Soluble polyelectrolytes based on copolymers of styrene with benzonitrile

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Data of the copolymerization of styrene with benzonitrile are presented. The effect of reactivity of monomers, catalyst nature, temperature and process duration on the composition and molecular weight of the formed polymers are discussed. The polymerization mechanism is suggested. Copolymers of different composition were used for synthesis of soluble polyelectrolytes. The conditions of their formation and principal physico-chemical characteristics were studied. The fields of application are discussed.

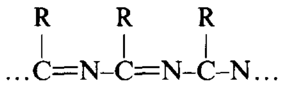
(Keywords: styrene; benzonitrile; polyelectrolyte; redox ion-exchanger; sorption)

INTRODUCTION

The chemical modification of inert polymers by different compounds provides great possibilities for the synthesis of high molecular compounds with ion-exchange properties[1].

New copolymers of styrene (St) with benzonitrile (BN) (developed at the Institute of Chemical Sciences, Academy of Science of the Republic of Kazakhstan[2]) were used for the synthesis of soluble polyelectrolytes. The presence of the highly polar group –C=N– gave valuable properties such as photoelectric sensitivity, paramagnetism, semiconductivity, heat resistance as well as complex-forming ability. However, the production of such polymers and their use in the synthesis of ion-exchange materials has not been discussed before. This was conditioned by low reactivity of the –C≡N group in the polymerization reactions in comparison with other vinyl monomers.

Kargin *et al.*[3] succeeded in polymerizing a series of nitriles using the principle of regularity of monomer molecules in solid complexes. The latter can be formed easily by nitriles with coordinated unsaturated metal halides. Polymerization of ordered molecules of nitrile occurs due to the considerable decrease of enthalpy of the system:



$$\ldots\overset{\overset{R}{|}}{C}=N-\overset{\overset{R}{|}}{C}=N-\overset{\overset{R}{|}}{C}-N\ldots$$

Other studies have been concerned with the mechanism of formation of polymers[4–8] and copolymers[9] of nitriles with vinyl monomers.

EXPERIMENTAL

Monomers (St, BN) were purified by known methods. Purity was controlled by chromatography. Stannic chloride was distilled twice above P_2O_5 and powdered Cu in argon current. Solvents were dried and used after purification and distillation.

For the synthesis of BN and St, a complex of BN with $SnCl_4$, prepared by mixing a stoichiometric quantity of both reagents in dry benzene, was used. The formed complex, with 2:1 $(2C_6H_5CN)$:$SnCl_4$ composition, was a white, hygroscopic substance. The chlorine content of the complex was analysed by reverse titration. Calculated for $C_{12}H_{10}N_2Cl_4Sn$:Cl, 30.45%; Sn, 25.39%. Found: Cl, 30.49%; Sn, 25.46%.

Copolymerization was carried out in sealed ampoules (10^{-2} mmHg) at 60±2°C. The concentration of monomer was 15–20 mol%. When the copolymerization was finished the contents of the ampoules were poured into methanol, and the precipitate was filtrated, washed with BN or dichloroethane, dissolved in dimethylformamide and precipitated by diethyl ether. Then it was dried to constant mass in vacuum at ambient temperature. For purification of the copolymers formed from residues of unreacted monomers and catalysts, the precipitation was carried out several times. The composition of the synthesized copolymers was determined on the basis of elemental analysis of nitrogen content. Copolymerization constants were calculated from copolymer composition values obtained at low degree of conversion (up to 10%) by the Mayo–Lewis method[10]. The molecular weight of samples was determined by viscosimetric and cryoscopic methods.

Polyelectrolytes with anion-exchange properties were prepared by amination of chloromethylated samples containing 16.0–18.3% of chlorine with amines of different basicity in organic solvents at different temperatures. Anion exchangers were purified by reprecipitation of samples from dimethylformamide in diethyl ether and by passing an aqueous solution of polymer through a column with cation exchanger in H-form. For conversion of polymer in OH-form, the aqueous solution of ion exchanger was transmitted through a column with the

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strong basic anion exchanger, AB-17. The yield of polymer was 82–85%.

Soluble sulfonic cation exchangers were synthesized by sulfonation of copolymer solution by sulfuric acid in dichloroethane at 80°C or by sulfochlorination with chlorosulfonic acid at 30°C for 3–5 h with further saponification with distilled water or 2% solution of caustic soda. When the reaction was finished, polyelectrolytes were precipitated by diethyl ether and filtered. For elimination of unreacted acid, the aqueous solution of polymer was transmitted through a column with resin AB-17 in OH-form.

Phosphorylation of St–BN copolymers or their chloromethyl derivatives was achieved by addition of excess of phosphorus trichloride to copolymer solution in dichloroethane in the presence of $AlCl_3$. The reaction product was hydrolysed and oxidized with 25% aqueous solution of nitric acid. For purification and conversion of the ion exchanger in OH-form, the aqueous solution of polymer was transmitted successively through columns with anion exchanger AB-17 in OH-form and cation exchanger KU-2 in H-form. To study structure and composition, the ion exchanger was precipitated in methyl alcohol and the dark-brown powder formed was dried to stable weight in a vacuum drier at 50°C.

Kinetics of sulfonation and amination of St–BN copolymers were studied at different temperatures by sampling at certain time intervals and determining contents of nitrogen and phosphorus by elemental analysis. Kinetics of phosphorylation was studied by reaction for 5, 10, 20, 30, 40 and 60 min at different temperatures.

Static exchange capacity (SEC) of polymers was determined by potentiometric titration curves on a multipurpose ionometer EV-75 at 25°C. The apparent dissociation degree of ion exchanger was calculated according to the Henderson–Hasselbach equation.

