

## Thermomechanical Behavior of a Polynorbornadiene

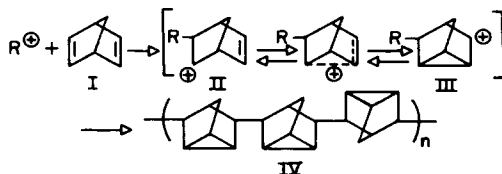
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### Synopsis

A high-temperature linear amorphous hydrocarbon polymer synthesized cationically from 2,5-norbornadiene (bicyclo[2.2.1]hepta-2,5-diene), was studied thermomechanically with respect to physical transitions and stability in nitrogen. The glass transition temperature was determined to be 320°C (at less than 1 cps), which is probably the highest known for a linear hydrocarbon addition polymer. The thermomechanical technique of torsional braid analysis, together with thermogravimetric analysis, differential thermal analysis, infrared analysis, and solubility studies, was used to investigate the sequential events of the glass transition and degradation. The polymer is of particular interest since it is a high-temperature plastic which in the bulk form would probably need to be processed at high speeds in the vicinity of  $T_g$  in an inert atmosphere. The presence of tertiary hydrogen atoms should render it amenable to degradation by the earth's environment.

### INTRODUCTION

The cationic polymerization of 2,5-norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) (structure I below) has been interpreted to lead predominantly to structure IV.<sup>1,2</sup> Ultraviolet, infrared, and proton magnetic resonance spectroscopy have been used for structure determination.<sup>1,2</sup> The proposed cationic reaction mechanism involves a transannular rearrangement (II  $\rightarrow$  III) of the initially formed intermediate (II), prior to the addition of another norbornadiene monomer<sup>1,2</sup>:



Probably for steric reasons, 1,2-enchainment does not occur. The product was found to be amorphous on the basis of x-ray examination<sup>1,2</sup>; the mechanism was therefore considered not to be stereospecific. An examination of models leads to the expectation that the bonds between cages would be

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equatorial-to-equatorial. The nortricyclene cage structure in the backbone confers a high degree of chain stiffness on the molecule and therefore a high glass transition temperature on the material. The highly strained substituted cyclopropane ring in the cage would be expected to reduce the overall thermal stability of the structure while the presence of tertiary hydrogens would be expected to provide sites for oxidative attack.

The present report presents a preliminary examination of the thermomechanical behavior and thermal stability of the polymer. The techniques used were torsional braid analysis (TBA) for the thermomechanical spectra,<sup>3-5</sup> differential thermal analysis (DTA) to monitor heat effects, thermogravimetric analysis (TGA) to study weight loss, infrared analysis (IR) to monitor chemical changes, and solubility studies to monitor crosslinking and/or chain stiffening. All the studies were carried out with a heating rate of 2°C/min, with the exception of DTA ( $\Delta T/\Delta t = 20^\circ\text{C}/\text{min}$ ), and all were performed in a dried nitrogen atmosphere. TGA was also studied in air.

## EXPERIMENTAL

### Synthesis

Norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) monomer (Matheson, Colman and Bell) was distilled before use. Gas-chromatographic analysis indicated greater than 98% purity and the presence of four or five minor impurities.

Polymerizations were carried out in a dry box in stirred glass reactors using a published procedure for obtaining noncrosslinked polymer.<sup>1</sup> The catalyst, aluminum chloride, was dissolved in ethyl chloride (2.5% solution) and was added slowly (1-2 ml every 2-3 min) to the reactor which initially contained a homogeneous solution of norbornadiene (19.8 g) in ethyl chloride (130 ml) at  $-127^\circ\text{C}$ . The temperature of the reaction medium increased to no higher than  $-125.5^\circ\text{C}$  during the course of the synthesis (>1 hour). Polymerization started immediately after introduction of

