

THE SYNTHESIS OF MACROPOROUS CROSSLINKED POLYSTYRENE AMIDOPHOSPHONIC ACID*

HE Binlin (何炳林), WANG Linfu (王林富) and CHEN Weizhu (陈伟朱)

(Department of Chemistry, Nankai University, Tianjin)

ABSTRACT

A series of macromolecular copolymers of styrene and divinyl-benzene were prepared in the presence of *iso*-octanol or 2-ethyl butyl alcohol. The factors which affected the physical structures of the copolymer were discussed. The macroporous amido-phosphonic acid resin was obtained after the acetylation, phosphorylation and amination of the crosslinked polystyrene. The factors which affected each reaction were studied and the change of physical structures of the copolymer were discussed.

The macroporous crosslinked polystyrene amidophosphonic acid resin has a strong tendency to form coordinate and chelate compounds with many heavy metals because the phosphorus atoms in the molecule and their bonds possess high polarization energy and there are many atoms with lone pairs of electrons in the molecule. Based on the fact that it possesses different activity toward different metallic ions, the resin may be used for the extraction and purification of the uranium, thorium, rare earth and transition metals. It may also be used for the treatment of pollution problems of electroplating and other enterprises.

In the meantime, the pore structures of the resin which depend on the method of preparation play an important role in the formation of coordinate compounds and chelates. There are many ways for the preparation of macroporous crosslinked polystyrene matrixes^[1]. The conventional methods for the preparation are to run the copolymerization in the presence of an inert organic solvent such as benzene, toluene, xylenes, 1,2-dichloroethane etc.^[2-10] known as good solvents for polystyrene and aliphatic hydrocarbons, aliphatic alcohols, aliphatic acids etc.^[11-16] known as the nonsolvents for polystyrene. In this paper, the preparation and physical properties of a series of styrene-divinylbenzene copolymers in the presence of *iso*-octanol or 2-ethyl butanol were investigated. The macroporous crosslinked polystyrene was then acetylated with either acetic anhydride or acetyl chloride in the presence of aluminum chloride followed by a reaction with phosphorus trichloride and decomposed with glacial acetic acid. To the final product was added excess amine and macroporous crosslinked polystyrene amidophosphonic acid was thus obtained.

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EXPERIMENTAL

1. *Preparation of styrene-divinylbenzene copolymer in the presence of an aliphatic alcohol as porogenic agent*

(1) Preparation of copolymer

Water, gelatin and sodium chloride were added into a three-necked flask equipped with a stirrer, reflux condenser and thermometer, followed by the addition of a mixture of styrene, divinylbenzene, benzoyl peroxide and *iso*-octanol or 2-ethyl butanol. The mixture was stirred at such a rate that it formed droplets approximately in the desired size. The temperature was raised slowly to 75°C and maintained there for 8 hours. The mixture was cooled, filtered and washed, and the resulting polymer beads were air-dried.

(2) Determination of the physical properties of copolymer

The apparent density and true density of samples were determined by the conventional pycnometer method with mercury and *n*-heptane respectively^[17,18].

The specific surface area was measured with a ST-03 surface area analyzer.

The porosity and average pore size of the resins were calculated from apparent density, true density and specific surface area^[19] measurements.

2. *Acetylation of the macroporous crosslinked polystyrene*

(1) Preparation of the macroporous crosslinked acetopolystyrene

The dried macroporous copolymer beads of styrene-divinylbenzene and suitable solvents were placed in a three-necked reaction flask, followed by the addition of aluminum chloride and acetic anhydride. After acetylation, the reaction mixture was cooled and decomposed with 12*M* HCl, the product was placed in a column and washed successively with distilled water, acetone, 15*M* NH₄OH, distilled water, 12*M* HCl, distilled water, methyl alcohol, filtered and finally air-dried.

(2) Determination of the macroporous crosslinked acetopolystyrene resin

(a) Infrared spectroscopy

The resin was ground and dried to constant weight in vacuum at room temperature; and determined by the KBr pellet method.

(b) Analysis of the nitrogen content of the resin

One gram of dried crosslinked acetopolystyrene resin was washed with 50 ml pyridine, 95% ethanol, dichloroethane, toluene, ethanol successively and filtered. Samples were dried to constant weight at 50°C in the vacuum oven; ground and finally their nitrogen content was determined by the Dumas method. The carbonyl group content of the macroporous cross-linked acetopolystyrene resin was calculated from the nitrogen content of the resin.