To study the complex-forming properties of synthesized soluble polyelectrolytes in relation to the metal cations, the aqueous solutions of corresponding salts were used. Precisely weighed samples of cation exchangers in OH-form were flooded by solutions of metal salts. Solutions with ionic strengths of 0.5 and 1.0 were obtained by addition of dry sodium chloride or sodium nitrate. When equilibrium of the reaction was reached the solution was titrated in the presence or absence of metal by 0.1 N solution of caustic soda.

RESULTS AND DISCUSSION

Synthesis of St–BN copolymers

It is known that the polymerization of nitriles is not possible thermodynamically. However, there are two ways to increase their activation. The first is by incorporation of electron-acceptor substituents in the organic molecule, which increases electrophilicity of carbon $-C{\equiv}N$ bond and increases the reactivity of nitriles in the processes occurring via cationic mechanism[9]. Another way is by the use of Lewis acids bonding inactive monomer in the complex, where the nitrile group becomes more reactive in the ionic reactions owing to the polarization strength in the presence of catalysts (homolytic rupture of π-bond of polarized nitrile group is hindered[11]).

There are no data in the literature concerning cationic polymerization of nitriles with vinyl monomers, therefore we studied the system BN–St.

Study of the dependence of copolymer composition on the composition of the initial monomer mixture showed that in the copolymerization reaction BN (M_1) was less active than St (M_2) (*Table 1*).

During cationic polymerization in non-polar solvents, bound carbo-cations were assumed[12] to be active centres and relative reactivity of monomers was determined by steric factors. In polar solvents the chain growth occurred on free carbo-cations; the steric effect in this case was insignificant. This hypothesis confirmed the results of experiments. Analysis of data concerning dependence of copolymer composition on the composition of the initial mixture (*Table 1*) showed that the nitrogen content of the copolymer increased with increase of BN fraction in the monomer mixture. However, in this case the 'polymerization limit' was reached, i.e. activity of carbocation of BN to its monomer was practically zero. Values of relative activities of monomers calculated on the basis of the elemental analysis of nitrogen content and the method of least squares are presented in *Table 2*. For BN and St, $r_1=0.012\pm0.001$ and $r_2=7.0\pm0.05$ (upon the calculation of copolymerization constants the conversion did not exceed 7%). The probabilities of formation of different structures in copolymers were calculated from these data[13]; then the average sequence length of chains of the same type (*Table 3*) was determined.

Table 1 Dependence of copolymer composition on composition of initial monomer mixture (BN, M_1; St, M_2; solvent, benzonitrile; concentration of monomers in the solution, 15%; $t=60$°C; monomer for the polymerization (BN) with styrene was added to the solution in the form of the complex with $SnCl_4$)

Initial mixture (mol %)		Copolymer composition (mol %)		Nitrogen contents
M_1	M_2	M_1	M_2	(%)
45	55	10.5	89.5	1.28
50	50	12.7	87.2	1.49
63	37	13.6	86.4	2.01
70	30	21.6	78.4	2.67
75	25	24.2	75.8	3.04
80	20	29.9	70.1	3.46

Table 2 Principal parameters of the copolymerization of BN and St

Solvent	r_1	r_2	r_1r_2	e_1	e_2	Q_1	Q_2
BN	0.012	7.0	0.084	−2.38	−0.8	0.51	1.0
Dichloroethane	0.002	5.1	0.012	2.94	−0.8	1.08	1.0

Table 3 Probabilities of the formation of different structures (f) in St–BN copolymers and average length of sequences (L) of elemental chains of the same type

	M_1	M_2	$f_{M_1M_1}$	$f_{M_1M_2}$	$f_{M_2M_2}$	$\bar{L}_1$	$\bar{L}_2$
BN–St	80	20	0.0126	0.2632	0.4607	1	2.7
$r_1=0.012$	75	25	0.0082	0.2288	0.5340	1	3.3
	70	30	0.0056	0.1989	0.5967	1	4.0
$r_2=7.0$	63	37	0.0033	0.1629	0.6708	1	5.0
	50	50	0.0013	0.1109	0.7767	1	8.0
	45	55	0.0009	0.0946	0.8097	1	9.6

Table 4 Properties of St–BN copolymers depending on composition of initial monomer mixture and conditions of copolymerization

Monomer content in initial mixture (mol %)		Duration of copolymerization (h)	Monomer content in copolymer (mol %)		f.p. (°C)	[η] (dl g^{-1})	ρ (Ω^{-1} cm^{-1})
St	BN		St	BN			
10.0	90.0	60	72	28	195–200	0.06	4×10^{-9}
17.0	83.0	54	74	26	180–190	0.07	6×10^{-9}
24.8	75.2	48	75	25	175–180	0.10	4×10^{-10}
50.0	50.0	42	78	22	160–180	0.12	2×10^{-12}
71.0	29.0	33	94	6	110–120	0.21	2×10^{-15}

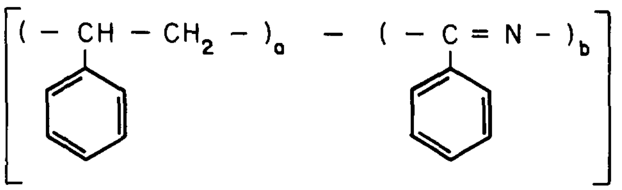
It was clear that during the copolymerization of BN with St at the initial composition of 50:50 mol%, one chain of BN in the copolymer accounted for eight chains of St whereas at 80:20 mol% one chain of BN accounted for three chains of St, i.e. the copolymer was enriched by BN.

