

Synthesis and Properties of Polyoxyethylated Amine Polyurethane Ionomers

XIN WEI, QUAN HE, XUEHAI YU

Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210093, People's Republic of China

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ABSTRACT: Based on polyoxyethylated amines ($M_n = 600, 1,200$) derived from *n*-butyl amine and ethylene oxide, 4,4'-diphenylmethane diisocyanate, and different chain extenders, two series of polyether-polyurethane (PU) ionomers with reasonable mechanical properties were synthesized. Chain-extended by 1,4-butanediol and subsequently reacted with 1,3-propane sultone, PU elastomers can be conveniently converted to PU zwitterionomers whose ions are located in polyether soft segments. Chain-extended by *N*-methyl diethanolamine or sodium-*S*-1,2-dihydroxypropyl sulfonate along with ionization by 1,3-propane sultone, PU ionomers with ions incorporated into both hard and soft domains can be prepared. Physical properties were studied by means of Fourier transform infrared spectra, differential scanning calorimetry, and uniaxial stress-strain testing. Complex impedance spectra were also measured to estimate solid-state ionic conductivity. The results show that ionization of both hard and soft segments induced a much decreased glass transition temperature and brought higher ionic conductivity at room temperature. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 67: 2179–2185, 1998

Key words: polyoxyethylated amine (NPEO); polyurethane ionomer; zwitterionomer; solid state ionic conductivity; single ion transport mechanism

INTRODUCTION

Because of their excellent mechanical properties, polyurethane (PU)-segmented copolymers are an important class of thermoplastic elastomers which consist of hard-segment-rich and soft-segment-rich domains.^{1,2} Due to specific properties of PEO, such as ready solubility in water and a number of organic solvents, chain flexibility and mobility, and strong tendency of association complex formation with neutral salts, polyethylene oxide (PEO) PU performs an important role as a very promising functional polymer for biomaterials, solid state ionic conductor, and so on.^{3–6}

Despite the increasing interest in PU ionomers

in many areas, relatively little synthetic work has been done in this fast-growing field. This laboratory,⁷ Cooper and associates,^{8–15} and Xu and Yang,³ have made great efforts to explore various ways of synthesizing and characterizing PU ionomers. Different kinds of samples, including zwitterionomers and sulfonated and carboxylated anionomers were synthesized. However, generally speaking, most of the ionization took place in hard domains (in urethane groups or chain extenders) because of the advantage that ions could be much more conveniently introduced there than in polyether soft segments. Recently, we have reported the synthesis of a series of sulfonated PU anionomers with ions located in the polyether (PTMO or PEO) soft segments by means of transesterification with sodium salt of dimethyl 5-sulfoisophthalate. Some interesting properties have been found in such PUs.⁷ Because tertiary amine

Correspondence to: X. Yu.

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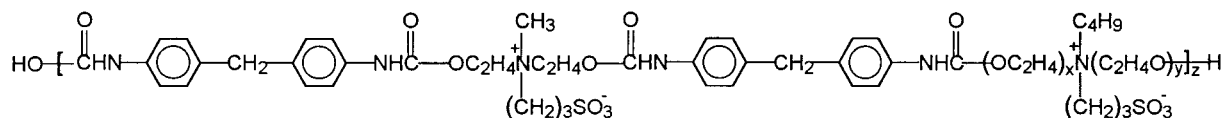


Figure 1 Chemical structures of NPEO PU zwitterionomer. Note that the structure of MM-NPEO600-Z is taken as an example.

presents an ideal ionization site to prepare cationomers, anionomers, quaternary ammonium sulfonate zwitterionomers,¹⁰ and carboxybetaine compounds,¹⁶ and because tertiary amine also supplies a sufficient catalyst for PU synthesis,⁵ polyoxyethylated amines (NPEOs) were prepared and utilized in this work as polyether soft segments to synthesize PU elastomers. In this investigation, ionization of the polyether soft segments was accomplished by quaternization of NPEOs with 1,3-propane sultone. Hard domains were ionized according to the methods reported by Miller and colleagues¹⁰ and Chui and coworkers.¹⁷ The purposes of this investigation were to present another option for preparing ionized-polyether PU and to study the effects of ion incorporation and ionization site on morphology and solid-state ionic conductivity.

