Rheological Investigation of Microphase Separation Transition of Polyurethane Elastomer

I-Kuan Yang, Pei Ju Wang, Ping Hung Tsai

Department of Chemical Engineering, Tunghai University, Taiwan

ABSTRACT: A technique of linear viscoelasticity measurements coupling with temperature scanning was found effective in the detection of microphase separation transition (MST) and in the determination of MST temperature. The validity and accuracy of the technique were confirmed and reinforced by atomic force microscopy and differential scanning calorimetry (DSC). The technique was applied to a study of the MST of a series of 13 polyurethane (PU) elastomers based on mixed toluene diisocyanate (TDI), 1,4 butadiol, and poly(tetramethylene oxide) (PTMO) of two different molecular weights; the MST temperatures of the PU elastomer samples were measured. Although each of the 13 polymer samples had distinct hard segment content and used PTMO of different chain lengths, or mixed PTMO, the MST temperatures of the 13 samples formed a linear master curve when the MST temperature was plotted against the fraction of hard segment. The master curve indicated that the MST temperature is independent of the length and type of PTMO. It was also found that 2,4 TDI prevailing over its isomer 2,6 TDI played a dominant role in the MST of this series of PU elastomers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2107–2112, 2007

Key words: atomic force microscopy (AFM); polyurethane; rheology; viscoelastic properties; microphase separation

INTRODUCTION

Polyurethane (PU) elastomers are an important class of thermoplastic elastomer and have been widely used in coating, binder resins, fibers, and high-performance elastomeric products. Typical PU elastomers are segmented copolymers composed of alternating hard and soft segments. The hard segments are usually PUs formed by diisocyanates and low-molar-mass diols, while the soft segments are mostly polyether or polyester. Owing to the thermodynamic incompatibility between the hard and soft segments, the elastomers show a microphase separated structure, which is responsible for the excellent elastomeric properties.

Industrially, diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI) are two of the most widely used aromatic diisocyanates. PU elastomer derived from MDI was found to have three distinct endotherms by differential scanning calorimetry (DSC)[1,2] and thermomechanical analysis.[3,4] The lowest-temperature endotherm (T_I) was attributed to the local restructuring of hard segment units in the hard microdomain. The intermediate temperature endotherm (T_{II}) was related to the onset of a microphase separation transition (MST) to a homogeneous phase, or an order-disorder transition.[3] The higher-temperature endotherm (T_{III}) was ascribed to the crystalline melting of the hard segments.

As compared with MDI-based PU elastomers, the counterpart derived from TDI attracted relatively less attention. Few studies were carried out on the thermal transition behavior of PU elastomers based on TDI. Scheider et al.[5] reported that PU elastomers based on 2,4 TDI also showed three distinct endotherms resembling MDI-based PU elastomers, but no intermediate endotherm, or T_{II} transition was observed for 2,6 TDI-based elastomers.

Mechanical methods, such as linear viscoelasticity measurements[6–8] and penetrometer,[5] have been shown to be more effective in identifying MST than calorimetry. Techniques based on linear viscoelasticity measurements to detect the MST for diblock and triblock copolymers have been well established,[9–11] but not for segmented copolymers such as PU elastomers and poly(ether block amide). In this study, we developed a rheological method based on linear viscoelasticity measurement to identify the MST temperature T_{II}. The validity and accuracy of the method were confirmed and reinforced by DSC and atomic force microscopy. The method was then used to measure the MST temperatures of a series of 13 PU elastomer samples made of mixed TDI and the effect of urethane concentration on the transition temperature was studied. A linear relation between the MST temperature

Correspondence to: I-K. Yang (ikyang@thu.edu.tw).

and the urethane content was found, and the relation could be useful to both academics and industries.