Depending on the copolymerization conditions and composition of the initial monomer mixture, copolymers were obtained with the properties given in *Table 4*. The colour of copolymers of different composition varied from yellow to brown and they were soluble in polar solvents.

In i.r. spectra, the intense peak of –C≡N at 2240 cm^{-1} disappeared, and a wide band appeared in the region of 1640 cm^{-1}; this is related to the deformation vibrations of –C=N bond in the linear chain. Bonds at 690 and 750 cm^{-1} were retained, i.e. depending on experimental conditions the interaction of the triple –C≡N bond occurred without destruction of the aromatic ring, as also evidenced by the absence of gaseous reaction products.

Addition of noble metal salts to the aqueous solution serves as evidence[14] for the presence of conjugated –C=N bonds in copolymers. It should be noted that under the conditions studied the BN itself does not polymerize[5].

On the basis of the data obtained, the structure of St–BN copolymers can be presented as:



It is known[9] that the structure of copolymers based on nitriles can be judged from hydrolysis data, as a result of which an acid is formed corresponding to the nitrile used, as well as compounds containing an amino group.

To confirm the above structure, alkaline hydrolysis of the copolymer was carried out with concentrated alkaline solution at 80°C for 30 h. Elemental analysis data (a copolymer with 1:1 composition was used as an example) and potentiometric titration of the hydrolysis product were in good agreement, the BN content obtained being 37.5% and 37.7%, respectively. Titration curves indicated the formation of weak basic anion exchanger obtained as a result of hydrolysis.

The presence of a primary amino group also confirmed the formation of a non-soluble product during hydrolysis.

Synthesis of ion exchangers based on St–BN copolymers was carried out through traditional stages of polymer activation by incorporation of reactive groups, chloromethyl or sulfonyl chloride, and by direct incorporation of ionogenic groups in the polymer structure.

Anion-exchange resins based on St–BN copolymers

Study of chloromethylation of copolymers of St with BN by monochlorodimethyl ether in the presence of Friedel–Kraft catalysts showed that stannic chloride was more active[15] and the largest quantity of chlorine (16.8–18.3%) was introduced when 0.4 mol of catalyst and 10 mol of ether were used over 3 h (the temperature was not higher than 50°C).

^{1}H n.m.r. spectra of St–BN copolymers contained signals in the region 7.05, 7.48 and 7.95 ppm, due to the protons of St and benzene nuclei. Absorption of methine and methylene protons as a result of higher screening was observed in the stronger fields, their chemical shifts being 2.3 and 1.9 ppm, respectively. Signals of the methylene group of chloromethylated copolymer appeared in the weaker field (4.98 ppm) owing to their descreening by the chlorine atom (*Figure 1*).

Amination of chloromethylated copolymers was achieved with aliphatic amines and pyridine in the presence of dimethylformamide. Study of the conditions of anion-exchanger synthesis showed that the reaction was usually complete in 2–3 h in the presence of 5 mol excess amine at 50°C, with the conversion degree 75–88% depending on amine type.

From kinetic curves of the interaction of chloromethylated copolymers with amines (*Figure 2*) calculated from a second order equation, it was shown that rate constants of the reaction changed considerably as the process was completed, and the relations obtained had the shape of broken curves (*Figure 2b*). This phenomenon seemed to be related to steric hindrances that arose under amination, i.e. due to the effect of neighbouring unreacted groups of macromolecules (configuration effects) and the accumulation of the charge of the amination product[16]. Incorporation of substituents in the polymer chain hindered the diffusion of amine to chloromethyl groups which appeared to be scfeened by reincorporated chains.

Alkyl-substituted amines differed a little in basicity but differed considerably in reaction rate. Comparison of the data obtained showed that change of rate depends on the nature of the aliphatic radical (*Table 5*). Thus, in the case of the least volumetric substituents (conversion from methylamine (MA) to diethylamine (DEA)) an increase in reaction rate was observed. It seemed to be related to the fact that a small steric hindrance effect was overlapped by its inductive effect, increasing the basicity upon incorporation of a second ethyl group, and it was wholly manifested by facilitating the formation of a new bond, i.e. by the rise of amination rate. Upon conversion from DEA to triethylamine (TEA), rate constants decreased owing to the increase of spatial screening of the nitrogen atom by more volumetric substituents. Spatial effects proved to influence the reactivity of alkylamines to a greater extent than the basicity. The rate decrease in the above sequence was explained by the different extent of localization of undivided electrons on nitrogen atoms on the amino group, and by the intensity of their steric screening by hydrogen substituents[8]. The thermodynamic parameters—enthalpy $\Delta H^{\neq}$, entropy $\Delta S^{\neq}$ and free activation energy $\Delta G^{\neq}$, calculated from the relation lg k on $1/T$ (*Table 6*) by means of the following equation[17]—confirmed the influence of spatial effects:

$$\Delta G = 4.576T\,(10.319 + \lg T - \lg K) \tag{1}$$

$$\lg K = \frac{\Delta G^{\neq}}{2.3RT} + \lg\frac{RT}{Nh} \tag{2}$$

$$\Delta H^{\neq} = E_{\text{act}} - RT \tag{3}$$

$$\Delta S = \frac{\Delta H^{\neq} - \Delta G^{\neq}}{T} \tag{4}$$

where R = gas constant, T = absolute temperature, N = Lodhmidt's number and h = Planck's constant.

