Substituted Oxetanes in Polymer Synthesis
Polyesters Based on 3,3-Bis(Chloromethyl) Oxetane and
5-Amino-Sodium Isophthalate

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ABSTRACT
The preparation of Polyesters based on 3,3-bis (chloromethyl) oxetane (BCMO) and 5-amino-sodium Isophthalate (5-AIP) under the phase transfer conditions is discussed, together with the influence of reaction conditions upon the properties of the obtained polymers. The anisotropic properties of the polyesters and their thermal behaviour are investigated by DSC, TG and optical polarizing microscopy.

Key Words
phase transfer, oxetane, polyesters, liquid crystals, polycondensation

INTRODUCTION
Phase transfer catalysis (PTC) is a widely used technique in synthesis of polycondensation polymers. It shows a remarkable efficiency in preparation of poly- and copolycarbonates [1-4], poly- and copolyethers [5-9], and also in nucleophilic substitution of halogen atoms in dihalogenated compounds by dicarboxylates [9-13]. Most of these polymers reveal interesting anisotropic properties.

The present work studies the experimental conditions in synthesis of polyesters based on 3,3-bis (chloromethyl) oxetane (BCMO) and 5-amino-sodium Isophthalate (5-AIP) under the PT-conditions and investigates their potential liquid-crystalline properties in the molten state.

EXPERIMENTAL
Materials
BCMO was synthesized by the method as described in ref.9. 5-AIP was obtained by usual titration of
the 5-amino-isophthalic acid with NaOH. Solvents (Fluka) and catalysts (Aldrich Co.) were used without further purification.

**Polymer Synthesis**

The polyesters from BCMO and 5-AIP were prepared in a round bottomed flask fitted with a refluxing condenser, nitrogen inlet tube and a magnetic stirrer. In a typical run, 3 mmol (0.675 g) 5-AIP and 3 mmol (0.465 g) BCMO were dissolved in 15 mL of NMP under stirring condition. After adding 0.5 mmol (0.169 g) tetraethyl ammonium hydrogensulfate (TBAHS), the reaction mixture was stirred for a prefixed time at 85 °C. The product was precipitated in acidified (HCl) methanol, washed with water and methanol to remove unreacted reagents and dried under vacuum (40°C).

**Polymer Characterization**

The IR spectra (KBr pellets) were registered on a SPECORD IR 71. The 60 MHz 1H-NMR spectra were recorded with a JEOL spectrometer from DMSO-d6 solution at 80°C using TMS as an internal standard. Thermal properties were evaluated by DSC on a SEIKO DSC 220 C at 10°C/min heating rate, under nitrogen flow, with data processing in UNIX system, version 3.0.

Conformational information were obtained from the calculations performed on a PC 486 computer by using a MMX program [14].

**RESULTS AND DISCUSSION**

Polyesters from BCMO and 5-AIP were prepared via the nucleophilic displacement route (Scheme I) under the PT-conditions in the presence of TBAHS as transfer agent:

![Scheme I](image)

Preferably, the reaction was carried out in N-methyl pyrrolidone (NMP) solvent, using a stoichiometric ratio of aminodicarboxylate and BCMO at a reaction temperature of 85°C. Good results were also obtained in dimethylformamide (DMF) and dimethylsulfoxide (DMSO), but no polymer was formed in nitrobenzene (Table 1).

It is important to note that reaction takes place in those liquids which are water miscible for polyesters and possess a high dielectric constant (DMSO-48.9, NMP-unknown). Only traces of the polymer were obtained when dioxane was used as reaction medium.

Much of the research effort in PT-catalysis has been aimed at the improvement of molecular weight and polymer yield, so that our research exploits also the efficiency of onium salts in nucleophilic displacement of halogen atoms in BCMO by dicarboxylates. Several catalysts have been used (triethylbenzylammoniumchloride, tetraethylammoniumchloride, cetylpyridylammoniumbromide, triphenylmethyolphosphoniumbromide, tetrabutylammoniumhydrogensulfate), but only TBAHS provided good results in polyester synthesis. From the data summarized in Table 2, it appears that the polymer yield increases with increasing concentration of TBAHS up to $6.66 \times 10^{-2}$ mol/L and subsequently the yield decreases almost linearly because of the increased in oligomer formation.

The nucleophilic substitution of chlorine in BCMO is positively influenced both by temperature and reaction time. The plot in Figure 1 shows that the main accumulation of the polymer occurs up to 90°C.

