

Preparation and Properties of Aqueous Polyurethane Dispersions

S. Mohammad Seyed Mohaghegh^{*1}, Mehdi Barikani¹, and
Ali Akbar Entezami²

(1) Department of Polyurethane and Advanced Materials, Iran Polymer and Petrochemical
Institute, P.O. Box: 14965/115, Tehran, I.R. Iran

(2) Faculty of Chemistry, Tabriz University, Tabriz-51664, I.R. Iran

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].

(*)To whom correspondence should be addressed.
E-mail: S.M.Mohaghegh@ippi.ac.ir

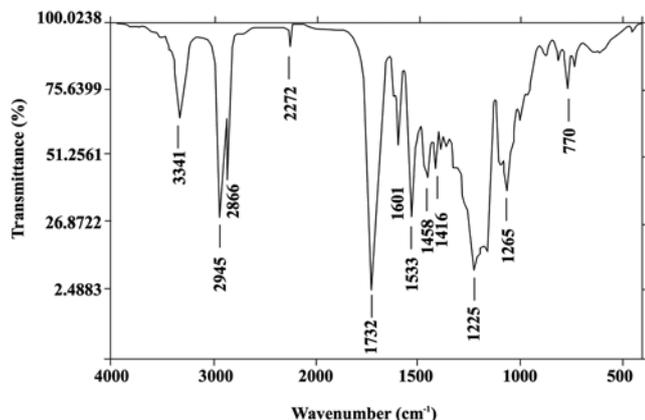


Figure 1. FTIR Spectrum of PU elastomer.

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-

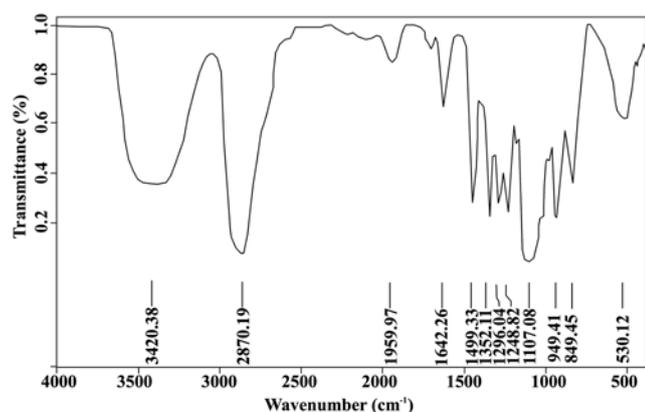


Figure 2. FTIR Spectrum of PEGMME.

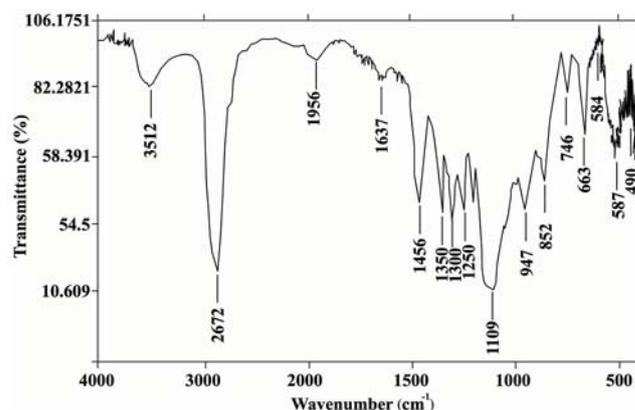


Figure 3. FTIR Spectrum of chlorinated PEGMME.

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 3300-3600 cm^{-1} .
- 2- Aliphatic C-H stretching mode of 2850-3000 cm^{-1} .
- 3- The carbonyl (C=O) stretching absorption band at 1600-1750 cm^{-1} .
- 4- C-O-C stretching absorption band at 1000-1150 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

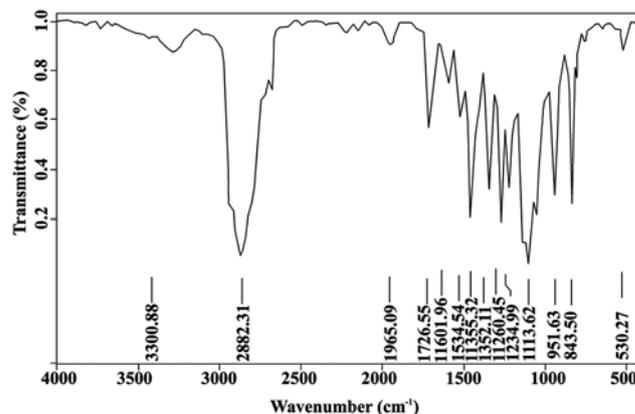


Figure 4. FTIR Spectrum of grafted PU.

