

# The Plasticizing Effect on the Thermal Transitions of the Toluenediisocyanate-Based Polyurethanes Monitored by Thermally Stimulated Current Technique

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Received 8 March 1999; revised 25 June 1999; accepted 5 September 1999

**ABSTRACT:** A liquefied curative in methylene-bis-ortho-chloroaniline/dioctyl or di-2-ethylhexyl phthalate (MOCA/DOP) was used as the substitute curative for the hot-melt MOCA curative in a two-component preparative system for the toluene diisocyanate (TDI)-based polyurethane elastomers. The polyurethane elastomer specimens based on this liquefied curative were prepared with three different soft segments with the addition of various plasticizers. The DOP-added specimens were evaluated by the depolarization technique in the thermally stimulated current/relaxation mapping analysis (TSC/RMA). The results were also compared with differential scanning calorimeter and dynamic mechanical analyzer on the observation on the changes in thermal transitions. Results indicated that at a low DOP content of less than 26 wt %, little disruption on the urethanic matrix was found in the TDI-polycaprolactone (PCL)/MOCA-DOP system. However, at a high DOP content of 47 wt %, a disruption in TDI-poly(tetramethylene) oxide (PTMO) amorphous phase by DOP was observed. The optimum weight ratio of MOCA/DOP was found to be 1 : 2 and this liquefied solution was stable at the ambient temperature, and can be applicable for use as a curative for the preparation of the TDI-based polyurethane elastomers at ambient temperature.

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**Key words:** liquefied curative; MOCA/DOP; plasticizers; polyurethane; TSC/RMA

## INTRODUCTION

Preparation of segmented polyurethane (PU) with the hot-melt method in the two-component system based on the toluenediisocyanate (TDI) often results in a transparent specimen. The linear methylene diphenylisocyanate (MDI)-based PU,<sup>1–5</sup> on the other hand, is opaque in appearance. The difference has been attributed to the separate arrangement in morphology.<sup>6</sup> The transparency of the TDI-based PU has been attributed to the well-mixed phenomenon<sup>7</sup> of the hard and the soft segments in the amorphous phase.

The two-component system that has been used and still is in use has many bottlenecks in its preparative procedures. There are two key steps in the hot-melt procedures that are considered to be critical for successful PU elastomers. First is the requirement of the melt curative, and second the speedy mixing of the melt methylene-bis-ortho-chloroaniline (MOCA) into the preheated TDI-prepolymer. The making of TDI-based PU elastomers is considered to be state of the art. Often this hot-melt step is the determining factor in the production of the PU elastomers. In addition, one of the difficulties lies in the unmeasurable quantity of the MOCA at the hot-melt state. The amount added is based on the experience and the size of the batch. As a result, the products varied in the batches.

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*Journal of Applied Polymer Science*, Vol. 76, 743–761 (2000)  
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**Table I Specimens and Formulations**

Specimens <sup>a</sup>	Formulation (%)		
	DOP	TDI-prepolymer	MOCA
		PCL <sup>b</sup>	
PU-PCL-0	—	88.7	11.3
PU-PCL-4	4.2	85.0	10.8
PU-PCL-8	8.2	81.4	10.4
PU-PCL-15	15.0	75.4	9.6
PU-PCL-21	21.1	70.0	8.9
PU-PCL-26	26.3	65.4	8.3
		PTMO <sup>c</sup>	
PU-PTMO-0	0.0	88.7	11.3
PU-PTMO-31	30.8	61.4	7.8
PU-PTMO-47	47.0	47.0	6.0
PU-PTMO-57	57.2	38.0	4.8
PU-PTMO-64	63.9	32.0	4.1
		PPG <sup>d</sup>	
PU-PPG-0	0.0	88.7	11.3
PU-PPG-31	30.8	61.4	7.8
PU-PPG-47	47.0	47.0	6.0
PU-PPG-57	57.2	38.0	4.8
PU-PPG-64	63.9	32.0	4.1

<sup>a</sup> % of DOP = wt DOP/total wt in the formulation.

<sup>b</sup> PCL has the Mw distribution of 683 to 1595 with main component of Mw = 1002 determined by MALDI-TOF, in Figure 1.

<sup>c</sup> PTMO has the Mw distribution of 522 to 1674 with main component of Mw = 1098 determined by MALDI-TOF, in Figure 1.

<sup>d</sup> PPG has the Mw distribution of 656 to 1468 with main component of Mw = 1004 determined by MALDI-TOF, in Figure 1.

The appearance of the TDI-based PU elastomer can be used as a preliminary indicator for screening. The change of the morphology can be detected easily in the transparent specimens such as the specimen being whitening or leaching out of the nonreactive materials. One of the modifications is the use of the nonreactive plasticizer such as DOP (dioctyl or di-2-ethylhexyl phthalate) to dissolve MOCA. With this step, the hot-melt conditions can be modified with the lowering of the processing temperature during the mixing stage. Consequently, it may provide the better mixing of the specimens at the lower temperature than the hot-melt method or even at the ambient temperature. The preparation procedures can be greatly simplified.

The addition of DOP to the making of the thermal setting PU elastomers needs to be evaluated on its thermal and mechanical properties if the

product is to be useful. DOP as the plasticizer may affect or interrupt the well-mixed soft-to-hard phenomenon and produce deteriorated and useless products that defeat the purpose of the modification.

Thermal properties were evaluated first in this investigation with the emphasis on the thermal evaluations of the Tg transitions because it may indicate the urethanic chain movement in response to the thermal analysis. Furthermore, an evaluation of the hydrogen bonding in the interaction of the soft and hard segments in amorphous phase may be important in the TDI-based PU elastomers. The hydrogen bonding may also contribute to the stabilization of this well-mixed amorphous phase.<sup>8-12</sup> Disruption of the hydrogen bonding formation between the soft and hard segments, may greatly affect the well-mixed soft-to-hard phenomenon in the amorphous phase.

A compatible plasticizer containing the carbonyl group, such as DOP, may compete with the soft segment in the formation of the hydrogen bonding with the NH-group of the urethanic linkage. If this occurs, the stability of the mixing of the hard-to-soft segments in amorphous phase may be altered or deteriorated.

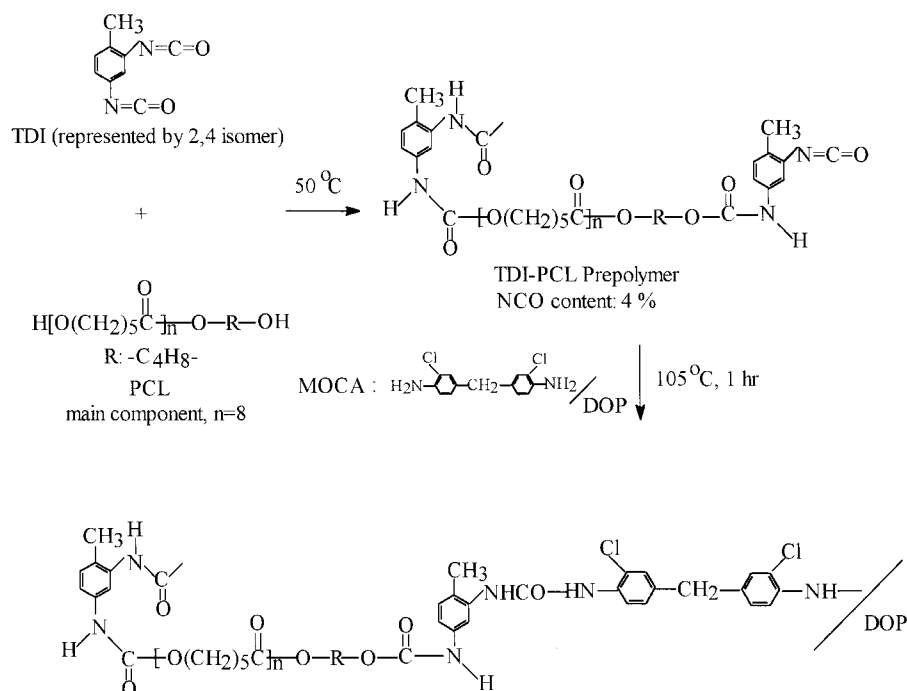
An addition of a plasticizer may provide a good medium<sup>13</sup> for the producing of the elastomers that may release the strain of the mixing,<sup>14</sup> particularly with a small dose of the plasticizer in the thermal curing condition during the preparation of the PUs.

**Table II Optimization of MOCA/DOP Ratio**

Sample #	Weight Ratio		Temperature (°C)	Note
	MOCA	DOP		
M2D1	2	1	100	Dissolved
			90	Dissolved
			80	Partial ppt
M1D1	1	1	Ambient	ppt <sup>b</sup>
			80	Dissolved
			60	Dissolved
M1D2 <sup>a</sup>	1	2	Ambient	Cloudy <sup>b</sup>
			80	Dissolved
			60	Dissolved
			Ambient	Clear <sup>b</sup>

<sup>a</sup> M1D2 contains less DOP than PU-PCL-26. In fact this M1D2 batch contains 9.7 g DOP less than 26.3 g DOP used for the same 8.3 g MOCA in PU-PCL-26 formulation.

<sup>b</sup> 24 h after dissolved at ambient temperature of 20°C. ppt = precipitate.



**Scheme I** Preparation and curing conditions of DOP-containing polyurethane elastomers.

It may be interesting to observe the effect of DOP if it acts differently towards the soft segments with the different structures such as the polyesterpolyol of the polycaprolactone (PCL), the polyetherpolyols of the poly(tetramethylene oxide) (PTMO) and the poly(propylene) glycols (PPG) with the constant hard-segment content of TDI-MOCA segment.

One of the effective methods to detect this plasticizing effect is to observe the change in the cooperative urethanic motion that often occurs in the glass transition region. The observation on the changes of the thermal transitions, the main chain motion in  $T_g$ , and the localized segmental motions in sub- $T_g$ , may be used to indicate the plasticizing effect on the PU matrix.

