

Poly(dichlorophosphazene): Thermomechanical Behavior

This report presents dynamic mechanical data (~ 1 Hz) for the inorganic polymer poly(dichlorophosphazene), $(\text{NPCl}_2)_n$, in the temperature range of $-180^\circ \leftrightarrow 350^\circ\text{C}$ in helium for the purposes of locating transitions and investigating the effect of high temperature on both the transitions and the thermomechanical behavior. The technique used was torsional braid analysis (TBA), which uses a composite of polymer and inert support as the specimen in a torsional pendulum experiment.^{1,2}

Linear poly(dichlorophosphazene) was obtained by heating hexachlorotriphosphazene, $(\text{NPCl}_2)_3$, in an evacuated glass tube at a maximum temperature of 270°C for 24 hr, extracting low molecular weight species with hexane, and drying in vacuo.^{3,4} Specimens for the thermomechanical experiments were made by impregnating heat-cleaned glass braids (length 2 in.) in 10% solutions (g polymer/ml benzene). Solvent was removed after mounting the specimen in the TBA apparatus by heating to 150°C in flowing helium. Oscillations were then induced intermit-

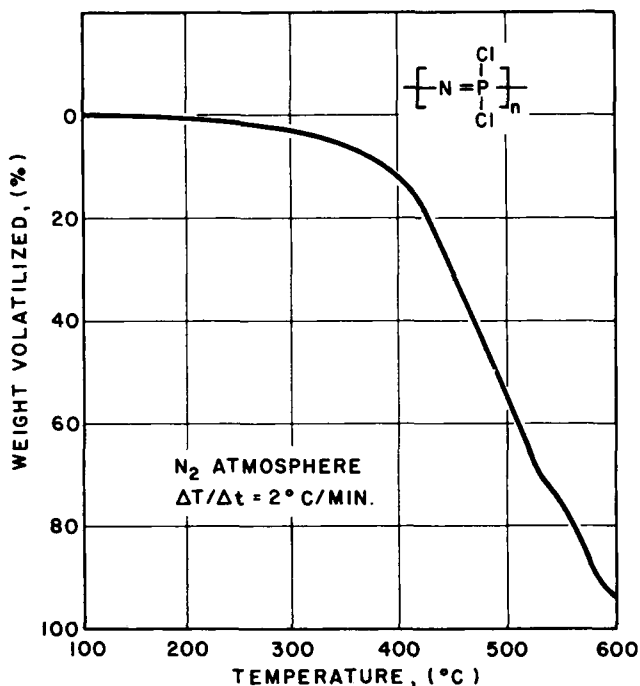


Fig. 1. Thermogravimetric analysis of poly(dichlorophosphazene) ($100^\circ \rightarrow 600^\circ\text{C}$). The pre-history of the specimen involved heating from 25° to 150°C at $2^\circ\text{C}/\text{min}$ immediately prior to the experiment.

tently during the temperature sequence $150^\circ \rightarrow -180^\circ \rightarrow 250^\circ \rightarrow -180^\circ \rightarrow 300^\circ \rightarrow -180^\circ \rightarrow 350^\circ \rightarrow -180^\circ \rightarrow 350^\circ\text{C}$ in order to obtain the thermomechanical data of the experiment. The rate of change of temperature for heating and for cooling modes was $2^\circ\text{C}/\text{min}$ above 0°C and $1.5^\circ\text{C}/\text{min}$ below 0°C for drying and the experiment. The weight loss-versus-temperature plot of Figure 1 was obtained in nitrogen at $2^\circ\text{C}/\text{min}$ using a thermogravimetric analyzer (du Pont Model 900) after heating the polymer in situ to 150°C at $2^\circ\text{C}/\text{min}$.

