TABLE III
TRANSITION TEMPERATURES^f OF POLY(2,6-DIPHENYL 1,4-PHENYLENE ETHER) BY VARIOUS METHODS

Method	Measurement	T_s,^{c} °C	T_g, °C	T_c,^{d} °C	T_{tr},^{e} °C	T_m, °C
Dsc	C_p	N.o.^{a}	225	258	N.o.	481
Tma	α	118	225	N.o.	350–375 (not distinct)	470
Dma	$E''^{\,b}$	130	230	285	N.o.	Not attainable by this method
Dsde	$\epsilon''^{\,b}$	125	N.o.	288	338	485

[a] N.o. = not observed. [b] Applied frequency = 110 cps. [c] Onset of a solid-state transition. [d] Temperature of maximum in crystallization exotherm. [e] Onset of premelt transition. [f] Reported values were all from measurements at a heating rate of 5 °C/min.

jump in the heat capacity for such a transition is more difficult to accept. However, since this transition is more gradual (*i.e.*, the dielectric loss peak extends over a 150° range) it is probably not detectable by heat capacity measurements.[18]

A summary of transition and relaxation temperatures is given in Table III. It was shown that a complete description of transitions and relaxations necessitates the use of samples of well-defined thermal histories and the application of various experimental techniques at comparable experimental conditions. The importance of heat capacity measurements in assigning the glass-transition temperature of this polymer was clearly demonstrated. In the absence of C_p data it would have been difficult to guess which of the four discontinuities in the thermal expansion curve corresponds to the T_g.

On the other hand, thermal expansion data lead to the assignment of a subglass and submelt transition which could not be detected by differential scanning calorimetry. Dynamic-mechanical and dielectric relaxation spectra were useful in identifying possible origins of motion in transition regions of this polymer and in demonstrating the effects of changing morphology on these time-dependent processes.

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(18) B. Wunderlich, *Kolloid-Z. Z. Polym.*, **231**, 605 (1969).

Thermal Transitions in Stereoisomers of Poly(*tert*-butyl ethylene oxide)

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ABSTRACT: Differential scanning calorimetry was used to study thermal transitions in isotactic and base-catalyzed poly(*tert*-butyl ethylene oxide). The isotactic polymer had an equilibrium melting point of 135 ± 1° and a glass transition of 58 ± 1° which was verified with vibrating-reed measurements. It could be quench cooled from the melt, however, to give an amorphous polymer with a glass transition of 40 ± 1°. Upon aging, the thermograms of the quenched polymer developed an (anomalous) endothermic T_g which was explained in terms of the rate processes involved in passing through the glass transition. Base-catalyzed polymer demonstrated an equilibrium melting point of 63 ± 1° and a normal-appearing glass transition of −9 ± 1° both for quenched and freeze-dried samples. Heat capacities were calculated and tabulated over the temperature range of 0–180°, and are shown graphically in the regions of the thermal transitions.

Preparations of two stereoisomers of poly(*tert*-butyl ethylene oxide) having distinctly different physical properties have been reported in the literature.[1–5] Price and Fukatani[1] interpreted from nmr and X-ray data that the crystalline polymer prepared by coordination catalyst (Et_2Zn–H_2O) is isotactic, and the crystalline polymer prepared by base catalyst (*tert*-BuOK) is syndiotactic. Further investigation in this laboratory[6] and by Tani and Oguni[7] showed, however, that there must be approximately equal percentages of isotactic and syndiotactic dyads in the base-catalyzed polymer. Since it is semicrystalline, it must be made up of stereoblocks of isotactic and syndiotactic placements.

Since the reported value[8] for the glass transition of the isotactic polymer (35°) was considerably different than the values determined in this laboratory (53°), we decided a careful study of the thermal transitions in both stereoisomers was called for. We thus determined the glass transition of an annealed semicrystalline isotactic poly(*tert*-BuEO) specimen using the vibrating-reed technique.[9] We also measured specific heats, heats of fusion, and glass transitions of annealed and quenched isotactic and base-catalyzed semicrystalline

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(1) C. C. Price and H. Fukutani, *J. Polym. Sci., Part A-1*, **6**, 2653 (1968).

