

Notes

**A NEW OPTICALLY ACTIVE POLYURETHANE DERIVED FROM
CHIRAL (2R, 3R) (+)-DIETHYL L-TARTRATE AND DIISOCYANATE***

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Abstract Optically active polyurethane was synthesized by the polyaddition of (2R, 3R)-(+)-diethyl L-tartrate (DET), 4,4'-diphenylmethane diisocyanate (MDI) and polyethylene glycol (PEG) with various molecular weights at 60°C in DMSO. The polymers were characterized by specific rotation, DSC and ¹H NMR spectra.

Keywords (2R, 3R)-(+)-Diethyl L-tartrate, Optically active polyurethane

INTRODUCTION

Okamoto et al. have reported the synthesis of optically active polytriphenylmethyl methacrylate (PTrMA) by chirally anionic complexes^[1], which were used as chiral stationary phase in high performance liquid chromatography (HPLC) for resolving various racemic compounds^[2]. However, when methanol was used as an eluent, the ester groups on PTrMA were slowly solvolyzed to form methyl triphenylmethyl ether^[3]. In order to diminish this defect, a new poly(triarylmethyl methacrylate) with electron-withdrawing substitutes on the phenyl ring of the trityl group was reported^[4]. In addition, the optically active polyurethane as chiral stationary phase was conducted for resolving racemic compounds in HPLC. Goodman *et al.*^[5] and Green *et al.*^[6] have synthesized optically active poly[(S)-(+)-2-methylbutyl isocyanate] and poly[(S)-2,2-dimethyl-1,3-dioxolane-4-methylene isocyanate] from corresponding monoisocyanates monomers which contain asymmetric carbon atoms in their side chain, respectively. Kobayashi *et al.*^[7] also reported that optically active polyurethanes obtained from the reaction of (1S, 3S)-diphenyl propanediol, (2R, 4R)-pentanediol and diisocyanates have been applied as the stationary phase of high performance liquid chromatography (HPLC) to separate racemic compounds. Cognet-Georjon *et al.* reported that optically active polyurethane obtained from 1,4 : 3,6 dianhydrosorbitol, 4,4'-diphenylmethane diisocyanate (MDI) and poly(tetramethylene glycol) (PTHF)^[8] was used in pharmaceuticals separation. In this paper, the optically active polyurethane was synthesized from the reaction of optically active short chain diol, i.e. (2R, 3R)-(+)-diethyl L-tartrate, MDI and poly(ethylene glycol) with various molecular weight and was characterized by specific rotation, DSC and ¹H-NMR spectra.

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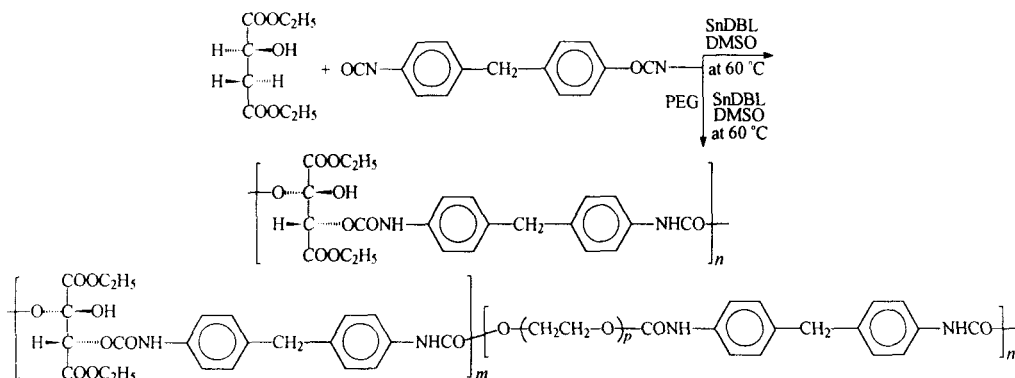
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EXPERIMENTAL

Optically Active Polyurethane

The synthesis of optically active polyurethane was described in Scheme 1.



Scheme 1 Preparation of optically active polyurethane

The reaction was carried out in a 100 mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser under inert atmosphere, (2R, 3R)-diethyl L-tartrate (DET) (Fluka Chemika) and poly(ethylene glycol) (PEG) together with 4,4'-diphenylmethane diisocyanate (ACROS Organics) were dissolved in DMSO. The flask was then placed in a thermoregulated oil bath. After the solution reached the desired reaction temperature, the catalyst, dibutyltin dilaurate (SnDBL) was added using a hypodermic syringe. After a short interval the polymer was precipitated from methanol, filtered and dried under vacuum. ¹H-NMR (DMSO-*d*₆) for sample **02**: δ 1.05~1.23 (*m*, -CH₃), 2.45~2.50 (*m*, -CH₂-), 2.8 (*s*, -CH₂-ary), 4.05~4.15 (*m*, =CH-), 7.05~7.4 (*m*, ary); for sample **06**: δ 1.05~1.23 (*m*, -CH₃), 2.45~2.50 (*m*, -CH₂-), 3.8 (*s*, -CH₂-ary), 3.5 (*s*, -CH₂OCH₂-), 4.05~4.15 (*m*, =CH-), 7.05~7.4 (*m*, -C₆H₄), 9.7~9.8 (*s*, -NH-).