The fully automated TBA apparatus controlled a repetitive sequence which consisted of alignment of the optical transducer by slow rotation of the pendulum head, initiation of free oscillations by step displacement of the pendulum head, and computation and immediate printout on

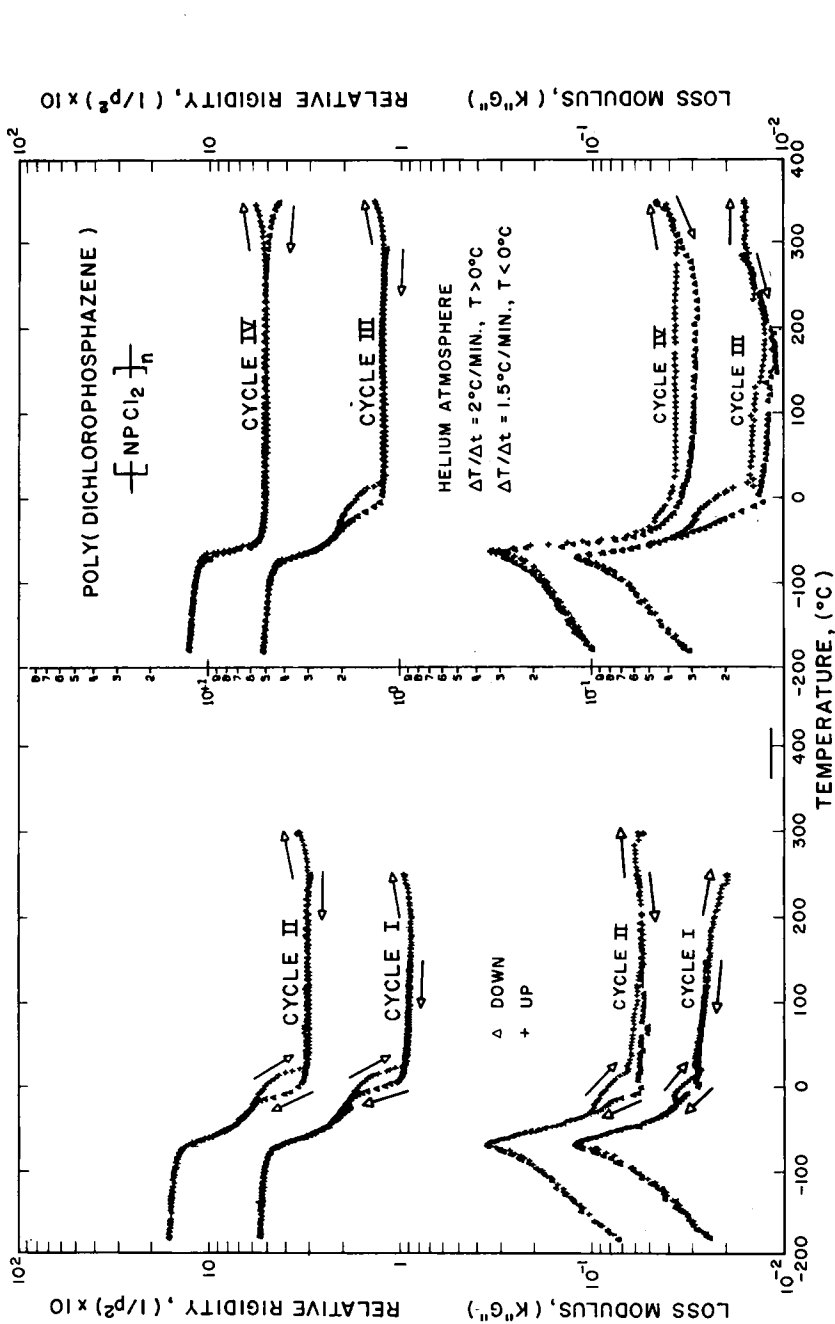


Fig. 2. Thermomechanical behavior of poly(dichlorophosphazene) during temperature sequence $150^\circ \rightarrow -180^\circ \rightarrow 250^\circ \rightarrow 300^\circ \rightarrow -180^\circ \rightarrow 300^\circ \rightarrow -180^\circ \rightarrow 350^\circ \rightarrow -180^\circ \rightarrow 300^\circ C$. The data are presented in four sets corresponding to four segments of the continuous sequence (i.e., cycle I, $150^\circ \rightarrow -180^\circ \rightarrow 250^\circ C$; cycle II, $250^\circ \rightarrow -180^\circ \rightarrow 300^\circ C$; cycle III, $300^\circ \rightarrow -180^\circ \rightarrow 350^\circ C$; cycle IV, $350^\circ \rightarrow -180^\circ \rightarrow 300^\circ C$). For purposes of presentation, the data for cycles II and IV have been displaced vertically by $\log_{10} 3.00$. The prehistory of the specimen involved heating from 25° to $150^\circ C$ immediately prior to the experiment.