(2) J. M. Bruce and S. J. Hurst, *Polymer*, **7**, 1 (1966).

(3) G. Allen, *et al.*, *ibid.*, **8**, 385 (1967).

(4) C. C. Price and D. Carmelite, *J. Amer. Chem. Soc.*, **88**, 4039 (1966).

(5) E. J. Vandenberg, U. S. Patent 3,285,861 (Nov 15, 1966).

(6) B. Furie, Ph.D. Thesis, Department of Chemistry, University of Pennsylvania.

(7) H. Tani and N. Oguni, *J. Polym. Sci., Part B*, **7**, 803 (1969).

(8) G. Allen, *et al.*, *Polymer*, **8**, 406 (1967).

(9) P. E. Wapner and W. C. Forsman, *Trans. Soc. Rheol.*, in press.

poly(*tert*-BuEO) using differential scanning calorimetry (dsc).

Experimental Section

Isotactic semicrystalline poly(*tert*-butyl ethylene oxide) was synthesized using zinc diethyl–water catalyst.[1] The polymerization was carried out for 5 days at 65° under nitrogen atmosphere in a sealed tube. The polymer was then dissolved in hot benzene and filtered through a medium-porosity sintered-glass funnel. The polymer solution was washed with a methanol–HCl mixture to remove traces of zinc oxide and finally precipitated completely with excess methanol. A part of the bulk polymer was dissolved in benzene and freeze-dried. The remaining bulk polymer was fractionated from benzene solution by cooling from 80° to room temperature. One fraction of number-average molecular weight 8.3×10^5 was selected for study. It was dried under vacuum at 25° for 48 hr. The base-catalyzed poly(*tert*-BuEO) was obtained by bulk polymerization with potassium *tert*-butoxide catalyst for 18 days at 96°. The polymer was dissolved in cyclohexane, neutralized with Dry Ice, isolated by evaporation of the solvent, and vacuum-dried for several days. The sample was then freeze-dried from benzene solution.

Number-average molecular weights of bulk isotactic and base-catalyzed polymers were determined with Mecrolab membrane and vapor pressure osmometers. They were 200,000 and 2200, respectively.

A Du Pont 900 differential scanning calorimeter was used to measure specific heats in the temperature range 0–180° at a heating rate of 20°/min. The instrument was calibrated with spectrographic aluminum. Specific heats were calculated from the following equation[10]

$$(C_p)_T = \frac{(\Delta T_x + \Delta T_{\text{blank}})E_T}{Ma}$$

where $(C_p)_T$ = specific heat at temperature T, in millicalories per milligram per °C; ΔT_x = absolute differential temperature for sample, in °C; ΔT_{blank} = absolute differential temperature under no sample condition, in °C; E_T = calibration coefficient at temperature T, in millicalories per °C per minute; M = sample mass, in milligrams; and a = heating rate, in °C per minute. Heats of fusion were calculated from the equation[10]

$$\Delta H = \frac{EA\Delta T_s T_s}{Ma}$$

where ΔH is in millicalories per milligram; A = area of the peak, in square inches; ΔT_s = y-axis sensitivity, in °C per inch; and T_s = x-axis sensitivity, in °C per inch.

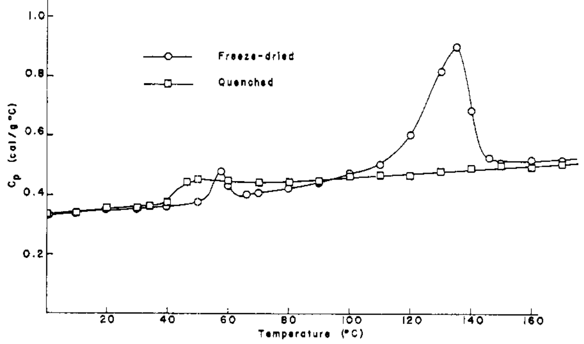

Figure 1. Variation of specific heat (C_p) with temperature of isotactic poly(*tert*-butyl ethylene oxide).

