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〈研究論文(學術)〉

Mesogen Unit를 포함하지 않는 Copolyurethane의 合成과 液晶性에 關한 硏究

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A Studey on the Synthesis and Physical Properties of Liquid-Crystalline Home and Copolyurethane Containing No Mesogenic Units.

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要 約

Mesogenic unit를 포함하고 있지 않는 1,4-phenylene diisocyanate, 2,6-bis(5-hydroxypentoxy) naphthalene, 1,4-bis(5-hydroxypentoxy)benzene을 重附加反應을 시킨 結果 生成된 co- polyurethane은 液晶性을 나타내었다. copolyurethane의 熱的 性質과 構造確認을 위하여 DSC, 編光顯微鏡, TG 및 FT-IR, ^{1}H-NMR로 測定하였다. DSC 測定結果 Tm및 Ti가 대부분 明確히 나타났다. 특히 液晶範圍는 copolyurethane은 homopolyurethane보다 약간 넓은 範圍에서 液晶性을 나타내었다. 예를 들면 copolyurethane(60/40) 및 homo- polyurethane(0/100)의 液晶 範圍는 각각 20℃ 및 11℃이다. 이러한 것은 homopolyurethane이 copolyurethane보다 熱的 安定性이 적다는 것을 나타낸다. 그리고 TG의 測定에서도 homopolyurethane보다 copolyurethane이 熱的으로 安定하다는 것을 알았다. 예를 들면 homopolyurethane(100/0) 및 copolyurethane(80/20)에서의 5% 에서의 TG 測定結果 각각 312℃ 및 327℃였다. 이러한 結果는 copolyurethane이 homopolyurethane보다 分子間 水素結合의 影響으로 熱的 安定性을 가져오는 것을 確認 할 수 있었다.

1. INTRODUCTION

Polyurethanes were prepared by a polyaddition reaction of diols and diisocyanates and they are unique polymers which have a wide range of application such as foams, coatings, adhesives, elastomers, and fibers because of their excellent properties. However, the mechanical properties are gradually diminish

above 100℃. The interaction between the hard and soft segments which usually provides the elastomeric properties are weakened, and then the breaking of urethane linkage takes place at about 200℃[1]. Some research group have reported the preparation and physical properties of a few liquid-crystalline polyurethanes comprised of rigid or mesogen unit in the main chain. Iimura and co-workers synthesized the liquid-crystalline polyurethanes for the first time[2]. After that, Tanaka, Nakaya, Kantor and co-workers reported the synthesis and the mesomorphic behavior of polyurethanes with biphenyl, azomethane or azobenzene moiety in the main chain[3-5]. Recently, Aharoni and co-workers reported liquid-crystalline polyamides containing no mesogenic core unit[6-7]. They revealed that the intermolecular hydrogen bond between amide groups plays an important role in regulation the mesomorphic behavior of polymers containing amide linkage.

In the previous paper, we reported that synthesis and thermotropic properties of a series of liquid-crystalline polyurethanes by a polyaddition reaction of para-substituted diisocyanate such as 1,4-phenylene diisocyanate (1,4-PDI) and 2,5-tolylene diisocyanate (2,5-TDI) with 2,6-bis(5-hydroxypentoxy) naphthalene or 1,4-bis(5-hydroxypentoxy) benzene[8-10].

In the present study, we report the synthesis and properties of a new series of thermotropic copolyurethanes by a polyaddition reaction of monomers 1,4-PDI with 2,6-bis(5-hydroxypentoxy) naphthalene (BHN5) and 1,4-bis(5-hydroxypentoxy) benzene (BHB5). These monomers having flexible spacers do not contain a rigid mesogenic core unit. The thermotropic liquid crystallinities of the synthesized polyurethanes were studied by using differential scanning calorimetry, a polarizing microscope equipped with a heating stage, and wide angle X-ray diffraction.

2. EXPERIMENTAL

Material : Diisocyanate monomer, 1,4-phenylene diisocyanate (1,4-PDI) was kindly supplied by Mitsui Toatsu Co., Ltd. This compound was used without further purification.

1,4-bis(5-hydroxypentoxy)benzene (BHB5) and 2,6-bis(5-hydroxypentoxy) naphthalene (BHN5). These compounds were synthesized by the methods reported in the literature[9-10].

