

NOTE

네마틱 폴리에스테르-수소화 폴리부타디엔의 블록 공중합체의 합성 및 성질

진 정 일 · 이 기 영 · 조 병 욱* · 심 홍 구**

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Synthesis and Properties of Block Copolymers Consisting of Nematic Polyester and Hydrogenated Polybutadiene Segments

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INTRODUCTION

Block copolymers consisting of incompatible blocks of hard and rubbery segments are known to exhibit unique biphasic morphologies which lead to materials being classified as thermoplastic elastomers.¹ These compositions have combined physical and mechanical properties of elastomers and thermoplastics. They usually possess excellent toughness and reveal very good recovery behavior. The hard segments form physical networks through the formation of glassy morphological domains. Styrene-isoprene-styrene and styrene-butadiene-styrene ABA block copolymers are representative thermoplastic elastomers commercially available.²

Recently, interest in liquid crystalline polyesters is rapidly increasing due to their many unique properties in mesophase as well as in solid.³⁻⁵ Some of thermotropic aromatic polyesters are in commercial production. We have been studying structure-property relationship of thermotropic polyesters containing flexible spacers.⁶ Liquid

crystalline properties of aromatic homo- and copolyesters also were subjects of our research.⁷

In this investigation block copolymers consisting of liquid crystalline polyesters and hydrogenated polybutadiene (PBDN) segments were prepared and their basic properties were studied.

— LC polyester block —

— hydrogenated PBDN block —

EXPERIMENTAL

Materials

All of the compounds including solvents were of reagent grade. Hydrogenated polybutadienes (GI2000-285A-1 and GI3000-319B-2-5) were kindly supplied by Nisso Co. (Japan). Thionyl chloride and some of the solvents such as reaction media were used after purification and drying according to the known methods.⁸

Synthesis of LCP

1,10-Bis (4-carboxyphenoxy) decane⁹ (6.624g : 0.016mol) was refluxed under a N₂ atmosphere for 4hrs in 30ml of thionyl chloride. Excess thionyl chloride was removed by vacuum distillation at room temperature. 1,10-Bis (4-chloroformylphenoxy) decane, thus prepared, was dissolved in 15ml of 1,1,2,2-tetrachloroethane (TCE). This solution was slowly added to a solution of 1,5-bis(4-hydroxyphenoxy) pentane(5.76g : 0.02mole) dissolved in 15ml of TCE. The solution was heated to 110°C. And then the reaction was allowed to proceed for 2.5 hrs at 110°C with a steady stream of N₂ gas bubbling through the reaction mixture. The precipitate was collected by filtration and washed with methanol.

Synthesis of Block Copolymers

Since the synthetic method was about the same for all of the block polymers investigated in the present work, only a representative procedure is described : Hydrogenated PBDN diol ($\bar{M}_n=2400$: 4.8g, 2.0mmole) and 1.001g(4.0 mmole) of MDI were reacted at 150°C for 30 min under a N₂ atmosphere. To this isocyanate-terminated PBDN polymer was added 5.4g (2 mmole) of the hydroxy-terminated LCP ($\bar{M}_n=2700$). Polymerization was conducted at 210°C for 2.5 hrs. Enough TCE was added to dissolve the formed polymer and The solution was poured into acetone. The precipitate was washed thoroughly with acetone and dried at 60°C under vacuum. The polymer yields ranged from 87 to 94%.

