

SYNTHESIS OF POLY(ETHER-URETHANE) CONTAINING PENDANT AMINO GROUP

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ABSTRACT

This paper is concerned with the synthesis of poly(ether-urethane) with pendant amino groups. The copolyether produced by ring opening copolymerization of tetrahydrofuran and epibromohydrin was treated with sodium azide in dimethylformamide to form azido substituted copolyether. The poly(ether-urethane) made from it was subjected to reduction reaction to convert azido group to amino group. The stress-strain behavior and dynamic-mechanical properties of poly(ether-urethane) containing pendant amino groups were studied.

INTRODUCTION

Segmented polyurethanes are linear block copolymers consisting of soft and hard segments. Its good biocompatibility and excellent mechanical properties make it particularly useful in biomedical application. Grafting of hydrophilic monomers onto the surface of polyurethane via free radical copolymerization or plasma treatment to improve the blood compatibility of these materials has been widely used^[1-3]. The incorporation of negatively charged group into polyurethane backbone produces materials known as polyurethane anionomers, which also possess improved hemocompatibility^[4-5]. Another approach is the immobilization of anticoagulating agents onto polyurethanes. Heyman synthesized the heparin-immobilized polyurethane through terminal amino groups formed by hydrolysis reduction on the polymer surface^[6].

In this study, a new type of polyurethane containing pendant amino group has been synthesized and characterized.

EXPERIMENTAL

1. Materials

21% fuming sulfuric acid was prepared by mixing 50% fuming sulfuric acid with concentrated sulfuric acid in proper portions adjusting the density to 1.920 (20 °C).

Tetrahydrofuran (THF) obtained from Beijing Chemical Company was dried with 3 Å molecular sieves for two days. It was then distilled under nitrogen (b. p. 66.5 — 66.7 °C).

Epibromohydrin (EBH), synthesized according to ref. [7, 8], was dried with 3Å molecular sieves for two days and then fractionally distilled under nitrogen (b. p. 135 °C).

4,4'-diphenylmethane diisocyanate (MDI) (Bayer Co.) was purified by distillation under reduced nitrogen pressure (191 °C / 1mmHg).

Sodium azide (NaN₃) (from Huang Yan Chemical Co.) and Sodium perchlorate (NaClO₄ · H₂O) (from Nanshanle Chemical Co., Beijing) were used as received.

