

SOLID-STATE VARIABLE-TEMPERATURE NMR STUDY ON THE PHASE SEPARATION OF POLYETHER POLYURETHANE ZWITTERIONOMERS*

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ABSTRACT

Polyether-polyurethane zwitterionomers based on 4, 4'-diphenylmethane diisocyanate (MDI), methyl diethanolamine (MDEA), and polytetramethylene oxide glycol (PTMO) were studied with variable-temperature wide-line ¹H NMR. It is found that upon ionization, degree of phase separation in the polymer system decreased at first due to the loss of hard segment regularity, while further ionization increased the degree of phase separation through increasing hard phase cohesion and difference of polarity between hard and soft segments.

INTRODUCTION

In the last decade, polyurethane elastomers have aroused a great deal of study interest for their increasing industrial importance. Polyurethane elastomers are (AB)_n-type block copolymers, which at service temperature, exhibit a two-phase microstructure. The main component of the soft phase is normally polyester, polyether, or polyalkyl-diol which is rubbery at room temperature and provides the polymer with elasticity. The hard phase which consists mainly of an aromatic diisocyanate extended with a low molecular weight diol or diamine, acts as physical crosslinks and gives the polymer strength and dimensional stability. As the same as other thermoplastic elastomers, some degree of phase separation is essential to the mechanical properties of the material. Many factors, including the contents and chemical structures of both hard and soft segments, incorporation of ionization functionality into hard segment, influence the phase separation

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and therefore the mechanical properties of the polymer.

Although many methods such as electron microscopy, SAXS, infrared dichroism, dynamic mechanical analysis, DSC and stress-strain testing have been used to study the morphology of these materials^[1], it still remains a subject of great debate. High resolution solid state ^{13}C NMR has proved to be useful in studying the microstructure of polyurethanes^[2]. However, due to the extremely broad line width of the hard segment, its application is highly restricted for polyether polyurethane studied herein. Wide-line ^1H NMR have also been used to study the microphase structures of polyurethanes^[3-5] and several polyurethanes were found to exhibit a two-component NMR free-induction decay (FID). Though some authors interpreted the two components to correspond to the hard and soft domains directly, effects of a very broad distribution of correlation time even in a single domain can not be ignored^[6]. Under such circumstances, results of FID decomposition do not exactly reflects the phase separation but the distribution of molecular motions in the system. So variable-temperature (VT) wide-line NMR can be used to study the change of distribution of molecular motions with temperature, which indirectly reflects the phase separation of the system. An additional benefit of employing VT NMR is that since the experiment is carried out over a relatively large temperature range, the results of the NMR experiment can be more easily compared with those of other methods, such as dynamic mechanical analysis, DSC and so on.

EXPERIMENTAL

Materials

Polyether polyurethane are based on PTMO with a molecular weight of 1000 and MDI extended with MDEA. Ratio of contents of three component is MDI:MDEA:PTMO=3:2:1. Ionization are incorporated into MDEA with addition of controlled amount of γ -propane sultone^[7]. Four samples with ionization degree of 0, 0.35, 0.65 and 0.95 are named PUA, PUB, PUC and PUD respectively. Samples for NMR studies are prepared by solution casting from DMF solution with no further disposal.

NMR Experiments

^1H NMR are performed on a Bruker MSL-300 spectrometer with resonance frequency at 300.13Mhz. FIDs are acquired with a windowless solid echo pulse sequence as shown in Fig. 1. Spin-lattice relaxation time T_1

is measured with inverse-recovery method. ^1H 90° pulse width is $2\mu\text{s}$ while number of scans is typically 4-8. All samples are studied at temperature extended from 173K to 353K, with FIDs acquired and T_1 measured. Temperature is controlled with a Bruker VT-1000 temperature control unit. Deviation of temperature is $\pm 1\text{K}$.

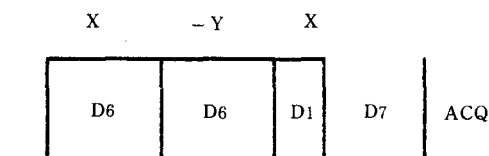


Fig. 1 Pulse sequence for windowless solid echo. D1 is 90° pulse. FID occurs when $D7 = D6 - 1/2D1$

RESULTS AND DISCUSSION

VT wide-line method

A typical FID of polyether polyurethane is plotted in Fig. 2. Obviously it can be decomposed into two components, one Gaussian fast decay and one Lorentzian slow decay. The variation of magnetization with time can be represented by the following expression:

$$M(t) = M_f \exp(-(t/T_{2f})^2) + M_s \exp(-t/T_{2s})$$

where M_f , M_s represent the initial values of magnetization of fast and slow decay respectively and T_{2f} , T_{2s} are the spin-spin relaxation time of corresponding components.

