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Thermal degradation of polystyrene – unperturbed chain dimensions of degraded polymers*)

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Summary

Intrinsic viscosity and viscosity average molecular weight data of thermally degraded polystyrene and its co-polymers have been used to determine the unperturbed chain dimensions. Analysis of these data according to Stockmayer and Fixman equation suggests that probably during thermal degradation in air no branched polymers are formed and the chain dimensions \([<r_0^2>/\bar{M}_o]^{1/2}\) remain as for the linear polymers.

Key words

Unperturbed chain dimensions, Thermal degradation, Polystyrene, High impact polystyrene, SAN, ABS, Steric factor.

Introduction

The thermal degradation of polystyrene (PS) in air is mainly a random chain scission due to the presence of thermolabile weak links in the polymer backbone (1). These thermolabile links are attacked by oxygen and peroxidic free radicals are formed which are unstable. These free radicals produce ketonic or peroxyester type structures on degradation. Similar observations were also made during oxidative \(\gamma\)-radiolytic degradation at low dose (2). The extent of degradation was determined by measuring the viscosity of the polymers in suitable solvents. The viscosity in various solvents can also be used to evaluate hydrodynamic parameters and unperturbed chain dimensions of the polymer chains. Thus in present communication we have analysed these data to determine the chain dimensions of the degraded PS and its copolymers in order to investigate the conformational changes, if any, during thermal degradation.

Unperturbed chain dimensions

The intrinsic viscosity, \([\eta]\), in a good solvent is related to the viscosity average molecular weight, \(\bar{M}_o\), by the relation (3),

\[
[\eta] = K \bar{M}_o^{\alpha} \alpha
\]

where \(\alpha\) is the viscosity expansion factor and \(K\) is Mark-Houwink constant. In a Theta solvent (\(\Theta\)-solvent) the factor \(\alpha\) is unity and equation [1] reduces to

\[
[\eta] = K_\Theta \bar{M}_o^{\frac{1}{2}}
\]

where \(K_\Theta\) is Flory constant and is given by

\[
K_\Theta = \phi_0 [<r_0^2>/\bar{M}_o]^{3/2}.
\]

In equation [3], \(\phi_0\) is universal viscosity constant, which has a theoretical value of \(2.86 \times 10^{23}\) cgs units, and \(<r_0^2>\) is the mean square end-to-end distance. Number of theoretical relations have been used to estimate \(K_\Theta\) from the knowledge of \([\eta]\) and \(\bar{M}_o\) (4–10). Recently Reddy et al. (11) have estimated unperturbed dimensions using these graphical methods for polystyrene and concluded that simplest Stockmayer-Fixman relation (6)

\[
[\eta]/\bar{M}_o^{\frac{1}{2}} = K_\Theta + 0.51 \phi_0 B \bar{M}_o^{\frac{1}{2}}
\]

*) Work done at Gorakhpur University, Gorakhpur, India.
gave the value of Flory constant closer to the value in a Θ-solvent. In equation [4], B is the thermodynamic interaction parameter and is related to binary cluster integral for a pair of chain segment, β, of mass m as

\[ B = \beta/m. \]  

Therefore, the unperturbed dimensions of thermally degraded polymers are estimated by using equation [4].

**Results and discussion**

Using following equations [6–9] \( \bar{M}_v \) of thermally degraded polystyrene (PS), high impact polystyrene (HIPS), styrene-acrylonitrile co-polymer (SAN) and acrylonitrile-butadiene-styrene co-polymer (ABS) were computed and have been reported in references 1 and 13.

\[
[\eta] = 0.94 \times 10^{-4} \; \bar{M}_v^{0.74} \text{ PS at 30 °C in benzene} \tag{6}
\]

\[
[\eta] = 1.13 \times 10^{-4} \; \bar{M}_v^{0.73} \text{ HIPS at 25 °C in benzene} \tag{7}
\]

According to equation [4], \( [\eta]/\bar{M}_v^{0.5} \) is plotted as a function of \( \bar{M}_v^{0.5} \) and the plots for PS, HIPS, SAN, and ABS are shown in figure 1. All the four plots are straight lines. These fit the data at all temperatures of the study. Using the values of the intercepts and slopes from figure 1, the thermodynamic interaction parameter B and Flory constant, \( K_\Theta \), are recorded in table 1. The

\[
[\eta] = 3.6 \times 10^{-4} \; \bar{M}_v^{0.62} \text{ SAN at 30°C in butanone-2} \tag{8}
\]

\[
[\eta] = 3.6 \times 10^{-4} \; \bar{M}_v^{0.62} \text{ ABS at 30°C in butanone-2} \tag{9}
\]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>( K_\Theta \times 10^4 ), dl/gm.</th>
<th>( B \times 10^{27} ), cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>Benzene</td>
<td>8.5</td>
<td>1.51</td>
</tr>
<tr>
<td>HIPS</td>
<td>Benzene</td>
<td>10.0</td>
<td>1.30</td>
</tr>
<tr>
<td>SAN</td>
<td>Butanone-2</td>
<td>12.6</td>
<td>0.46</td>
</tr>
<tr>
<td>ABS</td>
<td>Butanone-2</td>
<td>11.4</td>
<td>0.66</td>
</tr>
</tbody>
</table>