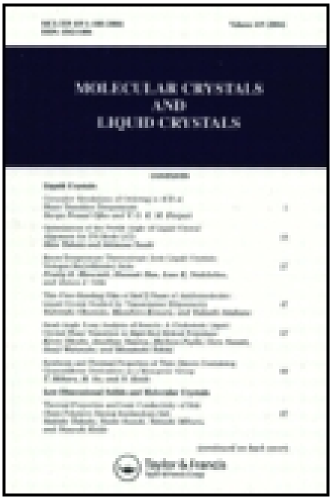


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Characterization of Poly(hydroxyamide-benzoxazole) Multi-Block Copolymers

Young Koo Kwon [a] & Young Jun Kim [a]
[a] Department of Chemical Engineering, Sungkyunkwan University, Suwon, South Korea

To cite this article: Young Koo Kwon & Young Jun Kim (2008) Synthesis and Characterization of Poly(hydroxyamide-benzoxazole) Multi-Block Copolymers, Molecular Crystals and Liquid Crystals, 492:1, 172/[536]-183/[547], DOI: 10.1080/15421400802330598

To link to this article: http://dx.doi.org/10.1080/15421400802330598

Mol. Cryst. Liq. Cryst., Vol. 492, pp. 172/[536]–183/[547], 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802330598

Synthesis and Characterization of Poly(hydroxyamide-benzoxazole) Multi-Block Copolymers

Young Koo Kwon and Young Jun Kim
Department of Chemical Engineering, Sungkyunkwan University,
Suwon, South Korea

Poly(hydroxyamide-benzoxazole) multi-block copolymers were prepared from the polymerization of 2,2′-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (6FAP) and 4,4′-oxydibenzoyl chloride (ODBC). N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) or N,O-bis(trimethylsilyl)acetamide (BSA) was used as a silylation agent to activate amine functional groups. The amine terminated hydroxyamide prepolymers (ATHA) were synthesized by employing the low temperature solution polymerization via the in situ *silylation method. p-Toluenesulfonic acid was added into the reaction mixture of ATHA, which in turn followed by cyclodehydration at 150 ~ 190°C 4 for 24 hrs to produce amine terminated benzoxazole oligomers (ATBO). Finally, the poly(hydroxyamide-benzoxazole) multi-block copolymers were prepared from the condensation of ATHA, ATBO and ODBC by employing the silylation method at relatively low temperature of 60°C. In the present work, properties of multi-block copolymers have been investigated.*

Keywords: *in situ* silylation; polybenzoxazole; poly(hydroxyamide-benzoxazole) block copolymer; positive working photo resist; silylation agent

1. INTRODUCTION

Polybenzoxazoles (PBOs) have special features which lower water absorption, dielectric constant, and power dissipation. Polybenzoxazoles precursors [o-hydroxy amide; PHA] have been used to prepare positive working photosensitive materials for microelectronics [1–5]. Polybenzoxazoles have good photolithographic performance, but they show dark film loss since the PBO precursors show high solubility in the aqueous base developer [6]. The dark film loss after development may be avoided by reducing the solubility of PBO precursors. In order

Address correspondence to Young Jun Kim, Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, South Korea. E-mail: youngkim@skku.edu

to protect dissolution of the prepolymer in the aqueous base developer we introduce small amount of PBO groups in the PBO precursors. PBOs could be prepared from the polymerization of bis(o-aminophenol)s with dicarboxylic acids in polyphosphoric acid(PPA) [7,8]. On the other hand, dicarboxylic acid chlorides can be used for the PBO synthesis by employing the direct solution polymerization technique. The solution polymerization technique involves polycondensation of bis(o-aminophenol)s with dicarboxylic acid chlorides in high boiling solvent to produce PHA precursors and subsequent thermal cyclodehydration of the PHAs to PBOs. However, it was found to be difficult to obtain high molecular weight PBOs especially when monomers with low reactivity such as 6FAP were involved [9]. The silylation of the amine functional group increases the electronic density on the nitrogen atom and decreases the activation energy of the reaction, which in turn increases the overall reaction rate [10]. The silylation method involving N,N′,O,O′-terakis(trimethylsilyl)-substituted bis(o-aminophenol)s was used for the synthesis of PBOs with high molecular weight. The hydrolytic susceptibility of the silylated bis(o-aminophenol) monomers was found to be a synthetic obstacle in the synthesis of PBOs [8,11,12]. Therefore, we have employed the *in situ* silylation method for the synthesis of PBOs using a silylation agent such as N,O′-bis(trimethylsilyl)acetamide (BSA) or N,O′-bis(trimethylsily)trifluoroacetamide (BSTFA).