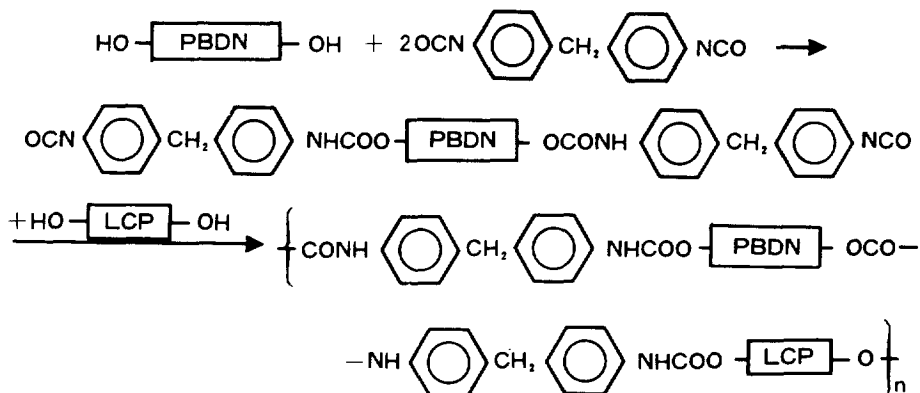
Characterization of Polymers

Inherent viscosities were determined at 30°C using a 0.4g/dl solution in TCE. The number average molecular weight(\bar{M}_n) of various polymers were measured on a Knauer vapor pressure osmometer at 56°C using TCE as a solvent. Benzil was employed as a standard material. IR spectra of the polymers were obtained on a Perkin Elmer IR Spectrometer 710 B. Transition temperatures were determined under a N₂ atmosphere on a Du Pont 910 DSC and Mettler DSC 3000 at a heating rate of 10°C / min.

Glass transition temperature, T_g, was taken as the temperature at which the initial slope change was observed on the DSC thermogram, while the peak maxima positions were taken as other transition temperatures, melting(T_m) and mesophase-to-isotropic transition temperatures(T_i). Optical textures of polymer melts were observed on a polarizing microscope(Leitz, Ortholux) equipped with a Mettler FP-5 hot stage.

RESULTS AND DISCUSSION

Hydroxy-terminated, hydrogenated PBDN prepolymer first was reacted with 4,4'-diphenylmethane diisocyanate(MDI) to convert the hydroxy endgroups to isocyanate groups. The polymer with isocyanate terminal groups thus prepared was reacted with pre-made liquid crystalline polyester (LCP) containing terminal hydroxy groups. The reaction scheme is the same as shown below.



Block Copolymers Containing Nematic Polyester Segment

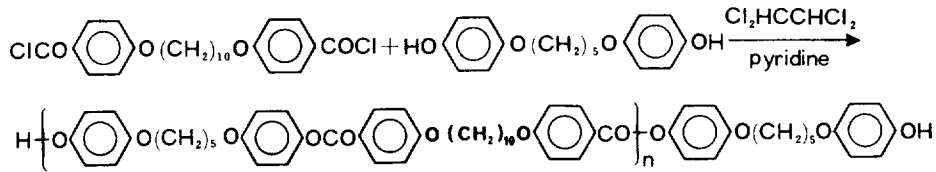


Table 1. General and Thermal Properties of Polymers

Block Copolymer	LCP				PBD			Block Copolymer				wt. % of PBD block
	\bar{M}_n^a (η^b)	T_g (°C)	T_m (°C)	T_i (°C)	\bar{M}_n^a (η^b)	T_g (°C)	Yield, wt. %	\bar{M}_n^a (η^b)	T_g (°C)	T_m (°C)	T_i (°C)	
BC-1	2,700 (0.22)	32	160	191	3,750 (0.099)	-34	94	11,500 (0.56)	-30, 22	165	206	58
BC-2	2,700 (0.22)	32	160	191	2,400 (0.076)	-37	88	11,500 (0.63)	-30, 27	169	205	47
BC-3	4,700 (0.33)	34	169	204	2,400 (0.076)	-37	87	21,000 (0.73)	-18, 22	174	214	34

^a Measured on a vapor pressure osmometer at 56°C.

^b Measured on a 0.4 g/dl solution in TCE at 30°C.

The LCP used in this investigation was prepared via the route shown above.

