

## Room Temperature Polymerization of Vinylic Monomers by Azo Initiator

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**ABSTRACT:** The azo initiator, sodium-{4-(4-hydroxy-phenylazo)-benzenesulfonate (SHPBS)}, has been synthesized by coupling reaction with sodium-(*p*-sulfonate benzene diazonium chloride) and phenol. Unsymmetrical azo group leading to weak azo bond in case of SHPBS resulted in dissociation at lower temperature (25°C) to produce free radicals. Its versatile solubility (soluble in aqueous and organic solvents), generation of free radicals at 25°C, and its application without mechanical stirring are the added greater advantage over commercially available azo initiators (AIBN, etc.). The SHPBS has been characterized by FTIR, <sup>1</sup>H-NMR spectroscopies, and thermal analysis. It has been observed that various monomers such as AM, AA, IPAM, and AMPS which have been polymerized with SHPBS have led to high molecular weight polymers at shorter reaction time. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1882–1887, 2013

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### INTRODUCTION

One of the terrific merits of free radical polymerization is the relative unreactivity toward monomer and media impurities, as compared to ionic polymerization. Thus, radical polymerization can be carried out under less energetic conditions, leading in reduced cost. Another advantage of this process is that it can be applicable to a wide range of monomers.<sup>1</sup> Many free radical polymerizations are carried out in relative organic solvents, which have been accountable for increasing air pollution.<sup>2</sup> Free radical polymerization is used for synthesizing high molecular weight polymer.<sup>3</sup> The initiator functionality can be considered by reason of the presence of functional polymer end groups, such as hydroxyl, carboxyl, azo, persulfate, and perester bonds,<sup>4</sup> which undergo dissociation to the alkyl, alkoxy, or acyloxy radicals under the influence of temperature or irradiation.<sup>5</sup> The functionality of initiators is exploited in diverse ways to accomplish particular purpose.

Azo initiator AIBN is commercially used for conventional free radical polymerization.<sup>6</sup> In AIBN, aliphatic symmetric azo group is exhibited. In case of SHPBS, the azo linkage is attached with unsymmetrical aromatic rings. Phenyl substituted azo compounds normally decompose by a nonconcentrated mechanism.<sup>7</sup> In this case, the sigma bond between azo linkage and aromatic carbon is weaker due to presence of electron-withdrawing sulfonate group and its preferred homolytic cleavage leading to formation of stable phenyl radical. The other

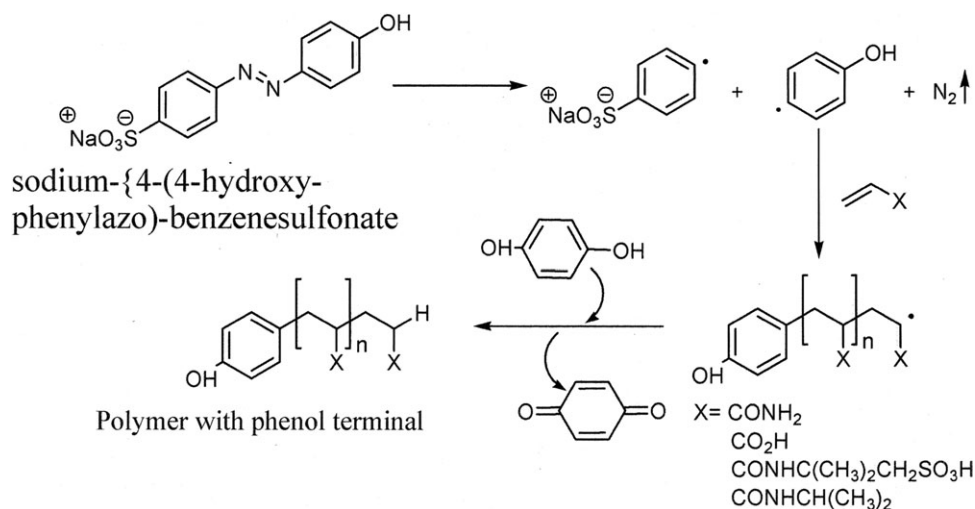
radical generated in azo nitrogen is very unstable and its leaves N<sub>2</sub> gas at lower temperature.