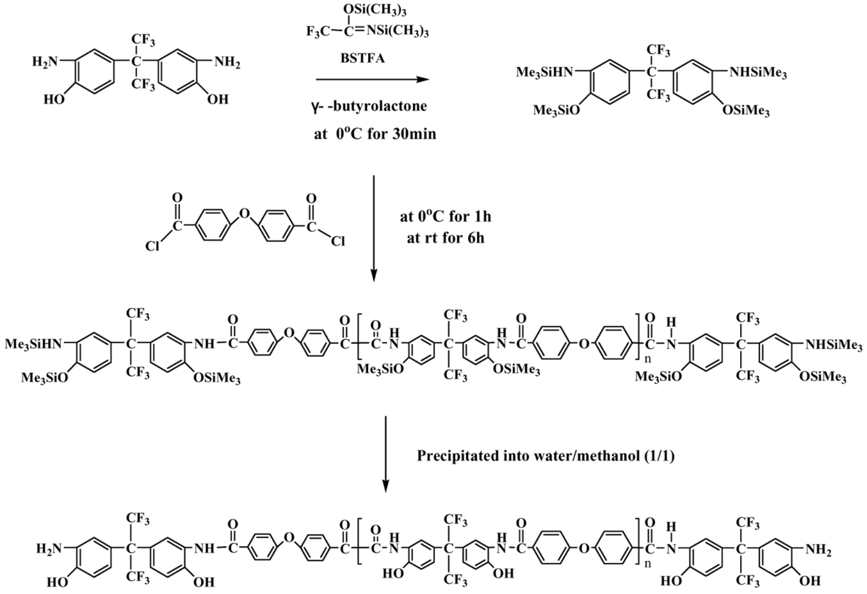
2. EXPERIMENTAL

2.1. Material

2,2′-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (6FAP) **(1)** was purchased from Chriskev Co. and dried in vacuum at 105°C for 24 h before use. 4,4′-Oxydibenzoyl chloride (ODBC) **(2)** was prepared by chlorination of 4,4′-oxydibenzoic acid with thionyl chloride according to the literature procedure [13]. N,O-bis(trimethylsilyltrifluoroacetamide) (BSTFA), N,O-bis(trimethylsilylacetamide) (BSA) and p-toluenesulfonic acid (p-TSA) **(3)** were purchased from Aldrich and used as received. Dichlorobenzene, N-methyl-2-pyrrolidinone (NMP), and γ-butyrolactone were obtained from Aldrich and dried by distillation over calcium hydride.

2.2. Synthesis of the Amine Terminated PBO Precursor [ATHA] ($\overline{Mn}$:8 K)

A typical example of the synthesis of the amine terminated PBO precursor with the theoretical number average molecular weight

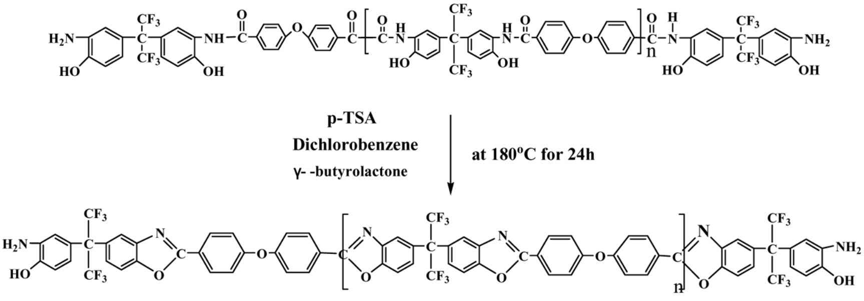


SCHEME 1 Synthesis of the amine terminated PBO precursor [ATHA] by silylation method.