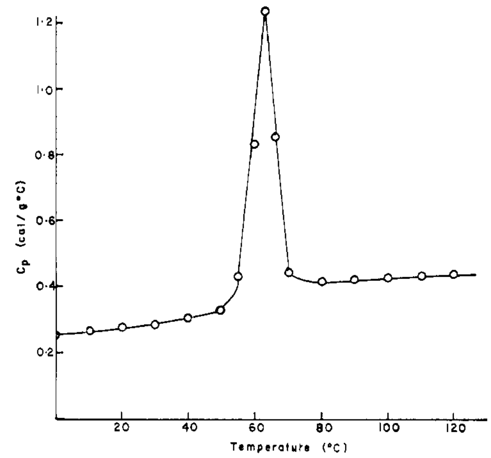

Figure 2. Variation of specific heat (C_p) with temperature of base-catalyzed poly(*tert*-BuEO).

Vibrating-reed measurements were made using an instrument and method of analysis described previously.[9] The reed was molded in a Preco platen press at 140° and 1000 psi. The mold was allowed to cool from the molding temperature to room temperature over a period of several hours—hopefully developing the highest degree of crystallinity practically attainable. Reed dimensions (free of the clamp) were 2.00 × 0.578 × 0.022 in. and its density was 0.980 gm/cm^3.

Results and Discussion

Two series of measurements were carried out both on isotactic and base-catalyzed poly(*tert*-BuEO). The former was examined from 0 to 180° and the latter from −10 to 120°. For the first experiment of each series, the freeze-dried sample as described above was used. The polymer melt from the first experiment was then quench cooled to 0°. Succeeding experiments in each series were done with quenched polymer that had been annealed for various times at various temperatures. Figures 1 and 2 show the variation of specific heat (C_p) with temperature of isotactic and base-catalyzed poly(*tert*-BuEO). The dependence of tan δ (mechanical loss tangent) on temperature measured by the vibrating-reed technique[9] is shown in Figure 3. The effect of aging time (annealing at room temperature) on the glass-transition temperature and the dependence of crystallinity on the high-temperature annealing time are shown in Figures 4 and 5.

Specific Heats and Melting Points. Specific heats for the freeze-dried bulk polymers are recorded in Table I. As seen in Figure 1, the C_p *vs.* T curve for semicrystalline freeze-dried

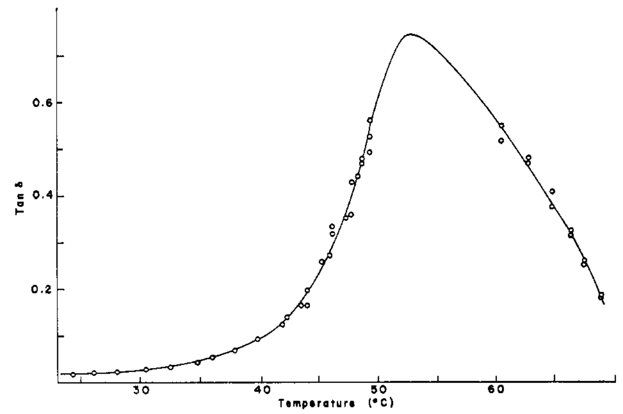

Figure 3. Dependence of mechanical loss tangent, tan δ, on temperature of annealed isotactic poly(*tert*-BuEO).

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(10) Instruction Manual of 900 Thermal Analyzer, E. I. du Pont de Nemours and Co., Wilmington, Del.