EXPERIMENTAL

TDI provided by Bayer Polymer Asiapacific (Taiwan) was a mixture of 80% 2,4 and 20% 2,6 isomers. Both the chain extender (1,4-butane diol [BDO]) and the polyol, PTMO, were provided by Korea PTG (Seoul, Korea). PTMO and BDO were dried in a vacuum oven for 24 h before usage and TDI was used as received. Synthesis of PU elastomers followed a one step solution polymerization method. Polyols of two different molecular weights were used. One had a nominal molar mass of 1000, while the other had a molar mass of 2000, referred to as PTMO1000 and PTMO2000, respectively. The molar feeding ratio of isocyanate to hydroxyl group for the series of PU elastomers synthesized in this work was fixed at 1.02 : 1. The chain extender and the polyol were first mixed with a suitable amount of methyl ethyl ketone in a 1-L jacket reactor with four necks. The mixture was heated to and kept at a temperature of 55°C until PTMO was completely dissolved then the isocyanate was introduced to start polymerization. After 4 h of polymerization, 0.1 wt % of dibutyl tin dilaurate (Bayer Polymer Asiapacific, Taiwan) was added to the reactor to accelerate the reaction and 2 h later, sample was taken out every 20 min for the titration of the NCO residue. The polymerization ended when no NCO residue was detected. Throughout the polymerization process, the reaction mixture was kept at 55°C by circulating water.

To prepare the samples for rheological measurements, solution casting was adopted. The product solution was poured into a flat pan and left in a hood for overnight; then the cast was transferred to an oven and stayed there at 80°C for another 4 days to drive out the solvent and bubbles. A sheet was obtained after the casting procedure. The sheet was then thermopressed at 110°C for 5 min to form a thinner sheet of 1-mm thickness, which was then subjected to DSC (Pyris 1 DSC, Perkin Elmer, Wellesley, MA) or cut into circular disks for linear viscoelasticity measurements.

Molecular weights of the PU elastomers synthesized were determined by a gel permeation apparatus using two columns (Jordi Gel DVB mixed bed, Jordi, Bellingham, MA) in series and a differential pressure detector (Viscotek T50A, Houston, TX) as a detector. A universal calibration curve was established by using polystyrene standards to calculate the absolute molecular weight distribution for the samples. Dimethyl formamide was used as the carrier.

The linear viscoelasticity measurement was performed on a torsion type rheometer (RDAII Rheometrics, Piscataway, NJ) with a fixture of 25-mm parallel plates. Isochronal measurement was performed at 1 rad/s and a cooling rate or heating rate of 1°C/min. The frequency and the temperature changing rate were so chosen because the combination offered the best identification of the intermediate transition temperature reported in this work. Isothermal measurements of linear viscoelasticity were also performed on RDAII with the same fixture.

Atomic force microscopy was conducted on a Solver P47-PRO provided by NT-MDT (Moscow, Russia). A taping mode was adopted to investigate the surface morphologies of the PU samples. The piece cutting from sheets prepared for the mechanical measurements were used for the microscopy. The pieces were

TABLE I
Constituents, Room Temperature Appearance, and Molecular Weights of PU Elastomers Synthesized*

Sample label	Type of polyol used	Feed mole ratio TDI/BDO/PTMO1000/ PTMO2000	M_n	M_n/M_w	Appearance at room temperature
1	PTMO2000	4.08/3.00/0.00/1.00	21900	5.36	Sticky viscous fluid
2		6.12/5.00/0.00/1.00	25600	5.46	Soft elastic rubber
3		7.14/6.00/0.00/1.00	24200	3.98	Tough elastic rubber
4		7.65/6.50/0.00/1.00	22600	4.21	Tough elastic rubber
5		9.18/8.00/0.00/1.00	33800	3.56	Tough elastic rubber
6		12.2/11.0/0.00/1.00	29100	3.82	Hard, plastic
7	PTMO1000	5.10/4.00/1.00/0.00	23000	2.66	Tough elastic rubber
8		7.14/6.00/1.00/0.00	30600	2.15	Hard plastic
9		9.18/8.00/1.00/0.00	24500	2.89	Fragile glass
10		11.2/10.0/1.00/0.00	18400	3.95	Fragile glass
11		16.3/15.0/1.00/0.00	23600	2.95	Fragile glass
12	Mixed polyol	7.14/6.00/0.34/0.66	16500	4.62	Tough elastic rubber
13		7.14/6.00/0.50/0.50	20000	4.40	Tough elastic rubber
14		7.14/6.00/0.66/0.34	26700	3.44	Tough elastic rubber

*Feeding ratio of NCO/OH is fixed at 1.02.

first annealed in an oven at a desired temperature for 30 min; they were then quenched by liquid nitrogen and stored in a liquid nitrogen pool. Microscopy was carried out immediately after the removal of the quenched sample pieces from the pool.

