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Synthesis and Characterization of Polyhydroxyamide Copolymers as Precursors of Polybenzoxazoles

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Abstract: Polyhydroxyamide (PHA) and its copolymers were synthesized *via* low-temperature solution polycondensation of 3,3'-dihydroxybenzidine (DHB) with terephthaloyl chloride (TPC) and/or isophthaloyl chloride (IPC) in N,N-dimethylacetamide (DMAc) with the aid of lithium chloride (LiCl). The synthesized PHA copolymers were characterized by ^{1}H-NMR spectroscopy, FT-IR spectroscopy, and thermogravimetric analyzer (TGA) in order to understand the relations between the chemical structures and the solubility and thermal properties of PHA copolymers. Thermal cyclization of PHA copolymers and the formation of polybenzoxazoles (PBOs) were investigated using FT-IR spectroscopy and TGA. The solubility test revealed that PHA copolymers containing IPC content over 20 mol% were readily dissolved in a variety of polar amide solvents with the aid of LiCl. TGA results showed that the thermal cyclization temperature, the thermal degradation temperatures of PHA copolymers and the thermal stabilities and the char yields of converted PBO copolymers were significantly reduced by the inclusion of meta-structure in the main chain especially when the IPC content was higher than 25 mol%.

Keywords: Polyhydroxyamides, Polybenzoxazoles, Copolymerization, Solubility, Thermal stability

Introduction

Polybenzoxazoles (PBOs) are well-known fire resistant polymers which have an excellent thermal stability, outstanding thermo-oxidative stability, and good mechanical properties. PBOs have been thus proposed as a good engineering material in a wide range of fields including mechanical rubber goods, protective cloths, ropes, and fiber reinforcing composites [1-5].

In general, PBOs can be directly prepared by one-step polymerization methods such as high-temperature solution polycondensation bewteen aromatic diamines and aromatic dicarboxylic acids in polyphosphoric acid (PPA) or methanesulfonic acid (MSA). However, PBOs can be also produced by thermal cyclization of polyhydroxyamides (PHAs) precursors which are prepared from aromatic diamines and aromatic diacyl chlorides in a variety of organic solvents [6-8]. In case of one-step methods, PBOs are soluble only in strong acids such as PPA and MSA which lead to a toxic environment, the corrosion of the equipment, and the difficulty in handling the manufacturing process. However, the precursor method is free from these difficulties because PHAs, typical precursors to PBOs, are soluble in many organic solvents with or without the aid of metal salts. Several studies have been reported on the fundamental research associated with precursor polymer preparation and the cyclization chemistry of them [9-18]. Since the precursor polymers do not have strong hydrogen bonding force between their molecules, they can be processed in various forms such as fibers, films, sheets, etc. However, the fundamental understanding of the relationship between the chemical structures and the solubility, thermal cyclization behavior, and properties of the precursor polymers is still limited.

In this study, we synthesized various PHA copolymers with different TPC/IPC mole ratios using low-temperature solution polycondensation of 3,3'-dihydroxybenzidine with terephthaloyl chloride and/or isophthaloyl chloride in N,N-dimethylacetamide with the aid of lithium chloride and tried to correlate their structures with their properties such as solubility in organic solvents, thermal cyclization behaviors, and thermal stabilities.

Experimental

Materials

3,3'-dihydroxybenzidine (DHB, 99.0 %) was purchased from Tokyo Chemical Ind. (Japan) and purified by recrystallization from ethanol/water/DMAc mixture. Terephthaloyl chloride (TPC, 99.0 %) and isophthaloyl chloride (IPC, 99.0 %), and anhydrous N,N-dimethyl acetamide (DMAc, 99.8 %) were purchased from Sigma-Aldrich Co. (USA) and lithium chloride (LiCl, 99.0 %) was purchased from Junsei Chemical Co. (Japan), respectively. N-methyl-2-pyrrolidinone (NMP, 99.5 %), N,N-dimethylformamide (DMF, 99.8 %), dimethyl sulfoxide (DMSO, 99.5 %), tetrahydrofuran (THF, 99.8 %), and sulfuric acid (H_2SO_4, 95.0 %) were purchased from Samchun Chemical Co. (Republic of Korea).