of 8 K is given below (Scheme 1). In a flame-dried flask, **1** (2.4 mmol) was dissolved in γ-butyrolactone (6 mL) while stirring under nitrogen. BSTFA (5 mmol) was added to this solution and stirred at room temperature for 1 h to prepare silylated monomers. 2 (2.05 mmol) was added all at once and stirred at room temperature for 6 h. A thin solution of amine terminate hydroxy-amide (ATHA) was obtained. The resulting ATHA solution poured into the water/methanol mixture (1:1 (v/v)). The precipitated ATHA **(4)** was collected, washed several times with the water/methanol mixture, and dried at 105°C for 24 h.

2.3. Synthesis of the Amine Terminated PBO Oligomer [ATBO] ($\overline{Mn}$:8 K)

At room temperature NMP (6 mL) was added to a 25 mL flame-dried reaction flask equipped with a Dean-Stark trap, nitrogen inlet, and a drying tube. Subsequently, **4** (2 mmol), azeotroping solvent, dichlorobenzene (1.4 ml) and p-TSA (0.48 mmol) were added to the reaction flask while stirring. After the addition of the p-TSA, polymerization temperature was increased to 180°C and the polymerization



SCHEME 2 Synthesis of the amine terminated PBO oligomer [ATBO].

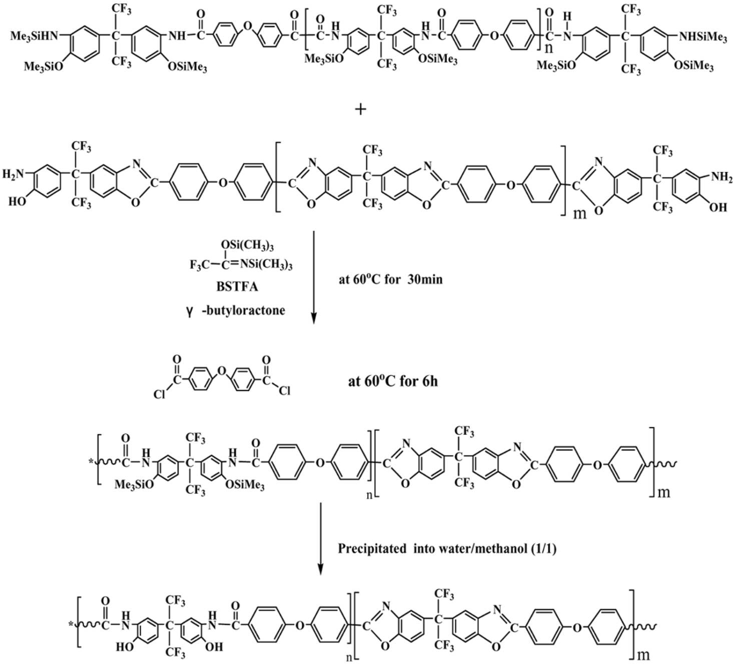
was allowed to proceed for 24 h at this temperature under nitrogen atmosphere. The resulting ATBO oligomer solution was poured into methanol. The ATBO **(5)** oligomer was collected and dried at 205°C for 24 h (Scheme 2).

2.4. Synthesis of Poly(hydroxyamide-benzoxazole) Multi-Block Copolymer [PHPB]

A typical example of the synthesis of poly(hydroxyamide-benzoxazole) multi-block copolymer in which the total mole % of ATHA and ATBO are 80 and 20, respectively, is given below. Into the flame-dried flask containing 8 K ATHA solution (4.638 g ATHA oligomer in 26 ml of NMP), **5** (1.018 g) was added. The reaction mixture was heated to 60°C in order to completely dissolve the oligomer **5**. The silylation agent, BSTFA was added to this solution and stirred for 30 min. to allow the silylation reaction to occur. Then **2** (0.7816 g) was added to the reaction mixture while stirring at 60°C. After the 6 hr reaction, highly viscose polymer solution was obtained. The resulting poly(hydroxyamide-benzoxazole) multi-block copolymer (PHPB) solution was poured into the mixed solvent of water/methanol (1:1 v/v). The precipitated polymer was collected by filtration, washed with the mixed solvent of water/methanol (1:1 v/v) and dried at 60°C 4 for 24 h (Scheme 3).

