Preparation and structure of polyether-block containing polymers

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Abstract: Block-copolymers were prepared by direct polycondensation of functional oligomers or by polycondensation of a functional oligomer with the precursors of another block. Three series of copolymers were prepared and characterized: poly(polyamide 12-block-copolyether)s, Polyisobutylene-block-polyoxyethylene-graft-polyoxyethylene and poly(semi-aromatic polyester-block-polyoxytetramethylene)s. The functional oligomers and the corresponding copoly-condensates were characterized by SEC, infra-red spectroscopy, mass spectrometry, \(^1\)H and \(^{13}\)C NMR (solution and solid state). Their thermal properties were analyzed and the extent of the segregation in poly(polyester semi-aromatic-block-polyoxytetramethylene)s was studied through visco-elastic properties.

INTRODUCTION

A large part of the activity of our laboratory is devoted to block copolycondensates (ref. 1-16). We use three main methods:

(i) direct polycondensation of a,w-difunctional oligomers:

\[
X-\text{[Oligomer 1]}-X + Y-\text{[Oligomer 2]}-Y \xrightarrow{\text{Block 1}} X'Y'-\text{[Block 2]}-Y'~
\]

(ii) polycondensation of an a,w-difunctional oligomer with the precursors of another block:

\[
X-\text{[Oligomer 1]}-X + A-A + B-B \xrightarrow{\text{Block 1}} X'Y'-\text{[Block 2]}-Y'~
\]

with \(Y'\)-[Block 2]-\(Y'\) is \(A'A'B'B'\)-[\(A'\)AIBIB]-[\(A'A'\)]

(iii) oligomer-coupling reactions:

\[
X-\text{[Oligo 1]}-X + Y-\text{[Oligo 2]}-Y + C-C \xrightarrow{\text{Block 1}} X'C'C'Y'[\text{Block 2]}-Y'~
\]

This lecture concerns the following copolymers:

Poly(polyamide 12-block-copolyether)s
Poly(polyisobutylene-block-polyoxyethylene-graft-polyoxyethylene)s
Poly(semi-aromatic polyester-block polyoxytetramethylene)s

SYNTHESES OF THE BLOCK-COPOLYMERS

Poly(polyamide-block-copolyether)s

They were prepared according to the following reaction scheme (general method I):

\[
\begin{align*}
n \text{HO-}\text{C-PA-C-OH} + n \text{HO-CE-OH} \rightarrow & \text{HO-C-\奥林匹a-\奥林匹a-O-C-O-CE-O} \text{H} + 2n-1 \text{H}_{2}\text{O} \\
\end{align*}
\]

where CE is the copolyether-block

Copolyethers

We used Synperonic® (ICI) and Pluronic® (BASF). In principle, they are triblock-copolymers (POE-POP-POE) but in fact they are mixtures of triblock and diblock copolymers and polyoxypropylene; however all of them are difunctional. Their \(\overline{M}_n\) (Table 1) was obtained by SEC, MS, and \(^1\)H NMR and the values obtained by these different techniques are in good agreement. Their composition and structure were essentially determined by \(^1\)H NMR and \(^{13}\)C NMR.
TABLE 1. Characteristics of the copolyethers. [OE] and [OP] are the concentrations of oxyethylene and oxypropylene units; pri-OH and sec-OH are the concentrations of the primary and secondary end hydroxy-groups of the oligomers.

<table>
<thead>
<tr>
<th>Oligomers</th>
<th>$\text{Mn}^1$</th>
<th>$\text{H NMR}^1$</th>
<th>[%OE]/[OP]</th>
<th>[%pri-OH]</th>
<th>[%sec-OH]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synperonic L-35</td>
<td>1920</td>
<td>1.26</td>
<td>90</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Synperonic L-44</td>
<td>2205</td>
<td>1.09</td>
<td>85</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Synperonic L-43</td>
<td>1840</td>
<td>0.77</td>
<td>80</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Pluronic 4300</td>
<td>1925</td>
<td>0.65</td>
<td>80</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Synperonic L-42</td>
<td>1570</td>
<td>0.26</td>
<td>75</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Synperonic L-61</td>
<td>1950</td>
<td>0.23</td>
<td>60</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Synperonic L-31</td>
<td>1090</td>
<td>0.25</td>
<td>50</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Pluronic 6100</td>
<td>1740</td>
<td>0.14</td>
<td>45</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>Pluronic 3100</td>
<td>1095</td>
<td>0.16</td>
<td>35</td>
<td>65</td>
<td></td>
</tr>
</tbody>
</table>