The polyester samples have been investigated by I.R spectroscopy on the registration, one may find absorptions of oxetane ring (930 cm⁻¹), of trisubstituted aromatic ring (1490-1600 cm⁻¹), and of primary free amine groups (3400-3500 cm⁻¹); also an absorption
Table 1. Polycondensation of BCMO and 5-AIP in different organic solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>DMF</th>
<th>DMSO</th>
<th>NMP</th>
<th>Dioxane</th>
<th>Nitrobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>38.0</td>
<td>48.9</td>
<td>-</td>
<td>2.2</td>
<td>35.7</td>
</tr>
<tr>
<td>Polymer yield, %</td>
<td>56.91</td>
<td>47.56</td>
<td>85.60</td>
<td>traces</td>
<td>-</td>
</tr>
</tbody>
</table>

Reaction conditions: \([\text{BCMO}] = [5\text{-AIP}] = 0.2 \text{ mol/L}; [\text{TBAHIS}] = 3.3 \times 10^{-3}\text{mol/L}; \text{time}=5\text{ h}; \text{T}=85^\circ\text{C}.

Table 2. The influence of catalyst concentration in polycondensation of BCMO with 5-AIP.

<table>
<thead>
<tr>
<th>Catalyst concentration (\times 10^2, \text{mol/L})</th>
<th>1.666</th>
<th>3.333</th>
<th>5.00</th>
<th>6.666</th>
<th>8.333</th>
<th>10.0</th>
<th>13.333</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer yield, %</td>
<td>15.67</td>
<td>44.83</td>
<td>59.16</td>
<td>63.60</td>
<td>57.95</td>
<td>53.87</td>
<td>40.25</td>
</tr>
</tbody>
</table>

Reaction conditions: \([\text{BCMO}] = [5\text{-AIP}] = 0.2 \text{ mol/L}; \text{Solvent-DMF}; \text{time}=3\text{ h}; \text{temperature}=85^\circ\text{C}.

attributable to ester linkage at 1700-1750 cm\(^{-1}\).

Figure 2 shows the \(^1\text{H}-\text{NMR}\) spectrum of the polymer with the assignment of various signals. It is worth mentioning that the signal at \(\delta=3.1\) ppm, assigned to aminic protons vanishes when the registration is made in trifluoroacetic acid (Figure 2b).

Thermal properties of the polyesters have

Fig.1. Conversion-time and conversion-temperature plots for the polycondensation of BCMO and 5-AIP.

Fig.2. \(^1\text{H}-\text{NMR}\) spectra of the polyester based on BCMO and 5-AIP in DMSO-\(d_6\) (a) and trifluoroacetic acid (b).
been studied by DSC and TG. The registered thermogram for the low molecular weight product $M_n \sim 2000\) displays two distinct thermal transitions at 161.4 °C which marks transition to LC state, and 208 °C for isotropization with endothermal effects of 6.4 mJ/mg and 8.8 mJ/mg, respectively (Figure 3).

It is worth mentioning that isotropization for polyesters of higher viscosities occurs above 250 °C and the process is accompanied by some cross-linking events occurring between-NH$_2$ groups and oxetane rings (Figure 4). The thermal transitions are less visible and beyond 250 °C, a pronounced exothermic reaction can be evidenced, which makes it impossible to continue. Similar reactions have been reported for epoxidic rings leading to thermoset LC-polymers [15,16].

The obtained polyesters show also a good thermal stability. The weight losses do not exceed 0.36% up to 315 °C, but represent almost 50% at 600 °C (Figure 5).

Shearing the sample between glass-slides at 210 °C showed that the prepared samples are in a liquid-crystalline state. From polarization microscopy studies (Figure 6) it appears that these polymers are in nematic arrangement.

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**Fig. 3.** DSC-thermogram of the 5-AIP-BCMO polyester ($M_n<2000$).

**Fig. 4.** DSC-thermogram of the 5-AIP-BCMO polyester ($M_n>2000$).
In order to explain the anisotropical properties, potential barriers upon rotation about the most important links were calculated with a MMX program on a PC-486 computer [14]. The repeating unit corresponds to Scheme II and its geometry was found to be very similar to that obtained for polyesters based on BCMO and unsubstituted isophthalates [11]. The macromolecular chain retains a semirigid character since the potential barriers upon rotation about links 3, 4, 7 and 8 range between 500 and 4000 kJ/mol and are much lower for the links 1, 2, 5 and 6. This suggests that the entire structural unit acts as a mesogenic group in the macromolecular chain.

It is noteworthy also that these polyesters are more rigid compared to those prepared from BCMO and potassium isophthalate. It might be that-NH$_2$ groups from 5-AIP are involved in hydrogen bonds which might restrict the rotation of the kinetic elements about the links.

CONCLUSION

The polyesters based on BCMO and 5-AIP exhibit a nematic liquid-crystalline phase above their glass transition temperatures. The macromolecular chain of such polymers bears a more rigid character compared to that of polyesters prepared from unsubstituted isophthalates. The-NH$_2$ groups might participate in hydrogen bonding and, above melting temperature of the polymer, might interact with oxetane rings to give cross-linked LC structures.

REFERENCES

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