Thus sodium-4-(4-hydroxy-phenylazo) benzene sulfonic acid (SHPBS) is one of the best alternative of AIBN which can resolve the problem of room temperature (25°C) polymerization reaction and less evaporation of organic solvent which causes air pollution. SHPBS polymerizes the vinylic monomer at room temperature without heating, stirring, and less evaporation of organic solvent. This approach belongs to the green polymer synthesis. SHPBS has more advantage over AIBN. It has *para*-hydroxyphenylene group which is applicable for polymer end analysis and also it is a cyanide-free initiator. Bulk batch synthesis of polymer is economic because heating is not necessary for initiation and thus is easy to use.

### EXPERIMENTAL

#### Materials

Sulfanilic acid and acrylamide were procured from E. Merck, India. Sodium nitrite, methanol, acetone, 1, 4-dioxane, and phenol were supplied by S.D Fine Chemicals, Mumbai, India. *N*-isopropyl acrylamide was procured by Sigma Aldrich, India. AMPS was procured from Himedia, Mumbai, India. Acrylic acid was procured from Loba Chemie, Mumbai, India. Tetrahydrofuran was obtained from Qualigens Fine Chemical, Mumbai, India.



**Figure 1.** Dissociation of initiator (SHPBS) and its initiation of polymerization process.

### Synthesis of Sodium-4-(4-hydroxy-phenylazo)-benzenesulfonic Acid (SHPBS)

Sulfanilic acid (4.33 g, 0.025 mol) and sodium carbonate (5.30 g, 0.05 mol) were taken in a 100 mL conical flask. Water (50 mL) was added and stirred at 60–70°C to dissolve the above. The solution was further cooled to 10–15°C and a cooled solution of sodium nitrite (1.725 g, 0.025 mol) in water (5 mL) was added. The mixture was poured into ice (350 g) containing conc. HCl (5.0 mL) at 5°C and stirred using mechanical stirrer for 30 min. The diazonium salt was added drop wise into a solution containing sodium hydroxide (30 g, 0.75 mol) and distilled phenol (2.65 g, 0.025 mol) in water (25 mL) at 5°C. The coupling reaction was continued by stirring for 3 h in the ice cold condition using a mechanical stirrer. The yellowish white precipitate was filtered using Buchner funnel, three times washed with water and then dried in a vacuum oven for 24 h at 40°C (0.1 mm of Hg).<sup>8</sup> Yield = 3.8 g (87.7%).

### Polymerization of AM, AA, IPAM, and AMPS with SHPBS

Initially 50 mL conical flask containing 20 mL distilled water was taken and dry N<sub>2</sub> was purged up to 30 min. About 5g of acrylamide (AM) was added and reaction mixture was stirred on magnetic stirrer. N<sub>2</sub> was purged for another 30 min followed by the addition of 50 mg SHPBS. The solution was adequately stirred till the initiator (SHPBS) completely dissolved. Subsequently, stirring was stopped and the flask was kept at room temperature till the solution became viscous. The polymerization was terminated by adding hydroquinone. The resulting viscous material was precipitated in excess of acetone until the unreacted AM and initiator were washed out. Polyacrylic acid (PAA) and poly-2-acrylamido-2-methylpropanesulfonic acid (PAMPS) were synthesized with above method in same solvent, but poly *N*-isopropyl acrylamide (PIPAM) was synthesized in methanol. Dissociation of initiator (SHPBS) and its initiation of polymerization process are shown in Figure 1. The synthesis details of polymers are given in Table I. To compare the effect of initiators (AIBN and SHPBS) on the polymer molecular weight, a series of polyacrylamide were synthesized by using

different concentration of SHPBS and AIBN initiators. The synthetic parameters are shown in Table II.

## CHARACTERIZATION

### FTIR

The spectrophotometer TERMO NICOLET FT-IR (Model jasco FT-IR 5300) was used to record IR spectra of SHPBS and polyacrylamide (PAM) within the range of 4000–400 cm<sup>-1</sup> by using solid-state KBr pellet method.

### <sup>1</sup>H-NMR

The spectrometer FT-NMR JEOL AL 300 FT-NMR was used to record <sup>1</sup>H-NMR of SHPBS and PAM. Tetramethylsilane was used as an internal reference. DMSO and D<sub>2</sub>O were used as solvents to record <sup>1</sup>H-NMR for SHPBS and PAM, respectively.