EXPERIMENTAL

Materials

4,4'-Diphenylmethane diisocyanate (MDI) was degassed and purified by vacuum distillation. PEO ($M_n = 600$) was dried at 70°C in a vacuum oven for 24 h. *N,N'*-Dimethylacetamide (DMA) and dimethyl sulfoxide were dried with molecular sieves and purified by distillation.

Ethylene oxide (EO), *n*-butylamine (98%), *N*-methyl diethanolamine (MDEA) (Fluka Chemie AG, Switzerland), 1,4-butanediol (BD) (99%, Aldrich Chemical Co., U.S.A.), 1,3-propane sultone (97%, Aldrich Chemical Co., U.S.A.), toluene, methanol, petroleum ether (boiling point, 60–90°C), and stannous octoate catalyst were used as received.

Sodium-*S*-1,2-dihydroxypropyl sulfonate (SDPS), which was used as an ionized chain-extender in this experiment, was prepared and purified according to the literature reported by Chui and colleagues¹⁷ (yield = 65–70%). The purity of SDPS was characterized by both elemental analysis (found C: 20.94%, H: 3.95%; calculated C: 20.23%, H: 3.96%) and induc-

tively coupled plasma (found Na: 12.50%; calculated Na: 12.91%) before use.

Preparation of NPEOs

A typical polymerization run is described as follows.^{4,5} A 2-L autoclave designed to stand 7.2 MPa was evacuated and purged with nitrogen twice, then the reactor was charged with a 500-g mixture of *n*-butyl amine and EO quantitatively. No additional catalyst such as caustic was used since the basic nature of *n*-butyl amine provided sufficient catalyst.⁵ The mixture was then stirred and the reaction temperature and pressure were gradually raised to the working range of 60–80°C at 0.8–1.2 MPa. During reaction, the temperature was carefully controlled to ensure that the pressure in the reaction kettle was never allowed to exceed the working range. The reaction continued steadily for 2–2.5 h. At the end of the run, the pressure in the reactor dropped to 0–0.1 MPa while the temperature increased to 110°C. To ensure a complete reaction, the mixture was kept at 110°C for another 30 min. The product was then cooled to 80°C and discharged. The yield is quantitative (yield > 96%). The main cause of the coloring of polyoxyethylated alkylamines is the reaction of acetaldehyde contained in EO, such as its polymerization and decomposition.¹⁸ The coloring can be depressed with the addition of primary amines.¹⁸ Since *n*-butylamine was used in this work, the produced NPEOs were lighter colored and no decolorization was necessary.¹⁸ The NPEOs were dried at 60°C in a vacuum oven for 24 h before use.

Preparation of PUs and PU Ionomers

Based on MDI and PEO ($M_n = 600$) and chain-extended by BD, MDEA, or SDPS, respectively, a series of PUs were synthesized using a typical two-step polymerization method.²

Based on MDI and NPEOs ($M_n = 600, 1,200$), another series of PU samples were prepared according to a so-called “one-shot” procedure,² which

Table I The Synthesized Polyurethanes

Sample Designation	Molar Ratio							1,3-Propane Sultone
	MDI	Polyethers			Chain Extenders			
		PEO60 0	NPEO60 0	NPEO120 0	BD	MDEA	SDPS	
MB-PEO600	2	1			1			
MB-NPEO600	2		1		1			
MB-NPEO600-Z	2		1		1			1
MM-PEO600-Z	2	1				1		1
MM-NPEO600-Z	2		1			1		2
MBS-NPEO600	2		1		0.368		0.632	
MBS-NPEO600-Z	2		1		0.368		0.632	1
MS-NPEO1200	2.35			1			1.35	
MS-NPEO1200-Z	2.35			1			1.35	1

meant the DMA solution of MDI was added dropwise to the DMA solution of NPEOs and chain-extendors.