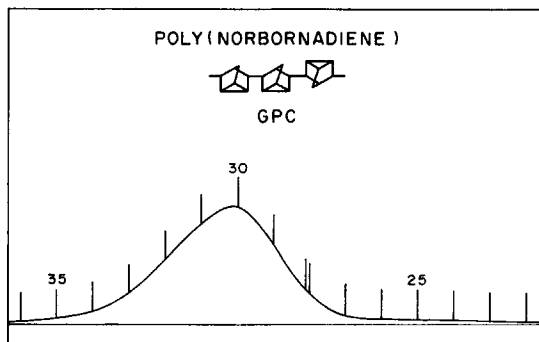


Fig. 1. Gel permeation chromatogram of polynorbornadiene in tetrahydrofuran solvent.

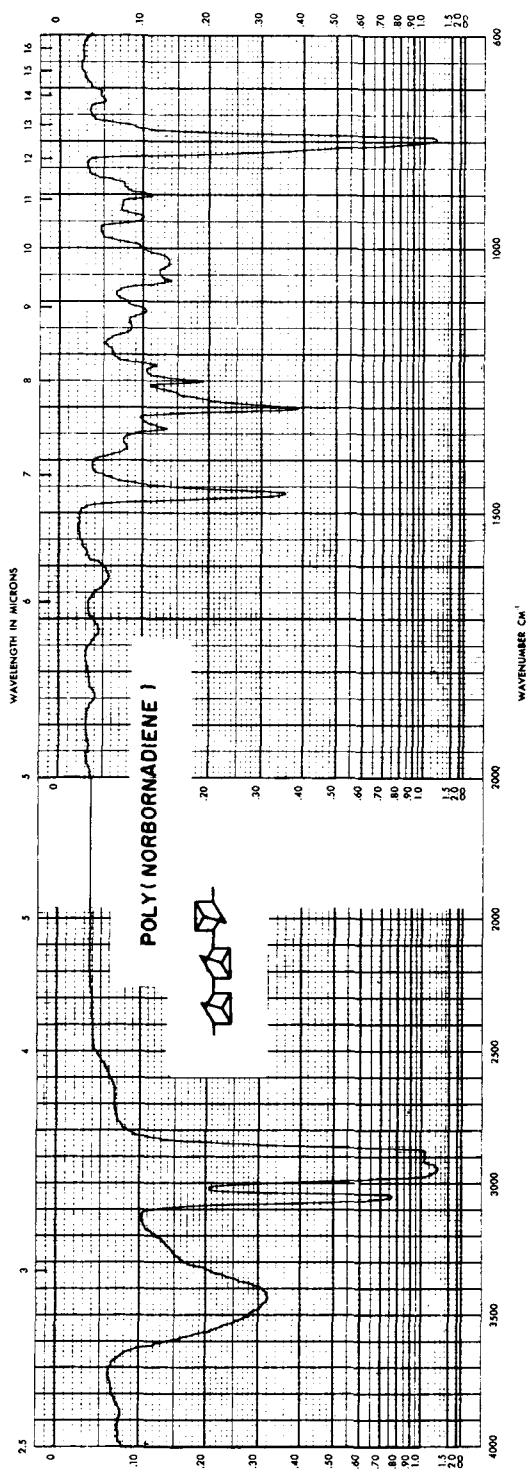


Fig. 2. Infrared spectrum of polynorbornadiene. Specimen was prepared by casting from a benzene solution at 50°C and forming a KBr pellet. Water present in the latter gives rise to absorption at 2.8 and 6.15 microns.

