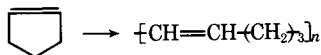


Thermomechanical Behavior of Uncrosslinked 1,5-Polypentenamers

1,5-Polypentenamers are synthesized by the ring-opening polymerization of cyclopentene using catalysts (e.g., $WCl_6 + AlR_3$):



Polymer microstructures ranging from essentially 100% cis to high trans (>80%) have been obtained by varying the catalyst and the temperature of synthesis. Extrapolation of values for the glass transition temperature obtained by differential scanning calorimetry (at 10°C/min) versus cis/trans composition shows that the pure 1,5-cis and the pure 1,5-trans amorphous linear polymers should have glass transition temperatures (T_g) at -106°C and -91°C, respectively.¹ Because of a reluctance to crystallize, high-cis 1,5-polypentenamer readily gives an amorphous material which displays elastomeric behavior to a lower temperature than do most other hydrocarbons. High-cis 1,5-polymer does crystallize in the course of a week at -40°C. High-trans polymer crystallizes readily; for example, cooling at 1°C/min produces considerable crystalline perfection and gives a material with a melting point (T_m) at about room temperature.¹ (The equilibrium melting point for the 100%-trans polymer has been estimated to be 40°C.¹) Crystallization occurs readily on straining at room temperature. The great current interest in 1,5-trans-polypentenamer is due to its similarity in behavior to natural rubber. Amorphous high-trans 1,5-polymer can be obtained by quenching with liquid nitrogen.¹

TABLE I
Characteristics of 1,5-Polypentenamers

Cis/trans ratio ^a	18/82	95/5	98/2
Inherent viscosity ^a (0.2 g/100 ml toluene, 25°C), dl/g	2.4	2.68	12.2
Polydispersity ^a Deviation from mono- dispersity	none	high MW shoulder	low MW peak
\bar{M}_w/\bar{M}_n	2.04	3.08	7.80
Transition data ^b			
$T_{\text{crystallization}}$, °C	-10 ^d , -19 ^e	—	—
T_{melting} , °C	11 ^f , 5 ^e	—	—
T_g (frequency) ^c			
decreasing temp., °C	-96 (0.64 Hz)	-109 (0.49 Hz)	-109 (0.50 Hz)
increasing temp., °C	-93 (0.63 Hz)	-109 (0.49 Hz)	-110 (0.50 Hz)
$T_{\text{secondary}}$ (frequency) ^c			
decreasing temp., °C	-147 (0.85 Hz)	-141 (0.87 Hz)	-143 (0.74 Hz)
increasing temp., °C	-149 (0.86 Hz)	-143 (0.87 Hz)	-144 (0.74 Hz)

^a Data provided by R. J. Minchak.

^b Determined during the temperature sequence 200° → -180° → 200°C ($\Delta T/\Delta t = \mp 1^\circ\text{C}/\text{min}$).

^c From maxima of logarithmic decrement.

^d From onset of rigidity increase on cooling.

^e From maximum rate of change of relative rigidity parameter.

^f From end of melting as determined by relative rigidity parameter.