All of the PUs based on NPEOs or chain-extended by MDEA can be quaternized by subsequently reacting with 1,3-propane sultone. As a result, PU zwitterionomers could be expected.

All the synthesized samples were recovered by precipitation in a 50/50 mixture of toluene and petroleum ether and washed several times in fresh toluene. The products were then extracted by methanol in a Soxhlet apparatus for 72 h. To prepare samples for further testing, the polymers were dissolved in DMA at 10 wt % and cast on a Teflon plate at 60°C to achieve transparent films. The films were kept under vacuum at 60°C for 48 h to remove residual solvent, and were stored at room temperature in a vacuum desiccator. The chemical structure is shown in Figure 1. The compositions and designations of the synthesized samples are listed in Table I. The nomenclature used in this paper describes the chemical structure of the polymer chain. As an example, the designation "MBS-NPEO600-Z" is interpreted as follows: The first group of letters defines the hard segment as "MBS," MDI chain-extended with BD and SDPS. The second group of letters indicates that the polyether soft segment is NPEO600. The subsequent "Z" means that this sample has been converted to its analogous zwitterionomer by reacting with 1,3-propane sultone.

Characterization

The number-average molecular weights (M_n) of NPEOs were determined by two conventional

methods. One of the methods for analysis involved the reaction in pyridine of phthalic anhydride with the end groups. The system was then titrated with sodium hydroxide to the phenolphthalein end point.⁴ Vapor phase osmometry (VPO) was also used to reaffirm the results, which was operated in a Knauer vapor phase osmometer at 45°C in a solution of toluene.

The effect of heating on solubility was studied in a 1% aqueous solution from room temperature (25°C) to 100°C at a heating rate of 10°C/min.⁵ Fourier transform infrared (FTIR) spectra were recorded on a Nicolet FTIR-170 SX at a resolution of 2 cm⁻¹. Samples for infrared studies were prepared by solution-casting on a NaCl plate and drying at 60°C in a vacuum oven for 24 h.

Differential scanning calorimetry (DSC) thermograms were recorded at a heating rate of 20 K/min from 120 to 480 K using a Perkin-Elmer DSC-2 equipped with a data-processing unit. The data-processing unit allows automatic subtract and normalization of the thermograms for sample weight.

Uniaxial stress-strain testing was performed at room temperature (25°C) using a Shimadzu

Table II The Synthesized Polyoxyethylated Amines (NPEOs)

Amine	M_n		Yield (%)	Effect of Heating on Solubility
	End-Group Analysis	VPO		
NPEO600	573	613	96	Clear at bp
NPEO1200	1,246	1,288	98	Clear at bp

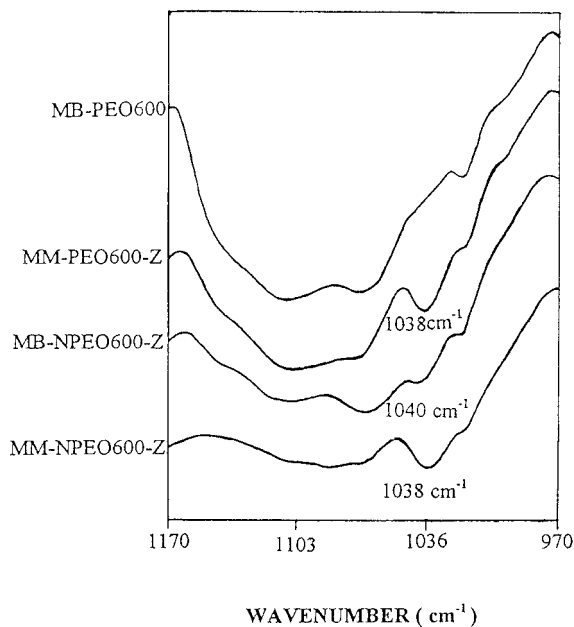


Figure 2 FTIR spectra of PU and PU ionomers.

AG-100KNE testing machine with a crosshead speed of 50 mm/min. The typical film thickness was about 0.5 mm. For each sample, three dumb-bell-shaped testing samples were cut from the film using an ASTM D1708 die. The reported values are the averaged results.