### Intrinsic Viscosity Measurement

The intrinsic viscosity of the polymer is determined with an Ubbelohde viscometer (CS/S: 0.00386) at 30 ± 0.1°C using the standard method to assess intrinsic viscosity.<sup>9</sup> About 0.5% aqueous solution of PAM and PAMPS were prepared to determine the intrinsic viscosity. PIPAM and PAA were prepared 0.5% solution in THF and 1,4-dioxane to find out the intrinsic viscosity, respectively.

### Molecular Weight Determination

The intrinsic viscosity [ $\eta$ ] values can be used to estimate the molecular weight of polymers. Mark–Houwink equation, [ $\eta$ ] =  $KM^a$  is broadly employed for the assessment of molecular

**Table I.** Synthetic Details of Polymers

Serial no.	Monomer	Initiator (SHPBS) (mg)	Time of polymerization (h)	Yield (%)	Molecular weight ( $\times 10^5$ )
1	AM	50	3	92.6	9.62
2	AA	50	6	96.3	790.00
3	AMPS	50	7	60.4	0.37
5	IPAM	50	28	68.0	59.32

**Table II.** Comparison of Molecular Weight and % Yield of PAM Obtained by AIBN and SHPBS Initiation

Serial no.	AM (g)	Initiator (mole $\times 10^{-4}$ )		Yield (%)		Molecular weight ( $\times 10^5$ )	
		AIBN (60°C)	SHPBS (25°C)	By AIBN	By SHPBS	By AIBN	By SHPBS
1	5	0.96	0.96	90.2	81.8	6.15	12.00
2	5	1.89	1.89	90.1	92.6	5.11	9.62
3	5	2.84	2.84	90.1	94.7	3.68	6.37
4	5	3.78	3.78	94.0	93.6	1.97	3.95

weight of polymers where  $K$  and  $\alpha$  values are constant for a specific polymer/solvent/ temperature system. Mark-Houwink constant ( $K$  and  $\alpha$ ) value of different polymers are as follows: PAM ( $6.31 \times 10^5$  dL/g and 0.8),<sup>10</sup> PAA ( $0.85 \times 10^5$  dL/g and 0.5),<sup>11</sup> PIPAM ( $9.59 \times 10^5$  dL/g and 0.65),<sup>12</sup> and PAMPS ( $12.3 \times 10^5$  dL/g and 0.757).<sup>13</sup>

### Thermal Analysis

DTG analysis of SHPBS was recorded by METTER-TOLEDO DSC/TGA 1 and it was carried out from 50 to 500°C, in a nitrogen atmosphere. The heating rate was 10°C per minute. DSC thermogram of SHPBS was recorded with a Mettler Toledo TC 15 TA differential scanning calorimeter at the rate of 10°C per minute under a nitrogen atmosphere using pure-grade indium as standard by taking samples in close-lid aluminium pans. The transition temperatures from DSC have been determined with an accuracy of  $\pm 0.1^\circ\text{C}$ .

## RESULT AND DISCUSSION

### Polymerization of AM, AA, IPAM, and AMPS with SHPBS

SHPBS is an aromatic azo initiator, which contains benzene sulfonic and phenolic group. The azo linkage dissociates in water at room temperature and liberates  $\text{N}_2$  gas by homolytic cleavage and generates two free radicals on aromatic *para*-carbon of benzene sulfonic and *para*-hydroxyphenylene group. According to the  $^1\text{H-NMR}$  spectrum of polymer phenolic (Ar-H) proton peaks are present at 6.7 and 7.4 ppm. Thus, its spectrum justifies that the *para*-hydroxyphenylene group free radical is striven to polymerization and high molecular weight polymers are