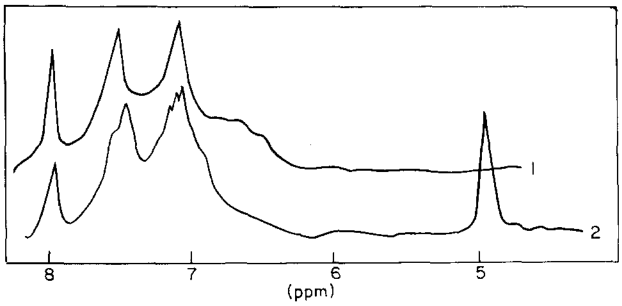


Figure 1 ^{1}H n.m.r. spectra of St–BN copolymers (1) and chloromethylated sample (2)

Table 5 Kinematic parameters of the amination of the chloromethylated St–BN copolymer

	$K(10^3\,\text{l mol}^{-1}\,\text{s}^{-1})$						
Amines	30	40	50	60	70	E_{act} (kJ mol^{-1})	$A \times 10^{-3}$
Methylamine	1.8	2.2	3.1	3.6	–	31.7	6.8
Diethylamine	1.7	2.4	3.9	4.1	–	29.2	7.3
Trimethylamine	1.1	1.3	1.8	2.3	–	36.7	5.0
Pyridine	–	1.3	2.6	3.0	3.4	34.8	5.9

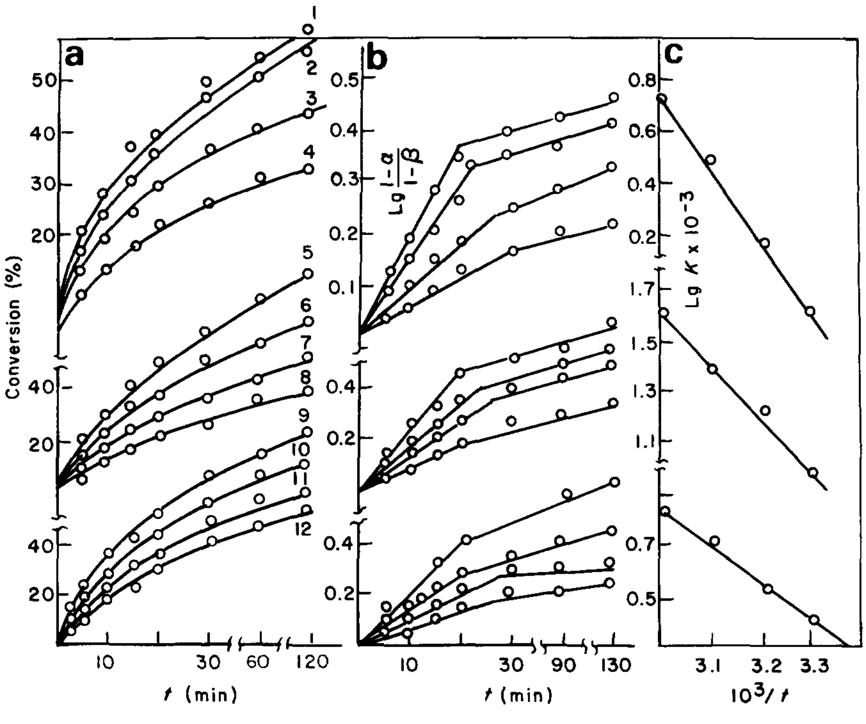


Figure 2 Kinetic amination curves of chloromethylated St–BN copolymer with trimethylamine (top), pyridine (middle) and diethylamine (bottom) at 30°C (4,12), 40°C (3,8,11), 50°C (2,7,10), 60°C (1,6,9) and 70°C (5). (a) Degree of conversion; (b) logarithm of ratio of reacted amino- and chloromethyl groups; (c) constants of amination

Table 6 Thermodynamic parameters of the amination reaction of chloromethylated St–BN copolymer (T = 50°C)

Amine	$\Delta G^{\neq}$ (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	pK_α of anion exchangers	Initial pK_α
Methylamine	94.75	31.88	−197.1	7.4	10.6
Diethylamine	94.13	28.58	−202.9	8.2	10.9
Trimethylamine	96.21	36.09	−186.1	9.0	9.8
Pyridine	95.60	34.21	−190.0	8.7	5.4

Enthalpy and entropy of activation increased as the size of the alkyl group increased, corresponding to the decrease of the overlapping ratio of the electron shell of the amine nitrogen and the alkyl atom of carbon in the transition state. Values of $\Delta G^{\neq}$ for the amination reaction of chloromethylated St–BN copolymer increased, depending on the nature of the amines used, in the following sequence: trimethylamine (TMA) > MA > DEA.

Comparison of spectra of the initial chloromethylated copolymer and anion exchanger shows the appearance of a series of absorption bands and considerable decrease in the intensity of bands of CH_2Cl groups (1270, 673 cm^{-1}). In spectra of ion exchangers based on TMA, the absorption of the *N*-methyl group appears at 2770 cm^{-1} and a series of intensive frequencies of valence vibrations of C–H aliphatic groups appears in the region of 2820 and 2970 cm^{-1}.

Values of dissociation constants of functional groups of synthesized anion exchangers, calculated from potentiometric titration curves with Henderson–Hasselbach's equation, are 7.4, 8.2, 9.0 and 8.7 (*Table 6*).

Cation-exchange resins based on St–BN copolymers

Synthesis of cation exchangers based on St–BN copolymers was achieved via chlorosulfonation or sulfonation of samples. A study of chlorosulfonation conditions showed that the increase in the temperature of the process and its duration, as well as the use of chloroacetic acid in excess, favoured cross-linking of the final product owing to the formation of sulfonic bridges, as a consequence of which cation-exchange capacity of ion exchangers decreased (after saponification) (*Figure 3*). Thus, it is 3.4 and 2.5 mg eq. g^{-1} at reaction temperatures of 30 and 60°C, respectively.

