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On the study of structure property of polypropylene-glycol based polyurethane ionomer

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Abstract: Water-based polyurethane ionomers which have been successfully synthesized at our lab are demonstrated to be polypropylene glycol-based polyurethane ionomers by FT-IR spectra. For polyurethane ionomers prepared at a fixed ratio of NCO to OH as a function of ionic content, their viscosities are seen to be higher for polypropylene glycol with molecular weight of 1500 (triols) than for polypropylene glycol with molecular weight of 1000 (diols) or 2000 diols based polyurethane ionomers, as a result of strong intra ionic chain interaction. On the other hand, the viscosities due to strong inter chain interaction appear to be higher for polypropylene glycol with molecular weight of 1000 than for polypropylene glycol with molecular weight of 1500 or 2000-based polyurethane ionomers made at a fixed ionic content and under the variation of the ratio of NCO/OH. Like surfactant, poly-propylene glycol-based polyurethane ionomers present in water can substantially reduce the surface tension of water. Thus, it may be considered as an ionomer-like surfactant.

Key words: Polyurethane ionomer

Introduction

The isocyanate polyaddition method which has long been used to prepare polyurethane ionomers is described in detail elsewhere. These polyurethane ionomers give rise to the structural change, as a result of strong electrostatic and hydrogen bonding interactions between their chains. Furthermore, this structural change not only depends upon the type, amount and chain length of diisocyanate and polyol used, but also upon the type and amount of ionic groups of PU ionomers present in the system and the solvent used. Since the structure property relationship can substantially affect the performance, particularly mechanical property of polyurethane ionomers, therefore, it has drawn a great deal of attention from researchers in both academia and industry. Although a number of papers on polyurethane ionomers has been published, information on the factors affecting the structures of these ionomers is still limited so far. Therefore, we attempt to explore the effect of the NCO (toluene diisocyanate)/OH (polypropylene glycol with other OH group) ratio and the amount of ionic chains on the structures of polyurethane ionomers in terms of surface tension and viscosity studies.

