

# Glass Transition Temperature ( $T_g$ ) versus Fractional Conversion for a Linear Thermosetting Polyamic Acid Ester–Polyimide System

R. A. VENDITTI,<sup>1</sup> J. K. GILLHAM,<sup>1\*</sup> E. CHIN,<sup>2</sup> and F. M. HOULIHAN<sup>2</sup>

<sup>1</sup>Polymer Materials Program, Department of Chemical Engineering, Princeton University, Princeton, NJ 08544, and  
<sup>2</sup>AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974

## SYNOPSIS

The relationship of the glass transition temperature,  $T_g$ , to fractional conversion,  $x$ , for the conversion of the cyclohexylmethyl ester of the benzophenone tetracarboxylic dianhydride–oxydianiline polyamic acid to polyimide has been investigated using dynamic mechanical analysis (torsion pendulum, TBA). The glass transition temperature and conversion measurements were obtained on a single solvent-free polyamic acid ester specimen during cooling after heating to successively higher cure temperatures. Conversion was determined from the intensity of a sub- $T_g$  mechanical relaxation peak that has been assigned to a relaxation of the cyclohexyl group. The resulting  $T_g$  versus  $x$  relationship is nonlinear. The  $T_g$  versus  $x$  relationship is adequately modeled using an expression derived by Couchman.

© 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The glass transition temperature,  $T_g$ , versus fractional conversion,  $x$ , is a key relationship in understanding the cure and properties of amorphous reactive thermosetting polymer systems. The curing behavior in many cases is characterized by a reaction stage that is kinetically controlled until  $T_g$  increases to the cure temperature (vitrification). A second stage follows after vitrification where the reaction rate significantly decreases due to the decreased mobility of unreacted groups (diffusion control). The effect of molecular mobility on the reaction rate has been discussed for linear polyimide systems.<sup>1–5</sup>

Data pertaining to  $T_g$  versus conversion for linear polyamic acid–polyimide systems are limited.<sup>3,4,6,7</sup> This is due to experimental complications that include (1) increases in  $T_g$  during its measurement, (2) the use of difficult-to-remove solvents (e.g., *N*-methyl pyrrolidinone), and (3) side reactions (isomerization and thermal degradation) occurring at high cure temperatures. Obtaining the value of

$T_g$  and conversion from a differential scanning calorimetric (DSC) experiment of a polyamic acid–polyimide-type polymer system is not practical because, in addition to the before-mentioned complications, the magnitude of change in specific heat at constant pressure at  $T_g$ ,  $\Delta c_p$ , of these materials is relatively small and may be dominated by other endothermic or exothermic events, e.g., solvent loss, by-product loss, or further reaction, occurring concurrently.

A method reported to measure the change in  $T_g$  with  $x$  for highly reactive polyamic acid–polyimide systems has been described in the literature;<sup>6</sup> it has been termed a stepwise pulse method. To determine the value of  $T_g$  of a specimen with a given conversion, a rapid heating (approximately 5 s) of a small segment of a film specimen in tension is performed by using a flow of preheated gas (at a known temperature) and measuring the deformation of the film. This is followed by another heating of an adjacent “fresh” part of the film with a higher temperature preheated gas and again the deformation is measured. This procedure is repeated at successively higher gas temperatures. A softening temperature, related to  $T_g$ , is then determined from the resulting thermomechanical curve of deformation versus

\* To whom correspondence should be addressed.

temperature. This procedure is performed for films cured to different fractional conversions. Determinations of  $x$  are performed by infrared (IR) spectroscopy on separate film specimens. This technique has the drawback that multiple specimens must be used and that parallel specimens (with the same thermal history) must be used to determine  $T_g$  and  $x$ . This technique also measures the softening point during heating where reaction and nonequilibrium effects may affect the measurement.

It is noted that polyimides physically age, which is the spontaneous nonchemical densification of a glassy material in the attempt to remove excess volume.<sup>8,9</sup> Physical aging can affect the measured value of  $T_g$  of a glassy material. For this reason, the value of  $T_g$  of a specimen should be determined on cooling directly after curing at a cure temperature ( $> T_g$ ) in order to avoid physical aging effects on the observed  $T_g$ .

