This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Effect of Soft Segment Molecular Weight and 3-Methyl Side Group on Microstructural Separation in Polyurethane Elastomers

Wen-Pin Chen[ab]; Kurt C. Frisch[b]; Donald J. Kenney[b]; Shaio-Wen Wong[b]; Ralph Moore[c]
[a] Polyurethanes International, Inc., Troy, Michigan [b] Department of Chemistry and Polymer, Institute University of Detroit, Detroit, Michigan [c] Chemicals and Pigments Department, E. I. du Pont de Nemours & Co., Wilmington, Delaware

To cite this Article Chen, Wen-Pin , Frisch, Kurt C. , Kenney, Donald J. , Wong, Shaio-Wen and Moore, Ralph(1992) 'Effect of Soft Segment Molecular Weight and 3-Methyl Side Group on Microstructural Separation in Polyurethane Elastomers', Journal of Macromolecular Science, Part A, 29: 7, 567 — 587
To link to this Article: DOI: 10.1080/10101329208052183
URL: http://dx.doi.org/10.1080/10101329208052183

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J.M.S.—PURE APPL. CHEM., A29(7), pp. 567–587 (1992)

EFFECT OF SOFT SEGMENT MOLECULAR WEIGHT AND 3-METHYL SIDE GROUP ON MICROSTRUCTURAL SEPARATION IN POLYURETHANE ELASTOMERS

WEN-PIN CHEN,*† KURT C. FRISCH, DONALD J. KENNEY, and SHAIO-WEN WONG

Department of Chemistry and Polymer Institute
University of Detroit
Detroit, Michigan 48221

RALPH MOORE

Chemicals and Pigments Department
E. I. du Pont de Nemours & Co.
Wilmington, Delaware 19898

Downloaded At: 17:02 24 January 2011

ABSTRACT

The object of this study was to assess the effect of the chain length and of the pendant 3-methyl side group in the soft segment of polyurethane (PU) elastomers. In addition, the effect of annealing–quenching on the degree of microstructural segregation between the hard and soft segments was also investigated. The study employed electron spin resonance (ESR), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). Samples for ESR measurements were spin-labeled with the nitroxide probe, 4-hydroxy-2,2′,6,6′-piperidine-1-oxyl (TEMPOL), by reaction of an isocyanate group with the hydroxyl group of TEMPOL. The nitroxide label is therefore located at a chain end. The PU's were based on 4,4′-diphenylmethane diisocyanate (MDI), po-

†Present address: Polyurethanes International, Inc., 4000 Livernois, STE 110, Troy, Michigan 48098.

Copyright © 1992 by Marcel Dekker, Inc.

ly(oxytetramethylene) glycols (PTMO), and hydroxyl-terminated random copolymers of tetrahydrofuran and 3-methyl-tetrahydrofuran (THF/Me-THF). Purified 1,4-butanediol (BD) was used as a chain extender. The elastomers made from higher molecular weight (MW) soft segments have better phase segregation than their lower MW counterparts. The 3-methyl side groups on the PTMO backbone have some effect on the arrangements of the two domains. ESR analysis indicated that the increase in the MW of THF/Me-THF decreased the degree of mixing between the hard and soft segments. In PU elastomers made from high MW soft segments, the presence of crystallinity was observed from the DSC measurements. The crystallinity of the soft segments was disrupted by the existence of the 3-methyl side groups.

INTRODUCTION

Downloaded At: 17:02 24 January 2011

Thermoplastic polyurethane (PU) elastomers are block copolymers of the $(AB)_n$ type, consisting of alternating soft and hard segments. At service temperatures, the soft segment is in a viscous or rubbery state, while the hard segment is in a glassy or semicrystalline state. The soft segment provides elastomeric character to the polymer. The hard segment provides dimensional stability by acting as a thermally reversible reinforcing filler. The unusual properties of these copolymers are directly related to their two-phase structures.

The domain morphology has been extensively studied in order to understand the molecular basis of the polymer properties [1–4]. The domain size and spacing can be determined by small-angle x-ray scattering [5–8] and electron microscopy [9–12]. Infrared spectroscopy [13–15] has been used to study the effect of temperature on hydrogen bonding, phase separation, and segmental orientation. Using differential scanning calorimetry (DSC) [16–18] to determine the glass transition temperature is also very effective for polymer characterization.

Brunette et al. [19] and Schneider et al. [20] used DSC and TMA to study the morphology of hydroxyl-terminated polybutadiene (HTPBO) based polyurethanes. These elastomers exhibited almost complete phase separation due to their T_g's being very close to those of the polyols. They attributed this complete phase separation to the absence of urethane hydrogen bonding in the soft segments of HTPBO.

The use of electron spin resonance (ESR) technique with nitroxide radicals to study motions in macromolecular systems was applied to homopolymers [21], block copolymers [22–24], and polymer blends [25]. The literature on spin labels in PU is limited; data obtained indicate that the ESR lineshapes are sensitive to the composition of the polymer and its degree of phase separation as well as its crystallinity. In a PU prepared from 4,4′-diphenylmethane diisocyanate (MDI), poly(oxytetramethylene) glycols (PTMO), and 4-hydroxy-2,2′6,6′-piperidine-1-oxyl (TEMPOL) [26], a clearly rapid motion spectrum was found at 100°C. The same spectrum was shown at 23°C when the same polymer was swollen. In a diol nitroxide spin-labeled PU hard segment based on MDI and 1,4-butanediol (BD) [27], the T_{50G} values of 410 and 450 K were calculated from ESR spectra. In a series of nitroxide spin labeled PU's made from MDI, PTMO, hydroxyl-terminated random copolymers of

tetrahydrofuran and 3-methyl-tetrahydrofuran (THF/Me-THF) as well as BD [23, 24], it was found that the microstructural morphology was affected by the soft-segment molecular weight, structure, and thermal history.

EXPERIMENTAL

Materials

The macroglycols (PTMO, MW = 650, 1000, 2000, 2900; THF/8% Me-THF, MW = 1000, 2000, 2900; THF/13% Me-THF, MW = 2900; and THF/15% Me-THF, MW = 1000, 2000, 3735) supplied by DuPont were dried overnight at 70°C under a vacuum of 5 mmHg. 1,4-Butanediol (DuPont) was purified by vacuum distillation with the first and last 5% discarded. The NCO content of MDI (Mobay) and of the prepolymers was measured by the di-*n*-butylamine titration method.

Preparation of PU Elastomers

The PU polymers were prepared in a two-step reaction. The prepolymers were obtained first by reacting MDI and the polyol. The reaction temperature was kept below 80°C. The ratios of MDI to polyol employed are listed in Table 1. The formation of the prepolymer from PTMO is shown in Scheme 1.

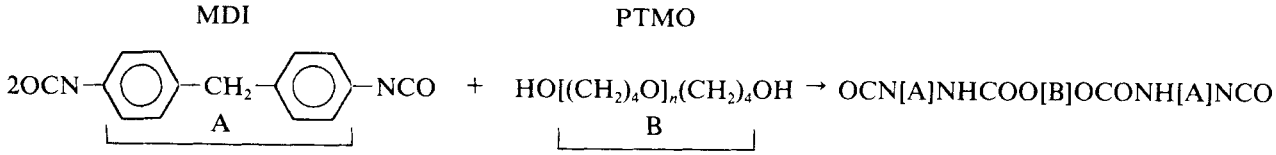
To prepare elastomers, the MDI/polyol-based prepolymers were chain-extended with BD to an NCO index of 105. The prepolymer and chain extender were kept at 70°C. A tin catalyst, dibutyltin dilaurate (T-12), was used to accelerate the curing reaction. The mixture was then immediately poured into a preheated mold. The mold was then placed on the heating platform of a Carver hydraulic press. The elastomer was then post-cured for 20 h at 90°C. The structure of the elastomer is shown in Scheme 2.