Synthesis of PHA and Its Copolymers

PHA and its copolymers were synthesized using low-temperature solution polycondensation. DHB (6.18 g, 0.029 mol) was dissolved in DMAc/LiCl solvent system (DMAc

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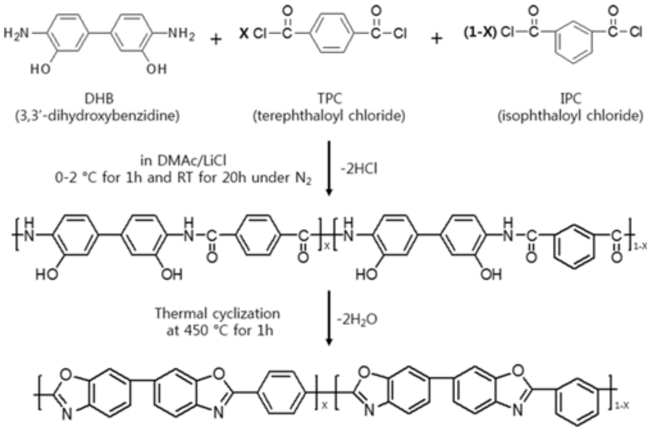

Scheme 1. The reaction scheme of the synthesis of PHA copolymers and the conversion of them to PBO copolymers on heating.

115 m*l*, LiCl 3.6 g, polymer concentration 8 wt%) using a mechanical overhead stirrer (Euro-Star CV P4, IKA German technology) and flakes of TPC and/or IPC were simultaneously added into the DHB solution. The solution was stirred under nitrogen atmosphere at a low temperature (0-2 °C) in ice bath for an hour and then at room temperature for 20 hours. The reaction mixture was poured into distilled water in order to remove the by-product (HCl). The products were washed for 10 hours and then finally dried in a vacuum oven at 110 °C for 24 hours. The synthetic route is shown in Scheme 1.

Characterization of PHA and Its Copolymers

The intrinsic viscosities of PHA and its copolymers were evaluated by means of Ubbelohode viscometer in sulfuric acid (95.0 %, 0.5 g/d*l*) at 30±0.1 °C. The chemical structures of PHA copolymers and their structural changes during heating were examined by proton nuclear magnetic resonance spectroscopy (400 MHz ^{1}H-NMR Spectroscopy, Bruker, Bruker Ascend 400, Germany) in dimethyl sulfoxide-d$_6$ and fourier transform infrared spectroscopy (FT-IR Spectroscopy, Thermo, Nicolet IS50, USA), respectively. To comprehend thermal properties as a function of IPC content in PHA copolymers, thermogravimetric analysis was carried out using thermogravimetric analyzer (TGA, TA instruments, Q50, USA) from 25 to 900 °C at the heating rate of 20 °C/min under nitrogen atmosphere.

Results and Discussion

Chemical Structural Analysis of PHA Copolymers

Figure 1 shows ^{1}H-NMR spectra of PHA copolymers. In Figure 1(A), it was found that the peaks of hydroxyl, amide, and aromatic protons of PHA-T0 were observed at 10.2, 9.9, and 8.7-7.0 ppm, respectively, where all the peaks could be assigned without difficulty as confirmed by our previous study [10]. The peak assignment of PHA copolymers were almost similar to those of PHA-T0 as shown in Figure 1(B), 1(C), and 1(D). It was observed that the peak intensity of meta-phenyl proton of IPC decreased with increasing TPC content in the copolymers, while that para-phenyl proton of TPC appeared at 7.4 ppm increased with increasing TPC content. The PHA-T100 was insoluble in NMR solvents. The sample identification and intrinsic viscosities of PHA and its copolymers are listed in Table 1.