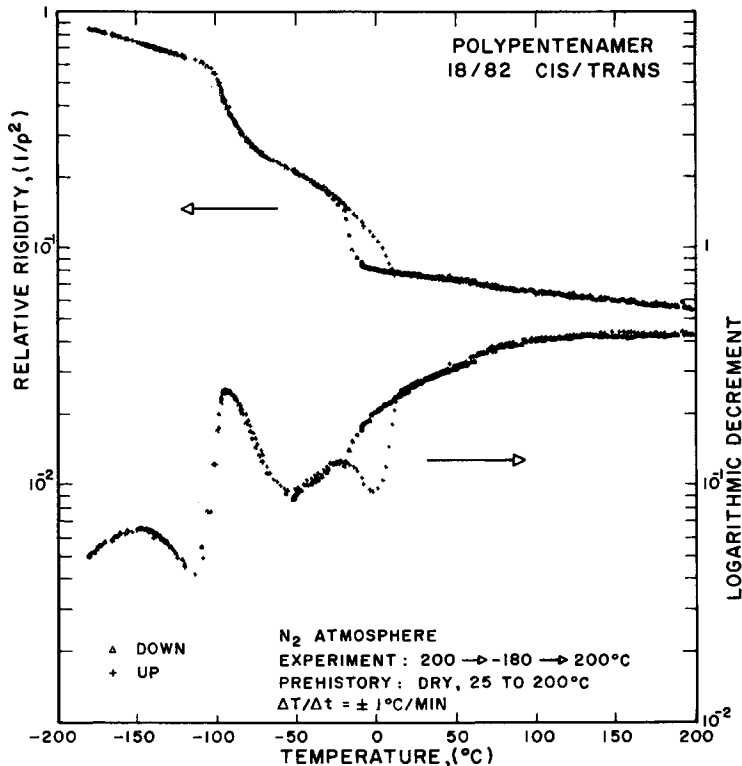


Fig. 1. 18/82 Cis/trans polypentenamer. Thermomechanical behavior: $200^{\circ} \rightarrow -180^{\circ} \rightarrow 200^{\circ}\text{C}$; (prehistory: $25^{\circ} \rightarrow 200^{\circ}\text{C}$); $\Delta T/\Delta t = \pm 1^{\circ}\text{C}/\text{min}$.

A definitive correlation of the transitions with microstructure of uncrossed pentenamer polymers has been made using differential scanning calorimetry.¹ The present communication deals with dynamic mechanical (<1 Hz) measurements of the transitions of unvulcanized gum high-cis and high-trans polymers with measured cis/trans content using a fully automated torsional pendulum apparatus with built-in data reduction facilities,² which employs polymer/glass braid composite specimens containing about 5 mg polymer.³

Three 1,5-polyentenamer samples with different ratios of cis to trans content (i.e., 18/82, 95/5, and 98/2) were provided by Dr. R. J. Minchak of the B. F. Goodrich Company. No vinyl was observed in the polymers. Cis to trans compositions had been determined by measurement of the $10.35\text{-}\mu$ and $13.60\text{-}\mu$ infrared bands according to a method for polybutadienes.⁴ The cis-to-trans ratios, inherent viscosities, and information on the molecular weight distributions obtained from gel permeation chromatography are summarized in Table I. The samples, as received, were stabilized with about 1% di-*tert*-butyl-*p*-cresol which was removed by precipitation of the polymers into methyl alcohol from benzene solutions. After drying under vacuum, they were stored under dry nitrogen in the dark.

Benzene solutions containing 3–5% polymer (g. polymer/ml. solvent) were used at room temperature for impregnating glass braids. Solvent was removed from the mounted specimens in the thermomechanical apparatus by heating to 200°C in dry nitrogen. (Thermogravimetric analyses showed that no weight was lost below 250°C from samples dried in this manner.) Thermomechanical data were then obtained in

