

CHEMICAL TRANSFORMATIONS OF POLYMERS. XII.*

REACTION OF POLYETHYLENE WITH CHLOROSULPHONIC ACID

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Received December 3rd, 1971

The reaction products of polyethylene with chlorosulphonic acid contain the $-\text{SO}_3^-$, $-\text{OSO}_3^-$, $-\text{Cl}$, $-\text{OH}$, $>\text{CO}$, $-\text{COO}^-$ groups and double bonds which during the reaction form cross-linking bridges and promote the entrance of further groups. The degree of transformation depends in particular on the branching of the polymer and the reaction temperature. At 25 and 50°C strongly acid cation-exchange polymers are formed having a high exchange capacity (up to 3 mval/g), while the products obtained under similar conditions and at temperatures $\leq 0^\circ\text{C}$ have no exchange capacity at all.

By treating polyethylene with chlorosulphonic acid ion-exchange membranes¹ were prepared and the surface of films was hydrophilized²; however, the chemical nature of these transformations has not been studied. The reactions of analogous low-molecular weight hydrocarbons with chlorosulphonic acid have not been described either; Young³ and Shepard, Henn and Midgley⁴ only mentioned that they had observed the formation of some undefined mixtures of products and pointed out a substantially weaker reactivity of n-paraffins compared to branched hydrocarbons.

In an earlier paper⁵ we described the reaction of chlorosulphonic acid with polystyrene and used the findings thus obtained to prepare cation-exchange capillaries based on polystyrene grafted on the internal surface of polyethylene tubes⁶. It seemed interesting to find out, in this connection, to what extent polyethylene participates in the reaction along with polystyrene, what structures are formed by the reaction and under what conditions the transformation of polyethylene can be eliminated.

EXPERIMENTAL

Materials

Chlorosulphonic acid (Spolek pro chemickou a hutní výrobu, Ústí nad Labem), twice distilled, b.p. $98^\circ\text{C}/41$ Torr. Heptane, a.p. grade (Lachema, Brno), was freed from isomers by washing with sulphuric acid and water and rectified after drying with calcium chloride, b.p. $98.0-98.5^\circ\text{C}$.

* Part XI: IUPAC International Conference (Chemical Transformations of Polymers) Bratislava 1971.

5-Ethylnonane, b.p. 76°C/15 Torr, n_D^{20} 1.4296, was prepared by reduction of 5-bromo-5-ethylnonane⁷. Branched polyethylene (10 g) was dissolved in boiling heptane (200 g), the polymer was precipitated by cooling to 25°C, filtered off, washed with methanol and water and dried at 25°C/0.1 Torr, d_4^{20} 0.925 (floatation method⁸), m.p. 112–115°C, content of methyl groups determined by IR spectrometry⁹ was 2.1 ± 0.1 CH₃ per 100 carbon atoms. A fraction with particle sizes ranging from 0.05 to 0.09 mm was used in the experiments.

Reaction of Chlorosulphonic Acid with Heptane and 5-Ethylnonane

A mixture of the hydrocarbon (335 or 21.65 mmol) with chlorosulphonic acid (369 or 20.25 mmol) was stirred at 50°C for an hour, then poured out onto ice and neutralized with sodium carbonate. The organic layer was dried with calcium chloride and subjected to fractional distillation. The dry residue (90.3 or 3.37 g) of the aqueous phase was dissolved in a minimum amount of water, precipitated with a fivefold amount of ethanol, and the salts were separated; evaporation and precipitation were repeated several times in order to separate the inorganic salts (the process of separation was checked by determination of the equivalent weight of the salt with a H⁺ cation exchanger) from organic components, which were analyzed by anion exchange and thin layer chromatography.

Reaction of Chlorosulphonic Acid with Polyethylene

Polyethylene (2 g) was first swollen at 25°C in 50 ml 1,2-dichloroethane; the suspension was then stirred for varying times with 5.3 g of chlorosulphonic acid and poured out onto ice. The chlorosulphonated polymer (intermediate *I*) was separated by filtration (the filtrate did not contain any soluble polymer), washed with water to remove Cl⁻ and SO₄²⁻, saponified with an excess of 1M-NaOH (80°C, 1 h), transformed into the H⁺-form on an ion-exchange column, regenerated with acid after repeated determination of the exchange capacity, washed with water and dried to constant weight at 78°C/0.1 Torr before the determination of the elementary composition and recording of the IR spectra. The intermediate *II* was obtained in a similar manner. Polyethylene (2 g) was dissolved in boiling tetrachloromethane (50 ml), precipitated with 1,2-dichloroethane (50 ml) and the suspension obtained was reacted with chlorosulphonic acid (17.7 g).