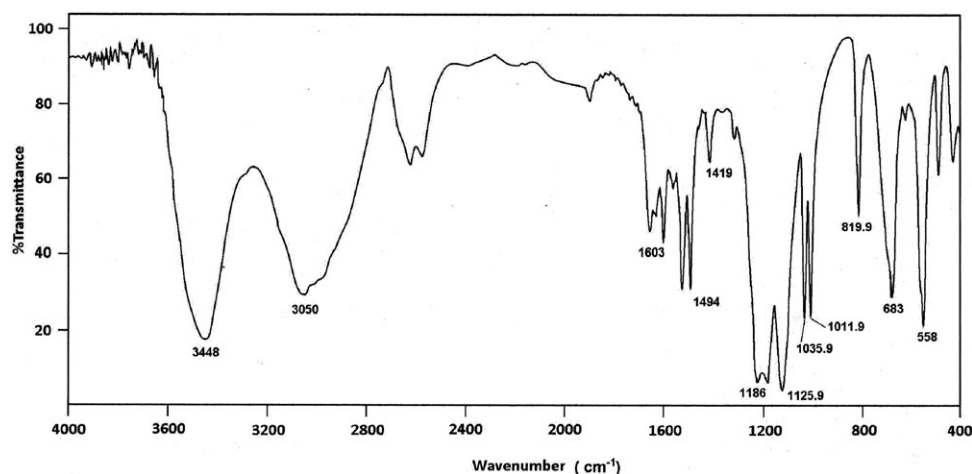
obtained. Table I gives the synthesis details of different vinylic monomer polymerized by SHPBS. Among all the monomers AM is polymerized in less time and high yield is obtained. IPAM takes more time to polymerize and less yield is obtained due to presence of bulky functional group attached to vinylic monomer.

### FTIR

Figure 2 shows the FTIR spectrum of SHPBS. The absorption peak at  $3448.5\text{ cm}^{-1}$  is attributed to  $\text{—OH}$  stretching frequency of *para*-hydroxyphenylene OH group of SHPBS. Absorption peak at  $3050\text{ cm}^{-1}$  is attributed to aromatic-H. Absorption peak at  $1603$  and  $1495\text{ cm}^{-1}$  are attributed to aromatic  $\text{C}=\text{C}$  and asymmetric  $\text{—N}=\text{N—}$ , respectively. Absorption peaks at  $1186$  and  $1125$  is attributed to sulfonic  $\text{S}=\text{O}$  stretching frequency. Absorption peak at  $819.9$ ,  $683.4$ , and  $558$  are attributed to  $=\text{C—H}$  bending vibration. Figure 3 shows the FTIR spectrum of PAM. A broad range of absorption peak around  $3433\text{ cm}^{-1}$  is attributed to combinations of  $\text{N—H}$ , phenolic-OH, and Ar-H stretching frequencies. Absorption peak at  $2933\text{ cm}^{-1}$  is attributed to  $\text{C—H}$  stretching frequency. A broad peak at  $1644\text{ cm}^{-1}$  is attributed to combination of amide-I and amide-II band.

### $^1\text{H-NMR}$

In Figure 4 shows the  $^1\text{H-NMR}$  spectrum of SHPBS.  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-d}_6$ ,  $\delta$ ) of SHPBS: 7.36 ppm (d,  $j = 8.4$  MHz, 2H, Ar-H); 7.73 (d,  $j = 8.4$  MHz, 2H, Ar-H); 8.09 ppm (d,  $j = 8.7$  MHz, 2H, Ar-H) 8.54 ppm (d,  $j = 8.7$  MHz, 2H, Ar-H). In Figure 5 shows the  $^1\text{H-NMR}$  (300 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ ) of PAM

**Figure 2.** FTIR spectrum of SHPBS.

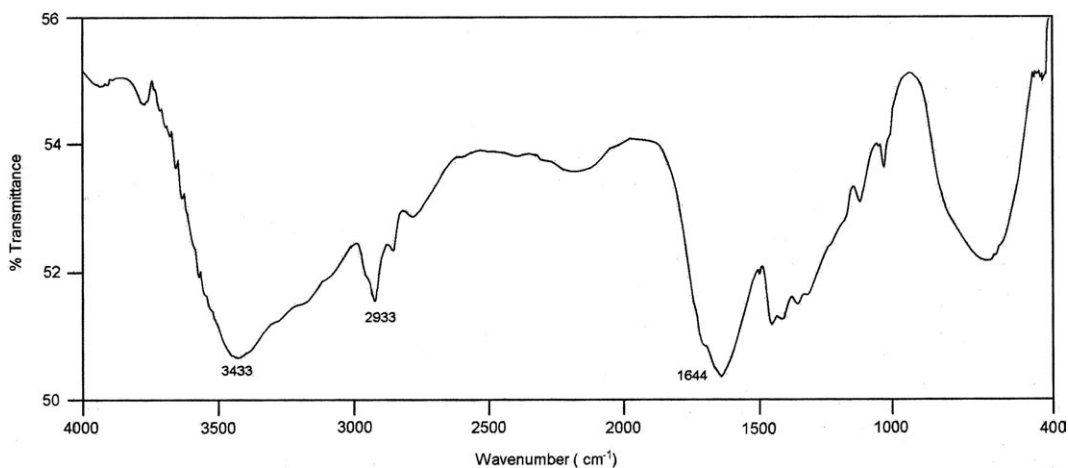


Figure 3. FTIR spectrum of PAM initiated by SHPBS.