In this report, a method for obtaining the change in  $T_g$  with  $x$  for a linear polyimide-type polymer is demonstrated. This technique utilizes a torsion pendulum and a composite specimen that allows multiple data points of  $x$  and  $T_g$  to be acquired on a single specimen. The use of a single specimen eliminates complications that would arise from the different dimensions of different specimens. Also,  $T_g$  is measured on cooling from a temperature above  $T_g$  rather than on heating to give a better assignment of  $T_g$  (i.e., relatively less reaction occurs and the effects of physical aging are minimized when measuring  $T_g$  during cooling from a temperature above  $T_g$  than during heating).

The particular system investigated in this report is the cyclohexylmethyl ester of the benzophenone

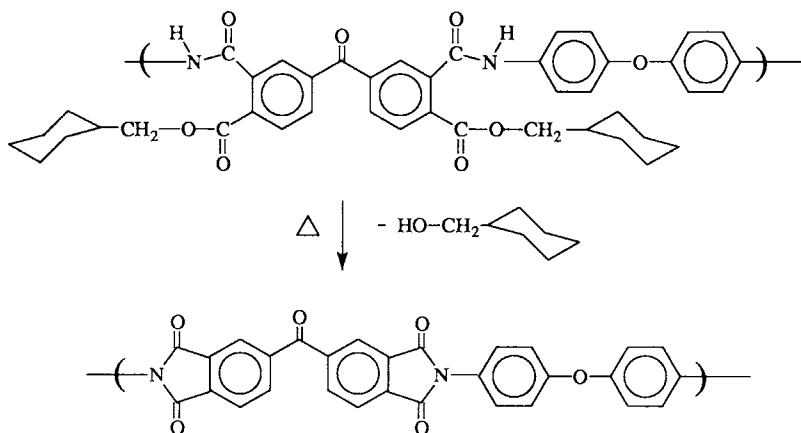
tetracarboxylic dianhydride–oxydianiline polyamic acid, which is thermally converted via intramolecular cyclization to the corresponding polyimide with the elimination of cyclohexylmethyl alcohol. This system has several advantages in the analysis of  $T_g$  versus  $x$  behavior: (1) the reaction rate is relatively lower than for typical polyamic acids, thus allowing measurements of  $T_g$  for partially cured samples, (2) the polyamic acid ester is readily isolated from relatively low-boiling solvents (e.g., tetrahydrofuran, b.p. = 67°C), (3) the value of  $T_g$  of the fully cured polyimide ( $T_{g\infty}$ ) is relatively low (i.e., 274°C), thus avoiding the need to use extreme curing temperatures where thermal degradation may occur, and (4) the intensity of the sub- $T_g$  cyclohexyl mechanical relaxation can be used as a measure of conversion on the same specimen whose  $T_g$  is being measured using a torsional pendulum. A previous study of the *n*-butyl ester form of this polymer has been reported and serves as a basis for the procedure reported here.<sup>7</sup>

## EXPERIMENTAL

### Material

The material investigated in this report is the cyclohexylmethyl ester of the benzophenone tetracarboxylic dianhydride–oxydianiline polyamic acid (abbreviated CHME-BTDA-ODA). The uncured and fully cured structures of CHME-BTDA-ODA are shown schematically in Figure 1 along with the thermally induced imidization reaction, which involves the loss of cyclohexylmethyl alcohol.

