

## PREPARATION OF IONOGENIC MEMBRANES BY RADIATION-INDUCED GRAFTING

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Conditions of preparation of ionogenic membranes based on the radiation induced polymerization of styrene on low-density polyethylene films (LDPE) were investigated. After optimization of the preparation conditions (radiation dose, concentration of the monomer solution, temperature of grafting), a series of samples with various degrees of grafting were prepared. Their sulfonation yielded cation-active membranes which were characterized by ion-exchange capacity, concentration membrane potentials, specific and area resistance, transport number of preferred ions, and permselectivity\*.

The procedure of preparation of ionogenic membranes by the method of radiation grafting of vinyl monomers on polymer films has been intensively studied. The main condition is that the trunk polymer for carrier films should possess satisfactory mechanical, chemical and thermal properties. By using the radiation induced polymerization, the required quantity of a further polymer which contains, either directly or after a consecutive reaction, the necessary concentration of cation- or anion-active groups can be grafted into the starting polymer. In this way, membranes possessing satisfactory mechanical and electrochemical properties can be prepared.

The mechanism of grafting process applied to four different types of copolymers has been described by Chen *et al.*<sup>1</sup>. Kinetic and theoretical studies of the radiation induced grafting in various systems have been carried out by many authors<sup>2-6</sup>. To obtain high-quality membranes, homogeneous grafting should proceed throughout the film. To achieve this, the amount of the diffused monomer should be higher than that needed for initiation and propagation in the reaction zone<sup>7</sup>, and the average time within which the diffused monomer molecules would reach the centre of the film should be shorter than the lifetime of radiation generated radicals. This condition can be ensured by a uniform swelling of the film before the grafting reaction and by adequate conditions of the grafting reaction (temperature, concentration of the monomer solution).

\* The results of this study were presented at the symposium Miners' Pfibram in Science and Technology 1986.

Radiation grafting can be carried out by two procedures: Directly, when the polymer film is immersed in the monomer or its solution, and the whole system is irradiated; or indirectly, by the so-called preirradiation procedure, consisting in a preliminary irradiation of the film, followed by the grafting reaction with the monomer. Direct procedure was used, *e.g.*, in grafting acrylic acid, methacrylic acid and N-vinylpyrrolidone on PE films<sup>8</sup>. Chakravorty *et al.*<sup>9</sup> describe the direct grafting of styrene on PE films and subsequent reactions used for the introduction of ionogenic groups. Omichi and Okamoto<sup>10</sup> investigated the grafting of methyl(2,3,3-trifluoroacrylate) on PE films and found that a much more homogeneous distribution of graft chains, and thus a decrease in the electric resistance of membranes can be achieved by the so-called co-grafting of an equimolar mixture of methyl(2,3,3-trifluoroacrylate) and propylene *in vacuo*. Preirradiation procedure was used in the grafting of acrylic acid on PE (ref.<sup>11</sup>), poly(tetrafluoroethylene-co-perfluorovinyl ether)<sup>12</sup>, poly(vinyl fluoride) and poly(tetrafluoroethylene-co-ethylene)<sup>6</sup>. Ellinghorst *et al.*<sup>6</sup> grafted also N-vinylpyrrolidone, styrene, vinyl acetate, dimethylaminoethyl methacrylate, vinylpyridine and vinylimidazole into the films mentioned above.

After experiments used to check advantages of the individual grafting procedures, the preirradiation procedure was used in this study in grafting styrene on LDPE films. The subsequent sulfonation gave cation-active membranes, the properties of which were evaluated by determining characteristic quantities.

## EXPERIMENTAL

### Materials

A PE film Bralen FB 4-18<sup>R</sup> (Slovnaft Bratislava, Czechoslovakia), 80 × 120 mm in size, 100 μm thick, was used as the trunk polymer. Prior to irradiation, the samples were swollen at 30°C in a benzene-ethanol solution (1 : 1 by vol.) for 28 h, then dried and weighed.