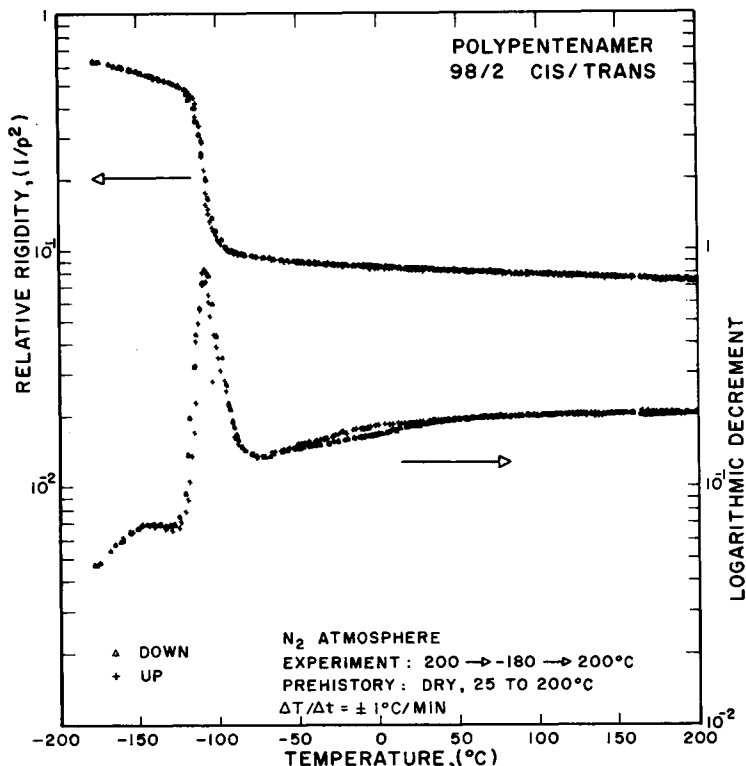


Fig. 2. 98/2 Cis/trans polypentenamer. Thermomechanical behavior: $200^{\circ} \rightarrow -180^{\circ} \rightarrow 200^{\circ}\text{C}$; (prehistory: $25^{\circ} \rightarrow 200^{\circ}\text{C}$); $\Delta T/\Delta t = \pm 1^{\circ}\text{C}/\text{min}$.

nitrogen throughout the temperature sequence $200^{\circ} \rightarrow -180^{\circ} \rightarrow 200^{\circ}\text{C}$. The heating and cooling rate for preparing the specimens and during the subsequent experiments was $1^{\circ}\text{C}/\text{min}$.

The thermomechanical characteristics in nitrogen of the 18/82 and 98/2 cis/trans polypentenamers are shown in Figures 1 and 2 in terms of relative rigidity ($=1/P^2$, where P is the period in seconds of the free oscillations of the damped wave³) and logarithmic decrement. The plots were made with a Calcomp Plotter using the digital readout from the printer of the data analyzer.² A summary of the transition data for the three polymers is included in Table I.

In displaying essentially reversible behavior on cooling and subsequent heating, the two high-cis polymers behave as amorphous materials. A glass transition at about -109°C and a glassy-state transition (T_{ee}) at about -143°C are displayed by each polymer.

The thermohysteresis displayed between the cooling and subsequent heating experiments for the 18/82 cis/trans polymer is considered to be the consequence of crystallization and melting. Crystallization is responsible for the increase in rigidity at about -10°C on cooling, whereas the end of the melting process occurs (on the basis of the rigidity data) by about $+11^{\circ}\text{C}$ on heating. The glass transition temperature is at about -95°C , and a glassy-state transition occurs at about -148°C . Crystallization is not considered to affect the value of the glass transition temperature for polypentenamers with less than about 80% trans content.¹

The present communication reports values for the glassy-state, glass, crystallization, and melting transitions of uncrosslinked polypentenamers which are in reasonable agreement with the literature. Precise comparisons with the literature are rendered difficult in consequence of the different measuring techniques, procedures for data analysis, thermal histories prior to measurement, and microstructures used by investigators. For example, previously reported thermomechanical spectra are for vulcanized high-trans 1,5-polypentamer specimens formed by quenching.⁵ The use of supported specimens, as reported herein, permits thermomechanical data to be obtained on uncrosslinked polymers in a continuous manner in both directions of temperature change, including the region through the load-limiting transition (T_g for amorphous materials, T_m for crystallizable materials). As an attempt at estimating consistency, glass transition temperatures for 18/82 and 98/2 cis/trans polypentenamers, measured by differential scanning calorimetry at 10°C/min heating rate after quenching with liquid nitrogen, are estimated to be -94°C (interpolated value) and -105°C (extrapolated value), respectively (reference 1, Fig. 7). The present results report -93°C and -110°C for the glass transition temperatures (on heating from -180°C) of 18/82 and 98/2 cis/trans polypentenamers for which the cooling and heating rates were 1°C/min. Again, the interpolated value (reference 1, Fig. 9) for T_m of 11°C is to be compared with that reported herein, namely 5° or 11°C (see Table I), for 18/82 cis/trans polypentamer, with the rate of change of temperature being 1°C/min during cooling and subsequent measurement.

In summary, the present communication reports the thermomechanical behavior (<1 Hz) of linear 1,5-polypentenamers with measured cis/trans ratios (i.e., 18/82, 95/5, and 98/2) during the temperature sequence 200° → -180° → 200°C ($\Delta T/\Delta t = \mp 1^\circ\text{C}/\text{min}$) using a fully automated torsional pendulum.

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