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Study of the Miscibility of Hard and Soft Segments of Optically Active Poly(amide-imide-ether-urethane) Copolymers based-L-Leucine with Different Soft Segments

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Summary

Three series of new optically active poly(amide-imide-ether-urethane) (PAIEU) copolymers with different soft segments including polyethylene glycol (PEG), polypropylene glycol (PPG) or polytetramethylene glycol (PTMG) of molecular weight (MW) of 1000 were successfully synthesized. These copolymers were prepared via direct polycondensation reaction of an aromatic diacid based on L-leucine (1), 4,4'-methylene-bis-(4-phenylisocyanate) (MDI) (2) and different polyether polyols. FTIR spectroscopy shows the different absorption bands of NH, urethane and imide-I, II groups that suggests the different intermolecular interactions due to hydrogen bonding in these PAIEUs. On the other hand, DSC analysis reveals that the glass transition temperature for hard segments (Tgh) of PAIEUs based on polyethers with higher ratio of O/CH_2 is higher than that of polyethers with lower ratio of O/CH_2 and it decreases with the soft segment length in PAIEUs consisting of the same type of PEG soft segments.

Introduction

Polyurethanes (PU)s are becoming increasingly important as engineering materials, because they have excellent abrasion resistance and properties of both elastomers and plastics [1–4]. However, the conventional PUs, are known to exhibit poor resistance to heat, e.g. the acceptable mechanical properties (strength, modulus, etc.) disappear above 80–90 °C [5]. Therefore, the poor heat-resistance of PUs largely limits their applications as engineering materials [6]. Research focused on improving the thermal stability of PUs has been tried by various ways. Especially combination of existing polymers has offered a mean of engineering into novel materials having certain combination of desired properties exhibited individually by each polymer component. For example, one method to improve the thermal stability of PUs is the incorporation of highly thermally stable segments such as polyimide, polyamide, poly(amide-imide)s (PAI) or their oligomers in PU backbones [7–9]. These units can be injected into PU backbone by a one-shot or sequential method resulting in an imide (PIU), amide (PAU) or PAI modified PUs (PAIU), which the consequent improvements in thermo-mechanical properties of PUs have been reported [10,11]. The presence of amide and imide functions bring about some new interactions and inter-chain H-bonding that can affect phase mixing and thus, other properties of modified PUs.

It is generally agreed that the unique mechanical properties of PUs, compared with other elastomers, are the result of a two-phase morphology of soft and hard segments [12,13]. Depending on the relative compatibility of hard and soft segments, phase segregation or phase mixing will occur during processing and post cure annealing with the hard domains acting as physical crosslinks. Thus, study of structure property relationships in segmented PUs has acquired importance due to the broad range of applications of segmented PUs [14-16]. Even though the structure and property relationships of PIUs or PAIUs have obtained extensive attention, most of the studies focused only on the thermal properties of these copolymers having various kinds and contents of hard and soft segments, in which the compatibility between hard and soft segments, play an important role. Usually, thermal analysis such as differential scanning calorimetry (DSC) is an effective method to evaluate the microphase separation between hard and soft segments in PUs and modified PUs [17–19]. In addition FTIR spectroscopy can be used as a convenient technique for studying the miscibility between hard and soft segments [20].

In addition, the synthesis of polymers containing amino acids is a subject of much interest [21-23]. Since amino acids are naturally occurring compounds, synthetic poly(α-amino acid)s and their copolymers are expected to be biodegradable, biocompatible, and nontoxic [24]. More over, amino acid-based chiral polymers can induce crystallinity with the ability to form higher ordered structures that exhibit enhanced solubility characteristics [25-26].

In this paper, we present the synthesis and properties of PAIEU segmented copolymers from the reaction of NCO-terminated oligoamide prepolymers with different soft segments and compare the compatibility between hard segment including amide, imide functionalities and soft segments with FTIR spectroscopy and DSC technique.