TABLE 1. Compositions of the Polyurethane Elastomers Based on MDI, BD, and Various Polyols

Designation	Macroglycol (MW)	Prepolymer NCO/OH	Hard segment, wt%
PU-0(06)-38	PTMO(650)	3/2	38.9
PU-0(1)-38	PTMO(1000)	2/1	38.0
PU-0(2)-38	PTMO(2000)	4/1	38.3
PU-0(3)-38	PTMO(2900)	11/2	38.1
PU-8(1)-38	THF/8% Me-THF(1000)	2/1	38.8
PU-8(2)-38	THF/8% Me-THF(2000)	4/1	37.3
PU-8(3)-38	THF/8% Me-THF(2900)	11/2	37.2
PU-13(3)-38	THF/13% Me-THF(2900)	11/2	37.2
PU-15(1)-38	THF/15% Me-THF(1000)	2/1	38.4
PU-15(2)-38	THF/15% Me-THF(2000)	4/1	38.3
PU-15(4)-38	THF/15% Me-THF(3735)	7/1	37.9

Downloaded At: 17:02 24 January 2011

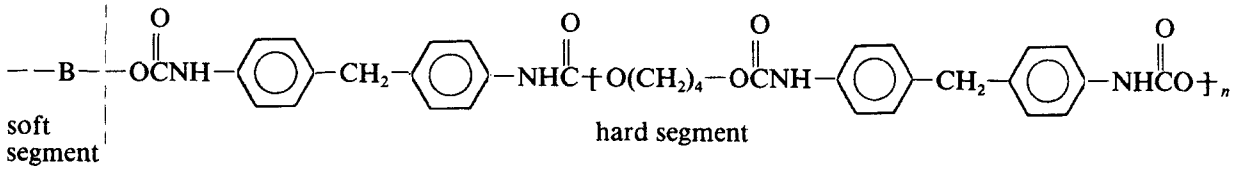
Downloaded At: 17:02 24 January 2011



SCHEME 1.

Downloaded At: 17:02 24 January 2011

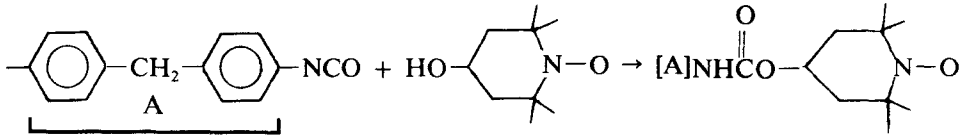
polyurethanes



where B = $H[O(CH_2)_4]_a[OCH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2]_b[O(CH_2)_4]_c[OCH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2]_dOH$

$(b + d)/(a + b + c + d) = 0, 0.08, 0.13$, and 0.15

SCHEME 2.



SCHEME 3.

Preparation of Spin-Labeled PU Elastomers

The preparation of spin-labeled MDI-BD, spin-probed PTMO, and THF/Me-THF as well as spin-labeled PU has been described in previous publications [23, 24].

For the preparation of spin-labeled PU, the prepolymer was labeled with TEMPOL. The reaction is shown as Scheme 3.

The spin-labeled prepolymer was then chain-extended with BD.

ESR Measurement

ESR spectra (x-band) were measured with a Bruker 2000 SRC spectrometer operating at 9.7 GHz (empty cavity at ambient temperature), using 100 kHz modulation. The samples were put into 3 mm i.d. Pyrex tubes. Spectra were measured from 100 to 425 K using the Bruker Variable Temperature Unit ER 411 VT. ESR spectra for MDI-BD were measured up to 460 K. Spectra at 77 K were taken in a liquid nitrogen Dewar inserted in the ESR cavity. The absolute value of the magnetic field was measured using a Bruker ER 035 NMR gaussmeter. The microwave frequency was measured with a Hewlett-Packard 5342 frequency counter. Calibration of g-values was based on 2,2′-diphenyl-1-picrylhydrazyl (DDPH, $g = 2.0036$) and Cr^{3+} in MgO ($g = 1.9796$).

Downloaded At: 17:02 24 January 2011

Differential Scanning Calorimetry (DSC)

A DuPont computer/thermal analyzer was used in conjunction with a 910 DSC module to obtain the thermograms. Samples (5.5 ± 0.05 mg) were cut from the test sheets and placed in an aluminum test pan for analysis. For the first run the cell was cooled from room temperature to 123 K by liquid nitrogen and then heated to 473 K in a nitrogen atmosphere at a rate of 20 K/min. The temperature was calibrated with the melting points of n-heptane and indium. The midpoint process was used to define the glass transition temperature of the sample. In the case of endothermic melting, the peak temperature was reported as the transition point.

To complete the annealing-quenching study, the sample was kept in the sample pan for annealing after the first run for 5 min. It was then quenched at the maximum cooling rate using liquid nitrogen. When the sample temperature reached 123 K, a second run was taken immediately using the same conditions as for the first run.

Dynamic Mechanical Analysis (DMA)

The storage modulus (E'), the loss modulus (E''), and the tan δ were measured by a Rheovibron Dynamic Viscoelastometer Model DDV-II-C (Imass, Inc.). Measurements were made at a frequency of 110 Hz. The temperature range was from 173 K to the softening of the sample. Liquid nitrogen was used to achieve the desired low temperature. The heating rate was controlled at about 1–2 K/min. The readings were taken every 3–5 K except in the transition regions, where the readings were taken every 1 K. The rectangular test specimens had dimensions of 1.2–1.7 inches in length and 0.07–0.1 inches in width. The thickness of the film was approximately 0.006–0.015 inches.

Mechanical Properties

Hardness was measured using durometers Shore A and Shore D (ASTM D2240-81). The stress-strain properties were measured by stretching the samples at a crosshead speed of 20 in./min (ASTM D412-80). Sample thickness ranged from 0.070 to 0.090 inches. A bench marker was used to measure the elongation at break. The tear resistance was measured while employing a crosshead speed of 20 in./min (ASTM D624-73 and ASTM D1938). A standard Die C was used to cut samples to measure the Graves tear strength. Rectangular shape specimens (1″ × 3″) with a 2-inch slit in the center were used for the split tear. Tests were performed on an Instron tester (Table Model A-1020). The reported data are the average of at least five readings.

RESULTS AND DISCUSSION

Model Homopolymers

ESR spectra of spin-probed THF/15% Me-THF 2000 in the temperature range of 120–360 K are shown in Fig. 1. The spectrum at 77 K is identical to that at 100 K. At temperatures below 240 K, the spectra indicate that the host polymer is very rigid. At temperatures above 260 K, the isotropic spectra appear. This means that certain motions take place in the homopolymer at this temperature. This will allow nitroxide tumbling. In the isotropic region, the only changes were in the linewidths for the three isotropic lines, which become narrower with increasing temperature. At 360 K the amplitudes of these lines approach the same height. We defined this as a complete isotropic state.