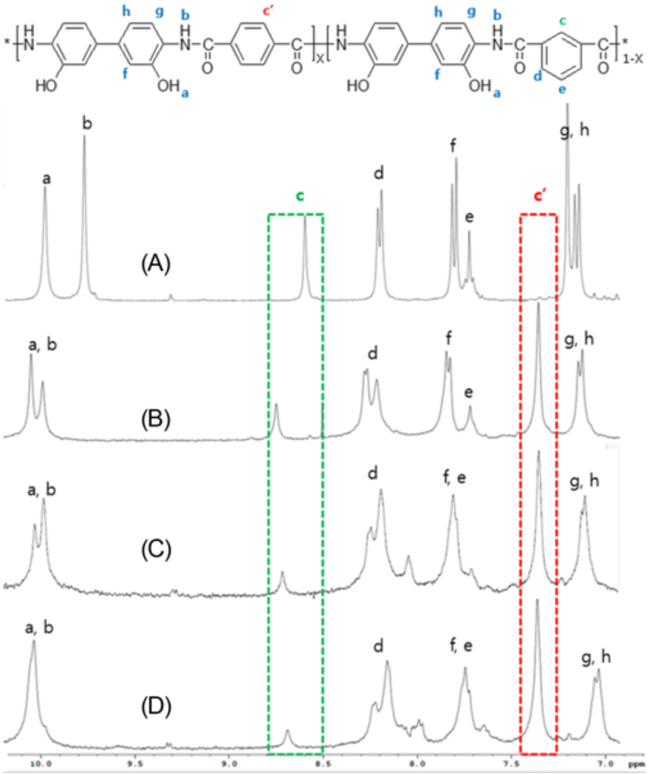

Figure 1. ^{1}H-NMR spectra of PHA copolymers; (A) PHA-T0, (B) PHA-T50, (C) PHA-T80, and (D) PHA-T90.

Table 1. Sample identification and the intrinsic viscosities of PHA copolymers

Sample code	TPC/IPC mole ratio (feed)	TPC/IPC mole ratio (calculated[a])	I.V. (d*l*/g)
PHA-T100	100/0	-	1.84
PHA-T90	90/10	88.1/11.9	1.68
PHA-T80	80/20	79.2/20.8	1.63
PHA-T75	75/25	75.5/24.5	1.57
PHA-T50	50/50	49.6/50.4	1.52
PHA-T0	0/100	-	1.50

[a] Calculated from ^{1}H-NMR results.

Figure 2(A) displays the FT-IR spectra of PHA copolymers. All the polymers showed typical IR bands at 3409 cm^{-1}, 3400-3000 cm^{-1}, 1650 cm^{-1}, and 1511 cm^{-1} corresponding to

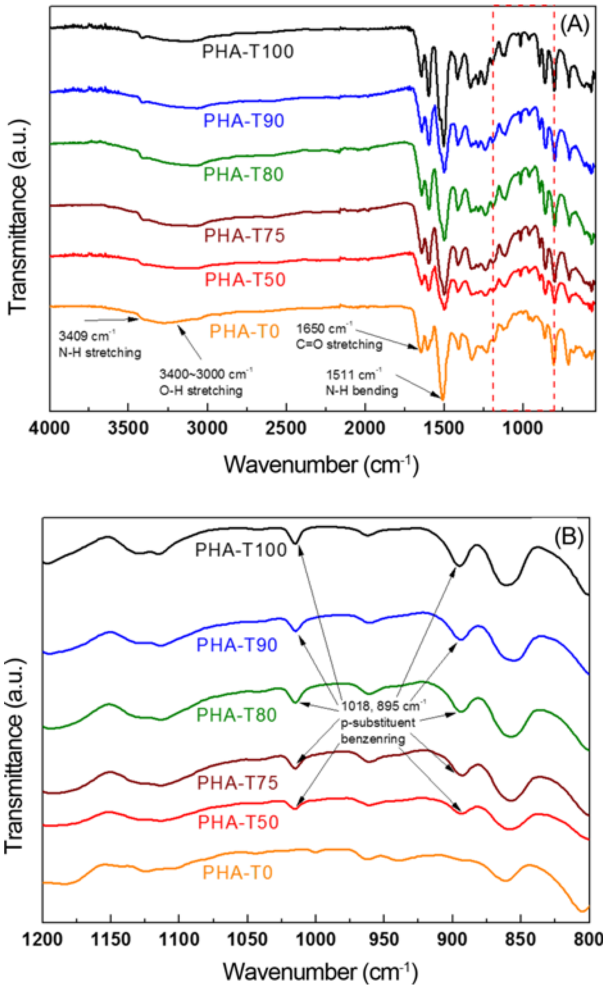

Figure 2. FT-IR spectra of PHA copolymers (A) and their expansion spectra between 1200 and 800 cm^{-1} (B).