RESULTS AND DISCUSSION

There are a total of 14 samples of different compositions investigated in this work. Their feeding constituents, molecular weights, polydispersities, and appearance are summarized in Table I. The samples can be divided into three categories by the polyol used. Samples 1–6 used PTMO2000 as the polyol, samples 7–11 used PTMO1000 as the polyol, and the rest of the samples used a mixture of the two polyols. Though feedings with a variety of constituent ratios were used, the molecular weights and polydispersities of the resulting PU elastomers were within a reasonably narrow range. This implies that the ratio of feeding constituents does not affect the molecular weight and its distribution, which is reasonable, since the molar ratio of the isocyanate to the hydroxyl group that controls the molecular weight of the resulting polymer was fixed at 1.02 for all 14 samples. At room temperature, the PU elastomers could be a sticky viscous fluid or a tough rubbery material or a fragile glass depending on the types of polyol and the molar ratio of polyol, chain extender, and isocyanate used.

We choose a typical example, sample 8, to present the following results and discussion section. In the following discussion, we will show that the isothermal frequency scan has inconvenience and difficulties to determine the MST temperature and for practical purpose, we propose a temperature scan method to determine the MST temperature and the measurement from the method is checked and found consistent with the observation of DSC and AFM. All 14 samples, except for sample 1, which is a sticky and viscous fluid at room temperature, show the similar behavior and results as those of sample 8.

The isothermal measurements of the storage and loss modulus for sample 8 are shown in Figure 1. Unfortunately, the measurements could not proceed to a temperature lower than 73°C because the stiffness of the test sample at these temperatures might damage the machine, especially at high frequencies and for prolong measurements. For the investigation of MST, the linear viscoelastic behavior at the terminal or low frequencies is the major concerns since the size of the microphase structure is of order of tens of nanometers and the linear viscoelasticity at low frequencies reflects the formation and change of the microphase structure. Homogeneous polymer melts follow typical terminal behavior, that is, $G' \propto \omega^2$ and $G'' \propto \omega$ as the frequency α approaches very small values.
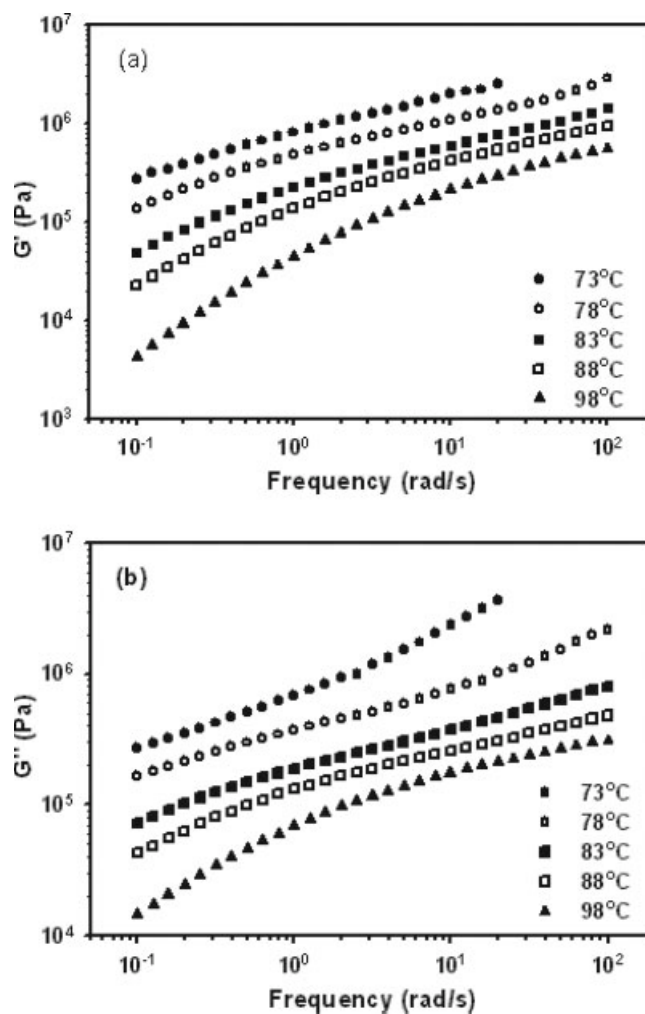

