

Optimization of the Thermomechanical Behavior of a Poly(Chromium(III) Trisphosphate)

J. K. GILLHAM, *Polymer Materials Program, Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08540*

Synopsis

A two-component reactive system consisting of a poly(chromium(III) bisphosphate) and dioctylphosphinic acid reacts to form a poly(chromium(III) trisphosphate). Extensive thermomechanical hysteresis is displayed throughout the temperature range -180°C to $>300^{\circ}\text{C}$ by specimens containing filaments of glass. Thermal pretreatment to about 400°C (the limit of thermal stability) eliminated these instabilities. These results correlate with the reported brittle and tough character of films of the poly(chromium(III) bisphosphate) and poly(chromium(III) trisphosphate), respectively. Regardless of thermal history (between 200°C and 400°C), the polymer system displayed three major transition regions: the glass transition centered at about 0°C , another centered at about 230°C , and a third at about -200°C .

INTRODUCTION

The problem of how to determine the thermal and chemical procedures which optimize material behavior is particularly difficult with new and reactive two-component systems. Conversion of a brittle poly(metal bisphosphate) into a tough poly(metal trisphosphate) represents such an example.¹ The method of solving the problem for a particular ratio of the two reactive components, which is presented herein, is based on an examination of thermohysteresis by torsional braid analysis.²

A poly(chromium(III) bisphosphate), $\{\text{Cr}(\text{H}_2\text{O})(\text{OH})[\text{OP}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{O}]_2\}_n$, with number-average molecular weight $\bar{M}_n = 60,000$, formed brittle films when cast from solution (CH_2Cl or *o*-dichlorobenzene). However, flexible and tough films could be formed by heating at 120°C a solution-cast mixture of the linear polymer and equal moles (per polymer repeat unit) of dioctylphosphinic acid. Compositions approximating the trisphosphate were formed upon heating at 150°C - 175°C for 2-3 hr.³

The reaction mechanism between the polymer and acid has been postulated to involve two steps³ each freeing 1 mole of water. Intra- and intermolecular reactions between the reactive groups would lead to a linear and a network structure, respectively (Fig. 1). A distinction between a truly linear and a network trisphosphate structure may possibly be made on the basis of solubility studies.

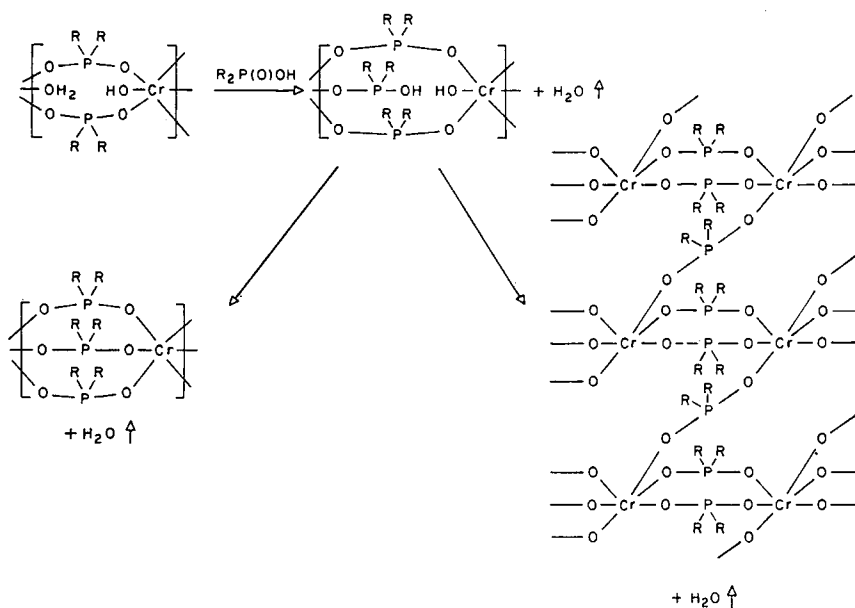


Fig. 1. Competitive intra- and intermolecular reactions in the conversion of poly(chromium(III) bisphosphinate) to poly(chromium(III) trisphosphinate).

EXPERIMENTAL

The two-component system was examined in dry nitrogen by torsional braid analysis,² the data for which are presented in Figure 2. For purposes of clarification, the three sets of data (curves I, II, and III) are displaced vertically on the logarithmic scales. The experimental procedures for each follow:

Thermal History for Curve I. A 20% solution in chloroform was advanced by heating at 45°C for 1½ hr. (Subsequent storage was in a refrigerator.) Chloroform was removed from the solution-impregnated glass braid in heating to 200°C in heating nitrogen at 3°C/min in the apparatus.

Curve I:

200°C → -180°C → 300°C in dried nitrogen,

$\Delta T/\Delta t = \pm 2^\circ\text{C}/\text{min}$ ($T < 25^\circ\text{C}$); $3^\circ\text{C}/\text{min}$ ($T > 25^\circ\text{C}$).

Thermal History for Curve II. A 20% solution in *o*-dichlorobenzene (bp 180°C) was formed and advanced to a thick solution before being used (and stored in a refrigerator). Solvent was removed from the solution-impregnated glass braid in heating to 300°C in nitrogen at 3°C/min in the apparatus.