### Polyamic Acid Ester/Polyimide Reaction Scheme



**Figure 1** Reaction scheme: polyamic acid ester (CHME-BTDA-ODA) to polyimide.

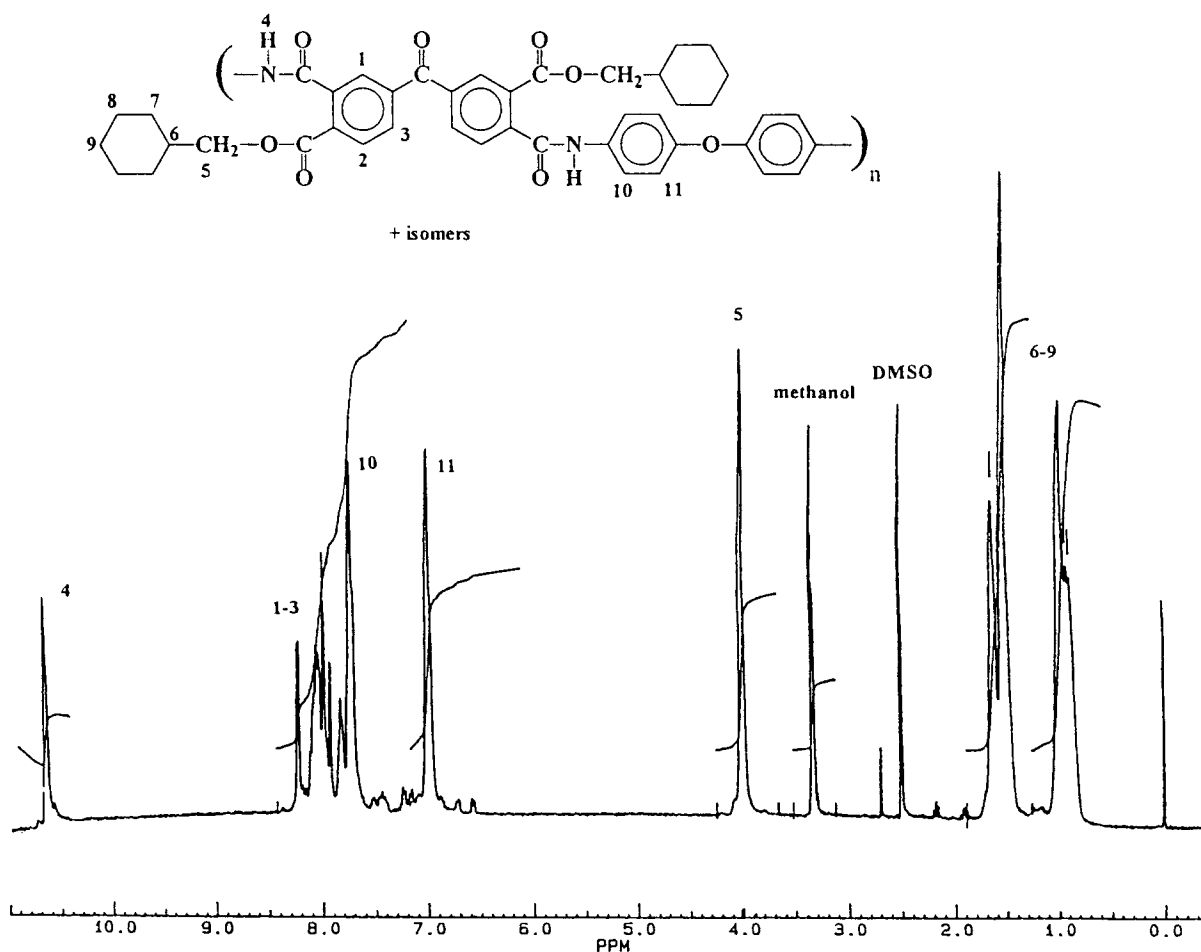
For the CHME-BTDA-ODA material investigated the number-average molecular weight,  $\bar{M}_n$ , was determined to be 22,000 and the value of the ratio of the weight-average molecular weight to the number-average molecular weight,  $\bar{M}_w/\bar{M}_n$ , to be 1.92 as determined by gel permeation chromatography. The synthesis and characterization of esters of BTDA-ODA have been published.<sup>10,11</sup> The characterization of the CHME-BTDA-ODA material showed it to be essentially pure. A  $^1\text{H-NMR}$  spectrum is shown in Figure 2, the caption for which provides chemical shift assignments. IR (cyclohexylmethanol/NaCl): 3280, 2920, 2850, 1720, 1660, 1600, 1530, 1490, 1220  $\text{cm}^{-1}$ . Anal: Calcd. for

$\text{C}_{43}\text{H}_{42}\text{O}_8\text{N}_2$ : C, 72.27; H, 5.92; N, 3.92. Found: C, 72.39; H, 5.92; N, 4.11.

### Procedure

The experimental technique used to determine the  $T_g$  versus  $x$  relationship for the imidization of CHME-BTDA-ODA was torsional braid analysis. In torsional braid analysis (TBA) a multi-filamented glass fiber braid impregnated with the material for analysis is used as the specimen. The TBA experiment provides the relative rigidity (proportional to the in-phase shear modulus,  $G'$ ), and the relative out-of-phase shear modulus (proportional to the out-of-phase shear modulus,  $G''$ ).

