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SYNTHESIS OF POLYURETHANES BEARING FLUORENE MOIETIES

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ABSTRACT

Several new polyurethanes bearing fluorene moieties were prepared by addition polymerization of bisphenoxyethanolfluorene (BPEF) with diisocyanates such as hexamethylene diisocyanate (HDI), 2,4-tolylene diisocyanate (TDI), and m-xylylene diisocyanate (XDI), respectively. The resulting polyurethanes, BPEF-HDI (**PU1**), BPEF-TDI (**PU2**), and BPEF-XDI (**PU3**), have the number average molecular weight $\overline{M}n$ of 11000, 9600, 14000 and intrinsic viscosities [η] of 0.142, 0.085, and 0.120 $dL \cdot g^{-1}$, respectively. Moreover, all of the resulting polymers could form brittle transparent films.

INTRODUCTION

There is considerable interest in polyurethanes, because polyurethanes are a versatile class of polymers with a variety of applications such as in biomedical implants, in electronic industry as transparent electric conducting films, and as organic semiconductor, organic ultraconductor, liquid

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crystalline materials, photo sensitive or therm sensitive materials. They are also used as adhesives, coatings, fibers, elastomers, foams and synthetic leather etc.[1-4]. The properties of polyurethanes can be tailored by varying the components from which they are constructed: rigid diols, flexible polydiols and polyisocyanates, respectively. We have recently reported some new polyurethanes based on phospholipid analogs [5-8], In this approach, we will report the synthesis and film-forming behavior of several new polyurethanes bearing fluorene moieties.

EXPERIMENTAL

Materials and physical measurements

Chlorobenzene, N,N-dimethylformamide (DMF), acetone, diethyl ether, methanol, hexamethylene diisocyanate (HDI), 4-methyl-1,3-phenylene diisocyanate (2,4-tolylene diisocyanate, TDI), and m-phenylenedimethyl diisocyanate (m-xylylene diisocyanate, XDI) were commercially obtained and purified by vacuum distillation. Bisphenoxyethanolfluorene (BPEF) was obtained from Osaka Gas Co., LTD. Japan and used as received.

IR spectra were recorded on a Jasco A 202 spectrometer. Viscosity measurements were performed in DMF at 30°C using an Ubbelohde dilution viscometer. Gel permeation chloromatography (GPC) measurements were carried on a HLC802UR GPC instrument with G4000H8 + G2000H8 columns, the samples were dissolved in DMF and using polystyrene as standard. The polarization microscopy measurements were carried out with a polarizing microscope with a Yanaco Model MP heating stage.

The polyurethanes were all synthesized by similar methods, therefore a representative synthesis is shown.

Polyurethane (**PU1**): Into a 300-cm^3 round-bottomed flask, equipped with a reflux condenser with a drying tube and a mechanical stirrer, were placed 4.38 g (10.0 mmol) of **BPEF**, 1.68 g (10.0 mmol) of HDI in 100 cm^3 of DMF under a nitrogen atmosphere. The mixture was stirred at 100 °C for 4 h. At the end of the reaction, the mixture was concentrated to one third of its original volume. The concentrate was poured into 200 cm^3 of diethyl ether by which polymer **PU1** precipitated. It was washed by diethyl ether three times.

White solid. mp.: 90-95°C. Yield: 3.81 g (62.8%).

IR (KBr): 3300 (-NH-), 2950, 1440, 750 (-CH_2-), 1710 (-CONH-), and 1600, 820 cm^{-1} (-C_6H_4-).

TABLE 1. Polyurethanes synthesized from **BPEF** and diisocyanates (HDI, TDI, XDI)[a)]

PU	amount in g				yield	Mn	$[\eta]$/dL·g^{-1}
	BPEF	HDI	TDI	XDI			
1	4.38	1.68			62.8	11000	0.142
2	4.38		1.74		67.5	9600	0.085
3	4.38			1.88	65.5	14000	0.120

[a)] Reaction conditions, N,N-dimethylformamide as solvent, 100°C; 4 h. HDI: hexamethylene diisocyanate, TDI: 2,4-tolylene diisocyanate, XDI: m-xylylene diisocyanate.

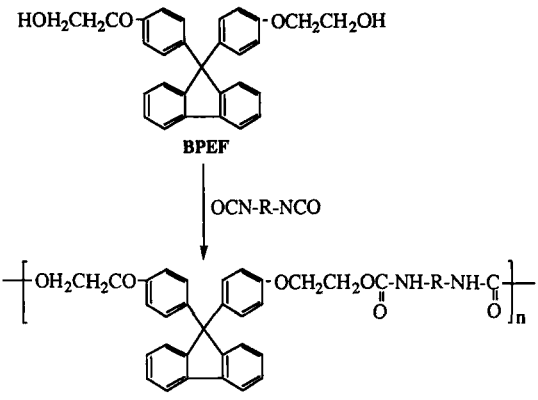
$(C_{37}H_{38}N_2O_6)_n$ $(606.7)_n$. Calculated: C, 73.25; H, 6.31; N, 4.62%. Found: C, 73.22; H, 6.30; N, 4.65%.

Using the same procedure as described for the preparation of polyurethane **PU1**, the reaction of **BPEF** with TDI, or XDI (mole ratios 1:1, respectively), in dry DMF at 100 °C for 4 h, afforded polyurethanes **PU2** and **PU3**, respectively. These results are summarized in TABLE 1.