By applying nonlinear least squares regression to the FID signals acquired under various temperatures, we can get T_{2s} and relative proton contents of the fast and slow decay components. Traditionally, only FID signals under room temperature are acquired and decomposed. Then the fast and slow decay components are related directly to hard and soft

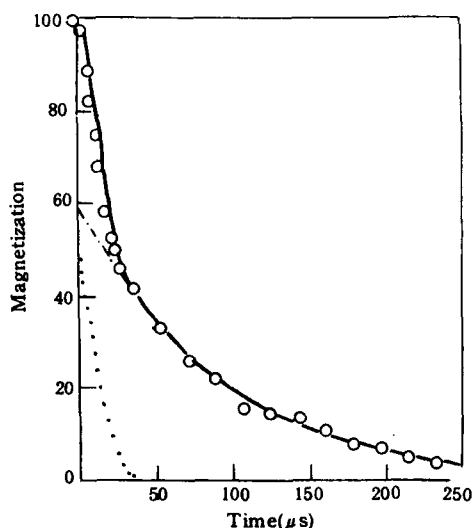


Fig. 2 Scheme of a typical FID decomposition

phases, whose contents are also determined from the result of FID decomposition. However, for the reasons we will discuss, we carried out the above procedure over a wide temperature range and presented the variation of T_{2s} and contents of Lorentzian component of four samples with

temperature in Fig. 4 and Fig. 3 respectively (Due to the extremely high contents of the slow decay, FIDs acquired at temperature above 333K can only be fitted well with a three—component GLL function. Thus, the T_{2s} of slow decay at higher temperatures are not presented in Fig. 4). T_2 of the Guassian component, which keeps constant over the whole experiment temperature range, is about $10\mu s$ for all samples.

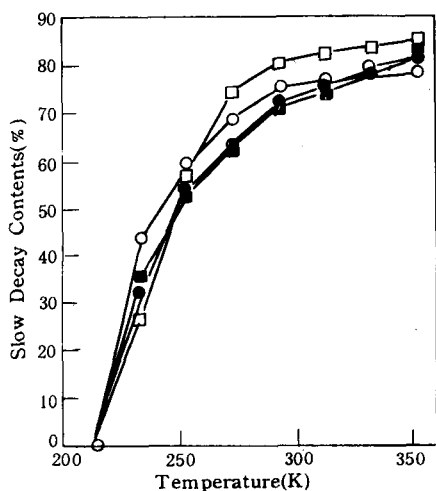


Fig. 3 T_{2s} of the slow decay component plotted against temperature

—○— PUA; —□— PUB;
—●— PUC; —■— PUD

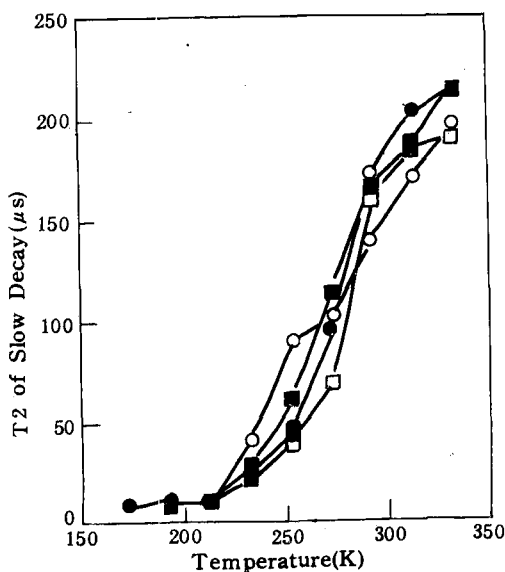


Fig. 4 Contents of the slow decay component plotted against temperature

—○— PUA; —□— PUB;
—●— PUC; —■— PUD

Since the experiment temperature is well below the T_g of the hard segment and the measurement of a sample is completed in several hours, the phase structure of the samples can be regarded invariable in the VT experiments. As a result, we do not use VT experiments to study the change of phase structure with temperature. Quite on the contrary, we use it to study the molecular motions of samples whose phase structure keeps unchanged with the temperature. Since the molecular motions of a sample are determined largely by the phase structure of the sample, we can use the information of the molecular motions to probe the phase structure of the system indirectly.

As mentioned above, the phase structure of the samples can be regarded unchanged with the temperature. However, from Fig. 4 and Fig. 3 we can see clearly that as the temperature changes, both the T_2 and content of the slow decay component change dramatically. Thus, it can be concluded

that traditional method of relating two FIDs components to hard and soft phases directly is not reliable, at least, in this system.

Phase separation in samples

It can be seen from Fig. 3 and Fig. 4 that at temperatures lower than 213K, both the hard segment and soft segment are in a rigid state, so only one Gaussian fast decay is presented in the FIDs of the samples. As the temperature increases, there emerges an exponential slow decay component, T_{2s} and contents of which increase with the temperature. The initial increase in T_{2s} and contents of the slow decay component is obviously caused by the onset of the segmental motions of the soft segment. Since PUA exhibits the highest content and the longest T_2 of the slow decay component in four samples at temperatures ranging from 220 to 250K, the segmental motions of the soft segment of it are the easiest. So it can be further concluded that PUA possesses the highest degree of phase separation, which renders the segmental motion of its soft segments least restricted by the hard segments. On the other hand, the fact that PUB exhibits the lowest content and the shortest T_2 of the slow decay component means the segmental motion of its soft segments are the most difficult due to the hindrance of the hard segment. Thus the phase separation in PUB is the worst among the four samples.

