NEW ANIONITES FROM COPOLYMERS OF STYRENE WITH SOME N,N'-ARYLENEDIMETHACRYLAMIDES

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The synthesis of ion-exchange polymers, which possess a high permeability and porosity, assumes constantly increasing importance, since such polymers find extensive use in sorption and the separation of metal ions, alkaloids and antibiotics [1-4]. Of especial interest are macroporous and macrosieve ionites with a high heat stability and mechanical strength, which contain groups in the macromolecule chain that are capable of forming complexes. Such properties could be expected from ion-exchange resins that are obtained from aromatic di- and tetramines. It is known [5, 6] that polymers are synthesized from such compounds that are resistant to heat, light, moisture, and radiation.

The purpose of the present paper was to synthesize and study the porperties of the anion-exchange that are obtained by the reaction of the halomethylated copolymers of styrene and N,N'-arylenedimethacrylamide with various amines.

EXPERIMENTAL

4,4'-Diaminodiphenyl sulfide was synthesized by treating aniline with sulfur in the presence of PbO [7], and it was recrystallized from aqueous alcohol (mp 105°C). 4,4'-Diaminodiphenylmethane was obtained by the reaction of aniline with CH_2O [8], and it was recrystallized from water (mp 90°). The other starting compounds (styrene, 4,4'-diaminodiphenyl ether, p- and m-phenylenediamine, methacrylic acid, and its acid chloride) were purified by known methods.

The N,N'-arylenedimethacrylamides were synthesized by the acylation of the indicated aromatic diamines (0.1 mole) with the acid chloride of methacrylic acid (0.2 mole), using either freshly distilled benzene or ether as the medium, in the presence of 0.2 mole of pyridine (1.5 h at 10-13°).

The copolymerization of styrene with N,N'-arylenedimethacrylamides (4, 8, 12, 16, or 20% on the weight of styrene) was run both in bulk and in suspension. As the solvent and pore-formation agent we used either n-butyl or isoamyl alcohol [3]. The chloromethylation was run with monochlorodimethyl ether in the presence of either 0.4 mole of $SnCl_4$ or $ZnCl_2$ (6-8 h at 55°). The amount of chlorine in the polymer is 25-26%, which corresponds to ~1.2 CH_2Cl groups per phenyl nucleus.

The chloromethylated copolymers of styrene and N,N'-arylenedimethacrylamide were aminated at 20-80° with the following amines: $NH_{3-n}(CH_3)_n$, $NH_{3-n}(CH_2CH_3)_n$, $NH_{3-n}(CH_2CH_2OH)_n$ ($n = 1$, 2, or 3), pyridine, picolines, and pyridinecarboxylic acids. The degree of conversion of the copolymers was determined by the amount of unreacted chlorine in the chloromethyl group and by the anion-exchange capacity of the anionite. The static exchange capacity SEC of the anionites obtained from the copolymers of styrene containing 8% of the dimethacrylamide of m-phenylenediamine (Ional A-2m8, Ional A-9m8, Ional A-Pm8), or containing 8% of the dimethacrylamide of 4,4'-diaminodiphenylmethane (Ional A-2M8, Ional A-9M8, Ional A-PM8), depending on the nature of the amines, is 1.3-5.0 mg-equiv/g when based on 0.1 N HCl solution (Table 1).

In the IR spectra of the starting styrene copolymers, containing the indicated arylenedimethacrylamides, are present the characteristic absorption bands (cm^{-1}) of the stretching (3470-3450) and deformation (1535-1500) vibrations of the N–H bond, the stretching vibrations (1700-1680) of the C=O bond of secondary unassociated amide groups, the antisymmetric (2950-2930) and symmetric (2875-2850) stretching

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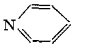
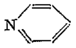
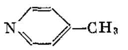
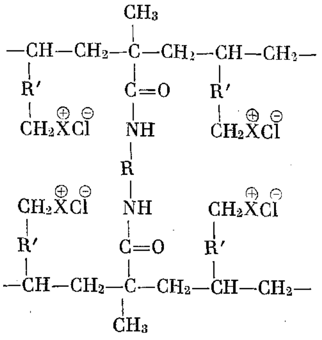
TABLE 1. Anion-Exchange Capacity of Macrosieve Anionites