Synthesized cation exchangers were soluble in water, dichloroethane and dimethylformamide. Hydrodynamic properties of aqueous solutions of sulfonic cation exchangers indicated the polyelectrolyte character of synthesized polymers (*Figure 4*).

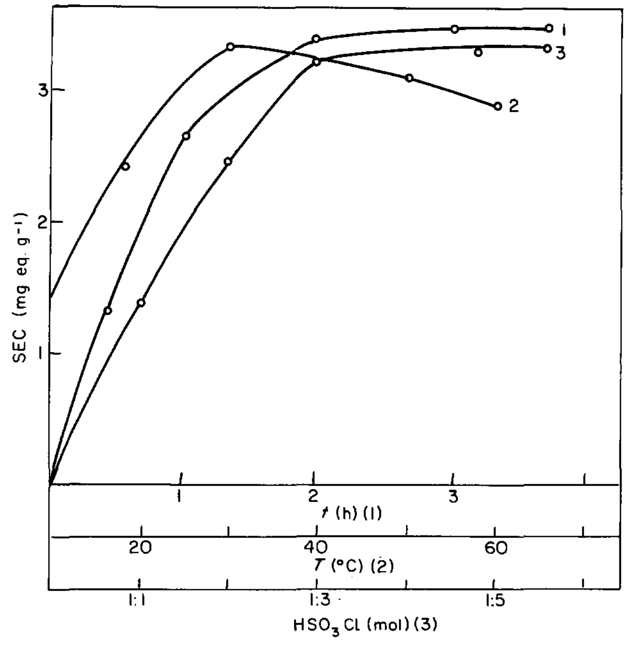


Figure 3 Dependence of exchange capacity of chlorosulfonated copolymer on the duration of the process (1) and temperature (2); polymer: ChSA ratio (3)

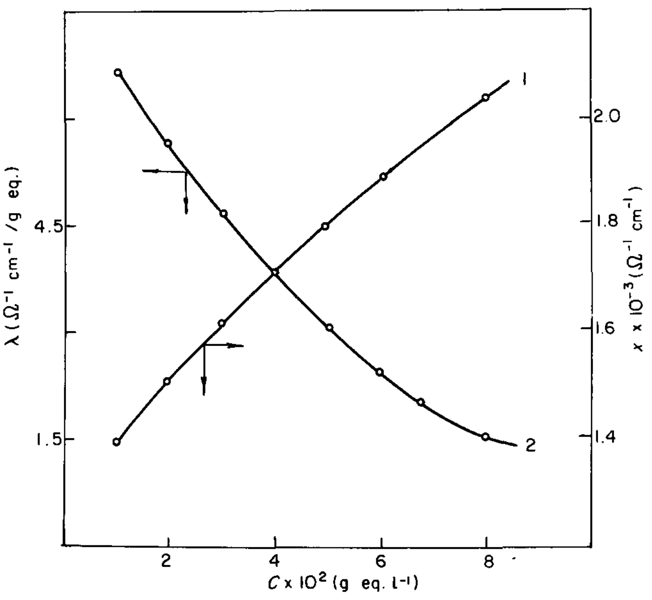


Figure 4 Dependence of reduced viscosity on the concentration of polymer based on chlorosulfonated St–BN copolymer (1) and on $\sqrt{c}$ (2)

I.r. spectra of chlorosulfonated samples contained intensive absorption bands of SO_2Cl groups (1375, 1190 and 1170 cm^{-1}) joined to polyalkylene chain in the *para*-position (840 cm^{-1}). In saponification products, characteristic bands of absorption of sulfo-groups appeared at 1210–1190, 1125, 1040 and 1010 cm^{-1}.

Study of sulfonation of St–BN copolymers with sulfuric acid in the presence and absence of catalyst (Ag_2SO_4) showed that its presence did not favour an increase in exchange capacity, but additional difficulties arose because of catalyst separation from the final product. A maximum value of exchange capacity of 4.1 mg eq. g^{-1} was achieved at 80°C with 5 mol excess of acid.

The shape of the potentiometric titration curve and value of the dissociation constant calculated from Henderson–Hasselbach's equation showed that the synthesized polymer represented a strong acid cation exchanger with pK = 2.4.

Reaction rate constants and activation energy of the process were calculated from kinetic curves for the initial stage. It was found that at the beginning the reaction proceeded vigorously; the rate constant was $(3.2\text{–}5.4) \times 10^{-3}$ s depending on temperature, and the activation energy was 26.6 kJ mol^{-1}.

I.r. spectra of sulfonic cation exchangers were analogous to the spectra of saponification products of chlorosulfonated samples.

