Synthesis and Characterization of N-Polyethylene Glycol Monomethyl Ether Substituted Polyurethane

S. Mohammad Seyed Mohaghegh¹, Mehdi Barikani²*, and Ali Akbar Entezami³

Departments of (1) Polymer Science and (2) Polyurethanes, Fibres and Nanopolymers, Iran Polymer and Petrochemical Institute, P.O. Box: 14965/115, Tehran, I.R. Iran
(3) Faculty of Chemistry, Tabriz University, Tabriz-51664, I.R. Iran

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A B S T R A C T

Poly(N-substituted urethane)s with different molecular weights of polyethylene glycol monomethyl ether side chain were synthesized form sodium hydride, chlorinated polyethylene glycol monomethyl ether (PEGMME), and polyether and poly ester urethane containing polytetrahydrofuran or polycaprolactone/toluene diisocyanate and 1,4-butanediol. The chemical structures were characterized with FTIR and FT-¹H NMR. To investigate the effect of different MW of N-substituted side chain on the morphology, thermal property and particle size distribution of the final product, we used differential scanning calorimetry and laser light scattering. N-Substitution of polyurethane had significant influences on thermal properties and solubility of the resulting material. Tg of the N-substituted urethane decreases with N-substitution and gradually increases with increasing molecular weight of the substituted side chain. This is more obvious in higher molecular weight. The particle size of final water borne PU emulsion also decreases with increasing MW of PEGMME. The decreasing particle size may be due to increased chain flexibility and or hydrophilicity of N-substituted polyurethanes.

INTRODUCTION

Polyurethanes are a unique class of polymers which have a wide range of applications because their properties can be readily tailored by the variation of their components. These versatile polymers are used extensively as elastomer, foams, coatings, adhesives, fibres, varnishes and sealants [1, 2]. Polyurethanes can be easily prepared by simple polyaddition reaction of polyols, isocyanates and chain extenders. Although these polymers are known by their excellent mechanical properties, depending on

Key Words: polyurethanes; N-modification; polyethylene glycol monomethyl ether; water borne.

(*)To whom correspondence should be addressed. E-mail: M.Barikani@ippi.ac.ir
the nature of the starting materials. However, a few disadvantages caused by the urethane group exist. During thermoplastic processing at temperature above 200°C, [3, 4], they are split back into starting polyols and isocyanates; they also show inadequate hydrolytic stability.

Many attempts have been made to improve the properties of polyurethanes. [5] One accepted approach is the chemical modification of its structure by grafting. So N-substitution of PU was used to overcome the preceding disadvantages and improve various typically desired properties of the materials, such as enhanced fire retardancy, flexibility and solubility [6, 7].

However, most of the research on N-substitution was carried out with the N-methylation of PU, and only a few limited studies have been reported on the N-substituted PU [5], especially thermoplastic PU, with alkyl or polyether side chains longer than methyl [8].

In this paper we report on the synthesis and characterization of a number of N-sub PEGMME PUs with various MW of PEGMME. Chlorinated PEGMME was prepared according to procedure described in experimental section, and then reacted with two series of polyurethane elastomer to obtain N-substituted polyurethanes.

The effect of various molecular weights of side chain morphology on the thermal properties of grafted PU is investigated.

EXPERIMENTAL

Materials
Poly(ethylene glycol monomethyl ether (PEGMME) (Mw= 350, 550, 750, 2000, 5000, Fluka) were dried at 80°C under vacuum overnight. Polytetrahydrofuran (PTHF, Merck, Mw=1000), polyCaprolactone (Capa 225, Interox Chemical Co Ltd., Mw = 2000) and 1,4-butane diol (1,4-BD, Merck) were dried under vacuum. Toluene diisocyanate (TDI, Merck) was distilled under vacuum before use. Dibutyl tin dilaurate (DBT, Merck) and sodium hydride (NaH, Akzo Chemie) were used without further purification. Dimethylformamide (DMF), thionyl chloride, toluene, n-hexane and chloroform (Merck) were dried and distilled before use.