2.5. Characterization

Intrinsic viscosity measurements were performed in NMP at 30°C by using Cannon-Ubbelohde viscometers. Molecule weight values were determined by gel permeation chromatography (GPC) on a Water GPC System equipped with polymethylmethacrylate gel columns. The measurements were performed at 35°C in DMF containing



SCHEME 3 Synthesis of poly(hydroxyamide-benzoxazole) multi-block copolymers [PHPB].

0.01 M LiBr. ^{1}H-NMR spectra were recorded on a Varian 500 MHz instrument using DMSO-d6 or $CDCl_3$ as solvents. Fourier transform infrared (FT-IR) spectra were recorded on KBr salt plates with a Perkin Elmer FT-IR Spectrometer Spectrum 2000. Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments 910. DSC scans were run under nitrogen atmosphere (100 ml/min) on powder samples. DSC scans were run from 30 to 300°C at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was performed on a TA Instuments 2950 thermogravimetric analyzer at a heating rate of 10°C/min under nitrogen atmosphere.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Poly(hydroxyamide-benzoxazole) Multi-Block Copolymer [PHPB]

It is reported by others that only oligomeric PBOs were obtained from monomers with low reactivity such as 6FAP. For example, oligomeric

PBOs were obtained either from the direct solution polycondensation of 6FAP or isophthaloyl chloride in dimethylacetamide at $0 \sim 5°C$ [9]. These experimental results imply that it is difficult to synthesize high m.w. PBO multi-block copolymers from low reactivity monomers through the direct solution polymerization technique. The synthetic obstacle could be overcome through the silylation method for the synthesis of poly(hydroxyamide-benzoxazole) multi-block copolymers. Figure 1 shows the GPC traces of ATBO prepolymer and poly (hydroxyamide-benzoxazole) multi-block copolymers and the molecular weight values are summarized in Table 1.

The number average molecular weight of ATBO, whose target molecular weight was 8,000 g/mol, was found to be 8,300 g/mol. It was impossible to cast a tough film with this oligomer. However, from the polymerization of 8 K ATHA, 8 K ATBO and ODBC as explained in the above experimental section, high molecular weight hydroxyl amide-bezoxazole multi-block copolymers were successfully synthesized. Dramatic molecular increase was observed. The block copolymers of PHPB10 and PHPB20 showed number average molecular weight of 117,000 and 70,000 g/mol, respectively. The intrinsic viscosity values of these polymers were 0.68 and 0.62 dL/g, respectively and these two block copolymers formed tough films.

In the cyclodehydration step in which the hydroxyl-amide groups were transformed to benzoxazole groups (Scheme 2), the addition of p-toluenesulfonic acid was critically important for achieving complete ring formation. This is demonstrated in the FTIR spectra shown in Figures 2 and 3. For the FTIR characterization, the 8 K ATHA prepolymer was cast on the KBr salt plate which in turn exposed to the thermal treatment at 100°C for 1 h, at 200°C for 1 h and at 300°C for 1 h (Fig. 2). Under these conditions the hydroxy amide groups were resistant to cyclization as evidenced by the fact that the oxazole C-O stretch vibration at $1051\,\mathrm{cm}^{-1}$ did not appear. Figure 3 shows FTIR spectra of 8 K ATHA prepolymer, 8 K ATBO, PHPB10 and PHPB20. In the synthesis of the 8 K ATBO oligomer, p-toluene sulfonic acid was used as a catalyst. As shown in Figure 3 the bands due to the oxazole C-O stretch were developed for the ATBO, PHPB10 and PHPB20 samples. The importance of the addition of the acid catalyst such as p-toluene sulfonic acid in PBO synthesis is reported elsewhere [12]. They reported that the attempts to cyclize the hydroxyl amide precursor without the addition of an acid resulted in less than 1% conversion over a 5 h period.