Synthesis of homo- and copolyurethanes 1,4-PDI with BHN5 and BHB5 . copolyurethanes of 1,4-PDI with BHB5 and BHN5 were prepared as fellows : A mixture of BHB5 and BHN5 with a total amount of 0.003 mol was dissolved in 10 mL of dry DMF in a round-bottom flask. 1,4-PDI (0.500g, 0.003mol) dissolved in10 mL of dry DMF was added dropwise to the solution of 1,4-PDI under a dry nitrogen atmosphere at 60℃. The reaction mixture was maintained at 80℃ for 24 h. The reaction was allowed at 80℃ for 24 h. The copolymer was precipitated in methanol, filtered, then washed well with methanol, and dried under vaccum pump at 60℃ for 20 h. Yield : 90~95%.

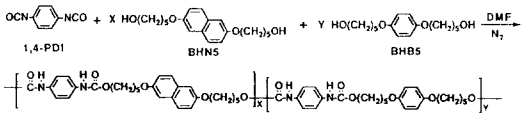
3. MEASUREMENTS

^{1}H-NMR spectra were obtained using DMSO-*d6* as the solvent by a JEOL JNM GX-270 spectrometer. Infrared spectra were taken by a Perkin Elmer FT/IR 1600 spectrometer. viscosities were measured at 25℃ with an ubbelohde viscometer in dichloromethane-trifluoroacetic acid (4:1, v/v) mixture solution of the polymer. Differential scanning calorimetry (DSC) experiments were performed on a Mettler DSC30. The scanning rate was 20℃/min. The maximum point of the endothermic was taken as the transition temperature. A polarizing microscope equipped with a Mettler FP82 hot stage was applied for visual observation. X-ray diffraction

measurements were carried out with a Rigaku RINT X-ray 2000 system using Ni-filtered Cu-Kα radiation. The thermogravimetric analysis was carried out by a Shimazu DT-40 at a heating rate of 10℃/min in air.

4. RESULT AND DISCUSSION

The general reaction equation and the structure of the various copolyurethanes 1,4-PDI with BHN5 and BHB5 are given in scheme 1. The original compositions of the starting material for the resulting homo- and copolyurethanes are summarized in Table 1. These copolyurethanes contained no mesogenic core unit in main chain. The reaction was allowed to proceed in dry DMF at 80℃ under dry nitrogen atmosphere for 24 h. The yields were 90~95%. The intrinsic viscosities of the polymers were within the range of 0.35~0.45 dL/g. The structure and composition of copolyurethanes were determined by ^{1}H-NMR and infrared spectra.



Scheme 1

Table 1. Synthesis of homo- and copolyurethanes based on 1,4-PDI, BHN5 and BHB5 by polyaddition reation[a])

Poly (x/y)	1,4-PDI (g)	mol ratio BHN5(g)	BHB5 (g)	Yield %	[η][b]) dl/g
Poly(100/0)	100[c])	100(1.038)	0	90	0.36
Poly(80/20)	100	80(0.830)	20(0.176)	90	0.46
Poly(60/40)	100	60(0.623)	40(0.353)	95	0.43
Poly(50/50)	100	50(0.519)	50(0.441)	95	0.42
Poly(40/60)	100	40(0.415)	60(0.529)	92	0.39
Poly(20/80)	100	20(0.208)	80(0.705)	93	0.41
Poly(0/100)	100	0	100(0.881)	92	0.35

a) 80℃, 24h., solvent : DMF, 20ml.
b) Intrinsic viscosity was measured in dichloromethane-trifluoroacetic acid(4 : 1 v/v) solution at 25℃.
c) Monomer weight(0.500g).

Fig. 1 shows 1H-NMR spectra of homo- and copolyurethanes. The spectra of polymers were obtained in a DMSO-d6 solution 30 and 100℃, respectively. For copolyurethane(B), a singlet N-H proton absorption of the urethane linkage was observed at 9.35 ppm because of the symmetric molecular structure. The structure was nearly identified by the peak area ratios between the aromatic and the aliphatic proton whose positions were 6.82~7.72, 4.08, 3.82, and 1.72~1.32 ppm, etc. Fig. 2 shows the infrared spectra of homo- and copolyurethanes within the range of 500/~4000 cm^{-1} at room temperature. Absorption peaks were characteristic of homo- and copolyurethanes. The N-H stretch bond of the urethane group in the region of 3200~3600 cm^{-1} and the carbonyl stretch band in the region of 1690~1720 cm^{-1} appeared in the spectra.

