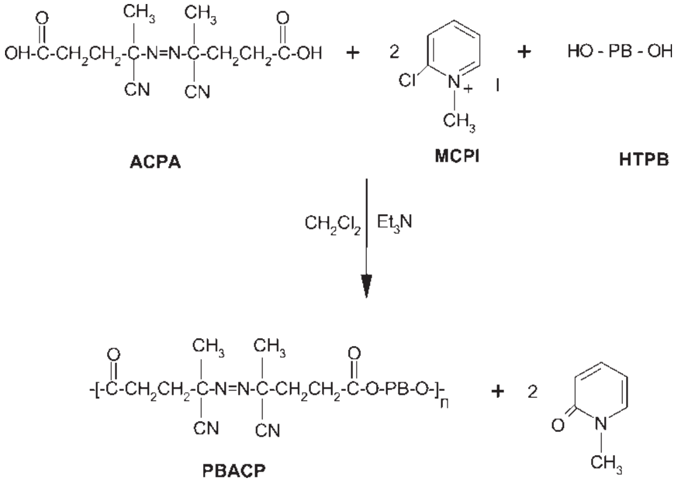
The viscosities of dilute chloroform solutions of PBACP and the block copolymers were determined using an Ubbelohde viscometer. The Huggins' and the Kraemer's equations (Equations (1) and (2) were used to determine intrinsic viscosity $[\eta]$, Huggins' constant, k' and Kraemer's constant, k'' (31).

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 C \quad (1)$$

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

where C is the concentration of polymer in gram/100 mL. The results of both equations were plotted using the same graph. The point of intersection of both the lines at the y-axis was taken as the intrinsic viscosity (31).

FTIR spectra of the products were recorded on a Perkin-Elmer Model 1430 spectrophotometer using KBr as dispersant. NMR spectrum was recorded on a Bruker DRX-300 FT-NMR spectrometer in a $CDCl_3$ solution. DSC analysis was done by the Mettler Toledo Star system under nitrogen atmosphere in temperature range from −70 to 500°C with a heating rate of 20°C/min.



Sch. 1. Synthesis of PBACP.

3 Results and Discussion

The details for the preparation of different samples of the MAI by direct polycondensation of ACPA with HTPB (Scheme 1) are summarized in Table 1. The block copolymers of 1,3-butadiene and AAm were synthesized with PBACP in different solvents at 60°C and the results are depicted in Table 2. Thermal polymerization of AAm did not occur under same reaction conditions in the presence of the prepolymer, HTPB. Hence, it was clearly evident that the block copolymerization occurred through the radicals formed by the scission of -N=N- units (Scheme 2). Polymerization of styrene initiated by PBACP proceeded smoothly in benzene (19). Acceptable results were obtained for AAm in chloroform, in which PBACP and AAm, as well as the block copolymer, was soluble. However, as the solubility of AAm was 2.6 g/100 mL in $CHCl_3$ at 60°C, this was the upper limit for the use of this monomer. Though AAm was soluble in acetone, PBACP was not. Similarly, DMF and DMSO dissolved PBACP but not AAm. Hence, polymerization of AAm could not be achieved by PBACP in these solvents. Since AAm is insoluble in benzene, mixed solvent systems were tried. Nevertheless, under the same conditions, a change of solvent from chloroform to benzene-chloroform (2:1) or benzene- water (2:1) in the presence of the emulsifier cetyl trimethyl ammonium bromide (CTAB) lowered the conversion from 50.2 to 6.5 and 1.3%, respectively. The conversion was higher in dioxane, which dissolved both PBACP and AAm, but the increase in viscosity over that of MAI was less than that in a chloroform medium. In dioxane, the viscosity increase was rather insignificant for the shorter reaction time (11 h, Table 2 run no. 10). Intrinsic viscosity $[\eta]$, a common measure of molecular mass, was higher for the product obtained in $CHCl_3$. This indicated that the mutual reaction of macroradicals was facilitated, as $CHCl_3$ was a poor solvent for AAm. It is noteworthy that the reaction mixture was homogeneous throughout the reaction in $CHCl_3$, whereas it became heterogeneous after a few