Experimental

Chemicals

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co. (Darmstadt, Germany). MDI **(2)** (Aldrich, 98%) was used as received. PEG-400, 600, 1000, 2000 (Merck), PPG-1000 (Fluka) and PTMG-1000 (Merck) were dried under vacuum at 80 ^{o}C for 8 h. pyridine (Py), triethylamine (TEA) and *N*-methyl pyrrolidone (NMP) (Merck) were distilled under reduced pressure over BaO. bis(*p*-amido benzoic acid)-*N*-trimellitylimido-*L*-leucine (BPABTL) **(1)** was prepared according to the reported procedure [27]. The yield of the diacid **(1)** was 98.0%, m.p.> 275 ^{o}C (dec) and $[\alpha]_D^{25}$ = +17.6 [0.0520 g in 10 mL of *N*,*N*-dimethyl formamide (DMF)].

Measurements

Proton nuclear magnetic resonance ^{1}H-NMR (500 MHz) spectra were recorded on a Bruker (Germany) Avance 500 instrument in DMSO-d_6 at room temperature (RT).

Multipilicities of proton resonance were designated as broad (br), singlet (s), doublet (d), multiplet (m) and doublet of doublet (dd). FTIR spectra were recorded on a Jasco FTIR spectrophotometer. Spectra of solids were carried out using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon-Fensk Routine Viscometer (Germany). Specific rotations were measured by a Jasco Polarimeter. DSC data were recorded on a DSC-PL-1200 instrument under N_2 atmosphere by the Research Institute of Polymer and Petrochemical of Iran (IPPI). Glass transition temperatures (Tg) were read at the middle of the transition in the heat capacity taken from the heating DSC traces. A sample was first scanned from room temperature to 150 °C and maintained for 1 min. followed by quenching to -100 °C at a cooling rate of 10 °C/min, and then a second heating scan was used to measure sample's glass transition temperatures of soft (Tgs) or hard segments (Tgh), respectively. A heating rate of 10 °C/min was applied to all samples. Wide angle X-ray diffraction recorded at ambient conditions on a Zimence D-5000 using Ni filtered Cu Kα radiation by IPPI. The supplied voltage and current were set to 40 kV and 25 mA, respectively. Samples were run at a scan rate of 2ø = 5°/min between 2ø = 5 and 70 °.

Synthesis of PAIEUs

A typical preparation of PAIEUs is as follow: Into a dried 25 mL round bottom flask **(1)** (0.696 g, 1.3×10^{-3} mol) and **(2)** (0.641 g, 2.6×10^{-3} mol) were dissolved in 1 mL of NMP and Py (0.25 mL, 3.1×10^{-3} mol) was added. The mixture was stirred for 1 h at RT, and then the temperature was raised gradually up to 120 °C. After cooling to RT, PPG-1000 (1.281 g, 1.3×10^{-3} mol) in 2 mL of NMP was added. The reaction mixture was stirred at RT for 1 h then heated up to 120 °C gradually. The viscous solution was poured into 10 mL of water/methanol, to isolate the polymer. The polymer was dissolved in DMF and precipitated in water/methanol again. The precipitated polymer was collected by filtration, and was dried at 80 °C for 10 h under vacuum to give 1.31 g (72%) of polymer PP-2.

^{1}H-NMR Peaks (ppm) : 0.92 (d, CH_3, J = 12 Hz), 1.02 (d, CH_3, J = 6.80 Hz), 1.91-2.31 (m, CH, CH_2 , br), 3.36-3.45 (m, CH), 3.47-3.49 (m, CH_2), 4.71-5.04 (dd, CH), 7.61-8.51 (Ar-H), 10.25-10.87 (s, br, NH). FTIR Peaks (KBr, cm^{-1}): 3350 (m, br) NH ν, 3127 (w, br), 3415 (s, br), 3028 (w), 2969 (w), 2930 (w), 2871 (w), 1774 (w) C=O urethane [amide I (symmetric stretching, imide I)] (non-H-bonded), 1720 (s) C=O urethane [amide I (anti-symmetric stretching, imide I)] (H bonded), 1684 (s) C=O amide (I), 1638 (s), 1599 (s), 1537 (s) C-N ν + NH (amide II), 1509 (s), 1410 (m), 1378 (m) (CNC axial stretching, imide II), 1315 (m) C-N ν + NH (amide IV), 1258 (w), 1235 (w) C-N ν + NH (amide V), 1203 (w), 1176 (w), 1101 (w) C-O-C ether, 1081 (w) O=C-O-C urethane and (CNC transverse stretching, imide III), 1017 (w), 940 (w), 858 (w), 771 (w) O=C-O, 729 (w) (CNC out-of-plane bending, imide IV), 710 (w), 693 (w), 668 (w), 549 (w), 418 (w), 405 (w).

