

AMPHIPHILIC POLYURETHANES WITH A NOVEL PEG-CONTAINING CHAIN EXTENDER

PART I: SYNTHESIS AND CHARACTERIZATION

Pham Ngoc Lan⁽¹⁾, Luu Van Boi⁽²⁾

⁽¹⁾*Polymer Research Center, Hanoi University of Technology*

⁽²⁾*Department of Chemistry, College of Science, VNU*

1. Introduction

Polyurethanes are block copolymers composed of alternating short hard segments and long flexible soft segments that are thermodynamically incompatible at the temperature of use [1,2]. Phase separation of segmented polyurethanes (SPU) with a limited hard segment content results in hard segment rich domains dispersed in a continuous matrix of the soft segments [3]. The hard domains act as physical crosslink providing the polymer with mechanical strength while the soft matrix contributes to the elastomeric properties [4,5]. The main factors influencing the hard domain cohesion and the resulting phase separation include hydrogen bonding and crystallization [4].

Several strategies have been proposed to further improve the surface properties for polyurethanes [5]. In this respect, polyethylene oxide rich surfaces that non selectively repel proteins and cells have been prepared and evaluated [6,7]. In the present work, a novel PEG-containing chain extender was synthesized and the potential use of this chain extender for the synthesis of segmented polyurethanes was investigated. Thus, a series of amphiphilic copolymers with PEG side chains of different MW were prepared. This article described the synthesis and chemical characterization of both the novel chain extender and the resultant grafted polyurethanes.

2. Experimental

2.1. Materials

All solvents were used as received, except for pyridine (dried on CaH₂) and dichloromethane (dried on P₂O₅). Poly(THF-CD), a special polyether polycarbonate diol with MW 2000 and based on Poly(THF) was obtained from BASF. The α -hydroxy- ω -methoxypolyethylene glycols (MPEG) were obtained from Jansen (MW350), Acros (MW550, 750, 1000) and Polymer Laboratories (MW 1900) respectively. Both

Poly(THF-CD) and the MPEG's were dried at 60°C for 6 hours under reduced pressure immediately before use. Hexamethylene diisocyanate (HMDDI), butane diol (BD), dibutyltin diacetate (DBTDAc), diethanol amine (DEA) and tosylchloride (TsCl) were used as received.

2.2. Characterization methods

¹H-NMR spectroscopy

All ¹H-NMR spectroscopy analyses were recorded in deuterated chloroform on a Bruker 360 MHz instrument. The chemical shift was expressed in ppm relative to tetramethyl silane as internal standard.

GPC analysis

GPC analyses were performed on 1% (w/v) solution in NMP. The styragel column (Polymer Laboratories, 10⁴-10⁵ Å) was operated at 45°C and a flow rate of 1 ml/min. A refractometer was used for detection and the data analysis was done with a Waters Data Module M730. The relative molecular weights and the polydispersity of the samples were calculated using a narrow molecular weight polystyrene standard calibration curve.

FT-IR spectroscopy

FT-IR spectroscopy was performed on thin films cast from a 1% (w/v) solution in chloroform directly onto KBr coins. The spectra were recorded on a Perkin-Elmer 1600 spectrometer and were the average of 16 scans at a resolution of 4 cm⁻¹.

3. Results and discussion

3.1. Synthesis of PEG-containing chain extender Ax

Starting materials used include α -hydroxy- ω -methoxypolyethylene glycols (MPEG) of molecular weights 350, 550, 750, 1000 and 1900.

The diol-terminated PEG macromer Ax is easily prepared via a two step reaction procedure (Fig.1). To a solution of MPEG in 25 ml of dichloromethane, 12 ml of dried pyridine and 0.08 mmoles tosylchloride were added in a period of 20 minutes. The mixture was reacted overnight at 4°C and subsequently cooled to 0°C. Then, 20 ml of concentrated HCl, 50 grams of ice and 20 ml dichloromethane were added. The organic phase was isolated and washed successively with a 3 M HCL solution, a saturated NaCl solution and a 5% NaHCO₃. After drying on MgSO₄ the solution was concentrated under reduced pressure and precipitated in hexane. The resulting α -hydroxy- ω -tosyl-polyethylene oxide (MPEG-Ts) was isolated by filtration and dried under reduced pressure at room temperature.