Table 1. Results of direct polycondensation of HTPB with ACPA[a]

	HTPB		ACPA				Yield		PBACP (Viscosity data)			
Run no.	(g)	(mmol)	(g)	(mmol)	CH_2Cl_2 (mL)	Time (h)	(g)	(%)	$[\eta]$	k′	k″	k′+k″
1	5.00	2.5	0.7006	2.5	36	12	4.96	87.0	0.512	0.324	0.165	0.488
2	5.00	2.5	0.7006	2.5	36	8	4.72	82.7	0.378	0.255	0.156	0.411
3	5.00	2.5	0.7006	2.5	50	8	4.36	76.4	0.342	0.396	0.122	0.518
4[b]	—	—	—	—	—	—	—	—	0.138	0.157	0.148	0.305

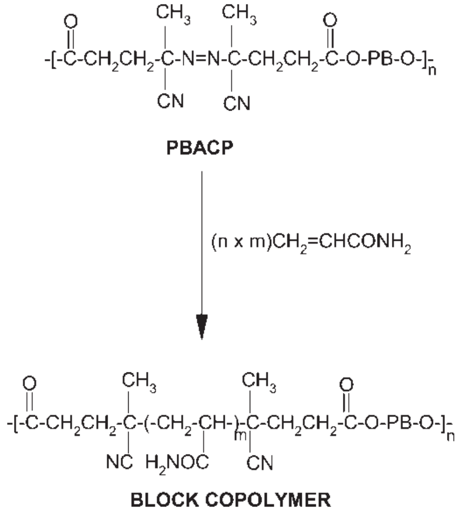
[a] MCPI: 5.25 mmol, Et_3N:5.25 mmol + 5.25 mmol, Temperature: 27°C.
[b] The viscosity measurements of HTPB alone were carried out.

hours in dioxane. Heitz et al. (32) in their study on the synthesis of block copolymer by use of polyazoesters discussed that for precipitation polymerization the focus of polymerization is mainly the precipitated polymer. Yamada et al. (33) reported that the polymer initiator, obtained by a reaction of p-isopropenyl-2,2′-azobis-2-cyanovalerate, initiated graft copolymerization of MMA in benzene. Quick polymerization proceeded heterogeneously, in the poor solvent, cyclohexane, to give a large amount of crosslinked polymer, since the macroradicals formed in the globule of polymer chains would readily react with each other. A perusal of Table 2 made it evident that with increasing MAI concentration, percent conversion increased, whereas viscosity decreased. This was expected behavior since at a constant monomer concentration, with an increase in the number of initiating species, the molecular mass should decrease. The percentage conversion, as well as intrinsic viscosity increased on varying AAm concentration, while keeping the concentration of MAI constant. When the polymerization of AAm by PBACP was compared with that of styrene (19), then at comparable reaction conditions, conversion for AAm (59.6%) was much higher than that for styrene (24.3%) reflecting greater reactivity of AAm. However, an increase in viscosity exhibited just the opposite trend, i.e., 17.1% for AAm as against 45.1% for styrene. This may be attributed to the termination in case of styrene by combination, which might be supplemented by the solvent cage phenomenon as well, in which solvent molecules restrain the diffusion of radicals so that combination becomes more probable. A similar cage effect was observed by Smith (34) in his study on decomposition of azonitrile compounds. Ueda and Nagai (35), while studying decomposition of azobis (cyanopentanaote) as a model of polymer containing azo linkages, concluded that the chain length of the polyamide block could be controlled by the use of a kind of solvent and concentration of styrene monomer as variable parameters. In another study, they (2) discussed that one of

Table 2. Polymerization of acrylamide initiated with MAI[a]