Instruments
Infrared measurements were performed on a Bruker IFS 48-FTIR spectrometer. The films for infrared analysis were prepared by casting 5% PU in DMF solution on to potassium bromide disk at room temperature. Following evaporation of the majority of the solvent, the films were placed in vacuum oven at about 80°C to remove residual solvent. The FT-H NMR spectra were recorded in dimethyl sulphoxide (DMSO-d6) solution using a Bruker Avance 500 MHz FT-NMR Instrument.

Differential scanning calorimetry (DSC) was recorded on a Polymer Laboratory DSC.

Particle size and its distribution were measured by laser light scattering (Sematech, He-Ne laser).

Preparation of Polyurethane

The required amounts of polylol (100g) and diisocyanate (25.1g) were placed in a round bottomed polymerization flask of 500 mL capacity and placed in an oil bath at 60°C which a steady flow of dry nitrogen was passed continuously through the apparatus. The flask was equipped with a dropping funnel, nitrogen inlet, and variable speed constant torque stirrer motor that was connected to the flask through an anchor stirrer with close fit to side of the flask. Nitrogen gas was used throughout and further dried by passing through silica gel guard tubes. The oil bath was a temperature controlled hot oil bath and the temperature was also monitored by using a thermometer immersed in the oil by the side of the polymerization flask. The reaction mixture was then continuously stirred for approximately 4 h. Then few drops of DBT and a required amount of predried chain extender (1,4-BD, 9 g) was added through the dropping funnel the reaction mixture was vigorously stirred for approximately 1h whilst maintaining the dry nitrogen.

Two different series of PU elastomers were prepared from the following molar ratio of linear polylol/diisocyanate /chain extender (Scheme I).

a) A PU series based on Capa 225/TDI/1/4-BD with molar ratio of 1/3/2.

b) A PU series based on PTHF/TDI/1/4 BD with molar ratio of 1/2/1.

Preparation of Chlorinated PEGMME

For preparation of chlorinated polyethylene glycol monomethyl ether with various molecular weight, 0.1mole of predried PEGMME was dissolved in 250 mL of dried toluene and placed in a 500 mL round-bottom
flask. A solution of 0.5 mole (59 g) of SOCl₂ in 50 mL of dried toluene was added drop-wise to the reaction flask. The solution was left for completion by finishing of gas evolution. The reaction mixture was then refluxed for 12 h. The excess SOCl₂ was removed by twice distillation in 130 mL dried toluene at low pressure in a rotary evaporator.

The resultant yellow coloured viscous liquid or solid (depending on the MW of the raw material) was dissolved in dried chloroform followed by extraction in dried n-hexane or diethyl ether to remove oil phase which was chlorinated PEGMME (scheme II).

**Preparation of Grafted PU**

A 5% DMF solution of prepared polyurethane was treated with stoichiometric quantities of NaH for 15 min at -40°C under nitrogen. An equivalent quantity of prepared chlorinated PEGMME was added at low temperature and the mixture was stirred. After 2 h heating at 50°C non-ionic grafted polyurethane was obtained (scheme III).

**RESULTS AND DISCUSSION**

Preparation of N-substituted polycaprolactone and polytetrahydrofuran based polyurethane with different molecular weights of poly(ethylene glycol monomethyl ether) using sodium hydride was achieved. The polyurethane elastomer was prepared by reaction of stoichiometric amount of polyol/diisocyanate/chain extender according to synthetic route as depicted in scheme I.

All poly(ethylene glycol monomethyl ether) with various molecular weights (350, 550, 750, 2000, 5000) were converted to their chloride analogues by using thionyl chloride in presence of dried toluene as a solvent, followed by distillation at low pressure, dissolving in chloroform and extracting in dried n-hexane (scheme II).

N-Substituted polyurethanes were synthesized by two step reaction from Capa or PTHF based PU as depicted in schem III.

In the first step, the catalyst generates the active anion sites on the polymer backbone. In the second step, the chlorinated PEGMME reacts with an anion site on the backbone to give N-substituted PU. The solvent influences the charge separation in the active chain end by solvation of the ions [10, 11]. Sodium hydride

\[
\begin{align*}
\text{CH}_3\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{H} & \xrightarrow{\text{SOCl}_2} \text{Toluene} \\
\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{Cl} & \xrightarrow{n-1} \text{CH}_2\text{CH}_2\text{Cl}
\end{align*}
\]  

**Scheme II. Chlorination of PEGMME.**
(NaH)/dimethylformamide (DMF) is commonly used as a catalyst/solvent in the N-substitution process of PUS. In the N-substitution of PUS, the overall reaction under the NaH/DMF condition was nearly completed within 2 h, determined by IR analysis. The prepared polymers were fully characterized and the results are brought in Tables 1 and 2.