There are many factors that may affect the  $T_g$  temperature, such as the composition changes, indicated by the NCO content,<sup>15</sup> and by the chain length variations of the soft segment.<sup>16</sup> Therefore, a system selected to examine the DOP effect on the degradation of the urethanic matrix is limited to the specimens containing the constant amount of NCO content, and similar distribution in the soft chain length for the preparation of the TDI-based PU elastomers.

A low NCO of 4% was selected to minimize the effect of the hard segment and the molecular

weight of 1000 in the soft segment was used. Three soft segments with the ether linkages having similar chain length distribution in PPG (PPG-1000), in PTMO (PTMO-1000), and in PCL (PCL-1000) were used for the comparison.

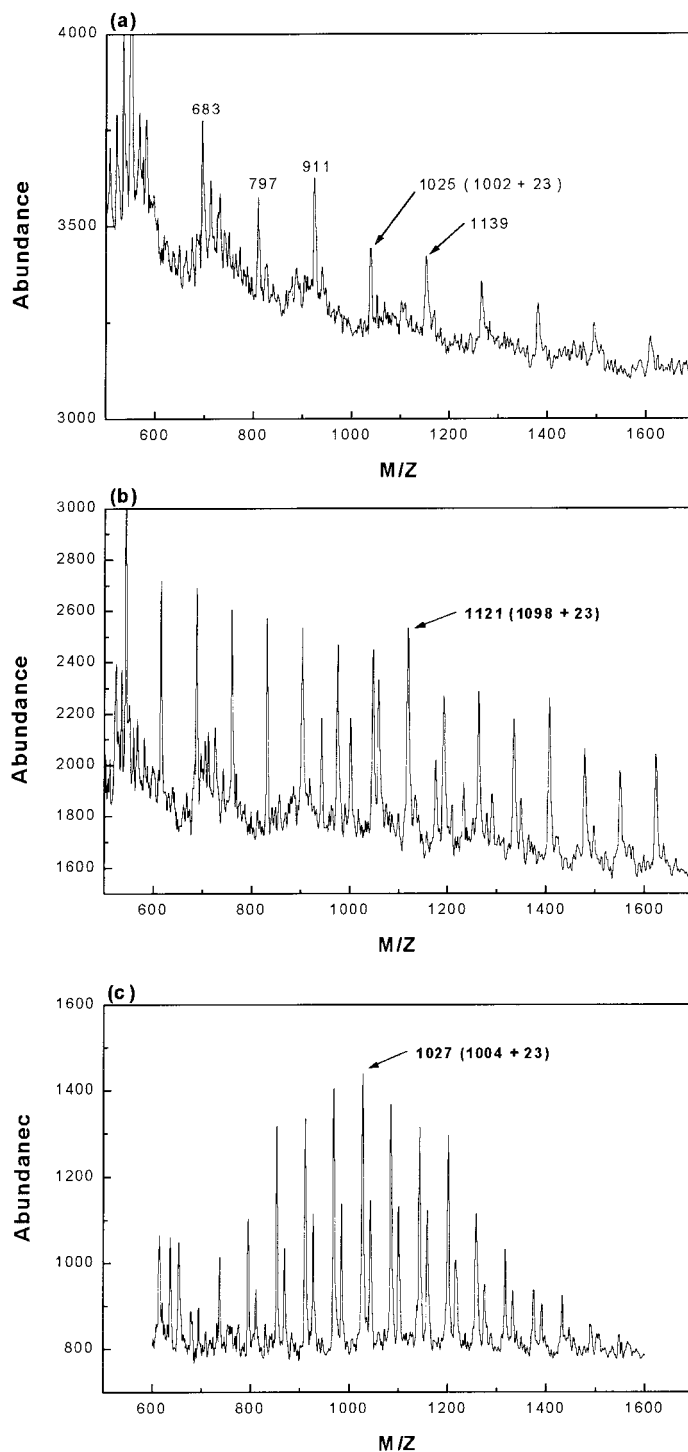
Thermal analyzers of the differential scanning calorimeter (DSC)<sup>17,18</sup> and the dynamic mechanical analyzer (DMA)<sup>19-23</sup> were used to compare the observations by the thermally stimulated current (TSC)<sup>24-27</sup> technique with the relaxation mapping analysis (RMA) in this investigation.

The purpose of this study is to investigate the plasticizing effect on the well-mixed amorphous phase of the PU elastomers, especially on the  $T_g$  measurement. A depolarization relaxation technique in TSC and the thermal windowing technique in the RMA were used. Comparison will be made with the measured data from DSC and DMA on the thermal transitions occurred in the glass transition region.

## EXPERIMENTAL

### Materials

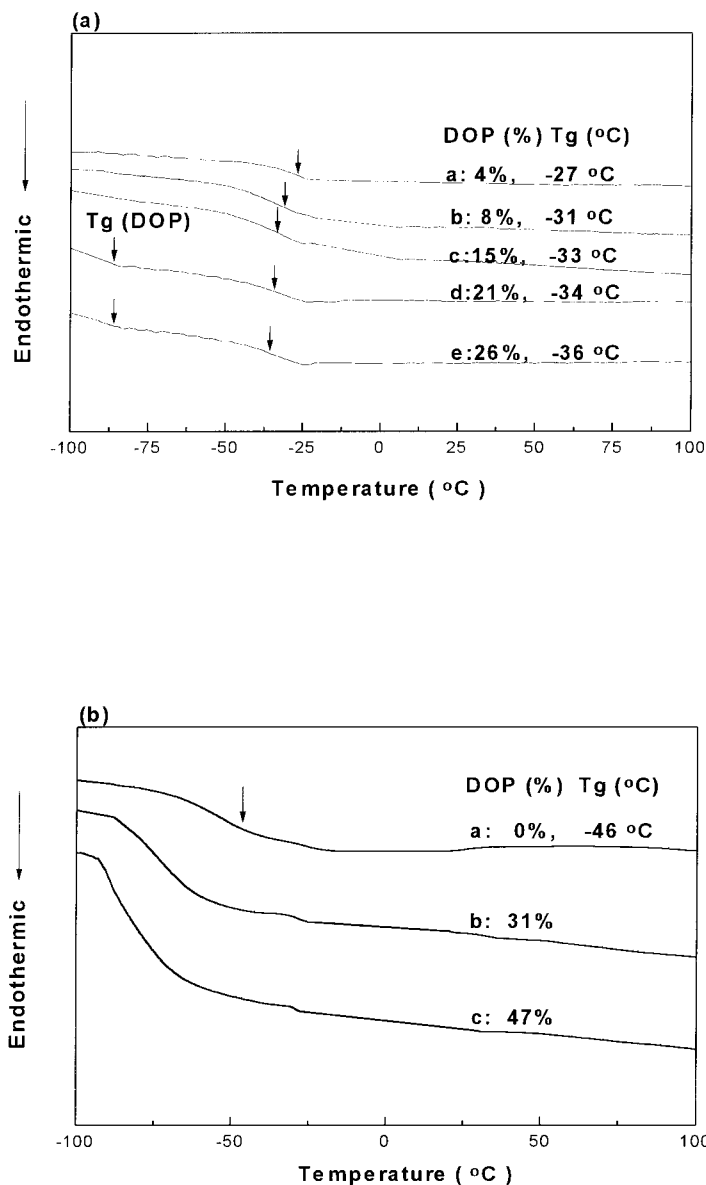
The PTMO diols and PCL diols of  $M_w$  in 1000, were supplied by Hon Yi Chemical Taiwan Co.,



**Figure 1** MALDI-TOF spectra of diols (a) PCL-1000, (b) PTMO-1000, and (c) PPG-1000.

Ltd., Taipei, Taiwan. PPG diols of Mw 1000, commonly known as PPG-1000, was supplied by ARCO Chemical Taiwan Co., Taipei, Taiwan. DOP plasticizer was purchased from Hayashi

Pure Chemical Industries Ltd., Osaka, Japan. A commercial asymmetric TDI (2,4/2,6 in 80/20 ratio) was purchased from First Chemical Taiwan Co. Ltd., Taipei, Taiwan. MOCA was purchased



**Figure 2** **a** DSC thermograms of PU-PCL-1000 specimens with the variation in wt % DOP (a) 4%, (b) 8%, (c) 15%, (d) 21%, and (e) 26%, respectively. Tg of DOP appeared at  $-85^{\circ}\text{C}$ . **b** DSC thermograms of PU-PTMO-1000 with variation in wt % DOP (a) 0%, (b) 31%, and (c) 47%, respectively.