Figure 1 Storage and loss modulus of sample 8. The feeding ratio of the sample is TDI/BDO/PTMO1000 = 7.14/6.00/1.00.

When a transition such as a phase separation occurs, a deviation from the terminal behavior, typically a relation of smaller exponent of frequency appears. It is seen that at mid- and high frequencies G' experiences no obvious drop or change of curve pattern over the temperature range investigated, while at frequencies of < 1 rad/s, the terminal slope decreases as the temperature decreases. Similarly for G'' one can see that as temperature decreases from 83 to 73°C it experiences a decrease in terminal slope. The leveling tendency of both G' and G'' at terminal frequencies indicates the occurrence of a structure change. To verify that the structure change is the MST and to determine the transition temperature, usually a branched master curve is constructed over a wide range of temperature by a frequency-temperature superposition[9] or the method suggested by Han and Kim.[10] Because of the risk of damaging the measuring apparatus, it is frequent that one is unable to obtain the isotherms covering a temperature range wide enough such that the branched master curve can be constructed. In some
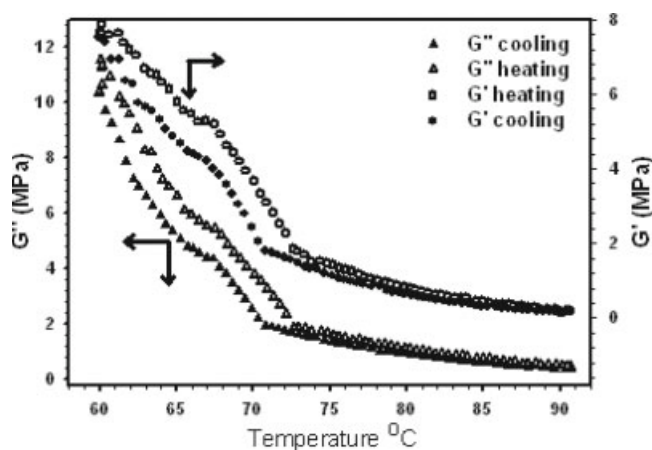
Figure 2 Temperature dependence of storage modulus and loss modulus of sample 8. The feeding ratio of the sample is TDI/BDO/PTMO1000 = 7.14/6.00/1.00. Both heating and cooling process are performed at a scanning rate of 1°C/min and at frequency of 1 rad/s.

fortunate cases in which the measurement can be completed, it is still inconvenient and extremely consuming in cost or time compared with the method proposed below, considering the large amount of data needed by the master curve methods.

The proposed isochronal technique is capable of investigating the transition and measuring the MST temperature of the PU elastomers. The temperature sweep measurement at a fixed frequency of 1 rad/s for the same sample is shown in Figure 2. The measurement was conducted such that the cooling scanning process was followed by a heating scanning process. It can easily be seen that a small hysteresis exists between heating and cooling process for both moduli and in both processes. The curves exhibit a drop in the values of both moduli followed by a kink or a discontinuity of the curve slope. The kink in the heating process locates at 73°C, while for the cooling process the kink occurs at a slightly lower temperature 71°C. The hysteresis can be resorted to the response lag to the temperature change for the polymer and we believe that by lowering the temperature sweeping rate the hysteresis will eventually diminish. It is also noteworthy that the storage and loss modulus experienced the discontinuity of slope at the same temperatures for both heating and cooling process. The drop and the slope discontinuity indicate a transition occurring in this temperature range. Similar results were observed by Ryan et al.[6] for MDI-based PU elastomers; using a thermomechanical analysis technique, Schneider et al.[5] showed that PU based on 2,4 TDI, BDO, and PTMO of molecular weight 1000 exhibited a transition from a microphase separation phase to a homogeneous melt, and no such transition was observed if 2,4 TDI was replaced by the 2,6 TDI isomer. Our PUs used mixed TDI with 2,4 TDI as the

major component and it is reasonable to believe that similar transition could happen.