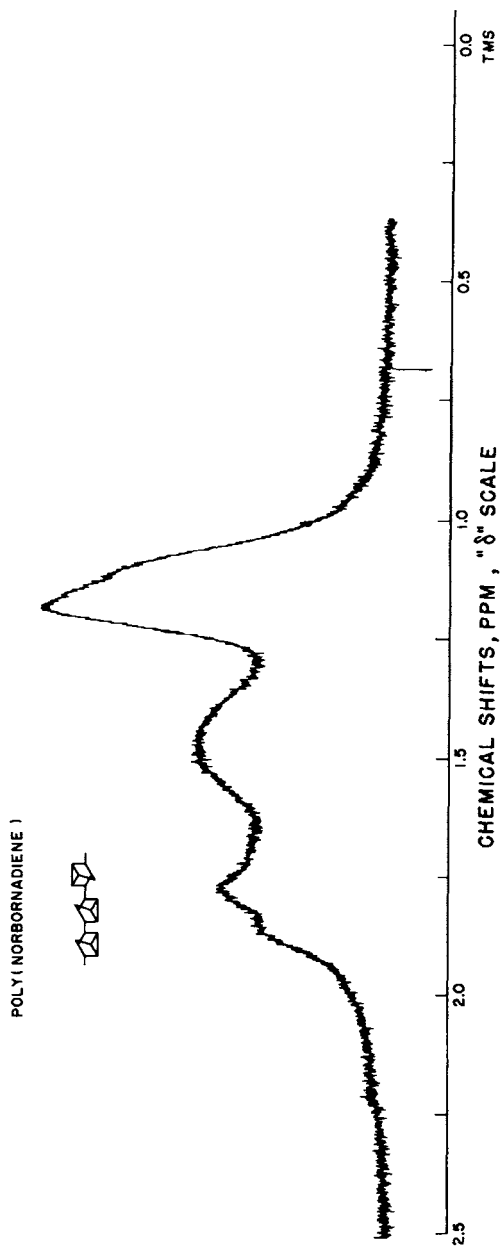


Fig. 3. NMR spectrum (100 MHz) of polynorbornadiene in hexachlorobutadiene (20%) at 90°C (lock signal, benzene). There was scarcely any absorption in the vinyl region (off scale).

catalyst, as detected by the development of haze. The reaction was terminated by introducing precooled *n*-propanol. The product was washed thoroughly with methanol, filtered, and dried under nitrogen at 50°C. The yield was 12.5% (2.5 g). The material was soluble in toluene, benzene, ether, and carbon tetrachloride. Its number-average molecular weight was 9850, as measured by vapor pressure osmometry, which corresponded to a degree of polymerization of about 100. Gel permeation chromatography (GPC) data are shown in Figure 1; when treated as polystyrene,  $\bar{M}_n = 14970$  and  $\bar{M}_w/\bar{M}_n = 3.73$ . The infrared and nuclear magnetic resonance spectra of the polymer are shown in Figures 2 and 3, respectively.

### Techniques

The low-strain thermomechanical data were determined at less than 1 cps throughout the range  $-180^\circ$  to  $+500^\circ\text{C}$  by the technique of torsional braid analysis.<sup>3-5</sup> The torsional braid analyzer is a free-hanging torsional pendulum with the specimen consisting of a multifilamented ( $\sim 3600$ ) glass braid impregnated with the sample polymer. The specimen is fabricated *in situ* by removing solvent from a braid that has been soaked in a polymer solution before mounting. The specimens for the pendulum were made by using a 10% (wt/vol) solution of the polymer in benzene. Solvent was removed from the composite specimens by heating in nitrogen to at least  $200^\circ\text{C}$  (see later) and cooling ( $\Delta T/\Delta t = \pm 2^\circ\text{C}/\text{min}$ ). Attached to the lower clamp is a polarizer disc, the inertial mass, which when coupled with another polarizer over a photocell, acts also as a "linear with angle" transducer to convert the mechanical oscillations into electrical signals.<sup>5</sup> The mechanical oscillations and the analogue signals approximate damped sine waves. The mechanical parameters are deduced from the character of the analogue signals. For isotropic, homogeneous specimens subject to small stains,

$$G' = K(1/P^2)$$

where  $G'$  is the in-phase elastic modulus,  $P$  is the period of oscillation, and  $K$  is a constant dependent upon the geometry. The logarithmic decrement, a measure of the ratio of energy dissipated to maximum energy stored on mechanical deformation, is defined as