### $^1\text{H-NMR}$ Spectrum of the Polyamic Acid Ester



**Figure 2**  $^1\text{H-NMR}$  spectrum of cyclohexylmethyl ester of the benzophenone tetracarboxylic dianhydride-oxidianiline polyamic acid.  $^1\text{H-NMR}$  (360 MHz, DMSO D-6)  $\delta$ : 10.70 (*s* broad, 2H, H#4), 8.20–7.80 (*m*, 6H, H#1–3), 7.70 (*m* broad, 4H, H#10), 7.00 (*m* broad, 4H, H#11), 4.00 (*m* broad, 4H, H#5), 1.60–0.80 (*m*, 22H, H#6–9). Also: chemical shifts from residual solvent (methanol) and from  $^1\text{H}$  DMSO.

tional to the out-of-phase shear modulus,  $G''$ ) of the specimen versus temperature in a torsional mode at a frequency of approximately 1 Hz. All experiments were performed under a steady purge of dry helium. Reviews of the TBA technique have been published.<sup>12,13</sup> The automated TBA torsion pendulum system is available from Plastics Analysis Instruments, Inc., Princeton, NJ 08540.

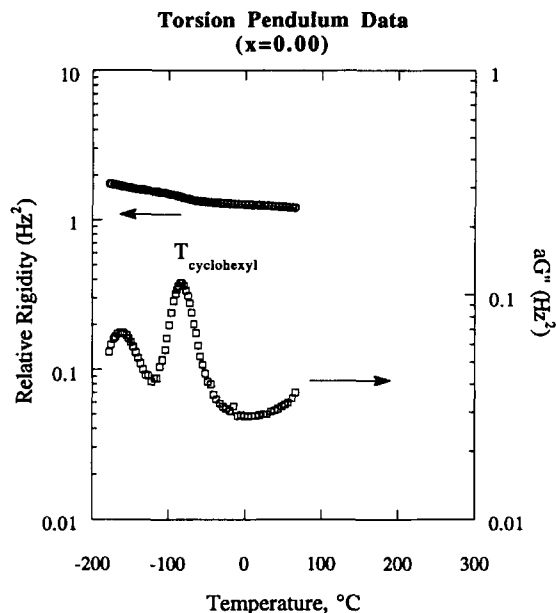
The procedure for making and curing a specimen was as follows. A heat-cleaned glass braid was impregnated with a solution of the polyamic ester in tetrahydrofuran (0.02 g/0.2 mL) for 1 h. Unlike some linear alkyl esters of BTDA-ODA and the acid form of BTDA-ODA, the cyclohexylmethyl ester of BTDA-ODA is readily soluble in tetrahydrofuran.<sup>10</sup> The impregnated specimen was then suspended vertically in methanol (approximately 300 mL) at room temperature for 20 h. The polymer precipitated on, and adhered to, the glass braid; during this processing the specimen changed visually from a transparent, light brown to an opaque, bright yellow color. (The dry polymer sample, amount used  $\approx 20$ mg, was a bright yellow powder.) The specimen (a cylinder approximately 5 cm in length and 1 mm in diameter) was then mounted in the TBA unit and held at 75°C for 5 h in flowing helium as the "drying" step. The specimen was then cooled and heated, at 1.5°C/m, between a minimum temperature ( $-185^\circ\text{C}$ ) and successively higher cure temperatures while data were collected. The final cure step was 300°C for 3 h. TBA data collected during cooling are reported here.

## RESULTS AND DISCUSSION

### Determination of $T_g$ and Fractional Conversion

TBA scans of the specimen for  $x = 0.00, 0.83,$  and  $0.99$  are shown in Figures 3, 4, and 5, respectively. The value of  $T_g$  was defined as the temperature location of the first maximum in the relative out-of-phase shear modulus,  $aG''$ , on cooling from the liquid/rubbery state;  $T_g$  is apparent only in Figures 4 and 5. In general, the second peak encountered on cooling an amorphous polymer is termed the  $\beta$ -relaxation ( $T_\beta$ ), which is apparent only in Figures 4 and 5. The third peak on cooling is associated with a relaxation of the cyclohexyl group ( $T_{\text{cyclohexyl}}$ ). A fourth peak is observed at approximately  $-170^\circ\text{C}$  and has been associated with a submolecular motion of a sequence of methylene groups.