paper tape of temperature (mV), logarithmic decrement Δ , and period P (sec) for each damped wave.⁵ Two parameters² were plotted versus temperature using a computer-driven plotter (Calcomp 565): the relative rigidity $1/P^2$ is a direct measure of the in-phase "storage" shear modulus G' of the composite specimen; a proportional measure $K''G''$ of the out-of-phase "loss" shear modulus G'' was computed as the product of the logarithmic decrement and relative rigidity (note: $G'' \approx G'\Delta/\pi$). Four sets of data appear in Figure 2 corresponding to segments of the continuous sequence of change in temperature. These are: cycle I, $150^\circ \rightarrow -180^\circ \rightarrow 250^\circ\text{C}$; cycle II, $250^\circ \rightarrow -180^\circ \rightarrow 300^\circ\text{C}$; cycle III, $300^\circ \rightarrow -180^\circ \rightarrow 350^\circ\text{C}$; cycle IV, $350^\circ \rightarrow -180^\circ \rightarrow 350^\circ\text{C}$.

The glass transition temperature T_g occurs at about -68°C (0.62 Hz) as measured by the peak in the loss curve (Fig. 2, cycle I). Its location and intensity are barely affected even after heating to 350°C . The thermohysteresis displayed in the vicinity of 0°C (cycles I, II, and III) marks the region of crystallizing/melting. The melting transition T_m in the initial polymer (cycle I) is 13°C (measured by the end of the abrupt change in the relative rigidity during heating), and the crystallization transition (T crystallization) in the initial polymer (cycle I) occurs at -10°C (measured by the inflection of the relative rigidity on cooling). Crystallization and melting occur after heating to 300°C but are absent after heating to 350°C . A glassy-state transition appears to be present below the glass transition (cycles II, III, and IV); however, the assignment of a transition temperature to it on the basis of the loss data is not warranted.

The level of the storage modulus increases above 200°C in a process which continues to the end of the experiment (350°) and which is observed particularly by the increase in relative rigidity at the end of each cycle. The level of the loss modulus above 20°C decreases after heating to 250°C and progressively decreases after heating to higher temperatures. The increase in storage modulus and concomitant decrease in loss modulus above the glass transition temperature are attributed to progressive chemical crosslinking in an elastomeric network. Although preheating to 350°C renders the material amorphous, the value of the glass transition temperature is unaffected.

The decrease in relative rigidity in the glassy state which is noted particularly after heating to 350°C (e.g., cf. cycle II and cycle IV) is caused by changes in the geometry of the specimen (shrinkage). Evidence for this is obtained from the results of thermogravimetric analysis (Fig. 1).

The literature⁶ comments that poly(dichlorophosphazene) crosslinks and turns black when heated at 300°C in evacuated sealed tubes and that heating from 260° to 400°C in helium produces volatile cyclic oligomers, $(\text{NPCl}_2)_{3-9}$. The specimen of the present experiment changed from white to yellow in being heated to 350°C in nitrogen.

In summary, on the basis of thermomechanical data obtained under defined rates of change of temperature, linear poly(dichlorophosphazene) displays a glass transition at about -68°C (0.6 Hz), a melting transition at about 13°C , and a crystallization transition at about -10°C . The high value of 0.72 for the ratio T_g/T_m ($^\circ\text{K}/^\circ\text{K}$) of the symmetrical polymer is noteworthy. Progressive heating from 180° to 350°C increases the storage modulus and decreases the loss modulus in the rubbery region through a process which is attributed to crosslinking which, after heating to 350°C , affects the ability of the polymer to crystallize but does not significantly affect the temperature assignment for the glass transition.

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