3. *Phosphonation of the macroporous crosslinked acetopolystyrene with phosphorus trichloride*

(1) Preparation of the macroporous crosslinked α -hydroxyl- α -methyl polystyrene phosphonic acid resin

The macroporous crosslinked acetopolystyrene resin was added into a three-necked

flask together with a suitable quantity of solvent and phosphorus trichloride. After reacting under a certain condition for some time, glacial acetic acid was added and the products were poured into a large quantity of water and thus α -hydroxyl- α -methyl polystyrene phosphonic acid resin was obtained. The extent of phosphorylation was calculated from the phosphorus content and exchange capacity of the product.

(2) Determination of the properties of crosslinked α -hydroxyl- α -methyl polystyrene phosphonic acid resin

(a) Infrared spectroscopy

The method was the same as above mentioned.

(b) Analysis of the phosphorus content

It was determined by the titration method with $\text{La}(\text{NO}_3)_3$ -EDTA.

(c) Measurement of the exchange capacity

0.2—0.3 g of resin was soaked for a few minutes with stirring in a mixture of 50 ml 0.1N sodium hydroxide and 20 ml 1M NaCl. Then 30 ml of this solution were taken out and titrated with a standard solution of hydrochloric acid.

4. *Amination of the macroporous crosslinked polystyrene phosphoryl chloride resin with di-n-butylamine*

(1) Preparation of the amidophosphonic acid resin

The macroporous crosslinked polystyrene phosphoryl chloride was made by the reaction of macroporous crosslinked acetopolystyrene with phosphorous trichloride followed by the decomposition of the product with glacial acetic acid. Excess di-n-butylamine was added dropwise and after amination the reaction products were poured into a large quantity of distilled water, filtered, washed successively with ethanol, distilled water, 5% HCl, distilled water, 5% NaOH, distilled water, ethanol and finally air dried.

(2) Determination of the properties of the amidophosphonic acid resin

The same procedure as before.

RESULTS AND DISCUSSION

1. *Factors affecting the physical structure of the copolymers*

The mechanism of pore structure formation during styrene-divinylbenzene copolymerization in the presence of inert diluents was investigated by Chen and Kunin^[20]. Their results indicated that the sequence of the onset of gelation and phase separation is crucial to the state of aggregation of the solvent modified copolymers.

According to Flory's theory on polymer network elasticity, the critical conditions for phase equilibrium during network copolymerizations were derived by Dusek^[21] and defined by the following equation:

$$\ln (1 - \alpha_c V_2^0) + \alpha_c V_2^0 + X_{13} (\alpha_c V_2^0)^2 = -V_1 (v_e/V_0)_c (\alpha_c V_c^0/2)$$

where α_c is the monomer conversion ratio at the onset of phase separation.

V_2^0 is the initial monomer concentration.

X_{13} is the polymer solvent interaction parameter.

V_1 is the molar volume of the solvent.

V_0 is the molar volume of the polymer formed.

V_c is the crosslinking density.

$(v_c / V_0)_c$ is the critical degree of crosslinking at the onset of phase separation.

This indicates that phase separation during network copolymerization in presence of inert diluents is mainly affected by the nature (X_{13} , V_1) and amount $(1 - \alpha_c V_2^0)$ of the inert solvent and the crosslinking density $(v_c / V_0)_c$ of the polymer network formed, which is consistent with our experimental results and indicated by the physical properties of the copolymers in Table 1.

Our results indicate that the evaluated physical properties of the copolymers are affected by the degree of crosslinking and the nature as well as the quantities of the inert solvents used.

(1) Influence of the degree of crosslinking on the physical properties of the copolymers

Copolymers made in the presence of *iso*-octanol or 2-ethyl butanol show increasing specific surface areas, true densities and porosities with increasing degree of crosslinking, whereas the apparent densities and the average pore size diameters decrease (Table 1).