The correlation times (τ_c) of the nitroxide in the three host polymers at various temperatures are listed in Table 2. The empirical method for calculating τ_c for the rigid spectra region is based on the following equation [28]:

$$\tau_c = a(1 - S)^b \tag{1}$$

where $S = 2A'_{zz}/2A_{zz}$; $2A'_{zz}$ is the extreme separation at various temperatures and $2A_{zz}$ is the extreme separation in the rigid limit at 77 K; the parameters a and b are motional model dependents. The model of diffusion was determined from the plot of H_+/H_- vs H_+ [28, 29], where H_+ and H_- are the shifts of the low and high field lines from their positions in the rigid limit, respectively. The plot for THF/15% Me-THF is shown in Fig. 2. The shape of the curve seems to suggest a Brownian diffusion mechanism. For this type of motional model with an intrinsic linewidth of 3 G, the suggested values of a and b are 5.4×10^{-10} s and -1.36, respectively [29]. The spin-probed PTMO and spin-labeled MDI-BD showed curves of very similar shapes to that of THF/15% Me-THF.

In the "isotropic spectra" regions, the correlation time can be calculated by the following equation [21]:

$$\tau_c = 0.65 \times 10^{-9}\, W_0[(h_0/h_1)^{1/2} + (h_0/h_{-1})^{1/2} - 2] \tag{2}$$

where W_0 is the linewidth of the center line in gauss, and h_1, h_0, and h_{-1} are the amplitudes of the ESR spectrum for low, center, and high field lines, respectively. At a temperature of 120 K, two spin-probed polyols exhibited nearly the same

Downloaded At: 17:02 24 January 2011

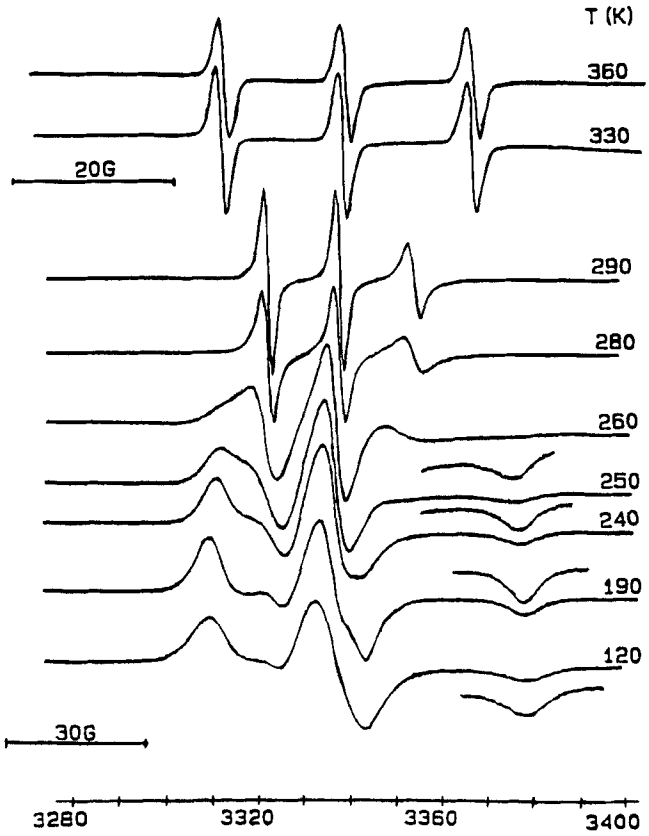


FIG. 1. ESR spectra of spin-labeled THF/15% Me-THF.

Downloaded At: 17:02 24 January 2011

TABLE 2. Correlation Time (τ_c) for Rotational Mobility of Nitroxides in the Host Homopolymers Measured by ESR

Temperature, K	τ_c of homopolymers, s		
	MDI-BD	THF/15% Me-THF 2000	PTMO 2000
120	1.239×10^{-6}	2.436×10^{-6}	1.867×10^{-6}
180	2.367×10^{-6}	2.289×10^{-7}	2.115×10^{-7}
240	3.479×10^{-7}	4.612×10^{-8}	2.484×10^{-8}
300	1.918×10^{-7}	2.841×10^{-10}	2.648×10^{-10}
360	4.319×10^{-8}	3.120×10^{-11}	2.244×10^{-11}

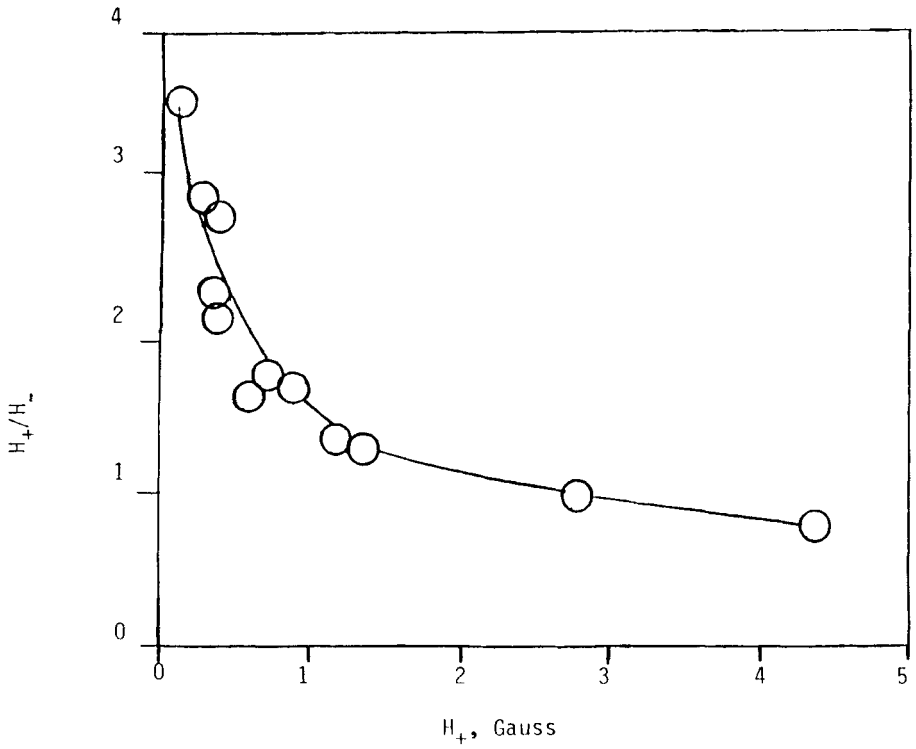


FIG. 2. The shift ratio H_+/H_- as a function of H_+ for the spin-probed THF/13% Me-THF.

Downloaded At: 17:02 24 January 2011

rotational correlation time as that of the spin-labeled MDI-BD in the range of 10^{-6} s (Table 2). This illustrated that the soft segment and the hard segment are very rigid at this low temperature.

At temperatures of 180 and 240 K, the spin-probed soft segments (PTMO 2000 and THF/15% Me-THF 2000) have a rotational correlation time of 10^{-7} and 10^{-8} s, an order of about one magnitude lower than the τ_c of the spin-labeled MDI-BD. This illustrates that the nitroxide tumbles more freely in the soft segment than in the hard segment at these temperatures.

At temperatures of 300 and 360 K, the slow-motional ESR spectra (10^{-9} s $\leq \tau_c \leq 10^{-6}$ s) still existed in the MDI-BD model compound, which has a strong hindrance to the rotation of the spin-labeled molecules. However, at these temperatures the spin-probed soft segments already allowed the nitroxides to tumble freely. The correlation time of the latter is about 1000 times lower than that of the MDI-BD.