Reaction on Chlorosulphonated Polyethylene *I* and *II*

0.3 g of the sample was used each time. The final products were dried at 78°C/0.1 Torr, the elementary composition was determined and the exchange capacity and the IR spectra were recorded: 1) A mixture of the sample with a solution of 5 g KOH in 30 ml of butanol was refluxed for a varying time, butanol was removed by steam distillation, the residue was refined by repeated (3 ×) swelling (in xylene) — deswelling (in methanol) and washing with water (product *III*). 2) A mixture of the sample, 0.6 g lithium aluminium hydride and 30 ml dry dibutyl ether was refluxed for one hour and the solvent was removed by distillation with water vapour; the residue was washed with 2M-HCl, water, and methanol, swollen in xylene while boiling and deswollen in methanol (product *IV*). 3) The sample was swollen 0.5 h in 20 ml of boiling xylene and the suspension (25°C) was saturated with hydrogen chloride after adding 1.4 g of zinc powder; when unreacted zinc had been dissolved in 30 ml of conc. HCl at 80°C (4 h), the polymer was filtered off, washed with 2M-HCl and methanol, swollen three times in xylene and deswollen in methanol (product *V*). 4) The sample was swollen for 0.5 h in 20 ml of boiling tetrachloromethane; at 25°C the solution of 0.161 g of bromine in 5 ml of tetrachloromethane was added, the mixture was shaken for a varying time with exclusion of day light, 20 ml of 20% KJ was added, and the iodine that separated was titrated after 5 min with 0.025M-Na₂S₂O₃; the undissolved fraction was filtered

and washed with 2M-HCl and water (product VI). 5) To a mixture of sample *Ic* or *Iib*, 0.3 g 2,4-dinitrophenylhydrazine and 10 mg *p*-toluenesulphonic acid were added after refluxing for half an hour; after another 1.5 h the insoluble fraction was filtered off, washed with methanol, swollen with xylene, deswollen in methanol and finally washed with methanol and water. Product *VIIa* from *Ic* contained 0.57% N, product *VIIb* from *Iib* contained 1.98% N. 6) Sample *Ic* was left half an hour in 20 ml of the refluxing xylene-pyridine mixture (5 : 1) and then refluxed for another half an hour with 0.3 g 3,5-dinitrobenzoyl chloride. The polymer after separation was swollen five times in boiling xylene and deswollen in methanol, then washed with methanol and water. Product *VIII* contained 0.72% N.

Analytical Methods

Gas chromatography: A Perkin-Elmer apparatus F 11, column (1 m) filled with squalane (15%) on silicagel, nitrogen as carrier gas. Thin layer chromatography: a silicagel layer with a light-sensitive indicator on an aluminium foil Silufol UV-254 (Kavalier, Czechoslovakia), elution with the chloroform-methanol-0.05M-H₂SO₄ mixture (7 : 3 : 0.6). Chromatography on an anion exchanger (modification of a procedure suggested by Mutter¹⁰): To a sample of alkylsulphonates (0.5 g) in a minimum amount of water, an equivalent amount of 0.1M-AgNO₃ with respect to the Cl⁻ ions present was added with potentiometric indication, the precipitate was separated, the filtrate evaporated and redissolved in 30 ml ethanol. The solution was filtered through an H⁺ cation exchanger (Dowex-X8, 30 ml) and an OH⁻ anion exchanger (DEAE Sephadex A-25, 30 ml); the non-ionic compounds that may have been present in the filtrate were isolated: The acids were gradually eluted from the anion-exchanger with aqueous 0.5M-NH₄HCO₃, 0.15M-NH₄HCO₃ in 60% propanol and eventually with aqueous 1M-NaOH, the eluates were adjusted with the H⁺ cation exchanger, titrated potentiostatically with 0.1M-NaOH, evaporated, and the salts thus obtained were weighed. From these amounts and from the titration values, the mean equivalent weights of the individual fractions were calculated.