The reaction was performed with different polyether polyols of MW 1000 as well as PEGs with different MW, in the presence of different catalysts or in the absence of any catalyst. All the polymers showed FTIR characteristic absorption peaks of amide, imide and urethane groups around 3404, 3323, 1774, 1721, 1679, 1602, 1538 cm^{-1}, peculiar to NH, C=O and C-N vibrations of urethane, amide (I, II) and imide groups.

Peaks at 1408, 1315, 756, 771, and 720 cm^{-1} show the presence of imide heterocyclic ring in the polymer structure.

Results and Discussion

Polymerization

The PAIEU copolymers based on polyether polyols such as PEG-400, 600, 1000, and 2000 as well as PPG-1000, and PTMG-1000 were prepared according to scheme 1 by pre-polymerization method. The reactions were performed in NMP in the presence of different catalysts such as Py, TEA, dibutyltin dilurate (DBTDL) or without catalyst, respectively. The ratio of NCO to OH was kept 1:1. These method furnished PAIEUs whose polyamide-imide blocks are connected with urethane linkages (polymers 1-20, Tables 1-2). It can be seen that in the case of PEG-1000, PPG-1000 and PTMG-1000 viscosities were relatively comparable with that of Py and no catalyst conditions (Table 1). The polymerization reactions were repeated for different MW of PEGs and in the case of each PEG, two set of best conditions have been presented in table 2.

Table 1. Some Physical Properties of PAIEUs based Different Polyether Polyols of MW 1000 and Reaction Conditions in NMP as Solvent.

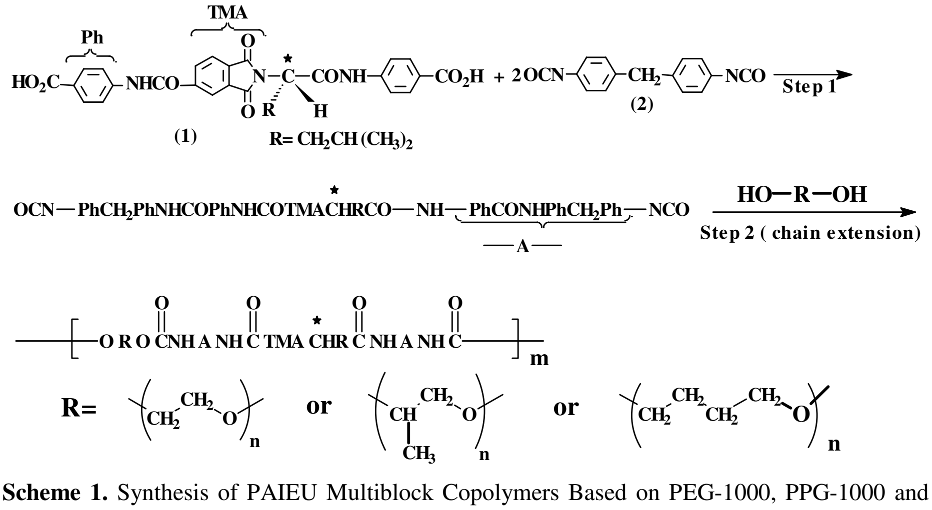
Polymer	Catalyst	Reaction condition (step 1)	Reaction condition (step 2)	yield (%)	η_{inh} (dL/g) [g]	[g] $[\alpha]_D^{25}$	[g, h] $[\alpha]_{Hg}^{25}$
PE1[a]	Py [d]	**A**	**B**	61	0.68	-3.02	-8.65
PP2[b]	Py	**A**	**B**	72	0.66	-1.77	-4.61
PT3[c]	Py	**A**	**B**	82	0.57	-0.90	-2.31
PE4	TEA[e]	**A**	**B**	80	0.54	+1.13	-2.15
PP5	TEA	**A**	**B**	70	0.43	-1.27	+0.52
PT6	TEA	**A**	**B**	67	0.45	-0.89	-14.62
PE7	DBTDL[f]	**A**	**B**	74	0.46	-0.93	-4.14
PP8	DBTDL	**A**	**B**	93	0.45	-2.87	+2.18
PT9	DBTDL	**A**	**B**	98	0.47	-1.06	+1.39
PE10	NO	**A**	**B**	68	0.58	-1.50	+2.45
PP11	NO	**A**	**B**	68	0.78	-2.87	+6.42
PT12	NO	**A**	**B**	81	0.55	-1.18	-7.47