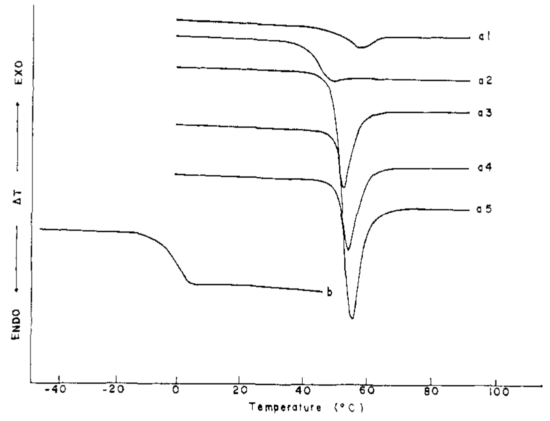

Figure 4. Dsc thermograms of (a) isotactic and (b) base-catalyzed polymers: (a1) freeze-dried sample, (a2) quenched sample, (a3, a4, and a5) aged for the periods 6, 34, and 240 days, respectively, at room temperature.

isotactic poly(*tert*-BuEO) is virtually linear between 0 and 45°. The effects of the glass transition and the first-order melting transition were then observed between 45 and 180°. The melting peak has a maximum at 135 ± 1° corresponding to the equilibrium melting point. In Figure 2, we see that from 0 to 120° only a first-order melting transition at 63 ± 1° is observed for base-catalyzed poly(*tert*-BuEO).

Within the temperature range between the glass transitions of the two stereoisomers, C_p for the isotactic polymer is 20–30% greater than that for the base-catalyzed polymer. The difference would be even greater below T_g of the base-catalyzed polymer. This behavior is the reverse of that reported for the stereoisomers of poly(methyl methacrylate),[11] and indeed it has been reported that C_p of polystyrene is independent of stereoregularity.[12,13] Full interpretation of these observations will have to be deferred until there is more detailed information on the structure of the base-catalyzed polymer and the results of thermal analyses of stereoisomers of other substituted polyethers have been reported.

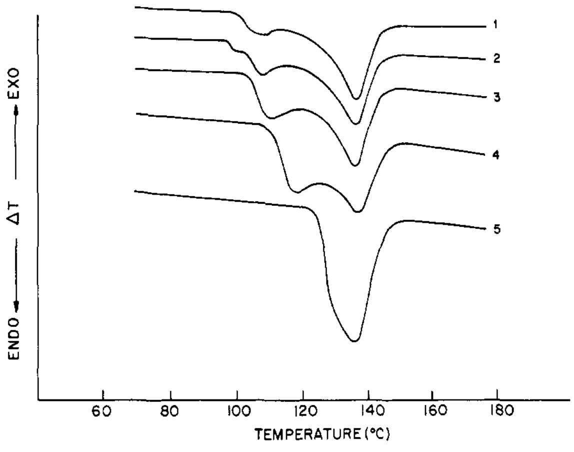

Figure 5. Dsc thermograms of isotactic polymer annealed at 94° for (1) 10 min, (2) 25 min, (3) 140 min, (4) 3.5 days, and (5) at 110° for 5 days. Heats of fusion for curves 1–5 were 3.3, 4.1, 4.6, 4.9, and 4.9 cal g^{-1}.

Table I
Specific Heats *vs.* Functions of Temperature for Freeze-Dried Bulk Polymer

	Specific Heat, cal g^{-1} deg^{-1}, of poly(*tert*-BuEO)	
Temp, °C	Isotactic	Base catalyzed
0	0.342	0.253
10	0.344	0.268
20	0.353	0.277
30	0.356	0.286
40	0.358	0.308
50	0.379	0.337
55		0.432
58	0.476	
60	0.433	0.834
63		1.235
66	0.404	0.857
70	0.411	0.447
80	0.427	0.415
90	0.447	0.424
100	0.479	0.433
110	0.507	0.437
120	0.608	0.439
130	0.821	
135	0.905	
140	0.689	
150	0.518	
160	0.527	
170	0.527	
180	0.542	

When the freeze-dried sample of isotactic poly(*tert*-BuEO) was melted, and then cooled and annealed at 20–30° below its melting temperature, the crystallinity increased with time. This effect is illustrated in thermograms shown in Figure 5. It is also observed that the melting peak has two minima. There is a small peak at 100° which moves to higher temperatures with increasing annealing time. After annealing the sample for 5 days at 110°, the small peak disappears with a corresponding increase in the area of the main fusion peak. The appearance of two minima is probably due to the presence of highly defected crystallites in the original freeze-dried polymer.