(2) Influence of the nature and amount of inert solvent on the physical properties of the copolymers

The difference in the structure parameters of copolymers made with the same amount of *iso*-octanol and 2-ethyl butyl alcohol and crosslinking agent can be contributed to the difference in solvating properties, polarity and molar volume of the inert solvent used. At 5% and 10% degree of crosslinking and other experimental conditions being the same copolymers made in the presence of *iso*-octanol have the larger specific surface area and higher porosity than those made with 2-ethyl butanol. However at 20% degree of crosslinking the porevolume of the copolymers made in the presence of *iso*-octanol are smaller than those made in the presence of 2-ethyl butanol. At 20% crosslinking or smaller, the specific surface area of the copolymers tends to increase with increasing quantities of the inert solvent, comes to a peak value and afterwards decreases. At 30% crosslinking or larger, the specific surface area decreases with increasing amount of inert solvent. The increase in the amount of inert solvent has an increasing effect on the porosity and average pore size but decreases the apparent density and slightly increases the true density.

2. Acetylation of the crosslinked polystyrene

Macroporous crosslinked polystyrene was acetylated with acetic anhydride or acetyl chloride in the presence of aluminum chloride. The reaction product and its hydroxylamine derivative were identified by infrared analysis and nitrogen determination.

The infrared spectra of the crosslinked polystyrene, its acetylated product and the hydroxylamine derivative are shown in Fig. 1. A strong peak appears at 1690 cm^{-1} after acetylation of the parent compound, indicating the existence of a carbonyl group but disappeared after the acetylated product was reacted with hydroxylamine. The absence of the aldehyde C—H bond stretch vibrational absorption near 2720 cm^{-1} in curve 2 further indicates the acetylated product to be crosslinked aceto-polystyrene.

Table 1 Physical properties of the copolymer

Number of resin	Degree of crosslinking (%)	Porogenic agent (%)	Specific surface area (M ² /g)	Apparite density (g/ml)	True density (g/ml)	Average pore size (Å) calculated value	Porosity (ml/g) calculated value	Appearance of copolymer
I × 5 ₁₀₀	5	150	8.64	0.3775	1.1152	4056	1.7523	Milky white
I × 5 ₁₀₀	5	100	47.84	0.5947	1.0845	317	0.7594	Milky white
I × 5 ₅₀	5	50	0.46	1.0256	1.0605	0	0.0321	Transparent
I × 5 ₂₅	5	25	0.45	1.0429	1.0520	0	0.0083	Transparent
E × 5 ₁₀₀	5	100	24.56	0.8884	1.0856	166	0.2045	Milky white
E × 5 ₅₀	5	50	0.33	1.0429	1.0453	0	0.0042	Transparent
I × 10 ₁₅₀	10	150	19.63	0.3687	1.1188	1853	1.8184	Milky white
I × 10 ₁₀₀	10	100	68.92	0.5601	1.0849	251	0.8637	Milky white
I × 10 ₅₀	10	50	0.38	0.8643	1.0748	0	0.2266	Transparent
E × 10 ₁₅₀	10	150	0.46	0.7977	1.0741	14026	0.3226	Milky white
E × 10 ₁₀₀	10	100	62.27	0.7266	1.1070	152	0.4729	Milky white
I × 20 ₁₅₀	20	150	31.41	0.3804	1.2354	1158	1.8194	Milky white
I × 20 ₁₀₀	20	100	99.89	0.5006	1.1395	224	1.1200	Milky white
I × 20 ₅₀	20	50	87.54	0.6788	1.1469	137	0.6013	Milky white
E × 20 ₁₅₀	20	150	28.07	0.3644	1.1310	1325	1.8601	Milky white
E × 20 ₁₀₀	20	100	91.61	0.4206	1.1292	325	1.4920	Milky white
E × 20 ₅₀	20	50	37.10	0.9012	1.1214	117	0.2179	Milky white
I × 30 ₁₅₀	30	150	59.88	0.3564	1.2354	667	1.9964	Milky white
I × 30 ₁₀₀	30	100	133.35	0.4206	1.1803	230	1.5303	Milky white
I × 30 ₅₀	30	50	163.73	0.6788	1.1469	73	0.6013	Milky white
I × 44 ₁₅₀	44	150	224.75	0.2912	1.2401	234	2.6277	Milky white
I × 44 ₁₀₀	44	100	263.57	0.3671	1.2012	144	1.8916	Milky white
I × 44 ₅₀	44	50	271.15	0.6442	1.1716	52	0.6988	Milky white
EI × 5 ₁₀₀	5	100	42.63	0.6446	1.0132	265	0.5644	Milky white
EI × 10 ₁₀₀	10	100	73.45	0.6046	1.1187	207	0.7601	Milky white
EI × 20 ₁₀₀	20	100	98.27	0.5346	1.1372	202	0.9912	Milky white

Note: I represents *iso*-octanol, E represents 2-ethyl butyl alcohol, and EI represents mixed solvents of *iso*-octanol and 2-ethyl butanol.

