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The Use of Polydisulfides and Copolymeric Disulfides in the Li/PEO/SRPE Battery System

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Abstract

Solid redox polymerization electrodes (SRPEs) have recently been used successfully as cathodes in lithium solid polymer electrolyte batteries. SRPEs contain organopolydisulfides -(SRS)n as the electroactive material; upon cell discharge these materials are reductively depolymerized via scission of the disulfide linkages to di- or trithiolate salts. The thiolate salts are reoxidized to the polymeric disulfides when the cell is recharged. Organopolydisulfides are easily synthesized via a one step process, are inexpensive, and exhibit high performance levels in batteries. A characteristic unique to the SRPE is the facile modification of physical and electrochemical properties simply by changing the organic group R, or the ability to combine the desirable features of several compounds by copolymerization. The discharge characteristics of several different polymeric and copolymeric disulfides are presented in this paper. In general aliphatic organopolydisulfides exhibit a flat discharge potential of about 2 V vs. Li, while others have higher cell voltages. The low equivalent weight and the high utilization of thick cathodes of -(SCH2CH2S)n (X8) translate into high energy densities for lithium polymer electrolyte cells.

Introduction

The solid redox polymerization electrode (SRPE) is a composite containing organopolydisulfides as the electroactive materials. These compounds undergo reductive depolymerization to di- or tri-thiolate salts upon cell discharge and are reoxidized to the polymeric disulfide upon cell charge.

\[ -(SRS)\_n \xrightarrow{2n \text{ e}^-} n (SRS)^{2-} \xrightarrow{-2n \text{ e}^-} \]

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While the excellent performance of the SRPEs in lithium polymer electrolyte batteries has attracted much attention\textsuperscript{1,2} other outstanding features include the low cost, low toxicity and ease of synthesis of the organopolydisulfides themselves. Additionally, polymers may be custom tailored for desired characteristics simply by changing the organic group, R; in principle, the number of polymers available is unlimited. In practice, the requirements for a thin film lithium battery system pose some restrictions; voltage vs. lithium, equivalent weight (and therefore energy density), electrode kinetic factors (power density) and physical characteristics of the polymers must all be considered. The polydisulfide of dimercaptothiadiazole, termed X1, has an open circuit potential of 3.0 V vs. lithium and an equivalent weight of 74.1 g/eq; because of its fast kinetic behavior, it may be discharged at high rates\textsuperscript{1,2} in a lithium-polyethylene oxide battery at 90\textdegree C. Simple aliphatic disulfides, however, exhibit slow electron transfer kinetics at room temperature with large energies of activation\textsuperscript{3,4}. For example, polyethylene disulfide, X8, shows slower redox kinetics than X1 and has an OCV of about 2.3 V vs. lithium, but its very low equivalent weight (46 g/eq) and the fact that very thick (30 C/cm\textsuperscript{2}) cathodes may be discharged efficiently imply a high energy density for lithium/polyethylene oxide/X8 batteries. Furthermore, by using copolymers or mixtures in cathodes, it is possible to design batteries with specialized features such as state of charge indication (e.g. the discharge profile is sloping or has a plateau region rather than being flat) or overcharge protection, as well as to improve performance by combining the desirable characteristics of several compounds. Mechanical and physical properties of materials can also be modified by copolymerization. For example, some copolymers of polyethylene disulfide/para-xylene disulfide are amorphous, yet polyethylene disulfide and polypara-xylene disulfide themselves are semicrystalline\textsuperscript{5}.

For this study, the behavior of several polymer, copolymer and mixed systems was examined in thin film lithium polymer electrolyte cells. For some experiments, the copolymers were synthesized chemically prior to incorporation into cathodes. For other experiments, copolymers were generated \textit{in situ} by combining cathodes of different polymers during cell assembly or by using a cathode containing two different polymers and then cycling the battery. The high level of performance of several of these polymers and copolymers in thin film lithium-polyethylene oxide

batteries demonstrates the versatility of the solid redox polymerization electrode and indicates that such batteries may be useful for a wide range of applications.