obtained with SHPBS initiation: 1.49 ppm (d, 2H, CH<sub>2</sub>); 2.06 (d, 1H, CH); 6.71 ppm (d, 2H, Ar-H); 7.43 ppm (d, 2H, Ar-H).

#### Thermal Analysis

DSC and DTG analysis are shown in Figures 6 and 7, respectively. Water content of SHPBS is checked by DSC and DTG analysis. In DTG analysis up to the 90–110°C no weight loss is observed, and in DSC analysis endothermic peak is absent in

this temperature range. DSC and DTG, both analyses prove that there is no water content in SHPBS. DSC and DTG analyses show that SHPBS is thermally stable up to the temperature 120°C. Therefore, in drying process at 40°C there is no decomposition. But in the solution (water), initiator decomposes at the low temperature. The initiator gains the energy from the solvation (ion–dipole interactions). Ionic interaction (ionic bond formation) is exothermic and this energy is used to cleave the azo linkage.

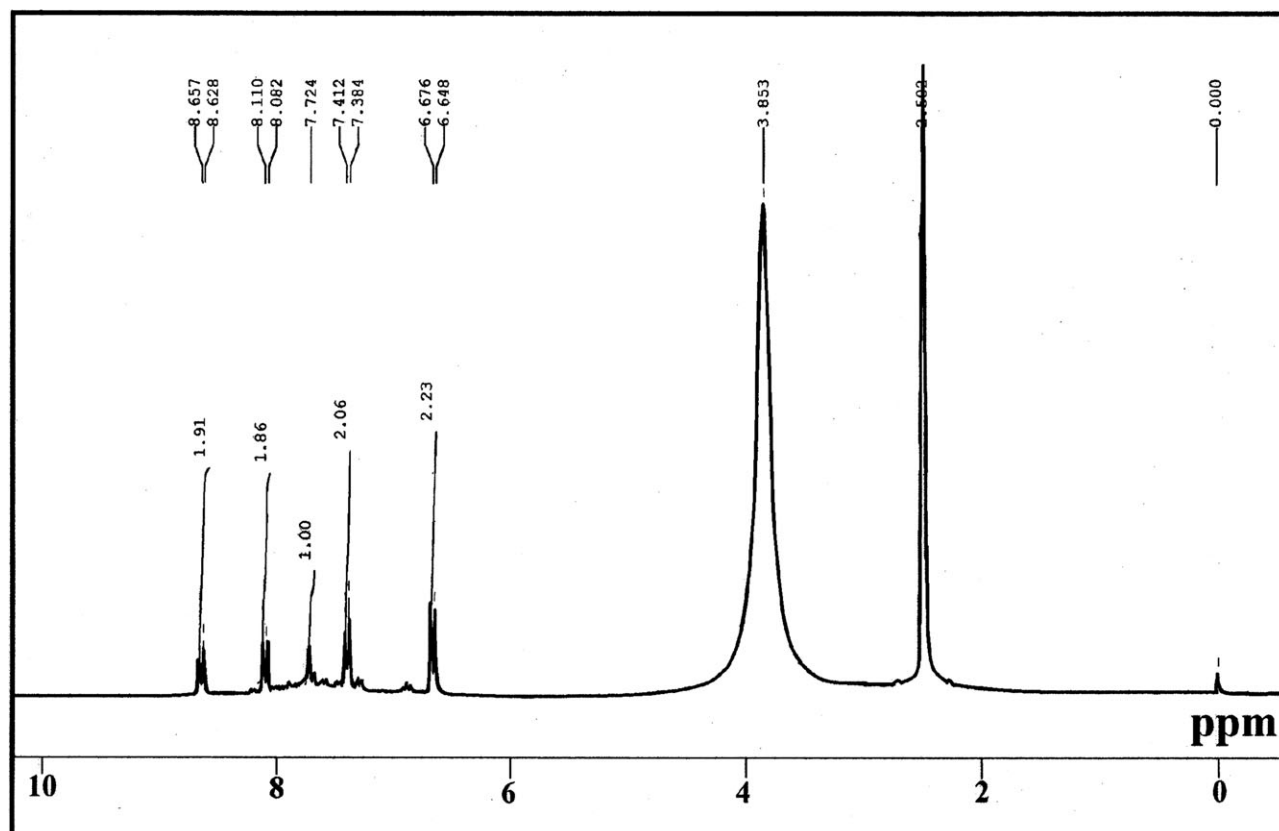


Figure 4. <sup>1</sup>H NMR spectrum of SHPBS.

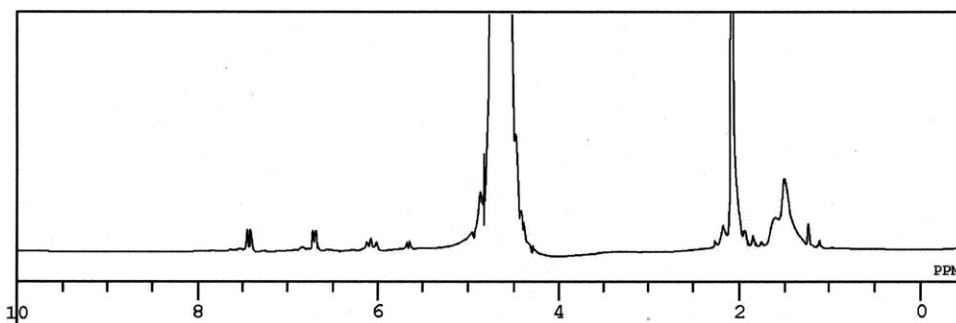


Figure 5.  $^1\text{H}$ NMR Spectrum of PAM initiated by SHPBS.

### Comparison Between SHPBS and AIBN by PAM Polymerization

Table II depicts the comparison between polymerization activity of AIBN and SHPBS. In this case, AM is used as the monomer polymerized with AIBN and SHPBS. SHPBS is more proficient to polymerize at lower temperature leading to high molecular