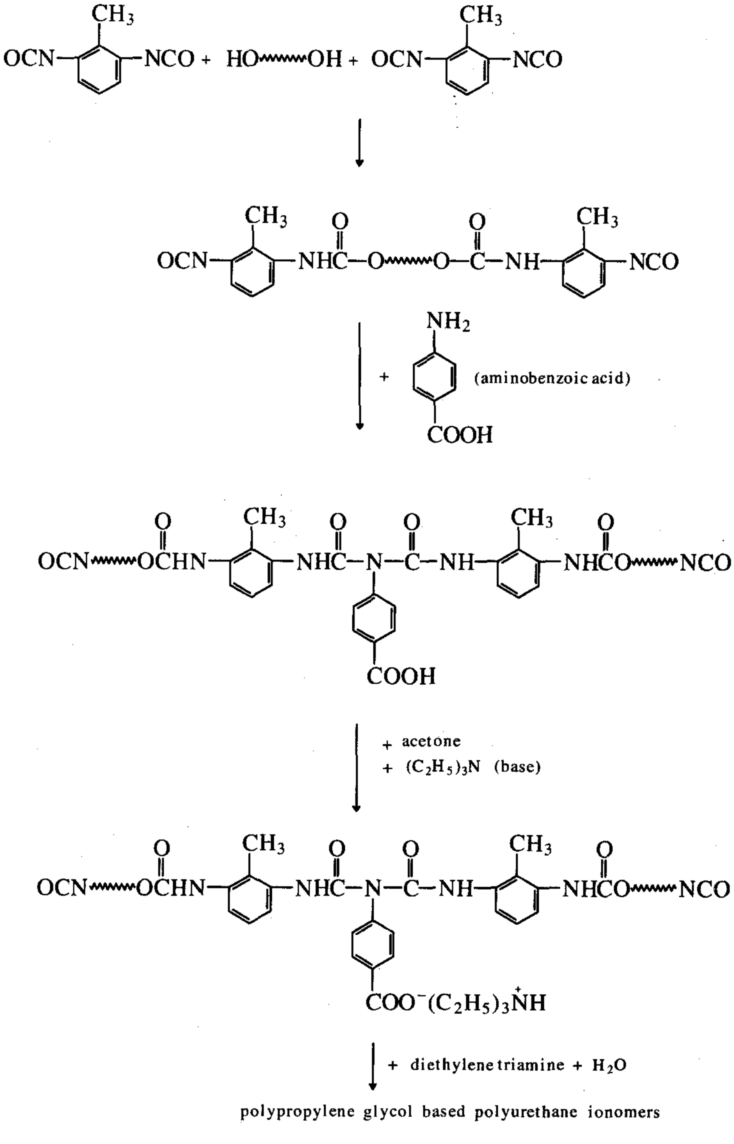
Experimental

Materials

Toluene diisocyanate, triethylamine, acetone, *N*,*N*-di-methylformamide, diethylene triamine and 4-aminobenzoic acid were purchased from Merck Co. Polypropylene glycol (PPG diols with molecular weight of 1000 and 2000; PPG triols with molecular weight of 1500) and polyester (with molecular weight of 2000) were supplied by Chiunglong Petrochemical Co. and by Dynasty Chemical Industries Co. Ltd., respectively. All of these materials were used without further purification.

Methods

Both PPG-2000 and acetone were dried before use. A 2-l fournecked reaction kettle equipped with a stirrer, thermometer, and condenser was charged with 0.1 or more than 0.1 equivalent of PPG-2000 (OH = 56), PPG-1500 (OH = 113), PPG-1000 (OH = 112), and polyester 2000 (OH = 56). Subsequently, 0.3 or less than 0.3 equivalent of toluene diisocyanate was added slowly and then reacted in the presence of 0.2% (by weight) dibutyltin dilaurate at 80–85 °C for about 3 h. Aminobenzoic acid (6.0–10.5% by-weight) in *N*,*N*-dimethylformamide was reacted with the above mixtures at about 55 °C for approximately 30 min to yield PU pre-polymer with different ionic content (6.0–10.5% percent by weight) and NCO/OH ratios. The amount of triethylamine was calculated (equivalent amount of triethylamine based on aminobenzoic acid used in preparing PU prepolymer) and then reacted with PU polymer dissolved in acetone (1.2 time of solid weight) to form quaternized PU prepolymer. This quaternized NCO-terminated prepolymers reacted further with diethylene triamine as a chain extender and water (0.6 time of solid weight) to form linear poly-urethane ionomers given as follows:



After removing the acetone by evaporation the viscosities and surface tension of the polyurethane (PU) ionomer liquids were studied at room temperature using a Brookfield viscometer and Du Nouy ring tensiometer, respectively. The experimental error for the measurements of these PU ionomers was estimated to be within ± 0.2.

Results and discussions

The OH group of PPG 1000 will rapidly react with TDI to form urethane linkage (–NH–COO–) illustrated by the disappearance of the absorbance peak at 3500 cm (OH) given in Fig. 1. It can be demonstrated that the reaction of aminobenzoic acid with TDI, followed with triethylamine, does, indeed, take place, since the OH absorbance peak is seen to disappear completely. Furthermore, the formation of NCO-prepolymer can also be demonstrated by the strong absorbance peak appearing at 3300 cm (NH) and by the weak absorbance peat at 2350 cm ($-N = C = O$).

The viscosities of polyurethane ionomers made by respective polypropylene glycol 1000 (PPG 1000), 1500 (PPG 1500), 2000 (PPG 2000) and polyester 2000 as a function of ionic content, given in Fig. 2, are seen to decrease with an increase in ionic content. Owing to electrostatic repulsion generating by ionic chains of PU ionomer molecules, increased electrostatic repulsion will substantially reduce the hydrogen bond formation and the interchain association between inter PU ionomer molecules, possibly forcing PU ionomer molecules in water to diffuse rapidly. Thus, the viscosity decreases.