**Poly(semi-aromatic polyester-block-polyoxytetramethylene)**

They were prepared according to the following reactionnal scheme (general method II):

$\begin{array}{c}
\text{HO-C-Ar-C-OH}+x \text{HO-A-OH}+y \text{HO-[(CH}_2\text{)}_4\text{O]_m-OH} \\
\text{C-Ar-C-O-A-O} \quad \text{C-Ar-C-O-[(CH}_2\text{)}_4\text{O]_m-OH} \\
\end{array}$

Six semi-aromatic copolymers were studied; in this lecture only the results relative to three of them are reported; they correspond to the scheme 3.

When $A$ is $(\text{CH}_2)_6$, $Ar$ can be:

When $A$ is $(\text{CH}_2)_6$, $Ar$ can be:

$y$ is the contribution of $N$ in $Ar$ (mol%)

The block-polyester can also be:

$\begin{array}{c}
\text{C-O-CH}^{-}_2\text{-CH-CH}^{-}_2\text{-CH}_2\text{-O} \quad \text{BMe} \\
\end{array}$

**Polyisobutylene-block-polyoxyethylene-graft-polyoxyethylene**

They were prepared according to the following reactionnal scheme (general method I):

$\text{PIB} \quad \text{HO-CH}_2\text{-POE} \quad \text{PB} \quad \text{POE}$

$\text{PIB} \quad \text{COO-CH}_2\text{-POE} \quad \text{PIB} \quad \text{COO-CH}_2\text{-POE}$

**Polyether-block containing polymers**

*a-monoanhydride and a*'-*dianhydride oligoisobutylene*

a-chloro oligoisobutenes were prepared according to Nguyen and Kennedy (ref. 17) and improved by Rodrigues (ref. 18); they were dechlorinated, giving a-isopropenyl oligoisobutenes, then reacted with maleic anhydride; these reactions were particularly studied by Tessier (ref. 19,20).

\[ 
\text{PIB} \quad \begin{array}{c} \text{C=CH}_2 \\ \text{CH}_2 \end{array} + \text{Bulk,Ar} \quad 190^\circ \text{C,16h} \quad \begin{array}{c} \text{O}=\text{C} \\ \text{O} \end{array} 
\]

**CHARACTERIZATION OF THE BLOCK COPOLYMERS**

**Poly(polyamide-block-copolyether)s**

The block-copolymer prepared from L-35 exhibits the following characteristics: \( [\eta] = 1.3 \text{ dL.g}^{-1} \) and \( \overline{M_n} \) is above 20000. The functional end group signals are no longer observed in the corresponding \( ^1\text{H} \) NMR spectrum and those of the methylene preceding (2.35 ppm) and following (4.25 ppm) the ester group confirm that the polycondensation took place. Solid state NMR spectroscopy provides interesting information on several copolymers.

The crystalline domains of the precursor oligoamide and of the polyamide-blocks are \( g \) monoclinic structures which is confirmed by X-ray diffractionmetry. The polyether-block of a poly[polyamide-block-polyoxytetramethylene] is amorphous when its \( M_n \) is 1000 and partially crystallized when \( M_n \) is 2000.

The polyether-block of a poly[polyamide-block-polyoxyethylene] contains a crystalline phase and an amorphous one. On the other hand the polyether blocks of poly[polyamide-block-polyoxypropylene] and of poly[polyamide-block-copolyether] are amorphous. Their thermal properties are reported in table 2.

**TABLE 2. Thermal properties of poly[polyamide-block-polyether].** Tg, Tm, Tr (°C); \( \overline{E_{\text{Hm}}} \), \( \overline{E_{\text{Hr}}} \) (J.g\(^{-1}\)) are respectively glass transition, melting and crystallisation temperatures, melting and crystallisation enthalpies.