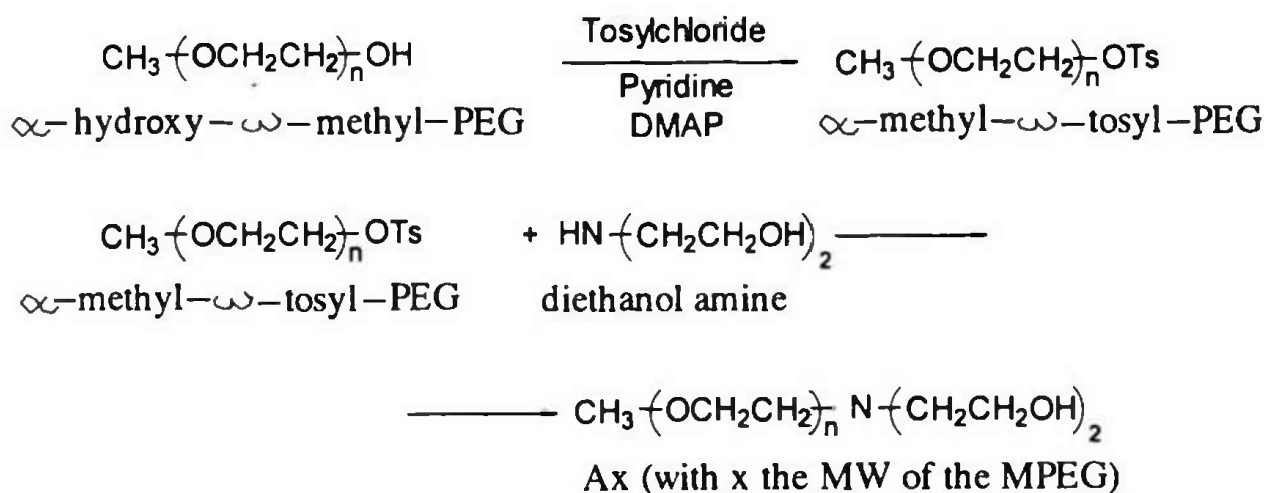


Fig.1. Synthesis of the PEG-containing chain extender Ax

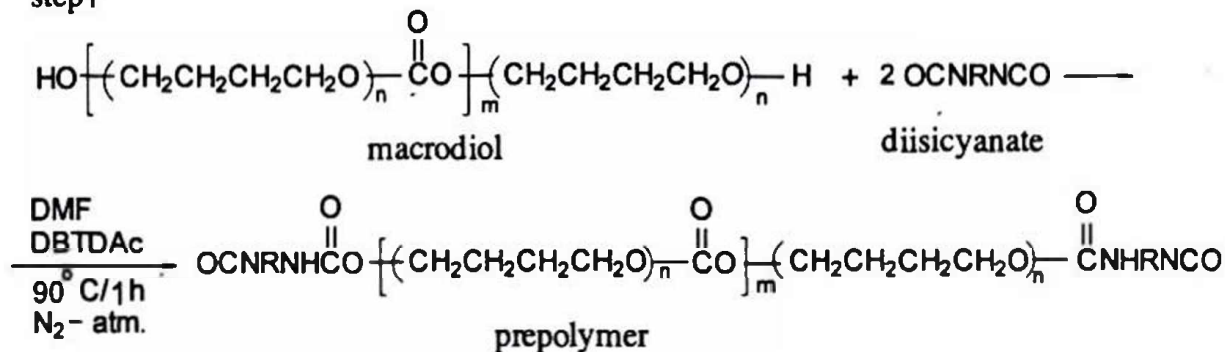
Two mmoles of MPEG-Ts and a large excess of DEA were reacted in bulk for 4 hours at 90°C. After the addition of 10 ml of distilled water, the reaction mixture was cooled to room temperature and the formed ammonium salt was converted to its free amine form with 10 ml of 0.5 M NaOH solution. After the extraction of the mixture with dichloromethane, the collected organic phases were dried on MgSO₄ and concentrated under reduced pressure. Further purification of the chain extender was varied with the MW of the MPEG chain. Chain extender A1900, A1000 (solid) and A750, A550 were purified by precipitation in a large excess diethylether at room temperature and 0°C respectively. Chain extender A350 (liquid) was extracted with 0.5 M NaOH solution. All structures were verified using ¹H-NMR spectroscopy. Peaks positions 2.68 and 2.73 ppm correspond to the α-N and β-O methylene protons of the PEG and non-PEG part of the chain extender respectively. The integrations for both peaks relate to each other as 1:2 indicating complete conversion.