$$\Delta = \ln(A_1/A_2) = \ln(A_2/A_3) \dots = \ln(A_i/A_{i+1})$$

where  $A$  is the amplitude of deformation. Due to the composite nature, the small size, and the irregular geometry of the specimens, the data discussed herein are presented in terms of the relative rigidity ( $=1/P^2$ ) replacing  $G'$ . The logarithmic decrement ( $\Delta$ ) is presented as the mechanical damping index,  $1/n$ , where  $n$  is the number of oscillations between two fixed but arbitrary boundary amplitudes in each wave (e.g.,  $A_i/A_{i+n} = 20$ ), taken constant over any thermomechanical experiment; and  $1/n$  is directly proportional to the logarithmic decrement ( $\Delta = 1/n \ln[A_i/A_{i+n}]$ ).

The thermogravimetric analyses were performed in nitrogen and in air using a du Pont 950 thermogravimetric analyzer. The differential thermal analyses were run on a Mettler thermoanalyzer at 20°C/min in nitrogen.

The infrared study was performed on a single film held between two sodium chloride plates. The holder, salt plates, and film were suspended in the TBA oven in a nitrogen atmosphere and were heated at 2°C/min to various "quench points," at which they were removed from the oven to a nitrogen chamber held at room temperature, without being exposed to air. The quenched specimen was examined at room temperature using a Perkin-Elmer Model 237B grating infrared spectrophotometer at low scan rate and normal slit opening. The specimen was returned to the nitrogen quench stream and purged before being returned to the oven at the quench point, after which the oven temperature was taken at 2°C/min to the next quench point. The quench points were taken as significant temperatures in the thermomechanical spectra.

The solubility studies used separate film specimens, each being taken at 2°C/min from room temperature to its quench point before being immersed in solvent. The behavior of the thermally treated films in excess benzene at 25°C was observed visually.

## RESULTS AND DISCUSSION

### Thermal Analyses (TGA and DTA)

A sample of the solution which was used to fabricate TBA specimens was examined by thermogravimetric analysis in nitrogen and air. After drying in nitrogen by heating at 2°C/min to 200°C, the specimen was cooled to room temperature and run at 2°C/min to 500°C. The thermogram in nitrogen shown in Figure 4 is essentially the same as those obtained in runs made on the dry, powdered, "as received" specimen. A small, slow weight loss started at 250°C and reached 6% by 370°C. The specimen started to lose weight rapidly at about 410°C and was reduced to about 29% of its original weight by 500°C where the rate of loss had diminished. In air, an initial gain in weight began at 150°C, reached a maximum weight of 102% of the original at 240°C, and returned to 100% by 275°C. The presence of the weight maximum was due to the competitive effects of the addition of oxygen (presumably due to the formation of hydroperoxides at the tertiary hydrogen sites) and the removal of both low molecular weight oligomers and of low molecular weight decomposition products. Just above 280°C there was an increase in the rate of oxidative weight loss which preceded a region of moderating rate. At about 425°C, there was another increase in rate of loss which approximately corresponds to the thermal degradation which was observed in nitrogen. The specimen was completely oxidized by 500°C and left no residue.

Differential thermal analyses (results not shown) were performed in nitrogen in two stages. The dry powder was first taken at 2°C/min to

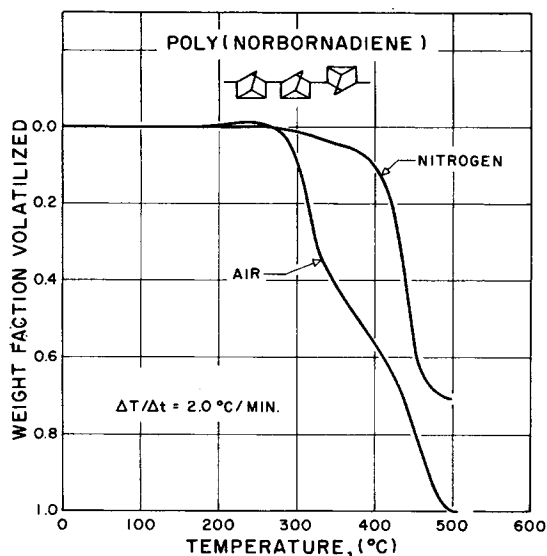


Fig. 4. Thermogravimetric analysis of polynorbornadiene in nitrogen and in air from 0° to 500°C at 2°C/min.