The conversion was determined by monitoring the sub- $T_g$  mechanical relaxation peak that has been associated with the cyclohexyl group.<sup>14-17</sup> For each



**Figure 3** Thermomechanical (TBA) data of the unreacted specimen.

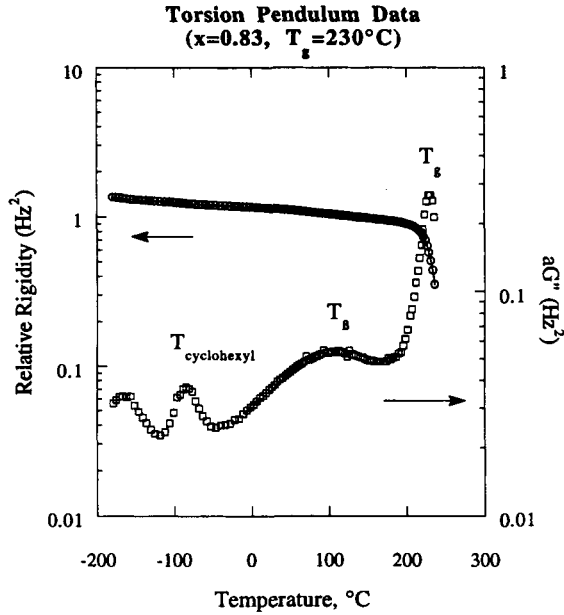
imidization reaction that occurs, cyclohexylmethyl alcohol is eliminated. Consequently, the intensity of the mechanical loss peak assigned to the cyclohexyl relaxation decreases with increasing conversion, as may be observed by comparing Figures 3, 4, and 5.

The following equation<sup>18,19</sup> utilizes the mechanical loss peak in  $G''$  versus the natural logarithm of frequency,  $\ln \omega$ , to calculate the relative concentration of a species undergoing a mechanical relaxation:

$$G'_U - G'_R = \frac{2}{\pi} \int_{\ln \omega = -\infty}^{\ln \omega = \infty} G''(\omega) d \ln \omega \quad (1)$$

where  $G'_U$  and  $G'_R$  are the unrelaxed and relaxed values of the in-phase shear modulus, respectively, and their difference is proportional to the concentration of mechanical elements that participate in the relaxation. In a TBA experiment, the relative out-of-phase shear modulus,  $aG''$ , where  $a$  is a constant depending on the geometry of the specimen which remains essentially unchanged throughout all the experiments, is obtained versus temperature at approximately 1 Hz (see Figs. 3-5). To transform Eq. (1) to temperature (or reciprocal temperature) coordinates, the Arrhenius relationship is invoked:<sup>17</sup>

$$\omega = \omega_0 \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$



**Figure 4** Thermomechanical (TBA) data for a partially cured specimen.

where  $\omega_0$  is a constant,  $E_a$  is the activation energy of the relaxation,  $R$  is the gas constant, and  $T$  is the temperature in Kelvin. Combining Eqs. (1) and (2),

$$G'_U - G'_R = c \int_{1/T=0}^{1/T=\infty} G''(T) d\left(\frac{1}{T}\right) \quad (3)$$

$$c = \frac{2E_a}{\pi R} \quad (4)$$

For Eq. (3) to be valid the relaxation must follow Arrhenius behavior as in Eq. (2). For Eq. (3) to be utilized in its simplest form, it is assumed that the activation energy of the relaxation is constant with respect to fractional conversion.

This last assumption is supported by the following observation. The temperature location of a mechanical loss peak at a constant frequency is related to  $E_a$  of the relaxation.<sup>17</sup> The temperature location of the maximum in the relative out-of-phase shear modulus,  $T_{\text{cyclohexyl}}$ , ranged from  $-83.4^\circ\text{C}$  at 1.19 Hz for  $x = 0.00$  to  $-83.7^\circ\text{C}$  at 1.09 Hz for  $x = 0.99$ . Thus, the approximate constancy of  $T_{\text{cyclohexyl}}$  versus  $x$  supports the assumption that  $E_a$  of the relaxation was also constant versus  $x$ . This suggests that the cyclohexyl relaxation is largely insensitive to the increasing stiffness of the polymer main-chain structure with increased conversion.

