Nuclear Substituent Effects on Hetero-cycle Containing Rigid-rod Polyimide

SEI-ICHI MUKAI

Mitsubishi Chemical Corporation, Yokohama research center
Yokohama 227, JAPAN

The nuclear-substituent effects on rigid-rod polyimide was discussed, through the benzobisthiazole containing poly p-phenylene pyromelliteimide (PIBT)-related system. The noticeable effect was observed in terms of the retrogressive gel forming tendency through the chemical cyclization of polyamide acid solution. The solubility-up of the partially imidized precursors is derived from the enhancement of the backbonechains' motional freedom and assumed to be effective for the backbone chains' re-alignments to build up the high-modulus ordered structures. Such assumption is certificated by the tensile improvement in PIBT-2-CH₃ (2-CH₃ -substituted) cast films as shown below, or the WAXD profile which is analogous to that of PIBT(non-substituted) uniaxially drawn films.

Young's modulus / Tensile strength for cast films

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>E (GPa)</th>
<th>Tensile Strength (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIBT (non substituted)</td>
<td>16</td>
<td>10.1</td>
</tr>
<tr>
<td>PIBT-2-CH₃ (2-methyl substituted)</td>
<td>21</td>
<td>10.4</td>
</tr>
</tbody>
</table>

Keywords; nuclear substitution, hetero-cycle containing rigid-rod polyimide, mechanical properties

1. Introduction
The mechanical evaluation of theoretical modulus for skeletal units has so far been an effective approach for the design of high-modulus polymeric materials. For example, 390 GPa for poly p-phenylene benzobisthiazole (PPBT) by W. Adams et al. or 505 GPa for poly p-phenylene pyromelliteimide (PPPI) by M. Kobayashi et al. [1], [2]

These numerical values are very advantageous for the rough mechanical estimation of the neighboring analogous skeletal units.

For example, polyimide p-phenylene benzobisthiazole (PIBT) is composed of the in-series combination of PPBT and PPPI unit as shown below. In other words, the following equation, based on the in-series mechanical model of two strong springs, can be applied there. [2]

\[
\frac{1}{K} = \frac{1}{K_1} + \frac{1}{K_2}
\]

\[
K_1 = \frac{E_1 S_1}{L_1}
\]

\[
E_1 \quad \text{theoretical modulus}
\]

\[
S_1 \quad \text{effective cross sectional area}
\]

\[
L_1 \quad \text{repeating unit length}
\]

As the result, the modulus as high as 430 GPa is estimated for PIBT, exceeding the value of PPBT. This means the introduction of p-phenylene pyromellite imide unit is very effective for the design of high-modulus polymeric materials.
But it is not all the merit coming from the imide-type modification. Generally, polyimides are synthesized via organic solvent-soluble intermediates like polyamide acids (PAA) or polyamideacid esters (PAE). It means that the fabrication can be carried out via such easily processable intermediates, which is industrially very advantageous. But the further important is on how easily such high mechanical potentials can be extracted through the actual molding.

In this paper, PIBT and its nuclear substituted derivatives are exemplified as high-modulus polymeric materials and these cast or uni-directionally drawn films are mechanically and thermally evaluated. From these results, what are essential for the high-mechanical potentials to be macroscopically extracted can get clarified.

2. Experimental
2.1 Materials
The corresponding benzobisthiazole containing diamine must be prepared for the synthesis of PIBT-related intermediates. In this paper, as an exemplary case, the synthesis of 2,6-bis(4-amino-2-methylphenyl) benzobisthiazole (DAPBT-2-CH₃) is introduced according to the following reaction scheme. As for other experimental details of the precursors synthesis, see the previous publication. [3]

Synthesis of DAPBT-2-CH₃ [II]
1) 2-cyano-5-nitrotoluene [4]
2-bromo-5-nitrotoluene(101.2g) and copper cyanide (50.7g) were added to N,N-
dimethylformamide (100 ml) and stirred under reflux for 4 hr. The reaction mixture was poured into aqueous solution consisted of iron (III) chloride 6-hydrate (200 g), 35% HCl and H2O (300 ml) at 60°C. After cooled, the mixture was filtered. The filter cake was washed with toluene. The filtrate was twice extracted with toluene (200 ml) and the filter cake was washed with extract. The resulting toluene solution was stripped, giving 69 g of pale yellow solid [II].