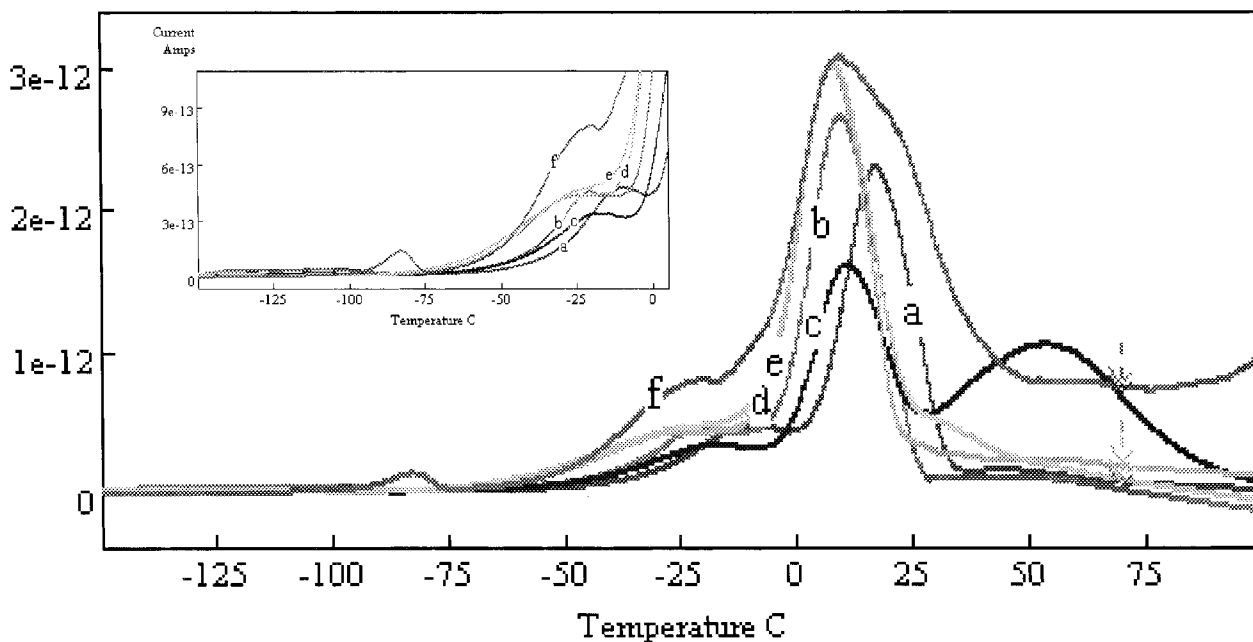
from Ihara Chemical Ind. Co. Ltd., Tokyo, Japan. The *n*-butylamine and *m*-Cresol purple was purchased from Janssen (Beerse, Belgium) and Merck Co. Ltd. (Darmstadt, Germany), respectively.

#### Preparations of TDI Prepolymers and PU Elastomers

The TDI prepolymer was prepared with the formulations listed in Table I. These ingredients

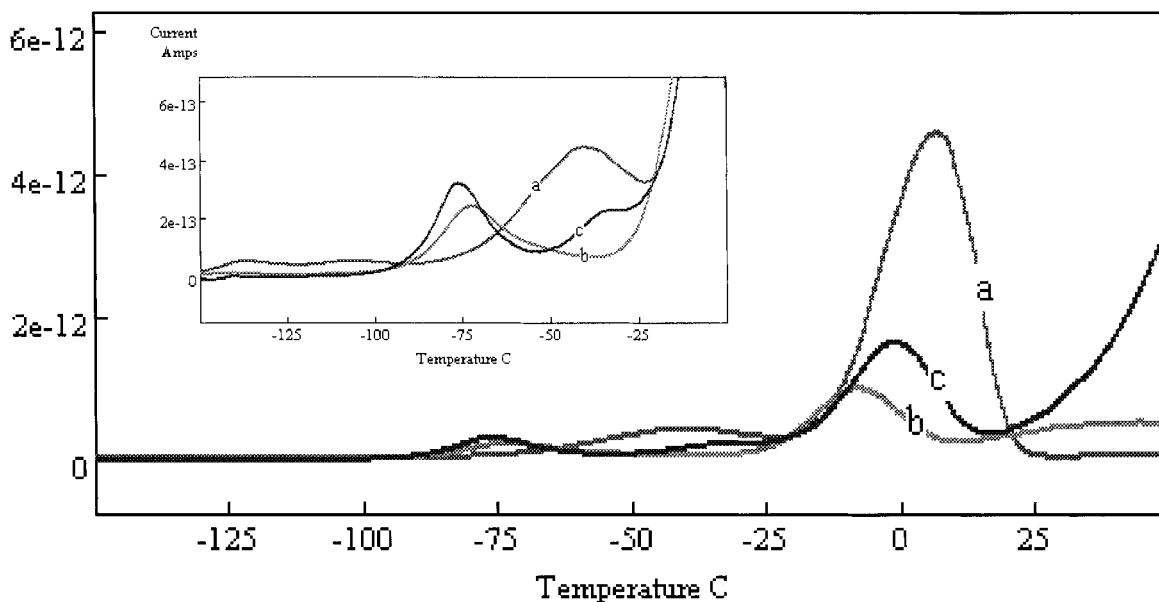
were placed in a flask and stirred under  $\text{N}_2$  atmosphere at  $50^{\circ}\text{C}$ . Aliquot at intervals was taken and the NCO content was determined by a back titration method (ASTM D1638-74). *m*-Cresol purple was used as the indicator, and was titrated until the desired NCO content was reached. The TDI prepolymer and the measured dissolved MOCA in DOP (Table II) were mixed at  $100^{\circ}\text{C}$ . The well-mixed mixture was transferred to a teflon plate and cured at  $105^{\circ}\text{C}$  for 1 h. Optimiza-

Current  
Amps

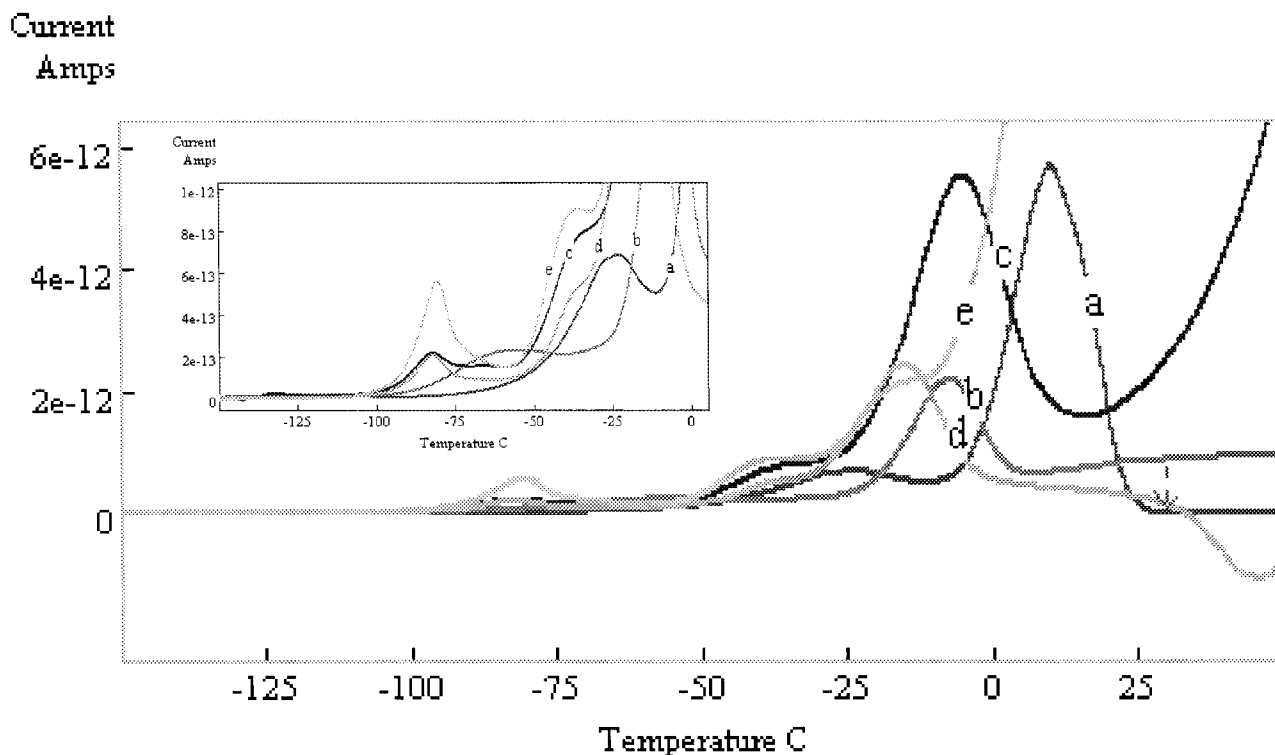


**Figure 3** TSC spectra of PU-PCL-1000 with variation in wt % DOP (a) 0%, (b) 4%, (c) 8%, (d) 15%, (e) 21%, and (f) 26%, respectively.

Current  
Amps



**Figure 4** TSC spectra of PU-PTMO-1000 with variation in wt % DOP (a) 0%, (b) 31%, and (c) 47%, respectively. DOP shows  $T_g$  at  $-80^\circ\text{C}$ .



**Figure 5** TSC spectra of PU-PPG-1000 with variation in wt % DOP (a) 0%, (b) 31%, (c) 47%, (d) 57%, and (e) 64%. DOP shows  $T_g$  at  $-80^\circ\text{C}$ .

tion of MOCA in DOP solution and a series of wt ratio of MOCA/DOP were prepared at  $100^\circ\text{C}$ . The results are shown in Table II.

#### Matrix-Assisted Laser Desorption/Ionization Time-of-Flight

The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometer (HP G2025A) used was equipped with a 337-nm nitrogen laser, with 3-ns pulse width duration, and an electron multiplier detector. The instrument was operated in positive ion reflection mode with an accelerating potential of +28 KV. The mass scale was calibrated with peptide standard. 2,5-Dihydroxybenzoic acid (DHB) was used as the matrix. The data was acquired in an average of 150 laser shots. Aqueous NaCl and KCl solution were added for mass peak identifications.

#### DSC

The  $T_g$  measurement was carried out by a Du Pont 900 (New Castle, USA) DSC instrument. The  $T_g$  was measured at a scanning speed of  $10^\circ\text{C}/\text{min}$ , in the temperature range of  $-120$ – $200^\circ\text{C}$ , and weighed approximately 5–10 mg.

