

Chloromethylation of the Polyethylene/Poly(Styrene-co-Divinylbenzene) System

INTRODUCTION

The polyethylene/poly(styrene-co-divinylbenzene) system [PE/poly(St-co-DVB)] obtained via interpolymerization of styrene and divinylbenzene in PE¹⁻³ is used as a starting material for the synthesis of ion-exchange membranes.^{4,5} Cation-exchange membranes are obtained by the direct sulfonation of this material,^{3,6,7} but the amine groups can be introduced into it by chloromethylation of polystyrene and, next, by amination of the chloromethylated intermediate.⁸⁻¹¹

Usually, the chloromethylation was carried out in refluxing chloromethyl methyl ether,¹² which is, however, very inconvenient in view of cancerogenic properties of this chemical.¹³

The purpose of this work was to investigate the possibilities of chloromethylation of the PE/poly(St-co-DVB) system at lower temperature than those used previously to obtain strong base anion exchange membranes with satisfactory physicochemical and mechanical properties.

EXPERIMENTAL

The PE/poly(St-co-DVB) system obtained by the continuous modification of PE with St and DVB in melt,³ containing 30 wt % of St and DVB crosslinked with 4 wt % of DVB in the monomer mixture, was used as a starting material. The blend was extruded with blowing to give a foil 0.2 mm thick.

The foil was chloromethylated by using chloromethyl methyl ether (CMME) in the presence of stannic chloride as a catalyst, and it was next aminated with *N,N*-dimethylaminoethanol (DMAE).

Anion-exchange capacity was determined by the OH⁻/Cl⁻ cycle by the standard procedure.¹⁴ Specific resistance was measured in a 0.1M sodium chloride solution by the modified procedure reported by Gryte and Gregor.¹⁵

The tensile strength of the water-swollen membranes in the chloride form was determined with a ZT-40 apparatus.

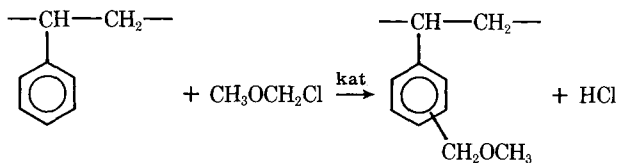
RESULTS AND DISCUSSION

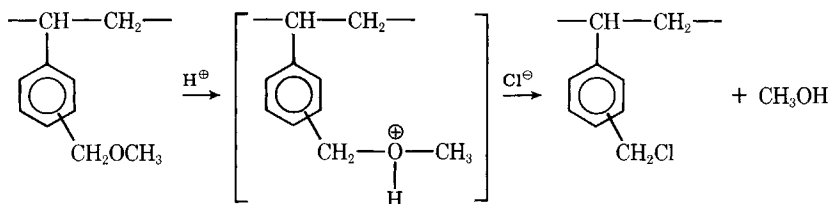
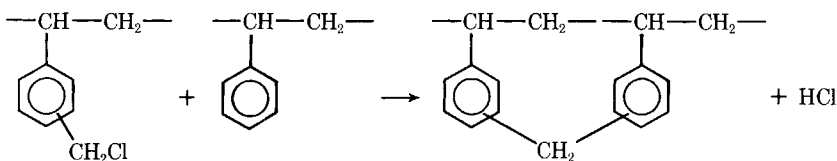
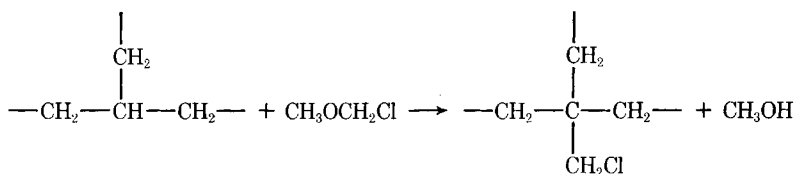
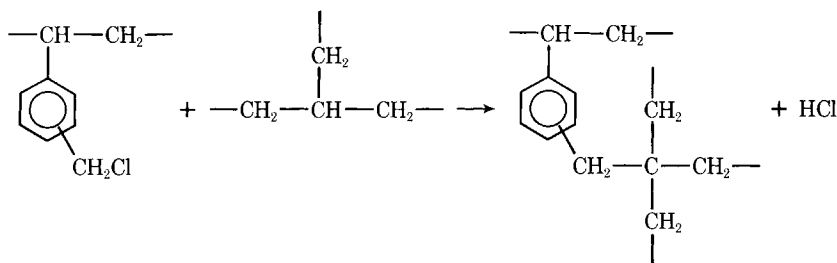
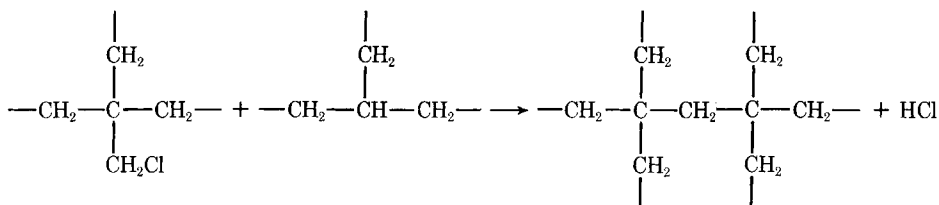
The results of chloromethylation of polymers depend mainly on polymer structure, the kind of chloromethylating agent, catalyst, the kind and amount of solvent, and other parameters of the process.