	PBACP			Acrylamide		Yield							
Run no.	-(-N=N-)[c]-	(g)	$[\eta]$	(g)	(Mol/L)	(g)	(%)	Conversion (%)	$[\eta]$ (dl/g)	Increase in $[\eta]$[b] (%)	k′	k″	k′ + k″
1	13.90	0.6232	0.378	0.2	0.093	0.6862	82.9	31.5	0.473	25.1	0.344	0.156	0.500
2	13.90	0.6232	0.378	0.4	0.187	0.8028	78.4	44.9	0.491	29.9	0.330	0.165	0.495
3	13.90	0.6232	0.378	0.6	0.281	0.9242	75.5	50.2	0.524	38.6	0.368	0.140	0.508
4	7.54	0.3382	0.378	0.6	0.281	0.4822	40.7	24.0	0.546	44.4	0.364	0.144	0.508
5	3.77	0.1692	0.378	0.6	0.281	0.2404	31.3	11.8	0.571	51.1	0.376	0.136	0.512
6	21.3	0.6232	0.512	0.6	0.281	0.9324	76.2	51.5	0.670	30.1	0.357	0.148	0.504
7	12.6	0.6232	0.342	0.6	0.281	0.9186	75.1	49.2	0.467	36.6	0.363	0.144	0.507
8[d,e]	4.20	0.2082	0.342	1.0	0.468	0.7218	59.7	51.4	0.360	5.17	0.329	0.170	0.499
9[d]	4.20	0.2082	0.342	1.5	0.702	1.1026	64.5	59.6	0.401	17.1	0.327	0.170	0.497
10[d]	4.20	0.2082	0.342	2.0	0.936	1.6404	74.3	71.6	0.490	43.4	0.331	0.166	0.496
11[f]	13.90	0.6232	0.342	0.6	0.281	0.6622	54.1	6.5	0.369	7.9	0.293	0.192	0.486
12[g]	13.90	0.6232	0.342	0.6	0.281	0.6312	51.6	1.3	0.353	3.2	0.359	0.143	0.502

[a] Reaction temperature: 60°C, Reaction time: 24 h, solvent for no. 1–7: Chloroform.
[b] Percentage increase in intrinsic viscosity of PBACP on copolymerization with acrylamide.
[c] Calculated from presumed formula mass per azo unit.
[d] Solvent: 1,4-Dioxane.
[e] Time: 11 h.
[f] Mixed solvent benzene-chloroform (2:1).
[g] Mixed solvent benzene-water (2:1), emulsifier CTAB (20 mg).



$$-[\overset{\overset{O}{\|}}{C}-CH_2CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-N=N-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_2-\overset{\overset{O}{\|}}{C}-O-PB-O-]_n$$

$$\xrightarrow{(n \times m)CH_2=CHCONH_2}$$

$$-[\overset{\overset{O}{\|}}{C}-CH_2CH_2-\underset{\underset{NC}{|}}{\overset{\overset{CH_3}{|}}{C}}-(-CH_2-\underset{\underset{H_2NOC}{|}}{CH}-)_m-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_2-\overset{\overset{O}{\|}}{C}-O-PB-O-]_n$$

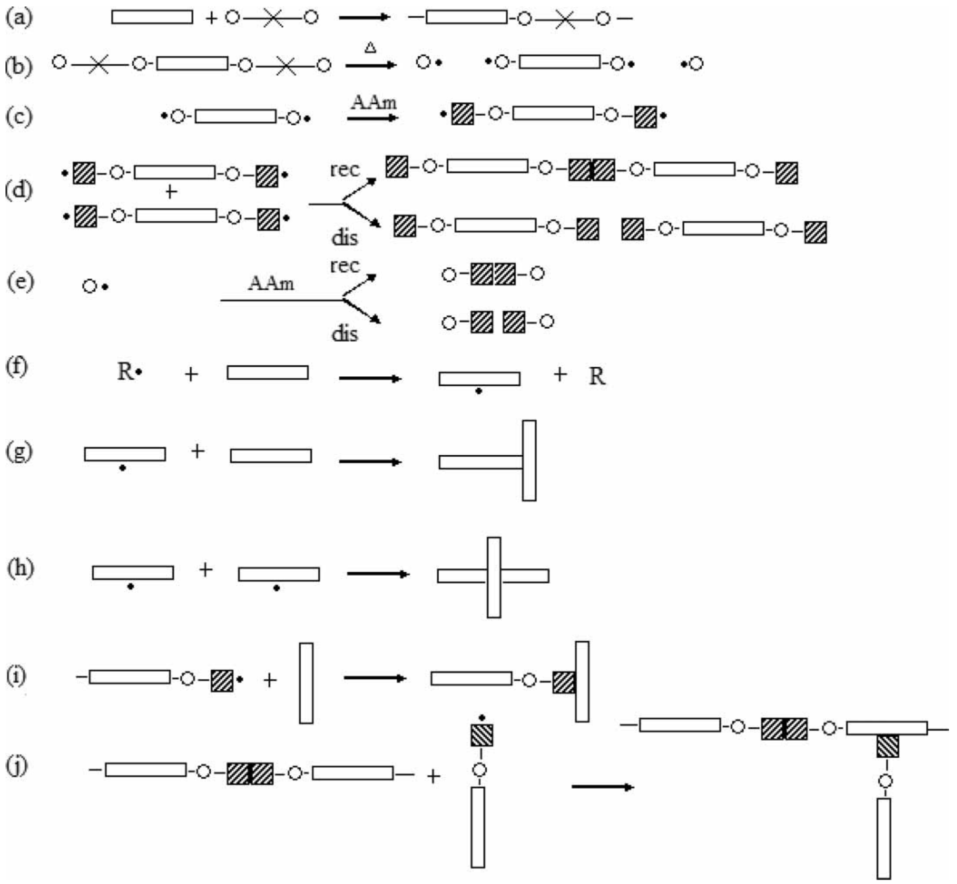
Sch. 2. Schematic representation of synthesis of block copolymer.