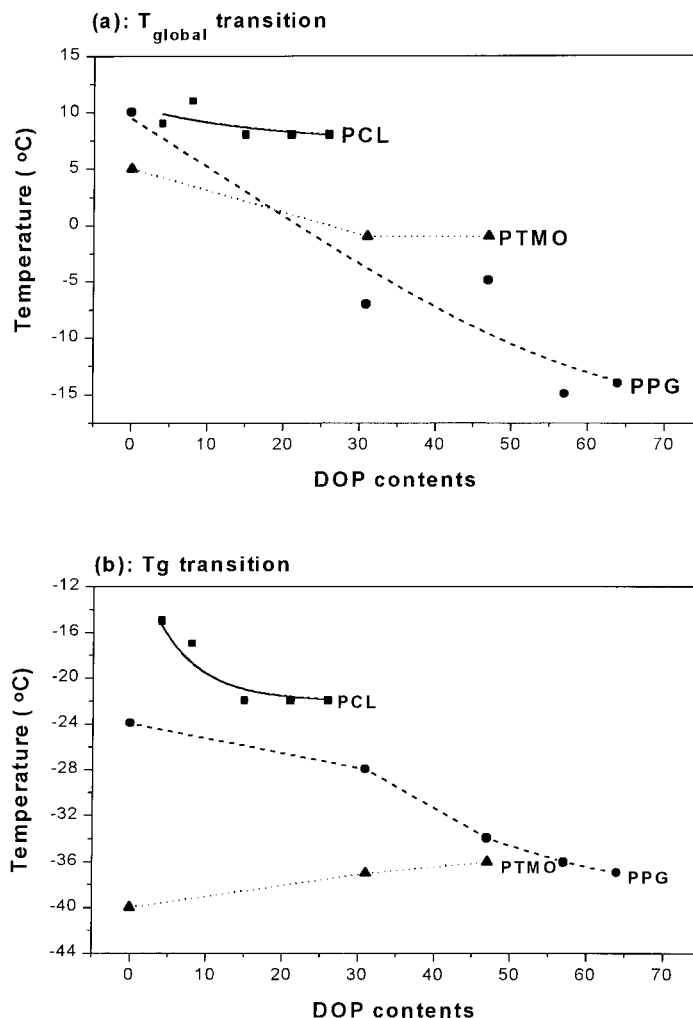
#### TSC/RMA

The TSC/RMA measurement was carried out with TherMold 9,000 (Stamfort, USA) instrument. The specimens were polarized at  $20$ – $30^\circ\text{C}$  above their respective  $T_g$ 's. A  $V_p$  of 100 V/mm was used. The depolarization measurement was carried out with a heating rate of  $7^\circ\text{C}/\text{min}$ . The sample thickness was 2 mm.

The voltage applied for RMA analysis during the polarization stage was 100 V/mm. The polarization temperature  $T_p$  was varied between raising and setting of peak for  $T_g$ . The window width was  $5^\circ\text{C}$ , and the time of polarization and depolarization was 2 min each. The ramp rate during recovery was  $7^\circ\text{C}/\text{min}$ . The depolarization curves were analyzed with the Debye integration option.<sup>28</sup>

#### DMA

A Polymer Laboratories MK II, frequency at 1 Hz and a constant heating rate at  $7^\circ\text{C}/\text{min}$ , was used for the dynamic analysis. The specimen dimensions were  $40\text{ mm} \times 8\text{ mm} \times 2\text{ mm}$ .



**Figure 6** DOP effect on the depolarization transitions of polyurethane elastomers: (a)  $T_{\text{global}}$  transition and (b)  $T_g$  transition.

## RESULTS AND DISCUSSION

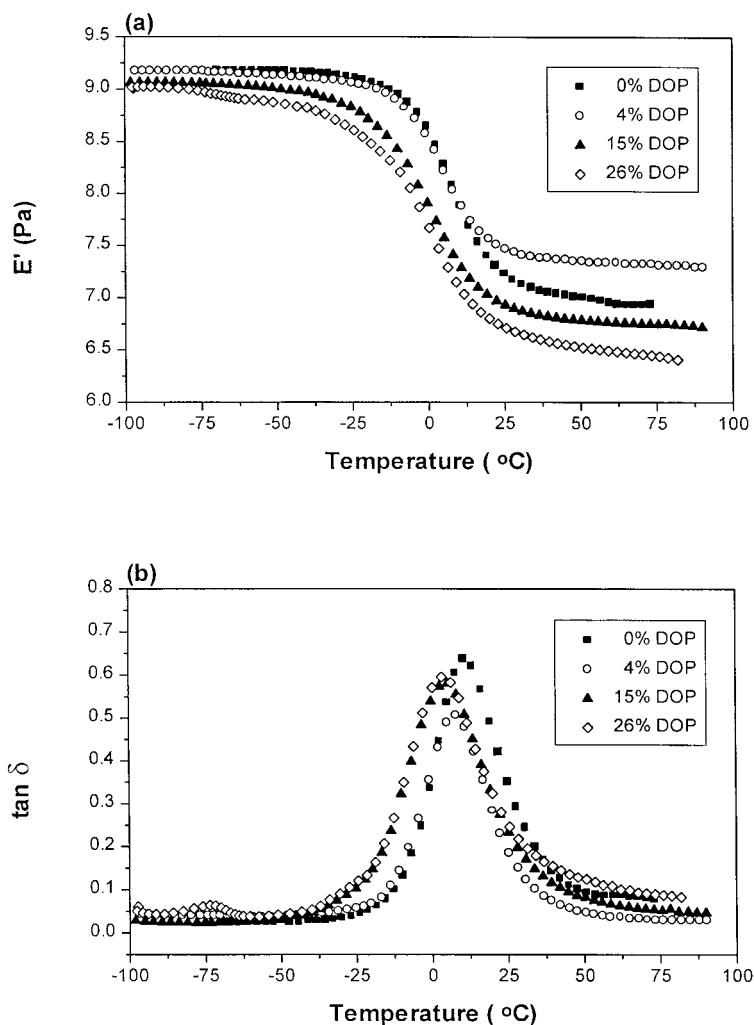
PU elastomers were prepared with three different soft segmented systems. They are PCL-1000, PTMO-1000, and PPG-1000. Table I lists the names and the compositions with the variations in DOP contents from 4 to 26 wt % for PCL-1000, 31 to 64 wt % for both PTMO-1000 and PPG-1000, respectively. The NCO content is maintained at 4%. PU specimens are all transparent. The preparation and curing conditions are shown in Scheme I with each system's representative structure being illustrated.

A MALDI-TOF mass spectrometer was used to examine the distributions of these soft segments. Figure 1 shows the individual distribution for PCL-1000, PTMO-1000, and PPG-1000 diols. The

distribution in the PCL-1000 diols is from 660 to 1572 with the main component of 1002 Da. The distribution of PTMO-1000 is 522 to 1674 with the main component of 1098 Da. PPG-1000 shows the distribution from mass of 656 to 1468 with the main component of 1004 Da. With this similarity in weight distribution and with the constant NCO content in 4%, the changes in  $T_g$  temperature may then be related to the effect of the DOP contents, because the effects associated with the compositional differences, among other pertinent factors, are kept at the minimum in these DOP-added specimens.

DOP is an ortho-diester of the phthalate with the structure of  $\text{C}_6\text{H}_4 [\text{C}(=\text{O})\text{OR}]_2$ , where  $\text{R} = -\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ . PCL has an ester linkage of  $-\text{O}(\text{CH}_2)_5-\text{C}(=\text{O})\text{O}-$ , an

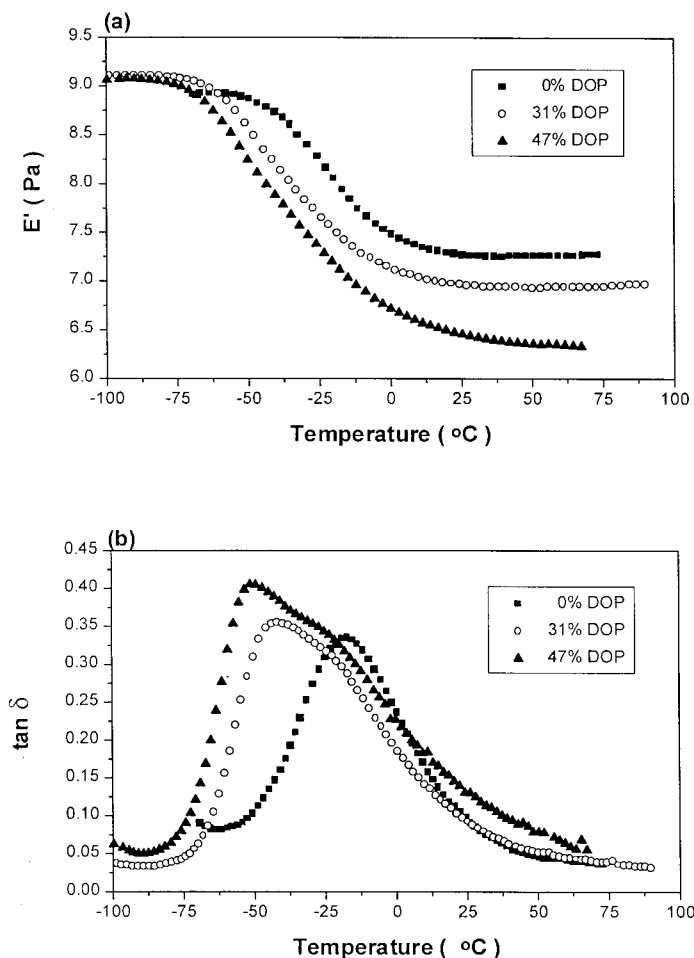




**Figure 7** DMA spectra of PU-PCL-1000 polyurethane elastomer (a) storage modulus ( $E'$ ) and (b)  $\tan \delta$ . Symbols of square, circle, triangle, and diamond represent 0, 4, 15, and 26% DOP additions, respectively.

opened chain unit of caprolactone in the main chain. Both PTMO and PPG possess ether linkages. PTMO has an aliphatic butylene ether linkage of  $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$  and PPG is with  $-\text{OCH}(\text{CH}_3)\text{CH}_2\text{O}-$ , a branched isopropyl ether linkage. These different structural units in the soft segment is expected to respond differently in the hydrogen bonding formation between these oxygenated soft segments and the NH in the urethanic linkage during the formation of the TDI-based PU matrix. It is expected that the DOP may show greater mixing effect with the PCL, if the general principle of the ester to ester in compatibility or the "like dissolves like" can be applied. In this case, the amount of the DOP added to the PU-PCL system will be in greater extent than the ether-linked PU-PTMO or PU-PPG systems.