Analysis Calc. C 59.3 H 3.7 N 17.3
Found C 59.03 H 3.52 N 17.01

2) 2-methyl-nitrobenzoic acid [III]

NaOH (39.7 g) and 40 g of [II] were added to H2O (200 ml), stirred for 1 hr under reflux and diluted to 700 ml of aqueous solution. The solution was acidified with 35% HCl, giving yellow brown precipitate. The precipitate was washed with H2O (500 ml), giving 35.1 g of beige solid [III].

Analysis Calc. C 53.0 H 3.9 N 7.7
Found C 51.87 H 3.52 N 7.84

3) 2-methyl-aminobenzoic acid [IV]

Iron [II] sulfate (630 g), 28% NH3 solution and 63.4 g of [III] were added to H2O (1300 ml), stirred for 7 hr under reflux and cooled. The reaction mixture was filtered out. The filter cake was washed with H2O (650 ml) and re-filtered. The filtrates were unified and slightly acidified with 35% HCl. The resulting precipitate was washed with small quantities of H2O and filtered out, giving 28.9 g of beige solid [IV].

Analysis Calc. C 63.6 H 6.0 N 9.3
Found C 63.06 H 6.01 N 9.47

4) DAPBT-2-CH3 [V]

To polyphosphoric acid (107 g), 2,5-diaminobenzene-dithiol dihydrochloride (17.2 g) was added under N2 stream, stirred at 80°C and finally allowed to stand under vacuum in order to perfectly remove HCL gas. It took about 80 hr in total. To the de-gassed mixture, 23.2 g of [IV] was added, heated at the rate of 10°C/min up to 180°C, held at that temperature for 9 hr and cooled to 110°C.

The condensation mixture was neutralized with 28% NH3 solution, giving yellow brown precipitate. The precipitate was washed successively with H2O (750 ml) and ethanol (750 ml) and dried, giving 27 g of olive green solid. The solid was re-dissolved in N-methyl pyrrolidone NMP (100 ml) at 80°C. The solution was filtered and allowed to stand at room temperature overnight. The resulting precipitate was re-dissolved in NMP (50 ml) and treated in a similar manner. The resulting precipitate was washed with methanol (200 ml).

Analysis Calc. C 65.67 H 4.48 N 13.92 S 15.92
Found C 64.96 H 4.67 N 13.90 S 15.37

Film fabrication

1) Cast films

Pre-determined quantities of chemical cyclization reagents (acetic anhydride/pyridine) were added into a polyamide acid solution and stirred under vacuum for 10 min. The solution was coated on a glass substrate, de-gassed under vacuum for 1 hr and heated 1 hr at 80°C. The dried film was peeled off the glass substrate, attached to a metal frame and heat-cured under the pre-determined heating condition. Film modulus was measured with tensile tester IM-20 (INTESCO) (specimen 80 mm x 5 mm)

2) Partially imidized polyamide acid (PAI)-drawn film

Uniaxial drawing was applied at the gelation stage in the chemical cyclization procedure. These gelled films are already so self-sustainable that can be peeled off the substrates and highly stretchable. These partially imidized film was washed with toluene and cut out to pre-determined shape (30 mm width). The cut out film was dried under the pre-determined load and further heat-cured under tension, based on a similar heating condition as in above cast films. Imposed load was set up highest possible before break.

3) polyamide acid (PAA)-drawn films

A coated polyamide acid solution similarly
prepared as in the cast film was condensed at 80 °C, under vacuum for 1 hr. (polymer concentration about 80%), immersed in a coagulation bath (H₂O/NMP=25/75 by volume) and peeled off the substrate (polymer concentration about 20%). The coagulated film was cut out to a pre-determined shape (30mm width), was stretched under pre-determined load and dried for 9 hr as it stood. And further, the stretched film was immersed in a chemical cyclization bath (acetic anhydride/pyridine=70/30 by vol.) under tension and partially imidized. The partially imidized film was heat-cured under tension in a similar manner as in PAI-drawn film.