Ional	Amine	Amination temperature, °C,	SEA*	Ional	Amine	Amination temperature, °C	SEA*
A-2m8	$NH(CH_3)_2$	40	4,5	A-2M8	$NH(CH_3)_2$	20	0,5
A-3m8	$N(CH_3)_3$	40	3,9	A-3M8	$N(CH_3)_3$	20	3,9
A-5m8	$NH(CH_2CH_3)_2$	55	4,3	A-5M8	$NH(CH_2CH_3)_2$	55	4,6
A-6m8	$N(CH_2CH_3)_3$	80	1,7	A-6M8	$N(CH_2CH_3)_3$	80	1,3
A-7m8	$NH_2(CH_2CH_2OH)$	60	4,0	A-7M8	$NH_2(CH_2CH_2OH)$	40	4,4
A-8m8	$NH(CH_2CH_2OH)_2$	60	3,8	A-8M8	$NH(CH_2CH_2OH)_2$	80	4,2
A-9m8	$N(CH_2CH_2OH)_3$	80	2,9	A-9M8	$N(CH_2CH_2OH)_3$	80	2,6
A-Pm8		80	2,7	A-PM8		60	2,6
A-P4M12		80	2,2				

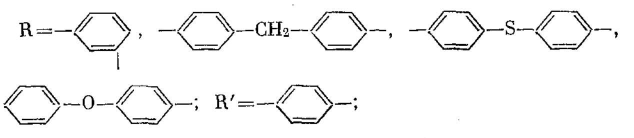
*Based on 0.1 N HCl solution, mg-equiv/g.

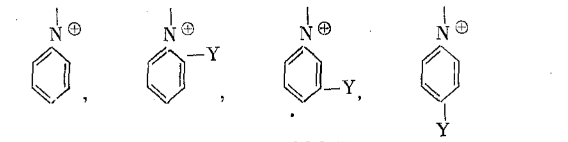
vibrations of $-CH_2-$ groups, the stretching vibrations of the C–H bond (3100-3000) and the deformation vibrations of the C=C bonds of the benzene rings (1610-1600 and 1535-1500), the out-of-plane deformation vibrations of monosubstituted phenyl nuclei (760, 700), the stretching vibrations of the C–N bond (1315-1300), the deformation vibrations of the $-CH_3$ and $-CH_2-$ groups (1460-1455), and also the corresponding absorption bands of the deformation vibrations of 1,4-substituted (1035, 1165, 845) and 1,3-substituted (1035, 1080, 1110-1200, 850) aromatic rings [9]. In the spectrum of the chloromethylated copolymer are present absorption bands that are characteristic for the CH_2Cl group (675, 1270), while absorption bands that are characteristic for the unsubstituted units of polystyrene are completely absent. In the spectra of the obtained anionites the intensity of the frequencies at 675 and 1270 cm^{-1} decreases sharply.

In harmony with the data of the spectral and chemical analyses, the structure of the obtained anionites can be depicted in the following manner:



where





$$X = -\overset{\oplus}{N}H_{3-n}(CH_3)_n,\ -\overset{\oplus}{N}H_{3-n}(CH_2CH_3)_n,\ -\overset{\oplus}{N}H_{3-n}(CH_2CH_2OH)_n;\ (n = 1,2 \text{ or } 3)$$

(Y = CH_3 or COOH)

The presence of heteroatoms and polar groups (–S–, –O–, $-SO_2-$, –NH–, >C=O, etc.) in the macromolecular chains of ion-exchange polymers can increase the selectivity of the anionites with respect to certain ions of organic and inorganic compounds. For this reason the use of such ionities for the sorption and separation of various metal ions is of both practical and theoretical interest. The greater length of the N,N'-arylenedimethacrylamides when compared with divinylbenzene makes it possible to increase the permeability of ion-exchange resins with respect to the ions of large organic molecules (alkaloids, antibiotics, etc.).

CONCLUSIONS

Various anion-exchange polymers were obtained from the copolymers of styrene and N,N'-arylenedimethacrylamides, with subsequent chloromethylation and amination.

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