[a]Poly(amide-imide-ether-urethane) based PEG-1000, the first PAIEU and etc. [b]Poly(amide-imide-ether-urethane) based PPG-1000, the 2nd PAIEU and etc. [c]Poly(amide-imide-ether-urethane) based PTMG-1000, the 3rd PAIEU and etc. [d] Pyridine. [e]Triethylamine. [f]Dibutyltin dilurate. [g]Measured at a concentration of 0.5 g/dL in 2% W/W LiCl/DMF as solvent. [h]Wide range was used (no filter was used for the Hg lamp), **A**: 1 h RT; 2h 50-60°C; 2h 60-80 °C; 4h 80 °C; 3h 80-100 °C; 2h 120 °C **B**: 1h RT; 2h 50-60°C; 2h 60-80 °C; 4h 80 °C; 2h 80-100 °C, 1h 120 °C.

Table 2. Some Physical Properties of PAIEUs based Different MW of PEG Polyether Polyols and Reaction Conditions in NMP as Solvent.

Polymer	Catalyst	Reaction condition (step 1)	Reaction condition (step 2)	Yield (%)	η_{inh} (dL/g)[d]	[d] $[\alpha]_D^{25}$	[d,e] $[\alpha]_{Hg}^{25}$
PE-40013[a]	Py[b]	**A**	**B**	60	0.55	-0.78	-3.61
PE-40014	NO	**A**	**B**	81	0.81	-1.55	+1.65
PE-60015	Py	**A**	**B**	66	0.52	-1.55	+1.65
PE-60016	NO	**A**	**B**	71	0.65	-1.22	-1.25
PE-100017	Py	**A**	**B**	61	0.64	-3.12	-8.67
PE-100018	NO	**A**	**B**	71	0.52	-1.23	+2.35
PE-200019	Py	**A**	**B**	68	0.51	-1.02	-2.55
PE-200020	DBTDL[c]	**A**	**B**	70	0.41	-1.97	-3.40

[a]Poly(amide-imide-ether-urethane) based PEG-400, the 13th PAIEU and etc (The numbers 400, 600, 1000 and 2000 represent PEG's MW). [b]Pyridine. [c] Dibutyltin dilurate. [d]Measured at a concentration of 0.5 g/dL in 2% W/W LiCl/DMF as solvent. [e]Wide rang was used (no filter was used for the Hg lamp), **A**: 1 h RT; 2h 50-60°C; 2h 60-80 °C; 4h 80 °C; 3h 80-100 °C; 2h 120 °C **B**: 1h RT; 2h 50-60°C; 2h 60-80 °C; 4h 80 °C; 2h 80-100 °C, 1h 120 °C.



Scheme 1. Synthesis of PAIEU Multiblock Copolymers Based on PEG-1000, PPG-1000 and PTMG-1000 or different MW of PEG by the Chain Extension of NCO-terminated Oligoamide-imide.