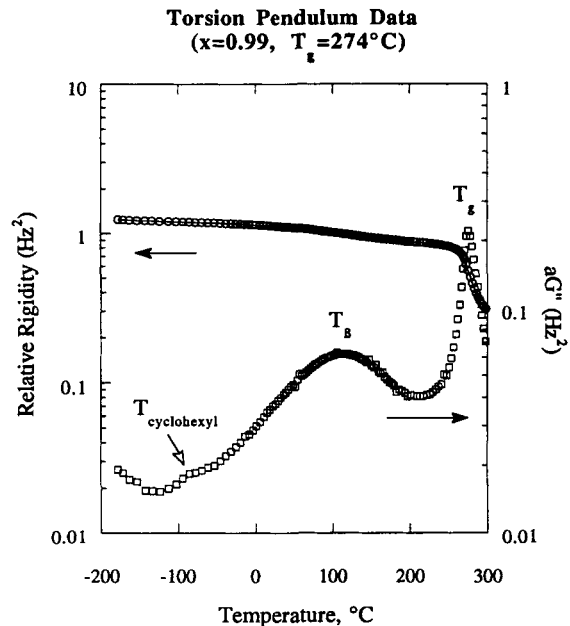
To determine the fractional conversion, an integration of the cyclohexyl mechanical loss peak,

$aG''$ , is performed with respect to the coordinate  $1/T$  (K) for each cooling ramp. The TBA data obtained during cooling for a partially cured specimen ( $x = 0.83$ ) versus  $1/T$  (K) are shown in Figure 6. To perform the integration, a baseline was constructed in Figure 6 consisting of a linear extrapolation of the low-temperature portion of the  $\beta$ -relaxation peak (or the glass transition peak if the  $\beta$ -relaxation peak is absent) and the high-temperature portion of the lowest temperature relaxation peak (peak at approximately  $-170^\circ\text{C}$ ). With this baseline subtracted, the cyclohexyl mechanical loss peak,  $aG''$  versus  $1/T$ , was then fit using a least-squares method to a Gaussian distribution. The best-fit Gaussian distribution was then substituted into Eq. (5):

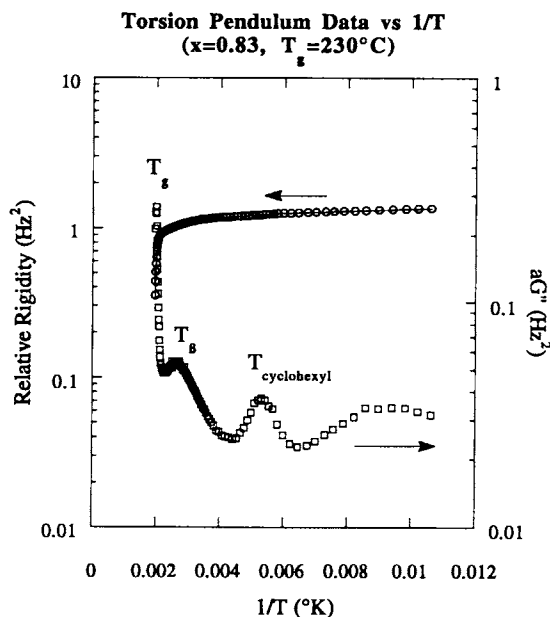
$$A = a(G'_U - G'_R) = c \int_{1/T=0}^{1/T=\infty} aG''(T) d\left(\frac{1}{T}\right) \quad (5)$$

