PROPERTIES AND PHASE TRANSITIONS IN POLYPHOSPHAZENES

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PROPERTIES AND PHASE TRANSITIONS IN POLYPHOSPHAZENES

Lecture Abstract presented at the Japanese High Polymer Conference

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by

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Properties and Phase Transitions in Polyphosphazenes

J. H. Magill

Technical

From July 28, 1987

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An overview of our work dealing with thermal, physical and related properties of polyphosphazenes of academic and technological interest.
Polyphosphazenes were first synthesised towards the end of the last century, but it was not until the mid 1960 that linear polyphosphazenes were prepared (1). Now, a wide variety of polymers and copolymers with alkoxy, aryloxy and aminoxy groups have been synthesised (see Figure 1). Recently, side chains have been connected directly to the backbone phosphorus modifying physical properties considerably (2). Variations in side group chemistry enables a wide span in properties to be covered ranging from glass temperatures approaching -100°C to melting points well above 300°C in some systems. Thermotropic behavior persists over a range of temperature from \(T_m\) to \(T(1)\) depicts the range of this disordered phase seen in Figure 2. Interestingly a useful empirical relationship (Figure 3) has been established (3) involving \(T_g\), \(T(1)\) and \(T_m\). The thermotropic range \([T_m-T(1)]\) scales with the side group chemistry for these polymers.

At this point it is appropriate to digress to some practical aspects of these polymers since my polyphosphazene research was first involved with the thermal stability and toxicity of these polymers. The lower toxicity of the degradation products of halogen-free polyphosphazenes (i.e. those closest to D.FIR in Figure 4) proved to be appealing, although it was also realized that specimens with halogen substituents normally raise the oxygen index of polymers generally, which is also desirable (4). This dichotomy may only be resolved through an appropriate hazard index involving critical parameters for the test evaluation. Analytical and animal testing procedures (5) established
patterns of behavior for polyphosphazenes in relation to other commercial polymers. It was further determined that degradation mechanisms were also important in determining thermal stability. For example, alkoxy phosphazenes degraded primarily via a "chain unzipping" process leaving little or no residue, whereas aryloxyphosphazenes mostly disintegrated through random chain scission (involving some chain transfer too) leaving a substantial residue (6). Materials that characteristically leave relatively large amounts of intumescent residues (~30 wt % or more) are invariably useful as substrate coatings since heat transfer is curtailed through the creation of such a layer. Poly(aminoxyphosphazenes) are most liable to cross-link creating the largest quantities of char in these polymers. Polyphosphazenes containing additives, have also been studied but exhibited no synergism between additives and polymers (7).

Flammability and flame spread are important commercially but are not well understood. Anyhow, our purpose here was to attempt to establish a useful potential hazard index scale (PHI) for comparing polyphosphazenes with other commercial plastics. Several such relationships have been established empirically (8). In our case the relation

\[
\text{PHI} = \left( \frac{W_{\text{max}}}{D_m} \right) \frac{(\Delta H_c)}{(L_{C50})} \text{O.I.} \left( T_{\text{max}} \right)
\]

proved useful where \( W_{\text{max}} \) is the maximum weight loss over 100°C interval, \( D_m \) is the smoke density, \( \Delta H_c \) is the heat of combustion, \( L_{C50} \) is the 50% mortality value O.I. is the oxygen index and \( T_{\text{max}} \) the temperature where maximum weight loss occurs. For comparative testing this relationship showed promise whenever a reference material like Douglas Fir was involved (see Table 1). However, it proved to experimentally demanding because of the many parameters involved.
The thermotropic or disordered nature of many polyphosphazenes usually covers a relatively wide range of temperature and imposes a degree of complexity greater than that which exists in semicrystalline homopolymers alone. Before turning to some of these results, it is important to note that short alkyl groups connected directly to the backbone phosphorus destroys thermotropic behavior.

Transitional changes in polyphosphazenes have been studied extensively by thermal techniques. Current investigations are concerned with the coexistence of different morphological forms and phases formed from the melt and from solution. Strikingly, the disappearance of $T_g$ after heat treatment close to or above $T_m$ is accompanied by a substantial increase in sample crystallinity (curve 5 in Figure 5) above 90%, compared to the level found in solution grown crystals (~40%). This behavior is elaborated upon in other papers (9,10) presented at this conference.