The FTIR and ¹H NMR analysis were used to identify changes in chemical structure of polyurethanes resulting from N-substitution. Figure 1 depicts the IR spectra for N-substituted polymers. The spectrum shows N-H stretching at around 3300 cm⁻¹ obviously decreased by N-substitution, the N-H in urethane groups is used for initiation of the N-substitution. Consequently, a successful reaction would result in a complete consumption of the N-H groups. It is evident that the IR bonds at 3300 cm⁻¹ (N-H stretching), 1540 cm⁻¹ (C-NH) and 1225 cm⁻¹ gradually disappeared according to the increase of N-substitution degree for polyurethanes.

The ¹H NMR spectra of PU and N-substituted PU in DMSO are shown in Figure 2. The N-H proton peak was observed at 8-9.6 ppm for polyurethanes and two new peaks can be observed at 3.26 ppm and 3.69 ppm (Figure 2b) assignable to protons of the methoxy group (OCH₃) and (CH₂CH₂O)n which are the end group and backbone of PEGMME side chain in the N-substitution urethane. However in all the spectra of N-substituted polyurethanes, the signal of the urethane proton (NH-CO-O-) virtually disappeared as expected (Figure 2b).

**Thermal Behaviours**
The thermal properties were investigated in the point of the substitution various molecular weights of PEGMME using DSC. The results are brought in Table 3. In the case of the N-substituted PEGMME PU (Fig-
Figure 3), Tg decreased with N-substitution comparing with original PU (Figure 4), but lower molecular weight of polyethylene monomethyl ether has more effect on Tg than higher MW (Table 3). The hydrogen bonding of the urethane NH to O- or C=O restricts the segmental motion of the chain and increases the Tg of the chain. Disappearance of the active hydrogen in the urethane linkage decreases the intermolecular interaction caused by hydrogen bonds between the urethane groups and polyether or polyester backbone and leads to a decreased Tg. [6, 7, 12].

The Tg of N-substituted PU increase with increasing MW of polyethylene monomethyl ether and this is more obvious for PEGMME with MW of 2000 and 5000. This may be due to chain folding on itself and segment-segment interactions as suggested by Yen et al. [13], when the molecular weight of pendant group is above 1200.

**Particle Size Distribution**
The effect of PEGMME molecular weight on particle

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**Table 1.** Polymer characterization (PU, polycaprolactone base).

<table>
<thead>
<tr>
<th>No</th>
<th>polymer</th>
<th>IR (KBr, cm⁻¹)</th>
<th>NMR (DMSO-d6, δ, 2.49, 3.3 H2O)</th>
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<tbody>
<tr>
<td>1</td>
<td>PU</td>
<td>3341, 2945</td>
<td>7.9H(Ar), 7.2H(N-H)</td>
</tr>
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<td></td>
<td></td>
<td>1450, 1225</td>
<td>1.6 CH₂</td>
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<td></td>
<td>PU(350)</td>
<td>2858, 1729</td>
<td>7.4H(Ar), 7.02H(Ar)</td>
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<td></td>
<td></td>
<td>1600, 1534</td>
<td>4.08 CH₂, 2.30CH₃(Ar)</td>
</tr>
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<td></td>
<td></td>
<td>1457, 1225</td>
<td>1.6 CH₂</td>
</tr>
<tr>
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<td>PU(550)</td>
<td>2860, 1728</td>
<td>7.9 H(Ar), 7.02H(Ar)</td>
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<td>1600, 1537</td>
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<td>1.6 CH₂</td>
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<td>PU(750)</td>
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<td>7.9 H(Ar), 7.02 H (Ar)</td>
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<td>1600, 1535</td>
<td>4.08 CH₂, 2.36 CH₃ (Ar)</td>
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<td></td>
<td>1455, 1227</td>
<td>1.6 CH₂</td>
</tr>
<tr>
<td>5</td>
<td>PU(2000)</td>
<td>2866, 1725</td>
<td>7.9 H(Ar), 7.02H(Ar)</td>
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<td>1601, 1535</td>
<td>4.08CH₂, 2.33 CH₃ (Ar)</td>
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<tr>
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<td></td>
<td>1463, 1236</td>
<td>1.6 CH₂</td>
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<tr>
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<td>PU(5000)</td>
<td>2882, 1727</td>
<td>7.9 H(Ar), 7.02H(Ar)</td>
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<td></td>
<td>1467, 1235</td>
<td>1.6 CH₂</td>
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**Table 2.** Polymer characterization (PU, PTHF base).