Equation (5) is integrated to result in the area under the  $aG''$  versus  $1/T$  peak, denoted  $A$ . The area  $A$  is directly proportional to  $G'_U - G'_R$  and is thus directly proportional to the concentration of cyclohexyl ester units that experience a relaxation during cooling. The fractional conversion,  $x$ , is then defined as

$$x = 1 - \frac{A - A_\infty}{A_0 - A_\infty} \quad (6)$$



**Figure 5** Thermomechanical (TBA) data for a specimen with  $x = 0.99$ .



**Figure 6** Thermomechanical data (TBA) of a partially cured specimen plotted vs.  $1/T$  (K).

where 0 and  $\infty$  indicate the values of  $A$  in the uncured state and fully cured state, respectively. The value of  $A_0$  was obtained after “drying” at  $75^\circ\text{C}$  for 5 h without heating to above  $T_{g0}$  (to avoid reaction). The data utilized to determine  $A_0$  are shown in Figure 3.  $A_\infty$  was not measured from the data in Figure 5, but was taken to equal 0 in this report. Note that the constant factors  $a$  and  $c$  (proportionality factors) may be factored out of both the numerator and denominator of Eq. (6) and cancel. Thus, the absolute determination of the quantities  $a$  and  $c$  is not necessary to calculate  $x$ .

### $T_g$ versus Conversion Relationship

The  $T_g$  versus  $x$  data are shown in Figure 7. Note the nonlinearity of the relationship. The data have been fit to an equation developed by Couchman<sup>20,21</sup> to predict the  $T_g$  versus compositional variation behavior in polymer systems:

$$\ln(T_g) = \frac{(1-x)\ln(T_{g0}) + \frac{\Delta c_{p\infty}}{\Delta c_{p0}} x \ln(T_{g\infty})}{(1-x) + \frac{\Delta c_{p\infty}}{\Delta c_{p0}} x} \quad (7)$$

where  $\Delta c_p$  is the difference in heat capacity between the liquid or rubbery state and the glassy state at  $T_g$ , and 0 and  $\infty$  denote the properties of the material in the uncured and fully cured states, respectively. A least-squares method of fitting Eq. (7) to the  $T_g$

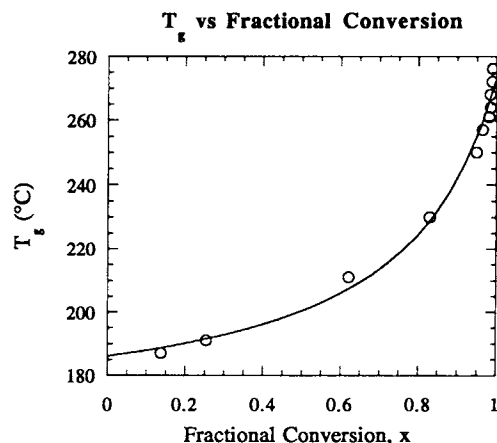
versus  $x$  data resulted in the parameters:  $T_{g0} = 186^\circ\text{C}$ ,  $T_{g\infty} = 274^\circ\text{C}$  and  $\Delta c_{p\infty}/\Delta c_{p0} = 0.22$ ; the resulting curve is shown in Figure 7. The curve adequately fits the data (the correlation coefficient is 0.99). It has been shown that Eq. (7) also fits  $T_g$  versus  $x$  data for other linear polyimide-type systems and also for crosslinking (network) thermosetting systems, such as epoxy-amine systems and cyanate ester to polycyanurate systems.<sup>22</sup> Further, where  $\Delta c_{p\infty}/\Delta c_{p0}$  values are available from DSC experiments, the best-fit values of  $\Delta c_{p\infty}/\Delta c_{p0}$  from fits of  $T_g$  versus  $x$  data agree with the independently determined DSC values.<sup>22</sup>

At conversions lower than  $x = 0.12$  values of  $T_g$  were not recorded. This is due to  $T_g$  rising above the maximum temperature (vitrification) during cure at low conversion.  $T_{g0}$  may be estimated by using Eq. (7) when an experimentally obtained value is not available.

At  $x > 0.95$  the value of  $T_g$  rises abruptly with respect to  $x$ .  $T_g$  is measured to better than  $1^\circ\text{C}$  and  $x$  may be measured to about 0.01. For this reason, it is not possible to conclude from these data whether the differences in the four highest measured values of  $T_g$  are caused by small changes in  $x$  (less than 0.01) or if they arise from effects such as side reactions or molecular ordering,<sup>6,23,24</sup> which may be independent of the detected conversion.

