PREPARATION OF CATION-EXCHANGE POLYCAPROAMIDE FIBERS

Yu. D. Andrichenko and T. V. Druzhinina

A characteristic feature of radical polymerization of ionizing monomers, particularly sulfonic acids and their salts, is the possibility of effective control of the kinetic parameters of this reaction by varying the ionic strength of the solution not only as a result of increasing the monomer concentration but also as a result of adding low-molecular nonpolymerizing electrolytes to the solution [1, 2]. At the same time, there are practically no data in the literature relating to studies of the heterophase graft polymerization of these monomers, in particular to polyamide fibers [3], despite the increasing interest in preparation of such fibrous chemisorptive materials.

In the present communication we give the results of investigating the radical graft polymerization of potassium styrenesulfonate (PSS) to chemically oxidized polycaproamide (PCA) fiber which had been prepared by treating fiber containing the copper complex of a triisoindolebenzene macro-ring [4] with a hydrogen peroxide solution.

The graft polymerization reaction was carried out in an aqueous PSS solution and in the presence of low-molecular electrolytes which are commonly used in studies of polymerization processes, particularly the chlorides of Li, Na, K, and Ca, and also in the presence of sodium acetate or sulfate.

Since there is no information in the literature about the use of UV-spectroscopy for the quantitative estimation of PSS concentration of potassium polystyrenesulfonate (PPSS) in a solution, we have carried out studies of these solutions using this method and have derived an equation which can justifiably be used to determine the concentration of PPSS (C, % by wt.) at a homopolymer concentration in the solution no greater than 1.65 moles per mole of PSS:

\[
C = \frac{(D - 0.0255) \cdot MP \cdot 500}{5839.21 \cdot 1000m} \cdot 100,
\]

where \(D\) is the optical density at \(\lambda = 250\) nm; \(P\) is the dilution; \(m\) is the sample weight of solution, in g (0.5-0.6); and 5839.21 is the molar absorption coefficient (pH = 11.2).

The deviation of the found value for PSS concentration from the calculated one thereupon does not exceed ±4%. At a larger PPSS content (4 moles/mole of PSS) the difference rises to +6%.

Studies showed that in an aqueous solution, the graft polymerization of PSS begins above 20°C (Fig. 1), and on varying the pH of the solution from 1.1 to 12.8, it takes place at a rate which does not exceed 1.90 \(\cdot 10^{-5}\) moles/(liter \(\cdot\) sec). It is to be noted that at a temperature which corresponds to carrying out the graft polymerization, PSS is characterized by a low affinity to PCA fiber as compared with its tendency to be sorbed on the surface of grafted PPSS. Thus, on immersing a modified PCA fiber containing 19.5% by wt. of grafted PPSS in a solution of PSS, the decrease in initial concentration of monomer after 30 min (pH = 11.2) reaches 35% instead of 2% in the case of the original PCA fiber. The increase in yield of graft polymer in an alkaline medium (Fig. 1, curve 2) is obviously connected both with a change in activity of the PCA–OOH–Cu initiating system and also with an increased reactivity of the PSS as a result of a change in state of the ionogenic groups and their effect on the electron density of the PSS double bond. The manifestation of an inductive effect (in combination with a resonance effect) of the sulfonate groups on the reactivity of the double bond in the polymerization process of sodium styrenesulfonate has been previously noted in [5].

For the graft polymerization reaction of PSS, just as for the polymerization of styrenesulfonic acid and its salts [1], a considerable dependence of the extent of reaction on the ionic strength of the solution is characteristic. On increasing the concentration of PSS (within the limits of its solubility) by a factor of 4, the yield of graft polymer rises approximately by a factor of 9 (Fig. 1, curve 3).

The studies performed have made it possible to establish an effect of the nature of the electrolyte on certain kinetic parameters of the graft polymerization of PSS. Specifically, the addition to an aqueous monomer solution of an equimolar quantity of singly charged metal ions, especially as the ionic activity coefficient decreases in the series LiCl > NaCl > KCl > \(\text{Na}_2\text{SO}_4\), helps increase the rate of reaction and the yield of graft polymer (Table 1).
Fig. 1. Effect of temperature (1), pH of grafting solution (2), and monomer concentration (3) on yield of grafted PPSS. Reaction conditions: pH\textsubscript{in} = 10.3; t = 75 ± 2°C; \( \tau \) = 120 min; liquid to solid ratio = 30; PSS concentration = 0.79 (1) or 0.50 (2) moles/liter.

TABLE 1. Effect of Nature of Electrolyte on the Graft Polymerization of PSS

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Ionic activity coefficient</th>
<th>Initial reaction rate, moles/(liter sec)</th>
<th>Yield of grafted PPSS, % of wt. of PCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>0.921</td>
<td>27.8</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>0.668</td>
<td>3.9·10\textsuperscript{-5}</td>
<td>37.9</td>
</tr>
<tr>
<td>CH\textsubscript{3}COONa</td>
<td>--</td>
<td>4.2·10\textsuperscript{-5}</td>
<td>33.2</td>
</tr>
<tr>
<td>KCl</td>
<td>0.573</td>
<td></td>
<td>37.9</td>
</tr>
<tr>
<td>Na\textsubscript{2}SO\textsubscript{4}</td>
<td>0.152</td>
<td>5.8·10\textsuperscript{-5}</td>
<td>43.5</td>
</tr>
<tr>
<td>None</td>
<td>--</td>
<td>1.9·10\textsuperscript{-5}</td>
<td>25.6</td>
</tr>
</tbody>
</table>

Note. [PSS] = 0.79 moles/liter; pH = 11.2; electrolyte corresponds to 1 mole per mole of PSS; t = 70°C; \( \tau \) = 120 min.

Fig. 2. Effect of chemical nature of electrolyte and of its content in the monomer solution on the graft polymerization of PSS. Reaction conditions: [PSS] = 0.79 moles/liter; pH = 11.2; t = 75 ± 2°C; \( \tau \) = 120 min; bath to fiber ratio = 30; electrolyte, CH\textsubscript{3}COONa (1), NaCl (2), or Na\textsubscript{2}SO\textsubscript{4} (3).

From the hypothesis about a kinetic role of ion pairs in the radical polymerization of ionizing monomers [6], this fact may be obviously explained by an increase in the rate of chain growth due to an increase in concentration and stability of ion pairs. Addition of a doubly charged Ca\textsuperscript{2+} cation (in the form of CaCl\textsubscript{2}) is also rather effective; this helps increase the yield of