

Preparation and Properties of Aqueous Polyurethane Dispersions

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Received 9 March 2004; accepted 25 August 2004

ABSTRACT

Waterborne polyurethane as a new polymer dispersion was synthesized by using relatively hydrophilic polyols. This polymer was prepared from polycaprolactone diol (Capa 225), toluene diisocyanate (TDI), 1,4-butane diol (BDO) as chain extender, and dibutyltin dilaurate catalyst. Grafted polyurethane was prepared with chlorinated poly(ethylene glycol monomethyl ether) (PEGMME) in the presence of sodium hydride (NaH). Chlorinated PEGMME was also prepared by reaction of PEGMME with thionyl chloride in dried toluene. FTIR and ¹H NMR of the waterborne polyurethanes were used to characterize the grafted PU. The effects of various molecular weights of PEGMME as non-ionic hydrophilic segments were studied. The particle size and viscosity of dispersions were systematically analyzed. It is found that by increasing the molecular weight of the grafted PEGMME, the particle size of dispersed polyurethane is decreased, and viscosity is increased.

Key Words:

polyurethane dispersions;
waterborne polyurethane;
grafted polyurethane;
particle size;
polyethylene glycol monomethyl
ether.

INTRODUCTION

Aqueous polyurethane (PU) dispersions have been widely used in coatings and adhesives mainly due to environmental considerations [1-3]. An aqueous polyurethane dispersion is a binary colloidal system in which PU particles are dispersed in a con-

tinuous aqueous media [2]. As conventional polyurethane is insoluble in aqueous media, for making it dispersible in water, ionic and/or non-ionic hydrophilic segments should be incorporated in its backbone structure [4-9].

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Pioneer works on aqueous PU dispersions have been performed by industrial laboratories [3, 9-16]. So detailed data on particle size and physical properties of emulsion cast films are rarely available in open literature [11, 13]. Particle size is governed by a number of internal and external factors. However, depending on specific applications, an optimum particle size exists, and therefore, it is important to be able to control the particle size via chemical compositions [5].

In this paper, preparation of aqueous PU dispersion based on polycaprolactone diol (Capa 225), toluene diisocyanate (TDI), and 1,4-butane diol with different molecular weights of poly(ethylene glycol monomethyl ether) (PEGMME) grafted on their structure is described, and effect of various molecular weights of PEGMME as a non-ionic hydrophilic segment on their particle size and viscosity are studied.

EXPERIMENTAL

Materials

Poly(ethylene glycol monomethyl ether) (PEGMME, Fluka) (MW= 350, 550, 750, 2000, 5000) were dried at 80°C under vacuum, overnight. Polycaprolactone diol (Capa 225, Introx Chemicals), and 1,4-butane diol (BDO, Merck) were dried under vacuum. Toluene diisocyanate (TDI, Merck) was distilled under vacuum before use. The catalyst utilized was dibutyltin dilaurate (DBT, Merck). DBT and sodium hydride (NaH 60% suspension in mineral oil, Akzochemie) were used without further purification. Dimethylformamide (DMF, Merck) was dried on molecular sieve (4 Å) and freshly distilled before use.

Procedure

Reactions were conducted in a 500 mL round-bottom, four-necked flask with a mechanical stirrer, and nitrogen inlet; condenser, and pipette outlet. Reactions were carried out in a constant temperature oil bath with $\pm 0.5^\circ\text{C}$ precision. Capa 225 (200 g) was charged to the reactor and heated to 60°C with stirring. While keeping the temperature at 60°C, TDI (52.2 g) and DBT (drops) were added to the mixture. The reaction proceeds over approximately 4 h. Chain extension was carried out with BDO (18 g) for a period of 1h.

