

# Notes

## *Continuous Modification of Polyethylene with Styrene and Divinylbenzene in Melt*

### INTRODUCTION

At present the majority of popular ion exchange membranes (IEMs) belong to the class of so-called "interpolymer" membranes,<sup>1,2</sup> which are produced by chemical transformations performed on polymer films obtained through the interpolymerization of a potentially reactive monomer with a crosslinking monomer inside an inert, thermoplastic supporting polymer. We have already reported the results of our studies on the preparation of a styrene-divinylbenzene-modified polyethylene film, PE(St-co-DVB), suitable for the synthesis of IEMs.<sup>3,4</sup> Although the electrical and mechanical properties of these membranes were good, their method of preparation was cumbersome and inefficient, and the yield of unusable by-products was high.<sup>3</sup>

In the present paper, we wish to report our initial results on a continuous method of preparation of PE(St-co-DVB) films by extruding a PE powder soaked with monomers in the presence of an initiator at high temperatures and continuous forming of the modified film. Some physicochemical and mechanical properties of sulfonic IEMs are also reported.

### EXPERIMENTAL

Powdered low-density polyethylene "Polythene LDS" for fluidization was purchased from Plastic Coatings, Ltd., Great Britain. Its number-average molecular weight was 19,600 as determined by vapor pressure osmometry, and the degree of crystallinity obtained by x-ray analysis<sup>5</sup> was 41 wt %. The degree of branching was found to be 49 branches per 1000 methylene units by IR spectroscopy.<sup>6</sup> Styrene, divinylbenzene (a commercial product containing 60.2 wt % of *m*- and *p*-isomers), and benzoyl peroxide were purified in the usual way.<sup>3</sup>

The modifications were carried out in a laboratory extruder (a Reifenhäuser model S.025 with a screw 25 mm in diam. and  $l = 20D$ ) equipped with a rod-forming die. The rods of modified polymers were subsequently pressed with a laboratory press to give films 50–500  $\mu\text{m}$  thick.

The IR spectra were recorded with a Specord model 71 spectrophotometer with a pure polystyrene film sample as reference, and the DTA analyses were made with a MOM model OD-102 apparatus. The tensile strengths of both polymer films and IEMs swollen in water were determined with a ZT-40 apparatus. The PE(St-co-DVB) film samples were extracted with ethyl acetate for ca. 100 hr in a Soxhlet apparatus.<sup>3</sup>

The modified polymer film samples were chlorosulfonated for 4 hr at room temperature with a 10 wt % solution of chlorosulfonic acid in 1,2-dichloroethane, followed by hydrolysis in a 20 wt % NaOH aqueous solution.

The IEMs were conditioned, and their water content, cation exchange capacity, and electrical resistance in a 0.5M KCl solution were determined as reported earlier.<sup>7,8</sup>

### RESULTS AND DISCUSSION

In Table I, the modification parameters and the determined properties of PE(St-co-DVB) films are presented. Samples are designated in such a way that in sample 20/40/1, for example, the first number represents the weight fraction of monomers in the initial mixture, the second is the content of DVB isomers in the monomer mixture, and the last is the concentration of benzoyl peroxide in the monomers.

On the thermal polymerization of styrene at higher temperatures, i.e., above 373–393 K, relatively little has been published,<sup>9,10</sup> let alone reported on the kinetics of the process in the presence of a crosslinking monomer. Experimental data suggest, however, that the thermal polymerization rate of styrene can be described even up to 433 K by the following equation<sup>11</sup>:

$$v = 10^{11.55} \times 10^{-4170/T}$$

TABLE I  
Principal Modified Polymer Product Characterization

Sample no.	Temp. of modification, K	Reaction time, min	St-co-DVB	St-co-DVB	Extr. loss, wt %	Tensile strength, MN/m <sup>2</sup>	Elongation at break, %	
			content by IR, wt %	content by DTA, wt %				
A	30/0/2	393	—	—	—	11.3	280	
B	30/1/2	393	—	—	—	11.7	190	
C	30/3/2	393	—	—	—	11.5	48	
D	30/5/2	393	28.6	26.8	—	11.9	10	
E	30/10/2	393	—	—	—	11.5	5	
H	40/1/2	393	—	—	—	11.6	125	
I	40/3/2	393	—	—	—	11.6	30	
J	40/5/2	393	36.4	36.5	—	12.0	5	
K	50/5/2	393	48.1	48.4	—	9.0	5	
	30/5/0	413	21	11.3	4.59	9.7	28	
	30/5/0	413	17	8.5	5.23	8.5	24	
	30/5/0	413	12	7.9	5.82	9.9	11	
G	30/5/1	413	19	18.2	4.06	10.6	110	
	30/5/1	413	13	17.8	4.28	9.8	97	
	30/5/1	413	8	16.2	5.14	9.6	39	
	30/5/2	413	14	24.7	3.81	10.5	79	
	30/5/2	413	11	22.2	4.09	10.3	58	
	30/5/2	413	7	23.7	4.67	10.1	54	
	30/5/2	413/433 <sup>a</sup>	21	23.4	4.26	11.1	66	
	30/5/2	413/433 <sup>a</sup>	19	25.1	4.92	10.4	64	
	30/5/2	413/433 <sup>a</sup>	13	22.0	5.11	9.8	27	
F	30/5/5	413	19	27.7	4.88	11.8	78	
	30/5/5	413	12	21.8	5.31	10.3	44	
	30/5/5	413	8	19.4	6.53	7.6	24	
	40/0/2	393	21	26.2	24.8	7.47	10.7	127
	40/0/2	393	17	25.2	—	9.13	9.9	118
	40/5/2	393	14	33.3	—	5.11	10.0	6
	40/5/2	393	10	32.8	—	5.90	9.6	5
L	PE	393	—	0	0	3.64	9.0	1060