Further increase in temperature enhances the segmental motion of the hard segments, thus makes MDEA and MDI begin to contribute to the slow decay component at temperature higher than 250K. Because of the poor phase separation of PUB, its hard segments are the most mobile among the four samples due to the influences of the soft segments. So when the temperature reaches 250 K, the content of the slow decay component of PUB begins to increase most quickly and soon becomes the highest in all the samples. Though the increase of the T_2 of the slow decay component of PUB is not as conspicuous, it is quite reasonable since the slow decay component of PUB possesses the highest amount of hard segments, which, despite their higher mobility compared with other samples, are much less mobile than the soft segments. At 293K, the content of the slow decay component of PUB surpasses 80%, which means the most rigid fragment, MDI, whose proton percentage content is 20.7%, begins to contribute partially to the slow decay component. This further supports the conclusion that PUB exhibits the lowest degree of phase separation.

As for PUC and PUD, it is shown in Fig. 3 and Fig. 4, the variation of content and T_2 of the slow decay components of the two samples are almost the same over the whole temperature range, so it can be concluded that they possess a similar degree of phase separation.

It can also be seen from Fig. 3 that when the temperature is higher than 293K, the content of the slow decay component of PUA almost keeps constant (ca. 75%). This result means that a large part of the hard segment of PUA is quite rigid even at a relative high temperature, which implies that the hard segment possesses a higher degree of regularity, or crystallinity. This crystallinity can be attributed to the high degree of symmetry of the hard segment and makes the hard segment of PUA less compatible with soft segment. Upon ionization, this regularity of hard segment is decreased greatly. This explains the increase of the degree of phase separation in PUB. As for PUC and PUD, though they possess a better phase separation than PUB they still show poor hard phase regularities since the contents of their slow decay component increase steadily as the temperature increases. Though the hard segment regularity is low due to the higher degree of ionization, the increase of the polarity of the hard segment also makes the hard segment less compatible with the soft segments in the system.

^1H spin - lattice relaxation of all samples can be presented in single - component exponential. Results of simulation are shown in Fig. 5, in which the relaxation rate $1/T_1$ is plotted against temperature. Since only one component is found in T_1 measurement for all samples, it can be known that the magnetization of the hard segments is relaxed through the mechanism of spin diffusion, while the soft segments, magnetization of which is relaxed quickly, form the relaxation centers in the polymer. Under such circumstances, PUB, which possesses the poorest phase separation and thus the quickest rate of spin diffusion, exhibits the shortest T_1 . For the same

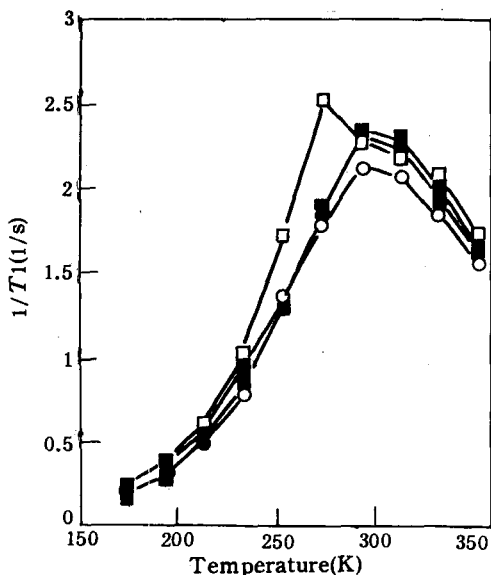


Fig. 5 T_{1s} plotted against temperature

—○— PUA; —□— PUB;
—●— PUC; —■— PUD

reason, PUA, which is most phase separated, displays the longest T_1 . This result agrees with that of T_2 experiments.

CONCLUSIONS

1. Initial introduction of ionization into the hard segment decreases the degree of phase separation by destructing the regularity of the hard segment, whereas further ionization helps to regain some degree of phase separation, probably due to the increase of the hard phase cohesion and the difference of polarity between hard and soft segments. When the degree of ionization excels 65%, further introduction of ionization into the hard segment bears only limited influence on the phase structure of the polymer. With ionization, degree of phase separation never reaches the level that PUA bears despite the increase of phase separation with higher degree of ionization. So for polyether polyurethane elastomers, incorporation of ionization groups into the hard segments is not always an effective way to increase the phase separation between hard and soft phase.

2. Although spin diffusion experiments have proved that the fast and slow decay components are related to hard and soft phase respectively, the relation is indirect and restricted to certain temperatures. At certain temperatures when the soft segments are sufficiently mobile but the hard segments are still so rigid as to contribute less to the slow decay component, the fast and slow decay components may mainly consist of spins in hard and soft phases respectively, which explains the results of the spin diffusion. However, it is never adequate to determine the relative contents of phases using the results of FID decomposition if no variable-temperature experiments are carried out and wherever a FID decomposition result is presented, the experimental temperature must be recorded and noticed.

Keywords:

Polyether polyurethane; Variable temperature; Wide-line NMR; Phase separation

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