3.2. Synthesis of the amphiphilic PEG-containing grafted polyurethanes

The segmented polyurethanes were prepared by a standard two-step solution polymerization in DMF (Fig.2). The catalyst used was dibutyltin diacetate (1%) and the total concentration of the reaction mixture was approximately 15% (w/v). The two reaction steps were carried out under a N₂ atmosphere at 90°C and with stirring, for 1 and 3 hours respectively. In the first step, the macrodiol (PTHF-CD, MW 2000) was reacted with the diisocyanate (HMDI) in a 1:2 molar ratio. The prepolymer thus obtained was subsequently reacted with the PEG-containing chain extender in equivalent amounts. The resulting polymer was isolated by precipitation in diethyl

ether or distilled water and dried under reduced pressure. Purification from low molecular weight products and catalyst was performed by dissolving the polymer in chloroform and precipitation in hexane.

step 1



step 2

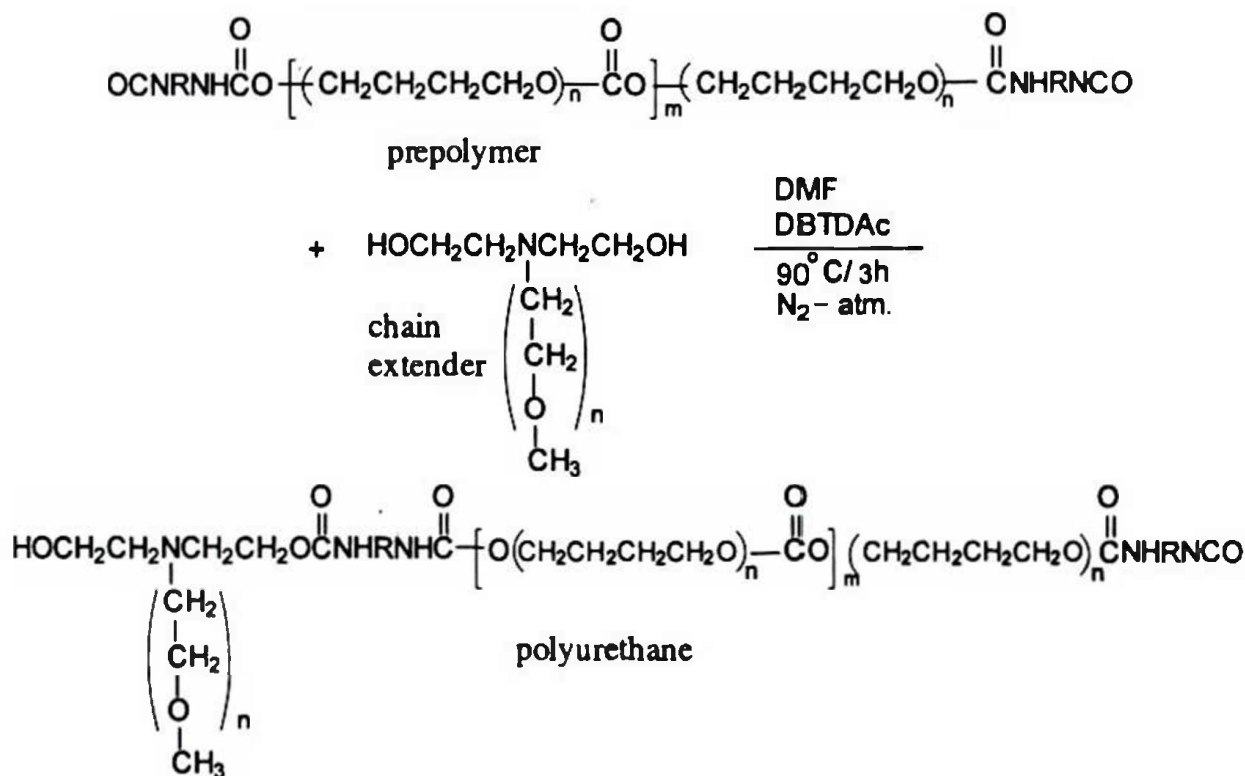


Fig.2. Synthesis of amphiphilic PEG-containing grafted polyurethanes

3.3. IR- spectra

