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Hot-stage wide-angle X-ray diffraction studies of the morphology of a polyurethane ionomer

Xin Wei, Bo Jin, 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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Summary

A polyurethane ionomer with a specific ionic structure was synthesized in an attempt to induce ionic aggregate dissociation at elevated, but observable temperatures. By means of hot-stage wide-angle x-ray diffraction (WAXD), the dissociation could be clearly detected before the onset of degradation.

Introduction

Ionomers define a class of polymers attached with 10 mol % or less of inorganic salt groups. It is generally accepted that the ion pairs in organic polymer matrix tend to aggregate into microdomains, which behave as physical crosslinks (1).

Although it has been found that ionomers could be made to flow at elevated temperatures with an "ion-hopping" model well established by A. Eisenberg (2,3), which means that ions can be transported between aggregates at raised temperatures, the persistence of the aggregates always leads to a much higher melt viscosity than analogous nonionic polymers. Therefore, observing an ionic aggregate dissociation has not only theoretical significance, but practical importance as well (4). However, many previous efforts to observe such a dissociation have failed (1,4,5).

In this paper, a tailor-made polyurethane ionomer with a specific ionic structure was synthesized. Both microion pairs (Na^+ and I^-) and macroion pairs (sulfonate groups and quaternary ammoniums) were incorporated in this system, hence the periodicity of the ions in the microdomains might be reduced. Moreover, since the macroion pairs were directly attached on the polymer chains, more neighboring hydrocarbon segments might be brought in the composition of ionic aggregates, which should provide a greater steric effect on the periodicity in aggregates and a better chance to observe a dissociation.

Wide-angle x-ray diffraction (WAXD) has long been recognized as a best characterization method for probing the morphology of the ionic domains (5). It has been suggested that the intensity of the ionic peak exactly reflects the corresponding salt content in ionic aggregates (5). In addition, the WAXD position of the ionic peak ($2\theta \approx 4°$) is relatively insensitive to ionic structures, which means that it is independent of the cations examined (5). Therefore, hot-stage WAXD was applied to the system, for in this work the total quantity of the different ion pairs in ionic aggregates will be studied as a whole, regardless of their individual properties. It could be clearly observed that the intensity of the ionic peak at $2\theta \approx 4°$ was decreased at 200 °C, indicating that the total salt content in ionic aggregates was reduced. This suggested that the ionic groups might be dispersed to the surrounding polymer matrix and the ionic aggregates were dissociated at raised temperatures.

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* Corresponding author

Experimental

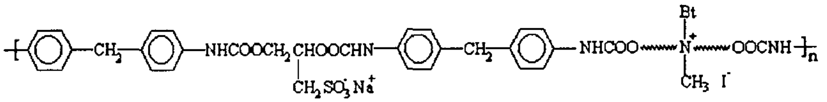
Materials

4,4'-Diphenylmethane diisocyanate (MDI) was degassed and purified by vacuum distillation. Sodium-S-1,2-dihydroxypropyl sulfonate (SDPS) as an ionized chain-extender was prepared and purified according to the literature (6). 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 inductively coupled plasma (ICP) (found Na$^+$: 12.50%; calculated Na$^+$: 12.91%) before use. Polyoxyethylated n-butyl amine (NPEO) (Mn = 572) was prepared as reported (7). Both NPEO and polyethylene oxide (PEO) (Mn = 600) were dried in a vacuum oven for 24 h at 70 °C. N,N'-dimethylacetamide (DMA) was dried with molecular sieves. Iodomethane was purified by distillation. 1,4-Butanediol (BD) (99%, Aldrich Chemical Co.), toluene, and petroleum ether (b.p. 60 ~ 90 °C) were used as received.

Sample Preparation

A 2 : 1 : 1 MDI : BD : PEO segmented polyurethane "PU" and a 2 : 1 : 1 MDI : BD : NPEO polyurethane copolymer "NPU" used as control polymers in this study were synthesized by a typical "one-shot" condensation reaction (7).

Based on the molar ratio of MDI : SDPS : NPEO : Iodomethane 2 : 1 : 1 : 1, the polyurethane ionomer "PUI" was also prepared by a one-shot procedure. A 15 wt % solution of MDI in DMA was added dropwise to a 15 wt % DMA solution of NPEO and SDPS. The solution was stirred for 1 h at 60 - 65 °C under dry nitrogen, then the mixture was stirred at 85 °C for 4 h. After cooling, a stoichiometric iodomethane was added and stirred for 8 h at room temperature. To ensure a complete reaction, the system was stirred for 5 h at 80 °C. The synthesized ionomer was recovered by precipitation into a solvent of 50 / 50 mixture of toluene and petroleum ether. Molecular structure of the produced ionomer is shown in Scheme 1. ICP result confirmed this structure (found Na$^+$: 1.68%; calculated Na$^+$: 1.65%).



Scheme 1. Molecular structure of the sample "PUI"

All the samples were dried under vacuum for 1 week at 60 °C to remove any residual solvent before characterization.