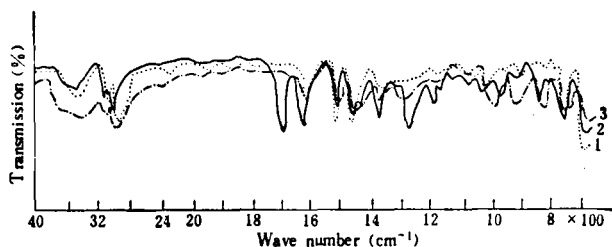


Fig. 1 Partial infrared spectrum of the crosslinked polystyrene, its acetylated product and the hydroxylamine derivative

1. Crosslinked polystyrene $\left(\text{C}_6\text{H}_5 \right)_n$;

2. Crosslinked acetopolystyrene $\left(\text{C}_6\text{H}_4\text{C}(=\text{O})\text{CH}_3 \right)_n$;

3. The derivative obtained from the reaction with hydroxylamine hydrochloride. $\left(\text{C}_6\text{H}_4\text{C}(\text{CH}_3)=\text{N}-\text{OH} \right)_n$.

The acetylation of crosslinked polystyrene is affected by many factors such as:

(1) The amount of acetic anhydride used

From Table 2, it is clear that the extent of reaction increases as the amount of acetic anhydride is increased. However, with too much excess of the acetic anhydride, the extent of reaction decreased.

(2) Solvent effects on the acetylation of crosslinked polystyrene

The extent of acetylation with acetic anhydride is influenced by the nature of the solvating medium (Table 3). Solvents with good solvating properties with respect to the polymer network and acetic anhydride greatly facilitate the extent of acetylation. This indicates that the reaction might be diffusion-controlled and therefore requires a considerable degree of swelling of the polymer network and miscibility of the acetic anhydride in the reaction medium (Table 4).

(3) Effect of temperature on the extent of acetylation

The effect of temperature on the acetylation reaction is shown in Table 5. It is obvious that the extent of reaction is favoured by higher reaction temperatures.

(4) Effect of reaction time

The effect of reaction time is shown in Table 6. The highest extent of reaction is obtained by running 4 hours of acetylation under the conditions given in Table 6. If the reaction is allowed to go on further, the extent of reaction decreased.

(5) Effect of catalyst on acetylation

The highest extent of reaction is obtained when the molar ratio of aluminum chloride and acetic anhydride is 2.2 (Table 7).

3. Phosphonation of crosslinked acetopolystyrene

The phosphonation products were identified by elemental analysis, IR spectroscopy and ion exchange capacity determination.

Table 2 Effect of acetic anhydride acetylation

Ratio of weight of acetic anhydride/copolymer	Ratio of weight of $AlCl_3$ /co-polymer	Solvent	Reaction time (h)	Reaction temperature ($^{\circ}C$)	Hydroxylamine deriv. nitrogen content (%)		Extent of reaction (%)
					Calculated value	Experimental value	
1	5.78	Dichloroethane	4	60	7.9	5.98	75.7
2	5.78	Dichloroethane	4	60	7.9	7.06	89.4
3	5.78	Dichloroethane	4	60	7.9	7.13	90.3
5	5.78	Dichloroethane	4	60	7.9	6.04	76.5

Table 3 Effect of solvent on acetylation

Solvent	Weight ratio: catalyst/acetic anhydride	Weight ratio: acetic anhydride/copolym.	Reaction time (h)	Reaction temp. ($^{\circ}C$)	Hydroxylamine deriv. nitrogen content (%)		Extent of reaction (%)
					Calculated value	Experimental value	
Carbon disulfide	1	2	2	40	7.9	5.80	73.4
Dichloroethane	1	2	2	40	7.9	3.10	39.2
Nitrobenzene	1	2	2	40	7.9	3.12	39.5