The cyclization reaction was also followed by ^{1}H-NMR. Figure 4 shows ^{1}H-NMR of 8 K ATHA (spectrum A) and 8 K ATBO (spectrum B) oligomers. As shown in Figure 4 the peaks at 10.5 ppm due to amide

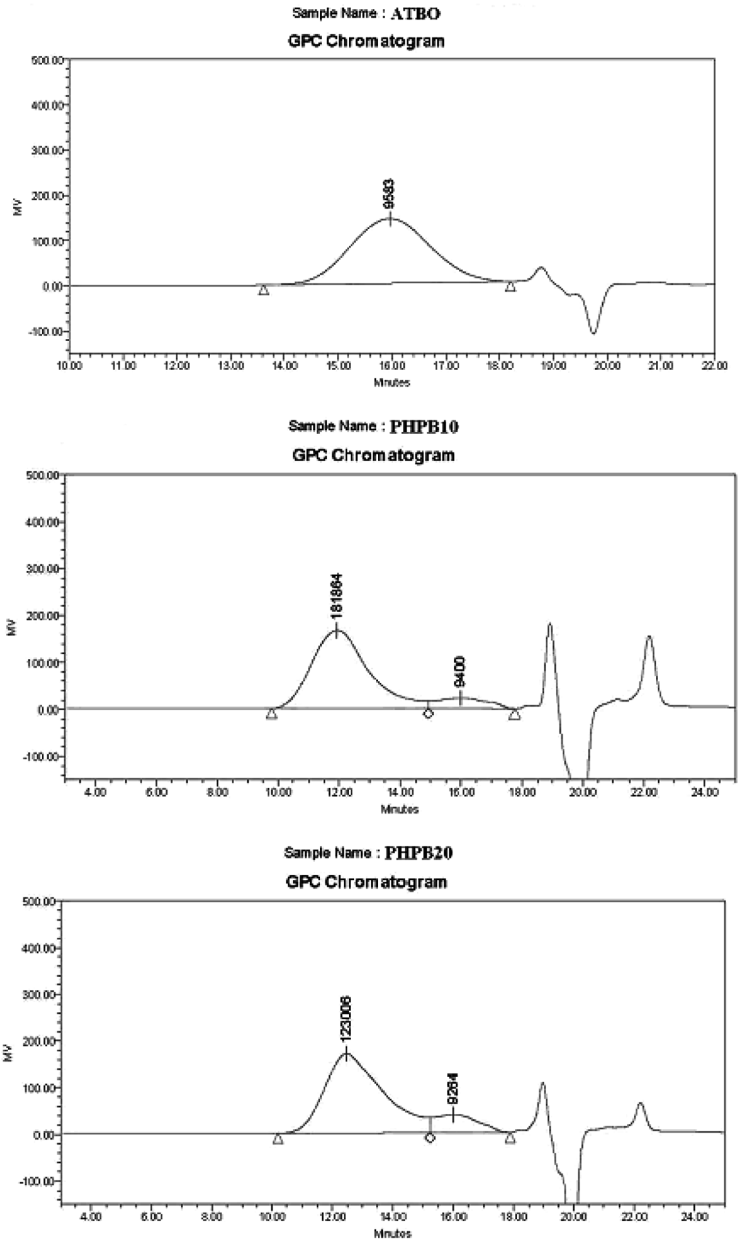


FIGURE 1 GPC traces of ATBO prepolymer and poly(hydroxyamide-benzoxazole) multi-block copolymers.

TABLE 1 Molecular Weight and Intrinsic Viscosity Values of ATBO Prepolymer and Poly(hydroxyamide-benzoxazole) Multi-Block Copolymers

Polymer systems	$\overline{Mn}$	$\overline{Mw}$	$\overline{Mw}/\overline{Mn}$	Intrinsic viscosity
ATBO (8 K)	8,300	10,600	1.3	–
PHPB10*	117,000	187,000	1.6	0.68
PHPB20**	70,000	113,000	1.6	0.62

*PHPB10: Poly(hydroxyamide-benzoxazole) multi-block copolymer synthesized from 8 K ATHA (90 mole%) and 8 K ATBO (10 mole%).