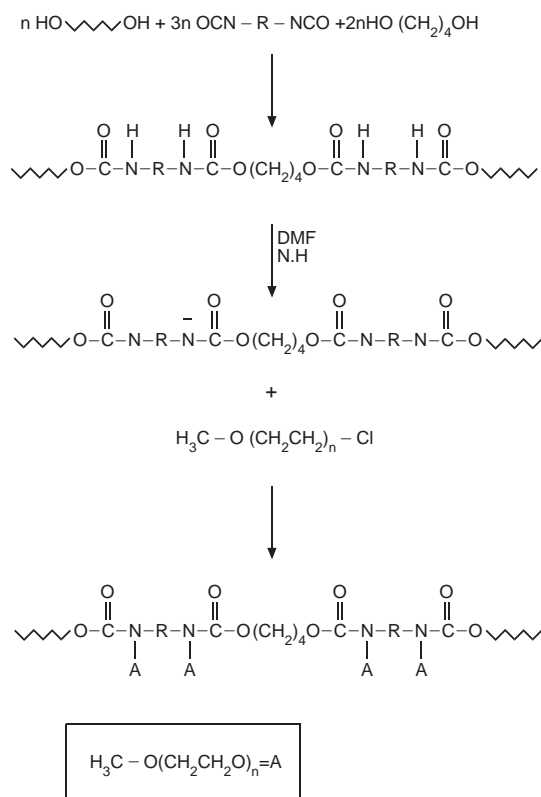
A 5% DMF solution of prepared polyurethane was

treated for 15 min at -5 to 0°C , under nitrogen, with stoichiometric quantities of NaH, counted on the basis of the $-\text{NH}-\text{COO}-$ group content in order to obtain the desired degree of substitution (Scheme 1). In this way, a polyurethane solution with ionic center was obtained. An equivalent quantity of prepared chlorinated PEGMME was added to the solution, at low temperature and the mixture was stirred. After 2 h heating at 50°C , nonionic grafted polyurethane was obtained. While stirring rapidly, demineralized water was added to the solution to form water dispersion.

For preparation of chlorinated PEGMME, was dissolved in dried toluene. An excess amount of thionyl chloride was added dropwise to the solvent. The reaction mixture was refluxed at least for 12 h at 60°C . After removing unreacted thionyl chloride by rotary evaporator, the oily phase (chlorinated PEGMME) is separated with dried n-hexane.

Characterization

Particle size and its distribution were measured by laser light scattering (Sematech, SEM-633, He-Ne laser). The sample was diluted by deionized water to 0.5% and then, the dispersion solution was homogenized.



Scheme 1. Preparation of grafted polyurethane elastomer.

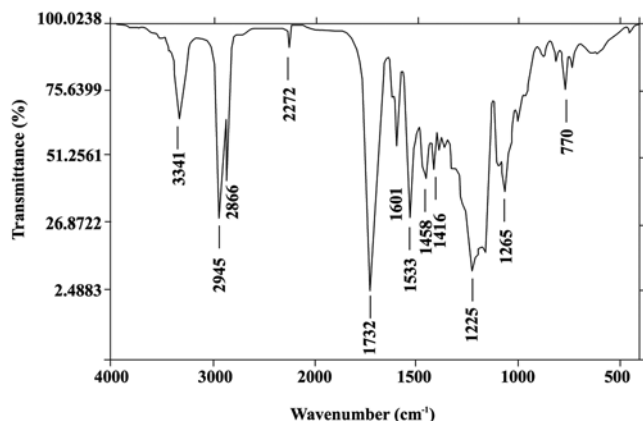


Figure 1. FTIR Spectrum of PU elastomer.

Films for infrared analysis were prepared by casting 5% PU in DMF solution onto potassium bromide pellets at room temperature. Following evaporation of the most of the solvent, the disks were placed in a vacuum oven at about 80°C for over 24 h to remove residual solvent. FTIR Spectra were recorded using an IFS-Brucker system. ^1H NMR was recorded with Bruker 500 MHz spectrometer and DMSO was used as a solvent. The viscosity of dispersion was measured with Brookfield viscometer 25°C.

RESULTS AND DISCUSSION

The reaction procedure of grafted polyurethane elastomer is given in Scheme I.

