SYNTHESIS AND CHARACTERIZATION OF SEGMENTED POLYURETHANES BASED ON POLYETHYLENE AND POLYTETRAMETHYLENE GLYCOLS

(Part I: Synthesis and characterization)

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1. Introduction

Segmented polyurethanes (SPUs) are multiblock $-\!\!\!\!+ X - Y +\!\!\!\!-_n$ copolymers which consist of thermodynamically incompatible segments. In these copolymers, X and Y are soft and hard segment sequences respectively. Due to the thermodynamic differences of the soft and hard segments, they usually segrate to form an agregated pseudo-two-phase structures [1]. SPUs have good biocompatibility due to the morphological two-phase structure and consequently have found extensive biomedical applications [2].

The relationship between the structures and properties of the SPUs has been extensively investigated [3,4,5].

In this paper we present the study on synthesis and characterization of SPUs based on macrodiols (polyethylene and polytetramethylene glycols), methylene 1,4-Di(cyclohexyl isocyanate) (MDCI) and 1,4-butane diol (BD)(chain extender). The effects of macrodiols, their molecular ratios on the morphology and properties of the resulting polymers were discussed.

2. Experimental

2.1. Materials

Polyethylene and polyteramethylene glycols selected for preparation of the polyurethanes are listed in the *table 1*. Before use they were carefully dried by azeotropic distillation of the toluene solution and subsequent removal of the solvent. *Figure 4a* shows the IR spectrum of polyol PEG-2000.

The hydroxyl number of polyetherdiols for calculation of molecular weights was determined by esterification of them with acetic anhydride and subsequent titrimetric analysis of the carboxylic acid groups according to the standard procedure [6].

Table 1: Polydiols for preparation of SPUs

Polyol	Mn (a)	Mn (b)	Tm, °C	Tg, °C
PEG-1000	1207	1100	40	-70 (very weak)
PEG-2000	2341	2070	55	-70 (very weak)
PEG-4000	4280	4109	62	-
PTMO-2000	2186	1950	25	-30

(a): Determined via GPC

(b): Determined via chemical titration

The molecular weights of the polydiols were also verified by means of gel permeation chromatography (PL columns, 103A°, 7mm i. d., 60 cm length, Polymer Laboratories Ltd, Shropshire, UK. Eluent: chloroform, Differential reflectometric detection (Model Waters 401, Millipore, MA, USA). Data analysis occurred on a Waters data module model M730. Calibration was based on a peak position calibration curve established using polystyrene standards (Millipore, Millford, MA, USA).

Diisocyanate (MDCI) (Aldrich Bornem, Belgium) was vacuum distilled and stored under dried conditions in a refrigerator prior to use. The IR spectrum of MDCI is shown in *figure 1*