FTIR Study

The FTIR spectra of synthesized PAIEUs have been presented in figure 1. Stretching vibration of two carbonyls that are weakly coupled is present in the FTIR spectra around 1780-1700 cm^{-1} of all PAIEUs samples. The absorption bands at about 1775 and 730-720 cm^{-1} that are characteristic bands of imide bond (I, IV) verify that the imide groups have been introduced into the PU backbone. Imides-II, III and IV are assigned to axial, transverse, and out-of-plane vibrations of cyclic imide structure. The wave numbers for urethane, imide-I, II absorption bands vary with the type and MW of soft segments (Table 3). The urethane, imide-I bands for PAIEUs based PPG-1000, PTMG-1000, and PEG-1000 arise at a higher wave numbers, respectively, that can be related to the miscibility of hard and soft segments in the order of PAIEUs based PPG>PTMG>PEG. This order can be confirmed by the peak of NH and imide-II bands shifts, to higher wave numbers from PPG to PEG (Table 3). In copolymers with better hard and soft segment compatibility the urethane carbonyls form the hydrogen bonding with NH groups in the hard segments and increase the compatibility between the soft and hard segments, which results in the shift of the average position of the imide-I carbonyl's band to a lower wave numbers in FTIR spectra. The formation of the hydrogen bonding (intermolecular and/or intramolecular) influences the vibration of N–H bands, as listed in table 3 and shown in figure 1. It can be seen that, the N–H band shifts from 3470 cm^{-1} to 3350 cm^{-1} and 3340 for the respective PAIEUs based PEG, PTMG and PPG. This also indicates that H-bonding increased with the incorporation of amide and imide groups via BPABTL (1) compared with conventional PUs (C=O band at 1780 cm^{-1}). It can be concluded that different interactions exist between molecular chains in the PAIEUs with different type and MW of soft segments.

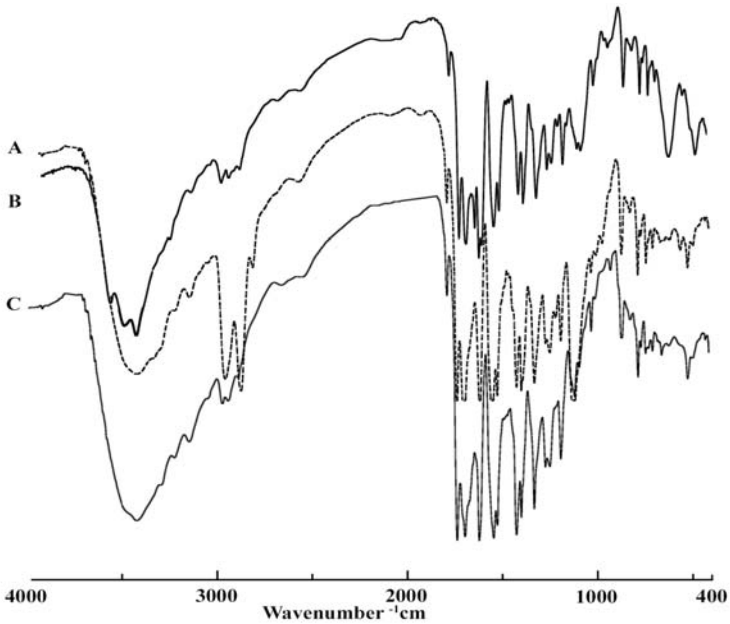


Figure 1. FTIR Spectra of PAIEUs with Different Soft Segments; (A) PP2, (B) PT3, (C) PE1.

It is inferred by comparing N-H stretching, C=O urethane (amide-I-imide-I), C=O amide–I, and imide-II band shifts, for PAIEUs based different MW of PEGs, there is some compatibility between hard and soft segments polyether–PUs with longer soft segments.

Table 3. FTIR Absorption Bands in Different PAIEUs, Wavenumber, Cm^{-1}.