Spin-Labeled Polyurethanes

ESR spectra for spin-labeled PU-15(4)-38 in a temperature range from 200 to 400 K are shown in Fig. 3. The shapes of these ESR spectra are different from those of the one-phase morphology of the model compounds. A clear intermediate spectrum appears at 300 K with one phase tumbling faster than the other phase. At

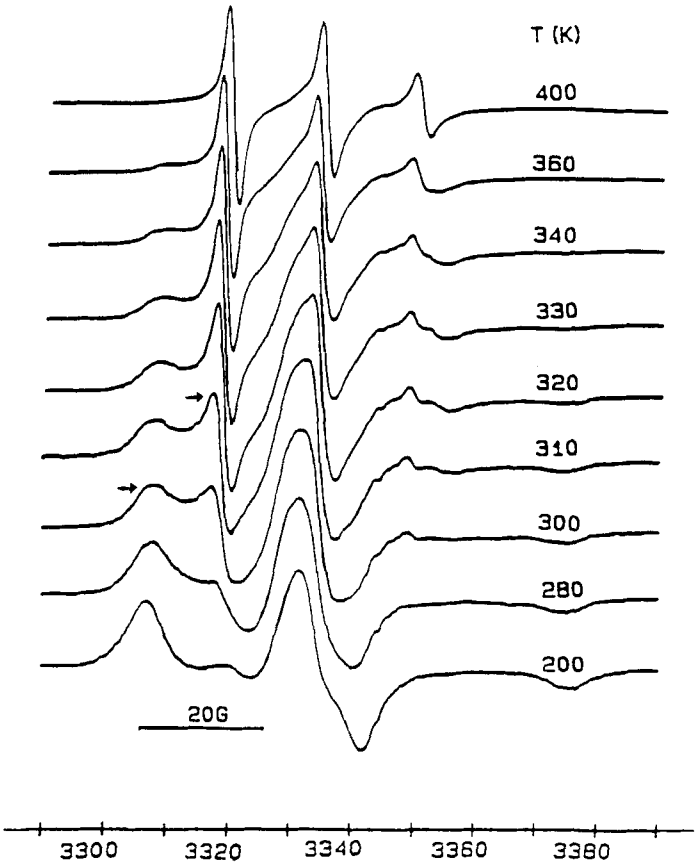


FIG. 3. ESR spectra of spin-labeled PU-15(4)-38.

Downloaded At: 17:02 24 January 2011

this temperature the more rigid or slow phase has an extreme separation at 65 G, and the fast phase is isotropic. This indicates that the spin-labels (chain ends) are able to tumble rapidly in the soft segment phase, while those spin-labels in the hard segment domains are still rigid. The definition of T_{iso} is the temperature at which the fast motion becomes isotropic. The T_{iso} for the spin-labeled PU-15(MW)-38 are listed in Table 3. It was found that T_{iso} decreased with the increasing length of the soft segment.

The temperature corresponding to the appearance of the "fast" component is higher for lower MW polyols. This indicates that a larger part of the hard segment is incorporated in the soft segment domains for polyurethane elastomers made from lower MW polyols. The extreme separation ($2A'_{zz}$) of the "fast" component, representing the soft domain as a function of temperature, is shown in Fig. 4. The temperature corresponding to an extreme separation of 50 G, T_{50G}, is approximately 262 K for THF/15% Me-THF. This value can be compared with the value of 300 K for PU-15(4)-38, 318 K for PU-15(2)-38, and 328 K for PU-15(1)-38. These temperatures are very close to those of the corresponding T_{iso}. The earlier occurrence of a dramatic drop in $2A'_{zz}$ with the onset of rapid rotation for PU's having higher MW polyols demonstrates that the degree of mixing increases with a decrease in the MW of the polyol.

TABLE 3. Effect of Soft Segment MW on the Thermal Transitions of Polyurethane Elastomers

Elastomers	DSC[a] T_1, K	T_2, K	T_3, K	T_4, K	H_f, J/g	ESR, T_{iso}, K
PU-15(1)-38	240.4		341.5	409.0	5.8	330
	(253.6)			(373.9)		
PU-15(2)-38	211.9			430.3	10.1	320
	(213.0)			(446.9)	(0.4)	
PU-13(3)-38	205.9			438.6	12.0	300
	(208.7)			(446.5)	(0.3)	
PU-15(4)-38	205.6	268.0		441.0	11.3	300
	(206.0)	(270.6)		(454.4)	(1.7)	

[a]The values in parentheses are for the annealed samples.

Downloaded At: 17:02 24 January 2011

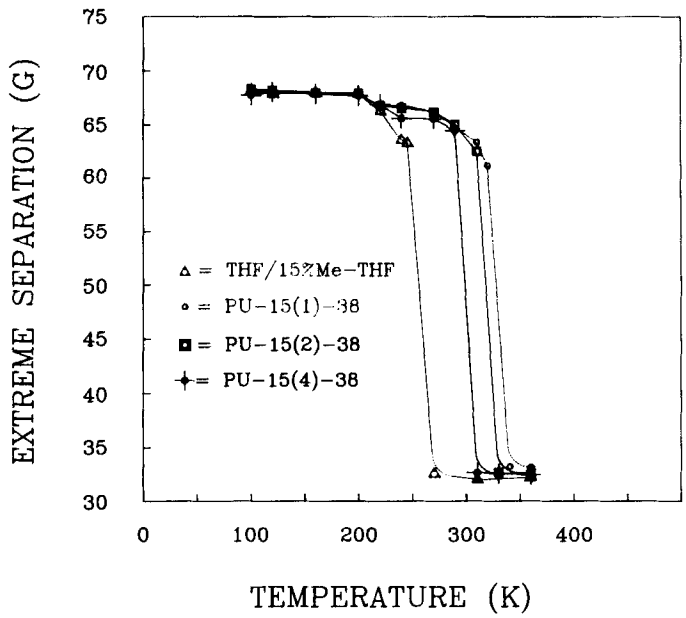


FIG. 4. The extreme separation $2A'_{zz}$ for THF/15% Me-THF and PU-15(MW)-38 elastomers as a function of temperature.

Soft Segment Behavior

Effect of Soft Segment Chain Length

DSC thermograms of polyurethane elastomers of the PU-15(MW)-38 series are shown in Fig. 5. The data are summarized in Table 3. The glass transition temperature (T_1) of the soft segments increases with the decreasing molecular weight

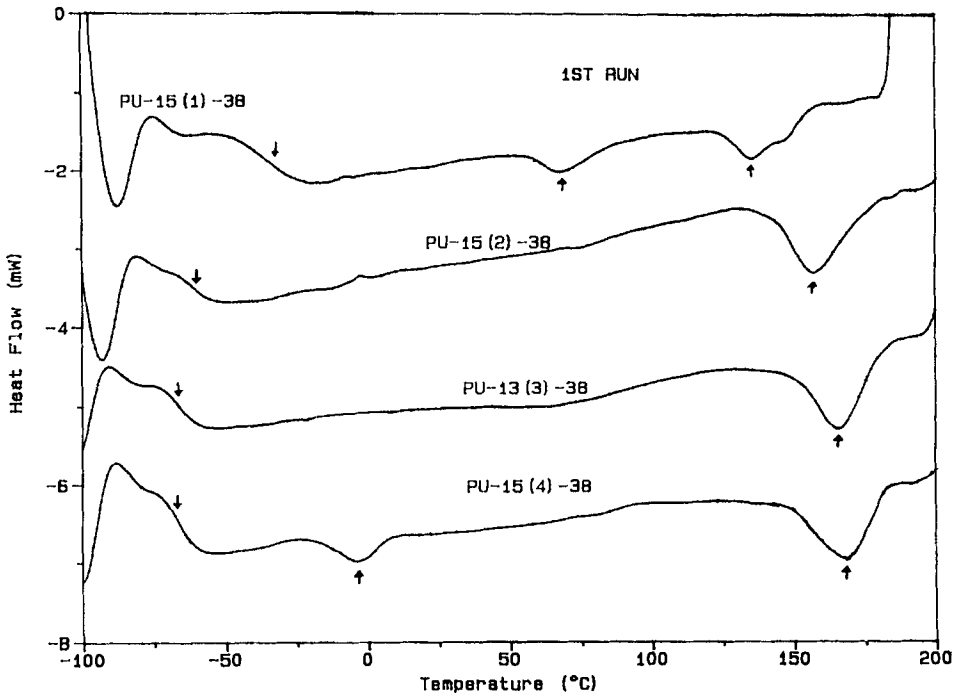


FIG. 5. DSC thermograms of PU-15(MW)-38 series (1st run).