FTIR

The FTIR spectrum of prepared polyurethane, chlori-

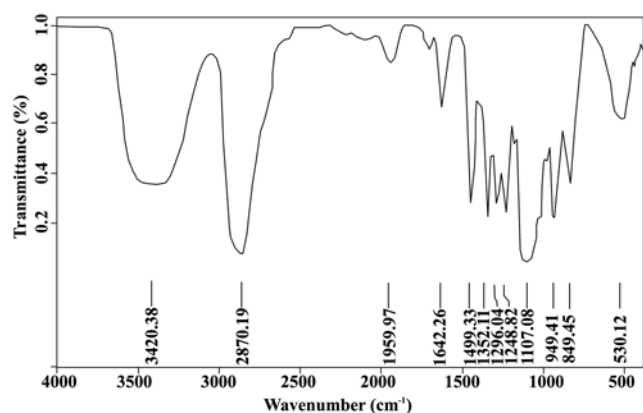


Figure 2. FTIR Spectrum of PEGMME.

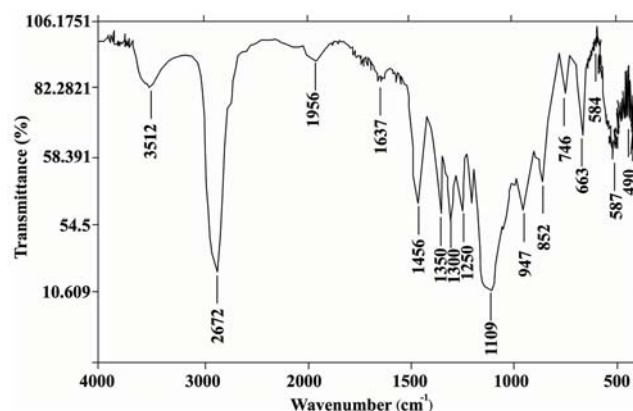


Figure 3. FTIR Spectrum of chlorinated PEGMME.

nated PEGMME and grafted PU are given in Figures 1, 2, and 3, respectively. Four main regions were assigned as follows:

- 1- A broad absorption band of the N-H stretching mode in $3300\text{--}3600\text{ cm}^{-1}$.
- 2- Aliphatic C-H stretching mode of $2850\text{--}3000\text{ cm}^{-1}$.
- 3- The carbonyl (C=O) stretching absorption band at $1600\text{--}1750\text{ cm}^{-1}$.
- 4- C-O-C stretching absorption band at $1000\text{--}1150\text{ cm}^{-1}$ corresponding to the ether oxygen of soft segment.

By comparing Figure 1 (spectrum of PU elastomer) and Figure 4 (spectrum of grafted PU) it can be concluded that N-H bond is substituted by N-PEGMME as the N-H absorption band is reduced [15].

^1H NMR

The ^1H NMR spectra are shown in Figures 5 and 6 for PU and grafted PU, respectively. In Figure 5 the N-H

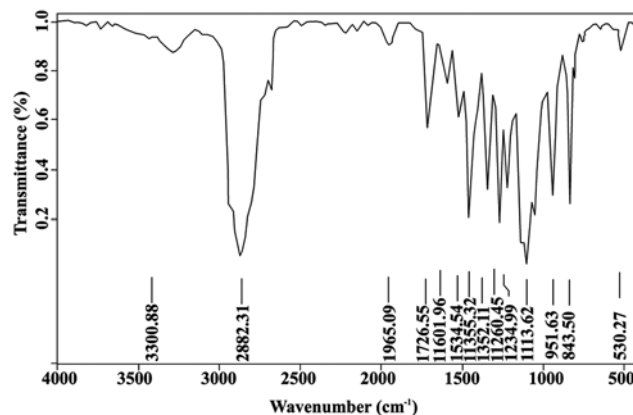


Figure 4. FTIR Spectrum of grafted PU.