To characterize the homogeneity of the polymeric products, thin slides (~0.1 mm) of reacted particles cast in paraffin were cut with a microtome, stained with methylene blue and photographed at a 200× magnification (microscope Meopta A 36 Bi). Neither positive enlargements nor the results of density measurements of the negative with a photodensitometer (Schnell-photometer II, Zeiss, Jena) indicated any macroheterogeneities in the substance of the particles. The IR spectra were recorded on a Zeiss UR-10 apparatus. Polyethylene was pressed into films 0.05–0.2 mm thick, the polymeric reaction products were measured by the KBr disc technique. The content of the carbonyl groups was determined using levulinic acid as the internal standard.

The other methods used: the relative and total weight exchange capacity were determined by decomposition of a neutral salt using a conventional method¹¹. The weight swelling in water was determined by measuring the sorption equilibria¹² within the region 5–95% of relative humidity on seven levels at 30.1°C; the value corresponding to 100% of relative humidity was then determined by extrapolation.

RESULTS AND DISCUSSION

Heptane and 5-ethylnonane, the low-molecular weight models of linear and branched polyethylene, yield with chlorosulphonic acid — along with isomeric mono- and polysulphonic acids — unsaturated hydrocarbons, high-molecular weight neutral compounds having a rather undefined composition with a maximum peak in their mass spectrum 428.5m/e and containing carbonyl groups. The branched 5-ethylnonane reacts much faster and gives more oligomeric hydrocarbons than heptane (Tables I, II).

TABLE I

Composition of Mixture after Reaction of Heptane and 5-Ethylnonane with Chlorosulphonic Acid

M_n mer of the residue derived from the original hydrocarbon; ξ_h , ξ_n % by weight of heptane and 5-ethylnonane.

Hydrocarbon	ξ_h	ξ_n	Alkyl sulphonate	ξ_h	ξ_n
Original	96.75	37.17	$M_1-(SO_3Na)_{>1}$	0.15	0
B.p. 87°C/15 Torr	0.10	24.77	M_1-SO_3Na	0.64	5.90
B.p. 90–98°C/0.3 Torr	0	20.65	M_2-SO_3Na oligomeric ^a	0.85 3.39	2.06 20.94

^a Equivalent weight > 375.

TABLE II

Sodium Alkylsulphonates Isolated on an Anion Exchange Column from the Reaction Mixture after Chlorosulphonation of Heptane or 5-Ethylnonane

W Amount, W_e equivalent weight determined with the cation exchanger.

W , g	R_F^a	Formula	W_e	
			found	theor.
For heptane				
0.05	0.00	$C_7H_{13}(SO_3Na)_3$	136.9	135.5
0.22	0.33	$C_7H_{15}SO_3Na$	202.2	202.3
0.29	—	$C_{14}H_{29}SO_3Na$	295.1	300.4
0.19	0.92	$C_{21}H_{43}SO_3Na$	375.7	398.6
0.12	0.97	—	1 094.9	—
For 5-ethylnonane				
0.20	0.92	$C_{11}H_{23}SO_3Na$	254.0	258.4
0.07	0.92	$C_{22}H_{45}SO_3Na$	410.0	412.6
0.71	0.92	$C_{44}H_{87}SO_3Na$	625.8	719.2

^a By thin-layer chromatography.

In contrast with its low-molecular weight models, polyethylene does not dissolve in the reaction medium, so that the way in which the transformation proceeds is also determined by the properties of the polymeric substrate (molecular weight, crystallin-

ity) and by the type of the swelling agent, or by the way in which the gel state is attained. Even though the reaction mixture is heterogeneous, the chemical transformation proceeds uniformly throughout the substrate, judging by the microphotometry of thin slices of the reacted particles. The reaction products are coloured light yellow to black depending on the degree of reaction attained, and are quite insoluble in solvents of the original polyethylene already at low conversions. The products swell in water proportionately with increasing conversion (18 mol of water per 1 mol of acid groups), but do not dissolve in it. Sulphur and chlorine appear in the elemental composition of the samples, the H : C ratio decreases (Table III) and the oxygen content increases (relative number of heteroatoms and groups (c_X) at each time related to 100 carbon atoms). Oxidation takes place along with the chlorosulphonation of polyethylene, as follows from the difference between c_0 found and c_0 corresponding to the concentration of the $-\text{SO}_3\text{H}$ groups (Fig. 1a).