the most important properties of macroinitiator for block copolymerization is its solubility in monomers. The homogeneous solution of monomers and macroinitiators is essential to precede polymerization. For MAI, having a long prepolymer structure linked with azo bonds, the solubility of the initiator depends on that of the prepolymer since the latter dominates in the composition or volume fraction of the initiator. It is suggested that low viscosity increases in the present case may be attributed to the formation of a ABA type block copolymer through disproprotionation. The values obtained for Huggins' constant, k′ and Kraemer's constant, k″ are in agreement with the acceptable value in good solvent and the constants satisfy the condition of Equation (3) also:

$$k' + k'' = 0.5 \tag{3}$$

It is known that for linear polymers in good solvents, the addition of k′ and k″ is often near 0.5. The k′ + k″ values for the resultant products are indicative of the linear nature of this polymer.

Besides the crosslinked product, the precipitated polymer may also contain the homopolymer, formation of which is unavoidable since the initiator radicals derived from the end of the polyazoester chain may form the homopolymer. The precipitated product was stirred with water for 6 h, but the homopolymer could not be separated due to the chemical heterogeneity and the strong emulsifying properties of the block



Sch. 3. Schematic presentation for the formation of (a) MAI, (b) Primary radicals, (c) non primary copolymer radicals, (d) (AB)$_n$ and ABA type block copolymers, (e) polyacrylamide homopolymer through terminal radicals, (f, g, h) pure crosslinks through residual double bonds of polybutadiene, (i, j) crosslinks through growing bock copolymer chains. [⨯, Scissile azo groups; ▭, polybutadiene; ▨, polyacrylamide; ○, cyanopentanoate groups; $\mathbf{R}^{\cdot}$, any radical present in the system; rec, combination; dis, disproprotionation.

copolymer. A possible mechanism for the formation of block copolymer, crosslinked product and homopolymer (PAN) is depicted in Scheme 3 in a blank run (in the absence of AAm) about 11% of the crosslinked product was formed. However, in the presence of AAm, it is expected that the amount of pure crosslinked product would be less because of greater reactivity of AAm on the basis of its Q and e values 36.

3.1 Characterization

The comparison of the IR spectra of HTPB, MAI, block copolymer (Figure 1) and polyacrylamide authenticated the formation of MAI and block copolymer. The representative samples (run no. 2 Table 1, run no. 2 Table 2) were used for characterization. The strong and broad absorption at 3380 cm^{-1} due to hydrogen bonded hydroxyl groups of HTPB and the broad intense OH stretching absorption of carboxylic groups from ACPA appeared with greatly reduced intensity in MAI. The appearance of the intense absorption, near 1738 cm^{-1} in MAI and the shoulder at 1785 cm^{-1} in block copolymer clearly showed the presence of ester linkages. The broad and strong absorption ascribed to out of plane CH bending of HTPB at 966 cm^{-1} appeared with considerably reduced intensity in MAI. The intense and broad absorption band due to NH stretching of AAm units appeared at 3440 cm^{-1}. A strong and broad splitted band at 1657 cm^{-1} involved amide I vibration of AAm and C=C stretching of butadiene units.