In Fig. 2, it indicates that the viscosities appear to be slightly higher for non-linear PPG 1500 (triols; $\overset{\text{OH}}{\text{OH} \quad \text{OH}}$) than for linear PPG 1000 (diols; HO OH) and linear PPG 2000 (diols; HO OH)-based PU ionomer solution. This may be attributed to non-linear PPG 1500 (triols)-based PU ionomer molecules with more ionic chains having strong electrostatic repulsion resulting from intra-ionomer molecules, and with more ionic chains occupying a slightly larger free volume. This repulsive interaction may force PPG 1500 based PU ionomer molecule to form expanded conformation (i.e., large aggregates) resulting in raising the viscosity with increasing ionic content. Figure 2 also shows that, at low ionic content (≤ 7% by weight), viscosities for both linear PPG 2000 (diols) and linear polyester 2000 (diols) based PU ionomer, under experimental error, decrease rapidly and their differences in viscosities are seen to be small. At high ionic content (> 7% by weight), on the other hand, the viscosities start to rise for both cases and the values are seen to be larger for polyester 2000 (i.e., more hydrogen bond formation) than for PPG 2000 based PU ionomer solutions. The ion association from inter- and intra-molecular electrostatic interactions between carboxyl anions (COO^-) and associated ammonium counterions

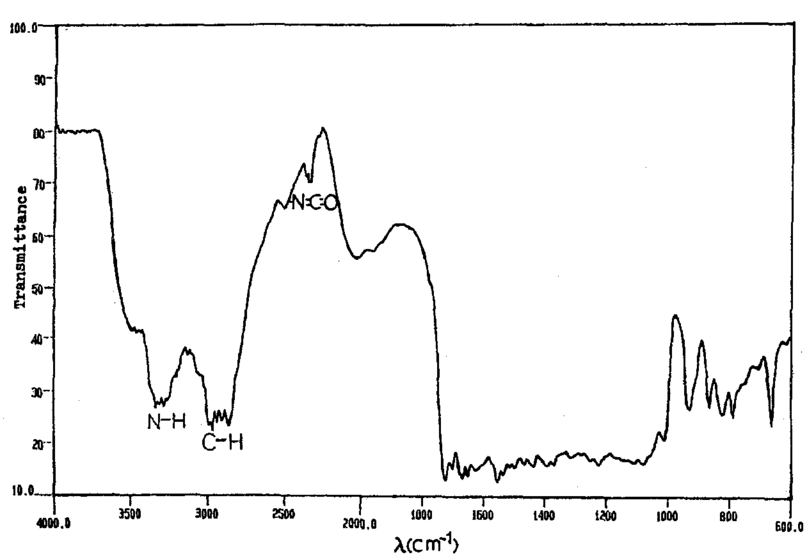


Fig. 1. Spectra of PPG 1000 based PU prepolymer at 20 ± 0.05 °C

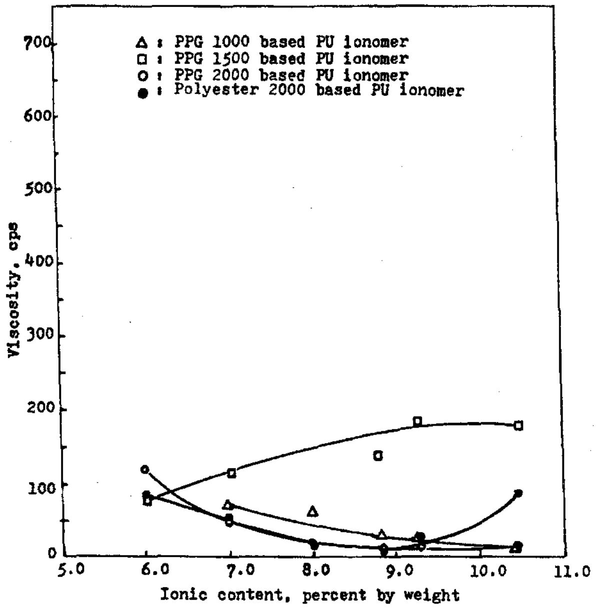


Fig. 2. Viscosity for PPG based PU ionomers prepared as a function of ionic content at 20 ± 0.05 °C