As shown in Figure 3, DSC was also applied to the sample, and there was also no melting peak at ∼ 160°C, at which crystallites of the hard segments of 2,6 TDI-based PU melts. The DSC study suggested that 2,6 TDI and 2,4 TDI were randomly distributed in the chain of the elastomer molecule and the ability to crystallization for 2,6 TDI-based hard segments was suppressed. There is one endothermic peak as well as one exothermic peak on the heating and cooling curve, respectively, for sample 8. Both peaks are broad, and for the rest of the samples in this series only few showed observable peaks. The thermohistory of a sample strongly affects the DSC spectra and proper annealing to the samples helps the emergence of the broad peak.[3,5] The maximum of the endothermic curve of sample 8 is located at 62°C, the same temperature at which the minimum of the exothermic curve occurs. Both the endothermic and the exothermic peaks can be related to microphase transition as being done by Leung and Koberstein.[3] However, because of uncertainty in the emergence of the peaks and their broadness, it is difficult to determine the transition temperature simply by using DSC spectra. If the peak temperature of the DSC spectra is defined as the temperature of microphase transition of the sample, it is ∼ 10°C less than the temperature at which discontinuity of slope occurs in the linear viscoelasticity measurement.

To confirm the occurrence of the MST, we performed an atomic force microscopy (AFM) on the same PU elastomer sample (sample 8) using a taping mode. The results of phase lag spectra are shown in Figure 4, in which one can clearly see that samples without annealing and annealed at 55°C, a temperature well below the slope discontinuity temperature, exhibited a heterogeneous morphology with soft
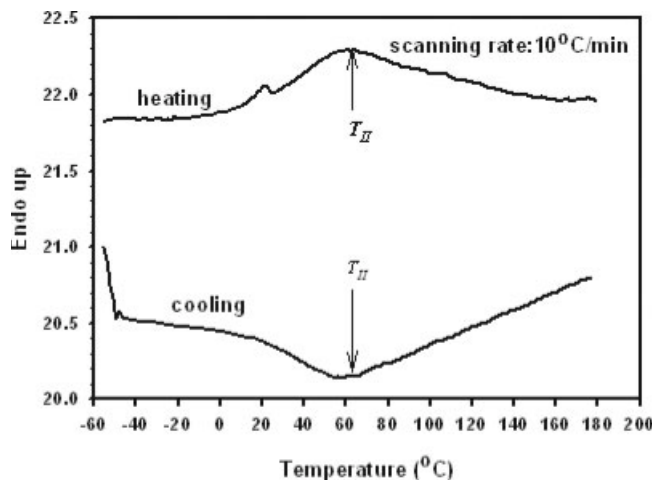