Films for conductivity measurements were cut to a required size and then painted with conductive Ag paste at both sides to form two Ag electrodes (diameter 1.0 cm). The typical film thickness was about 0.5 mm. The painted films were dried at 60°C in a vacuum oven for 24 h before measurement. Solid-state ionic conductivity measurements with alternating current were carried out with a 378 Electrochemical Impedance System (EG & G Princeton Applied Research, U.S.A.) interfaced with an IBM XT computer in the frequency range from 5 to 10^5 Hz. The cell was kept in a temperature-controlled dry box and the conductivity was measured at each temperature after equilibration for 30 min.³

RESULTS AND DISCUSSION

Properties of the Synthesized NPEOs

The nomenclature of the produced NPEOs, the M_n measured by means of end-group analysis and VPO, and the effect of heating on solubility are

listed in Table II. It can be noted that the results of end-group analysis and VPO were comparable and the yield was satisfactory, indicating that the polymerization was successful and quantitative. It can also be noted that no turbidity point was observed upon two NPEOs until boiling point, demonstrating that the produced polyethers did not tend to associate with each other at higher temperature, thus providing suitable intermediate materials for the synthesis of PU elastomers.

Synthesis of NPEO PUs

When applying NPEOs ($M_n = 600, 1,200$) as polyether soft segments to synthesize PU elastomers in a typical two-step method,² abruptly increased viscosity or even gel formation was frequently observed at about 60°C. This is an unusual phenomenon and is definitely not beneficial to the preparation of linear PU elastomers. In such a two-step preparation process, a DMA solution of NPEO was dropped to the solution of MDI in the first step. The added NPEO should react with MDI to produce urethane groups. But at the same time it might also catalyze the reaction between the excess isocyanate groups and the produced urethane groups, thus resulting in a crosslinked allophanate structure.² However, when a one-shot procedure was used, a DMA solution of MDI was dropped slowly to the DMA solution of NPEO and chain-extenders. The excess hydroxyl groups and the tertiary amine in NPEO guaranteed that the added MDI reacted with hydroxyl groups quickly and thoroughly and no residual MDI could be remained, ensuring no gel formation at reacting temperatures and successful synthesis of linear PU elastomers.

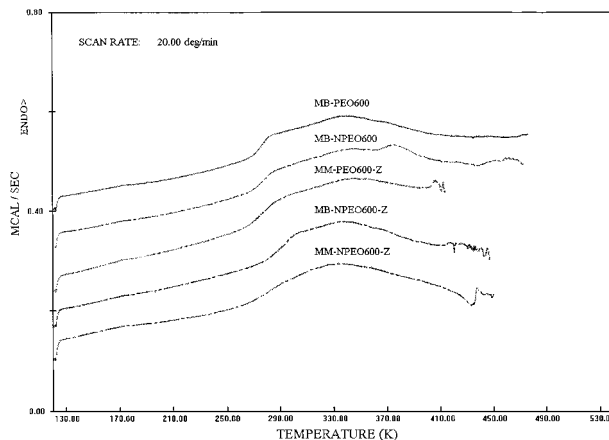


Figure 3 DSC traces of PU and PU ionomers.

Table III DSC Parameters of Polyurethanes

Sample	MB-PEO600	MM-PEO600-Z	MB-NPEO600	MB-NPEO600-Z	MM-NPEO600-Z
T_g (K)	274.4	274.9	274.3	287.8	258.1
Δc_p (cal g ⁻¹ deg ⁻¹)	0.122	0.131	0.098	0.137	0.012

Fourier Transform Infrared Spectra

Figure 2 shows the FTIR spectra of PU zwitterionomers compared with the nonionized PU. A peak at 1038–1040 cm⁻¹ attributable to the symmetric vibration absorption of sulfonate groups can be clearly detected in all the zwitterionomer samples, indicating that sulfonate groups have been successfully introduced into the PU zwitterionomers.¹⁴