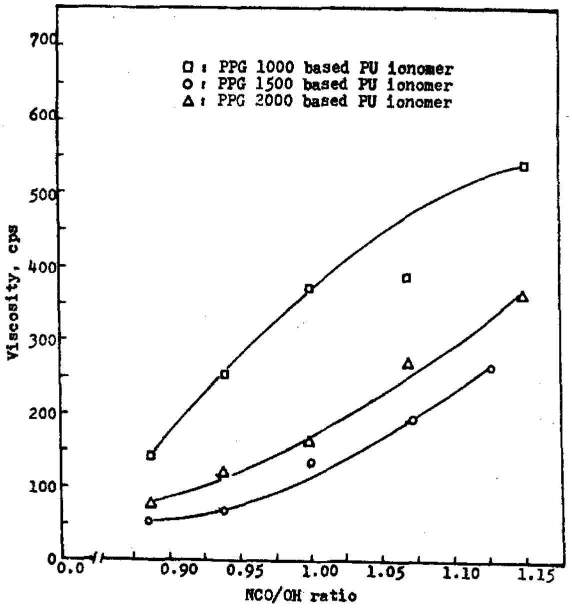


Fig. 3. Viscosity for PPG based PU ionomers prepared as a function of NCO/OH ratio at 20 ± 0.05 °C

may lead to form large or cross-linking-like conformation, coupled with more hydrogen bond formation with increasing ionic content. These factors are probably responsible for rising viscosity.

The viscosity for PPG based PU ionomers made at a fixed ionic content, given in Fig. 3, appears to gradually increase with increasing the ratio of NCO/OH, as a result of more hydrogen bond formation between urethane groups themselves and between urethane and water molecules. Figure 3 clearly shows that the values of viscosities are seen to be higher for low molecular weight PPG 1000 than for high molecular weight PPG 2000 based PU ionomers. This is because PPG 1000 based PU ionomer with short soft segments (i.e., PPG 1000) has more hard segments (i.e., –NH–CO–O) than PPG 2000 based PU ionomer with long soft segments (i.e., PPG 2000). These inter-hard segments may readily cross-link to form large aggregates resulting in increasing the viscosity of PU ionomers solution. It is important to point out that, since PPG 1500 (triols)-based PU ionomers, having more hard segments than PPG 1000 based PU ionomer (diols), readily form small aggregates owing to intra-hard segments interaction, therefore, viscosities become smaller for PPG 1500 than for PPG 1000 and PPG 2000-based PU ionomers.

The effect of water on the viscosity of PPG 1000-based PU ionomers present in acetone is shown in Fig. 4. It clearly illustrates that the viscosity of PU ionomer solution drastically increases and then rapidly drops as the amount of water in the system is largely increased. This is because at first a small amount of water equal to or less than 10% (by weight) added to PPG 1000 based PU ionomer system may replace part of acetones surrounding PU ionomers, possibly making such ionomers to form large aggregates, as a result of rapid formation of hydrogen bonding between water and ionomer molecules. These aggregates having large free volume move slowly in aqueous organic solution and are responsible for viscosity rising sharply. However, addition of water larger than 10% (by weight) to the above ionomer system results in decreasing the viscosity of PU ionomers in aqueous organic solution considerably, although the PU ionomer concentration decreases. Since the amount of acetone present in the system may largely decrease and PU ionomers due to intra chain association may form compact aggregates, therefore, the viscosity decreases. As soon as the viscosity of PU ionomer solution reaches a plateau, further addition of water to the system appears not to affect the viscosity significantly. The reason for this is

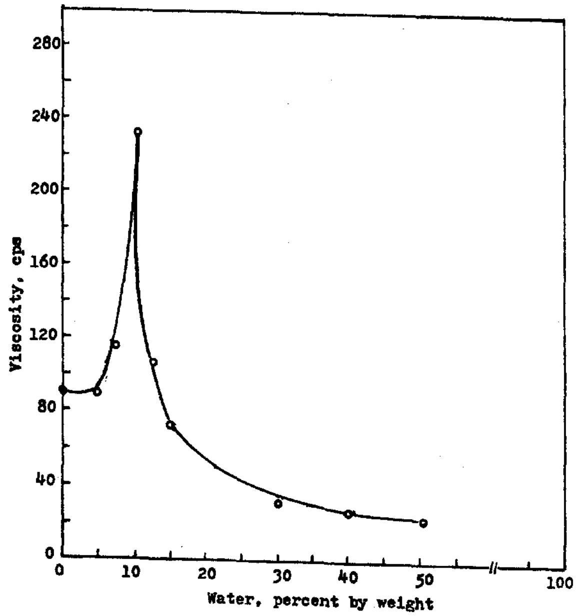


Fig. 4. Viscosity for PPG 1000 based PU ionomer prepared as a function of water at 20 ± 0.05 °C