Experimental

2,5 dimercapto-1,3,4-thiadiazole (Aceto Corp.), 2,4-Dithiopyrimidine (Sigma), 2-mercaptoethyl ether (Aldrich, tech. grade), 2-mercaptoethyl sulfide (Aldrich, 95%), trithiocyanuric acid (Aldrich, 95%), 1,2 ethanedithiol (Aldrich, 99%), potassium ferricyanide (Aldrich, 99+%), lithium hydroxide (Aldrich, 99.9+%), iodine (Baker, sublimed) and acetonitrile (Aldrich, HPLC grade) were used as supplied. Polyethylene oxide (avg. m.w. = 5 x 10⁶, Aldrich), carbon black (Shawinigan acetylene black, Chevron) and lithium trifluoromethylsulfonate (lithium triflate, hereafter abbreviated LiTf) were dried under vacuum at 50° C for several days and stored under an inert atmosphere. Lithium foil of either 1 or 5 mil thickness (Lithco Co., battery grade) was stored under helium and cut into disks 3 cm² immediately prior to use.

Disulfide polymers and copolymers were synthesized by converting the di- or trithiol to a soluble lithium di- or trithiolate salt and then oxidizing the salt to the polydisulfide. The reactions are shown below for X8, polyethylene disulfide.

\[
\begin{align*}
1a) \quad & HSCH_2CH_2SH + 2LiOH (aq) \rightarrow Li_2SCH_2CH_2S(aq) + 2H_2O \\
1b) \quad & nSCH_2CH_2S^2- \rightarrow (SCH_2CH_2S)_n \quad [O] = I_2, K_3Fe(CN)_6
\end{align*}
\]

All reactions proceeded rapidly at ambient temperature in aqueous solution. Copolymers were produced chemically by co-reacting the appropriate di- or trithiols as above. The resulting polymers and copolymers were washed with copious amounts of water and suitable organic solvents and dried in vacuo at 50° C.

Positive electrodes were prepared from a mixture of the polydisulfide(s) of interest (30 or 45 wt %), carbon black (7-10 wt %), carbon dispersant (2-3 wt. %) and remainder polyethylene oxide or P(EO)₂₀LiTf. A viscous slurry, typically about 2-3 wt. % solids in acetonitrile was obtained after several days of stirring. Films of 20-80 μm thickness were cast and air-dried on a clean Teflon surface, then vacuum dried for several days at 50° C. P(EO)₂₀LiTf films (30-50 μm thickness) were prepared in a similar fashion.

Cells were assembled under an inert atmosphere and tested at 90-100° C or 110° C (X8). In some cases a 2 cm² cathode was shielded to an area of 1 cm² by using a 19 μm thick polypropylene spacer, otherwise the full 2 cm² cathode area was used in the battery. The Li electrode capacity in all cells exceeded that of the positive electrode by more than 400% (by stacking Li foils if necessary) and therefore did not limit cell performance. Discharge and cycling characteristics were examined with a PAR 173 or 371 potentiostat/galvanostat utilizing software
developed in this laboratory. Cell impedances (typically 20-50 ohm-cm², resistance times area) were determined in situ by a pulse technique described elsewhere. Galvanostatic cell discharges were performed at 0.25-0.5 mA/cm² with cell OCVs monitored periodically.

Results and Discussion

Structures, equivalent weights and OCV's of disulfide polymers are listed in the table below.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Formula</th>
<th>eq. wt. (g/eq)</th>
<th>OCV in Li/P(EO)₅LITf/polymer cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>X0</td>
<td>-(SCH₂CH₂OCH₂CH₂S)ₙ</td>
<td>68.1</td>
<td>2.5</td>
</tr>
<tr>
<td>X1</td>
<td>(N-N)</td>
<td>74.1</td>
<td>3.0</td>
</tr>
<tr>
<td>X5</td>
<td>(N=N)</td>
<td>58</td>
<td>3.0</td>
</tr>
<tr>
<td>X7</td>
<td>-(S-S)</td>
<td>71</td>
<td>2.5-2.8</td>
</tr>
<tr>
<td>X8</td>
<td>-(SCH₂CH₂S)ₙ</td>
<td>46.1</td>
<td>2.3-2.8</td>
</tr>
<tr>
<td>X9</td>
<td>-(SCH₂CH₂SCH₂CH₂S)ₙ</td>
<td>76.2</td>
<td>2.3</td>
</tr>
</tbody>
</table>