The PE/poly(St-co-DVB) system was found to be a heterogeneous one^{12,16,17}; it is composed of polyethylene homopolymer, grafted polyethylene, styrene-divinylbenzene copolymer, and polystyrene homopolymer. It was assumed that poly(St-co-DVB) in this system exhibits properties similar to those of styrene-divinylbenzene copolymer obtained via suspension copolymerization.^{16,17} Thus, the problem of chloromethylation resolves itself into a reaction on this copolymer and determining the behavior of PE under these conditions.

On chloromethylating the studied system the following reactions can take place:

(i) The introduction of chloromethyl groups into the benzene ring of polystyrene¹⁸:



(ii) Crosslinking of the copolymer^{9,12,19}:(iii) The introduction of chloromethyl groups into a PE chain¹²:(iv) Crosslinking of PE with poly(St-co-DVB)¹²:(v) Crosslinking of PE¹²:

The yield of chloromethylation is determined by the content of crosslinking agent in styrene-divinylbenzene copolymer. In the studied system the mode of poly(St-co-DVB) distribution in PE should also be taken into account. It was found previously that the DVB content in the monomer mixture was higher than 2 wt % and up to 20 wt % a macroscopically continuous poly(St-co-DVB) phase in PE was formed^{12,16,17}; thus in such case the probability of crosslinking via reaction (ii) is lower. This reaction enhances mechanical properties of the membranes, but brings about a decrease in the ion-exchange sites content.

The reaction of PE chloromethylation [scheme (iii)] proceeds to a very low degree only; the determined content of chlorine does not exceed 0.5 wt %, since in this case the reaction of PE crosslinking [scheme (v)] prevails. This conclusion was confirmed by the results of extraction of chloromethylated PE—the polymer contained about 35 wt % of a heptane-insoluble fraction.

TABLE I
Dependence of Some Properties of Membranes on Chloromethylation Parameters^a

Amount of catalyst (mol/mol St)	Temp of reaction (K)	Reaction time (h)	Amount of CMME ^b (vol %)	Chlorine content (wt %)	Specific resistance ^c (Ω m)	Exchange capacity (mmol/g dry membrane)	Tensile strength (MPa)	Elongation at break (%)
2.0	298	20	60	6.1	37.2	0.43	10.2	208
			80	5.2	17.4	0.55	10.5	211
3.5	298	20	100	4.8	10.5	0.65	10.9	215
			60	10.5	7.0	1.42	10.5	138
3.03	303	6	60	10.7	7.8	1.52	11.4	111
			80	9.7	8.9	1.47	11.8	93
3.03	323	9	100	7.1	8.8	1.32	12.9	153
			60	10.8	6.3	1.47	11.4	123
3.03	323	12	80	8.9	6.3	1.40	12.1	146
			100	9.9	6.2	1.38	13.6	144
5.0	303	6	60	11.2	7.5	1.15	11.7	167
			80	10.8	7.2	1.06	13.2	218
6.0	303	6	100	6.9	6.9	0.93	13.5	99
			80	8.1	6.7	1.25	—	—
6.0	323	9	100	6.7	9.5	0.98	—	—
			60	9.8	5.1	1.57	—	—
6.0	323	6	100	8.2	7.4	1.27	—	—
			60	10.5	5.8	1.46	—	—
6.0	323	6	100	6.1	8.9	1.05	—	—

^a Aminated with a 50 vol % aqueous solution of DMAE, 298 K, 3 days.

^b In CCl_4 solution.

^c Determined at 0.1M NaCl.

TABLE II
Dependence of Some Properties of Membranes on Chloromethylation Parameters^a

Amount of CMME ^b (vol %)	Reaction time (h)	Exchange capacity (mmol/g dry membrane)	Water content (g H ₂ O/g dry membrane)	Specific resistance ^c (Ω m)	Tensile strength (MPa)	Elongation at break (%)
100	10	0.92	0.12	10.5	12.1	167
	15	1.15	0.15	7.9	11.5	154
80	10	0.93	0.20	11.6	10.8	201
	15	1.22	0.21	9.5	10.7	198
	20	1.36	0.32	4.8	10.8	186
60	10	1.23	0.30	6.9	11.4	218
	15	1.35	0.32	5.7	11.4	192
	20	1.45	0.34	4.8	12.5	176

^a Aminated with a 50 vol % aqueous solution of DMAE, 298 K, 3 days.