The amount of crystallinity developed in the sample depends on the crystallization process. The fraction which was crystallized from solution during stirring had a melting point of 144° and a heat of fusion of 11.0 cal g^{-1} compared with values of 135° and 7.3 cal g^{-1} for the freeze-dried sample. We propose that these effects are due to orientation induced by the shearing stresses present during crystallization.

Values of melting temperature, glass-transition temperature, heat of fusion, entropy of fusion, and heat capacity increment at the glass transition [$\Delta C_p(T_g)$] are summarized in Table II.

Heats of Fusion. The heats of fusion (Table II) calculated from the areas under melting peaks for annealed isotactic and base-catalyzed semicrystalline poly(*tert*-BuEO) are 7.3 and 6.8 cal g^{-1}, respectively. Heat of fusion of a 100% crystalline poly(propylene oxide) (PPO) was reported[14] to be slightly less than 31 cal g^{-1}. In the case of poly(*tert*-BuEO), a 100% crystalline sample would have an even somewhat lower heat of fusion than PPO because of the bulky *tert*-butyl group. This indicates that the semicrystalline poly(*tert*-BuEO) has low degree of crystallinity (possible 20–25%). The entropies of fusion for isotactic and base-catalyzed polymers are 0.0179 and 0.202 cal g^{-1} deg^{-1}, respectively.

Glass Transitions. Figure 3 shows that annealed isotactic

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(11) J. M. O'Reilly and F. E. Karasz, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **6**, 731 (1965).

(12) F. E. Karasz, H. E. Bair, and J. M. O'Reilly, *J. Phys. Chem.*, **69**, 2657 (1965).

(13) I. Abu-Isa and M. Dole, *ibid.*, **69**, 2668 (1965).

(14) R. H. Beaumont, *et al.*, *Polymer*, **7**, 401 (1966).

TABLE II
VALUES MELTING TEMPERATURE, GLASS-TRANSITION TEMPERATURE, HEAT OF FUSION, ENTROPY OF FUSION, AND HEAT CAPACITY INCREMENT AT THE GLASS TRANSITION [$\Delta C_p(T_g)$]

	Isotactic poly(*tert*-BuEO)	Base-catalyzed Poly(*tert*-BuEO)
Heat of fusion, ΔH_f, cal g^{-1}	7.30	6.83
Entropy of fusion, ΔS_f, cal g^{-1} deg^{-1}	0.0179	0.0202
Heat capacity increment, $\Delta C_p(T_g)$, cal deg^{-1} bead^{-1}	2.66	2.53
Glass temperature, °C	53 ± 2 40 ± 1[a]	−9 ± 1
Melting temperature, °C	135 ± 1	63 ± 1

[a] For amorphous sample (quench cooled).

poly(*tert*-BuEO) demonstrates a major dispersion peak in its tan δ *vs.* T curve at 53 ± 2° corresponding to the glass transition.[15] Likewise, the C_p *vs.* T curve (Figure 1) for the same polymer shows a small endothermic peak at 58 ± 1° which must therefore be associated with the glass transition.

Quenched poly(*tert*-BuEO) demonstrates a C_p–T curve typical of an amorphous polymer with a glass transition of 40 ± 1°. That the 40 and 58° dsc transitions both are associated with T_g is shown in the aging experiments illustrated in Figure 4. Curve a2 represents a part of the thermogram used to calculate the specific heats of the quenched cooled isotactic polymer that are shown in Figure 1, and it shows the 40° glass transition. Curves a3–a5 are thermograms of the same polymer sample taken to 100° after various periods of aging at room temperature. After 6 days, the transition was again endothermic, with a heat absorption of 1.5 cal g^{-1}, and T_g had increased to 48°. After 240 days, heat absorption had increased to 2.2 cal g^{-1} and T_g to 58°, which is the same glass transition as demonstrated by the original freeze-dried sample.