Differential Scanning Calorimetry

DSC traces are shown in Figure 3. Data obtained from the DSC traces are listed in Table III, where T_g is defined as the midpoint of the transition. Comparing the results of MB-PEO600 and MM-PEO600-Z, it can be concluded that ionization of the hard domains brought better phase compatibility between hard and soft segments, which is typical for PEO PUs³ and is confirmed by the increased T_g and the increased magnitude of Δc_p , the heat capacity change at the transition.¹³ Comparing the data of MB-NPEO600 with MB-NPEO600-Z, it can also be observed that ionization of polyether soft segments caused better phase mixing in a larger degree than ionization of hard domains, which is supported by the much-enhanced values of T_g and Δc_p and also consistent with the reported literature.⁷

What is unexpected and much more interesting is that ionization of both hard and soft segments induced a sample MM-NPEO600-Z with a complicated domain structure. Both the much-decreased T_g and the much-decreased Δc_p values provided evidence for a better phase-separated morphology. However, as shown in Figure 3, the wider range of T_g suggested a better phase-mixing morphology. It is still difficult to explain this phenom-

enon and we believe much more work should be done to explore this field in the future. Around 60–70°C all of the samples exhibited an endotherm whose magnitude is about the same for all the materials. This has been suggested to be ascribed to the dissociation of the short-range ordering in hard domains of PUs.¹⁰ No evidence of a transition attributable to a hard-phase glass transition was found in the DSC traces, which is typical for PUs.¹³

Mechanical Properties

Young's modulus extracted from the maximum slope of the data and the results of elongation at break from uniaxial stress–strain testing are summarized in Table IV. Upon ionization of either hard or soft domains, PU samples exhibited an increased elongation at break and a decreased Young's modulus, which should be taken as another evidence of better phase compatibility and which reaffirmed the DSC results. When both hard and soft segments were ionized, the sample MM-NPEO600-Z possessed a much-increased Young's modulus while still exhibiting a reasonable elongation at break, supporting the better phase-separated morphology suggested by the much-decreased T_g and Δc_p values from DSC measurements.

Complex Impedance Spectra and Solid-State Ionic Conductivity Measurements

In general, solid ionic conductive polymers characterized by bi-ionic transport mechanism (such as the complexes of PEO–lithium salts) suffered a significant decrease in ionic conductivity under direct current polarization so that more stable

Table IV Mechanical Properties of Polyurethanes

Sample	MB-PEO600	MM-PEO600-Z	MB-NPEO600-Z	MM-NPEO600-Z
Young's modulus (MPa)	3.68	2.48	2.48	18.5
Elongation at break (%)	160	1000	1150	210

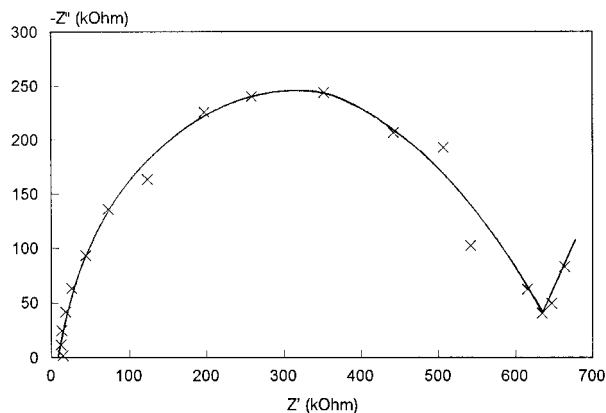


Figure 4 Complex impedance spectrum of MS-NPEO1200 at 26°C.