The PU-PCL-1000, PU-PTMO-1000, and PU-PPG-1000 specimens were made with the addition of DOP. A DOP of up to 64 wt % with some leaching out of the specimens but still can be used for the testing. The 64 wt % DOP-added specimens of PU-PTMO-1000 and PU-PPG-1000 remain transparent. But only 26 wt % of DOP that can be added to the PU-PCL-1000 without the appearance of the whitening in the specimen. The results are somewhat unexpected but not unexplainable. The explanation may lie in the fact that the matrix of the PCL contains a rigid carbonyl group. It may due to the formation of the hydrogen bonding in which the carbonyl groups in PCL are bounded to the NH group of the urethanic segment and not available to the interaction with the DOP plasticizer. Apparently, the DOP fails to



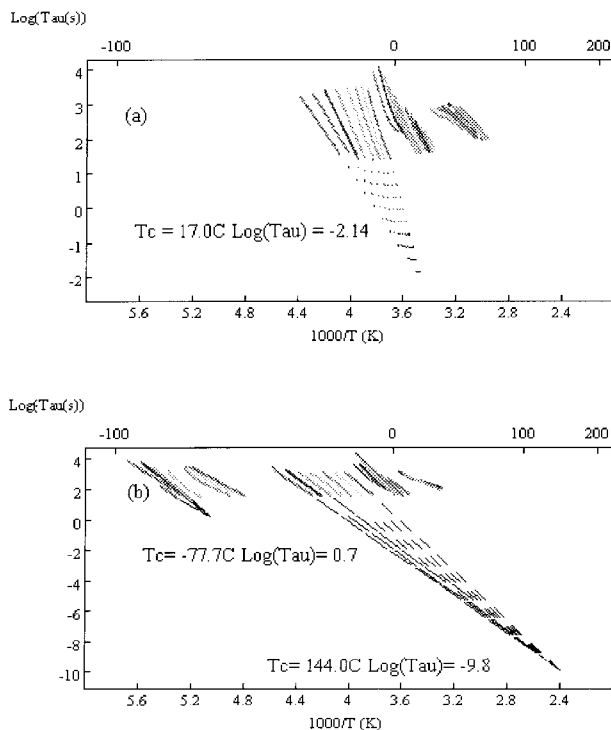
**Figure 8** DMA spectra of PU-PTMO-1000 polyurethane elastomers (a) storage modulus ( $E'$ ) and (b)  $\tan \delta$ . Symbols of square, circle and triangle represent 0, 31, and 47% DOP additions, respectively.

compete with PCL in the hydrogen bonding formation with the NH group in the urethanic linkage. An implication from the preparation of these DOP-added specimens is that the DOP must exist in the hard segment region as the aromatic moieties of TDI. Furthermore, MOCA may have better compatibility with the phthalate group in DOP.

#### The Plasticizing Effect of the DOP

First, the DSC thermograms contained PU-PCL-1000 and PU-PTMO-1000 specimens are shown in Figure 2. The curves of the DOP-added PU-PCL-1000 specimens as shown in Figure 2a indicate that  $T_g$  initially dropped then flattened out without the additional plasticizing effect with the increases in DOP con-

tent. For the specimen with 26 wt % DOP addition, a weak but new  $T_g$  may be seen around  $-85^{\circ}\text{C}$ , indicating the  $T_g$  for the DOP. However, DOP-added specimens of PU-PTMO-1000's  $T_g$  demonstrated a broadening curve with much better intensities in Figure 2b. Unlike the detection of the  $T_g$  for DOP in PCL-system, a broad DSC curve was observed in Figure 2b for PU-PTMO-1000 system. Apparently, the DSC curve leads to the DOP  $T_g$  at  $-85^{\circ}\text{C}$  is merged with the curve leads the  $T_g$  at  $-49^{\circ}\text{C}$  for the PU-PTMO-1000 specimen without any DOP added. The merge of two  $T_g$  curves of DOP at  $-85^{\circ}\text{C}$  and PU-PTMO at  $-49^{\circ}\text{C}$  occurred and resulted in a broad curve in DSC thermogram. This leads to no clear  $T_g$  measurement in DSC thermogram for PU-PTMO-1000 with the additions of DOP plasticizer in the specimens.



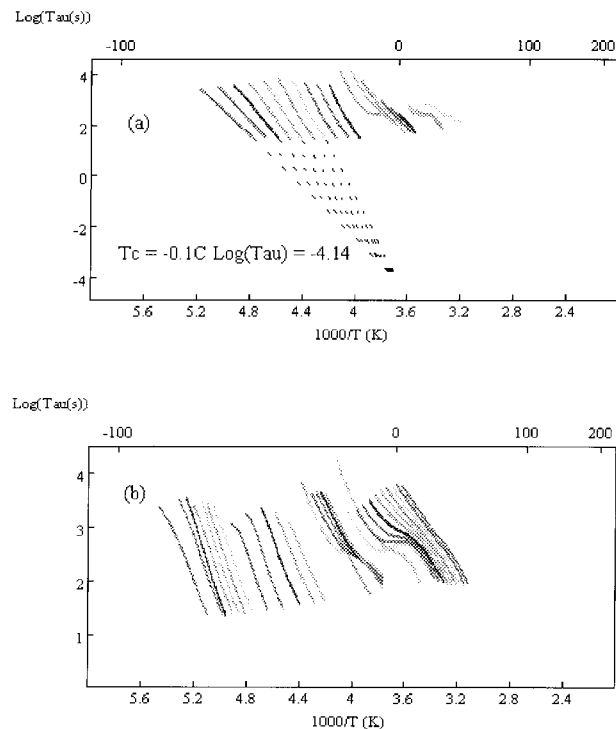
**Figure 9** Arrhenius lines of PU-PCL-1000 (a) without DOP addition and (b) with 26 wt % DOP addition.

The same specimens were then examined by the TSC technique. TSC spectra of PU-PCL-1000 with the variation in DOP additions are shown in Figure 3. Other TSC spectra of the DOP-added PU-PTMO-1000 and the similarly DOP-added PU-PPG-1000 are shown in Figures 4 and 5, respectively. Each of the TSC depolarization spectra indicate that these PU specimens possess two relaxations of the  $T_g$  and the  $T_{\text{global}}$  transitions.<sup>16</sup> The discussion of this  $T_{\text{global}}$  transition has been presented elsewhere.<sup>15</sup> Briefly, the  $T_{\text{global}}$  transition is similar to the maximum temperature observed on the tangent  $\delta$  curve in DMA. Both are describing thermal macromolecular nature of the specimens.

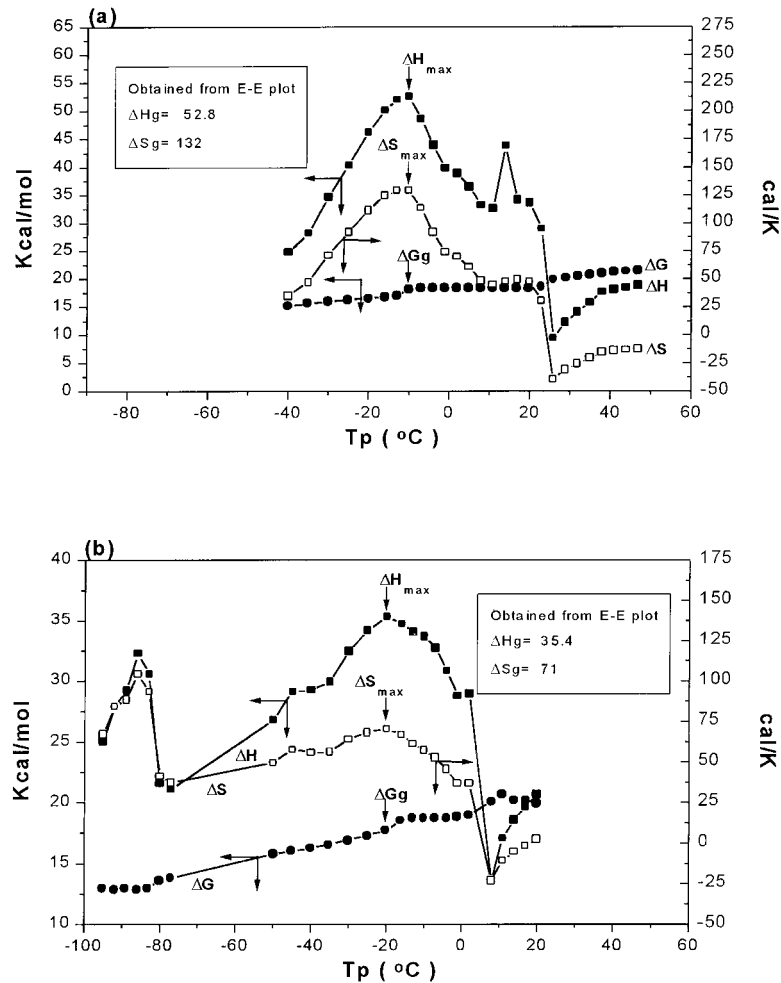
A general feature of these TSC curves is the lowering of the  $T_{\text{global}}$  transition temperature that demonstrated as merging peaks between the  $T_g$  and the  $T_{\text{global}}$  transitions of the PU specimens at the high content of the DOP addition. The  $T_g$  of the DOP can be clearly seen in the TSC spectrum in PU-PCL-1000 specimens with the addition of the DOP plasticizer, whereas the  $T_g$  of DOP and  $T_g$  of PU-PTMO-1000 were somewhat overlapped, partially due to the low  $T_g$  of the PTMO-contained PU. The DOP effect on these two relaxation transitions by the depolarization are sum-

marized in Figure 6, showing the DOP effect on (a) the  $T_{\text{global}}$  transitions and on (b) the  $T_g$  transition. The existence of the  $T_g$  of the DOP in the PU matrix will be discussed later.