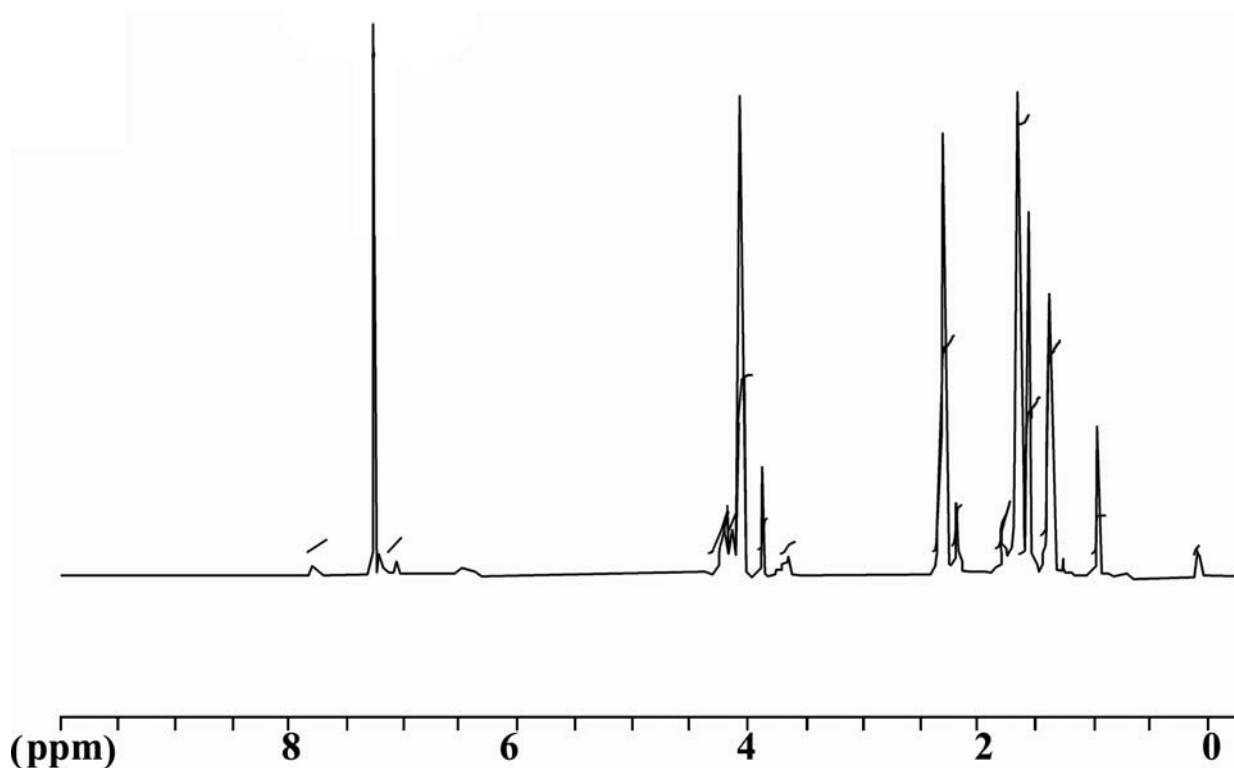


Figure 5. ^1H NMR Spectrum of PU elastomer.