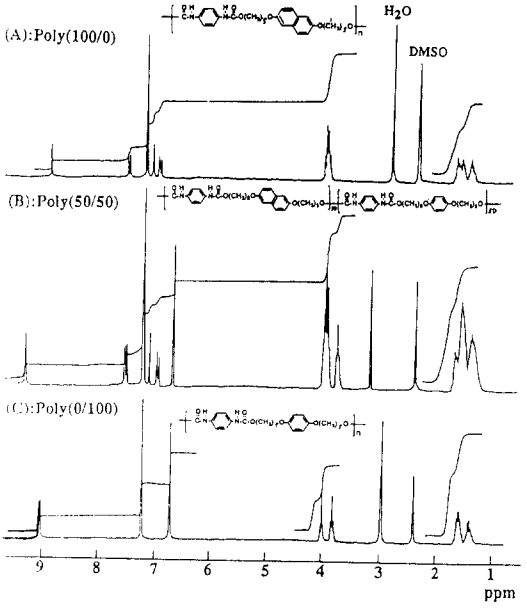


Fig. 1. ^{1}H-NMR spectra of (A) poly(100/0) in DMSO-*d6* at 100℃ and (B) poly(50/50) in DMSO-*d6* at 30℃ and (C) poly(0/100) in DMSO-*d6* at 100℃.

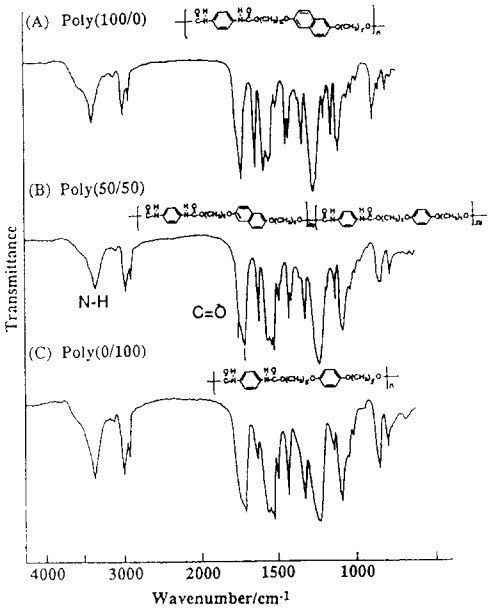


Fig. 2. IR spectra of (A) poly(100/0) and (B) poly(50/50) and (C) poly(0/100).

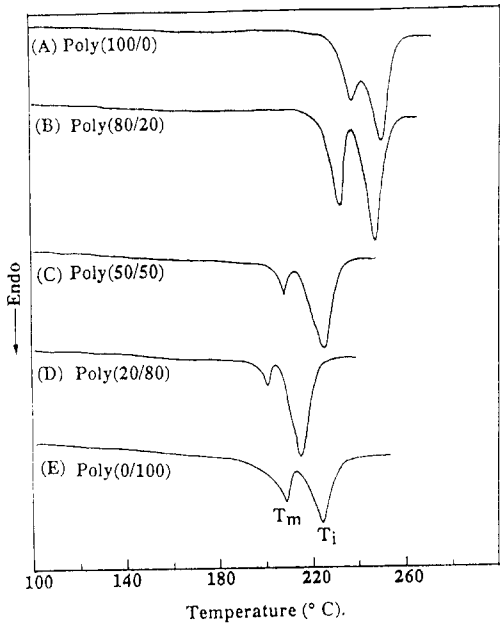


Fig. 3. DSC curves of homo- and copolyurethanes : rate : 20℃/min in second heating.

