Vinyl acetate polymerization by ionizing radiation

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Abstract

For this work an irradiation system to be used in the polymerization of the vinyl acetate in methylethylketone and in ethyl alcohol solution using the gamma radiation as initiator was projected and built. The molecular weights of the polymers obtained by irradiation with gamma rays in methylethylketone and in ethyl alcohol solution were 33,000 and 44,000 g/mol, respectively. From the characterization by infrared spectroscopy it was possible to verify that the polymers obtained in two studied cases actually correspond to poly(vinyl acetate).

Keywords: Polymerization; Poly(vinyl acetate); Radiation

1. Introduction

Poly(vinyl acetate) (PVAc) is obtained by the free-radical polymerization of vinyl acetate. Polymerization is carried out commercially by bulk, solution, suspension or emulsion polymerization techniques (Ravve, 1995).

Polymerization can be initiated by organic and inorganic peroxides, azo compounds, redox systems, light and high-energy radiation (Cordeiro, 1997).

Polymerization of a monomer comprises three major steps—initiation, propagation, termination—possibly modified by other reactions such as transfer. In radiation-induced polymerization attention is essentially confined to the first step, where radiation can often be considered as an attractive alternative to chemical initiation by a thermally activated catalyst. Major advantages include the following (Charlesby, 1987):

1. absence of any residue as from the decomposition of a chemical catalyst;
2. an immense range of intensities and, hence, initiation rates;
3. little or no temperature effect, so that the choice of an operating temperature may be fixed by other considerations (e.g., propagation rate);
4. there is no danger of runaway reaction due to the energy released in the propagation step reacting to enhance the initiation rate of the catalyst;
5. unusual features such as the possibility of initiation in the solid state, polymerization of oriented monomers, and so on.

The aim of this work is to polymerize vinyl acetate to produce PVAc by gamma radiation to obtain a product without initiators and with a high degree of purity, qualities that are required when this polymer is applied in medicine and in the food industry (Ebdon and Eastmond, 1995).

The vinyl acetate polymerization was carried out, in solution, using a Gammacell-220 with a dose rate of 6.7 kGy/h, at different doses. The PVAc was characterized by FTIR-spectroscopy.

The PVAc molecular weight obtained by ionizing radiation in solution agrees with the values obtained by chemical processes.
2. Experimental

The irradiations were accomplished with gamma rays coming from an irradiator of $^{60}$Co (Challa et al., 1985), “Gammacell-220” of Atomic Energy of Canada Limited”, with a dose rate of 6.7 kGy/h. For the samples irradiation a polymerization reactor was used. This reactor has two paths (inlet and outlet) for the circulation of the monomer solution, containing in the center a type tube well for introduction of the thermocouple that is used to control the temperature of the polymerization reaction (Fig. 1).

Initially, samples of vinyl acetate monomer in solution were prepared, with methylethylketone as solvent, in a proportion in volume of 1:1. This sample was irradiated for 6 h corresponding to a radiation dose of 40.2 kGy.

Later, a bracket of the sample was taken and put in a rectangular-form glide of stainless steel, where the heating for evaporation of the solvent occurred and PVAc free from solvent was obtained.

The same procedure previously described was accomplished for the polymerization by gamma radiation of the vinyl acetate using ethyl alcohol as solvent, following the same proportion of 1:1 in relation to the monomer. The reaction was interrupted after 2 h of irradiation, corresponding to a radiation dose of 13.4 kGy. Later, the solvent was also evaporated to yield the PVAc free from solvent.

Then the molecular weight of both polymers obtained by gamma radiation was determined, using a liquid chromatography HPLC.

Finally, the samples were analyzed by infrared absorption spectroscopy, in agreement with the norm ASTM-AND 1252-98, using the equipment Great Nicolet—IR 550. The samples were applied in crystals of KBr and analyzed directly.

3. Results and discussion

The results of molecular weight of PVAc obtained by gamma radiation acting as initiator of the polymerization of vinyl acetate in methylethylketone and in ethyl alcohol solution are given in Table 1.

<table>
<thead>
<tr>
<th>Samples of PVAc</th>
<th>Irradiation time (h)</th>
<th>Radiation dose (kGy)</th>
<th>Molecular weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylethylketone</td>
<td>6</td>
<td>40.2</td>
<td>33,000</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>2</td>
<td>13.4</td>
<td>44,000</td>
</tr>
</tbody>
</table>

The molecular weight of the PVAc obtained by the gamma radiation was compared with that obtained industrially that is of 44,000 g/mol. It was observed that the polymer obtained by gamma radiation of the monomer in solution of ethyl alcohol was similar to that obtained industrially by the traditional chemical method.

Figs. 2 and 3 present the absorption spectra in the infrared area of the PVAc obtained by gamma radiation in methylethylketone solution and ethyl alcohol, respectively. These spectra showed characteristic absorption bands in 1735 cm$^{-1}$, corresponding to the axial deformation C=O, and in 1244 cm$^{-1}$, corresponding to the axial deformation C–O, characterizing the presence of an acetate.

Comparing the spectra obtained to those of the Library “Hummel Polymer and Additives”, of the equipment, it can be affirmed that both samples analyzed correspond to a PVAc due to the peaks presented in Figs. 2 and 3, corresponding to the absorption spectrum in the infrared area of the poly(vinyl acetate) obtained industrially (Fig. 4). It was observed that these spectra are coincident. Therefore, it can be concluded that the products obtained by irradiation of gamma rays with the vinyl acetate in methylethylketone and in ethyl alcohol solution really correspond to the polymer of PVAc.

The results of the polymerization for radiation range demonstrated that the method is viable with same small changes of practical order in the polymerization system projected, built and used in this work, to make the polymerization process faster and more efficient.
Fig. 2. Spectrum of PVAc obtained in solution of methylethylketone.

Fig. 3. Spectrum of PVAc obtained in solution of ethyl alcohol.
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References


Fig. 4. Spectrum of PVAc obtained industrially.