polymer electrolytes with single ion transport mechanism are required.^{3,7} Until now, most of these sorts of materials are polyblends of ionomer and polyether or copolymers of ionomer oligomer with polyether-low molecular ionomers. Because they showed either poor mechanical properties or low conductivity, PEO PU ionomers with sodium sulfonate groups in hard domains were synthesized in this laboratory and the conductivity of 10^{-6} – 10^{-5} S/cm was obtained at 70–80°C.³ However, the conductivity near room temperature (25°C) was still unsatisfactory (around 10^{-9} – 10^{-8} S/cm).³ Recently, we have reported the synthesis and conductive properties of another kind of sodium sulfonated PEO PU ionomer with ions incorporated in soft segments. Relatively higher conductivity (10^{-8} – 10^{-7} S/cm) was achieved at room temperature.⁷ However, as PEO PUs are concerned, it is well known that ionization of either hard or soft domains always causes better phase mixing,^{3,7} thus increasing the T_g of PEO soft segments to a certain degree. This could be a negative influence of the flexibility and chain mobility of PEO segments and definitely restrained the efforts to improve the ionic conductivity. In this experiment, lower T_g has been observed when both hard and soft domains were ionized. As a result, the samples MBS-NPEO600-Z and MS-NPEO1200-Z with optimized sodium content for conductivity ($\text{Na}^+ : \text{EO} = 1 : 20$) were synthesized and complex impedance spectra were measured. The typical complex impedance spectrum for the control sample MS-NPEO1200 sandwiched between Ag electrodes at 26°C is shown in Figure 4. There are a high-frequency semicircle arc and a low-frequency sharp slope in the spectrum. The high-frequency arc results from the

combination of the PU resistance and the geometry capacity of the sample. The low-frequency sharp slope is caused by the boundary impedance, which is due to the double-layer capacity of the electrode and the sample.^{3,7} There usually exist two arcs on an impedance spectrum for non-blocking electrodes coupled with an electrolyte with two mobile ions.^{19,20} Since Ag electrodes were used as ion-blocking electrodes in this work, the arc at lower frequency disappeared and only one arc was observed, which suggests that there were no electrode reactions.^{3,7}

The Z' value at the minimum of $-Z''$ on impedance spectra has been recommended to be the best estimation of the sample's resistance.²¹ Figure 5 shows the temperature dependence of ionic conductivity. It should be noted that in the whole range of testing temperature the conductivity of the samples MBS-NPEO600-Z and MS-NPEO1200-Z were obviously higher than the conductivity of MBS-NPEO600 and MS-NPEO1200, respectively, which might be attributed to the decrease of T_g upon ionization of both hard and soft segments and the increased polarity of the polyether matrix. This result also suggested higher chain mobility and flexibility brought by the better phase separation, which has been indicated by the much-decreased T_g and Δc_p values from DSC tests. It should also be noted that the conductivities of MS-NPEO1200 and MS-NPEO1200-Z were higher than the conductivities of MBS-NPEO600 and MBS-NPEO600-Z, demonstrating that the longer polyether chain supplied higher flexibility and chain mobility. At room temperature, comparing with the reported results, the highest ionic conductivity for ionomers with single ion transport mechanism has been achieved (1×10^{-7} S/cm) in the sample MS-NPEO1200-Z.

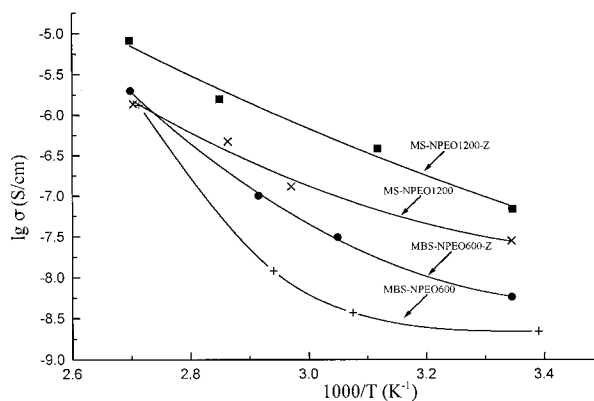


Figure 5 Temperature dependence of ionic conductivity for PU ionomers.

CONCLUSIONS

1. A novel series of PU ionomers using NPEOs with different molecular weights were synthesized. Their physical properties were characterized by FTIR, DSC, and uniaxial stress-strain testing.
2. When ions were incorporated in either hard or soft segments, better phase compatibility can be expected. However, once ionizing both hard and soft domains, the PU ionomer exhibited a complicated morphology.
3. The new PU ionomers possess higher ionic conductivity at room temperature than previously synthesized PUs and are characterized by a single ion transport mechanism.

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