Polymer	Polyol	Polyol MW	N-H Stretching	C=O Urethane (amide-I-imide-I)	C=O Amide -I	Imide-II
PE1	PEG	1000	3406	1776, 1722	1681	1384
PP2	PPG	1000	3349	1774, 1720	1684	1378
PT3	PTMG	1000	3398	1775, 1721	1680	1383
PE-40013	PEG	400	3474	1776, 1722	1682	1411
PE-60015	PEG	600	3474	1776, 1721	1680	1410
PE-100018	PEG	1000	3406	1776, 1720	1680	1384
PE-200019	PEG	2000	3346	1775, 1720	1678	1383

DSC Study

Thermal properties of PAIEUs were studied with DSC (Figures 2-3, Table 4). It can be seen that Tgs of PAIEUs consisting of the same type of PEG soft segments increased with the increasing of the length of the soft segments. Because Tgs in PU samples vary greatly, better information about interaction between soft and hard segments could be indicated by the changes in Tgh, specially by ΔTg = Tgh-Tgs. DSC data (Table 4) show that the Tgs of PAIEUs samples with different MW of PEGs were in the range of 33-90 ^{o}C. Comparing these transitions data, with Tg,s (ranging from -60 to -53 ^{o}C) and melting temperature (Tm) of pure PEGs (PEG-400; 4-8 ^{o}C, PEG-600; 17-22 ^{o}C, PEG-1000; 33-40 ^{o}C, respectively), great shifts to higher temperatures can be observed. Such results as well as decreasing ΔTg, indicate that the presence of BPABTL in PU backbone caused to more interaction and compatibility between hard and soft segments and more restriction of internal rotation in soft segments. Decreasing ΔTg, through PAIEUs based PEG, PTMG and PPG-1000, suggests domain separation according to PEG > PTMG > PPG. The distinct and sharp peak of PT3 at 140 ^{o}C compared to PP2 and PE-100018 suggests more crystalline structure for hard segment, and its more cohesiveness. Also it can be concluded from the sharp endotherm of PT3 at 26.8 ^{o}C, short range reorganization within the hard segment distributed in the soft phase and crystalline region of soft segment is more than that of PP2 and PE-18.

It is noteworthy to mention that according to our detailed study on the preparation of these kinds of modified PUs based different polyols, via introducing structures such as BPABTL, the morphology, phase miscibility, and other physical properties of these copolymers affected by polymerization reaction parameters, such as polymerization method, pre-polymerzation method and etc [28].

Table 4. DSC Data of PAIEUs with Different Soft Segments.

Polymer	Tgh[a] / Tmh[b]	Tgs[c] / Tms[d]	ΔTg = Tgh-Tgs
PE-40013	170 [a]	52 [c]	118
PE-60015	152 [a]	60 [c]	92
PE-100018	166 [a]	90 [c]	76
PT3	107 [a] / 140 [b]	26.8 [d]	70
PP2	80 [a]	26.4 [d]	54

[a] Glass transition temperature of hard segments (HS). [b] Melting transition temperature of crystalline domain of hard segments. [c] Glass transition temperature of soft segments (SS). [d] Melting temperature of crystalline domain of SS and /or crystalline microdomin of HS distributed in SS.

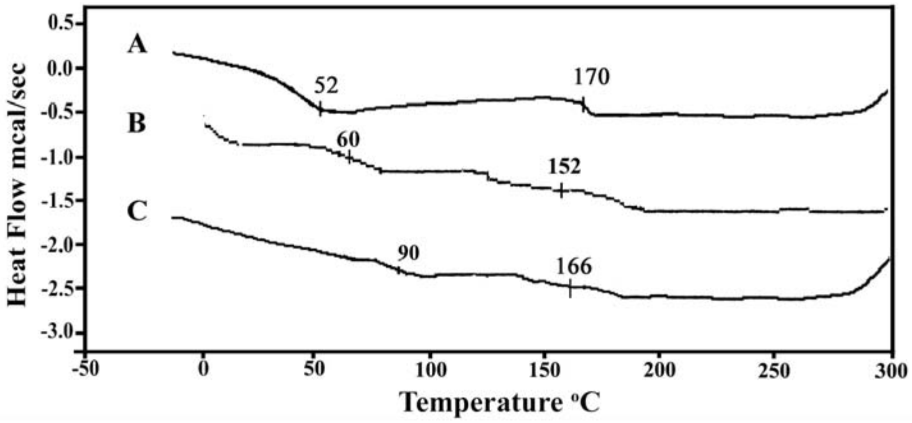


Figure 2. DSC Curves of PE-400-13 (A), PE-600-15 (B) and PE-1000-18 (C) under N_2 Atmosphere.