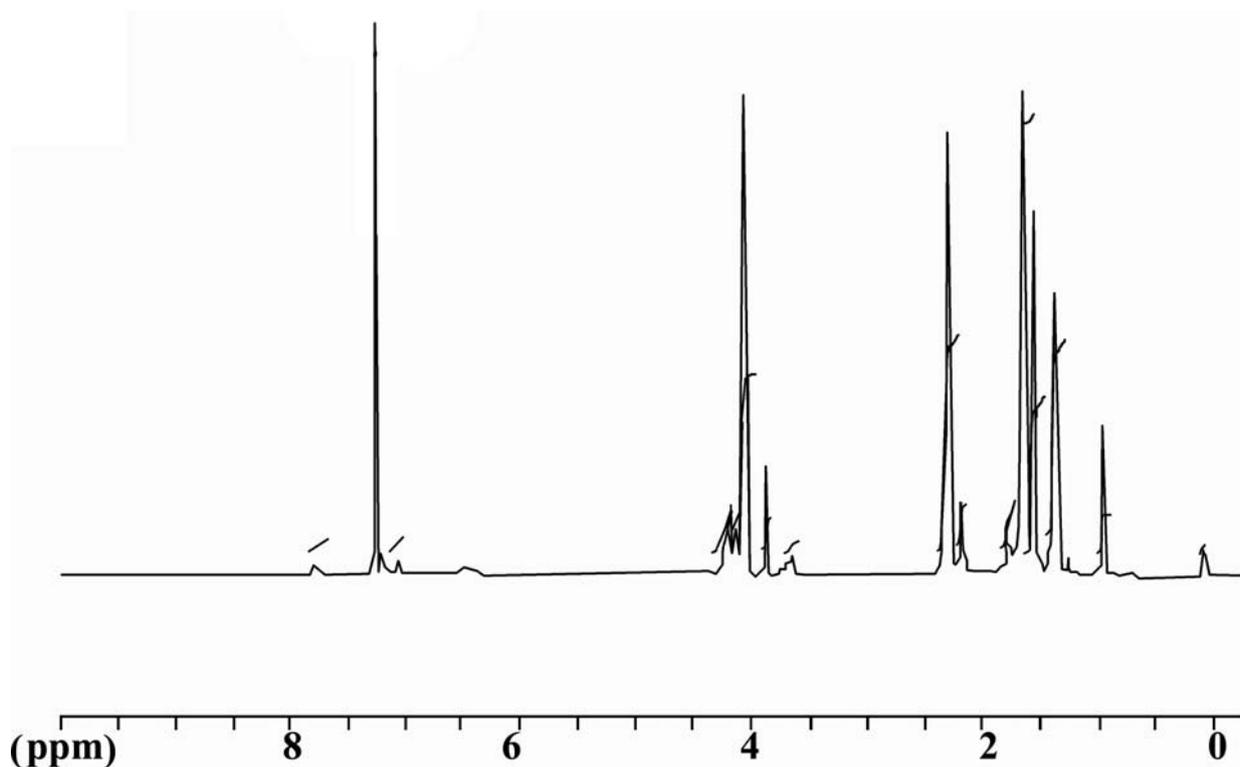


Figure 5. ^1H NMR Spectrum of PU elastomer.

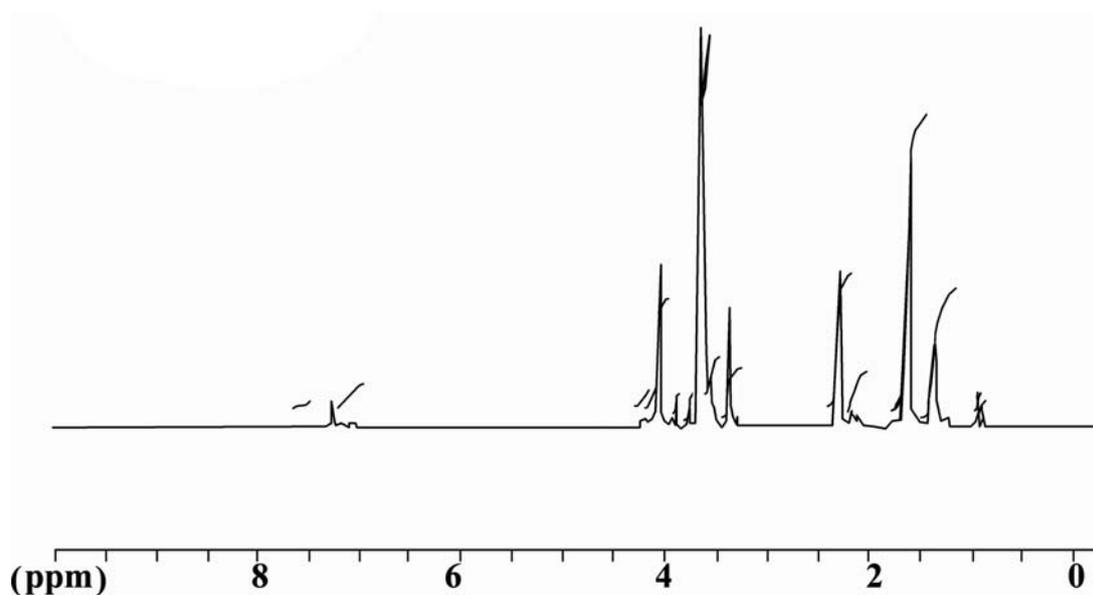


Figure 6. ^1H NMR Spectrum of grafted PU.