Figure 3 shows the IR spectrum of a polyurethane (PU) obtained. The typical functional groups of the PU are shown clearly in the spectrum. For example, NH-groups absorb at 1522.6 cm^{-1} , 3377.9 cm^{-1} and 3330.7 cm^{-1} . The bands at 3377.9 cm^{-1} and 3330.7 cm^{-1} correspond to the non-bonded and bonded NH-groups respectively. The

peaks at 1713.6 cm^{-1} and 1719.7 cm^{-1} belong to the non-bonded and bonded carbonyl groups respectively. The ether groups appear at 1040.4 cm^{-1} . Very strong peak at 1257.3 cm^{-1} corresponds to the C-O- group adjacent to carbonyl group. Partially bonded NH- and -C=O groups in PU possibly make it partially phase separated [8].

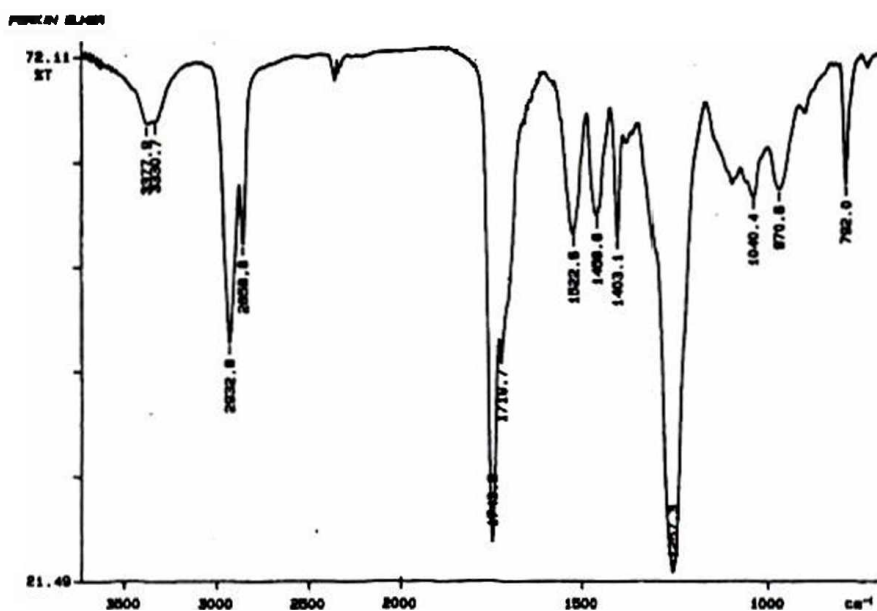


Fig.3. IR spectrum of a polyurethane

3.4. $^1\text{H-NMR}$ spectra and GPC analysis

The typical $^1\text{H-NMR}$ spectrum of a PU are shown in *figure 4*. In the spectrum NH-group (1) appears at about 8 ppm. The CH_2 -group (2) adjacent to ether group appears at about 4.2 ppm. The other CH_2 - group (3) gives strong peak at 1.8 ppm. It is seen that the obtained PU are very well characterized.