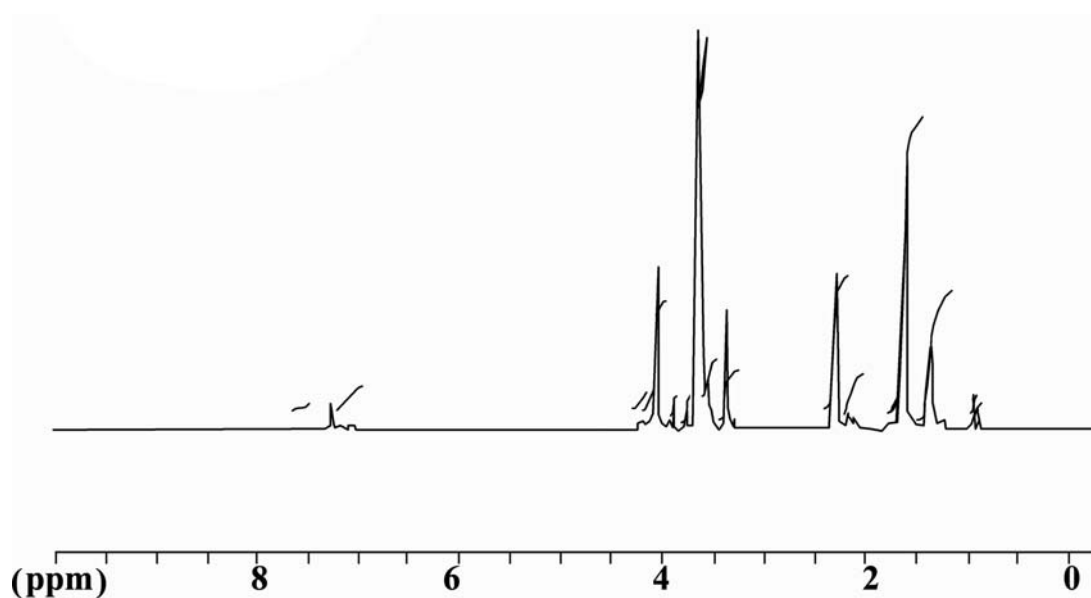


Figure 6. ^1H NMR Spectrum of grafted PU.

peak of PU elastomer was observed at $\delta = 7.2$, but according to Figure 6, N-H bonds were successfully substituted through grafting reaction.

Particle Size and Viscosity

The particle size distribution and viscosity of grafted

PU with different molecular weights of PEGMME are shown in Figures 7 and 8. it is needed to say that all samples for this part have the same concentrations [6].

It can be seen from Figure 7 that with increasing molecular weight of PEGMME the particle size is decreased. The dispersion viscosity is increased with

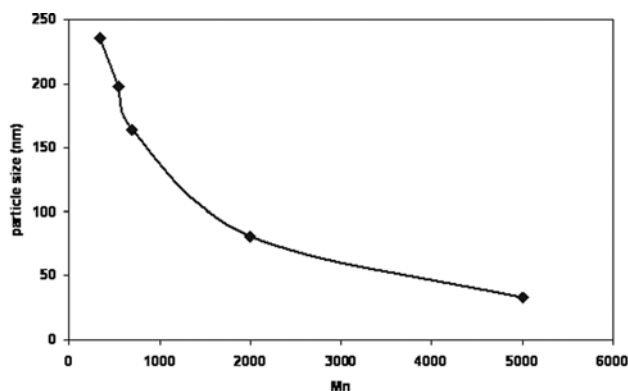


Figure 7. Particle size as a function of various molecular weights of PEGMME.

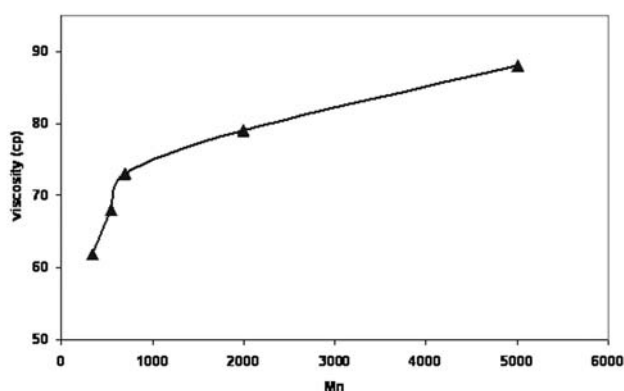


Figure 8. Viscosity as a function of various molecular weights of PEGMME.

increasing of PEGMME molecular weight (Figure 8), The decreased particle size and increased viscosity are due to increasing hydrophilicity of the polyurethane elastomers due to grafting of PEGMME to PU backbone structure.

CONCLUSION

A new method for producing non-ionic polyurethanes is consisted of preparing PU of polycaprolactone diol (Capa 225), toluene diisocyanate (TDI), butane diol (BDO), chlorinated PEGMME and sodium hydride (NaH) as an ionization agent was established. It is shown that with increasing molecular weight of PGMME, its particle size is decreased, so the average particle size is directly related to molecular weight of PEGMME. It is concluded that particle size decreases,

as the amount of hydrophilicity increases. The viscosity of dispersion is also increase with increasing of PEGMME molecular weight. Thus, by increasing hydrophilicity, particle size of prepared PU decreases and its viscosity increases.

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