<sup>a</sup> Temperature of I/II heating zone of extruder.

where  $v$  = polymerization rate in wt %/hr and  $T$  = absolute temperature in K. From this relation, polymer yields of 8.5, 28.4, and 83.1 wt %/hr at 393, 413 and 433 K, respectively, were calculated. Thus, a much higher reaction rate should be expected in the presence of both benzoyl peroxide and DVB at these temperatures.<sup>12</sup> Precise kinetic determinations, although attempted, were irreproducible because of the partial evaporation of monomers during the feeding operation and the very rapid reaction rate in these conditions. Nevertheless, given the short time of reaction, the St-co-DVB copolymer contents found in our samples are surprisingly high. GLC determinations of the unreacted monomer content in the PE(St-co-DVB) gave generally very low values of styrene concentration, all in the range of 0.025–0.09 wt %, although, again, partial evaporation of styrene from the hot product leaving the extruder cannot be excluded.

It can be seen from Table I that the concentration of DVB has the most pronounced effect on the copolymerization yield. The mechanical properties measurements showed that although the modified polymer films have good tensile strength, 20–30% higher than for pure PE film, their elongation at break decreases sharply with increasing DVB content. Despite this, their elongation at the usual DVB content in commercial membranes, i.e., 3–6 wt %, is still satisfactory and allows for their application in larger-scale electrolysers.

The linear polystyrene extraction results indicate very good bonding of modifying St-co-DVB copolymer within the PE matrix, for in the same extraction conditions approximately 3.6 wt % of the pure PE film could be extracted—these were probably the low molecular weight fractions of PE.

TABLE II  
Properties of Sulfonic PE(St-co-DVB) Membranes in H<sup>+</sup> State

Sample no.	Cation exchange capacity, meq/g dry membrane	Water content, g H <sub>2</sub> O/g dry membrane	Electrical resistance in 0.5M KCl, Ω m	Tensile strength of wet membrane, MN/m <sup>2</sup>	Elongation at break, %
A 30/0/2	1.79	0.55	1.61	34.0	122
B 30/1/2	1.79	0.46	1.47	35.4	60
C 30/3/2	1.82	0.38	1.55	38.8	31
D 30/5/2	1.70	0.30	1.90	41.4	29
E 30/10/2	1.66	0.21	2.55	53.1	32
F 30/5/5	1.71	0.39	1.76	32.9	25
G 30/5/1	1.78	0.30	1.77	38.0	24
H 40/1/2	2.07	0.61	0.71	27.5	37
I 40/3/2	2.17	0.47	1.10	37.7	25
J 40/5/2	2.07	0.39	1.25	41.9	25
K 50/5/2	2.37	0.46	0.86	19.0	5
L PE	0.02	0.15	10,800	49.7	670

It is also noteworthy that PE(St-co-DVB) can be easily molded by pressing or extrusion, probably because the three-dimensional network of the grafted St-co-DVB copolymer is partially broken down during extrusion. On the other hand, PE, making up 60–85 wt % of the product, considerably decreases the viscosity of the melt. At higher DVB contents, however, e.g., 8–10 wt %, the product obtained by extruding or onefold pressing was visually inhomogeneous.

In Table II some important properties of IEMs are shown. It can be seen that in the relatively mild chlorosulfonation conditions IEMs having good electrical properties were obtained. The electrical resistance of the membranes in 0.5M KCl was in the range of 0.7–2.5 Ω m, which is comparable with the values reported for commercial IEMs of this type.<sup>13,14</sup>

### CONCLUSIONS

It has been shown that the continuous modification of polyethylene with crosslinked styrene-divinylbenzene copolymer through *in situ* graft copolymerization of these monomers, in the presence of a free-radical initiator in the polyethylene melt, leads to a modified polymer product suitable for the preparation of ion exchange membranes with good electrical and mechanical properties. The modified polymer film can be obtained from this product by pressing or extrusion molding.

Studies on the extrusion blow molding of the modified polymer products and long-term investigations of these IEMs in the electro dialysis process are in progress.

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