Table 1 summarizes the hard segment contents and molecular weights of the different amphiphilic polyurethanes. Codes for samples are as follows. e.g. PU-HT-A550, where H, T and 550 represent HMDI, PTHF-CD and a chain extender with a PEG MW of 550 respectively. The reference polymer PU-HT-BD was synthesized with butanediol as chain extender and as such it does not contain a PEG side chain. A model compound PU-HT was also included. This was prepared by reacting HMDI and PTHF-CD in equivalent amounts under the same conditions as for the preparation of the polyurethanes. The weight percentage of hard segments (wt% HS) was calculated by combining the weight of the diisocyanate and BD or the non-PEG part of the PEG-containing chain extender Ax.

Table 1. GPC analysis and $^1\text{H-NMR}$ spectroscopy of the PEG containing grafted polyurethanes and a model compound

Polymer	Chain extender	Wt% HS	Mn (GPC method)	d
PU-HT-BD	BD	18.3	75,300	1.4
PU-HT-A350	A350	12.6	69,000	1.8
PU-HT-A550	A550	14.3	51,200	1.7
PU-HT-A750	A750	13.2	26,200	1.8
PU-HT-A1000	A1000	12.7	36,500	1.5
PU-HT-A1900	A1900	10.0	47,400	1.4
PU-HT	-	7.9	67,200	1.5

As can be seen from the GPC data, all polymers have sufficiently high molecular weight and narrow polydispersity to provide polymer films with good elastomeric properties.