Three different compositions of block copolymers were prepared from LCP and PBDN prepolymers whose properties are summarized in Table 1. The two LCP prepolymers used in the preparation of block polymers had \bar{M}_n of 2,700 or 4,700. The glass transition temperature (T_g) of LCP was 32°C for low MW prepolymer and 34°C for high MW one, while that of PBDN was much lower, -37 or -34°C depending on \bar{M}_n . LCP polymers were thermotropic, nematic and exhibited melting as well as isotropization transitions. The values

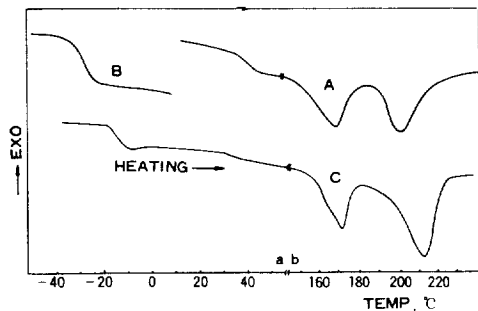
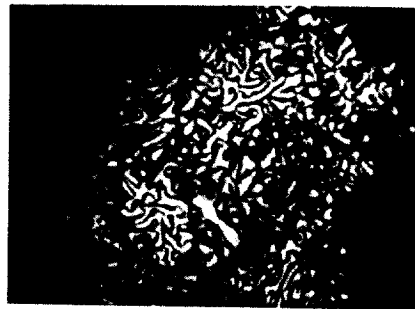
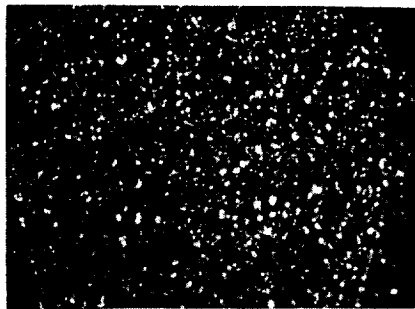


Fig. 1. DSC thermograms of LCP(A), hydrogenated PBDN(B) and block copolymer BC-3(C).



(A)



(B)

Fig. 2. Photomicrographs of LCP taken at 170°C (A) and block copolymer BC-1 taken at 192°C (B) (magnification 150x).

of T_m and T_i for high MW LCP were slightly higher than those for low MW LCP, which is a general phenomenon for most of the relatively low MW polymers.

Block copolymers(BC) were obtained in satisfactory yield, 87-94%. Much enhanced MW's of the final polymers compared with those of the starting prepolymers can be taken as a proof that we indeed were able to make block copolymers. According to the MW's of final block copolymers and the two starting prepolymers, it appears that BC-1 and BC-2 were approximately of ABAB tetra block on an average and BC-3 was of ABABAB. For the preparation of block copolymers, 1 : 1 mole ratio of LCP and PBDN was utilized. Figure 1 shows DSC thermograms of LCP (\bar{M}_n : 4,700), hydrogenated PBDN (\bar{M}_n : 2,400) and BC-3. We can clearly see two glass transitions at -18 and 28°C , and T_m and T_i at 174°C and 214°C , respectively, for BC-3. The values of T_m and T_i were confirmed by microscopy. The results of DSC analyses of block copolymers are tabulated in Table 1. In general, T_g 's of the rubber segments were slightly raised by the formation of a block structure, while those of LCP segments were slightly reduced.

We can think of two possible reasons for such shift in T_g values. The first one is a partial compatibility of the two segments which was proved by two different experimental observations : partial miscibility of polymer solutions in TCE and shift in T_g values on DSC analyses of the polyblends of the two prepolymers. The second reason is the formation of interfacial zone between rubber and LCP domains, which, in turn, influences the free volume of each segment. The latter theory

was put forward separately by Imai, et al.¹⁰, Baers,¹¹ and Couchman and Karasz¹² for the glass transition behavior of block copolymers consisting of hard segments and soft segments.

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