**PHPB20: Poly(hydroxyamide-benzoxazole) multi-block copolymer synthesized from 8 K ATHA (80 mole%) and 8 K ATBO (20 mole%).

NH groups and 9.6 ppm due to the hydroxy groups were completely disappeared in case of the ATBO sample, which confirms complete cyclization of the hydroxy amide groups.

3.2. Characterization of Poly(hydroxyamide-benzoxazole) Block Copolymers [PHPB]

The solubility of the poly(hydroxyamide) prepolymer and PHPB multi-block copolymers (PHPB10 and PHPB20) was investigated in

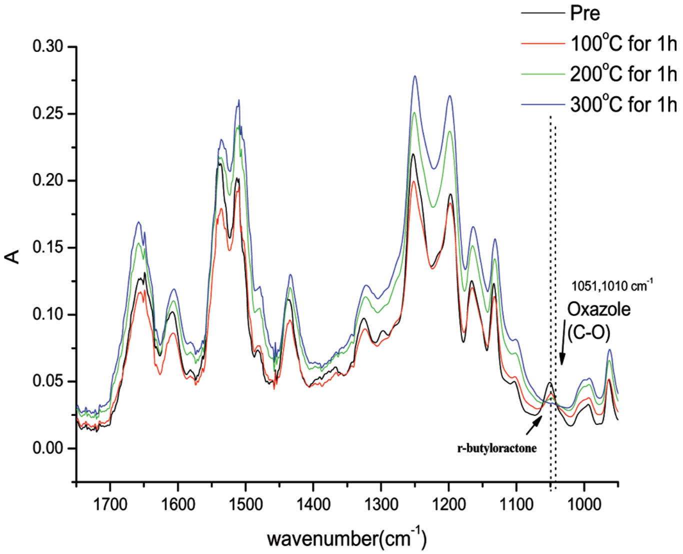


FIGURE 2 FTIR spectra of 8 K ATHA prepolymer measured at the different stages of thermal treatment. The ATHA prepolymer was cast on the KBr salt plate which in turn exposed to the thermal treatment at 100°C for 1 h, at 200°C for 1 h and at 300°C for 1 h.

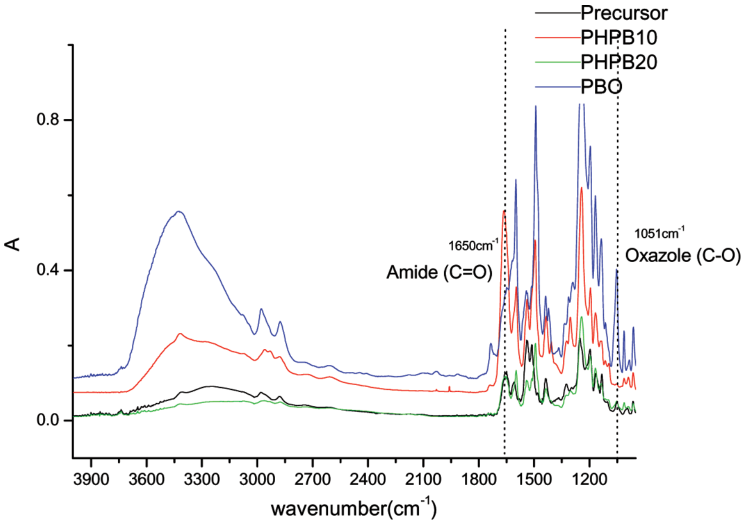


FIGURE 3 FTIR spectra of 8 K (precursor), PBO (8 K ATBO), PHPB10 and PHPB20.