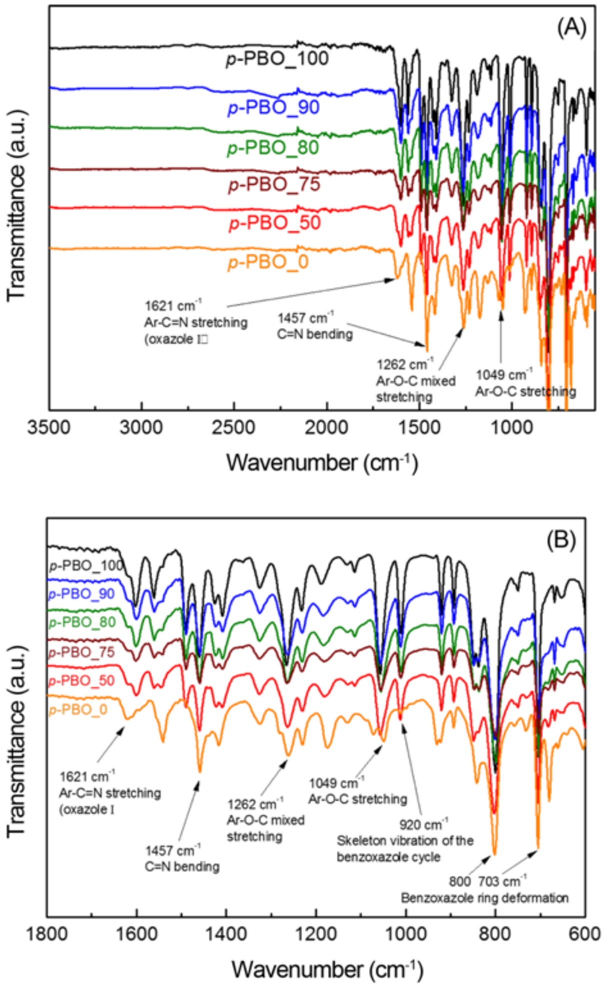

Figure 3. (A) FT-IR spectra of PBOs and its copolymer and (B) their expansion spectra between 1800 and 600 cm^{-1}.

Table 2. The FT-IR characteristic bands of PHA and PBO and their possible assignments

Wavenumber (cm^{-1})		Possible assignment of the bands
PHA	PBO	
3400-3000	-	O-H stretching
-	1621	Benzoxazole ring C=N stretching
1511	-	N-H bending
-	1049	Benzoxazole ring Ar-O-C stretching
-	800, 703	Benzoxazole ring deformation

N-H stretching, O-H stretching, amide C=O stretching, and aromatic N-H bending, respectively [19]. In order to identify the effects of IPC content in PHA copolymers, the high resolution FT-IR spectra were observed from 1200 to 800 cm^{-1} as shown in Figure 2(B). It was confirmed that two characteristic peaks of para substitution of benzene ring clearly indicated the absorption bands at 1018 cm^{-1} and 895 cm^{-1}, respectively [20]. The intensities of the two characteristic bands gradually decreased with an increment of IPC content in the copolymers and disappeared at the spectrum of PHA-T0.

Figure 3 shows the FT-IR spectra of PBO and its copolymers obtained through thermal cyclization of PHA copolymers. It was observed that the typical characteristic bands of PHA copolymers disappeared completely and the characteristic bands of the oxazole ring appeared at 1621 cm^{-1}, 1457 cm^{-1}, 1262 cm^{-1}, and 1049 cm^{-1} corresponding to Ar-C=N stretching (oxazole I bending, C=N bending, Ar-O-C mixed stretching, and Ar-C-O stretching, respectively) [21]. It means that PHA and its copolymers have been successfully converted to PBO and its copolymers after heat treatment. The FT-IR characteristic band assignments of PHA and PBO are summarized in Table 2.

Solubility Study of PHA and PBO Copolymers

The solubility results of the synthesized PHA copolymers

Table 3. The solubility results of the synthesized PHA copolymers and the converted PBO copolymers

Sample code	Polar solvents					Non-polar solvents	
	H_2SO_4	NMP	DMAc	DMF	DMSO	Chloroform	THF
PHA-T100	***	-	-	-	-	-	-
PHA-T90	***	*	*	-	-	-	-
PHA-T80	***	**	**	*	*	-	-
PHA-T75	***	**	**	*	*	-	-
PHA-T50	***	**	**	*	*	-	-
PHA-T0	***	**	**	**	**	-	-
PBO-T100	***	-	-	-	-	-	-
PBO-T90	***	-	-	-	-	-	-
PBO-T80	***	-	-	-	-	-	-
PBO-T75	***	-	-	-	-	-	-
PBO-T50	***	-	-	-	-	-	-
PBO-T0	***	-	-	-	-	-	-