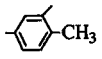
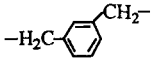
RESULTS AND DISCUSSION

The bisphenoxyethanolfluorene (BPEF) containing fluorene moieties was obtained from Osaka Gas Co., LTD. Japan, the structure of BPEF and resulting polyurethanes is outlined in Scheme 1:

Polyurethanes **1-3** were synthesized by reaction of BPEF with diisocyanates such as hexamethylene diisocyanate (HDI), 2,4-tolylene diisocyanate (TDI), and m-xylylene diisocyanate (XDI), respectively. Polyurethanes were obtained at 100 °C in DMF or chlorobenzene in the absence of any catalyst. All of the resulting polyurethanes were soluble in DMF and acetone when being slightly heated but insoluble in methanol and diethyl ether. In addition, all of synthesized polyurethanes formed transparent films from the corresponding warm acetone casting solutions on the glass plates, although the obtained films were brittle. The synthesized polyurethanes were characterized by their IR and elemental analyses. Element analyses of the resulting polyurethanes were in good agreement with theory. The IR spectra of polyurethanes **1-3** are shown in Figure 1. As can be seen, adsorption bands due to -NH- at 3300, -CH_2- at 2950, 1440, 750, -CONH- at 1710, and -C_6H_4- at 1600, 820 cm^{-1} appeared respectively. During the preparation of the polyurethanes, DMF was found to be a better solvent than chlorobenzene, because the residual NCO peak at 2260 cm^{-1} on the IR spectra of the resulting polymers was found when the chlorobenzene was used as solvent but DMF was not under the same reaction condition.



PU 1-3

	PU1	PU2	PU3
R	-$(CH_2)_6$-		

SCHEME 1. Synthesis of polyurethanes bearing fluorene moieties

Viscosity measurements on the polyurethanes were performed in DMF at 30 °C. The polyurethanes **1-3** had the intrinsic viscosities [η] of 0.142, 0.085, and 0.120 $dL \cdot g^{-1}$, respectively.

Gel permeation chromatography (GPC) measurements of these polyurethanes were carried out. From the relationship between retention time and molecular weights derived for narrow-distributed standard polystyrene, the number average molecular weights of polyurethanes **1-3** were 11000, 9600, and 14000, respectively.

The thermal properties of the resulting polymers were studied by polarizing microscopy. The polarization microscopy measurements were carried out with a polarizing microscope with a Yanaco Model MP heating stage. The melting points of polyurethanes **1-3** were 90-95, 60-65, and 65-70 °C, respectively. Moreover, the polyurethane **1** was found to exhibit slight liquid crystalline behavior from room temperature to 90°C but polyurethanes **2** and **3** were not.

CONCLUSION

Several new polyurethanes bearing fluorene moieties were synthesized by addition polymerization of

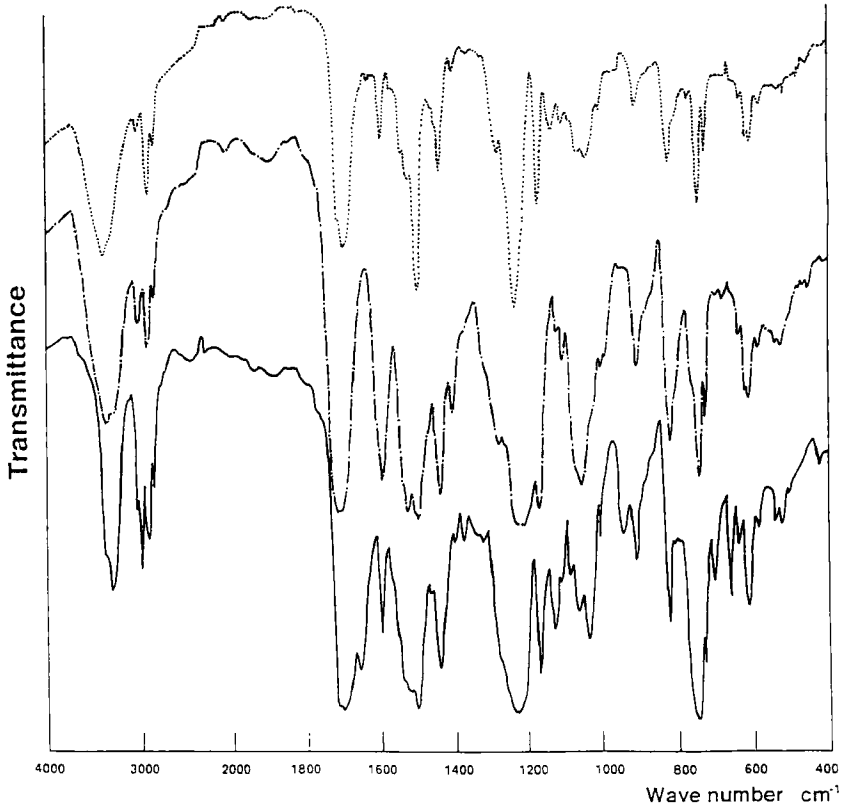


Figure 1. IR spectra of **PU1** (---), **PU2** (-·-), and **PU3** (—)

bisphenoxyethanolfluorene with diisocyanates such as hexamethylene diisocyanate, 2,4-tolylene diisocyanate, and m-xylylene diisocyanate, respectively. The number average molecular weights of resulting polyurethanes were in the range of 9600 to 14000 and all of the resulting polymers could form brittle transparent films.

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