Characterization

It has been demonstrated that MDI-based polyurethanes will not undergo the degradation process until 220 °C (8). In addition, it has been reported that tetramethylammonium iodide, which possesses a very similar ionic structure with the quaternary ammonium salts in the synthesized ionomer, will be sufficiently stable until 230 °C (9). Moreover, it has also been reported that a potassium analog of SDPS was very stable up to 270 °C (6). Therefore, in this experiment WAXD patterns were obtained up to 200 °C to ensure no material degradation, which is also consistent with our previous experimental method (4). The

WAXD testing was performed using a Rigaku D/MAX-RA rotating anode x-ray generator with a copper target, at 40 KV cathode potential and 150 mA emission current. X-rays were collimated into a beam 10 mm × 70 μm with a Kratky camera and the x-rays were detected with a SC-30 scintillation counter probe. CuKa x-rays were selected by detector pulse-height analysis.

Results and Discussion

The WAXD testing was performed in a range from 2θ = 2° to 35°. To emphasize the changes in ionic peak and make WAXD patterns more apparent, selected spectral regions were shown in Figure 1 and Figure 2 respectively, instead of the whole survey spectrum.

As shown in Figure 1, WAXD testing resulted in a similar diffraction peak in all the samples that was quite diffuse with a maximum of 2θ at about 20°, indicating a spacing of 4.5 Å, which was characteristic of an average distance between two neighboring polymeric chains (10). It should be noted that the intensity of the peak was not reduced when the temperature reached 200 °C, meaning that no degradation or flow of samples took place at elevated temperatures.

What was different in their WAXD patterns could be clearly revealed in Figure 2. A peak with a maximum of 2θ at about 4° could be clearly detected in the sample of "PUI" at 17°C. As a contrast, as to nonionic analogous polymers were concerned, both "PU" and "NPU" just exhibited smooth curves at room temperatures between 2θ = 2° and 6°. Then it could be concluded that ionic aggregates exist in the synthesized ionomer at room temperature, for the peak position was consistent with the reported values (5). The ionic peak looked somewhat diffuse, demonstrating that the incorporated macroions together with their connecting hydrocarbon chains might lower the efficiency to achieve a higher degree of order in ionic aggregates.

It should be noted that upon heating, although the ionic peak intensity of "PUI" remained unchanged at 100 °C, both the peak intensity at 2θ ≈ 4° and the integrated area in a range from 2θ = 3° to 5° were obviously decreased at 200 °C (The intensity at 2θ ≈ 4° was dropped from about 550 CPS to 300 CPS.). Since the intensity of the WAXD ionic peak exactly reflects the salt content in the aggregates (5), its decrease should be interpreted as the ionic transportation from microdomains to the surrounding polymer matrix. This is a process different from the proposed "ion-hopping" process, for in the ion-hopping process the ions are transported between aggregates (2), which should result in an unchanged ion content in ionic microdomains and no decrease of WAXD ionic peak can be expected. Therefore it was reasonable to draw such a conclusion that at about 200 °C, the ionic aggregates in the studied system tended to dissociate.

Such an observation might be explained as follows. First, certain macroions might participate in the ionic aggregate formation, causing a lower degree of microdomain order. Second, other "free" macroions in the system could constitute a continuous phase in which isolated regions of microions is dispersed and electrostatically associated with the macroions (11). The interaction between the "free" macroions and the microions might further weaken the cohesive energe in the aggregates. Third, such an disordered ionic structure might also be ascribed to the high percentage of hydrocarbon segments mixed in the ionic aggregates which was brought in by the connecting macroions. Consequently, sufficiently high temperatures could induce such a dissociation.

It should also be noted that as the intensity of the WAXD ionic peak was decreased at 200 °C, this peak was also broadened. This might be associated with the "ion-hopping" process which caused a lower degree of order in ionic aggregates. It means that although the dissociation process is different from the ion-hopping process, there might exist some relationship between them.

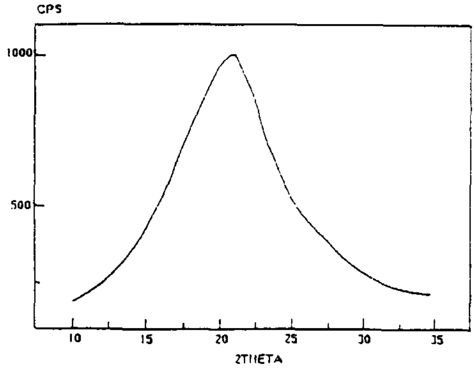


Figure 1. A typical WAXD peak attributable to the amorphous polymer matrix. Note that the WAXD pattern of "PU" is taken as example, for all the tested samples exhibited a quite resembling peak in this region.

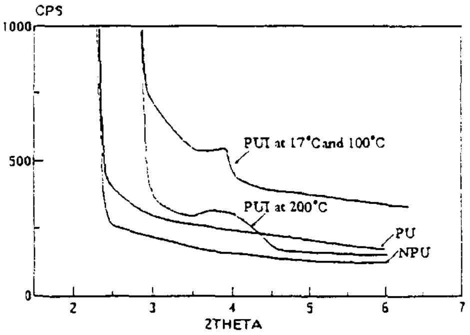


Figure 2. Hot-stage WAXD patterns of "PUI" at 17, 100, and 200 °C comparing with WAXD patterns of "PU" and "NPU" at 17 °C.

Conclusion

By means of applying hot-stage WAXD on a polyurethane ionomer with an unorderly ionic structure, it could be clearly detected that ionic aggregates were dissociated at elevated temperatures. Comparing with previous literatures (1,4,5), it can be concluded that the orderliness of ionic structure determines whether ionic microdomains can be dissociated at high but observable temperatures.

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