The sulphur content of the reaction products of polyethylene with chlorosulphonic acid increases in the experiments described here up to $c_S \sim 5$; it depends in particular on the reaction temperature, the way in which the gel state has been attained, and on the excess of chlorosulphonic acid (Table III). The content of acid groups (c_{H^+}) calculated from the exchange capacity C and from the carbon content determined by elemental analysis also increases linearly in the polymeric products with increasing c_S (Fig. 1b); at the highest sulphur content c_S 4.73, c_{H^+} was 3.35 ($C = 1.65$ mval/g).

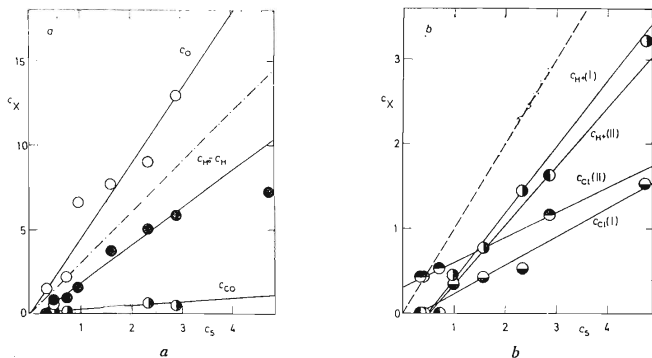


FIG. 1

Dependence of the Course of the Oxidation Reactions (a) and of the Content of Acid and Chloro Groups (b) on the Sulphur Content (c_S) in Chlorosulphonated Polyethylene

— c_0 corresponding to the concentration of the $-\text{SO}_3\text{H}$ groups equal to c_S . c_{H^+} related to the starting polyethylene.

The acid exchange groups are strongly dissociated: identical capacities were determined both by neutralization with an alkali and by splitting of a neutral salt, and the titration curves obtained correspond¹³ to monobasic strong acids (pK'_a 2.75 in 0.1M-NaCl). With respect to the fact that both sodium polyethylene sulphonate and sodium polyvinyl sulphate were stable in the model alkaline hydrolysis (0.1M-NaOH, 80°C, 6 h), it can be expected that the groups of both types will be preserved in the polymer even after alkaline saponification of sulphochlorides and will participate in the exchange capacities. In accordance with the presence of the more labile $-\text{OSO}_3\text{H}$ groups in addition to the more stable $-\text{SO}_3\text{H}$ groups the exchange capacity C decreases during all subsequent transformations (Table IV). In the infrared spectra the $-\text{SO}_2$ -groups are best fitted by the bands at 1040 and 1180 cm^{-1} (Fig. 2, correlation coefficients 0.93 and 0.97), while in the vicinity of 905 and 1380 cm^{-1} vibrations of the C—H bonds also play their role, along with the $-\text{SO}_2$ -groups (Fig. 2, correlation coefficients 0.86 and 0.82).

The zero capacity of products with a very low sulphur content ($c_s < 0.75$) is assigned to an insufficient swelling in water. The differences ($c_s - c_{H^+}$) observed with polymers having a higher degree of reaction with chlorosulphonic acid are interpreted in terms of the existence of closed regions in the structure of the product which contain sulphur in non-ionic forms (especially sulphochlorides and carbylsulphates). Inaccessible sites can be produced by non-uniform deswelling of the heterogeneous substrate with crystalline regions during the reaction of polyethylene with

TABLE III

Conditions of Chlorosulphonation of Polyethylene and Elemental Composition of the Polymer
 C Total exchange capacity. For the initial polyethylene found: 84.86% C, 14.28% H.

τ , h T , °C	Polymer	% C % H	% S % Cl	C mval g ⁻¹	τ , h T , °C	Polymer	% C % H	% S % Cl	C mval g ⁻¹
24 ^a	<i>Ia</i>	77.45	2.42	0.300	4	<i>IIa</i>	82.55	0.78	<0.002
25		12.80	0.61		—30		13.96	1.06	
1	<i>Ib</i>	76.29	2.88	0.499	4	<i>IIb</i>	82.98	1.07	<0.002
40		12.27	0.82		0		13.91	1.31	
1	<i>Ic</i>	73.02	4.35	0.879	24	<i>IIc</i>	81.40	1.58	<0.002
50		12.85	1.10		0		13.36	1.29	
1	<i>Id</i>	59.15	7.48	1.650	24 ^b	<i>IIId</i>	73.99	3.96	0.317
60		9.52	2.68		25		12.35	0.84	
					24	<i>IIe</i>	69.41	5.31	0.944
					25		10.99	2.41	