In the PCL and PPG systems, the DOP shows some effect on the  $T_g$  transition of the PU matrix after the initial drop of the  $T_g$  temperature and then levelled off. Approximately  $7^\circ\text{C}$  lowering for PU-PCL system of 0–26 wt % of DOP and a lowering of approximately  $8^\circ\text{C}$  for 0–64 wt % of DOP for the PU-PPG system were observed, whereas a slight increase in  $T_g$  at  $-40$  to  $-35^\circ\text{C}$  for the DOP-added content of 0–47 wt % was observed for the PU-PTMO system. Apparently, DOP with aromatic phthalate groups may restrict the motion of the tetramethylene aliphatic chain when the 2-ethylhexyl group in the added DOP comes in contact with the tetramethylene of the soft segment in PU-PTMO-1000 matrix. The high-DOP-content specimens of up to 64 wt % in this system can be made. The specimen maintained the shape even with some of the DOP leaching off the specimen. The DOP must enter the region and mingle with the soft-to-hard segments at this high DOP content in 64 wt %. The disruption in this  $T_g$  region of the PU matrix will be examined



**Figure 10** Arrhenius lines of PU-PTMO-1000 (a) without DOP addition and (b) with 57 wt % DOP addition.



**Figure 11** The correlation of  $\Delta H$ ,  $\Delta G$ , and  $\Delta S$  values vs  $T_p$  of polarization temperature ( $^{\circ}\text{C}$ ) for PU-PCL-1000 with variation in wt % DOP additions (a) 0% and (b) 26%.

by the thermal windowing technique in the RMA, which will be described later.

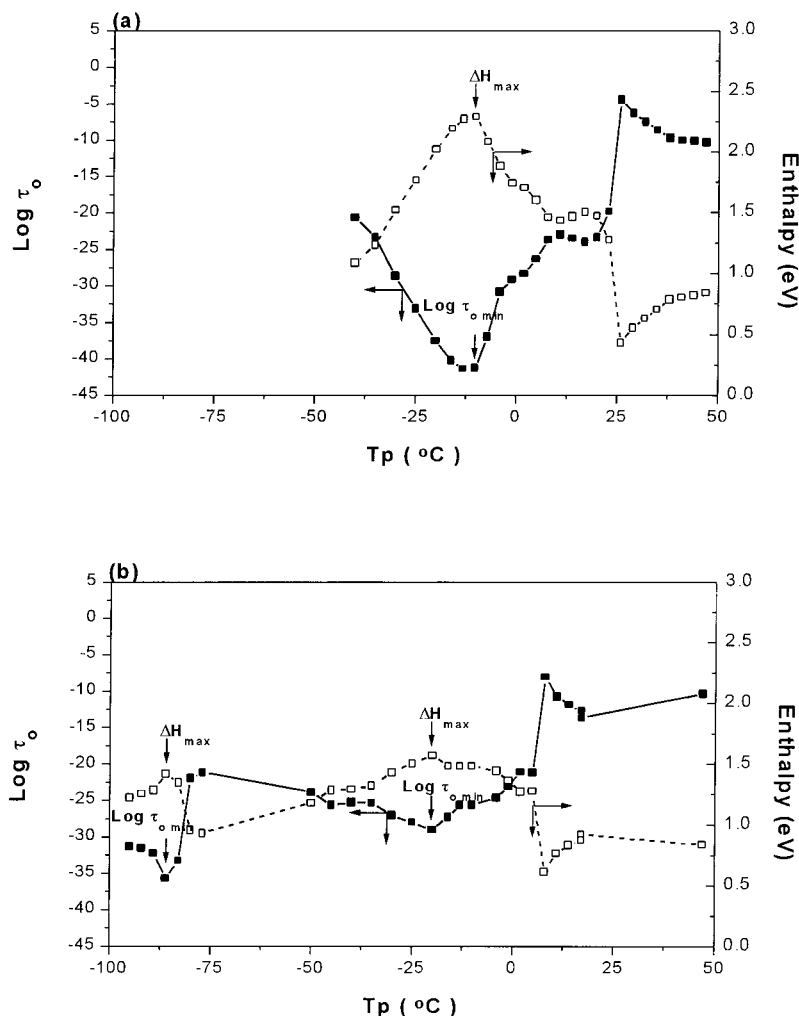
DMA data on the DOP-added PU-PCL-1000 specimens are shown in Figure 7. The corresponding DMA data of the DOP-added PU-PTMO-1000 are shown in Figure 8. From Figures 7 and 8, the DOP softens the specimens with the lowering of the  $E'$  (Pa), and the ease of the slopes of the DMA curves can be seen in Figures 7a and 8a for both systems. A slight lowering of the maximum peak in the tangent  $\delta$  curves was observed for the PU-PCL-1000, whereas an apparent merging of the tangent  $\delta$  curves was observed for the PU-PTMO-1000. A small peak at  $-75^{\circ}\text{C}$  was also observed corresponding to the  $T_g$  of the DOP. In PTMO system, the observed merging peak was mainly due to the increasing intensity of the DOP  $T_g$  peak that occurred in the vicinity of the  $-75^{\circ}\text{C}$  region. There is no real merging of the  $T_g$  peak

but overlapping curves did occur. It would be clarified with the data from the RMA measurements. A comparative discussion on these thermal data will be presented after the RMA measurements on these two specimens.

A thermal windowing technique was carried out in the RMA. One of the advantages of the RMA measurement is the dynamic evaluation of the relaxation transition on the observation of the narrowed region on the peak observed in the global spectrum. Thus each resolved Debye peak can be treated with Arrhenius eq. (1):

$$\tau_i(T) = \tau_{oi} \exp(\Delta H/kT) \quad (1)$$

where  $\tau_{oi}$  is the pre-exponential factor,  $\Delta H$  and  $k$  are the activation enthalpy and Boltzmann's constant, respectively.



**Figure 12** The correlation of  $\text{Log } \tau_0$  and Enthalpy ( $\Delta H$ : eV) vs  $T_p$  of polarization temperature for PU-PCL-1000 with variation in wt % DOP additions (a) 0% and (b) 26%.

Eyring<sup>29</sup> has indicated that the pre-exponential factor in the Arrhenius equation is directly related to the entropy of activation.

The relaxation time can be expressed as:

$$\text{Log } \tau_i = \text{Log}(\tau_{oi}) + \Delta G/kT \quad (2)$$

With Eyring eq. (4)<sup>29</sup>:

$$\text{Log}(\tau_{oi}) = -\text{Log}(kT/h) \quad (3)$$

where  $k$  and  $h$  are the Boltzmann and Planck's constants, respectively.

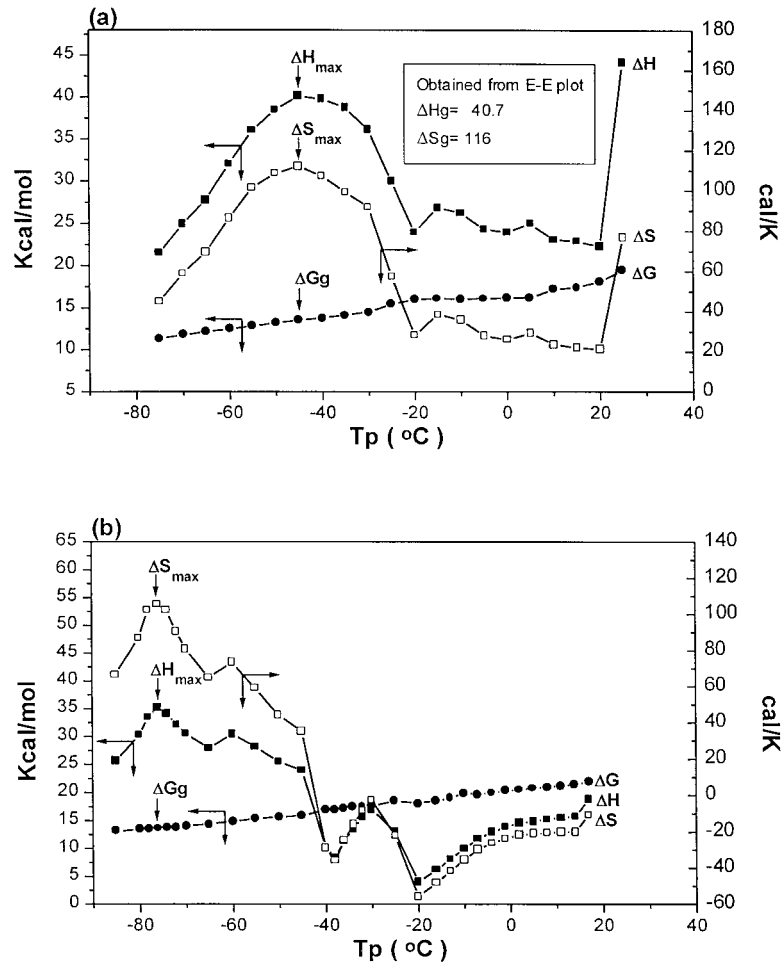
$$\Delta G = \Delta H_p - T\Delta S_p \quad (4)$$

where  $p$  indicates that these variables are a function of the polarization temperature.

Eq. (5) is the combined equation:

$$\tau_i = (h/kT) \exp(-\Delta S_p/k) \exp(\Delta H_p/kT) \quad (5)$$

$\Delta H$  and  $\Delta S$  values can be obtained from the plot of  $[\text{Log } \tau_i + \text{Log } T + \text{Log}(k/h)]$  versus polarization temperature ( $T_p$ ). If the Arrhenius or Eyring lines converge to a single point, then the point of convergence is called the compensation point,  $T_c$ .  $T_c$  is always higher than  $T_g$ . The values of the compensation point's coordinates ( $T_c$ ,  $\text{Log } \tau_c$ ) is important because it may transcribe the cooperative characteristics of relaxation as Arrhenius lines converge to a single point. Conse-



**Figure 13** The correlation of  $\Delta H$ ,  $\Delta G$ , and  $\Delta S$  values vs  $T_p$  of polarization temperature ( $^{\circ}\text{C}$ ) for PU-PTMO-1000 with variation in wt % DOP additions (a) 0% and (b) 57%.