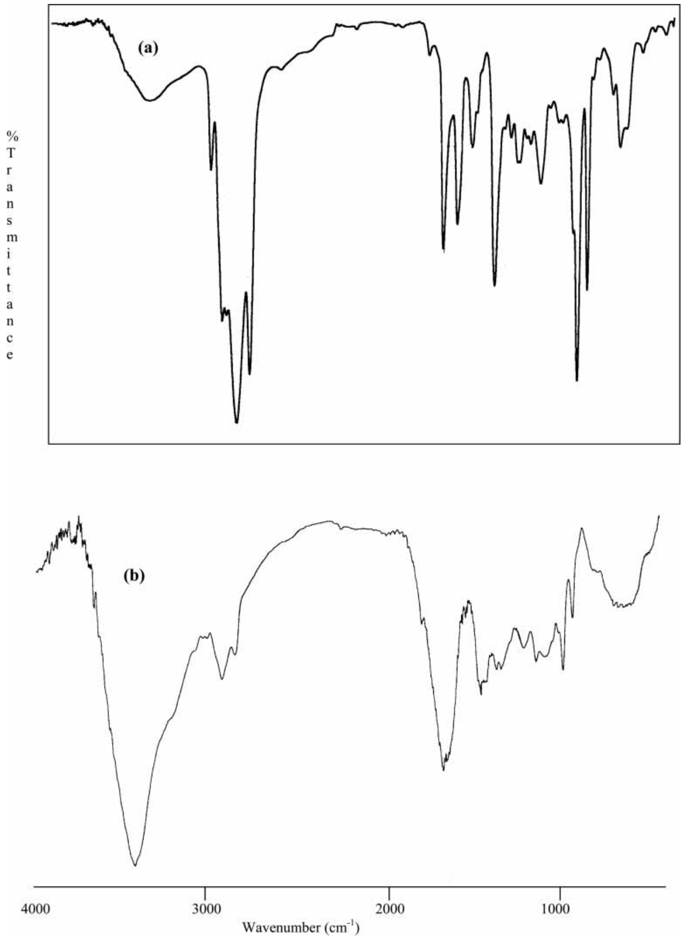


Fig. 1. IR spectra of (a) PBACP and (b) block copolymer.

The ^{1}H-NMR spectrum of the block copolymer is depicted in Figure 2. Signals due to methine protons of AAm appeared near the 4.91–4.98 ppm range and those owing to vinyl protons of butadiene in 5.38–5.56 ppm range. The proportion of butadiene and AAm units present in the block copolymer was computed by comparing the intensities of vinyl protons of butadiene and methine protons of AAm units. This proportion was found to be 64:36. The signals in the 2.24–2.03 ppm range must be from the CH_2 groups of polybutadiene blocks and those in the 1.72–1.20 ppm range must be from the CH_2 groups of PAAm blocks. When the proportion of butadiene and AAm units was calculated from intensities of these signals, it was then found to be 61:39. It is evident that the signals observed below 2 ppm involved contribution from solvent molecules (methanol) also because the complete removal of the solvent from the sample rendered it insoluble in chloroform. The DSC thermogram of PBd-*block*-PAAm is presented in Figure 3. DSC indicated the phase separation in block copolymer. T_g for polybutadiene block determined from thermogram as intercept of two asymptotes was found to be −15°C. Considerable deviation in the base line is an indication of the amorphous nature of the block copolymer. The broad endotherm in 70–130°C range must be associated with the melting transition of the polybutadiene block. T_g for PAAm block was observed near 185°C at a slightly higher value than that for the homopolymer (165°C), certainly reflecting somewhat restricted movement of PAAm chains due to self-assembly. PAAm may self assemble through H-bonding. Lightly crosslinked PAAm has widely been used as hydrogels. In PBd-*b*-PAAm crosslinking is possible through the unsaturation in butadiene. Furthermore, the hydrophobic PBd blocks may assemble to act as the

