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

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ABSTRACT

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 polyester and polyster urethane containing polytetrahydrofuran or polycaprolactone/toluene diisocyanate and 1,4-butandiol. 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. T_g 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

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

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the nature of the starting materials. However, a few dis-
advantages caused by the urethane group exist. During
thermoplastic processing at temperature above 200°C,
[3, 4], they are split back into starting polyols and iso-
cyanates; 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 pre-
ceding 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-sub-
tituted PU [5], especially thermoplastic PU, with alkyl
or polyether side chains longer than methyl [8].

In this paper we report on the synthesis and charac-
terization of a number of N-sub PEGMME PUs with
various MW of PEGMME. Chlorinated PEGMME was
prepared according to procedure described in experimen-
tal 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)
(M_w= 350, 550, 750, 2000, 5000, Fluka) were dried at
80℃ under vacuum overnight. Polytetrahydrofuran
(PTHF, Merck, M_w=1000), polyCaprolactone (Capa
225, Interox Chemical Co Ltd., M_w = 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 chlor-
form (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 solu-
tion 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℃ 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 polyl(100g) and diisocyanate
(25.1g) were placed in a round bottomed polymeriza-
tion flask of 500 mL capacity and placed in an oil bath
at 60℃ 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 con-
trolled hot oil bath and the temperature was also moni-
tored by using a thermometer immersed in the oil by
the side of the polymerization flask. The reaction mix-
ture 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 main-
taining the dry nitrogen.

Two different series of PU elastomers were pre-
pared from the following molar ratio of linear
polyol/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 scheme 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 back bone 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
(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 \(^1\)H 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 \(^1\)H 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 \((OCH_3)\) and \((CH_2CH_2O)_n\) 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-
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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<tr>
<td>1</td>
<td>PU</td>
<td>3341, 2945</td>
<td>7.9H(Ar), 7.2H(N-H)</td>
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<td></td>
<td></td>
<td>1732, 1513</td>
<td>4.07 CH₂, 2.28CH₃(Ar)</td>
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<td></td>
<td></td>
<td>1450, 1225</td>
<td>1.6 CH₂</td>
</tr>
<tr>
<td>2</td>
<td>PU(350)</td>
<td>2858, 1729</td>
<td>7.4H(Ar), 7.02H(Ar)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1600, 1534</td>
<td>4.08 CH₂, 2.30CH₃(Ar)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1457, 1225</td>
<td>1.6 CH₂</td>
</tr>
<tr>
<td>3</td>
<td>PU(550)</td>
<td>2860, 1728</td>
<td>7.9 H(Ar), 7.02H(Ar)</td>
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<tr>
<td></td>
<td></td>
<td>1600, 1537</td>
<td>4.08CH₂, 2.33 CH₃ (Ar)</td>
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<tr>
<td></td>
<td></td>
<td>1454, 1225</td>
<td>1.6 CH₂</td>
</tr>
<tr>
<td>4</td>
<td>PU(750)</td>
<td>2861, 1726</td>
<td>7.9 H(Ar), 7.02 H (Ar)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1600, 1535</td>
<td>4.08 CH₅, 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></td>
<td></td>
<td>1601, 1535</td>
<td>4.08CH₂, 2.33 CH₃ (Ar)</td>
</tr>
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<td></td>
<td></td>
<td>1463, 1236</td>
<td>1.6 CH₂</td>
</tr>
<tr>
<td>6</td>
<td>PU(5000)</td>
<td>2882, 1727</td>
<td>7.9 H(Ar), 7.02H(Ar)</td>
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<tr>
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<td></td>
<td>1601, 1534</td>
<td>4.08CH₂, 2.33 CH₃ (Ar)</td>
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<td></td>
<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>8.5-9.5H(N-H), 7.9H(Ar)</td>
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<td></td>
<td></td>
<td>1732, 1533</td>
<td>4.08 CH₂, 2.30CH₃(Ar)</td>
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<td>1456, 1225</td>
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<tr>
<td>2</td>
<td>PU(350)</td>
<td>2866, 1732</td>
<td>7.94H(Ar), 7.02H(Ar)</td>
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<td>1601, 1533</td>
<td>4.08 CH₂, 2.35CH₃(Ar)</td>
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<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>1601, 1532</td>
<td>4.08CH₂, 2.35 CH₃ (Ar)</td>
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<tr>
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<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>
</tr>
<tr>
<td></td>
<td></td>
<td>1600, 1533</td>
<td>4.08 CH₂, 2.33CH₃ (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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<td>1601, 1530</td>
<td>4.08CH₂, 2.35 CH₃ (Ar)</td>
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<td></td>
<td></td>
<td>1459, 1230</td>
<td>1.6 CH₂</td>
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<tr>
<td>6</td>
<td>PU(5000)</td>
<td>2869, 1735</td>
<td>7.9 H(Ar), 7.03H(Ar)</td>
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<tr>
<td></td>
<td></td>
<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>
</table>

Figure 3, T₉ decreased with N-substitution comparing with original PU(Figure 4), but lower molecular weight of polyethylene monomethyl ether has more effect on T₉ 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 T₉ 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 back bone and leads to a decreased T₉, [6, 7, 12].

The T₉ 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
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 polyether and polyester polyol/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 Tₐ 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**