Table 4 Degree of swelling of polystyrene in various solvents

Solvent	Swelling (ml/g)	Solvent	Swelling (ml/g)
Carbon disulfide	7.4	Carbon disulfide + acetic anhydride (5:2)	7.4
Dichloroethane	7.2	Dichloroethane + acetic anhydride (5:2)	6.1
Nitrobenzene	6.0	Nitrobenzene + acetic anhydride (5:2)	6.1

Table 5 Effect of temperature for acetylation

Reaction temp. (°C)	Mole ratio of AlCl ₃ /acetic anhydride	Ratio of weight: acetic anhydride/copolymer	Solvent	Reaction time (h)	Hydroxylamine deriv. nitrogen content (%)		Extent of reaction (%)
					Calculated value	Experimental value	
20	2.2	2	dichloroethane	4	7.9	6.17	78.1
40	2.2	2	dichloroethane	4	7.9	6.70	84.8
60	2.2	2	dichloroethane	4	7.9	7.06	89.4
80	2.2	2	dichloroethane	4	7.9	7.34	92.9

Table 6 Effect of reaction time for acetylation

Reaction time (h)	Mole ratio of AlCl ₃ /acetic anhydride	Weight ratio of acetic anhydride/copolymer	Solvent	Reaction temp. (°C)	Hydroxylamine deriv. nitrogen content (%)		Extent of reaction (%)
					Calculated value	Experimental value	
2	2.2	2	Dichloroethane	60	7.9	7.04	89.1
4	2.2	2	Dichloroethane	60	7.9	7.06	89.4
6	2.2	2	Dichloroethane	60	7.9	6.81	86.2
8	2.2	2	Dichloroethane	60	7.9	5.12	64.8

Table 7 Effect of catalyst on the extent of acetic anhydride ratio

Mole ratio of AlCl ₃ /acetic anhydride	Weight ratio of acetic anhydride/copolymer	Solvent	Reaction time (h)	Reaction temp. (°C)	Hydroxylamine deriv. nitrogen content (%)		Extent of reaction (%)
					Calculated value	Experimental value	
0.46	2	Dichloroethane	4	60	7.9	2.60	32.9
0.84	2	Dichloroethane	4	60	7.9	4.44	56.2
1.22	2	Dichloroethane	4	60	7.9	5.61	71.0
2.23	2	Dichloroethane	4	60	7.9	7.06	89.4

The IR spectrum of the phosphonation product show absorption peaks at 1240 cm^{-1} , 990 cm^{-1} and 920 cm^{-1} which are characteristic of the stretch vibrational absorption of the $\text{P}=\text{O}$, $\text{P}-\text{O}$ and $\text{P}-\text{C}$ bonds respectively (Fig. 2). The phosphonation reaction was further confirmed by phosphorus content determination.

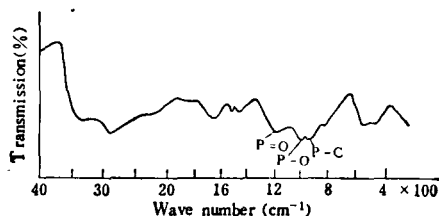
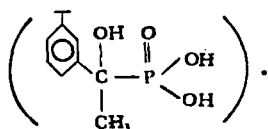


Fig. 2 Partial infrared spectrum of the crosslinked α -hydroxyl- α -methyl polystyrene phosphonic acid resin



The transformation of acetopolystyrene to polystyrene phosphonic acid is affected by several reaction conditions.

The nature of the solvating media showed to have some influence on the phosphonation reaction but to a much lesser extent as compared with the phosphonation of polymethylvinyl ketone^[22] (see Table 8). Temperature effects on phosphonation is shown in Table 9. The results indicate that the reaction of crosslinked acetopolystyrene and phosphorus trichloride show fair results at lower temperatures but the extent of reaction is increased at higher reaction temperatures. The extent of phosphonation increases slowly with reaction time and was the highest at 24 hrs; any more prolongation of the reaction time decreased the extent of transformation (Table 10). This is consistent with the phosphonation of polypropenyl aldehyde^[23], but not with polymethylvinyl ketone^[22].