Styrene (Chemopetrol, conc. enterprise, Kaučuk Kralupy n. Vltavou, Czechoslovakia) used as the grafting monomer was purified by washing three times in 20% NaOH, then in distilled water to neutral reaction, by distillation *in vacuo*, and drying.

### Preirradiation Grafting

PE films were irradiated in the air by using the RCHM apparatus (U.S.S.R.), with <sup>60</sup>Co radiation, dose rate 1.07 kGy/h. Prior to grafting, the styrene solution in methanol was freed from oxygen by bubbling with argon. PE films were placed in the monomer solution prepared in advance immediately after the irradiation. The grafting temperature was 60–70°C, the grafting time was 2–10 h. On completion of the reaction, the samples were extracted with benzene at 30°C for 28 h and dried to constant mass. The degree of grafting was determined gravimetrically.

### Sulfonation and Characterization of Membranes

Grafted samples were sulfonated in a 7% vol. solution of chlorosulfonic acid in dichloroethane at room temperature for 2 h (ref.<sup>13</sup>). After that, they were washed with distilled water to neutral reaction.

The membrane properties were characterized by determining the total exchange capacity (meq/g), area resistance ( $\Omega \text{ cm}^2$ ), specific resistance ( $\Omega \text{ cm}$ ), transport number of the preferred ion in the membrane, and permselectivity (%). Electrochemical measurements were performed at 25°C in a special cell described by Kùdela *et al.*<sup>14</sup>. The electrical conductivity of membranes was measured by means of an LF 2000/C conductometer, manufactured by WTW, F.R.G., at the frequency 4 kHz, in 0.5M-NaCl. The membrane thickness varied in the range 140–150  $\mu\text{m}$ . The concentration membrane potentials were measured with a pMX 2 000/pH WTW millivoltmeter with Ag/AgCl electrodes in the system 0.1 m KCl/0.2 m KCl. The transport numbers and permselectivities of the membranes were calculated from their concentration potentials.

## RESULTS AND DISCUSSION

The initial experiments were carried out in order to check advantages and disadvantages of the individual procedures during the actual grafting of styrene on PE films. The advantage of the direct procedure were higher yields of grafting, due to a considerably higher probability of an early penetration of the monomer to the radicals formed. A disadvantage of the same procedure is seen in the excessive formation of the undesired homopolymer which is accumulated around the grafted chains and is difficult to remove. The advantage of the preirradiation procedure was an easier manipulation with the films during irradiation, a better possibility of checking conditions of the two reactions and only an insignificant formation of the homopolymer. It is however necessary to apply higher radiation doses. This procedure gives better results in grafting on semicrystalline polymers, because macroradicals formed by radiation have a considerably longer life-time in crystalline regions. Diffusion of the monomer in the amorphous part is sufficiently quick, so that in the vicinity and on the surface of crystallites grafting proceeds more readily. Basing on the results of the analysis, we decided to prepare the membranes by employing the preirradiation procedure.

First, the individual parameters which may affect the process of grafting (irradiation dose, concentration of the grafting monomer, temperature and time of grafting)

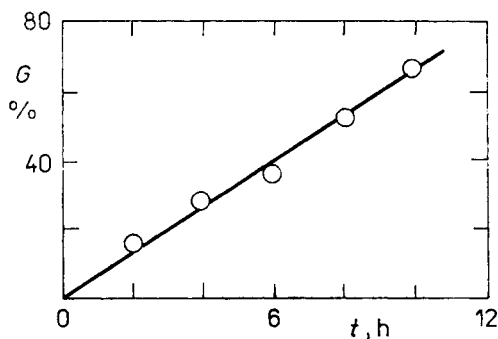


FIG. 1

Dependence of the degree of grafting on the time of grafting. Conditions: 70°C, 80 vol. % styrene in methanol, radiation dose  $^{60}\text{Co}$  25 kGy

were changed so as to optimize the conditions which would eventually lead to a uniform grafting of the samples. The best results were obtained at the total absorbed dose of  $\gamma$ -radiation 25 kGy, by using an 80 vol. % styrene solution in methanol and at the grafting temperature 70°C. A series of samples with various degrees of grafting were prepared under these conditions. The dependence of the degree of grafting on the reaction time is virtually linear up to a high polystyrene content,