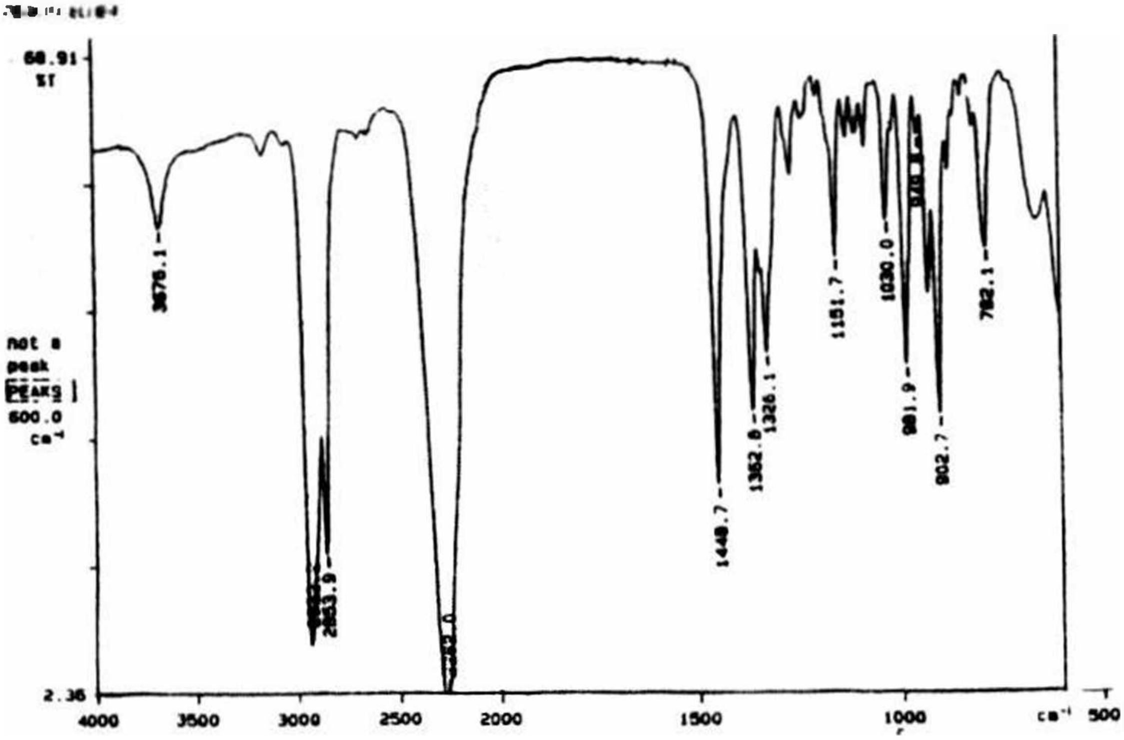

Figure 1: IR spectrum of diisocyanate: MCDI

1,4-butane diol (Aldrich, Bornem, Belgium) was dried over calcium hydride for 2 days, distilled and stored under nitrogen.

Dibutyl tin diacetate was obtained from Aldrich (Bornem, Belgium) and used without further purification.

Dimethyl formamide (DMF) (Aldrich Bornem, Belgium) was dried over calcium hydride for 2 days and then vacuum distilled.

2.2. Characterization methods

IR spectra were recorded using a Perkin-Elmer Model 1600 Spectrophotometer.

NMR spectra were recorded in DMSO-d_6 using tetramethyl silane (TMS) as internal standards, on an Aspect 3000 spectrophotometer.

The molecular weights and molecular weight distribution of the polymers were determined by gel permeation chromatography (Waters associates, model 510) at 60° C. The flow rate of the solvent, 1-methyl-2-pyrrolidinone (NMP), was 1 ml.min^{-1}. For calculation, monodispersed polystyrene standards were used.

DSC thermograms were recorded on a Perkin-Elmer DSC under nitrogen purging (heating rate 10°C.min^{-1}, from -100°C to 100°C). The unit was equipped with a data processing module that allows substraction of the background and normalization for sample weight.

2.3. Polymer preparation

Solutions of polydiol and diisocyanate were prepared separately in DMF. The concentration was approximately 15% (w/w). A four-necked flask, equipped with a stirrer, a nitrogen inlet and outlet and a thermometer, was charged with the diisocyanate solution. The polyetherdiol solution, containing 0.5 wt % of catalyst (dibutyl tin diacetate) based on the weight of the reactant, was added slowly to the diisocyanate solution. The molar ratio NCO:OH was set to 2:1. The reaction was carried out at 90° C under nitrogen purge and was allowed to proceed until the theoretical isocyanate content was reached as determined by the di-n-butyl amine titration method [7]. Then the reaction mixture was cooled down to room temperature and the chain extender (BD) was added slowly. The overall NCO:OH ratio was 1:1. The chain extension reaction was carried out at 90° C and continued until all NCO groups were reacted, as confirmed by the disappearance of the IR absorption band at 2262 cm^{-1}. The reaction mixture was then precipitated in water and the final polymer was dried under vacuum at 60° C. After drying it was redissolved in THF and reprecipitated in the solvent mixture hexane-ether (1/1). The copolymer product was dried under vacuum at 60°C at least for 2 days.

3. Results and discusion

3.1. Synthesis of segmented polyurethanes

Segmented polyurethanes (SPUs) were synthesized by a two-step polymerization (*Figure 2*). Polyol first reacted with two equivalents of the diisocyanate. Subsequent chain extension was obtained by reaction with an equivalent amount of 1,4-butane diol. The final polymer was purified properly by precipitation, vacuum dried and then characterized. The molecular weights of the SPUs determined by GPC method and are listed in *table 2*.