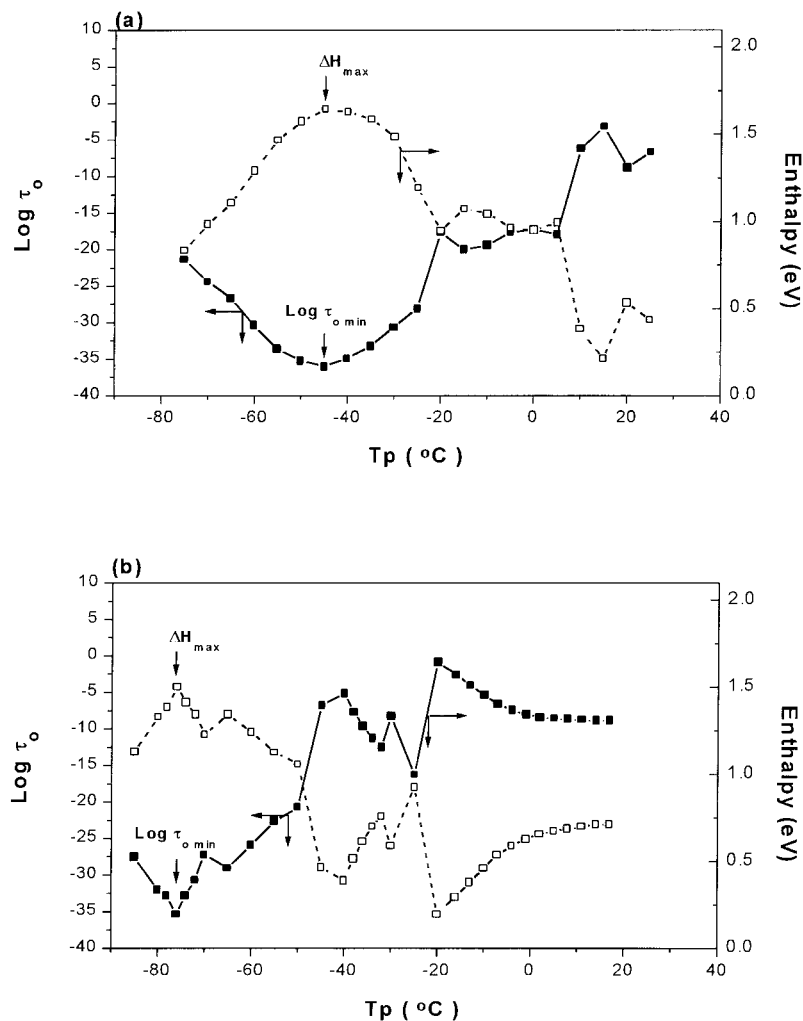
quently, a  $T_g$  transition must accompany a  $T_c$  in RMA measurement.

PU-PCL-1000 and PU-PTMO-1000 specimens were subjected to RMA measurements. The Arrhenius lines with the compensation search on the PU-PCL-1000 are shown in Figure 9, showing (a) with no DOP added and (b) with 26 wt % DOP. The corresponding RMA spectra for PU-PTMO-1000 are shown in Figure 10, showing (a) the specimen without DOP and (b) with 57 wt % DOP. Figure 9 shows that both specimens with or without DOP addition lead to the  $T_c$ . In addition, a new  $T_c$  at ( $\log \tau = 0.7$ ,  $T_c$  at  $-77.7^{\circ}\text{C}$ ) was observed for the DOP in Figure 9b. This confirms the  $T_g$  of DOP at  $-85^{\circ}\text{C}$ , because the  $T_c$  is always higher than the  $T_g$ . On the other hand, the Arrhenius lines no longer lead to the  $T_c$  in PU-PTMO-1000 after the addition of the DOP to the PU-PTMO-1000 formulation. Thus, the effect of DOP at this region is therefore indicated.

#### Verification on the $T_g$ Transition under the Influence of Plasticizing Effect of the DOP

Thermal windowing technique provides a method to obtain the thermokinetic data of enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) in terms of polarization temperature ( $T_p$ ). Figure 11 shows the maximum values of  $\Delta H$  and  $\Delta S$  that occurred at the  $T_g$  transition for PU-PCL-1000 with the different DOP contents at (a) 0% DOP and (b) 26% DOP. Similar maximum  $\Delta H$  but with the minimum  $\text{Log } \tau_0$  at  $T_g$  can also be observed in Figure 12. Figures 13 and 14 are thermokinetics plots for PU-PTMO-1000. A brief summarized data for these thermokinetic treatments lead to the verification of the  $T_g$  data is listed in Table III.

Figures 15 and 16 show the thermal analyzed data from DSC, TSC, and DMA on PU-PCL-1000 and PU-PTMO-1000 PU elastomers.



**Figure 14** The correlation of  $\text{Log } \tau_0$  and Enthalpy ( $\Delta H$ : eV) vs  $T_p$  of polarization temperature for PU-PTMO-1000 with variation in wt % DOP additions (a) 0% and (b) 57%.

With these data, the DOP plasticizing effect on the TDI-based PU elastomers may be summarized as follows:

1. The minimum deteriorated effect of the DOP on the PU matrix was observed as illustrated in the PU-PCL-1000 elastomer at the low DOP content.

The addition of the DOP in the PU elastomers was found to slightly deteriorate the PU matrix. If a wt % in the range from 0 to 26% in the formulation was added to the highly structured PCL-TDI-MOCA system, the fundamental soft-to-hard segment structure was not affected. The matrix may be somewhat enlarged but not disinte-

grated. The evidences support the following conclusion:

The addition of the DOP to the PU-PCL-1000 was limited to 26 wt % in the formulation. The  $T_g$  measurement for DSC or TSC showed a 5–8 $^{\circ}\text{C}$  lowering of the  $T_g$  (Fig. 6). The compensation points of the specimens with and without DOP shifted slightly. The amorphous phase indicated by the  $T_g$  transition is being retained with the evidence of the Arrhenius-Eyring lines remaining intact (Fig. 9). The straight Arrhenius-Eyring lines from the thermal windowing data indicated that no DOP has entered the  $T_g$  region in the PU-PCL system. The enthalpy, entropy, and  $\text{Log } \tau_0$

**Table III Tg Confirmations by Thermal Techniques**

Specimens	TSC <sup>a</sup> $\beta$ (°C)	RMA <sup>b</sup>									DSC <sup>c</sup>		
		Method 1	Method 2			Methods 3			Method 4			Tg (°C)	Tg (°C)
			$\Delta H_g$ (Kcal/mol)	$\Delta S_g$ (cal/K)	Tg (°C)	$\Delta H_{max}$ (Kcal/mol)	$\Delta S_{max}$ (cal/K)	Tg (°C)	$\Delta H_{max}$ (eV)	Log $\tau_{0\ min}$ (s)	Tg (°C)		
PU-PCL-0	-10	-11.6	52.8	132	-10.2	52.4	129	-10	2.29	-41.35	-10	-9	
PU-PCL-4	-15	—	—	—	—	—	—	—	—	—	—	-27	
PU-PCL-8	-17	—	—	—	—	—	—	—	—	—	—	-31	
PU-PCL-15	-22	—	—	—	—	—	—	—	—	—	—	-33	
PU-PCL-21	-22	—	—	—	—	—	—	—	—	—	—	-34	
PU-PCL-26	-22	-21.9	35.4	71	-22.3	35.3	71	-20	1.57	-29.05	-20	-36	
PU-PTMO-0	-40	-41.8	40.7	116	-39.5	40.1	112	-45	1.64	-36.08	-45	-46	
PU-PTMO-31	-38	—	—	—	—	—	—	—	—	—	—	—	
PU-PTMO-47	-36	—	—	—	—	—	—	—	—	—	—	—	
PU-PTMO-57	-35	—	—	—	—	—	—	—	—	—	—	—	
PU-PTMO-64	-34	—	—	—	—	—	—	—	—	—	—	—	
PU-PPG-0	-24	-26	47.2	121	-23.3	46.8	115	-25	2.03	-38.55	-25	-26	
PU-PPG-31	-28	—	—	—	—	—	—	—	—	—	—	—	
PU-PPG-47	-34	—	—	—	—	—	—	—	—	—	—	—	
PU-PPG-57	-36	—	—	—	—	—	—	—	—	—	—	—	
PU-PPG-64	-37	—	—	—	—	—	—	—	—	—	—	—	

<sup>a</sup> Measured with  $V_p = 100$  V/mm, with depolarization 7°C/min from -150 to 100°C.

<sup>b</sup> RMA measured by thermal windowing technique with  $V_p = 100$  V/mm, with width of 5°C. Method 1: Based on RMA data,  $T_g = (\Delta H_g + a)/(\Delta S_g + b)$ , where  $a = 0$ ,  $b = 0.07$  Kcal/K/m, reference 28. Method 2: Based on maximum data of  $\Delta H_g$  and  $\Delta S_g$  on Entropy-Enthalpy plot (E-E plot). Method 3: Based on Eyring transform. Method 4: Based on Arrhenius transform.

<sup>c</sup> Measured at 10°C/min.

plots were shifted but retained the shapes, clearly showing the maximum or minimum values (Figs. 11 and 12). The DMA measurement on the DOP-added specimens showed little deterioration of  $E'$  or the change in tangent  $\delta$  (Figs. 7 and 8). Figures 15 and 16 show that the TSC curves are clearer than the DSC on Tg data and  $T_{global}$  is compatible to the tangent  $\delta_{max}$ .

