Synthesis of telechelic monodispersed diols

2. Telomerization of undecylenol with bis(2-mercapto ethyl) ether and bis(2-mercapto ethyl) sulfide and physical properties

Bruno Ameduri¹, Khalid Berrada¹, Bernard Boutevin¹, and Roy D. Bowden²

¹URA D11930 CNRS, Ecole Nationale Supérieure de Chimie de Montpellier, 8, Rue Ecole Normale, F-34053 Montpellier Cédex 1, France
²I.C.I. Materials, Research and Technology Department, The Heath, Runcorn, Cheshire WA7 4QD, UK

Summary

The synthesis of telechelic monodispersed diols produced from the radical telomerization of an excess of undecylenol with commercially available α,ω-dithiols HSC₂H₄XC₂H₄SH (X = O,S or CH₂) initiated by peroxides is presented. In each case, the diols were obtained selectively and quantitatively and they were characterized by both ¹H and ¹³C NMR. Their physical characteristics (Tg, Tm and decomposition temperatures) were determined. Such compounds are thermally more stable than polydispersed telechelic commercially available diols.

Introduction

In previous articles (1-3) we detailed the bibliography about the synthesis of monodispersed telechelic diols performed by several international teams (4-7) or in our group (1-3,8) by alkalyl catalyzed addition of epoxy (7) or by telomerization of undecylenic monomers with α,ω-dithiols (3,9,10). We showed that the radicalar initiation of such telomerization led to the expected diols selectively and quantitatively.

It was noticed that polymethylenedithiols (3) and bis(2-mercaptop- ethyl) ether (9,10) were mainly employed but only one article (7) mentions the use of dithiols which exhibit a thioether group. Furthermore, almost no data about the physical properties of these oligomers have been reported in the literature.
The goal of this paper concerns the synthesis of novel monodispersed telechelic diols prepared from the bismonoaddition of undecylenol onto HS(CH₂)ₓ X(CH₂)₂ SH telogens where X = oxygen, sulfur. Furthermore, the comparison of their physical properties (melting, glass transition and decomposition temperatures) to those of the diol obtained from the 1,5-pentanediol (where X designates a methylene group) and to those of a commercially available polydisperse diol is also described.

Results and Discussion

The synthesis of telechelic monodispersed hydroxyl-terminated polythioether, whether exhibiting an ether group or not, has been performed in batch. This deals with the addition of an excess of undecylenol onto bis(2-mercaptoethyl) sulfide, bis(2-mercaptoethyl) ether or 1,5-pentanediol, in the presence of initiator, according to the following scheme:

\[
\text{HS(CH}_2\text{)}_2 \ X \ (\text{CH}_2\text{)}_2 \text{SH} + \text{H}_2\text{C}=\text{CH-} \ (\text{CH}_2\text{)}_9 \text{OH} \xrightarrow{\text{rad}} \HO\text{(CH}_2\text{)}_1\text{lS(CH}_2\text{)}_2 \ X \ (\text{CH}_2\text{)}_2 \ S \ (\text{CH}_2\text{)}_1\text{l OH}
\]

<table>
<thead>
<tr>
<th>X</th>
<th>diol</th>
<th>FW</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>1</td>
<td>494</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>478</td>
</tr>
<tr>
<td>CH₂</td>
<td>3</td>
<td>476</td>
</tr>
</tbody>
</table>

1) Synthesis of telechelic monodispersed diols

The reaction involving 1,5-pentanediol was described in a previous article (3) and we detail below the synthesis of the diols in which the other dithiols were utilized. We used the t-butyl peroxypivalate as initiator because of its efficiency and its low half-life even at 70°C. An initial [dithiol]/[undecylenol] molar ratio of 0.45 was chosen and the reactions were carried out at 70°C in acetonitrile.

After 3 hours of reaction, the diols were precipitated and recrystallized from acetonitrile to eliminate any residual starting materials. The GPC chromatograms of both crystalline products show a unique sharp peak (11). Then, they were characterized by 1H and 13C NMR.

The 1H-NMR spectra (Figure 1) of both diols show:
- a broad peak in the 1.1 - 1.4 \times 10^{-6} range corresponding to the methylenic chain;
- a triplet centered at about 2.5 \times 10^{-6} which is assigned to the methylene group in the position about the sulfur;
- a signal at about 3.5 \times 10^{-6} characteristic of the methylene group adjacent to the hydroxyl end-group.