weight polymers. With increase in initiator concentration, decrease in molecular weight is observed. It is due to the fact that at fixed monomer amount, higher number of monomers free radicals are initiated at higher initiator concentration leading to shorter chain lengths. Figure 8 shows the change in molecular weight of PAM synthesized with different initiator (AIBN and SHPBS) concentration. Molecular weight of PAM obtained by SHPBS initiation is higher than that of PAM obtained by AIBN initiation at all the initiator concentration. From this plot, predetermination of molecular weight at particular initiator concentration is possible. This can lead to tailor-made synthesis of polymer with desired molecular weight.

### CONCLUSION

SHPBS worked as an efficient azo initiator, which could polymerize vinylic monomer at room temperature ( $25^\circ\text{C}$ ) without any mechanical stirring and with lesser polymerization time. It fabricated high molecular weight polymers compared to AIBN. Presence of *para*-hydroxyphenylene group as end groups and absence of cyanide group gave it extra advantage over AIBN.

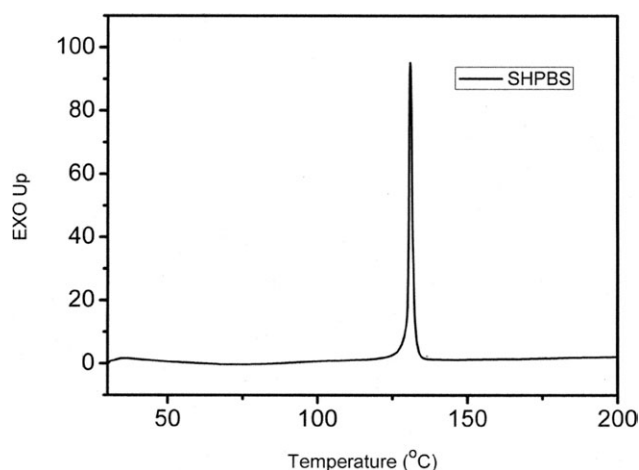


Figure 6. DSC analysis of SHPBS.

Thus, this free radical polymerization process shows vast commercial prospective due to its lower temperature initiation to obtain higher yield and molecular weight in a simple cost-effective way.