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

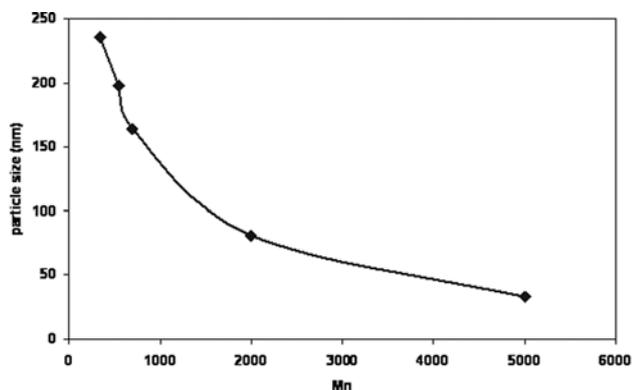


Figure 7. Particle size as a function of various molecular weights of PEGMME.

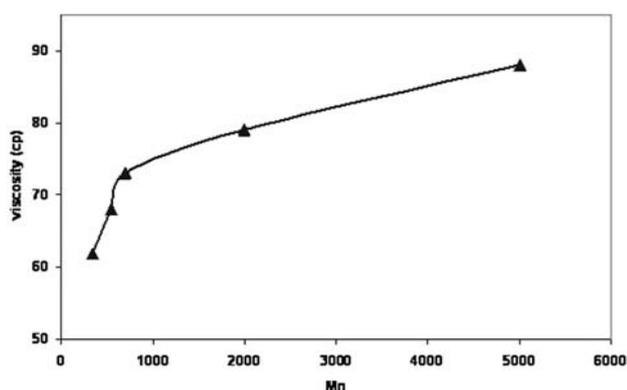


Figure 8. Viscosity as a function of various molecular weights of PEGMME.

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.

REFERENCES

1. Dietrich D., Aqueous emulsion, dispersions, and solutions of polyurethanes; synthesis and properties, *Progr. Org. Coat.*, **9**, 281-340(1981).
2. Dieterich D., Polyurethane ionomers a new class of block polymers, *Angew. Chem. Int. Eng. Ed.*, **9**, 40-50 (1996).
3. Kim B.K., Aqueous polyurethane dispersions, *Coll. Polym. Sci.*, **275**, 599-611(1996).
4. Frisch K.C. and Klempner D., *Advances in Urethane Science and Technology*, Technomic, Westport, 121-162 (1987).
5. Oertel G., *Polyurethane Handbook*, New York, Hanser Publishers (1985).
6. Kim B.K, lee S.Y., and Lee S.J., Preparation and properties of water-borne polyurethane, *Polym. Int.*, **42**, 67-76 (1997).
7. Dieterich D., Nevere wāBrige PUR-systeme, *Angew. Makromol. Chem.*, **98**, 133-165 (1981).
8. David D.J., and Staley B., *Analytical Chemistry of Polyurethanes, High Polymer Series. XVI*, Part III. New York., Wiley-Interscience (1969).
9. Lee Y.M., Kim T.K., and Kim B.K., Aqueous polyurethane Dispersions: Effect of DMPA and bisphenol A polyol on dispersion and physical properties of emulsion cast films, *Polym. Int.*, **28**, 157-162 (1992).
10. Kim B.K. and Kim T.K., Aqueous dispersion of polyurethanes from H₁₂ MDI, PTAd/PPG, and DMPA: Particle size of dispersion and physical of emulsion cast films, *J. Appl. Polym. Sci.*, **43**, 393-399(1991).
11. Kim C.K. and Kim B.K., IPDI-based polyurethane ionomer dispersion: effect of Ionic, Nonionic hydrophilic segments, and Extender on particle size and physical properties of emulsion cast film, *J. Appl. Polym. Sci.*, **43**, 2295-2301 (1991).
12. Hepburn C., *Polyurethane Elastomers, Appl., Sci. Publishers*, New York, Ch. 10 (1992).
13. Markusch P., Noll K., and Dieterich D., Cationic electrolyte-stable dispersions and process for producing polyurethanes useful therein, *US patent* 4,238,378 (1980).

14. Weyland P., Haeberle K., and Treiber R., Aqueous polyurethane formulation, *US patent* 5,401,582 (1995).
15. Sang-Sik B., and Nam Ju Jo, The effect of aggregation states on ionic conductivity of solid polymer electrolytes based on waterborne polyurethane, *Korea Polym. J.*, **9**, 332-338 (2001).
16. Digar M., Hung S.L., Wang H.L., Wen T.C., and Gopalan, A., Study of ionic conductivity and microstructure of a cross-linked polyurethane acrylate electrolyte, *Polymer*, **43**, 681-691(2002).