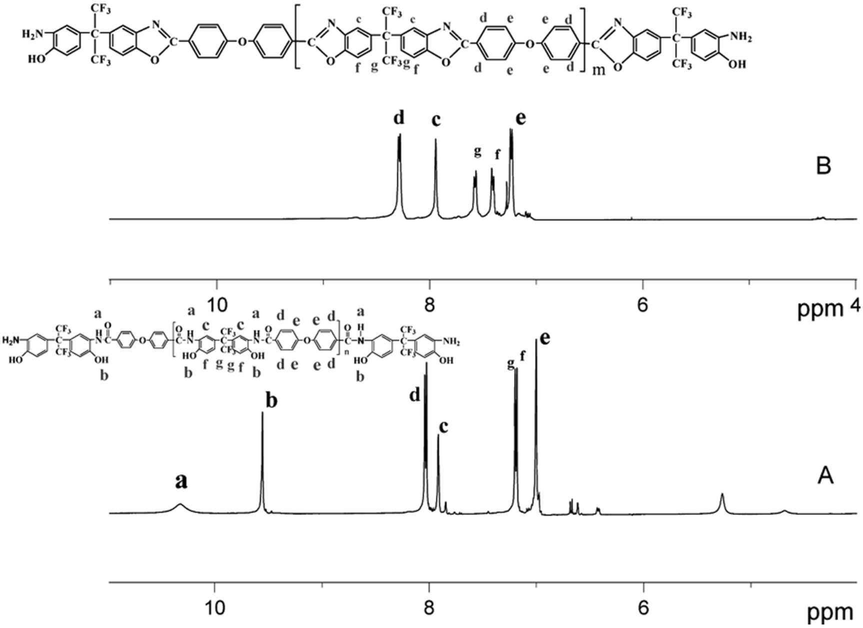


FIGURE 4 ^{1}H-NMR spectra of 8 K ATHA (spectrum A) and 8 K ATBO (spectrum B) oligomers.

TABLE 2 Solubilty Behavior of 6FAP/ODBC Based Hydroxyamide Prepolymer and Hydroxyamide-Benzoxazole Multi-Block Copolymers

Solvent	Solubility* of polybenzoxazole precursor**	Solubility of PHPB10 and PHPB20 multi-block copolymers
NMP	+	+
DMAC	+	+
DMF	+	+
THF	+	+
DMSO	+	+
Acetone	+	−
Ethanol	−	−
Methanol	+	−
TMAH***	+	−

*+: soluble; −: insoluble.

**High molecular weight poly(hydroxyamide) precursor based 6FAP/ODBC (intrinsic viscosity: 0.6 dl/g measured at 30°C in NMP).

***10% (w/w) aqueous solution of tetramethyl ammonium hydroxide.

various solvents as shown in Table 2. Both of the block copolymers were soluble in all of the solvent under investigation except ethanol and methanol. TGA curve of PHPB10 is shown in Figure 5. The weight loss up to 200°C corresponds to the vaporization of solvent. The TGA trace levels off around 360°C and stays at constant level up to 510°C from which dramatic weight loss is observed due to thermal

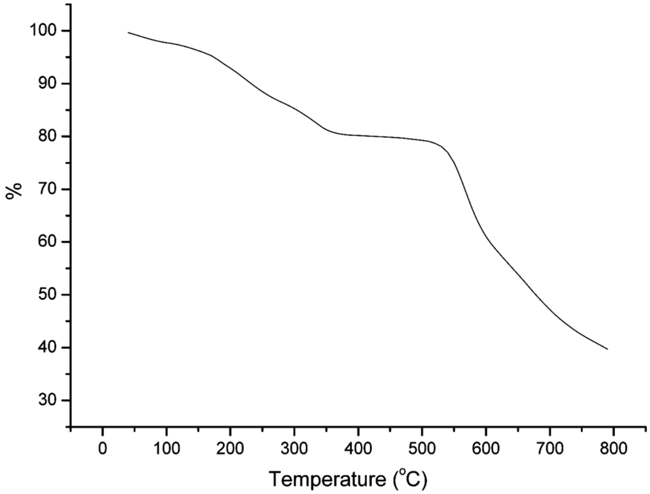


FIGURE 5 TGA trace of PHPB10.