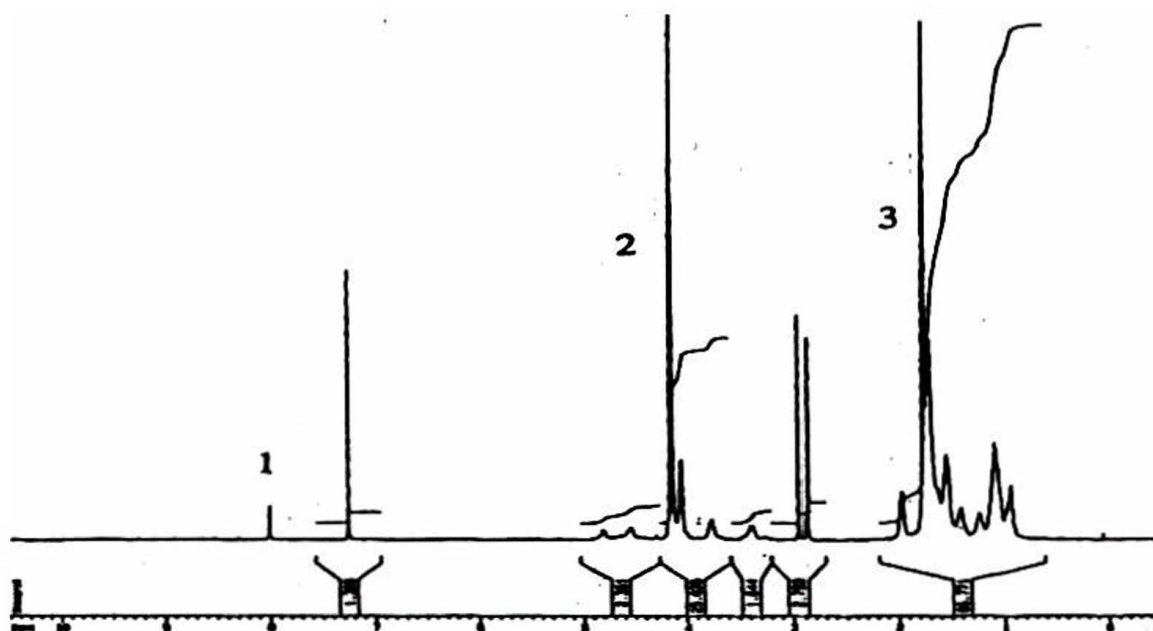


Fig. 4. $^1\text{H-NMR}$ spectra of polyurethane

Conclusion

In this article, the synthesis and characterization of a new, PEG-containing chain extender Ax are described. A series of amphiphilic PEG-grafted polyurethanes with different PEG chain length was subsequently prepared and well characterized by IR and $^1\text{H-NMR}$ spectroscopy. All polymers containing this new chain extender had high molecular weights and narrow polydispersity to provide polymer films with good elastomeric properties.

REFERENCES

1. Estes GM., Cooper SL. and Tobolsky AV., *J. Macromol.Sci.*, **C4** (1970), 313-320.
2. Li Y., Yang LH. Ma D. and Chu B., *J. Polym. Sci., Part B: Polymer physics*, **31** (1993), 853-867.
3. Chang Y.J.P and Wilkes GL., Superstructure in Segmented Polyurethanes, *J. Polym. Sci.: Polym. Phys. Ed.*, **13** (1975), 455-476.
4. Chang AL and Thomas EL., *ACS Adv. Chem.*, **176** (1979), 31-39.
5. Lelah MD., Grasel TG., Pierce JA. and Cooper SL., Exvivo interactions and surface property relationships of polyurethanes, *J. Biomed. Mater. Res.*, **20** (1986) 433-468.
6. Cooper SL. and Tobolsky AV., Properties of linear elastomeric polyurethanes, *J. Appl. Polym. Sci.*, **10** (1966) 1837-1844.
7. Takahara A., Tashita J., Kajiyama T. and Takayanagi M., Blood compatibility and microphase separated structure of segmented poly(urethane urea) with various soft segment componemts, *Rept. Progr. Polym. Phys. Japan*, **25** (1982) 841-844.
8. Pham Ngoc Lan, Corneillie S., Schacht E., Davies M. and Shard A., Synthesis and characterization of segmented polyurethanes based on amphiphilic polyether diol, *Biomaterials*, **17** (1996) 2273-2279.

TẠP CHÍ KHOA HỌC ĐHQGHN, KHTN & CN, T.XXIII, SỐ 1, 2007

POLYURETAN AMPHIPHILIC VỚI HỢP CHẤT NỐI DÀI MẠCH CHỨA POLYETYLEN GLYCOL

PHẦN I: TỔNG HỢP VÀ ĐẶC TRƯNG TÍNH CHẤT

Phạm Ngọc Lân⁽¹⁾, Lưu Văn Bôi⁽²⁾

⁽¹⁾*Trung tâm Nghiên cứu Vật liệu Polyme, Trường Đại học Bách khoa Hà Nội*

⁽²⁾*Khoa Hóa học, Trường Đại học Khoa học Tự nhiên, ĐHQGHN*

Bài báo trình bày về nghiên cứu tổng hợp và đặc trưng tính chất của một loại chất nối dài mạch mới Ax. Chất nối dài mạch loại mới này được dùng để tổng hợp một số polyuretan ghép PEG có độ dài mạch PEG thay đổi (từ 350 đến 1900 Da). Đã sử dụng macrodiol PTHF-CD là một polyete diol đặc biệt với độ phân cực tăng dần do có mặt một lượng nhỏ nhóm cacbonat để tổng hợp các polyuretan. Tất cả sản phẩm polyuretan thu được có khối lượng phân tử khá cao và độ đa phân tán tương đối thấp. Cấu trúc polyme được xác định bằng phương pháp phổ hồng ngoại và cộng hưởng từ hạt nhân proton.

Từ khóa: *Polyuretan ghép PEG, chất nối dài mạch, khối lượng phân tử, độ đa phân tán.*