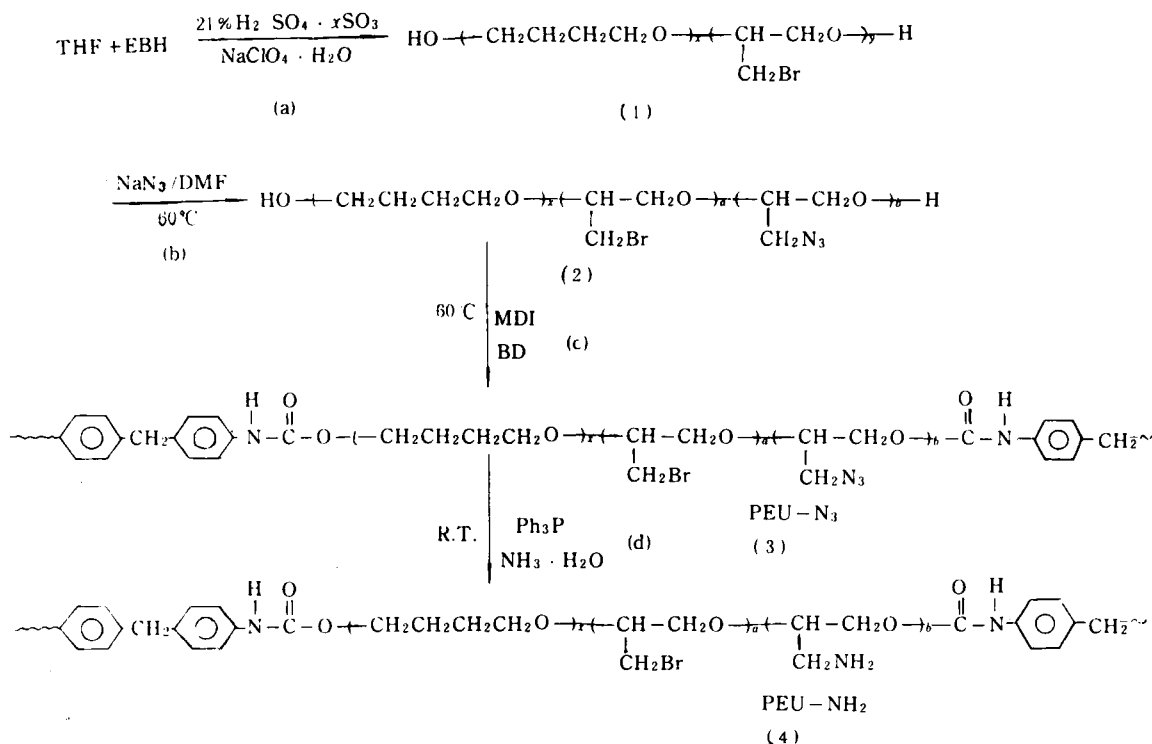


Fig. 1 Synthesis scheme of PEU containing pendant amino group

2. Preparation of copolyether (step a)

In a 250ml, three-necked, round-bottomed flask, 2.0g of NaClO₄ · H₂O was dissolved in 50g of newly distilled THF. When the mixture was cooled below -10 °C, 10g of 21% H₂SO₄ · xSO₃ was added gradually at such a rate that the temperature was maintained in the range of 0 ± 2 °C. After the addition, epibromohydrin (EBH) was added gradually at the same temperature. Two hours later, 100ml of distilled water was added to terminate the reaction.

The unreacted THF and EBH were removed by distillation. Then, the crude polyether was hydrolyzed at 100 °C for two hours and extracted with CH₂Cl₂. The organic layer was washed with distilled water until it was neutral.

After the solvent removed, the product was dried under vacuum at 80 °C. The copolyether of THF and EBH was an oily liquid and became a white, waxy solid when cooling.

Molecular weight of the copolyether was measured according to ref. [9, 10].

The composition of the copolyether was determined by elemental analysis .

3 . Preparation of azido substituted copolyether (step b)

A mixture of 20.1g copolyether (M . W . = 830) , 2.5g of sodium azide and 60ml of redistilled DMF was stirred at 60 °C for 48hrs . After the solvent evaporated , CH_2Cl_2 was added . The mixture was filtrated and the filtrate was washed with distilled water for several times . The azido substituted copolyether was a light yellow , oily liquid . The substitution percentage of the azido group was calculated on the basis of elemental analysis data .

4 . Preparation of poly (ether-urethane) containing pendant azido group (PEU- N_3) (step c)

A mixture of 4.02g azido substituted copolyether glycol (4.85mmol) and 3.79g of MDI (15.2mmol) was stirred at 60 °C for three hours . This was followed by addition of 0.873g of redistilled BD (9.69mmol) diluted with 15ml anhydrous DMF . Two hours later , the reaction was stopped by adding 2ml of methanol .

The product was precipitated in distilled water and was then extracted with alcohol for several times at room temperature .

5 . Preparation of poly (ether-urethane) containing pendant amino group (PEU- NH_2) (step d)

5.0 g of PEU- N_3 was treated with 7.5 g. triphenylphosphine (Ph_3P) in 90ml tetrahydrofuran at room temperature for 24hrs , followed by addition of 60ml tetrahydrofuran , 350ml pyridine and 120ml concentrated ammonium hydroxide . The mixture was stirred at room temperature for 48hrs . After the solution was concentrated , the mixture was precipitated with methanol /ether mixed solvent (50v/50v) . A white precipitate was obtained .

6 . Stress-strain and dynamic-mechanical tests

The stress-strain behaviour of synthesized polymers were observed at ambient temperature with an electronic tensile tester , Model DL-1000B . Rectangular-shaped specimens of the approximate average dimension $60 \times 10 \times 0.2\text{mm}$ were used . Elongation rate was 250mm /min and loading weight was 10Kg .