<table>
<thead>
<tr>
<th>No</th>
<th>polymer</th>
<th>IR (KBr, cm⁻¹)</th>
<th>NMR (DMSO-d6, δ, 2.49, 3.3 H₂O)</th>
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<tr>
<td>1</td>
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<td>1732, 1533</td>
<td>4.08 CH₂, 2.30 CH₃(Ar)</td>
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<td>1456, 1225</td>
<td>1.6 CH₂</td>
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<td>7.9H(Ar), 7.02H(Ar)</td>
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<td>1601, 1533</td>
<td>4.08 CH₂, 2.35 CH₃(Ar)</td>
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<td></td>
<td>1458, 1225</td>
<td>1.6 CH₂</td>
</tr>
<tr>
<td>3</td>
<td>PU(550)</td>
<td>2868, 1731</td>
<td>7.9 H(Ar), 7.02H(Ar)</td>
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<td></td>
<td>1601, 1532</td>
<td>4.08 CH₂, 2.35 CH₃ (Ar)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1456, 1225</td>
<td>1.62 CH₂</td>
</tr>
<tr>
<td>4</td>
<td>PU(750)</td>
<td>2869, 1733</td>
<td>7.9 H(Ar), 7.03 H (Ar)</td>
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<td></td>
<td></td>
<td>1600, 1533</td>
<td>4.08 CH₂, 2.33 CH₃ (Ar)</td>
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<td></td>
<td>1456, 1228</td>
<td>1.63 CH₂</td>
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<tr>
<td>5</td>
<td>PU(2000)</td>
<td>2868, 1731</td>
<td>7.9 H(Ar), 7.02H(Ar)</td>
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<tr>
<td></td>
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<td>1601, 1530</td>
<td>4.08CH₂, 2.35 CH₃ (Ar)</td>
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<td>1459, 1230</td>
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<td>6</td>
<td>PU(5000)</td>
<td>2869, 1735</td>
<td>7.9 H(Ar), 7.03H(Ar)</td>
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<td>1602, 1534</td>
<td>4.08CH₂, 2.33 CH₃ (Ar)</td>
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<tr>
<td></td>
<td></td>
<td>1459, 1233</td>
<td>1.63 CH₂</td>
</tr>
</tbody>
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**Figure 1.** FTIR Spectrum: (a) PU elastomer and (b) PEG-MME grafted PU.
size are given in Figure 5. The particle size decrease with increasing molecular weight of PEGMME [14]. Control of particle size is important with regard to the particular application of aqueous PU, relatively larger particles are preferred in surface coating for rapid drying, and smaller ones are desirable when the deep penetration of dispersion into a substrate is an essential step [15].

### CONCLUSION

A new method established to prepare non-ionic water borne, PU elastomer. In this method polyethylene gly-
col monomethyl ether was chlorinated in the presence of SOCl₂ and used for N-substitution of prepared polyurethanes based on polyester and polyether polyl/toluene diisocyanate/1,4-pentane diol. N-Substituted PUs with PEGMME side chains were successively synthesized through a two-step process: first by generation of active anion sites on the polymer backbone, second, by treating the obtained urethane polyanion with corresponding chlorinated PEGMME in DMF. N-Substitution of PU had significant influences on thermal properties and solubility of the final products.

The T_g decreased along with the increase of the N-substitution as a result of weakened intermolecular interactions between the polymer chain caused by the decrease in the number of hydrogen bonds between them. Successful preparation of water borne PU elastomer based on CaPa 225 as well as PTHF proved that, both ester and ether based polyurethane can be used for preparation of non-ionic water-borne polyurethane elastomers.

REFERENCES