Polyurethane Characterizations

Glass transition temperatures were determined by DSC on a Shimadzu DSC-41 model apparatus under nitrogen using a heating rate of 20 °C/min. ¹H-NMR spectra were recorded with a Varian XL-200 (200 Hz) on deuterated DMSO solution at 45 °C with TMS as the internal standard. Specific rotation was measured by WZZ-15 spectropolarimeter at 25 °C.

RESULTS AND DISCUSSION

In the polyaddition reaction of (2R, 3R)-(+)-diethyl L-tartrate (DET), two factors could effect the reactivity of hydroxyl group towards diisocyanate: the intramolecular hydrogen bond between the hydroxyl and CO groups on DET, and the steric hindrance of ester groups on DET react the same way as the hydroxyl group on isosorbite towards diisocyanates^[9]. Therefore, the obtained polyurethanes would have lower specific viscosities as shown in Table 1. It is very interesting to inspect the chiral feature of the optically active polyurethanes obtained. The specific rotations of hard-segmented polyurethane has negative values, distinguishing itself from the positive values of the fraction of the polyurethane composite, (2R, 3R)-(+)-diethyl L-tartrate ($[\alpha]_D^{25}$, +26°). The block polyether-polyurethane with soft-segmented PEG has positive optical activity, which is different from that of the hard-segmented polyurethanes. Therefore, the polycondensation process is very complex. Thiem *et al.*^[10] reported that the optically active polyesters obtained from 1,4 : 3,6-dianhydro-D-sorbitol (DAS) with exo- and endo- hydroxyl group and terephthalic acid dichloride would have positive or negative specific rotation due to change of main configuration

Table 1 Synthesis and characterization of optically active polyurethane^a

Run No.	DET (mol)	MDI (mol)	PEG (mol)	<i>T</i> (°C)	<i>t</i> (h)	Yield (%)	η_{sp}/C^b (dL/g)	<i>T_g</i> (°C)	$[\alpha]_D^{25c}$
01	1.00	1.00	0	65	20	94.0	0.17	—	-36.0°
02	1.00	1.00	0	60~65	24	81.0	0.14	136.8	-34.0°
03	0.74	1.00	0.26(600)	60~65	48	76.7	0.12	—	+17.0°
04	0.82	1.00	0.18(600)	60~65	48	55.0	—	20.4	+16.7°
05	0.86	1.00	0.14(1000)	65	24	44.0	0.16	—	+27.1°
06	0.86	1.00	0.14(1000)	63	24	87.0	0.09	-9.1	+35.2°
07	0.87	1.00	0.13(1000)	60~65	48	71.3	0.08	—	+34.2°
08	0.92	1.00	0.08(2000)	60~65	48	69.3	—	-12.2	+33.0°
09	0.84	1.00	0.16(2000)	60~65	47	40.5	—	—	—

a) Polymerization condition: solvent, DMSO; *C* = 0.66 mol/L; catalyst, dibutyltin dilaurate (SnDB);

b) 0.5g/dL in DMF; c) $[\alpha]_D^{25}$ unit: deg · cm²/g in DMF, at 25°C; *C* = 0.5 g/dL

during the polycondensation process. Therefore, the influence of various chiral structure elements on the polymer properties, especially the chiral feature, are very important. In addition, the amphiphilic polyurethane gels obtained by hydrolysis and modified by polyethylene glycol has been known to have pH sensitive features^[11]. Hydrophilic polyurethane as a waterbearing coating has been widely utilized recently in industrial coatings which has made it possible to control pollution, to reduce risks of fire, and to improve aspects of occupational health and safety, especially with regard to water-dispersible UV curing resin^[12]. Polyethylene glycol-polyurethane-based electrolyte system would be useful in batteries to provide ion transport^[13] and for drug carrier to control release^[14]. Our investigation of the hydrophilic polyurethanes obtained by hydrolysis of hard-segmented polyurethane and polyethylene-glycol-polyurethane to be used as waterbearing coating, polyelectrolyte and drug carrier will be continued in the future.

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