^b In CCl₄ solution.

^c Determinated at 0.1M NaCl.

An additional crosslinking of styrene-divinylbenzene copolymer with PE according to reaction (iv) allows for better linking of the aromatic material with PE, which is advantageous in view of a higher stability of properties of such membranes.

It has been found previously¹² that from among catalysts of chloromethylation, stannic chloride brings the highest crosslinking of PE with poly(St-co-DVB).

Chloromethyl methyl ether is the most often used chloromethylating agent since poly(St-co-DVB) swells very well in it¹⁸⁻²¹; it is well documented that diffusion of the reagents into a polymer phase is the critical parameters in various heterogeneous reactions.

TABLE III
Properties of Membranes Obtained by Amination in Various Media at 298 K

Aminating medium	Reaction time (h)	Exchange capacity (mmol/g dry membrane)	Water content (g H ₂ O/g dry membrane)	Specific resistance in 0.1M NaCl (Ω m)
30 vol % aqueous solution DMAE	20	—	—	>>1000
30 vol % aqueous solution DMAE/methanol 2:1 vol ratio	20	—	—	>>1000
30 vol % aqueous solution DMAE/dioxane 2:1 vol ratio	20	—	—	>>1000
30 vol % aqueous solution DMAE/acetone	5	—	—	>>1000
	10	—	—	>>1000
	20	1.41	0.31	4.5
	5	—	—	>>1000
	10	1.48	0.32	5.2
	20	1.45	0.32	4.5
20 vol % aqueous solution DMAE/acetone	5	—	—	>>1000
	10	—	—	>>1000
	20	1.07	0.29	5.9
	5	—	—	>>1000
	10	—	—	>>1000
	20	1.04	0.30	5.6

Table I shows the used parameters of chloromethylation and some properties of strong base membranes obtained by aminating the chloromethylated derivatives under constant conditions, i.e., using a 50 vol % aqueous DMAE solution at 298 K (room temp) for 3 days.

We believe that properties of a membrane are better criteria of optimization of chloromethylation than are properties of the product of direct chloromethylation (of course, only a 100% yield of amination is attained).

The obtained results indicate that by lowering the content of SnCl_4 below 3,5 mol/mol of styrene during chloromethylation at 298 K, a product having a low degree of chloromethylation is obtained, thus leading to poor-quality membranes (specific resistance more than 10 Ωm , exchange capacity about 0.5 mmol/g dry membrane). At higher catalyst concentration the reaction equilibrium is drifted toward the formation of an ether-catalyst complex, which is the first stage in the chloromethylation of aromatic hydrocarbons.¹⁸ More active centers are formed on the polymer, thus increasing the yield of chloromethylation and improving properties of the membranes.

The higher the ether concentration, the higher the crosslinking of poly(St-co-DVB)²²⁻²⁴; this rule is confirmed by a decrease in chlorine content in chloromethylated derivatives as well as by lower exchange capacities and higher tensile strength values of these membranes. Similar results were obtained by increasing the time of chloromethylation or reaction temperature (Table I).

By assuming a temperature of chloromethylation of 298 K (room temp) as a convenient one from the practical point of view, we determined the necessary dilution of CMME by carbon tetrachloride and minimum time of chloromethylation.

Results are reported in Table II. By diluting CMME with CCl_4 the diffusion conditions in the system are improved and the possibility of crosslinking via reaction (ii) is lowered. It was found that weight swelling of the starting material PE/poly(St-co-DVB) in a 60 vol % CMME solution in CCl_4 was higher by 12% than that in pure CMME.

It was found that, by using a 60 vol % solution CMME in CCl_4 in the presence of 3.5 mol SnCl_4 /mol styrene, the sufficient time of chloromethylation of PE/poly(St-co-DVB) system is about 10 h (Table II).

The chloromethylated derivatives obtained under the above conditions were next reacted with various solutions of DMAE (Table III). By using solvents in which the chloromethylated derivatives swell very well, not only are the costs of amination lowered, but also amination time is shortened. Acetone was found to be the best diluent. The minimum time of amination in a 30 vol % aqueous solution of DMAE diluted with acetone in a 2:1 vol ratio is about 10 h (Table III).

CONCLUSIONS

It has been shown that the PE/poly(St-co-DVB) system can be chloromethylated at 298 K (room temperature). The so-obtained derivative can be aminated to give strong base membranes whose properties correspond to those of the AMF-A-60- and AMF-A-100-type commercial products.

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