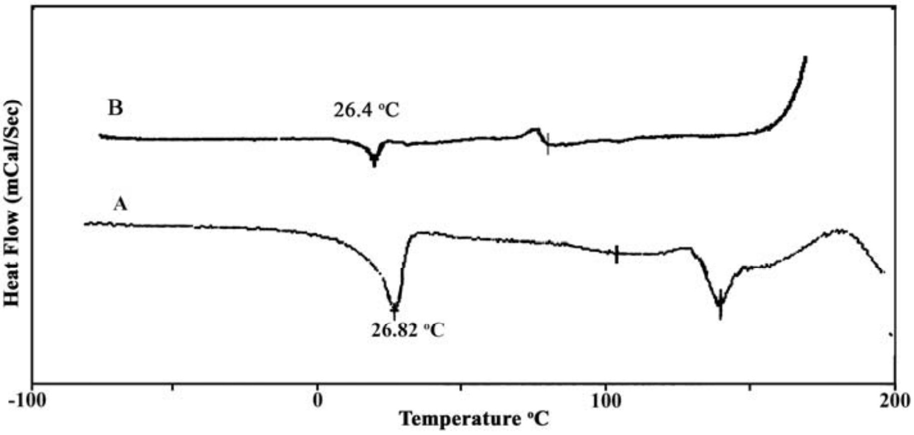


Figure 3. DSC Curve of (A)-PT3, and (B)-PP2.

Wide angle X-ray Diffraction Study (WAXS)

WAXS study for PAIEU based PTMG-1000 is presented in figure 4. The diffraction patterns for PT3 shows two main crystalline regions A and B divided into 1, 2, 3, 4 and 5 maxima as main peaks as well as amorphous region. The peaks at 2ø = 16.4, 21.2 and 24.1 (^{o}) that overlap with B region can be matched to literature values for MDI, MDI-O(CH$_2$)$_4$-O-, and PTMG crystallinity [29-31]. The other peaks can be due to BPABTL and MDI+BPABTL segments. It can be inferred that the introduction of BPABTL because of having planar structure as well as tacticity induced by chiral center has resulted in more crystallinity in new regions. The percentage of crystallinity obtained for PT3 at A and B regions is 5% and 66%, respectively.

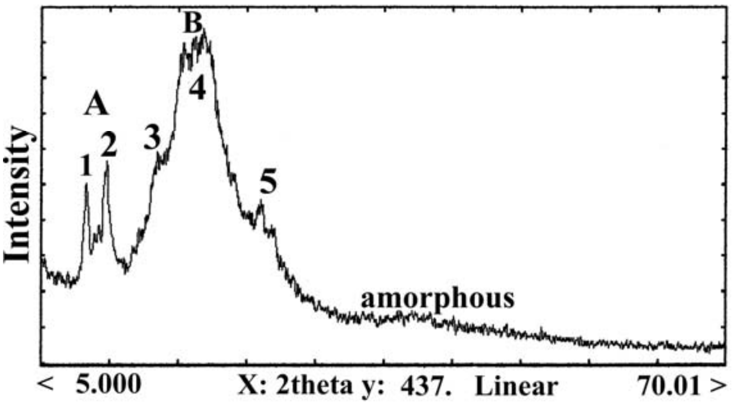


Figure 4. The Diffraction Patterns of WAXS Study for PT3.

As it can be seen the chiral center from amino acid moiety has induced crystallinity as well as optical activity in resulting copolymers. All the samples have shown optical rotation and expected to be environmentally degradable.