Downloaded At: 17:02 24 January 2011

of the soft segments. This indicates that the polyurethanes made from lower MW polyols have more miscibility between the hard and soft segments. The more hard segments are dispersed in the soft segments, the more restrictive the soft segment. These results are in agreement with ESR studies.

Figure 6 shows T_g data based on tan δ as determined by means of a rheovibron. The T_g of PU-0(MW)-38 which were prepared from PTMO exhibited the same trend as that of PU-15(MW)-38 which were made from copolyols of THF/15% Me-THF. More phase separation can be expected as the soft segment MW increases.

The DSC thermograms for the annealed samples are shown in Fig. 7. The thermal transitions are listed in Table 3 (in parentheses). The T_g of the soft segment domains, as previously mentioned, is an indication of the degree of phase separation. The same general trend is found in the annealed samples as in the unannealed samples. However, it was found that the soft segment T_g increases with annealing. This suggests that annealing promotes phase mixing and that the soft domains become less pure after annealing. This observation is in agreement with the studies by Wilkes et al. [30, 31]. They proposed that upon heating, the extended soft segments contract or relax, causing additional hard segments to be pulled out of the hard domains and phase mixing to occur. This effect is more pronounced in PU-15(1)-38 than in polymers which have a soft segment with MW $\geq$ 2000. The former has a 13 K change in T_g, but the latter have only a 0–3 K change in T_g. In the study by Hesketh et al. [17] on two polyurethane systems, MDI/BD/PTMO and piperazine/1,4-butanediol bischloroformate/PTMO, they suggested two possible

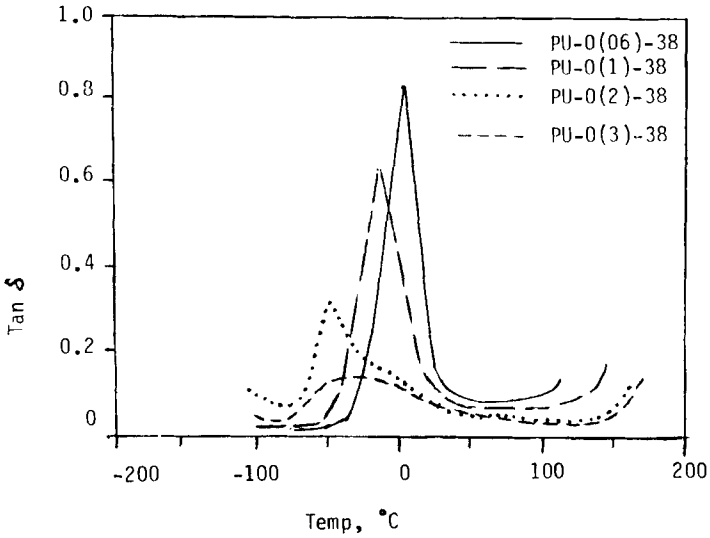


FIG. 6. Tan δ as a function of temperature for PU-0(MW)-38.

Downloaded At: 17:02 24 January 2011

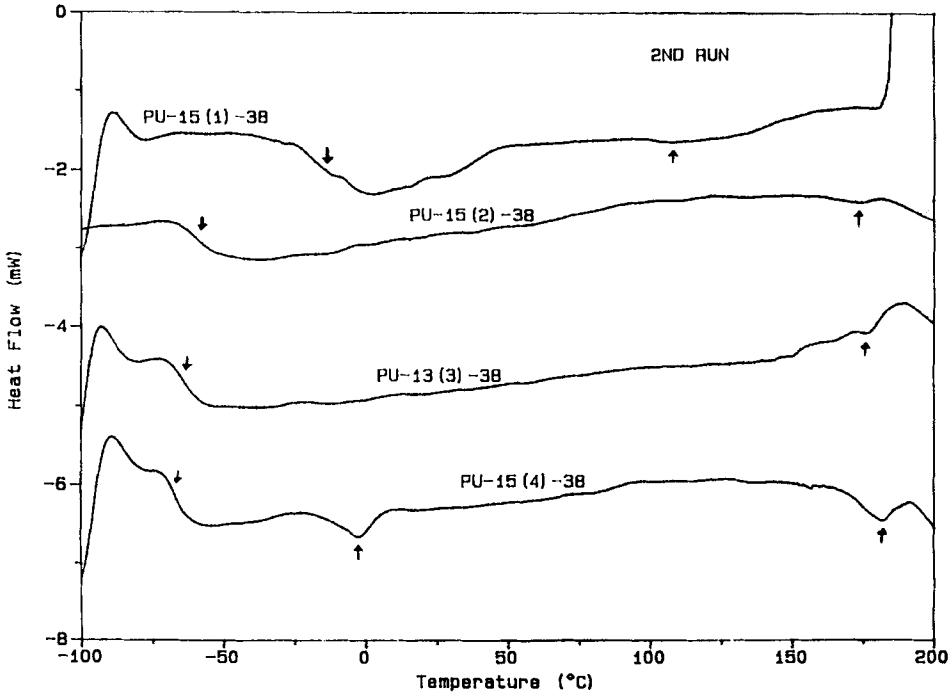


FIG. 7. DSC thermograms of PU-15(MW)-38 series (2nd run); annealing-quenching study.

explanations for small T_g changes in the annealed samples. Either increased phase mixing was not occurring during annealing or demixing upon quenching occurred on a time scale much shorter than that of the experiment.

In ESR studies for the PU-15(MW)-38 series (Fig. 8), it was found that all spectra exhibited a certain degree of isotropy at 400 K. This means that all samples exhibited a certain degree of phase mixing at this temperature. Thus, we suggest that the small changes in T_g for the annealed samples having soft segment MW $\geq$ 2000 are due to the fact that the demixing time upon quenching is much shorter than the cooling rate in the experiment.