<table>
<thead>
<tr>
<th>Polymer, Mn</th>
<th>Heating</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TgPE</td>
<td>TmPE</td>
</tr>
<tr>
<td>PA12DC (2100)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>POE (1015)</td>
<td>-</td>
<td>47</td>
</tr>
<tr>
<td>POP (928)</td>
<td>-52</td>
<td>-</td>
</tr>
<tr>
<td>PTOM (1075)</td>
<td>-83</td>
<td>27</td>
</tr>
<tr>
<td>PA-POE</td>
<td>-40</td>
<td>7</td>
</tr>
<tr>
<td>PA-POP</td>
<td>-47</td>
<td>-</td>
</tr>
<tr>
<td>PA-POTM</td>
<td>-50</td>
<td>11</td>
</tr>
<tr>
<td>L31</td>
<td>-55</td>
<td>-</td>
</tr>
<tr>
<td>L35</td>
<td>-52</td>
<td>28</td>
</tr>
<tr>
<td>PA-L31</td>
<td>-44</td>
<td>164</td>
</tr>
<tr>
<td>PA-L35</td>
<td>-44</td>
<td>168</td>
</tr>
</tbody>
</table>

TmPA, E\(\overline{\text{Hm}}\)PA, TrPA and E\(\overline{\text{Hr}}\)PA little depend on polyether nature and \( \overline{M_n} \). The polyether block Tg is above that of the precursor.

**Poly(semi-aromatic polyester-block-polyoxytetramethylene)s**

Their structure is given by formula 6:

\[
\sim\left[\begin{array}{c}
\text{Ar} - C - O - A - O - [O - (CH_2)_n - ]_x
\end{array}\right]
\]

\[
R \text{ is } \left[\begin{array}{c}
\text{Ar} - C - O - A - O - [O - (CH_2)_n - ]_x
\end{array}\right] \quad \text{and} \quad F \text{ is } \left[\begin{array}{c}
\text{O - (CH_2)_n - ]_m}
\end{array}\right]
\]

Ar and A structures are given in scheme 3. The average \( \text{Mn} \) of \( R \) blocks (\(^1\)H NMR) is given in table 3. The \( \text{Mn} \) of \( F \) is 2100 and their thermal and mesomorphic properties are reported in table 4.

**TABLE 3.** \( \text{Mn} \) of the blocks in the copolycondensates. Theoretical values are given in brackets. \( w \) is the weight percentage of \( F \) in \( R - F \)

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>( x )</th>
<th>( \text{Mn of } R )</th>
<th>( F(\text{w}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-F</td>
<td>31 (28)</td>
<td>7650 (6860)</td>
<td>23 (25)</td>
</tr>
<tr>
<td>B-F(27)</td>
<td>20 (22)</td>
<td>6440 (7092)</td>
<td>27 (25)</td>
</tr>
<tr>
<td>BN(26)-F</td>
<td>23 (22)</td>
<td>7365 (7070)</td>
<td>24 (25)</td>
</tr>
<tr>
<td>BMe-F</td>
<td>15 (15)</td>
<td>4670 (4730)</td>
<td>34 (33)</td>
</tr>
</tbody>
</table>