X1 and X5 are free-flowing off-white to yellow powders, X7, X8 and X9 are white powders, and X0 is a colorless or beige amorphous, viscous polymer. In general, these polymers are insoluble in common solvents, making molecular weight distribution analysis difficult. Figure 1 shows typical

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discharge curves of these polymers in lithium-polyethylene oxide cells at 95° C (X8 at 110° C) at 0.5 mA/cm² (0.25 mA/cm² for X5). In general, those polymers containing nitrogen (X1, X5 and X7) tend to have higher OCV's than those without (X0, X8 and X9), and all show nearly flat discharge profiles. In some cases, particularly for X1 and X8, voltage plateaus are evident; these may be attributed to the different chemical species that are generated during discharge (trimers, dimers etc). For some of the lower voltage systems (X0 and X8) starting OCV's were as high as 3 V, but dropped immediately at the beginning of discharge; this may be attributed to small amounts of an impurity.

Polarization for many of these cells tended to increase with increasing depth of discharge (see, for example, X8 in Figure 1). After resting several minutes, however, discharged cells showed normal or lower than normal internal resistances as measured by the current pulse tests. This time dependent behavior is characteristic of concentration polarization; i.e. the relatively low ionic conductivity of the PEO limits the performance of the cells. (It should be noted, however, that a salting out effect due to the production of lithium dithiolate salts during discharge may contribute to this as well).

For these experiments, cathode capacities were 2 to 5 C/cm² (30% loading) and utilizations ranged from slightly over 40% (X7 at 95° C) to nearly 100% (X8 at 110° C) of this capacity. (Note that utilizations varied somewhat depending upon the voltage limits chosen, however. Also, the extreme sensitivity of X8 to small changes in temperature tended to result in larger than normal experimental variation in terms of utilization for this compound.) Although X1 exhibits the best performance at 95° C and 0.5 mA/cm², excellent results were also obtained with X5 by lowering the discharge rate, and with X8 by raising the temperature to 110° C. This variation in behavior most likely can be attributed to differences in electrode kinetics among the polymers. X1 appears to be the fastest of these systems; it can be discharged at high rates (several mA/cm²) in lithium-polyethylene oxide cells at 90-100° C² and efficiently at 50-200 µA/cm² in modified cells at room temperature⁷. X1 is also notable for its cyclability in both room temperature and higher temperature Li polymer electrolyte cells.

Table 2 gives the theoretical coulometric and gravimetric film capacity and energy densities for X0, X1 and X8. Although X8 has a lower discharge voltage than X1, its very low equivalent weight compensates, resulting in similar energy densities. X0 has a higher equivalent weight than X8, and thus a lower energy density.