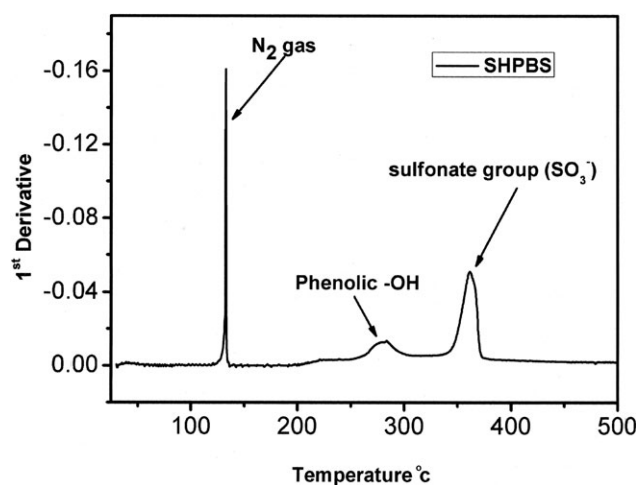


Figure 7. DTG analysis of SHPBS.

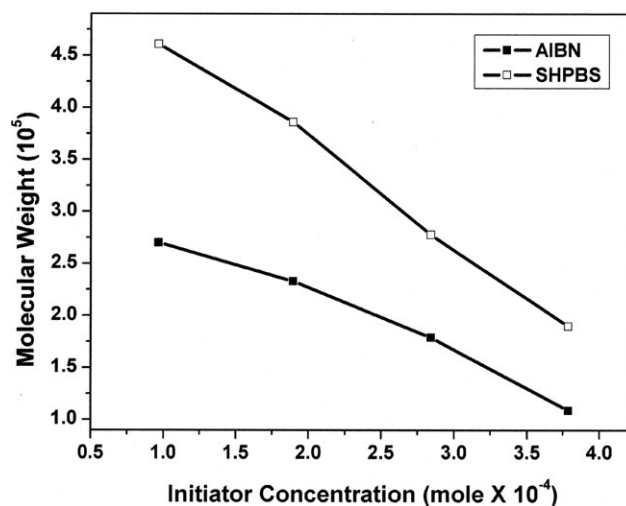


Figure 8. Change of molecular weight of PAM with different initiator concentration.

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## REFERENCES

- Hong, K.; Zhang, H.; Mays, J. W.; Visser, A. E.; Brazel, C. S.; Holbrey, J. D.; Reichert, W. M.; Rogers, R. D. *Chem. Commun.* **2002**, 13, 1368.
- Hawker, C. J. *Acc. Chem. Res.* **1997**, 30, 373.
- Wang, J. S.; Matyjaszewski, K. J. *Am. Chem. Soc.* **1995**, 117, 5614.
- Pabin-Szafko, B.; Wisniewska, E.; Hefczyc, B.; Zawadiak, J. *Euro. Polym. J.* **2009**, 45, 1476.
- Wahl, R. U.; Zeng, R. L.; Madison, S. A.; DePinto, R. L.; Shay, B. J. *J. Chem. Soc., Perkin Trans., 2*, **1998**, 9, 2009.
- Czech, Z.; Butwin, A.; Herko1, E.; Hefczyc, B.; Zawadiak, J. *Polym. Lett.* **2008**, 2, 277.
- Denisov, E. T.; Denisova T. G.; Pokidova T. S. *Handbook of Free Radical Initiators*, John Wiley & Sons: New York, **2003**.
- Jayakannan, M.; Anil Kumar, P.; Sanju, A. *Euro. Polym. J.* **2006**, 42, 2623.
- Krishnamoorthi, S.; Adhikary, P.; Mal, D.; Singh, R. P. *J. Appl. Polym. Sci.* **2010**, 118, 3539.
- Krishnamoorthi, S.; Mal, D.; Singh, R. P. *Carbohydr. Polym.* **2007**, 69, 371.
- Newman, S.; Krigbaum, W. R.; Laugier, C.; Flory, P. J. *J. Polym. Sci.* **1954**, 14, 451.
- Ali, S. *Euro. Polym. J.* **1979**, 15, 685.
- Coviello, T.; Burchard, W.; Dentini, M.; Crescenzi, V. *Macromolecules* **1987**, 20, 1102.