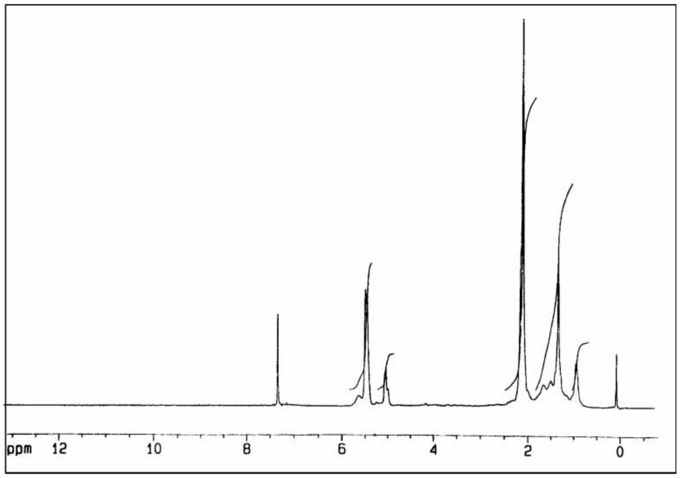


Fig. 2. NMR spectra of block copolymer.

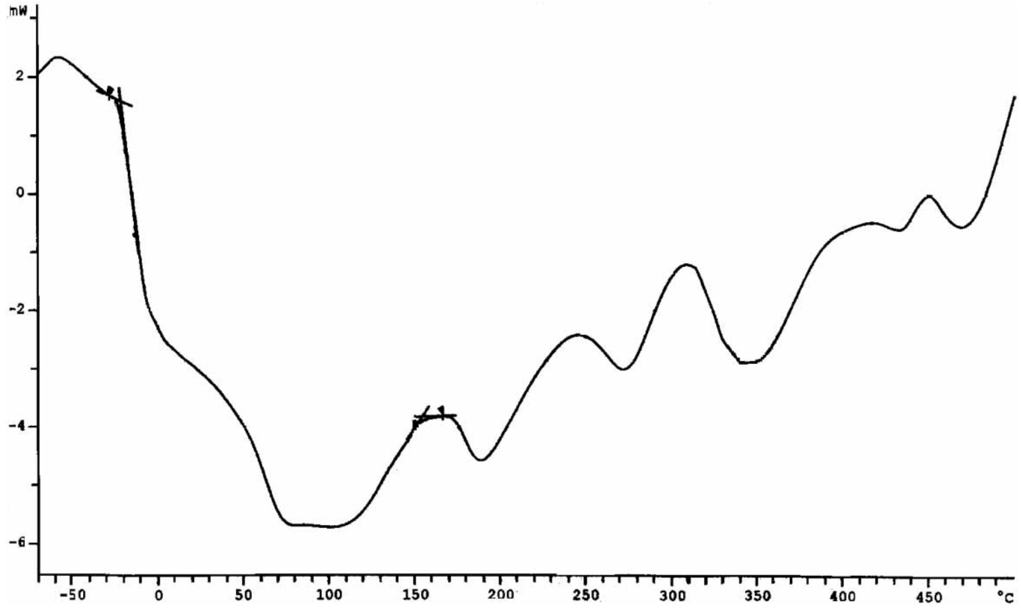


Fig. 3. DSC thermogram of block copolymer.

crosslinks. The next endotherm in 250–300°C signified the melting transition of PAAm blocks. The deeper endotherm above 300°C indicated the crosslinking and cyclization reactions in the polybutadiene blocks.

4 Conclusions

The macroazoinitiator, PBACP efficiently initiated polymerization of AAm in chloroform, but due to low solubility of AAm in chloroform, incorporation of AAm in the block copolymer was limited. Though dioxane was a better solvent for AAm, it could not dissolve the block copolymer to sufficient extent, hence, the reaction mixture became heterogeneous leading to crosslinked product formation. The block copolymer obtained in the chloroform solution was linear with definite phase segregation as was inferred from DSC analysis. Hence, it can be concluded that to control the structure of block copolymer solubility of MAI, monomer and the product was essential.

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