X-ray structure diffraction alone has not been very useful in establishing the many polymorphic forms found recently in polyphosphazenes by electron microscopy and diffraction (11,12). However, physical differences sometimes arise between thin and thick specimens for morphological and other reasons relating to the framework of heat treatment used in sample preparation. For instance, Figure 6 shows the crystal modifications found for poly(bisphenoxyphosphazene)(13). The lamellar crystals formed from solution ($\alpha$-form) transform upon heating into a 2D hexagonal 6-form which may be quenched in this disordered state(11). Only when it is annealed just below $T(1)$ does it crystallize as a 3D hexagonal form - designated as $\epsilon$-form. However, when the $\alpha$-form is heated through $T(1)$ (but $<T_m$) and cooled again, it is further stabilized to a $\lambda$ chain-extended form (14).
Tensile and dynamic mechanical properties also undergo significant changes on passing through the T(1) transition which represents an upper limit to the engineering properties of polyphosphazenes. Figure 7 illustrates the change in dynamic moduli \( E' \) (storage) and \( E'' \) (loss) as well as the significant variation in \( \tan \delta \) at \( T_g \) and \( T(1) \) respectively\(^{15}\). Consistent with these properties is a change in density which is about 6% at each of \( T(1) \) and \( T_m \) even though the corresponding change in thermal and associated properties is much less\(^{16}\). Creep, refractive index and other properties also exhibit transitional behavior.

Another important feature is the kinetics of phase transformations in polyphosphazenes as measured by DSC \(^{17}\) and X-ray scattering (small and wide angle) techniques\(^{18}\). The transformation from the isotropic phase to the 2D form below \( T_m \) is too rapid to follow even using synchrotron radiation. However, the isothermal 2D to 3D transition associated with \( T(1) \) has been investigated successfully by both methods. The extent of this phase change followed by thermal analysis is dependent upon undercooling. The half-time values (Figure 8) of the transformations are independent of the X-ray scattering technique even though each has inherently different sensitivities. Phase kinetics are internally consistent, and this broad properties approach serves as an overview of our work which will be discussed in more detail in the lecture.

**Acknowledgement**

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References

Figure 1
Synthesis Scheme

Figure 2  Transitions in polyphosphazenes

Figure 3  Correlation between T_g, T(1) and T_m
Figure 4 LC<sub>50</sub> values

Figure 5 T<sub>g</sub> and T<sub>1</sub> transitions in Poly(biophenoxy-phosphazene)

Figure 6 Phase transitions in Poly(bisphenoxy-phosphazene)
Figure 7  Phase Transitions in Poly (bistrifluoroethoxyphosphazene)

Figure 8  Crystallization rates for 2D → 3D Transition in Poly(bis-p-methylphenoxyphosphazene)
<table>
<thead>
<tr>
<th>MATERIALS DESCRIPTION</th>
<th>T</th>
<th>$\Delta H_{c}$ (kJ/g)</th>
<th>$D_m$</th>
<th>$T_{max}$ (f)</th>
<th>$W_{max}$ (b)</th>
<th>LC50 (g/m$^3$)</th>
<th>PHI (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM21, flexible polyurethane foam</td>
<td>18</td>
<td>28.2(a)</td>
<td>204(a)</td>
<td>713(3)</td>
<td>74</td>
<td>13.0(a)</td>
<td>28</td>
</tr>
<tr>
<td>GM25, High resilience flexible polyurethane foam</td>
<td>27</td>
<td>26.6(a)</td>
<td>127(a)</td>
<td>693(a)</td>
<td>65</td>
<td>8.3(a)</td>
<td>17</td>
</tr>
<tr>
<td>GM31, rigid polyurethane foam with fire retardants</td>
<td>24</td>
<td>26.4(a)</td>
<td>775(a)</td>
<td>593(a)</td>
<td>30</td>
<td>8.2(a)</td>
<td>60</td>
</tr>
<tr>
<td>APN, polyaeryloxyphosphaene(d)</td>
<td>32</td>
<td>28.0(a)</td>
<td>180</td>
<td>693</td>
<td>15</td>
<td>23.8(2)</td>
<td>2</td>
</tr>
<tr>
<td>and $\text{NH}_2(\text{OH})_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Douglas Fir</td>
<td>22</td>
<td>19.0</td>
<td>160</td>
<td>623</td>
<td>30</td>
<td>63.7(1)</td>
<td></td>
</tr>
</tbody>
</table>

- a: estimated value.
- b: maximum weight loss over any 100°C interval.
- c: value relative to Douglas Fir
- d: phenoxy-ethylenepolycopolymer
- e: reference 633
- f: sample temperature where maximum weight loss occurs.

**Table 1** Potential Hazard Index Values for Selected Polymers
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