## CONCLUSIONS

The glass transition temperature,  $T_g$ , versus fractional conversion,  $x$ , data for a polyamic acid cyclohexylmethyl ester-polyimide system has been experimentally determined using a torsion pendu-



**Figure 7**  $T_g$  vs. conversion data (symbols). Also plotted is Eq. (7) with best-fit parameters (full curve).

lum (TBA).  $T_g$  and  $x$  measurements were obtained on a single solvent-free specimen during cooling after heating to successively higher cure temperatures. The fractional conversion was determined by monitoring a sub- $T_g$  mechanical relaxation peak that has been assigned to a relaxation of the cyclohexyl group. The resulting  $T_g$  versus  $x$  relationship is nonlinear. The  $T_g$  versus  $x$  relationship is adequately modeled using an expression derived by Couchman to predict the  $T_g$  versus compositional variation behavior in polymer systems.

## REFERENCES

1. J. A. Kreuz, A. L. Endrey, T. P. Gay, and C. E. Sroog, *J. Polym. Sci., A-1*, **4**, 2607 (1966).
2. L. A. Laius, M. I. Bessonov, E. V. Kallistova, N. A. Adrova, and F. S. Florinskii, *Vysokomol. Soedin.*, **A9**, 2185 (1967).
3. L. A. Laius, M. I. Bessonov, and F. S. Florinskii, *Vysokomol. Soedin.*, **A13**, 2006 (1971).
4. L. A. Laius and M. I. Tsapovetsky, in *Polyimides: Synthesis, Characterization and Applications*, Vol. 1, K. L. Mittal, ed., Plenum Press, New York, 1984, p. 295.
5. G. R. Palmese and J. K. Gillham, *J. Appl. Polym. Sci.*, **34**, 1925 (1987).
6. M. I. Bessonov, M. M. Koton, V. V. Kudryavtsev, and L. A. Laius, in *Polyimides: Thermally Stable Polymers*, Plenum Publishing, New York, 1987.
7. R. A. Venditti, J. K. Gillham, E. Chin, and F. M. Houlihan, in *Advances in Polyimide Science and Technology*, C. Feger, ed., Technomic Publ., Lancaster, PA, 1992, pp. 336-350.
8. R. A. Venditti and J. K. Gillham, *J. Appl. Polym. Sci.*, **45**, 1501 (1992).
9. G. Levita and L. C. E. Struik, *Polymer*, **24**, 1071 (1983).
10. E. Chin, F. M. Houlihan, R. A. Venditti, and J. K. Gillham, in *Advances in Polyimide Science and Technology*, C. Feger, ed., Technomic Publ., Lancaster, PA, 1992, pp. 201-212.
11. F. M. Houlihan, B. J. Bachman, C. W. Wilkins, Jr., and C. A. Pryde, *Macromolecules*, **22**, 4477 (1989).
12. J. K. Gillham, in *Developments in Polymer Characterisation*, Vol. 3, J. V. Dawkins, ed., Applied Science Publishers, London, 1982, Chapter 5, pp. 159-227.
13. J. B. Enns and J. K. Gillham, in *Computer Applications in Applied Polymer Science*, Am. Chem. Soc., Symposium Series, No. 197, Theodore Provder, ed., American Chemical Society, Washington D.C., 1982, pp. 329-352.
14. J. Heijboer, *Kolloid Z.*, **134**, 149 (1956).
15. J. Heijboer, *Kolloid Z.*, **148**, 36 (1956).
16. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymer Solids*, Wiley, London, 1967.
17. J. Heijboer, *Internatl. J. Polymeric Materials*, **6**, 11 (1977).
18. I. M. Ward, *Mechanical Properties of Solid Polymers*, Wiley, New York, 1983, p. 107.
19. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1970, p. 59.
20. P. R. Couchman and F. E. Karasz, *Macromolecules*, **11**, 117 (1978).
21. P. R. Couchman, *Polym. Eng. Sci.*, **24**(2), 135 (1984).
22. R. A. Venditti and J. K. Gillham, *J. Appl. Polym. Sci.*, to appear. See also: R. A. Venditti and J. K. Gillham, *Proc. Am. Chem. Soc. Div. of Polymeric Materials: Sci. Eng.*, **69**, pp. 434-435 (1993).
23. C. J. Lee, *JMS-Rev. Macromol. Chem. Phys.*, **C29**(4), 431 (1989).
24. J. K. Gillham and H. C. Gillham, *Polym. Eng. Sci.*, **13**(6), 447 (1973).

Received April 27, 1993

Accepted January 18, 1994