Conclusions

The DSC measurement's and FTIR spectroscopy results suggest that the soft segments become more compatible with the hard segments as their lengths are longer. These studies showed there is a different intermolecular interaction due to hydrogen bonding in these PAIEUs. On the other hand, the Tgh of PAIEUs based on polyethers with higher ratio of O/CH$_2$ as well as lower molecular weight, is higher than that of polyethers with lower ratio of O/CH$_2$. Also BPABTL containing preformed amide and imide functions, has caused to more interaction and compatibility between hard and soft segments and more restriction of internal rotation in soft segments.

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References

1. Keiji I.editor. (1987) Handbook of polyurethane resins, Japan: The Nikkan Kogyo Shimmbun Ltd, Chapter 1
2. Saunders JH, Frisch KC (1962) Polyurethane Chemistry; part I. New York: Interscience, Chapter 6
3. Legge NR, Holden E, Schroeder HE (1987) Thermoplastic elastomers. Meckel W, Goyert, W., Wider, W. editors. Munich: Hanser, Chapter 2
4. Comstock MJ, (1981) Urethane chemistry and application. ACS Symposium Series, Chapter 2: 172
5. Min Z, Tsutomu (1999) Polymer 40: 5153
6. Masiulanis B, Zielinski R (1985) J Appl Polym Sci 30: 2731
7. Masiulanis B, Zielinski R (1985) J Appl Polym Sci 30: 2731
8. Sendijarevic A, Sendijarevic V, Frisch KC (1990) J Polym Sci: Part A: Polym Chem 28: 3603
9. Liao DC, Heieh KH (1994) J Polym Sci: Part A: Polym Chem 32: 1665
10. Bogumila M (1985) J Appl Polym Sci 30: 2731
11. Radhakrishnan NP, Reghunadhan NCP, Francis DJ (1998) J Appl Polym Sci 70: 1483
12. Cooper SL, Tobolsky AV, (1966) J Appl Polym Sic 10: 1837
13. Kwei TK, (1982) J Appl Polym Sci 27: 2891
14. Gower LA, Lyman DJ (1995) J Po!vm Sci Polym Chem Ed. 33: 2257
15. Goddar RJ, Cooper SL (1995) Macromolecules 28: 1390
16. Chang SL, Yub TL, Huang CC, Chen WC, Linliu K, Lind TL (1998) Polymer 39: 3479
17. Lin MF, Shu YC, Tsen WC (1999) Polym Int 48: 433
18. Philip GT, Sultan NA, Padmanabha IN, Radhakrishnan G (2000) J Polym Sci, Part A: Polym Chem 38: 4032
19. Asai K, Inoue SI, Okamoto H (2000) J Polym Sci, Part A: Polym Chem 38: 715
20. Liu J, Ma D, Li Z (2002) Eur Polym J 38: 661
21. Mallakpour S, Shahmohammadi MH, (2005) Iran Polym J, 14 (5): 473
22. Mallakpour SE, Hajipour AR, Zamanlou MR (2002) J Polym Sci, Part A: Polym Chem, 22: 177
23. Mallakpour S, Rafiemanzelat F (2004) J Appl Poly Sci 93:1647
24. Okada M (2002) Prog Polym Sci 27: 87
25. Birchall AC, Bush SM, North M, (2001) Polymer 42: 375
26. Sanda F, Endo T (1999) Macromol Chem Phys 200: 2651
27. Mallakpour SE; Hajipour AR; Vahabi R (2002) J Appl Polym Sci 84: 35
28. Mallakpour S; Rafiemanzelat F (2005) Iran Polym J, Accepted for publication
29. Vasanthan, N.; Shin, D.; Tonelli, A. E. (1995) J Polym Sci Part B, Polym Physics 33 (9): 1385
30. Martin, D. J.; Meijs, G. F.; Renwick, G. M.; McCarthy, S. J.; Gunatillake, P. A. (1996) J Appl Polym Sci 62 (9): 1377
31. Quay, J.R.; Sun, Z.; Black, J.; Briber, R. M.; Thomas, E. L. (1990) Polymer 31 (6): 1003