Evaluation of films
As for the mechanical and thermal evaluation and WAXD analysis, see the previous publication. [3]

3. Result and discussion
3.1 Polyamide acid solution properties
Table 1 shows the NMP solution properties of polyamide acids prepared from DAPBT including its several nuclear substituents and pyromellitic anhydride (PMDA). PPBT solution is well known to be lyotropic, on the other hand, these solutions don't show such lyotropicity in spite of containing the similar rigid-rod components.

Probably, polyamide acids are composed of around fifty/fifty based meta/paraamide linkage as the randomizing factor in the repeating chains. [5] But such randomizing factor may be restrained by the ortho-substitution towards the amide linkage. The case is testified by the example of PIBT-3-CH₃, where the polycondensation is interfered by the less homogeneity of the reaction medium, in other words, solubility-down.

Table 1 Solution properties of PIBT-related polyamide acids

<table>
<thead>
<tr>
<th>substituent</th>
<th>polymerization of polyamide acid</th>
<th>polyamide acid</th>
<th>imide conv. at gelation</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-substituent</td>
<td>OK</td>
<td>3.64</td>
<td>8%</td>
</tr>
<tr>
<td>2-CH₃</td>
<td>OK</td>
<td>2.62</td>
<td>21%</td>
</tr>
<tr>
<td>3-CH₃</td>
<td>non (precipitate)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2-Cl</td>
<td>non</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

chemical cyclization reagent
pyridine/ acetic anhydride = 1) 0.04 eq. / 6 eq. // benzobis thiazole unit
2) 0.80 eq. / 6 eq. // benzobithiazole unit
3.2 Mechanical and thermal properties of cast films

Table 2 shows the mechanical properties for the cast films from PIBT and PIBT-2-CH₃. As far as the cast films are concerned, the mechanical properties for PIBT-2-CH₃ is exceeding that for PIBT (non-substituted). But these results should be inconsistent with their own original mechanical potentials because the introduction of nuclear substituent leads to the increase of effective molecular cross-sectional area, in other words, the retrogression of theoretical modulus.

The featurestic phenomena through the cast film fabrication for both systems can be seen in TMA diagrams. That is, shrinkage mode is for PIBT and elongational mode is for PIBT-2-CH₃, in the temperature range of through 120 to 200°C as shown in Fig. 1.

On the other hand, the imide conversion along with the cast film forming process is shown in Table 3. According to these results, the imide conversion of the TMA starting materials, that is, at the 80°C pre-cured stage, is around 8% for PIBT and 21% for PIBT-2-CH₃.

Additionally speaking, at the stage, in films around 20% of NMP is still remained. It means that the temperature range of through 120 to 200°C should be basically shrinkage mode dominant. Nevertheless, PIBT-2-CH₃ system shows the elongational mode, and further higher modulus than that of PIBT.

It means the elongational mode is the reflection of the self-organization leading to the texture with high modulus.

3.3 Tensile properties for PIBT drawn films

Tensile properties of PIBT uni-axially drawn films are summarized in Table 4., where one group is prepared from partially imidized films (PAI film) and the other is from non-imidized films (PAA film). Fig. 2. is the plots vs. total draw down ratio during whole the drawing process, based on these above results. These results show the drawing during polyamide acid stage is remarkably effective compared with that during the partially imidized stage.