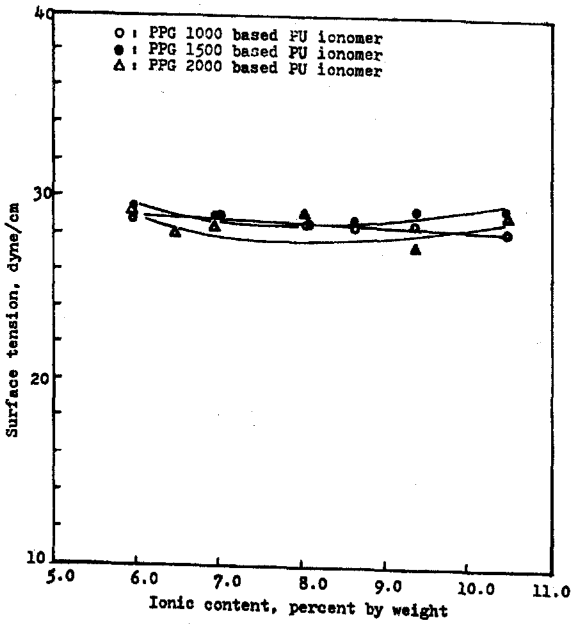


Fig. 5. Surface tension for PPG based PU ionomers prepared as a function of ionic content at 20 ± 0.05°C

attributed to the formation of micro-sphere of dispersants present in aqueous organic solution.

The surface tension measurements for PPG-based PU ionomer aqueous solution as a function of ionic content are given in Fig. 5. Figure 5 shows that the surface tensions gradually increase with increasing ionic content for PPG 1500 and PPG 2000-based PU ionomer solutions, but not for PPG 1000-based PU ionomer solution. Increased ionic content for PU ionomer molecules, leading to generation of strong electrostatic repulsion, may enable the hydrophobics of PPG 1500 (triols) and PPG 2000 (diols)-based PU ionomers to adsorb at the air-water interface to become even more ordered. Thus, the surface tension increases. For PPG 1000 (diols)-based PU ionomer molecules, the adsorption of hydrophobics of these molecules at the air-water interface may already rearrange to become ordered, as a result of their relatively short soft segments which are considered to be hydrophobics diffusing to the interface. For this reason, increased electrostatic repulsion resulting from increasing ionic content does not significantly affect the surface tension of an ionomer solution. It is also interesting to point out that, like surfactant, PPG-based PU ionomer present in water can substantially lower the surface tension of water (i.e., around 30 dyne/cm). In this respect, it may considered as an ionomer-like surfactant.

Conclusion

Water-based polyurethanes which have been successfully synthesized at our lab are demonstrated to be PPG based polyurethane ionomers by FT-IR spectra. Non-linear PPG 1500 (triols) based PU ionomers, made at a fixed ratio of NCO to OH as a function of ionic content, have more ionic chains than linear PPG 1000 (diols) and linear PPG 2000 (diols)-based PU ionomers. These intra-ionic chains due to their strong electrostatic repulsion may lead PPG 1500-based PU ionomer molecule to form large aggregates resulting in rising the viscosity. Contrarily, the viscosity is seen to be higher for PPG 1000 than for PPG 1500-based PU ionomers made at a fixed ionic content and under the variation of NCO/OH, as a result of strong inter-chain associations between ionomer molecules. Since intra-chain associations may cause PPG 1500-based PU ionomer molecules to form compact conformation, therefore, the viscosity decreases. In addition, PPG-based PU ionomer present in water can substantially reduce the surface tension of water. For this reason, it may be considered as an ionomer-like surfactant.

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