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### Table 2

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Loading (wt %)</th>
<th>Film Density (g/ml)</th>
<th>Volumetric Capacity Density (Ah/ml)</th>
<th>Gravimetric Capacity Density (Ah/g)</th>
<th>Volumetric Energy Density (Wh/ml)</th>
<th>Gravimetric Energy Density (Wh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X0</td>
<td>30</td>
<td>1.27</td>
<td>0.15</td>
<td>0.12</td>
<td>0.30</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>1.27</td>
<td>0.15</td>
<td>0.23</td>
<td>0.45</td>
<td>0.35</td>
</tr>
<tr>
<td>X1</td>
<td>30</td>
<td>1.45</td>
<td>0.16</td>
<td>0.11</td>
<td>0.47</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>1.54</td>
<td>0.25</td>
<td>0.16</td>
<td>0.75</td>
<td>0.49</td>
</tr>
<tr>
<td>X8</td>
<td>30</td>
<td>1.39</td>
<td>0.24</td>
<td>0.17</td>
<td>0.48</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>1.45</td>
<td>0.38</td>
<td>0.26</td>
<td>0.76</td>
<td>0.52</td>
</tr>
<tr>
<td>Li</td>
<td>100</td>
<td>0.53</td>
<td>2.0</td>
<td>3.8</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Some of the most interesting results were obtained with X8, polyethylene disulfide. These cells had very low internal resistances as measured by the current pulse tests, frequently dropping to as low as 7-8 ohm-cm² (resistance times area) after discharge. Utilization appeared to be nearly independent of either loading level (30 or 45%) or thickness (total capacity) of the cathode to nearly 30 C/cm² for discharge rates of 0.5 mA/cm² (Figure 2). Thus it should be possible to increase practical energy densities for X8 cells by using thick cathodes with high loading levels. Figure 3 shows practical volumetric and gravimetric energy densities for X1 and X8 cells having cathodes of variable thicknesses and loading levels, 30 μm thick P(EO)₆LiTf separators, lithium anodes with four times the capacity of the cathodes and metallized plastic current collectors 5 μm thick. (These materials are widely used in the capacitor industry and have recently been proposed for use in batteries⁸, ⁹). X1 has slightly better energy densities than X8 for cathode capacities below 5 C/cm². However, the highest practical volumetric and gravimetric energy densities are obtained for thick X8 cathodes (values of almost 400 Wh/L and 350 Wh/kg for capacities of 30 C/cm²); X1 cannot yet be discharged to this extent.

Figure 4 shows several cycles of a Li/P(EO)₆LiTf/X8 (30%) cell, discharged at 0.5 mA/cm² and charged at 0.25 mA/cm². This figure also illustrates the temperature sensitivity of X8; utilization for

the first cycle (90°C) was less than 30% whereas utilization for the second cycle, at 108°C, was over 90%. Although the first few cycles were quite good, subsequent discharges showed capacity losses of about 10% per discharge. Overcharging the cell by 10% or more ameliorated this to some extent. Li/P(EO)9LiTf/X8 cells did not polarize at the end of charge; indeed, it was possible to overcharge them indefinitely at 0.25 mA/cm² without evidence of polarization or deterioration. This characteristic suggests that a shuttle mechanism may be operating in the cell; i.e. an intermediate product produced upon partial discharge or charge (for example, a dimeric anion) diffuses through the PEO and is chemically reduced by lithium. It is highly unlikely that the X8 polymer itself is mobile; furthermore, there is no evidence of self-discharge of assembled cells that have not been discharged.

The rather high mobility of anions in PEO has been noted by several researchers. Transference numbers as large as 0.82 have been measured for ClO₄⁻ in P(EO)9LiClO₄ at 112°C. Although transference numbers have not yet been measured for thiolate anions in PEO, there is visual evidence of their mobility. Post-mortem inspections of discharged X1 cells show the characteristic yellow color of the X1 dimer or dithiolate anion in the slightly oversized separator. When an electrode containing X1 salt or dimer (but no polymer) is layered on top of an oversized PEO separator, placed between two pieces of clear plastic and heated to 90°C, the yellow color appears beyond the electrode in about two hours. Unfortunately, the salts of X8 are not colored, so it is not possible to tell whether the anions are moving in the cells simply by visual inspection. However, it is not unreasonable to expect that these salts would be even more mobile than those of X1, due to the similarity in structure to PEO itself (X8 dithiolate salt “SCH₂CH₂S; ethylene oxide unit CH₂CH₂O). This characteristic suggests that X8 may be used to advantage as an overcharge protection material for thin film polymer electrolyte cells arranged in series, provided self-discharge rates are acceptable.