Dynamic-mechanical measurements were carried out on a Vibron Dynamic Viscoelastometer , Model DDV-II-EA (Shimadzu Co .) . Frequency employed was 3.5Hz . Samples were heated at a nominal rate of 2 °C /min under dry nitrogen atmosphere .

RESULTS AND DISCUSSION

1 . Synthesis of PEU- NH_2

Zhang et al.^[9] reported that ring opening copolymerization of THF and ECH using 70% $\text{HClO}_4 - \text{H}_2\text{SO}_4 \cdot \text{xSO}_3$ as initiator yielded the copolyether with no cyclic oligomer , and the end groups were proved to be primary hydroxyl groups with bifunctionality . Han^[10] discovered that instead of 70% HClO_4 by using $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ in the above mentioned initiator obviously enhanced the reaction rate .

Table 1 indicates that in the case of low EBH feed ratio , monomer ratio in

copolyether almost equals to the feed ratio . But further increase of the EBH feed ratio would not much increase its content in the copolymer . This indicates that the reactivity of EBH in ring opening polymerization is lower than that of THF .

Table 1 Ring-opening copolymerization of EBH /THF

Sample No .	1	2	3	4	5	6
Feed molar percentage of EBH	0.0617	0.116	0.165	0.208	0.296	0.345
Monomer molar percentage of EBH in copolymer	0.0622	0.110	0.140	0.176	0.229	0.251
Molecular weight	1210	1130	880	980	830	840
Yield (%)	54.7	66.2	66.0	56.3	64.2	55.7

$t = 0 \pm 2^\circ \text{C}$, 21% $\text{H}_2\text{SO}_4 \cdot x\text{SO}_3 \cdot \text{NaClO}_4 \cdot \text{H}_2\text{O}$ initiation

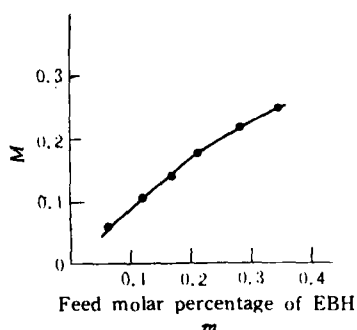


Fig. 2 Relationships between feed molar percentage of EBH (m) and monomer molar percentage of EBH in copolymer (M)

Conversion of azides to primary amines has been become one of the most important methods to prepare primary amine from halide^[11] . We found that the displacement reaction of bromide in copolyether with sodium azide could not occur in THF , but it could proceed easily in DMF or DMSO . Under this condition , about 65% of the bromide could be substituted by azido group .

From Fig. 3 , it can be seen that there is a characteristic absorption band at 2100cm^{-1} indicating the presence of azido group .

It is well known that azides can be converted to amines by catalytic hydrogenation^[12] . However , azido group pendant on the poly (ether-urethane) backbone exhibited resistance to hydrogenation, either by Lindle Cat ., Raney Nickel or Pd /C (5%) . It had been reported that treatment of azides with triphenylphosphine and concentrated ammonium hydroxide yielded corresponding amines with no observable by-products . By using this method , the azido groups in PEU were easily reduced to amino groups . Fig. 4 showed that the characteristic absorption band at 2100cm^{-1} completely disappeared . The reaction yield was

very high .

Table 2 also showed that the conversion of azido group to amino group was proceeded rather satisfactory .

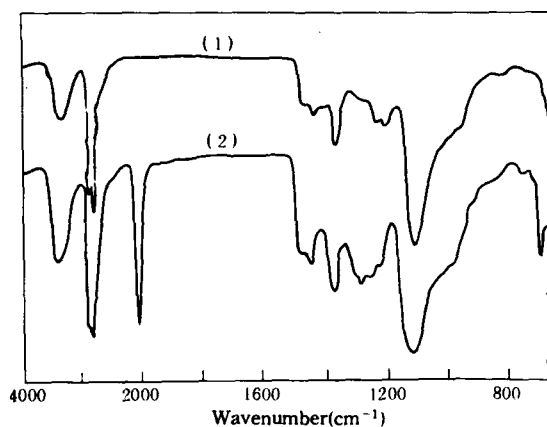


Fig. 3 Infrared spectra of copolyether (1) and azido substituted copolyether (2)