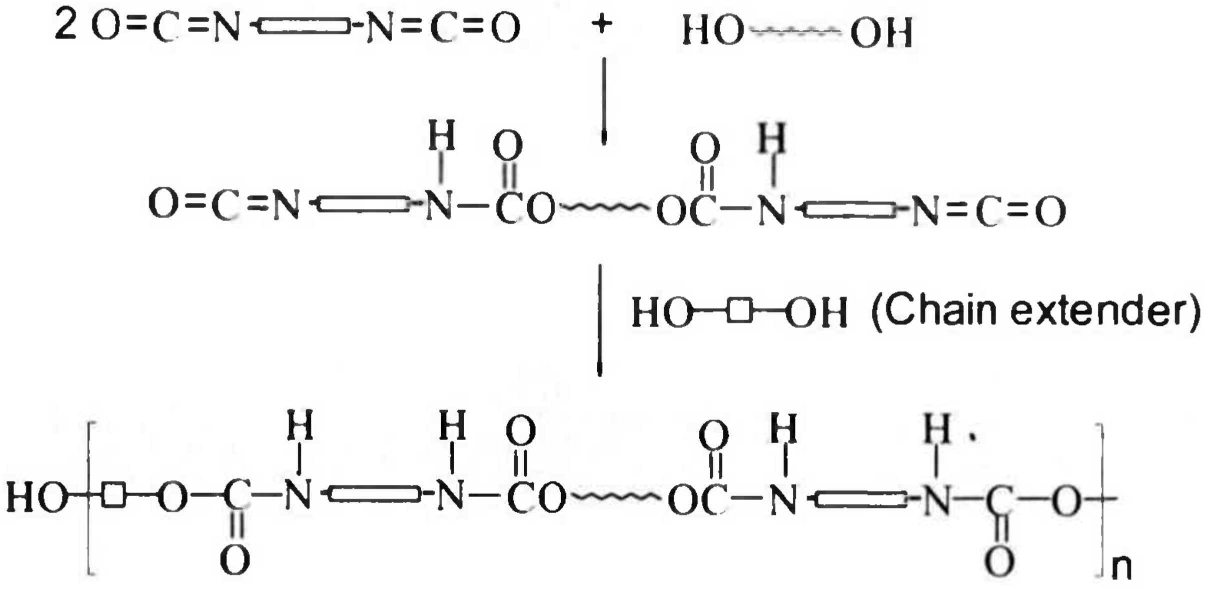

Figure 2: Schematic procedure of segmented polyurethane formation

We can see from the *table 2* that all the SPUs have quite high molecular weights and the molecular weight distribution (d) is relatively narrow. The materials obtained are strong as will be shown in the next publication.

Table 2: Molecular weights of SPUs

Code	Polyol ratio	Diiso-cyanate	Chain extender	Mw	d
PU-1	PEG-1000 + PTMO-2000 (1/1)	MCDI	BD	60027	2.0
PU-2	PEG-2000 + PTMO-2000 (1/1)	MCDI	BD	70815	1.9
PU-3	PEG-4000 + PTMO-2000 (1/1)	MCDI	BD	61593	1.8
PU-4	PEG-2000 + PTMO-2000 (2/1)	MCDI	BD	108533	2.1
PU-5	PEG-2000 + PTMO-2000 (1/2)	MCDI	BD	66242	2.0

3.2. NMR spectra

The structure of the SPUs obtained was confirmed by proton NMR spectra. *Figure 3* shows the NMR spectrum of polyurethane PU-2. We can see that the spectrum shows clearly the peak at δ = 1.6 ppm corresponding to β-CH of PTMO and a peak at δ = 3.4 - 3.7 ppm corresponding to α-CH_2 of PTMO and PEG.