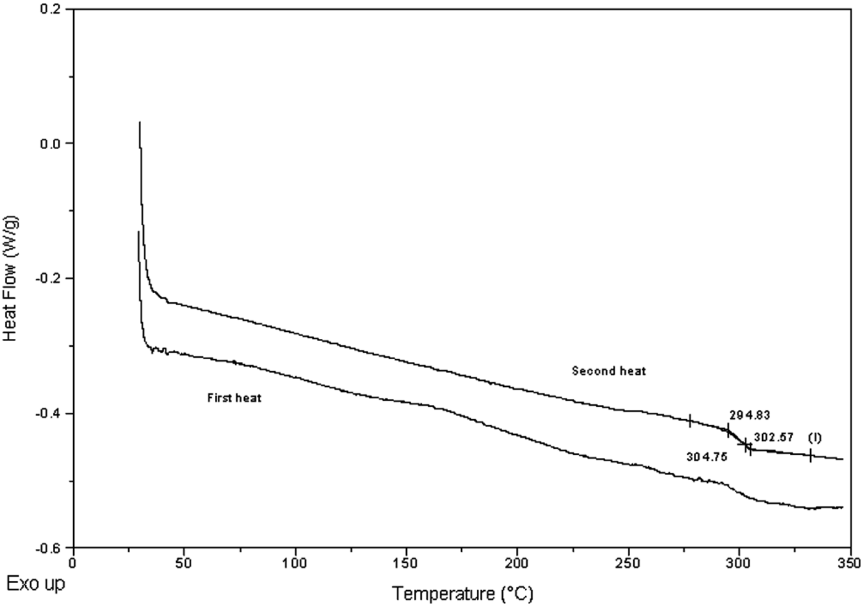


FIGURE 6 DSC thermogram of PHPB10.

degradation. Figure 6 shows the DSC thermogram of PHPB10 where the glass transition is observed at 302°C.

4. CONCLUSION

Poly(hydroxyamide-benzoxazole) multi-block copolymers [PHPB] were synthesized from the coupling reaction of amine terminated hydroxyl amide oligomers, amine terminated benzoxazole oligomers and ODBA by employing the *in situ* silylation method. GPC, FTIR and ^{1}H-NMR spectroscopic data confirmed the synthesis of the multi-block copolymers. The cyclization conditions for transformation of hydroxy amide groups to benzoxazole groups were investigated. It was found that catalytic amount of p-toluene sulfonic acid should be added in the solution cyclization technique for effective cyclization.

REFERENCES

[1] Makabe, H., Banba, T., & Hirano, J. (1997). *Photopholym. Sci. Technol.*, *10*(2), 307–311.
[2] Tokoh, A. (1999). *Photosensitive Polymers*, Kansai Research Institute, Kyoto, Japan, 89–90.

[3] Maier, G. (2001). *Prog. Polym. Sci.*, *3*, 26.

[4] Ahne, H., Kuhn, E., & Rubner, R. (1982). *US Patent*, *4*, 339, 521.

[5] Mueller, W. H., Khanna, D. N., & Hupfer, B. (1993). *US Patent*, *5*, 240, 819.

[6] Hsu, S. L. C. & Chen, W. C. (2002). *Polymer*, *43*, 6743.

[7] Imai, Y., Taoka, I., Uno, K., & Iwakura, Y. (1965). *Makromol. Chem.*, *83*, 167.

[8] Ueda, M., Sugita, H., & Sato, M. (1986). *J. Polym. Sci. Polym. Chem. Ed.*, *24*, 1019.

[9] Maruyama, Y., Oishi, Y., Kakimoto, M., & Imai, Y. (1988). *Macromol.*, *21*, 2305.

[10] Lozano, A. E., Abajo, J., & Campa, J. G. (1998). *Macromol. Theory Simul.*, *7*, 41.

[11] Joseph, W. D., Mercier, R., Prasad, A., Marand, H., & McGrath, J. E. (1993). *Polymer*, *34*, 866.

[12] Joseph, W. D., Abed, J. C., Mercier, R., & McGrath, J. E. (1993). *Polymer*, *35*, 5046.

[13] Hsiao, S.-H. & Yu, C.-H. (1998). *J. Polym. Sci. Polym. Chem. Ed.*, *36*, 1847.