Figure 3 DSC spectra of sample 8. The feeding ratio of the sample is TDI/BDO/PTMO1000 = 7.14/6.00/1.00.
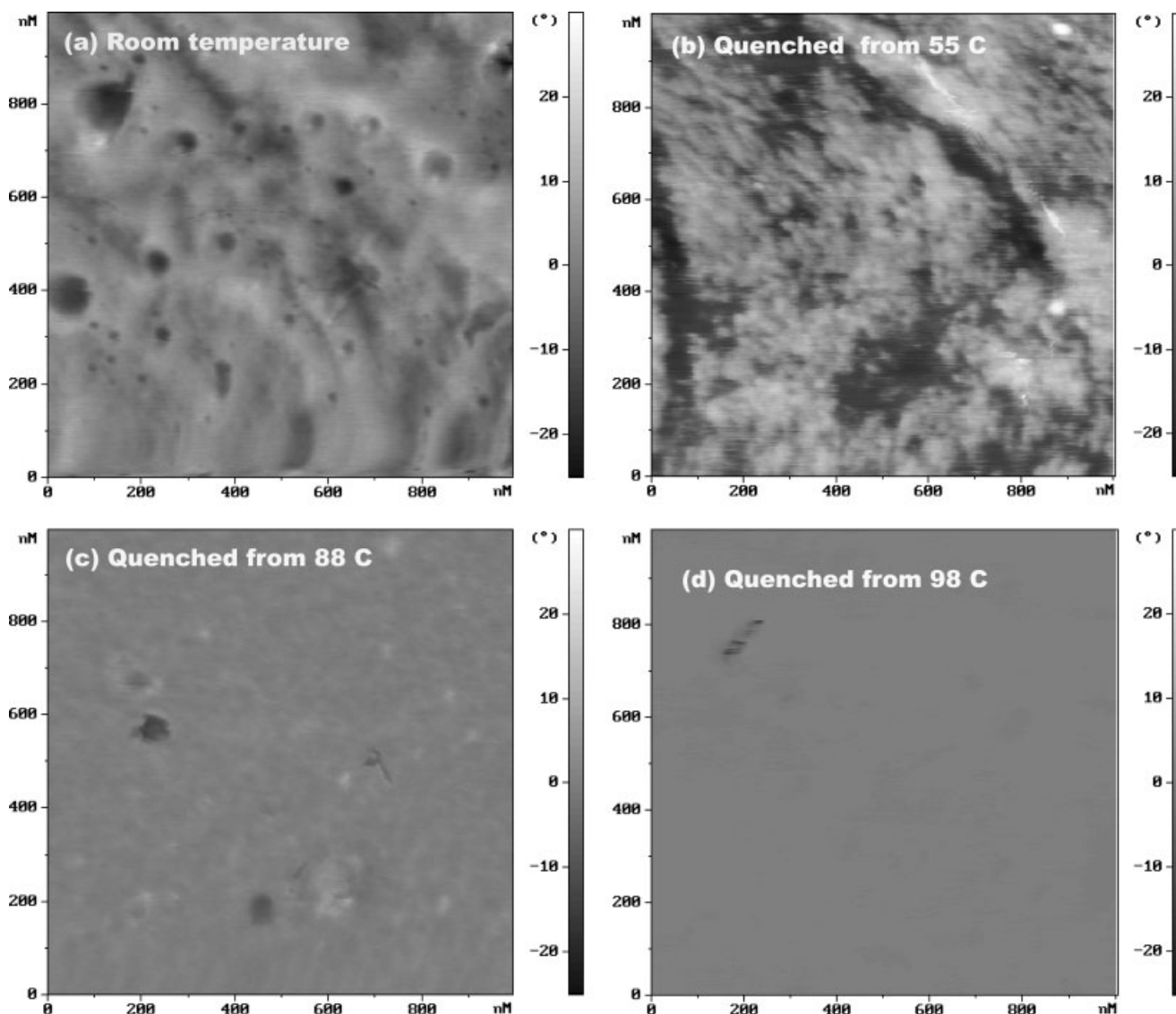
Figure 4 Atomic force microscopy of sample 8 quenched from different annealing temperatures. The feeding ratio of the sample is TDI/BDO/PTMO1000 = 7.14/6.00/1.00.

domains of irregular shapes (dark area) randomly dispersed in a hard matrix (gray area). The soft domains were soft segment rich regions that were composed predominantly of PTMO, while the hard matrix was rich in segments made of chain extenders and isocyanates. For sample quenched from an annealing temperature of 88°C, which is above the temperature where the slope discontinuity occurs, a homogeneous morphology was observed. For the sample quenched from a higher annealing temperature 98°C a much more homogeneous picture was obtained. The morphological changes demonstrated the destruction of domain morphology and the complete mixing of the soft and hard segments. Thus, the AFM results confirmed that the slope discontinuity in the isochronal temperature sweep measurement is indeed a signature of MST.