**TABLE 4.** Thermal and mesomorphic properties of the copolymers. \( T_i \) is the isotropization temperature and \( \Delta T \) is the temperature mesomorphic domain.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( T_g,F )</th>
<th>( T_m,F )</th>
<th>( T_m,R )</th>
<th>( T_i )</th>
<th>( \Delta T )</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>-83</td>
<td>35</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>-</td>
<td>-</td>
<td>147</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>T-F(34)</td>
<td>-74</td>
<td>17</td>
<td>144</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>-</td>
<td>214</td>
<td>241</td>
<td>27</td>
<td>Smectic A</td>
</tr>
<tr>
<td>B-F(27)</td>
<td>-76</td>
<td>28</td>
<td>223</td>
<td>231</td>
<td>8</td>
<td>Smectic A</td>
</tr>
<tr>
<td>B-F(50)</td>
<td>-78</td>
<td>25</td>
<td>224</td>
<td>233</td>
<td>9</td>
<td>Smectic A</td>
</tr>
<tr>
<td>BN(25)</td>
<td>-</td>
<td>-</td>
<td>192</td>
<td>227</td>
<td>35</td>
<td>Smectic A</td>
</tr>
<tr>
<td>BN(26)-F(24)</td>
<td>-77</td>
<td>29</td>
<td>197</td>
<td>209</td>
<td>12</td>
<td>Smectic A</td>
</tr>
<tr>
<td>BMe</td>
<td>-</td>
<td>-</td>
<td>214</td>
<td>232</td>
<td>18</td>
<td>Nematic</td>
</tr>
<tr>
<td>BMe-F(26)</td>
<td>-81</td>
<td>26</td>
<td>215</td>
<td>231</td>
<td>16</td>
<td>Nematic</td>
</tr>
</tbody>
</table>

We compared the segregation extent when Ar is benzenic ring (the copolycondensate is not mesomorphic) and when the copolycondensate exhibits mesomorphic properties \( B, BN, BMe \); in this purpose their viscoelastic properties were studied (table 5).

**TABLE 5.** Temperature \( T_E^{\max} \) \(^{\circ}\)C; 1 Hz; 10°C min\(^{-1}\).)\n
<table>
<thead>
<tr>
<th>Copolymer</th>
<th>( T_E^{\max} )</th>
<th>Copolymer</th>
<th>( T_E^{\max} )</th>
<th>Copolymer</th>
<th>( T_E^{\max} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-F(23)</td>
<td>-4</td>
<td>T-F(34)</td>
<td>-37</td>
<td>T-F(43)</td>
<td>-63</td>
</tr>
<tr>
<td>B-F(27)</td>
<td>-51</td>
<td>B-F(33)</td>
<td>-53</td>
<td>B-F(50)</td>
<td>-46</td>
</tr>
<tr>
<td>BN(26)-F(24)</td>
<td>-46/-20</td>
<td>BN(30)-F(34)</td>
<td>-46/-20</td>
<td>BN(28)-F(49)</td>
<td>-47/-20</td>
</tr>
<tr>
<td>BMe-F(20)</td>
<td>-49</td>
<td>BMe-F(26)</td>
<td>-55</td>
<td>BMe-F(34)</td>
<td>-56</td>
</tr>
</tbody>
</table>

The rheological properties in the melt were studied. With T the solid/liquid transition characteristic of an isotropic material; \( G'' \) is always far above \( G' \) and its value is proportional to the pulsation \( (\omega) \) whatever T. On the other hand with B or BN \( G' \) is above \( G'' \) when T is below \( T_m \) showing it is an elastic solid material.
When \( T_m < T < T_i \), \( G' \) and \( G'' \) are very close and rapidly decrease with \( T \) increasing which is characteristic of a smectic phase; in this domain \( G'' \) is roughly proportional to \( T^{0.5} \). When \( T > T_i \), the corresponding isotropic liquid is characterized by \( G'' > G' \). The nematic state of B-Me-copolymers is characterized by a weak decrease of \( G' \) and \( G'' \) when \( T \) increases.

**Polyisobutylene-block-polyoxyethylene-graft-polyoxyethylene**

The reaction product of anhydride-oligoisobutenylones with a-hydroxy-polyoxyethylene (7) was characterized by infra-red spectroscopy, mass spectrometry and SEC.

![Diagram of reaction product](image)

characteristics do not depend on the structure of the oligoisobutylene. When the \( M_n \) of POE is 815 Tg is -64°C, crystallisation temperature is -45.5°C and \( T_m \) is 24.5 °C; when it is 2015 Tg is -65°C, \( T_m \) is 49 °C. Some of their amphiphilic properties were determined and particularly cloud-point and surface-tension. Their water solubility is high due to the fact that the hydrophobic block has a low molar mass; they have a classical behaviour of non-ionic surfactant.

**REFERENCES**