Effect of 3-Methyl Side Groups

The glass transition temperatures (T_g's) for PU-R(1)-38 by means of DSC, DMA, TMA, and ESR are shown in Table 4. In this series, the one with more 3-methyl side groups on the PTMO backbone produces a higher T_g. The glass

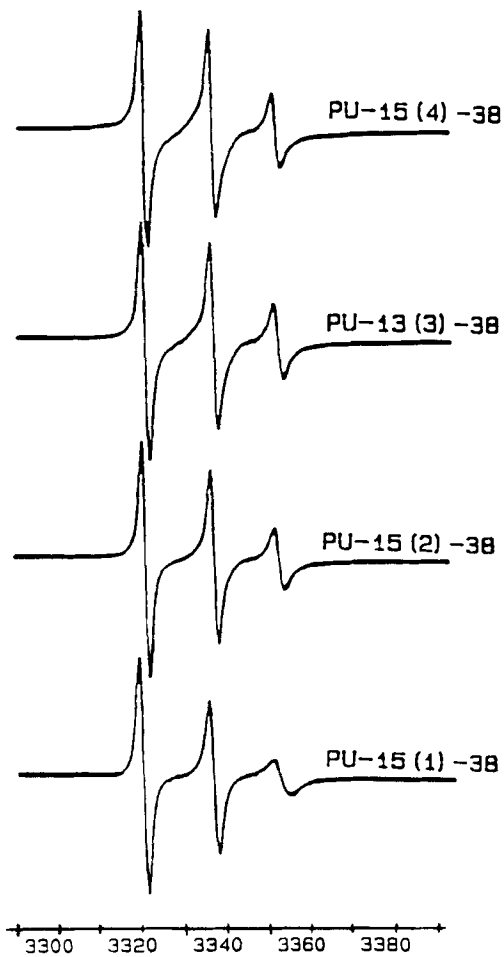


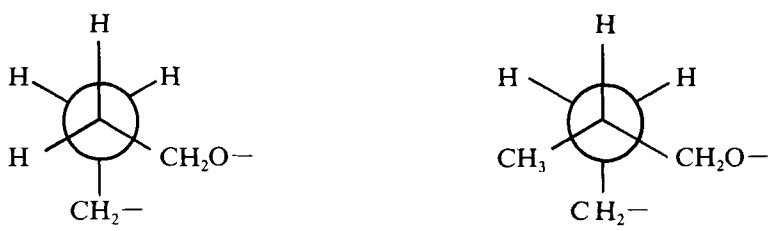
FIG. 8. ESR spectra of spin-labeled PU-15(MW)-38 series at 400 K.

Downloaded At: 17:02 24 January 2011

TABLE 4. Effect of Methyl Side Groups of Soft Segment on the Thermal Transitions of Polyurethane Elastomers

Samples	DSC, T_g, K	DMA T_g (E''), K	DMA T_g (tan δ), K	TMA, T_g, K	ESR, T_{iso}, K
PU-O(1)-38	238.2	239.0	257.0	226.8	310
PU-8(1)-38	239.9	240.0	259.0	234.6	330
PU-15(1)-38	241.0	240.0	263.0	237.6	330
PTMO 1000	192.5	–	–	187.8	260
THF/15% Me-THF	195.5	–	–	191.2	265

transition temperatures of PTMO and THF/15% Me-THF are listed in Table 4. This clearly shows that T_g of THF/Me-THF was higher than that of PTMO. The factor which increased T_g of the soft segment is the steric hindrance of the 3-methyl side groups restricting the motion of the soft segment. This effect can be clearly explained by means of two Newman projections of $-CH_2CH_2CH_2CH_2O-$ and $-CH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_2O-$ through number 2 and 3 carbon atoms.



(a) (b)

The energy barriers of chain rotation in (b) is larger than in (a) due to the steric hindrance of the methyl group. This will lead to an increase in the soft segment T_g.

Crystalline Melting of the Soft Segment

Crystallinity melting endotherms for PU-0(MW)-38 are presented in Fig. 9. The crystallinity in the soft segment results from the highly symmetrical PTMO polyols with higher molecular weights. There is no soft segment crystallinity for the polyurethanes made from a soft segment of MW $\leq$ 1000.

The effects of 3-methyl side groups on the soft segment crystallinity are summarized in Table 5 and shown in Fig. 10. With 3-methyl side groups $\leq$8%, the samples having a soft segment of MW 2900 can have some crystallinity. The crystallinity, however, disappears when 3-methyl side groups increase to 13%. This illustrates the fact that the chain length and the 3-methyl side groups are two opposing

Downloaded At: 17:02 24 January 2011

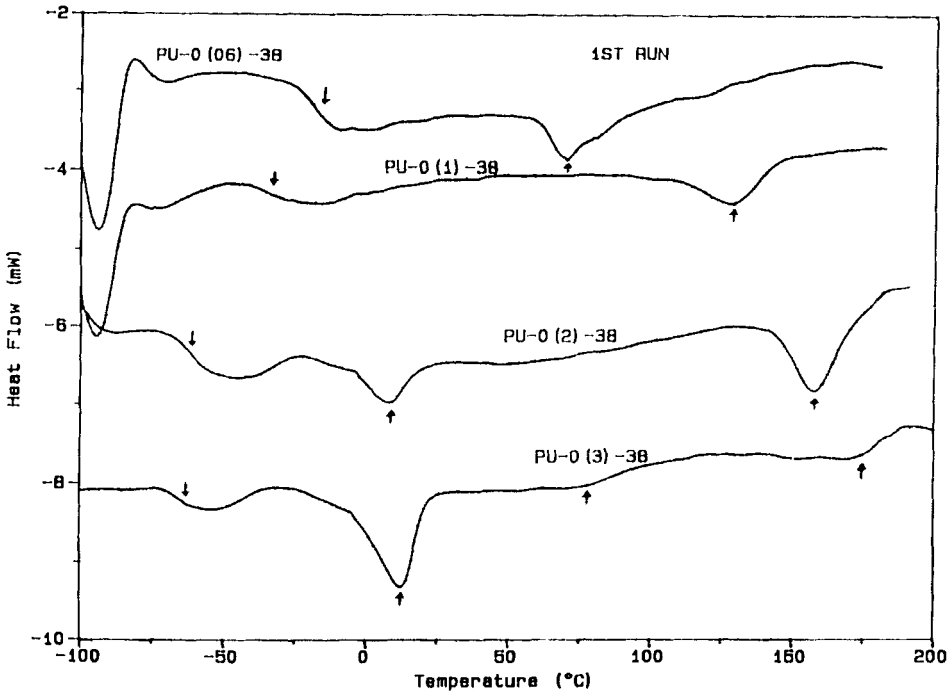


FIG. 9. DSC thermograms of PU-0(MW)-38 series; crystallinity melting endotherms.

Downloaded At: 17:02 24 January 2011

TABLE 5. Effect of the Soft Segment Structure on the Crystallinity of the Soft Segment in the Polyurethane Elastomers

	1st Run		2nd Run[a]	
Elastomers	H, J/g	Crystallinity, %	H, J/g	Crystallinity, %
PU-0(2)-38	3.5	2.0	0	0
PU-8(2)-38	0	0	0	0
PU-15(2)-38	0	0	0	0
PU-0(3)-38	11.6	6.0	7.8	4.0
PU-8(3)-38	3.7	2.0	1.8	1.0
PU-13(3)-38	0	0	0	0

[a]After annealing.