Curve II:

300°C → -180°C → 400°C in dried nitrogen,

$\Delta T/\Delta t = \pm 2^\circ\text{C}/\text{min}$ ($T < 25^\circ\text{C}$); $3^\circ\text{C}/\text{min}$ ($T > 25^\circ\text{C}$).

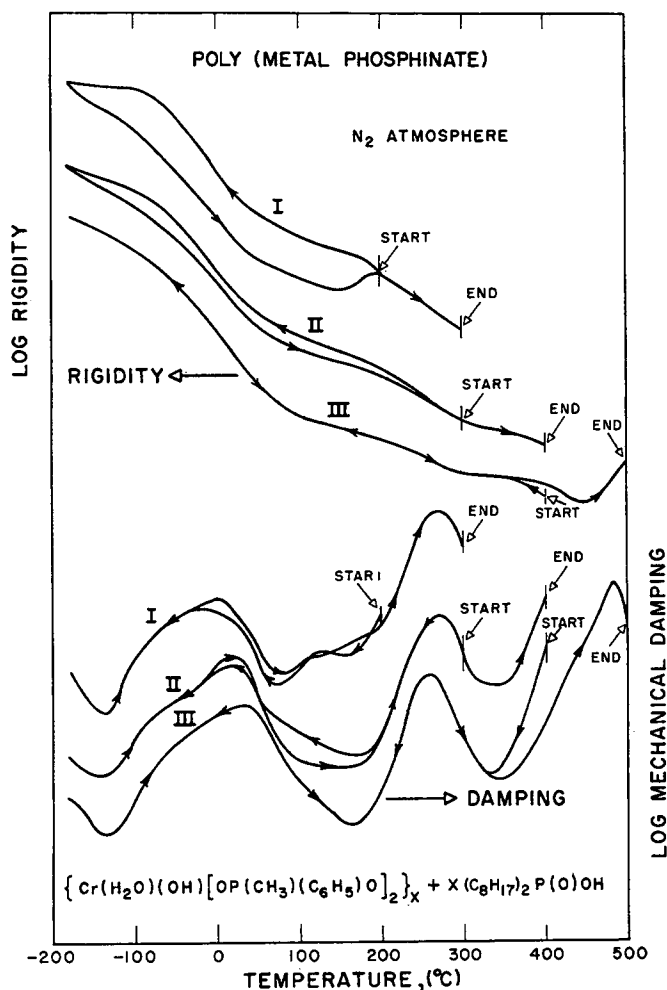


Fig. 2. Thermomechanical behavior of the poly(chromium(III) phosphinate) system.

Thermal History for Curve III. Same as for Curve II (same specimen) including $300^{\circ}\text{C} \rightarrow -180^{\circ}\text{C} \rightarrow 400^{\circ}\text{C}$.

Curve III:

$400^{\circ}\text{C} \rightarrow -180^{\circ}\text{C} \rightarrow 500^{\circ}\text{C}$ in dried nitrogen,
 $\Delta T/\Delta t = \pm 2^{\circ}\text{C}/\text{min}$ ($T < 25^{\circ}\text{C}$); $3^{\circ}\text{C}/\text{min}$ ($T > 25^{\circ}\text{C}$).

RESULTS AND DISCUSSION

The polymer system displays extensive hysteresis in mechanical rigidity between cooling to -180°C and subsequent heating to temperatures below 400°C (curves I and II). The lower the maximum temperature in an hysteresis cycle, the greater the differences between the results for

cooling and heating. It appears that the mechanical properties are stabilized by preheating the system to close to 400°C (curve III). In contrast to the behavior of the modulus, the mechanical damping changes but little with pretreatment in the temperature range 200° to 400°C.

The trisphosphinate and the precursor polymers display major transitions centered at about 0° and 250°C. The form of the modulus curves suggests that the former is a very broad glass transition with glass-like properties being displayed only below -100°C and leathery behavior being displayed at room temperature. A glassy state transition is rendered apparent by the high damping at -190°C; relaxations which precede degradation are made apparent by the rising damping above 350°C. The trisphosphinate is stable to above 400°C in nitrogen: the system loses less than 3% of its solvent-free weight in being heated to 400°C, and films remain intact and green to above 400°C.

The thermohysteresis in mechanical behavior can be explained by considering increases in modulus (to 400°C) (which counteract thermal softening and close the hysteresis loops) as being the consequence of chemical reaction—presumably of changing the bisphosphinate to trisphosphinate. Since the damping curves are not sensitive to these reactions, the latter do not severely restrict the mobility of the submolecular motions. Extensive crosslinking is therefore not of prime importance, since this would significantly alter the temperature of the transitions and alter the loss curves. The reaction scheme proposed above involving change of double-stranded flexible ($-\text{O}-\text{P}-\text{O}-$) linkages to triple-stranded flexible linkages or to a network would be expected to produce an increase in elastic modulus and yet not necessarily produce a change in localized submolecular mobility and in the dissipative modulus (damping).

The decrease in rigidity, which is the other factor producing the hysteresis in the modulus curves, presumably arises from microcracking of the composite specimens. In contrast to the bisphosphinate, the trisphosphinate can withstand the thermal stresses induced in the composite specimen by changes (decreases) in temperature.

Determination of thermal procedures which give optimal material behavior in the polyphosphinate was aided by the ability to determine mechanical behavior with both increasing and decreasing temperature modes. In contrast with most mechanical apparatus, the author's torsional pendulum² is suited to this type of experiment.

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References

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