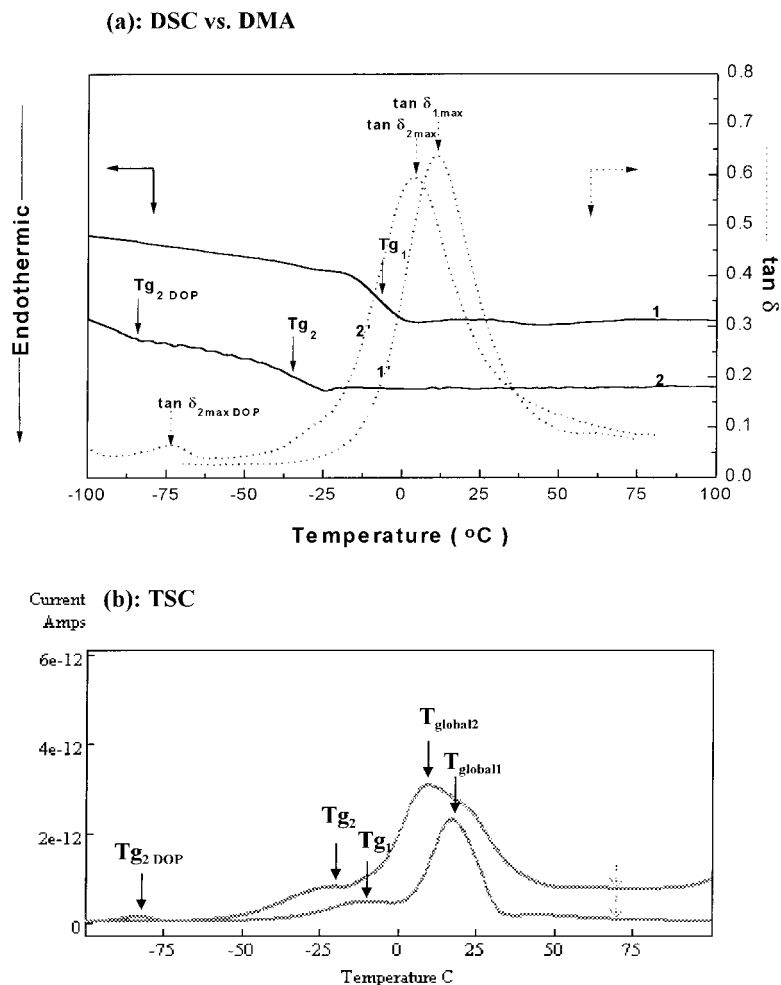
2. The visible deteriorated effect of the DOP at the high DOP content on the PU matrix was observed as illustrated in the PU-PTMO-1000 elastomer.

In the DOP-plasticized PU-PTMO-1000 elastomer, DOP was found to enter the interfacial layer of the urethanic matrix and was mingled with the soft and hard segments. Some disintegration of the matrix was indicated by the merging of the Tg transition with the Tg of the DOP in DSC (Fig. 2b), or in the TSC curves (Fig. 4). DMA showed a large shift of the tangent  $\delta$  to the lower temperature with the loss of the  $E'$  in Figure 8. The RMA measurement showed the loss of the Arrhenius lines and failed to converge to the once well-formed

compensation point on addition of DOP (Fig. 10). In addition, the Arrhenius-Eyring lines were randomized. Enthalpy, entropy, and Log  $\tau_0$  plots no longer displayed a maximum or minimum. The Tg transition was greatly disrupted by the presence of the DOP plasticizer. Apparently, at 47 wt % of the DOP in the formulation, the octyl aliphatic chain (2-ethylhexyl segment) may mix with the tetramethylene segment in PTMO chain. The phthalate aromatic moiety of the DOP was also mixed with the hard segment of TDI-MOCA segment. The maximum temperature of tangent  $\delta$  shifted to the lower temperature and did not measure the same properties as the TSC's  $T_{global}$ . Apparently, the macroproperties changed with the large amount of DOP added in the amorphous phase. Therefore, disruption of the well-mixed soft-to-hard segments of the urethanic matrix by DOP was observed.

3. The different behaviors of the PU elastomers with the structural variation in the soft segment may lie in the presence of the hydrogen bonding between the NH— of the





**Figure 15** Comparative thermal data from DSC, DMA, and TSC on PU-PCL specimens (a) DSC vs. DMA and (b) TSC. 1 and 2 represent 0 wt % and 26 wt % DOP additions.

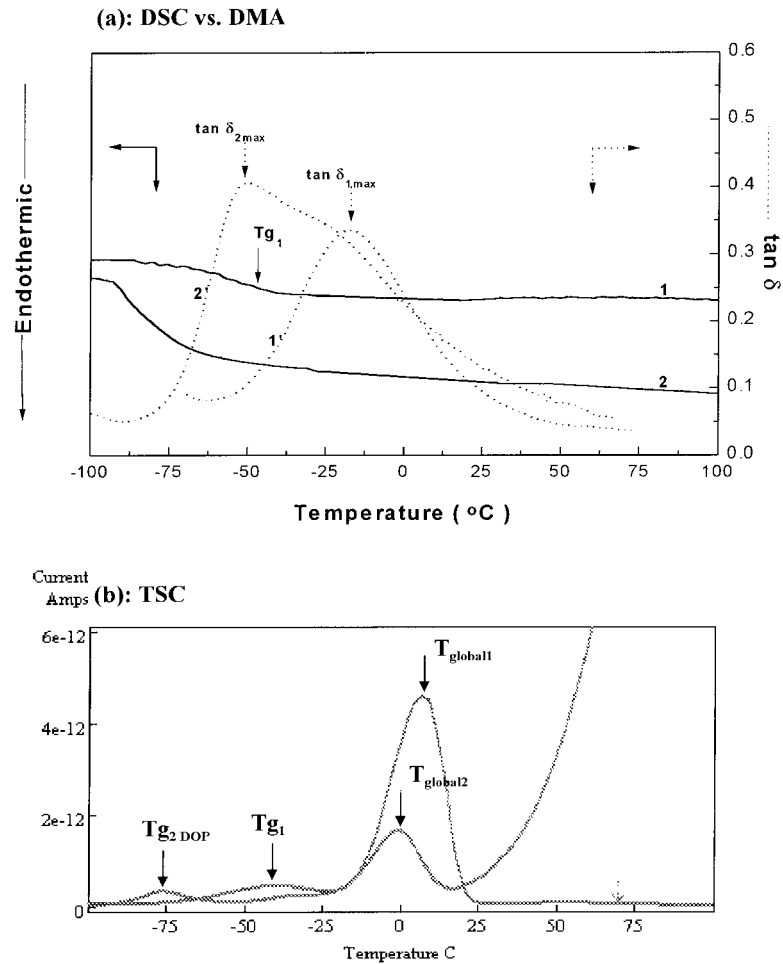
hard segment in TDI and MOCA to the C=O group in the PCL soft segment in PU-PCL-1000. There is a lack of the C=O group in the polyether-linkaged PTMO as the soft segment in PU-PTMO-1000. The addition of the DOP may mingle freely with soft and hard segments because there is no strong hydrogen bonding between the hard and soft segments. Thus, disintegration of the well-mixed soft-to-hard segments in PTMO-TDI/MOCA linkages was observed.

- The optimum M1D2 (MOCA/DOP = 1/2 ratio) batch depicts a clear and stable liquefied MOCA at ambient temperature as shown in Table II. Taking PU-PCL-26 formulation as the example, PU-PCL-26 contains more DOP (26 g) whereas the M1D2

only contains 16.6 g of DOP. This indicates that MOCA/DOP may be used as the ambient curative for low-temperature PU applications.

- There is an argument on the observation of the Tg transition of the DOP plasticizer. DOP is a nonpolymeric small molecule and has the known Tm at  $-55^{\circ}\text{C}$ .<sup>30</sup> Our polyurethane specimens with three different soft segments of PCL, PTMO and PPG failed to observe the melting point of the DOP in DSC.

Contrary, thermal analyzers of DSC (Fig. 2), TSC (Figs. 3 to 5) and RMA (Fig. 9) showed clearly the existence of the Tg transition at  $-75^{\circ}\text{C}$  for the added DOP in the PU system. One explanation may lie on the well-mixed amorphous



**Figure 16** Comparative thermal data from DSC, DMA, and TSC on PU-PTMO specimens (a) DSC vs. DMA and (b) TSC. 1 and 2 represent 0 wt % and 47 wt % DOP additions.

phase of the DOP with the TDI-based PU system. DOP as discussed above is mingled in the PU matrix with its phthalate aromatic group to the TDI-MOCA segment and the 2-ethylhexyl chain to the PCL, PTMO, and PPG soft segment. Another explanation<sup>1</sup> may be due to the lack of the crystalline structure with the rapid cooling effect on the DOP in the DSC or TSC testing procedures. A syndo-Tg transition<sup>1</sup> may be resulted in this supercooling condition.

## CONCLUSION

A feasibility on the liquefied MOCA in DOP as a substitute for the hot-melt curative in the conven-

tional two-component system was studied. MOCA can remain in clear solution at ambient temperature in 1 : 2 weight ratio. This amount of DOP in respect to the use of MOCA can be safely used for all formulations tested. With DOP content in less than 26 wt % in the formulation, the plasticizing effect was minimal and no disruption in the urethane linkage was observed. At the higher DOP content with 47 wt %, the disintegrated matrix was observed in the TSC and the RMA data.

The authors are pleased to acknowledge the financial support from the National Science Council, Taipei, Taiwan, R.O.C. through Grant No. NSC 86-2216-E-011-002. Acknowledgments are also due to Professor K. N. Chen of Tam Kang University for discussion on the DMA data and J. C. Huang and J. Z. Lai for their assistance in the DMA measurements.

<sup>1</sup> Suggested by the reviewer.

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