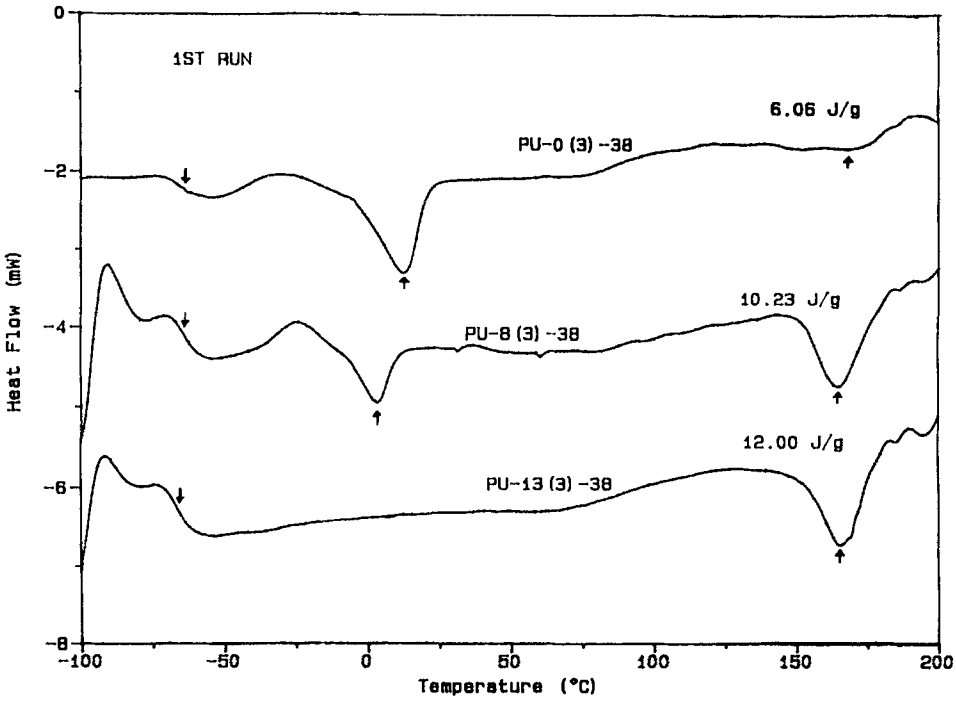


FIG. 10. Effect of 3-methyl side groups on formation of order in soft domains and hard domains.

Downloaded At: 17:02 24 January 2011

factors leading to crystallization. The quantitative analysis of DSC curves can further indicate the effect of these two competitive factors. The reported heat of fusion of pure PTMO is 200 J/g [32]. The weight fraction of soft segment crystallinity is approximately 2 wt% for PU-0(2)-38, 6 wt% for PU-0(3)-38, and 2 wt% for PU-8(3)-38. This is based on the area under the endotherms due to soft segment melting. The highest crystallinity content in PU-0(3)-38 illustrates the highest symmetrical structure in the soft domains.

In the annealed samples, the crystallinity remains in PU-0(3)-38 and PU-8(3)-38. The crystalline melting peaks disappear for PU-0(2)-38. This behavior is explained by the fact that the crystallization process is time dependent. Since the crystallinity is disrupted by heat treatment, the soft segment is amorphous at the start of the second run. Hence it is not surprising to see a crystallization exotherm in the DSC thermogram of PU-0(3)-38 above the soft segment T_g, followed by melting (Fig. 11, last thermogram). Evidently there is insufficient time for a complete nucleation to occur. Thus, it is found that the crystallinity is only 4 wt% for the annealed PU-0(3)-38.

The phenomena of soft segment crystallinity can be further described by the shape of the tan δ peak (Fig. 6). It is observed that the tan δ peak of these elastomers becomes lower and broader as the degree of crystallinity in the soft segment increases. A second relaxation around 273 K is observed in the elastomer of PTMO 2000 as a shoulder of the tan δ peak, and the elastomer of PTMO 2900 showed a broad transition peak.

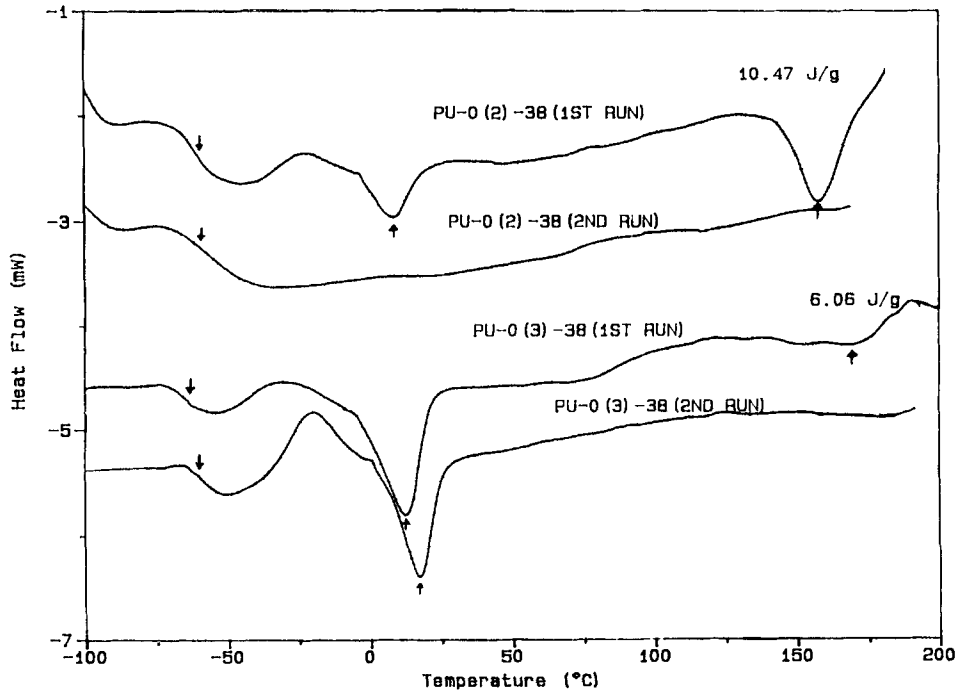


FIG. 11. Effect of annealing-quenching on soft segment crystallinity and hard domain.

Downloaded At: 17:02 24 January 2011

Hard Segment Domain Dissociation: T_3 and T_4

In the PU-15(MW)-38 series, PU-15(1)-38 has a third transition (T_3), which appears at 341 K (Fig. 5 and Table 3). This endotherm is ascribed to the dissociation of short-range order in hard segment domains [16, 33]. This transition disappears on the second run of the DSC scans (Fig. 7), which are taken immediately after quenching the samples from the annealing temperature. It is suggested that the disappearance of these endotherms was due to the phase mixing process during annealing.

The T_4 of DSC endotherms is assigned to the dissociation of the long-range order in hard segment domains. Figure 5 and Table 3 show that this endotherm shifts to higher temperatures with increasing soft segment molecular weight. This indicates that the improved phase separation in the polyurethanes made from soft segment MW $\geq$ 2000 contributes to the formation of well-defined hard segment domains. Further evidence is that the heats of fusion of the crystalline hard domains are 10–12 J/g for polyurethanes made from soft segment MW $\geq$ 2000. This is twice as much as those for polyurethanes made from soft segment MW 1000 (5.8 J/g). It is suggested that the polyurethanes made from higher MW with the same hard segment content can have bigger and more ordered hard segment domains than their lower molecular weight counterparts.

One exception is PU-0(3)-38, which has a broad endotherm (6.06 J/g) which is much less than that for PU-0(2)-38 (Fig. 11). The small size of the endotherm

indicates that only a small portion of the hard segment is crystalline. The limited number of ordered hard segment domains is attributed to the high crystallinity in the soft segments, which constrain movement in the hard segment needed to stack closely.

As discussed above, the demixing time of annealed samples having a higher soft segment MW is much shorter than in the lower molecular weight analogues. Thus, it is found that the endotherms for annealed samples disappear or become a transition with a small width (Figs. 7 and 11). It is also acknowledged that heating the polymer above its MST may destroy the crystallinity of the hard domain.

The effect of 3-methyl side groups on the formation of the orderly hard domains is shown in Fig. 10. It is found that the endotherm of hard domains increases with increasing numbers of 3-methyl side groups. This indicates less crystallinity in the soft segments, which leads to the formation of hard segments with long-range order.