The higher value of T_g demonstrated by the semicrystalline specimen is to be expected and is a reflection of loss of mobility of chains in the amorphous regions due to constraint placed upon them by crystallites. The endothermic response, however, is anomalous, in that no latent heat is associated with the glass transition. Expected behavior of the C_p–T curve at T_g would be similar to that for the quenched cooled specimen. McKinney and Foltz[16,17] obtained similar results with slightly crystalline poly (vinyl chloride). They interpreted the endothermic nature of the glass transition to be due to physical orientation (very low degree of crystallinity). However, since the melting point of poly(*tert*-BuEO) is higher by 77° than the (apparently endothermic) glass transition, it is highly unlikely that it could be associated with the disruption of even highly defected crystallites. Similar endothermic response near the glass transition was also observed by Maurer[18] in an ethylene–propylene copolymer, and the interpretation given was the same as that of McKinney and Foltz.[16,17]

The *apparently* endothermic response in dsc heating thermograms has, however, been satisfactorily explained by Ellerstein,[19] who took into account the kinetics of volume change during heating. He further pointed out that the increasing *apparent* ΔH with annealing time could be explained by considering the long-time bulk relaxation processes discussed by Kovacs.[20]

Allen,[8] *et al.*, have studied dynamic mechanical properties of isotactic poly(*tert*-BuEO), and they observed a dispersion at 46° which they assigned as a β-relaxation process corresponding to the glass-transition temperature. However, they also have reported, from dilotometric measurements, 35 ± 1° for T_g, which is close to the T_g observed in our laboratory for the amorphous (quench cooled) sample. Their differing results can therefore be attributed to differing thermal history.

The increase in C_p, as isotactic poly(*tert*-BuEO) passes through T_g, is 0.08 cal g^{-1} deg^{-1} or 2.66 cal deg^{-1} mol^{-1} of beads (as defined by Wunderlich[21]). The heat capacity increment at T_g for the base-catalyzed polymer is 2.53 cal deg^{-1} mol^{-1} of beads. These two values are consistent with Wunderlich's[21] rule of constant heat capacity increment.

Semicrystalline base-catalyzed poly(*tert*-BuEO) demonstrates a normal-appearing glass transition at −9 ± 1°, as is shown in Figure 4. This value is surely somewhat low, since the number-average molecular weight is only 2200. A T_g more characteristic of the base-catalyzed chain can be obtained only when polymer of much higher molecular weight is available. Although most often T_g has been reported to be independent of tacticity,[11–13,22] Shetter[23] has shown that T_g for the lower methacrylate polymers is sensitive to tacticity because of steric effects of the pendent groups. Since the backbone structure of the base-catalyzed polymer is not fully understood, we cannot offer any detailed interpretation of the differences in glass transition of the two stereoisomers of poly(*tert*-butyl ethylene oxide).

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(15) J. D. Ferry, "Viscoelastic Properties of Polymers," Wiley, New York, N. Y., 1970.

(16) P. V. McKinney and C. R. Foltz, *J. Appl. Polym. Sci.*, **11**, 1189 (1967).

(17) C. R. Foltz and P. V. McKinney, *Anal. Chem.*, **41**, 687 (1969).

(18) J. J. Maurer, "Analytical Calorimetry," R. S. Porter and J. F. Johnson, Ed., Plenum Press, New York, N. Y., 1968.

(19) S. M. Ellerstein, *Appl. Polym. Symp.*, No. 2, 111 (1966).

(20) A. J. Kovacs, *Fortschr. Hochpolym.-Forsch.*, 3, 394 (1963).

(21) B. Wunderlich, *J. Phys. Chem.*, **64**, 1052 (1960).

(22) R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).

(23) J. A. Shetter, *J. Polym. Sci., Part B*, 1, 209 (1963).