Phosphorus-containing cation exchangers based on St–BN copolymers

Bifunctional phosphorus-containing cation-exchange polymers with ionogenic groups $-PO(OH)_2$, intermediate between weak and strong acid ion exchangers in degree of dissociation, were of interest because of their specific selectivity under sorption process. St–BN copolymers or their chloromethylated derivatives were phosphorylated under conditions of the Friedel–Kraft reaction by phosphorus trichloride via oxidation of groups of phosphoneous acid, formed at the first stage. For the synthesis of cation exchangers, the ratio of initial components, temperature and duration of the process were varied widely (*Figure 5*) to assure complete solubility

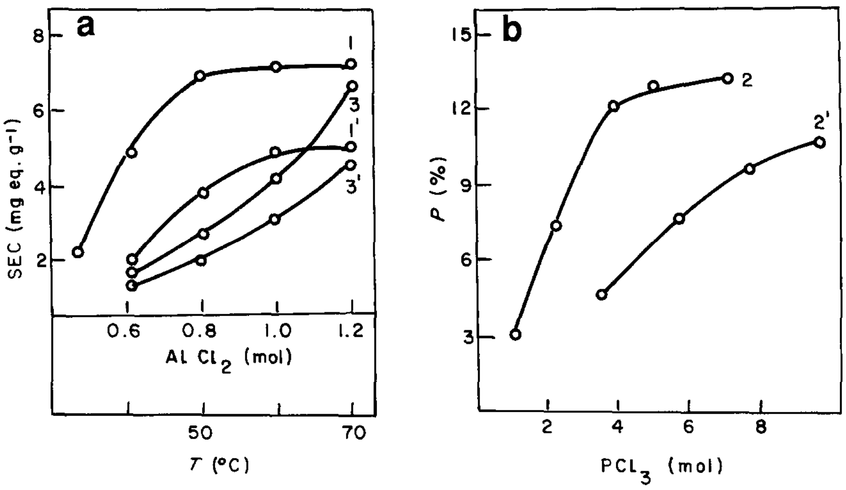


Figure 5 Dependence of phosphorylation rate of St–BN copolymers (1,2,3) and their chloromethylated derivatives (1′,2′,3) on the process temperature (a,3,3′), amount of catalyst (a,1,1′) and PCl_3 (b,2,2′) in the reaction medium

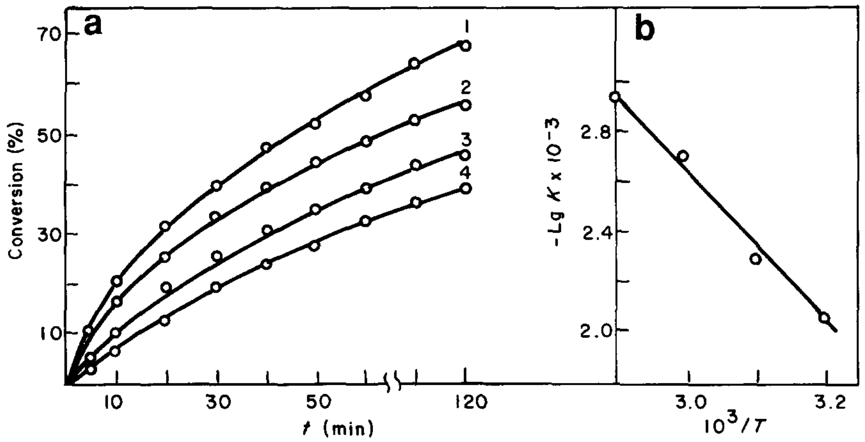


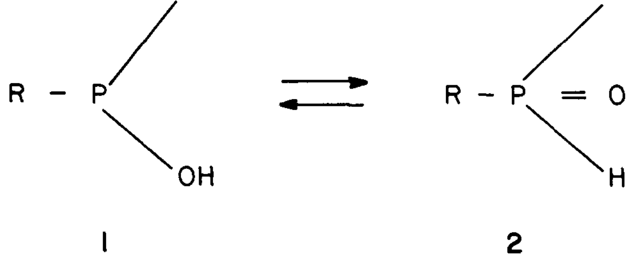
Figure 6 (a) Kinetic phosphorylation curves of St–BN copolymer at 70°C (1), 60°C (2), 50°C (3) and 40°C (4); (b) dependence of $-\lg K \times 10^{-3}$ on $10^3/T$

of the initial components in the reaction medium and to avoid cross-linking of macromolecules. The maximum conversion of initial samples was 82.6–90.1%; in this case the degree of phosphorylation of chloromethylated copolymers was somewhat lower in comparison with the initial copolymers, apparently due to the fact that in the first case the process occurred only by chloromethylated groups. Substitution of hydrogen atoms of the nucleus in the *ortho*-position relative to the polyalkylene chain and phosphorylation of benzonitrile chains did not occur.

From kinetic curves, it was established by the Want–Goff method and semitransformation period[18] that phosphorylation of initial copolymers with PCl_3 in excess followed a first-order equation. As a process was completed, reaction rate constants changed and decresed considerably. This was probably because in the initial stage the reaction took place on the surface of statistic coils of macromolecules and was subsequently displaced to the inner layers, where the process rate decreased due to the increased diffusion hindrances within static coils of the macromolecules.

The dependence of rate constants in Arrhenius coordinates initially had a linear character (*Figure 6b*); in this case the activation energy was 54.1 kJ mol^{-1}.

The nature of the functional groups before and after oxidation with 25% aqueous solution of HNO_3 was determined by potentiometric titration (*Figure 7*). The titration curve of the hydrolysis product of the phosphorylated copolymer characterized the product as a weak monobasic acid (*Figure 7*, curve 1) with an exchange capacity of 3.5 mg eq. g^{-1}. In the non-oxidized product, the functional group RPO_2H_2 was able to exist in the form of two modifications in mobile equilibrium[19]:



Equilibrium form 2 predominated at 95%, therefore the non-oxidized product behaved as a monobasic acid.

