Polymere

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Effects of Degree of Crystallinity upon Dielectric Behaviors in Some Aromatic Polyesters

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With 25 figures and 2 tables
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Introduction

Recently, the dielectric behaviors of the amorphous polymers have been investigated by many authors and the various relationships between the dielectric behaviors and the chemical structures have been established rather in details. The dielectric behaviors of the semicrystalline polymers, however, depend on the fine structures as well as on the chemical structures of these polymers. It is, therefore, important to know how the dielectric properties are affected by the fine structures. Among the quantities which define the fine structures of semi-crystalline polymers, the degree of crystallinity seems to be the most important one. The first step to clarify the relationship between the dielectric properties and the fine structures is, therefore, to investigate how the dielectric properties depend on the degree of crystallinity. For this purpose, it is desirable to use the semi-crystalline polymer whose degree of crystallinity can be altered as wide as possible. Polyethylene terephthalate (PET) or polyparaethylene oxybenzoate (PEOB) seems to be one of the most desired ones.

The dielectric behaviors of PET have already been measured by Reddish (1), Krum and Müller (2), Saito and Nakajima (3), Heilwege and Langbein (4) and others. As a result of these measurements, two kinds of the dielectric absorption have been found, that is, the higher and the lower temperature absolutions. These two absorptions are confirmed to come from the amorphous part. The apparent activation energy of the higher temperature absorption is much larger than that of the lower temperature absorption. With the increase of the degree of crystallinity, the peak of the higher temperature absorption moves to the higher temperature side and the shape of the higher temperature absorption becomes broader.

The mechanism of the higher temperature absorption has already been established (1). The higher temperature absorption is attributed to the reorientation of the permanent dipoles due to the segmental micro-Brownian motions of the main chains. On the other hand, the mechanism of the lower temperature absorption has not yet been confirmed. Reddish (1) suggested that the lower temperature absorption is attributed to the response of the OH dipoles at the ends of the main chains. His suggestion seems, however, to be inconsistent with observations and then we expressed a different view in the previous papers (5, 6, 7). We considered that the lower temperature absorption might be attributed to the local visco-elastic re-orientation of the permanent dipoles of the main chains in the vicinities of their equilibrium positions.

In this paper, we discuss the dielectric properties of PEOB together with those of PET. Since PEOB has similar dielectric properties and chemical structures to PET, it seems to be reasonable to assign the same molecular mechanisms as those of PET for the two dielectric absorptions of PEOB.

We shall discuss the effects of the degree of crystallinity upon the dielectric behaviors of PET and PEOB from such a view for the molecular mechanism of these absorptions.

Experimental

The samples of polyethylene terephthalate (PET) and polyparaethylene oxybenzoate (POEB) used in this experiment were provided from Teikoku Jinken Co. Ltd. and Kokoku Jinken Co. Ltd. respectively. The samples with different degrees of crystallinity are prepared by annealing the amorphous samples at different temperatures, where the annealing is made till the degree of crystallinity of each sample reaches to the equilibrium value at that temperature. The degree of crystallinity of each sample is calculated from its density (8, 9) and shown in table 1.
Table 1

The degree of crystallinity of each sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>PET I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>PEOB I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>degree of crystallinity</td>
<td>0.05</td>
<td>0.32</td>
<td>0.41</td>
<td>0.51</td>
<td>0.27</td>
<td>0.34</td>
<td>0.38</td>
<td></td>
</tr>
</tbody>
</table>

The method of measurement is similar to the previous report (10).

Results

Every sample of PEOB also shows two kinds of the dielectric absorptions as well as PET. For simplicity, we shall call the higher temperature absorption the $\alpha$-absorption and the lower temperature absorption the $\beta$-absorption. As the examples of the observed results, the frequency dependences of $\varepsilon''$ for PET-I, PET-IV, PEOB-I and PEOB-IV are shown in fig. 1 to 8.