Copolymeric polydisulfides can be made via several different routes; either by chemical oxidation of a mixture of di- or trithiolates or electrochemical oxidation in situ by discharging and

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recharging a cell in which mixtures of polymers are used, or cathodes of different polymers are stacked. Copolymers may take the following forms:¹³

- Block copolymer: \(-A_nB_m\)
- Regular copolymer: \(-\left(A-B-A-B-A-B\right)_n\)
- Random copolymer: \(-\left(A-A-B-A-B-B-A-B-A\right)_n\)

The type of copolymeric disulfide formed initially during chemical or electrochemical oxidation (or, whether copolymers can form at all) might be expected to be dependent upon the relative rates of reaction (electrochemical potentials) of the dithiolates "SRS" and "SR'S" and their concentrations. For example, a large disparity in reactivity rates should lead to a block copolymer or two separate polymers. The disulfide linkages in copolydisulfides are known to redistribute rapidly, however, resulting in randomization.¹⁴ Mechanisms for this are shown in schemes 1 and 2 below.

\[
\begin{align*}
-(SRSSRS)_n + \text{"SR'(SSR'S)_n} & \rightarrow -(SRSSR'S)_n + \text{"SR(SSRS)_n} \\
\text{Scheme 1}
\end{align*}
\]

\[
\begin{align*}
(SRS \quad SRS)_n + (SRS \quad SRS)_n & \rightarrow (SRS \quad SRS)_n + (SRS \quad SRS)_n \\
\text{Scheme 2}
\end{align*}
\]

Scheme 1 involves an \(S_n2\) type reaction in which nucleophilic displacement by a thiolate anion occurs. The reaction rate for displacement is expected to be dependent upon the concentration of free thiolate anions and the basicity of the thiolate anions.¹⁵ Thus, scheme 1 is expected to play an important role in cases where large differences in redox potentials exist, and when high concentrations of thiolate anions are present. If the reaction is occurring in the solid state (for example, in the cathode of a lithium polymer electrolyte battery), the rate should also depend upon the relative mobilities of the anions. Scheme 2 shows a free radical process in which exchange takes place via a 4S ring intermediate. This mode of reaction would tend to increase in importance if the reaction mixture is heated or subjected to light. The relative dominance of one process

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(whether simple redox, free radical or nucleophilic displacement) in a copolymer system is undoubtedly dependent upon a number of factors, including concentration and type of the reactants as well as reaction conditions. The nature of the scrambling is undoubtedly complex, and several processes may occur simultaneously or concurrently in some cases. A full determination of mechanism was considered beyond the scope of this paper. No formal attempt was made to identify products as random, regular or block copolymers, due to the difficulties inherent in analyzing these intractable materials.

The process of copolymerization is sometimes directly observable in the discharge curves. Figure 5 shows discharge curves of X8 alone (a) and X1 alone (b) as well as several cells in which X1 and X8 were mixed in various ways. Curves c, d and e are the first discharge, recharge and second discharge respectively of a cell in which a circular 1 cm² X1 cathode was placed inside an X8 cathode with a 1 cm² hole in the center (total area 2 cm², X1 capacity 50% of total). As expected this resulted in a mixed potential discharge curve; i.e. a plateau at about 2.8 V which could be attributed to X1 and a lower plateau attributable to X8. (The difficulty encountered in aligning the cathodes probably contributed to the rather poor utilization shown by this cell). The subsequent charge and discharge, however, was sloping, as might be expected for a random copolymer of X1 and X8. Surprisingly, when a cell with a cathode containing a 50:50 mixture of X1 and X8 (loading 30 wt. % electroactive material) was discharged, plateaus were not seen; instead the profile was sloping. Similar behavior was seen for a cell containing an X1 cathode stacked on top of an X8 cathode (X1 50% of total cell capacity). Scrambling leading to random copolymers essentially occurs before the full discharge of the cell whenever X1 and X8 are in intimate contact. This may occur via free radical processes when the cell is heated in preparation for discharge, and/or via nucleophilic displacement during discharge as free thiolate anion concentration increases. In the absence of these scrambling processes the random copolymerization of X1 and X8 probably would not be favored due to the large difference in redox potentials (about 1 V); the tendency instead would be towards forming block copolymers or separate polymers. Clearly, randomization processes such as are depicted in schemes 1 and 2 dominate the chemistry of the X1/X8 system and allow copolymers to form readily.
In some cases, it is advantageous to copolymerize materials by chemical oxidation prior to incorporation in cathodes due to processing considerations. X0, a viscous, amorphous polymer, is difficult to handle because of its physical properties. A harder material is obtained when X0 is crosslinked by addition of 5 wt. % X5. A copolymer made from a 50:50 mixture of X1 and X0 dithiolate anions is a yellow-white powder similar in appearance to X1. The homogeneity of the products and change in physical properties from the simple polymers was interpreted as positive evidence that copolymers had formed. In some cases, however, attempted chemical copolymerization was unsuccessful. For example, oxidation of a 50:50 mixture of X0 and X5 led to two separate phases. Apparently, randomization reactions are slow or nonexistent for this system, and the large voltage difference between X0 and X5 thiolate anions discourages copolymerization leading to the production of two separate polymers instead.