After oxidation by 25% nitric acid solution, the exchange capacity of cation exchangers in 0.1 N solution of NaOH increased to 5.3–6.8 mg eq. g^{-1}. The character of the potentiometric titration curve indicated that during oxidation, polyphosphoneous acid converted into dibasic phosphonic acid with functional group $PO(OH)_2$ having

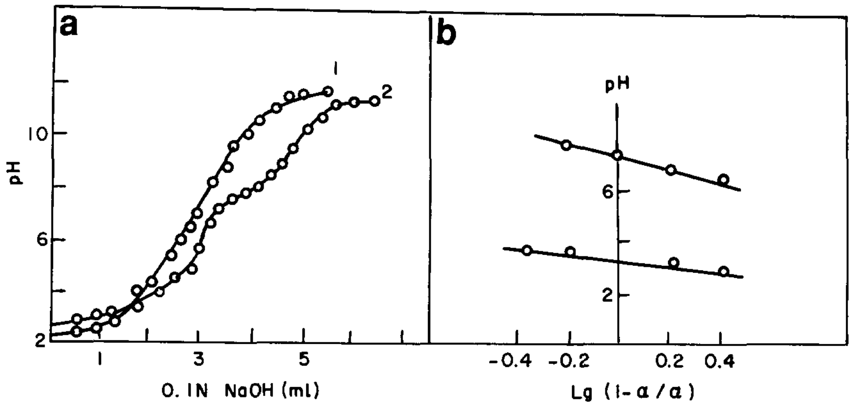


Figure 7 (a) Potentiometric titration curves of phosphorylated cation exchangers before (1) and after (2) oxidation; (b) dependence of pH on lg (1 − α/α)

two degrees of dissociation, corresponding to $pK_{\alpha 1}$ and $pK_{\alpha 2}$ values of 3.5 and 7.3, respectively (*Figure 7*, curve 2).

Saponification of the interaction products of the chloromethylated copolymer of St with PCl_3 resulted in the formation of groups of phosphoneous acid (phosphorus content was 8–10%, exchange capacity in 0.1 N solution of NaOH was 2.3–3.8 mg eq. g^{-1}). During oxidation of the obtained product the exchange capacity of cation exchanger increased to 4.8 mg eq. g^{-1}; the formed polymeric dibasic acid had $pK_{\alpha 1}$ and $pK_{\alpha 2}$ values of 4.0 and 8.1, respectively.

Study of the hydrodynamic properties of the water-soluble polymers obtained showed that the dilution of their solutions increased the reduced viscosity relative to the change of macromolecular conformation, owing to the electrostatic repulsion in polyions of the same charge. After the addition of low molecular polyelectrolyte, this relationship acquired a linear character.

Measurement of specific and equivalent conductivity of phosphorylated St–BN copolymers indicated the presence of ionogenic groups in the macromolecules. It was known that the value of polyelectrolyte conductivity was dependent on its degree of dissociation and was determined by free polyions with fixed charges and by their mobility. After dilution of copolymer solutions, equivalent conductivity increased (*Figure 8*). This was apparently because the degree of dissociation increased with decrease of polyelectrolyte concentration owing to the decrease of intermolecular interaction of polyions with counterions.

In i.r. spectra of phosphorylated ion exchanger, characteristic absorption bands of valence vibrations of P=O bond were present in the region of 1190 cm^{-1} and P–OH groups in the region of 1020–1040 and 995 cm^{-1}.

Thus, from these studies it is concluded that during phosphorylation of St–BN copolymers by phosphorus trichloride in the presence of anhydrous $AlCl_3$, water-soluble polyelectrolytes with phosphonic acid groups are formed. This occurs via the formation of an active complex in which Lewis acid can be present in dimeric form, $PCl_3^{\delta+}$—$AlCl_3$—$AlCl_3^{\delta-}$, and the monomeric state, $PCl_3^{\delta+}$—$AlCl_3^{\delta-}$. We studied ^{31}P and ^{27}Al n.m.r. spectra of initial compounds and their complexes. The signal of ^{31}P (219 ppm) was not observed to shift (*Figure 9*). The deficit of electron density on the phosphorus atom that arose during complex formation seemed to be supplied by electrons of the chlorine atom, bonded with the phosphorus atom.

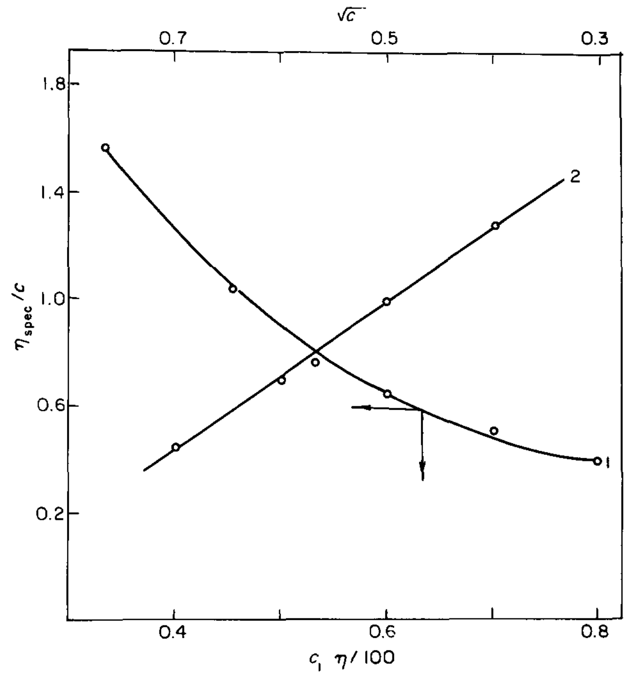


Figure 8 Concentration dependence of specific (1) and equivalent (2) conductivity of aqueous solutions of phosphorylated St–BN copolymer