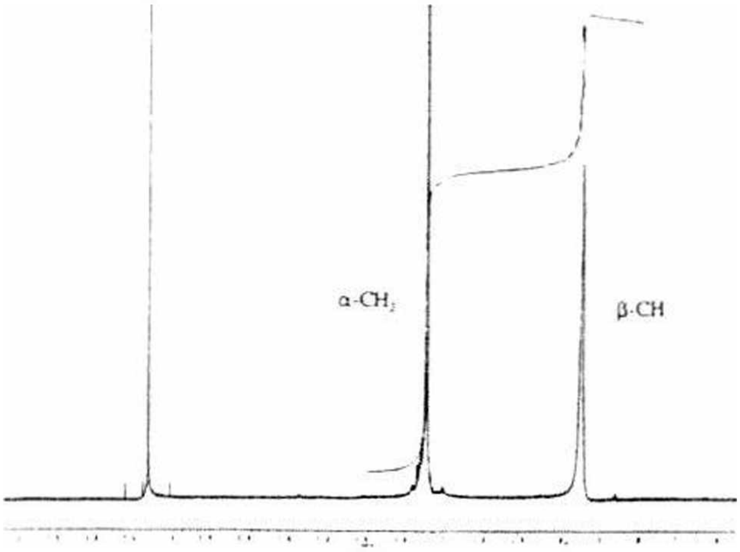

Figure 3: 1H-NMR spectrum of PU-2 (PEG-2000 + PTMO-2000 (1/1)), Solvent: Chloroform

3.3. IR analysis

For comparision, *figure 4a* shows the IR spectrum of polyol PEG-2000. We can see clearly the characteristic absorption band of the OH-group at 3447.9 cm^{-1} which was almost disappeared in polyurethane formation and the ether group at 1119.5 cm^{-1}. By polyurethane forming, the NCO group of diisocyanate disappeared (2262.0 cm-1) (see *figure 1*), but there appeared two new characteristic groups: the NH-group at 3323.1 cm^{-1} and C=O group at 1712.8 cm^{-1} (*Figure 4b*).

The polyurethanes are segmented copolymers containing flexible polyether segments and hard segments of isocyanate moeties. In the hard segments of the SPUs, hydrogen bonds occur due to the interaction of hydrogen atoms of NH-groups with carbonyl groups. In the polyether polyurethane copolymers, the NH groups form hydrogen bonds with the C=O groups of the urethane linkages making the hard segments good packed consequently the copolymer well phase separated. At the same time the hydrogen bonds can occur due to the interaction between the NH groups and the oxygen atoms of the soft segment ether groups. In this case the copolymer becomes less phase separated. It is known from the literature [8, 9] that the IR absorption of the NH- and C=O groups (free and bonded) in the SPUs occurs in the following range:

-NH- (H-bonded) → 3200 - 3350 cm^{-1}

-NH- (H-free) → 3360 - 3500 cm^{-1}

-C=O (H-bonded) → 1700 - 1714 cm^{-1}

-C=O (H-free) → 1715 - 1740 cm^{-1}

As we can see from the *figure 4b* that the PU-5 is quite well phase separated. The same good phase separation can also be seen in the other SPUs investigated in this work. The question concerning phase separation of the SPUs will be discussed in more details in the part II.