200°C (to simulate the drying step in the TBA analysis) and then, after cooling, was taken at 20°C/min to 500°C. An endothermic dip typical of the glass transition temperature was evident in the vicinity of 300°C. The exact position of the glass transition temperature was difficult to determine. A large exotherm began at 420°C. The data were somewhat ambiguous due to the large baseline drift and therefore are not shown. It is noteworthy that at 20°C/min, the glass transition temperature and the degradation processes were distinguishable.

#### Thermomechanical Analysis

The thermomechanical behavior of the polymer in dried nitrogen was determined over the range  $-180^{\circ}$  to  $+500^{\circ}\text{C}$ . Figure 5 shows the behavior of the specimen from  $-180^{\circ}$  to  $350^{\circ}$  to  $25^{\circ}\text{C}$  after it had been preheated to  $200^{\circ}\text{C}$  in order to remove the benzene solvent and then precooled to  $-180^{\circ}\text{C}$ . The data for the latter precooling (not shown) and subsequent reheating were not absolutely reproducible, although changes occurred at the same temperatures. In the low-temperature region, there were multiple damping peaks with maxima at  $-60^{\circ}$  (see Fig. 6) and  $-140^{\circ}\text{C}$  which were accompanied by changes in the slope of the rigidity curve. A shoulder in the broad glass transition damping peak at  $225^{\circ}\text{C}$  was also accompanied by a drop in modulus. The glass transition ( $T_g$ ) was characterized by the large drop in rigidity and intense damping maximum at  $320^{\circ}\text{C}$ . The previously cited DTA study indicated an endothermic shift in this region which is typical of  $T_g$ . The glass transition temperature region was rendered even more pronounced after heating to  $350^{\circ}\text{C}$ , as is shown by the cool-

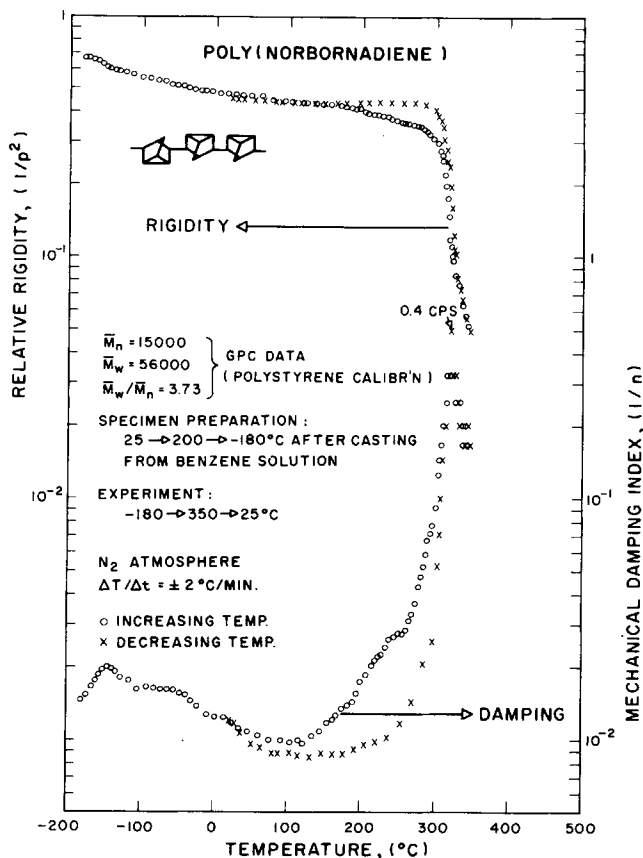


Fig. 5. Thermomechanical spectra of polynorbornadiene in nitrogen.