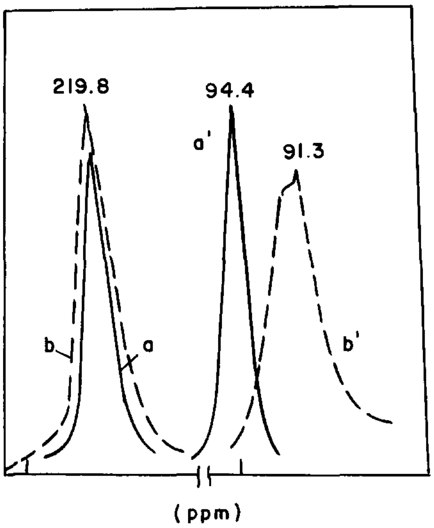


Figure 9 ^{31}P and ^{27}Al n.m.r. spectra of phosphorus trichloride (a, b) and aluminium chloride (a', b') before (——) and after (– – –) complex formation

The change in character of chemical shift of ^{27}Al in the PCl_3 solution (*Figure 9*) indicated complex formation. The ^{27}Al signal in the complex shifted in the direction of the strong field due to the increased screening (91.3 ppm).

Soluble redox polymers based on St–BN copolymers

To obtain electron exchangers, the polymers with active –OH, CH_2Cl, $-SO_2Cl$, $-NH_2$ and other groups were modified by compounds capable of reversible reduction–oxidation (quinones, di- and trioxybenzenes and other polynuclear aromatic compounds, nitrogen-containing reagents, dyes, etc). In this field the majority of studies were devoted to the hydroquinone–quinone containing redox ion exchangers; compounds and their derivatives have been studied in detail and reversibility of the quinone–hydroquinone system has been known for a long time[20,21].

Synthesis of redox polymers based on St–BN copolymers was achieved by condensation of chloromethylated samples with quinones and hydroquinones in the presence of Friedel–Kraft catalyst; organic solvents were used as the medium for initial reagents[22,23].

The effect of the ratio of the initial components on the extent of chlorine atom substitution was studied; quinone in excess was not seen to influence the degree of substitution. When the ratio of chloromethylated copolymer to quinone was 1:1, 1:3 and 1:5, the conversion of initial samples was 72.1, 74.3 and 77.0%, respectively. The maximum degree of conversion, 78.2%, was reached at 80°C; at higher temperatures cross-linking of the macromolecules occurred.

Kinetic studies of the interaction of chloromethylated St–BN copolymers with quinone in excess showed that the activation energy of the process at the initial stage was $51.5\,kJ\,mol^{-1}$; this value was slightly higher for the analogous process with chloromethylated polystyrene[23]. This seemed to be due to the electron-acceptor effect on the nitrile group of the aromatic nucleus. The lower chlorine content in chloromethylated St–BN copolymer in comparison with polystyrene also indicated this phenomenon (19–19.9%).

The capacity of electron exchangers for redox reactions was characterized by the redox capacity and the determination of redox potentials (*Table 7*). They are dark brown powders, soluble in organic solvents, and showing a change in colour during conversion from one form to the other.

Comparison of the i.r. spectra of model compounds and condensation products showed their identity: the spectrum of quinone and polymer on its base contained an intensive absorption band of carbonyl groups in 1,4-quinone at $1660\,cm^{-1}$.

To accelerate the redox process it was necessary for the polymer system to be reversible. Such redox exchangers were prepared by the incorporation of hydrophilic ionogenic groups in the final product by sulfonation and amination[23].

Table 7 Principal properties of redox polymers based on St–BN copolymers

Group in redox exchangers	SEC in 0.1 N NaOH $(mg\,eq.\,g^{-1})$	SEC in 0.1 N HCl $(mg\,eq.\,g^{-1})$	Redox capacity $(mg\,eq.\,g^{-1})$	E_n (mV)
Sulfo-	2.1	–	2.40	708
Phosphoric acid	2.5	–	2.61	715
Dimethylamine	–	0.92	2.87	706
Trimethylamine	–	1.15	2.95	703

Phosphorylated redox exchangers were prepared by treating them with PCl_3 in the presence of $AlCl_3$ at the polymer: PCl_3:$AlCl_3$ ratio of 1:4:1 at 70°C for 6 h. The dark brown product was hydrolysed and oxidized by nitric acid (25%), and the colour of the polymer became red–brown.

The apparent dissociation constants of the polymers obtained were determined from potentiometric titration curves. Values of $pK_{\alpha 1}$ and $pK_{\alpha 2}$ were 3.0 and 6.2, respectively. Complete cation-exchange capacity was $2.5\,mg\,eq.\,g^{-1}$.

Redox cation exchangers sulfonated with sulfuric acid were characterized from potentiometric titration curves as strongly acidic, with $pK_\alpha = 1.78$ and exchange capacity of $2.1\,mg\,eq.\,g^{-1}$.

In spectra of sulfonated redox ion exchangers, the absorption bands corresponding to the bond –C–S– (1380, 1360 and $1130\,cm^{-1}$) appeared; in phosphorylated redox ion exchangers, bands at 1280 and $1220\,cm^{-1}$ were due to the valence vibrations of P=O.

The principal characteristics of redox exchangers are given in *Table 7*.

Thus, these studies showed that it is possible to use new copolymers of styrene with benzonitrile for the synthesis of various types of soluble ion exchangers. It was found that they were less susceptible to cross-linking during prolonged storage in comparison with polystyrene polyelectrolytes. Phosphorylated ion exchangers showed a high sorption capacity upon recovery of uranyl ions and cuprum from solutions of nitric acid (3.9 and $2.0\,mg\,eq.\,g^{-1}$, respectively). Redox ion exchangers were efficient at stabilizing the potential on the membrane-current tap surface in ion-selective membranes without liquid filling.

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