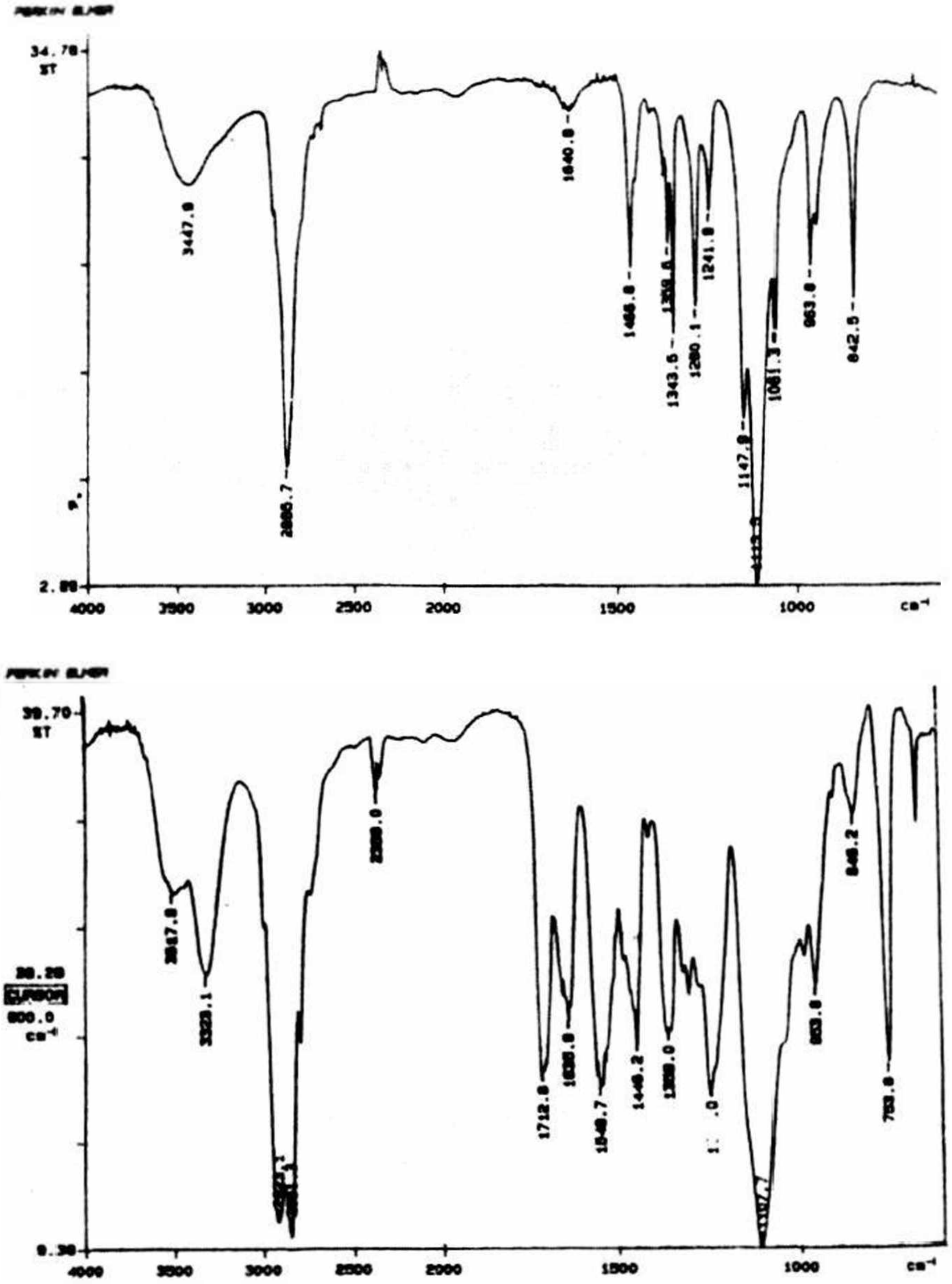

Figure 4: IR spectrum of polyol (4a) and polyurethane PU-5 (4b)

4. Conclusion

In this study, the synthesis and characterization of polyethylene and polytetramethylene glycol based SPUs were described. The structure of the SPUs obtained was confirmed by the NMR and IR spectra. It was shown that the selected SPUs for this study had quite good phase separation.

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TỔNG HỢP VÀ KHẢO SÁT TÍNH CHẤT CỦA CÁC POLYURETAN PHÂN ĐOẠN (PU) TRÊN CƠ SỞ POLYETYLENGLYCOL VÀ POLYTETRAMETYLENGLYCOL

(Phần 1: Tổng hợp và khảo sát tính chất)

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Bài báo đề cập về nghiên cứu và khảo sát tính chất của các polyuretan phân đoạn trên cơ sở polyetylenglycol và polytetrametylenglycol. Đã sử dụng phương pháp phổ hồng ngoại (IR) và cộng hưởng từ hạt nhân proton (1H-NMR) để xác định cấu trúc của các polyuretan thu được. Đã nghiên cứu ảnh hưởng của các macrodiol và tỷ lệ mol của chúng lên hình thái học và tính chất của sản phẩm polyuretan.

Từ khóa: macrodiol, polyuretan phân đoạn, tách pha.