***: soluble without LiCl, **: soluble with LiCl, *: partially soluble with LiCl, and -: insoluble.

and the converted PBO copolymers are listed in Table 3. As shown in Table 3, the copolymers were insoluble or partially soluble in NMP or DMAc when the TPC content was 90 % or higher, while they were readily soluble when the TPC content was reduced below 80 %. They were less soluble in DMF or DMSO as compared to NMP or DMAc. In case of chloroform and THF, all the polymers were insoluble. It is believed that the improvement of solubility of PHA copolymers with increasing IPC content is caused by the reduction of hydrogen bonding force and the chain packing efficiency in the main chain as well as the differences in the free volume between the para- and the meta- position on the benzene ring [22]. All the synthesized polymers were easily soluble in sulfuric acid regardless of the presence of the LiCl. Increased solubility could extend the application field to film, coatings, and blend.

Thermal Properties of PHA and PBO Copolymers

Figure 4 presents TGA and derivative TGA curves of PHA copolymers, where there shows a typical two-step weight loss during heating. The first weight loss in the range of 215-440 °C region was due to the thermal cyclization of PHA copolymers and the second one in the vicinity of 590-715 °C region was due to the thermal decomposition of PBO copolymers converted from PHA copolymers during heating [23]. It was observed that thermal cyclization temperature and decomposition temperature gradually shifted to lower temperature range with increasing IPC content in the copolymers, which was thought to be due to the structural characteristic of IPC and well consistent with the solubility test results. To evaluate the thermal stabilities of the converted PBO copolymers during heating PHA copolymer, TGA and derivative TGA curves of PBO copolymers are shown in Figure 5. The thermal degradation characteristics such as

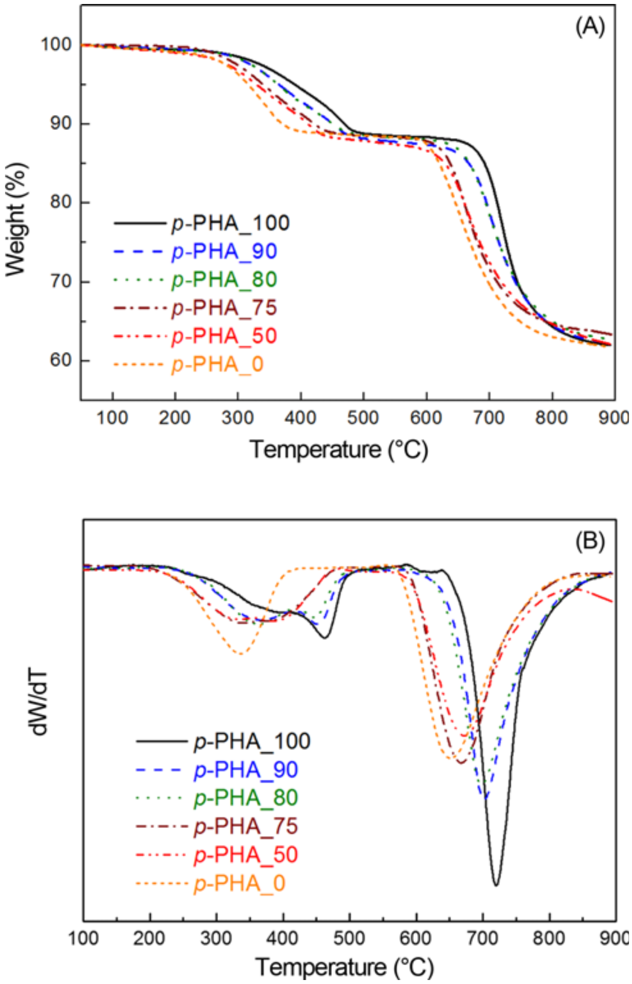

Figure 4. TGA (A) and derivative TGA curves (B) of PHA copolymers under nitrogen atmosphere.

