

NOTES

Thermomechanical Behavior of "BBB" Polymer

The synthesis of double-stranded, thermally stable, linear polymers has been the main goal in the high-temperature field of plastics during the past fifteen years. Unfortunately, reversible thermal processibility and high-temperature rigidity seem to be incompatible because of irreversible high-temperature thermal reactions and the low extent of fusibility.

One of the more recently developed polymers is "BBB" polymer, which is synthesized¹ from the condensation reaction of naphthalene-1,4,5,8-tetracarboxylic acid and 3,3'-diaminobenzidine, with the repeat unit shown in Figure 1. The geometric structural

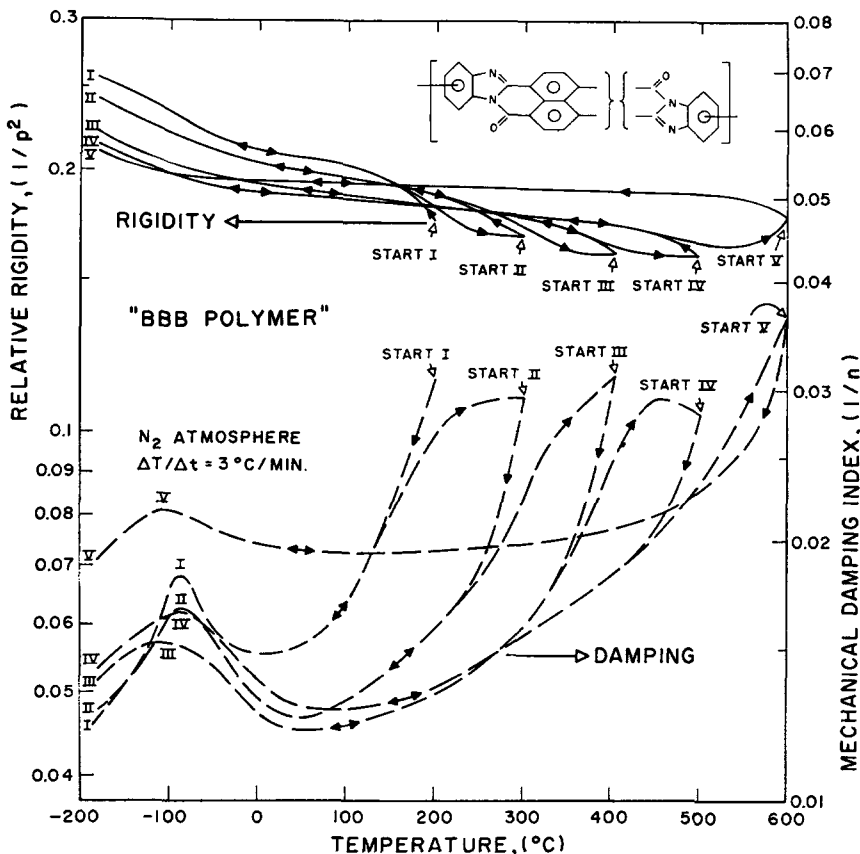


Fig. 1. Thermomechanical behavior of "BBB" polymer during temperature sequence 200° → -180° → 300° → -180° → 400° → -180° → 500° → -180° → 600° → -180° → 130°C.

irregularity of the repeat unit arises from the nonsymmetry of the several competing equivalent reactions.

Unpublished dynamic thermomechanical experiments² in flowing dried nitrogen (at about 1 cps), using the technique of torsional braid analysis,^{3,4} employed specimens that were prepared by impregnating a glass braid with solutions (5% w/v) of polymer in methanesulfonic acid (bp 167°C). The thermomechanical behavior (e.g., see p. 155 of reference 4) of polymers which had been preheated to 300°C in an attempt to remove solvent was interpreted on the basis of irreversible crosslinking reactions which caused the observed increase in rigidity above 450°C. The softening, which occurred prior to 450°C, was considered to be partially the consequence of retained solvent which plasticized the linear polymer and lowered the temperature of the glass transition region. At finite heating rates, the glass transition, T_g , was considered to be inaccessible for the unsolvated polymer because of the thermal reactions. The presence of a low-temperature (< -100°C) damping peak and the fact of solubility and plasticization were the consequence of some degree of molecular flexibility.

The particular solvent, methanesulfonic acid, is difficult to remove via evaporation from the polymer film and reacts with it⁴ in the attempt to remove it thermally. The thermomechanical behavior² could well have been that of reacted polymer.⁴ Therefore, another method involving precipitation (see acknowledgment) rather than thermal evaporation was used to prepare an impregnated polymer/glass braid composite. The results are presented and discussed herein. A solution of "BBB" polymer in methanesulfonic acid was precipitated in a swollen form⁵ upon the braid. The specimen was then repeatedly washed with water to remove acid and subsequently was washed with dilute ammonium hydroxide, water, and anhydrous methanol before being air dried at 120°C for three days. The thermomechanical behavior of the specimen was obtained in flowing dried nitrogen throughout the following sequence of changes in temperature ($\Delta T/\Delta t = \pm 3^\circ\text{C}/\text{min}$ above 25°C, $\Delta T/\Delta t = \pm 1^\circ\text{C}/\text{min}$ below 25°C): 200° → -180° → 300° → -180° → 400° → -180° → 500° → -180° → 600° → -180° → 130°C. The results are shown in Figure 1.

The fact that thermohysteresis is displayed (especially between cooling and subsequent heating) above 100°C demonstrates that irreversible processes are thermally active. Stiffening occurs by crosslinking, completion of intramolecular ring-closing reactions, or physical organizational processes related to crystallization and/or removal of still-retained solvent. The presence of the -100°C glassy-state transition reveals the presence of motion which is not "frozen out" by the high-temperature thermal processes. These results differ only qualitatively from those obtained by using specimens that had been prepared by thermal evaporation.²

In summary, the present communication reports the thermomechanical spectra of a "dried" form of "BBB" polymer throughout the temperature range -180° to 600°C at about 1 cps, points out problems in preparing solvent-free specimens with infusible polymer, and demonstrates application of the technique of torsional braid analysis in investigating thermally irreversible changes by examining thermohysteresis effects.

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