The liquid-crystalline properties of these polymers have been studied by DSC, polarized optical microscopy. In Fig. 3, the heating scans of DSC thermograms of homo- and copolyurethanes were shown, which were representative thermograms for the series of polymers. Polymer samples were heated to 30℃ above their melting temperatures and then cooled to room temperature for the DSC measurements. Two endothermic peaks were observed in the thermograms. The microscopic observation suggested that the two endothermic corresponded to melting and isotropization transitions, respectively. The thermal properties of copolyurethanes are listed in Table 2 where all of the copolyurethanes exhibited liquid-crystalline phases. The phase transition temperatures determined by the DSC method were correlated with the polarizing microscope observations and the phase transition enthalpies. A polarizing optical photomicrograph of copolyurethane (50/50) taken at 215℃ shows the existence of an anisotropic melt state at the temperature between two endothermic peaks (Fig. 4).

Table 2. Thermal properties for homo- and copolyurethanes based on 1,4-PDI, BHN5 and BHB5[a])

Poly (x/y)	BHN5/BHB5 mol ratio X : Y	Tm ℃	Ti ℃	Ti-Tm deg	△Hm J/g	△Hi J/g
Poly(100/0)	100 : 0	239	250	11	25.1	35.9
Poly(80/20)	80 : 20	231	248	17	20.1	44.4
Poly(60/40)	60 : 40	215	235	20	7.7	39.3
Poly(50/50)	50 : 50	208	226	18	4.8	34.3
Poly(40/60)	40 : 60	201	219	18	5.2	34.9
Poly(20/80)	20 : 80	198	215	17	3.5	38.2
Poly(0/100)	0 : 100	208	224	16	17.0	27.0

a) Transition temperatures were determined by DSC measurement with a heating rate of 20℃/min.

Fig. 4. Polarizing optical photomicrograph of thermotropic copolyurethane[poly(50/50)]. (Tm=208, Ti=226℃)

Threaded textures were observed for this copolymer. Homopolymer 1,4-PDI/BHN5 with naphthalene unit came from BHN5, and homopolymer 1,4-PDI/BHB5 with phenylene unit came from BHB5 exhibited liquid-crystalline properties within the range of 239~250℃ and 208~224℃, respectively. However, for example, in the case of copolymer(40/60) comprising the aromatic units came from BHN5 and BHB5, a little wider mesophase range as compared with those of the homopolymers was observed between 201℃ and 219℃. The mesophase temperature range (Ti-Tm) was 11 and 20℃. The widest range (20℃) was observed for copolyurethane(60/40). The copolyurethanes exhibited some what increasing tendency for temperature range of liquid-crystalline phase although the extent was not very remarkable (Fig. 5). For example, in the case of copolyurethane(40/50) comprising the aromatic units came from BHN and BHB5, a little wider mesophase range as compared with those of the homopolyurethanes. This indicated that the mesophase of the homopolyurethanes are more unstable than those of the copolyurethanes. It is worthwhile to point out that the clearing enthalpy (△Hi) is large than the enthalpy of fusion (△Hm) for homo- and copolyurethanes. Fig. 6 displays the X-ray powder pattern of homo- and copolyurethane (50/50) measured at room temperature. The diffraction patterns of all investigated homo- and copolyurethane differed slightly from each other. The highest crystallinity appeared in the homopolyurethanes, whereas the pattern of copolyurethane appear low crystallinity.

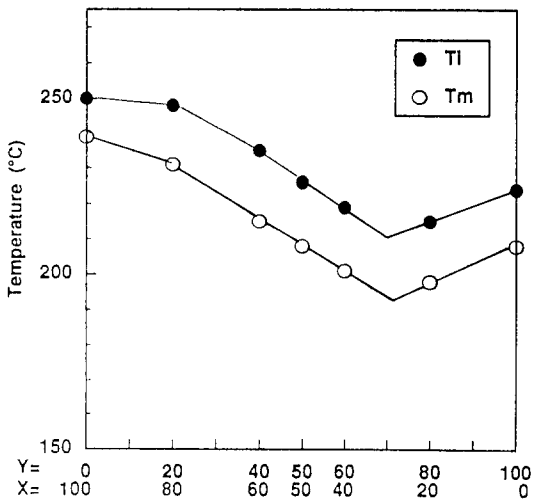


Fig. 5. Phase transition temperatures of thermotropic liquid crystalline copolyurethanes with various compositions.