Mechanical Properties

Downloaded At: 17:02 24 January 2011

The mechanical properties of PU elastomers are reported in Table 6. Generally, it is well accepted that the hard segment domains are held together by intermolecular secondary forces, which function as tie-down points or physical crosslinks for a rubbery soft segment matrix and impart high strength. For the elastomers containing the same 38% hard segment content, the ones using the polyols with a higher molecular weight exhibited a higher value in mechanical properties. This may suggest that the optimal mechanical properties can be improved by an increased phase separation. Samples labeled by nitroxide showed comparable properties to the unlabeled samples. This may be due to the small amount of nitroxide probe (only 10^{-5} grams per gram polymer).

TABLE 6. Comparison Mechanical Properties of Polyurethane Elastomers between Labeled and Unlabeled Samples

		Unlabeled		Labeled	
Mechanical properties		PU-0(1)-38	PU-0(2)-38	PU-0(1)-38	PU-0(2)-38
Shore hardness	A	85	92	86	92
	D	36	46	36	45
Stress-strain:					
100% Modulus, psi		751 ± 20	1201 ± 21	743 ± 41	1188 ± 52
300% Modulus, psi		1361 ± 204	2013 ± 21	1370 ± 158	2042 ± 86
Stress at break, psi		3842 ± 259	4270 ± 54	3802 ± 324	4170 ± 125
Elongation, %		486 ± 34	615 ± 53	475 ± 48	627 ± 48
Tear strength:					
Graves die C, pli		516 ± 53	594 ± 37	519 ± 20	582 ± 65
Split tear, pli		248 ± 19	271 ± 28	245 ± 25	281 ± 31

CONCLUSIONS

1. The spin-probed polyols and spin-labeled MDI-BD were studied by means of ESR. MDI-BD is very rigid, as could be expected, with a correlation time of three orders of magnitude higher than that of polyols at 300 K.

2. Polyurethane elastomers were spin-labeled at the terminal isocyanate groups. The ESR spectra showed composite spectra, with fast and slow components.

3. Polyurethane elastomers having 38% hard segment content made from higher MW soft segments have greater phase separation than their lower MW analogues.

4. Two opposing factors lead to crystallization in the soft segments. A higher molecular weight of the soft segment with symmetric structure favors crystallization, whereas a high concentration of 3-methyl side groups restricts crystallization due to steric hindrance.

5. The 3-methyl side groups on the polyol backbone act as steric hindrance which increases the chain rotational energy, leading to an increase in the T_g of the soft segment.

6. T_g's of the annealed sample are usually higher than those of the unannealed samples. The difference in T_g's became smaller as the molecular weight of polyol increased. This is due to the demixing process during quenching. This time-dependent process is faster for the elastomers having longer soft segments.

7. The ESR spectra of spin-labeled polyurethanes showed that the polyurethanes made from higher MW soft segments exhibited more phase separation than their lower MW analogues.

Downloaded At: 17:02 24 January 2011

ACKNOWLEDGMENTS

The authors would like to thank Ms. Maryann Andrews and Mr. David R. Willis of Mearthane Products Corporation for their help in the data arrangement.

REFERENCES

[1] V. V. Shilov, V. N. Blinznyuk, and S. Yu. Lipatov, *J. Mater. Sci., 22*, 1563 (1987).

[2] L. M. Leung and J. T. Koberstein, *Macromolecules, 19*, 706 (1986).

[3] J. T. Koberstein, I. Gancarz, and T. C. Clarke, *J. Polym. Sci., Polym. Phys. Ed., 24*, 2487 (1986).

[4] A. Kintanar, L. W. Jelinski, I. Gancarz, and J. T. Koberstein, *Macromolecules, 19*, 1876 (1986).

[5] Y. S. Ding, S. R. Hubbard, K. O. Hodgsen, R. A. Register, and S. L. Cooper, *Ibid., 21*, 1698 (1988).

[6] Y. J. P. Chang and G. Wilkes, *J. Polym. Sci., Polym. Phy. Ed., 13*, 455 (1975).

[7] S. B. Clough, N. S. Schneider, and A. O. King, *J. Macromol. Sci.—Phys., B2*, 641 (1968).

[8] R. Bonart and E. H. Muller, *Ibid.*, *B10*, 177 (1974).
[9] N. S. Schneider, C. R. Desper, J. L. Illinger, A. O. King, and D. Barr, *Ibid.*, *B11*, 527 (1975).
[10] A. L. Chang and E. L. Thomas, *Adv. Chem. Ser.*, *176*, 13 (1979).
[11] R. M. Briber and E. L. Thomas, *J. Macromol. Sci.—Phys.*, *B22*, 509 (1983).
[12] C. Li and S. L. Cooper, *Polymer*, *31*, 3 (1990).
[13] C. S. Paik Sung and N. S. Schneider, *Macromolecules*, *8*, 68 (1975).
[14] M. M. Coleman, K. H. Lee, D. J. Skrovanek, and P. C. Painter, *Ibid.*, *19*, 2149 (1986).
[15] H. S. Lee, Y. K. Wang, and S. L. Hsu, *Ibid.*, *20*, 2089 (1987).
[16] R. W. Seymour and S. L. Cooper, *Ibid.*, *6*, 48 (1973).
[17] T. R. Hesketh, J. W. C. Van Bogart, and S. L. Cooper, *Polym. Eng. Sci.*, *20*, 190 (1980).
[18] C. Li, X. Yu, T. A. Speckhard, and S. L. Cooper, *J. Polym. Sci., Polym. Phy. Ed.*, *26*, 315 (1988).
[19] C. M. Brunette and W. J. MacKnight, *Rubber Chem. Technol.*, *55*, 1413 (1982).
[20] N. S. Schneider and R. W. Matton, *Polym. Eng. Sci.*, *19*, 1122 (1971).
[21] S. C. Gross, *J. Polym. Sci., Part A-1*, *9*, 3327 (1971).
[22] P. L. Kumler and R. F. Boyer, *Macromolecules*, *9*, 903 (1976).
[23] W.-P. Chen and S. Schlick, *Polymer*, *31*, 308 (1990).
[24] W.-P. Chen, D. J. Kenney, K. C. Frisch, S. Wong, and R. Moore, *J. Polym. Sci., Polym. Phys. Ed.*, *29*, 1513 (1991).
[25] O. Pekcan, Y. Kaptan, and Y. Demir, *J. Colloid Interface Sci.*, *111*, 269 (1986).
[26] T. C. Ward and J. T. Books, *Macromolecules*, *7*, 207 (1974).
[27] F. Lembicz, J. Slonecki, and J. Skolimowski, *Ser. Fiz. (Univ. A. Mickiewicza, Poznan)*, *54*, 317 (1985).
[28] S. A. Boldman, G. V. Bruno, and J. H. Freed, *J. Phys. Chem.*, *76*, 1858 (1972).
[29] A. N. Kuznetsov and B. Ebert, *Chem. Phys. Lett.*, *25*, 342 (1974).
[30] G. L. Wilkes, S. Bargrodia, W. Humphries, and R. Wildnauer, *J. Polym. Sci., Polym. Lett. Ed.*, *13*, 321 (1975).
[31] S. Abouzahr, G. L. Wilkes, and Z. Ophir, *Polymer*, *23*, 1077 (1982).
[32] I. J. Bowman, D. S. Brown, and R. E. Wetton, *Ibid.*, *10*, 715 (1969).
[33] R. W. Seymour and S. L. Cooper, *J. Polym. Sci., Part B*, *9*, 689 (1971).

Received September 23, 1991
Revision received December 12, 1991

Downloaded At: 17:02 24 January 2011