^a After 168 h and using 71.8 g chlorosulphonic acid found: 43.71% C, 4.15% H, 11.84% S, 2.68% Cl, $C = 3.07$ mval/g. ^b Content of chlorosulphonic acid in the reaction mixture was the same as during preparation of *I*.

chlorosulphonic acid. In accordance with this, the intermediates *II*, the preparation of which started with a higher initial degree of swelling of the polymeric substrate, exhibit a larger difference ($c_S - c_{H^+}$) and a higher c_{Cl} than samples *I*. The assumed existence of closed regions is supported by additional reactions of sulphonated polyethylenes with potassium hydroxide in the butanol medium. Both c_{H^+} and c_S decrease during these experiments; however, these variables tend to a comparable value and c_{Cl} decreases (Fig. 3). Owing to the more intensive swelling effect of butane compared with water upon polyethylene chlorosulphonated to a low degree the regions that were closed before become more accessible, the non-ionized sulphur-containing groups are transformed into ionizable groups and at the same time undergo a partial splitting-off.

TABLE IV

Transformations of Sulphonated Polyethylene and Elemental Composition of Products
C Total exchange capacity.

Initial polymer ^a	Agent ^b (τ , h)	Product	% C % H	% S % Cl	C mval g ⁻¹
<i>Ic</i>	KOH (4)	<i>IIIa</i>	78.88 12.70	2.00 0.67	0.626
<i>Ic</i>	KOH (8)	<i>IIIb</i>	77.98 12.31	1.51 0.66	0.435
<i>Ic</i>	KOH (16)	<i>IIIc</i>	80.99 12.20	1.50 0.48	0.389
<i>IIb</i>	KOH (4)	<i>III d</i>	81.15 13.52	0.80 0.51	<0.002
<i>Ic</i>	LiAlH ₄ (1)	<i>IVa</i>	76.64 12.50	2.85 0.39	0.624
<i>IIb</i>	LiAlH ₄ (1)	<i>IVb</i>	79.71 13.66	0.72 0.86	<0.002
<i>Ic</i>	Zn + HCl (1)	<i>Va</i>	77.91 11.89	2.56 0.96	0.449
<i>IIc</i>	Zn + HCl (1)	<i>Vb</i>	81.54 13.18	1.10 —	<0.002
<i>Ic</i>	Br ₂ (0.17)	<i>VIa</i>	73.90 11.78	3.55 1.74	0.466
<i>Ic</i>	Br ₂ (0.50)	<i>VIb</i>	72.88 11.56	3.46 1.68	0.384
<i>Ic</i>	Br ₂ (1.00)	<i>VIc</i>	73.69 11.68	3.37 1.90	0.505
<i>IIe</i>	Br ₂ (0.17)	<i>VI d</i>	69.81 10.62	4.52 2.59	0.795

^a Cf. Table III; ^b Detailed conditions cf. Experimental.

Since the decrease in c_{Cl} is smaller than the original difference $c_S - c_{H^+}$ (0.89 in the case of the sample in Fig. 3), the non-exchanging groups involve not only sulphochlorides, but probably also carbylsulphates or sulphonic and hydrogensulphate groups in closed regions.

The chlorine content in the samples increases with the content of sulphur. At $c_S \leq 0.5$ is $c_{Cl} \sim c_S$, but the ratio c_{Cl}/c_S decreases with increasing c_S ; for the highest sulphonated samples c_{Cl} is 1.53 and c_S is 4.73. The decrease in the chlorine content was observed not only during the treatment of the butanol medium with potassium hydroxide described above (Fig. 3), but particularly during reduction with lithium aluminium hydride and with the Zn-HCl system (Table IV). Chlorine is bonded in the polymer not exclusively by means of the sulphochloride groups: due to potassium hydroxide in the butanol medium comparable values of c_{H^+} and c_S are attained already when c_{Cl} has dropped to half its initial value and before the lowest c_{Cl} value

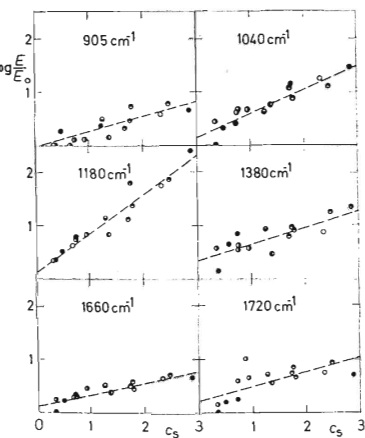


FIG. 2

Dependence of Relative Intensities of Selected Bands in the IR Spectra on the Sulphur Content (c_S)

E_0 Extinction of the band of the C—H vibration at 724 cm^{-1} . Assignment of data to the products: \circ Ic, \bullet IIa—c,e, \ominus IIIa—d, \bullet IVa, \ominus Va, \bullet VIa—d. Positions of the curves were calculated using the least squares method.