The discharge characteristics of the 5% X5/95% X0 and 50% X1/50% X0 copolymers as well as those of X1 and X0 alone are shown in Figure 6. The profile of the X1/X0 copolymer is similar to that of X1 alone, but is slightly more sloping. Electrochemical copolymerization of X1 and X0 gave a product with discharge characteristics identical to that of the chemical product. Because of the strong resemblance of the X1/X0 copolymer discharge curves to that of X1 alone, it is not possible to observe the copolymerization of X0 with X1 as readily as with X1/X8. The discharge profile of X0/X5 is similar to that of X0 alone. In general, utilization of X0/X5 and X0/X1 copolymer cathodes (whether chemically or electrochemically produced) was slightly better than that of the X0 alone.

Conclusions

The discharge characteristics of several types of polydisulfides and copolymeric polydisulfides have been presented. Properties such as cell voltage, utilization, and electrode kinetics vary as a function of R group in the polydisulfides, allowing Li batteries to be "custom tailored" for desired features. Although X1 may be discharged at the highest rates, X8 is extremely promising in terms of energy density and utilizable of thick cathodes. Copolymers may be made by chemically oxidizing two different dithiolates together, or, in some cases, by combining two polymers in one cell and subjecting the cell to discharge. Copolymerization allows the desirable features of two or more polydisulfides to be combined in one battery; and, in some cases, results in improved cell performance over the single polydisulfide cells. The facile modification of properties by changing R group or by copolymerization is a characteristic unique to the solid redox polymerization electrode, and is a decided advantage in the design of thin film Li solid polymer electrolyte cells.
Figure Captions

Figure 1. Discharge curves of organopolydisulfides in Li/P(EO)9LiTf cells. Loading levels were 30 wt. % in all cases. The temperature was 95° C for X0, X1, X5, X7 and X9 and 110° C for X8. The current density was 0.5 mA/cm² for X0, X1, X7, X8 and X9 and 0.25 mA/cm² for X5.

Figure 2. Discharges at 0.5 mA/cm² for Li/P(EO)9LiTf/X8 cells as a function of capacity (cathode thickness). Loading of X8 in the cathode was 45 wt. %.

Figure 3. Practical volumetric and gravimetric energy densities for X1 and X8 cells as a function of cathode thickness. Cells consist of cathodes of varying capacities and loading levels, 30 μm P(EO)9LiTf separators, lithium anode four times the capacity of the cathodes and two metallized plastic current collectors 5 μm thick.

Figure 4. Five cycles of a Li/P(EO)9LiTf/X8 cell discharged at 0.5 mA/cm² and charged at 0.25 mA/cm². The temperature was 90° C for the first cycle and 108° C for the subsequent cycles.

Figure 5. Copolymerization of X1 with X8 in Li/P(EO)9LiTf cells. All cells had 30 wt. % electroactive material in the cathode and were discharged at 0.5 mA/cm² at 105° C. a) X8 alone (110° C). b) X1 alone (95° C). c) 1 cm² X1 cathode placed inside an X8 ring cathode, so that the total cathode area was 2 cm². Electroactive material was 50 mol % X1. d) recharge of c. e) second discharge of c. f) X1 and X8 mixed in the cathode. Electroactive material was 50 mol % X1. g) X1 cathode placed on top of an X8 cathode in the cell. Electroactive material was 50 mol % X1.

Figure 6. Discharge profiles at 0.5 mA/cm² of X0, X1 and copolymers of X0/X5 and X1/X0. The temperature was 95° C.
Figure 1
Figure 2
Figure 3
Figure 4