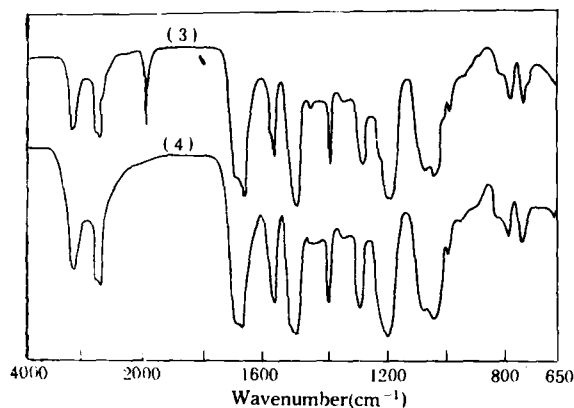


Fig. 4 Infrared spectra of PEU-N₃ (3) and PEU-NH₂ (4)

Table 2 Elemental analysis of PEU-N₃ and PEU-NH₂

	Calculated			Found		
	C	H	N	C	H	N
PEU-N ₃	60.71	6.97	8.31	61.88	6.72	8.36
PEU-NH ₂	63.44	7.05	6.10	63.98	7.48	6.02

2 . Stress-strain behaviour and dynamic-mechanical properties of PEU-NH₂

The effect of soft segment structure on the stress-strain behaviour of these poly (ether-urethane) was investigated . The results are summarized in Table 3 .

It is clear that tensile strength and ultimate elongation decreased when the unsymmetrical ($-\overset{\text{CH}_2\text{X}}{\underset{\text{CH}}{\text{CH}}} - \text{CH}_2\text{O} -$) units ($\text{X} = \text{N}_3, \text{NH}_2$) were incorporated into the

soft segment. The tensile strength increased when azido groups were converted to amino groups, because the hydrogen bonding interaction between carbonyl and amino group in $\text{PEU}-\text{NH}_2$ is much stronger than that of carbonyl with N_3 in $\text{PEU}-\text{N}_3$.

As shown in Table 4, the value of the soft segment glass transition temperature (T_g s) of $\text{PEU}-\text{NH}_2$ was the highest among the three specimens. This indicates that hydrogen bonding interaction between amino group and carbonyl group in $\text{PEU}-\text{NH}_2$ increased the compatibility of the two phases and decreased the degree of phase separation. The polar units of ($-\overset{\text{CH}_2\text{N}_3}{\underset{\text{CH}}{\text{CH}}} -$) incorporated into the soft

segment also increased the interaction between the two phases and decreased the degree of phase separation.

Table 3 Physico-mechanical properties of $\text{PEU}-\text{N}_3$ and $\text{PEU}-\text{NH}_2$

Sample	$(\eta)^*$	$\sigma t (\text{Kg}/\text{cm}^2)$	$\epsilon t (\%)$
PEU (PTMG) **	0.572	342	400
$\text{PEU}-\text{N}_3$	0.558	199	283
$\text{PEU}-\text{NH}_2$		268	283

* 30°C , in DMF

** PTMG $M.W.$ = 1100 ; MDI : PTMG : BD = 3 : 1 : 2

Table 4 Dynamic-mechanical data for polyurethanes

Sample	T_g s $^*(^\circ\text{C})$	$\tan \delta_{(\max)}$
PEU (PTMG)	1.1	0.183
$\text{PEU}-\text{N}_3$	33.7	0.255
$\text{PEU}-\text{NH}_2$	66.7	0.495

* T_g s = soft segment glass transition temperature

We have carried out the graft reaction of PEO (polyethylene oxide) on $\text{PEU}-\text{NH}_2$ through diisocyanate coupling and found that the hydrophilicity of the PEU surface was improved. The detailed grafting results and biological properties of grafted PEU will be reported later.

Keywords :

Poly (ether-urethane) ; Ring – opening copolymerization ; Azide reduction ; Dynamic -mechanical properties .

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