

## New approach to the preparation of grafted ion exchange membranes based on UV-oxidized polymer films and sulfonated polystyrene

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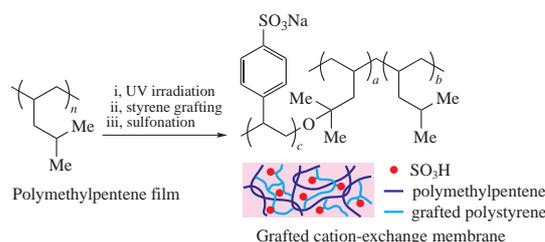
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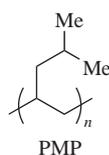
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The new way for the synthesis of advanced functional materials for water purification and alternative energy, namely, grafted cation-exchange membranes based on UV-oxidized aliphatic polymers (polypropylene and polymethylpentene) and sulfonated polystyrene, is proposed.



Ion-exchange membranes are among the main functional materials in membrane processes for water purification<sup>1,2</sup> and alternative energy.<sup>3–5</sup> In the state-of-the-art membrane technology, the task to obtain thin and relatively cheap membrane materials is of interest.<sup>6</sup> The graft polymerization of polar monomers on a nonpolar base film is a promising and convenient method for obtaining such membranes.<sup>7–9</sup> However, the use of high-energy gamma radiation for the generation of active centers in the base film reduces the attractiveness of this method in comparison with traditional chemical methods for the preparation of ion-exchange membranes.<sup>10</sup> Consequently, reducing the energy of activation radiation, for example, to the relatively safe UV range is an important problem. Moreover, UV radiation is more commonly applied in science and industry, for example, for water treatment<sup>11,12</sup> and chemical synthesis.<sup>13–15</sup>

It is well known that the UV activation of polypropylene for post-graft copolymerization can be used for its surface modification.<sup>16</sup> The surface nature of the grafted polymer distribution is due to the low oxygen permeability of polypropylene, which does not allow the active C–OOH group to be formed in the volume of material upon UV treatment. Polymethylpentene (PMP) is an analogue of polypropylene with tertiary carbon atoms necessary for UV oxidation and with enhanced gas permeability.<sup>17</sup> We consider that PMP can be used to produce UV-irradiated post-grafted ion-exchange membranes.



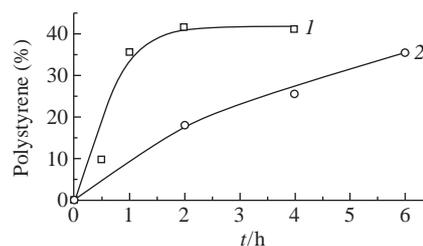
The polypropylene and PMP films were oxidized for 2 h in a custom-made reactor using an UV lamp. Since irradiation leads to the intense heating of films (up to polymer softening), they were cooled with an airflow. The post-graft copolymerization of

styrene onto a base film was carried out according to a published procedure.<sup>18</sup> The grafted polystyrene was sulfonated with 1.5 vol% chlorosulfonic acid in 1,2-dichloroethane. After that, the chlorosulfonic groups were hydrolyzed, and the resulting membrane was converted into the Na<sup>+</sup> form by immersing in a 1 wt% solution of NaOH.

The UV oxidation of films for 2 h did not lead to a noticeable change in their mechanical properties indicating that the radiation doses did not cause significant polymer degradation. At the same time, the doses provided a sufficient number of active C–OOH groups for successful polystyrene grafting.

Polystyrene is grafted onto PMP much faster than onto polypropylene (Figure 1). However, the inverse relationship is known for these polymers from published data on  $\gamma$ -induced grafting.<sup>19</sup> The observed differences are related to the fact that styrene is irregularly grafted onto polypropylene in terms of both area and thickness, as shown by electron microscopy. This is apparently observed due to the nonuniform formation of peroxy groups resulting from a much lower gas permeability of polypropylene.

In addition, the inhomogeneity of the conducting phase distribution affects the conductivity of membranes based on polypropylene. Therefore, the conductivity of the neighboring areas of a film can vary by orders of magnitude. An increase in the dose of UV irradiation or the duration of synthesis does not lead to an improvement of this feature.



**Figure 1** Grafted polystyrene content on (1) PMP and (2) polypropylene films vs. synthesis time.

**Table 1** Physicochemical properties of the ion-exchange membranes based on sulfonated grafted polystyrene and PMP (Na<sup>+</sup> form, 23±1 °C).

Polystyrene content (wt%)	Thickness (0.5 M NaCl)/μm	Water uptake (%)	Ion exchange capacity/mmol g <sup>-1</sup> (for the dry membrane)	Conductivity in 0.5 M NaCl/Ω <sup>-1</sup> cm <sup>-1</sup> (25 °C)	Young's modulus/MPa	Tensile strength/MPa	Strain at break (%)
					RH = 95%		
0	50	–	–	–	1090	19	280
10.0	55	16.4	0.5	6.2×10 <sup>-4</sup>	860	18	5
35.5	77	53.1	2.5	3.0×10 <sup>-2</sup>	460	16	8
41.0	87	53.7	2.6	3.4×10 <sup>-2</sup>	290	13	11

We studied the physicochemical properties of ion exchange membranes based on PMP (Table 1). An increase of grafted polystyrene content up to 41 wt% makes it possible to achieve an ion-exchange capacity of 2.6 mmol per gram of the dry membrane and a water uptake of 53.7 wt%. The through-plane ionic conductivity was measured by impedance spectroscopy with a P-40X potentiostat galvanostat (Elins) in a four-electrode cell.<sup>20</sup> The Na<sup>+</sup> conductivity of the membranes was 3.4×10<sup>-2</sup> Ω<sup>-1</sup> cm<sup>-1</sup>. With a thickness of 70–80 μm, this provides a low surface resistance around 0.26 Ω cm<sup>2</sup>, which is better than that of commercially available materials.<sup>5</sup> However, with an increase in the fraction of a sulfated polystyrene phase, the Young's modulus and the tensile strength decreased significantly due to the low strength characteristics of the conductive phase containing water. Despite this, the membranes obtained have mechanical properties satisfactory for a number of applications. For example, they can be used in neutralization dialysis<sup>21</sup> or reverse electrodialysis.<sup>22</sup>

Thus, we have developed a new approach to the synthesis of ion-exchange membranes based on sulfonated polystyrene grafted onto UV-oxidized polymethylpentene. An increase in the polystyrene content leads to an increase in water uptake and conductivity.

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