ing curves in Figure 5. Preheating the polymer to 350°C simplified the pre- $T_g$  region by eliminating the damping shoulder and increasing the modulus in the 200–250°C temperature range. Later studies, involving the low-temperature casting of films, showed that the polymer was a poor film former; heating above  $T_g$  probably altered the morphology and perhaps improved the material properties of the polymer. A new specimen was heated to 350°C in nitrogen and data were taken from +350° to -180° to +500°C (Fig. 6, curves 1). Unlike the previous specimen, the data were reversible on cooling from 350°C and subsequent reheating. On heating above 350°C, the rigidity began to increase at about 370°C, displayed a small maximum at 415°C, a large sigmoidal rise between 435° and 470°C, and then decreased slightly to 500°C. The increase in rigidity at 435°C was accompanied by a damping peak at 453°C after which the damping decreased sharply. The stiffening reactions were also detected as a large exotherm by DTA (described above). Visual examination of the cooled pyrolyzed specimen indicated that the polymeric material had been converted to a smooth, glossy, black and opaque coating on the braid.



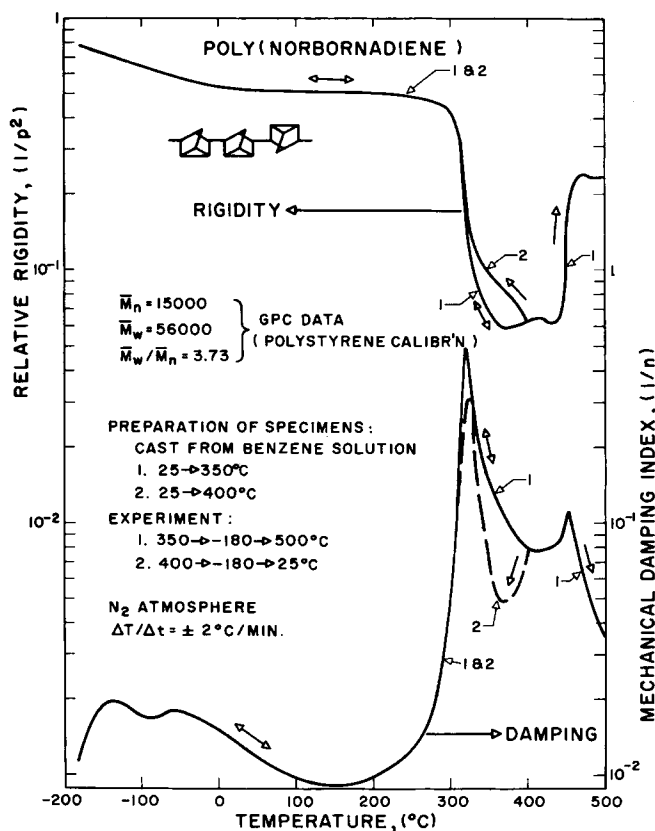


Fig. 6. Thermomechanical spectra of polynorbornadiene in nitrogen.

Curve 2 in Figure 6 represents the cooling behavior of another specimen after heating to 400°C. Note that preheating to 400°C shifted the glass transition up 7°C to 327°C, and the damping peak was rendered narrower and less intense than for the previous specimen which had been preheated to 350°C. The region below  $T_g$  was unaffected. Increase in the temperature of the glass transition and decrease in the intensity of the damping peak are typical of the effect of increasing crosslink density in a polymeric system. Narrowing of the damping peak is not typical but need not be unexpected if some of the skewness of the peak was due to reactions occurring in the vicinity of the glass transition temperature. The region below  $T_g$  was unaffected, presumably for the reason that the crosslink density, although sufficient to affect the longer-range motions associated with the glass transition, was insufficient to affect the more localized motions which are revealed by the damping pattern below  $T_g$ .<sup>5,6</sup>