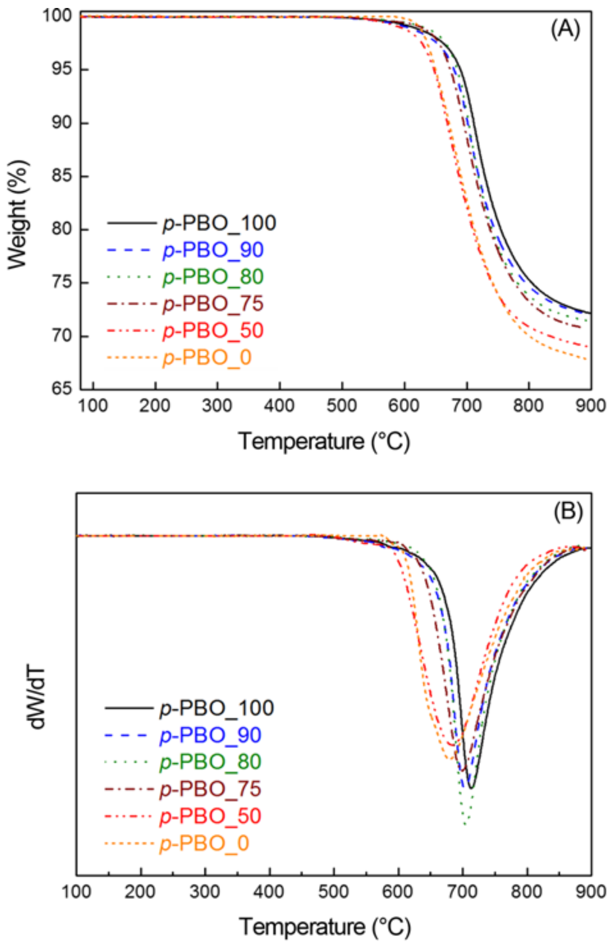

Figure 5. TGA (A) and derivative TGA curves (B) of PBO copolymers under nitrogen atmosphere.

Table 4. TGA results of PBO copolymers

Sample code	$T_{d5\%}{}^{a)}$ (°C)	$DTG^{b)}{}_{max}$ (°C)	$Char^{c)}$ (%)
PBO-T100	687.87	713.04	72.23
PBO-T90	683.31	703.06	72.11
PBO-T80	679.12	704.49	71.45
PBO-T75	668.88	696.34	69.79
PBO-T50	648.90	682.91	68.31
PBO-T0	646.04	675.17	67.67

$^{a)}$5 % weight loss temperature, $^{b)}$derivative TGA peak temperature, and $^{c)}$residue at 900 °C.

5 % weight loss temperature, DTG_{max} temperature, and char residue at 900 °C are listed in Table 4. There showed monotonic decrease of the thermal decomposition temperature and the char yields of the PBO copolymers with increasing IPC content in the PHA copolymers. Especially, 5 % weight loss temperature, DTG_{max} temperature, and char of PBO copolymers having IPC content of above 25 mol% were much lower than those of PBO-T100 about 20-40 °C, 17-30 °C, and 2-4 %, respectively. Considering solubility and thermal stability results, PHA-T80 is thought to be the promising candidate for a precursor polymer to PBO copolymer which has a good solubility in organic solvents and a reasonably low thermal cyclization temperature and good thermal stabilities as compared with PBO-T100.

Conclusion

We have successfully synthesized organic solvent-soluble PHA copolymers with different IPC content *via* low-temperature solution polycondensation in DMAc/LiCl solvent system, which can be used as precursors of PBO copolymers. ^{1}H-NMR results confirmed that the chemical shifts of all the protons were well consistent with the proposed structures of PHA copolymers. FT-IR spectra identified that the characteristic peaks of *p*-PHA and *p*-PBO copolymers distinctly revealed. The solubility results confirmed that PHA copolymers with a higher IPC content over 20 mol% could be readily dissolved in DMAc and NMP with the aid of LiCl. TGA results revealed that thermal cyclization temperature of PHA copolymers decreased with increasing IPC content, while the thermal stabilities of PBO copolymers decreased with IPC content increment. Considering solubility and thermal stability results, PHA-T80 was thought to be the promising candidate for a precursor polymer to PBO copolymer which had a good solubility in organic solvents and a reasonably low thermal cyclization temperature and good thermal stabilities as compared with PBO-T100. It was found that the incorporation of IPC in PHA copolymers could affect the solubility in organic solvents, the thermal cyclization behavior, and the thermal stabilities of both PHA and PBO copolymers.

Acknowledgements

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