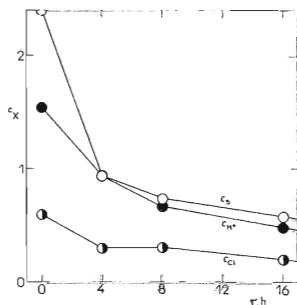


FIG. 3

Changes in the Participation of the Characteristics Groups in Sulphonated Polyethylene Ic During Reaction of KOH in Butanol

of this experimental series is reached. Consequently, one part of chlorine forms bonds of various stability with carbon (Fig. 3). The splitting-off of chlorine caused by the Zn-HCl system indicates the presence of the —Cl groups vicinal to the —SO₃H groups¹⁴. With respect to the imperfect contact between the reaction components during this reaction it is not possible to preclude that the actual content of the vicinal groups mentioned above will be higher than that found from the chlorine content (Table IV).

Formation of the double bonds in polymeric products can be assumed on the grounds of the behaviour of the low-molecular weight models (Table I), of the deepening of the colouration of samples, and also of the absorption at 1640–1660 cm⁻¹. Determination of the double bonds by bromination was unsuccessful. According to the degree of transformation, a band at 1640 cm⁻¹ was first observed in the infrared spectra; the band was later overlapped by a stronger band at 1660 cm⁻¹. This change in the spectra can be interpreted¹⁵ by a different position of the double bonds arising during the transformation. At the initial reaction step, side or end vinyl groups (1640 cm⁻¹) are formed in the first place; this is followed by the formation of double bonds in the main polyethylene chain (1660 cm⁻¹).

Along with the double bonds, carbonyl groups are also formed in the polymeric products (band at 1720 cm⁻¹). The formation of these groups has also been observed during the oxidation of polyethylene with air¹⁶. However, the participation of these groups in all oxidation products is comparatively low (Figs 1a, 2). The carboxyl groups were detected by means of the infrared spectra (a band at 1540 cm⁻¹) of a deuterated sample in the Na⁺ form but their presence was not reflected in the shape of the titration curves. The presence of the hydroxyl groups proved by a reaction with 3,5-dinitrobenzoyl chloride is not at variance with the spectra and can be derived indirectly from the values of the oxygen content.

The insolubility of the polymeric substrate that suddenly appears already at very low degrees of transformation is explained by chemical crosslinking. The formation of sulphones is not likely¹⁷ and has not even been proved¹⁸ in our experiments. The spectra exhibit a band at 1120 cm⁻¹ for the —C—O—C—bond which is used to explain¹⁶ the crosslinking of polyethylene during the oxidation with air. With respect to the fact that it was not possible to restore the solubility of the polymeric products by their reaction with lithium aluminium hydride and potassium hydroxide in butanol analogously to the case of polyethylene oxidized with air¹⁹, the other bonds are not regarded as the only crosslinking bridges. The most likely cause of the crosslinking is the polymerization of the double bonds formed by oxidation which has also been observed with the model compounds (Table I).

The reaction of polyethylene with chlorosulphonic acid can be suppressed by lowering the degree of branching of the substrate and by depressing the reaction temperature. According to an earlier communication⁵, almost 70% of the structural units of polystyrene have reacted with chlorosulphonic acid at 0°C after one hour, while for branched polyethylene under similar conditions (Table III) c_s was 0.48 and c_{H+} could not be determined. It can be seen that a sufficient decrease in the reaction temperature allows virtually to preclude the transformation of polyethylene during chlorosulphonation of a grafted styrene-polyethylene copolymer. On the contrary, by increasing the temperature to 50°C it is possible to obtain a strongly acid cation exchange polymer with exchange capacity C equal up to 3 mval/g, insoluble, swelling

to a limited degree and having a sufficient mechanical strength to be used in columns. Its exchange properties will be dealt with in a forthcoming paper.

The authors are indebted to Dr P. Schmidt for measuring of the infrared spectra, to the colleagues from the Analytical Department for the elemental analyses and to Mrs E. Kociánová for experimental assistance.

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Translated by L. Kopecká.