### Solubility Study

A study was undertaken to determine the temperature region to which a film of the polymer must be heated in order to become insolubilized by

chemical reactions (e.g., crosslinking or chain stiffening). Seven solutions were prepared in small vials. The benzene in the solutions was removed at reduced pressure overnight at 50°C. One specimen was kept as a control. The other dried films were suspended in the TBA oven and taken, one at a time, at 2°C/min from room temperature to various quench temperatures in nitrogen. The quench temperatures were room temperature (control), 100°, 180°, 260°, 320°, 360°, and 400°C. These temperatures correspond to significant points on the TBA, DTA, or TGA plots. After quenching, excess benzene was added to the vials, and after standing for a day the contents of the vials were compared. The colorless control and 100°C specimens were virtually the same. Thereafter, a yellow color developed in the liquid which intensified with degree of heating to 320°C, without the formation of visible gel. A small amount of swelled gel was evident in the 360°C specimen, indicating that chemical crosslinking or chain stiffening occurred above  $T_g$ . A major portion of the 400°C specimen had gelled and a brownish char was also visible. The fractions of polymer which had been insolubilized by the thermal treatment were not determined.

### Infrared Study

A qualitative infrared study was undertaken so as to correlate chemical changes with those monitored by the other techniques. A film of the polymer, formed by predrying slowly from a benzene solution to prevent bubbling before being further dried at reduced pressure at 50°C, was placed between two sodium chloride plates which were held together in an aluminum holder. After obtaining an infrared spectrum (which was similar to that of Fig. 2), the specimen was placed in the TBA oven and heated at 2°C/min in nitrogen to quench points: 100°, 180°, 260°, 320°, 370°, 440°, and 500°C. Each infrared scan (not shown) was made after heating from the previous quench point to the new one. There were no apparent changes in the scans until 440°C, when the 3050  $\text{cm}^{-1}$  band, the 2875  $\text{cm}^{-1}$  shoulder, the 1730  $\text{cm}^{-1}$  band, the 1300  $\text{cm}^{-1}$  band, and the 800  $\text{cm}^{-1}$  band decreased significantly relative to the 2925  $\text{cm}^{-1}$  band. Several bands in the 1200 to 850  $\text{cm}^{-1}$  region also appeared to be less intense. A new band appeared in the 1600  $\text{cm}^{-1}$  region and indicated unsaturation.<sup>7</sup> The 800  $\text{cm}^{-1}$  band has been attributed to the 2,6-disubstituted nortricyclene structure.<sup>8-10</sup> The changes observed at the 440°C quench point show that a major breakdown in the original nortricyclene structure had occurred, but the large-peak remaining in the 2925  $\text{cm}^{-1}$  region suggests that a hydrocarbon structure still remains. The 500°C specimen scan displayed an almost total disappearance of all but the most prominent of the original peaks which were rendered weak.

### CONCLUSIONS

The thermomechanical spectra of poly(bicyclo[2.2.1]hepta-2.5-diene), or polynorbornadiene, reveal the glass transition temperature of 320°C (at

less than 1 cps). This is probably the highest known  $T_g$  for a linear, soluble, and fusible addition-type hydrocarbon polymer. It is also noteworthy that by utilizing suitable heating rates, the glass transition and subsequent degradation reactions can be separated. The onset of degradation at temperatures just above  $T_g$  is not unusual for high-temperature plastics where the submolecular motions (and therefore diffusive processes), which are characteristic of polymeric materials, increase by orders of magnitude.<sup>5,6</sup>

The presence of low-temperature glassy-state relaxations indicates that some mechanism of energy dissipation is active at these low temperatures. Yet, the types of submolecular motions (crankshaft, rotations, oscillations) which are currently considered to be the intramolecular origin of these relaxations must be limited in such a structure.

The polymer is of particular interest since it might be a high-temperature plastic processible at high speeds in an inert atmosphere, provided that it could be prepared at sufficiently high molecular weights with satisfactory mechanical properties. The presence of tertiary hydrogen atoms in its structure should render it amenable to degradation by the earth's environment.

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