It means that the ordered textures must be preferentially arranged to macro-scopically extract the high mechanical potentials of rigid-rod polymeric materials. In other words, the ordering of rigid-rod polymer chains is much effectively carried out throughout the chain alignment done during the less rigid intermediate stage.
Table 3: Imide conversion through cast film curing steps

<table>
<thead>
<tr>
<th>Curing step</th>
<th>NMP content in cast film (%)</th>
<th>PIBT (%)</th>
<th>PIBT-2-CH₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80°C 1 hr</td>
<td>25</td>
<td>8.1</td>
<td>20.6</td>
</tr>
<tr>
<td>150°C 15 min.</td>
<td>15</td>
<td>32.8</td>
<td>40.7</td>
</tr>
<tr>
<td>200°C 15 min.</td>
<td>5</td>
<td>88.4</td>
<td>93.6</td>
</tr>
<tr>
<td>300°C 10 min.</td>
<td>—</td>
<td>95.7</td>
<td>98.0</td>
</tr>
<tr>
<td>350°C 10 min.</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Imide conversion: \( \frac{(I_{1780}/I_{1510})_T}{(I_{1780}/I_{1510})_{350°C}} \) by IR basis

Fig. 1. TMA diagrams for PIBT and PIBT-CH₃ pre-cured film
Table 4. Tensile modulus of uniaxially drawn films from PIBT

<table>
<thead>
<tr>
<th>Polyamide acid</th>
<th>Drawn ratio 1)</th>
<th>Thickness (μm)</th>
<th>TM (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAI-1</td>
<td>1.2 1.0 1.2</td>
<td>50</td>
<td>19.2</td>
</tr>
<tr>
<td>PAI-2</td>
<td>1.2 1.3 1.6</td>
<td>30</td>
<td>27.0</td>
</tr>
<tr>
<td>PAI-3</td>
<td>1.2 1.5 1.8</td>
<td>28</td>
<td>54.9</td>
</tr>
<tr>
<td>PAI-4</td>
<td>1.2 2.0 2.4</td>
<td>29</td>
<td>51.9</td>
</tr>
<tr>
<td>PAA-1</td>
<td>1.9 1.5 2.85</td>
<td>24</td>
<td>61.6</td>
</tr>
<tr>
<td>PAA-2</td>
<td>2.6 1.2 3.12</td>
<td>24</td>
<td>72.0</td>
</tr>
<tr>
<td>PAA-3</td>
<td>2.8 1.1 3.08</td>
<td>22</td>
<td>91.4</td>
</tr>
<tr>
<td>PAA-4</td>
<td>2.9 1.1 3.19</td>
<td>22</td>
<td>103.0</td>
</tr>
<tr>
<td>PAA-5</td>
<td>2.9 1.2 3.48</td>
<td>21</td>
<td>116.0</td>
</tr>
<tr>
<td>PAA-6</td>
<td>2.9 1.4 4.06</td>
<td>20</td>
<td>130.0</td>
</tr>
</tbody>
</table>

1) A at pre-curing, B at post-curing

Starting film: PAI chemically cyclized, PAA polyamide acid non-imidized

Fig. 2. TM vs. DR of uni-axially drawn films from PIBT
3.4 WAXD observation

Fig. 3. shows the three kinds of WAXD profiles, where X-ray beam incidence is vertically scanned towards the film edge side (edge-view).

One is for PIBT cast film, second for PIBT-2-CH₃ cast film and the last for PIBT uni-axially drawn film prepared via polyamide acid film (PAA film). We can see here, the peak at around $2\theta = 14^\circ$ as a characteristic peak. The important is, here, for PIBT system, that the peak is not appeared without any assistances of external force, that is the presence of the drawing process.

This means that partially imidized PIBT system is already too less flexible to induce the polymer chains' spontaneous self-alignments leading to the further ordered textures, compared with that of PIBT-2-CH₃.

4. Conclusion

For the layout of high-modulus polymeric materials, the prerequisite of the rigidity in first order structure is a matter of course. But the further important is that such first-order structure must be integrated into the highly regulated one. In this paper, what to be pointed out are as follows.

First one is that the higher tensile modulus of cast films are obtained from PIBT-2-CH₃ rather than PIBT (non-substituted). Second one is that the stretching during non-imidized polyamide acid stage is remarkably effective for the uni-axially oriented ultra high-modulus PIBT films. These results certificate that the high-modulus structure needs the fine combinational play between less rigid and the following rigid generation.

References