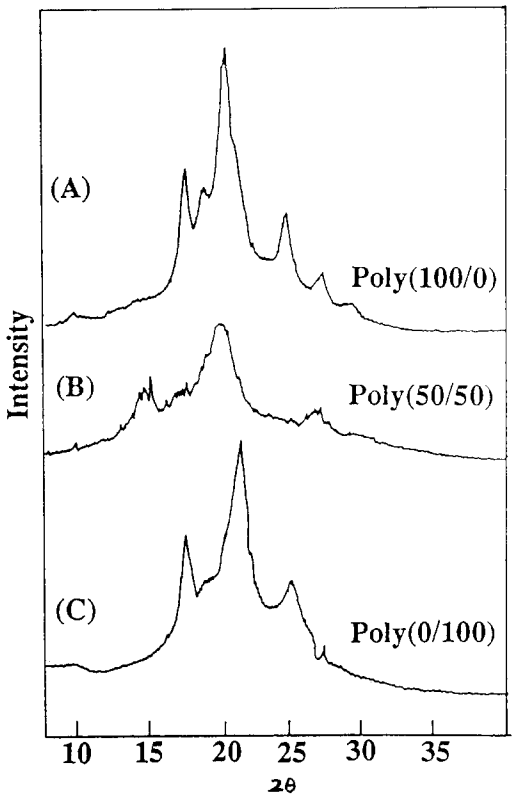


Fig. 6. Wide-angle X-ray diffraction pattern of homo- and copolyurethanes. (A) : poly(100/0) (B) : poly(50/50) (C) : poly(0/100)

This means that in the homo- and copolyurethanes the liquid-crystalline to isotropic state phase transition involved stronger intermolecular interaction due to hydrogen bonding of urethane linkages than the solid to liquid-crystalline phase transition. Schematic illustration of an anisotropic state proposed for the thermotropic copolyurethane is shown in Fig. 7. These copolyurethane showed liquid-crystalline properties, though for very repeating unit they were composed of nonmesogenic naphthalene and phenylene units that are connected by alkylene spacers. These results suggest that the mesomorphic behavior of the copolyurethanes is greatly dependent on the hydrogen bonds between the urethane linkage. Thermogravimetric analysis was performed for the polyurethanes. For homopolyurethane (1,4-PDI/BHN5) and copolyurethane (80/20), the temperatures of 5% weight loss in air were 312℃ and 327℃, respectively(Fig. 8). According of thermogravimetric results, homopolyurethanes and copolyurethanes were thermally stable up to around 310℃.

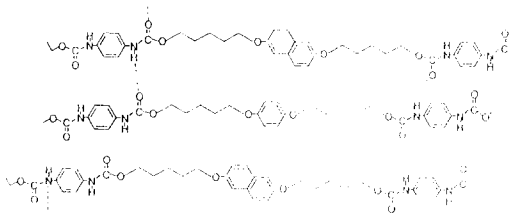


Fig. 7. Proposed structure for thermotropic copolyurethanes containing no mesogenic group.

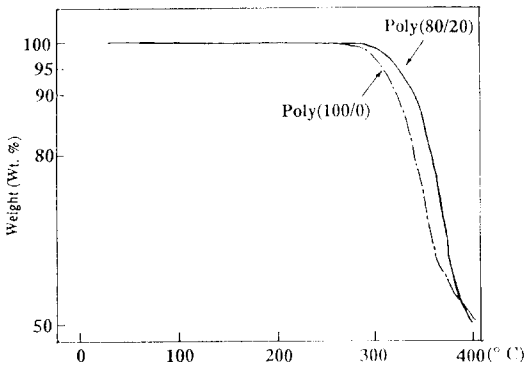


Fig. 8. Thermogravimetry conducted at a heating rate of 10℃/min in an air atmosphere.

5. CONCLUSIONS

Homo- and copolyurethanes were obtained by the reaction of para substituted monomer 1,4-PDI with BHN5 and BHB5. These copolyurethanes contained no mesogenic core unit in main chain. Melting and isotropization transitions are clearly observed in DSC thermograms. The copolyurethanes exhibited

somewhat increasing tendency for temperature range of liquid-crystalline phase although the extent was not very remarkable. According to the thermogravimetric results, homopolyurethanes and copolyurethanes were thermally stable up to around 310℃. Notwithstanding the absence of mesogenic unit in the copolyurethane, it is possible that by way of some intermolecular interaction such as hydrogen bonding, liquid crystallinity could be formed from the results of this work.

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