We defined the average of the slope discontinuity temperatures for heating and cooling process as the temperature of MST. For sample 1 the temperature sweep measurement did not detect any discontinuity in slope for either modulus between room temperature and 80°C. At room temperature the sample is a sticky liquid and we believe that its MST temperature is below room temperature which is out of the capability of the testing machine. For the rest of samples their MST temperatures are summarized in Figure 5. As shown in Table I, these 13 samples are of different feeding ratios and thus different hard and soft segment contents. The samples also use PTMO of different molecular weights or mixed PTMO. It is interesting to find that when the MST temperatures of the 13 PU elastomers are plotted against the urethane content, which is defined as the weight fraction of the
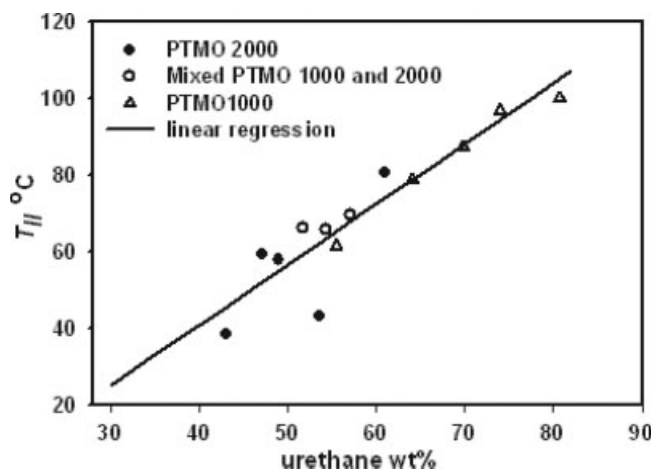
Figure 5 Microphase transition temperature of TDI-based polyurethane elastomer.

hard segment formed by the chain extender and the mixed TDI, a master curve in the form of straight line appears despite the apparent differences in PTMO length and in composition. The master curve indicates that either the length of PTMO or the composition of the mixed PTMO has no effect on the MST of this series of elastomers. This could be interpreted as follows. In the series of elastomers, the molar feeding ratio of NCO to OH is fixed at 1.02. Two polymerization processes of PU elastomers with the same urethane content, but one uses PTMO1000 and the other uses PTMO2000, are considered for the convenience of the interpretation. In the former polymerization process, the amount of NCO expected to react with PTMO1000 would be twice of that in the latter process using PTMO2000. Consequently one would expect that the extra TDI in the former process will on average link PTMO1000 in pair, which effectively makes the soft segment of the product in the former polymerization process have the average lengths as that of the latter in which PTMO2000 is used as the polyol. The MST temperature for this series of elastomers increases linearly with the increasing the urethane weight fraction of the polymers. The slope of the best-fit straight line in Figure 5 is 1.6. Schneider et al.[5] also found that for a series of PU elastomer made of 2.4 TDI, PTMO1000

and BDO the plot of the MST temperature and urethane fraction formed a straight line with a slope at ~ 2.2. Our PU elastomers used mixed TDI in contrast to pure 2.4 TDI used by Schneider et al. The ratio of the slope in our results to the slope from the work of Schneider et al. is 0.73, which is very close to the fraction of the 2,4 TDI in the mixed TDI. The coincidence implies that the hard segment derived from 2,4 TDI is the only active component and 2,6 TDI played no role in the MST observed in our polymers.

CONCLUSION

A series of PU elastomers based on mixed TDI, BDO, and PTMO of two different molecular weights were synthesized. A technique based on linear viscoelasticity measurement was developed and it successfully detected the microphase separation transition of the elastomers. The transition temperatures of the elastomers using PTMO of different molecular weights and the transition temperatures of the elastomers using mixed PTMO were found to form a master curve which was linearly dependent on the weight fraction of hard segments. The results indicated that the length and composition of PTMO has no effect on the microphase separation transition of this series of PU elastomers. A hard segment based on 2,4 TDI was found to prevailing over that based on 2,6 TDI in the control of the transition behavior.

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