TABLE I

Properties of cation-active membranes prepared by grafting styrene on LDPE films followed by sulfonation. Symbols:  $G$  degree of grafting,  $C$  ion exchange capacity,  $V$  membrane potential (of samples A and B),  $t_{\pm}$  transport number of preferred ions,  $S$  permselectivity

$G$ mass %	$C$ mequiv/g	$V$ , mV		$t_{\pm}$	$S$ %
		A	B		
12.8	1.10	-15.89	-15.90	0.994	98.8
25.2	1.45	-15.84	-15.90	0.993	98.6
34.2	1.92	-15.70	-15.70	0.988	97.6
42.3	2.13	-15.50	-15.48	0.981	96.3
55.5	2.45	-15.40	-15.33	0.977	95.5

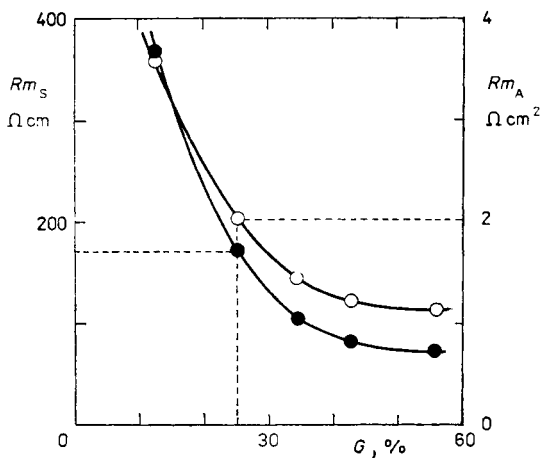


FIG. 2

Effect of the degree of grafting on the specific ( $Rm_s$ , ●) and surface ( $Rm_A$ , ○) resistance of membranes

c. 65% (Fig. 1). This indicates a good swelling through the PE film before irradiation, and, consequently, a sufficiently quick diffusion of the monomer in the reaction. Extraction of the grafted samples with benzene was used to investigate the homopolymer content. Its quantity varied in the range between 0.5 and 2% (related to the mass of polystyrene), which can be regarded as negligible.

Sulfonation was used to introduce cation-active sulfo groups into the samples. As expected, their concentration (expressed in Table I in the form of ion-exchange capacity) increases linearly with the degree of grafting. Table I also shows the electrochemical characteristics of the membranes thus obtained. The concentration membrane potentials determined in parallel using two samples (A and B) taken in various places of the membrane allow us to assume a very good homogeneity of distribution in the membrane area. It can be seen, moreover, that the higher polystyrene content in the membrane raises somewhat its total permeability, as reflected in a light decrease in permselectivity. It should be mentioned, however, that the selectivity of permeability of the cations is very good in all samples of the membranes.

With increasing degree of grafting, and thus also with increasing concentration of the introduced sulfo groups the specific and surface resistance of the membranes decreases (Fig. 2). It is quite obvious that approximately starting from a 25% degree of grafting of polystyrene and more, the procedure allows membranes to be obtained, the parameters of which are very suitable for electrodialysis from the economic point of view.

The surface area of the film which can be irradiated by using the apparatus mentioned above is very limited, however. Large-size membranes which might be applied in an electrodialysis unit on an industrial scale would have to be prepared by using an electron accelerator. By employing such procedure, it would be possible to irradiate continuously films passing under a beam of accelerated electrons, which would be followed by grafting in an adequately arranged apparatus.

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