Table 8 Effect of solvent on phosphonation reaction

Solvent	Exchange capacity (meq./g)		Phosphorus content (%)		Extent of reaction (%)	
	Calculated value	Experimental value	Calculated value	Experimental value	Calculated from exchange capacity	Calculated from phosphorus content
Trichloro-methane	7.95	5.39	12.33	9.17	67.9	74.4
Dichloro-ethane	7.95	5.62	12.33	9.39	66.2	76.2
Dioxane	7.95	7.10	12.33	9.72	89.3	78.8
Nitrobenzene	7.95	6.00	12.33	9.41	75.5	76.3
Phosphorous chloride	7.95	5.98	12.33	9.19	75.2	74.5

Table 9 Effect of temperature on phosphonation reaction

Reaction temp. (°C)	Exchange capacity (meq./g)		Phosphorus content (%)		Extent of reaction (%)	
	Calculated value	Experimental value	Calculated value	Experimental value	Calculated from exchange capacity	Calculated from phosphorus content
20	7.95	5.14	12.33	9.30	64.7	75.4
40	7.95	5.26	12.33	9.39	66.2	76.2
60	7.95	5.56	12.33	9.56	69.9	77.5

Table 10 Effect of time on phosphonation

Reaction time (h)	Exchange capacity (meq./g)		Phosphorus content (%)		Reaction extent (%)	
	Calculated value	Experimental value	Calculated value	Experimental value	Calculated from exchange capacity	Calculated from phosphorus content
6	7.95	5.08	12.33	9.29	63.9	75.3
12	7.95	5.26	12.33	9.39	66.2	76.2
24	7.95	5.30	12.33	9.43	67.1	76.5
48	7.95	4.50	12.33	8.12	56.6	65.9

4. Amination of the crosslinked polystyrene phosphonyl chloride

The structure of the final products were determined by elemental analysis and infrared spectroscopy.

The infrared spectra of the crosslinked polystyrene phosphonic acid resin and the polystyrene amidophosphonic acid resin are shown in Fig. 3. The stretch vibrational absorption band of the amidophosphonic acid resin appears at 990 cm^{-1} (P—O bond), a little bit lower than that of the phosphonic acid. However, a new absorption band appears at 1050 cm^{-1} which indicates the presence of a P—N (RR') group. This can be explained by the possibility that one of the hydroxy groups in the phosphonic acid resin has been replaced by the

—N $\begin{matrix} \diagup \text{C}_6\text{H}_5 \\ \diagdown \text{C}_6\text{H}_5 \end{matrix}$ group. The amination was further confirmed by nitrogen determination of

the final products. Amination is also affected by solvent, temperature and reaction time.

Solvent effects seem to have a distinct influence on the amination reaction (Table 11). Tetrahydrofuran was the best among the solvents used which might be due to the good

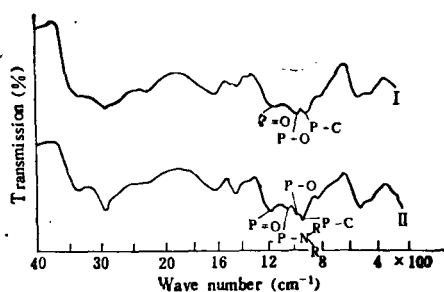
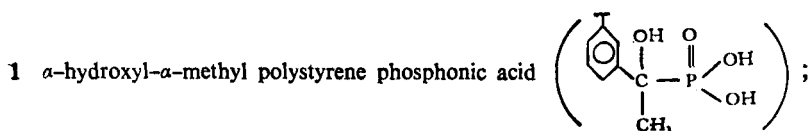


Fig. 3 Partial infrared spectra of the crosslinked polystyrene phosphonic acid and the polystyrene amidophosphonic acid resin



compatibility of THF with both polystyrene phosphonylchloride and *di-n*-butylamine. The effect of temperature on amination is shown in Table 12. The extent of reaction decreased with increasing temperature. Under the specified conditions in Table 13, the highest extent of reaction was obtained after 15 hrs and decreased with further increase of reaction time.

As shown in Table 14, the specific surface area and porosity of the macroporous copolymer decreased and apparent density and true density increased after amination. However, the specific surface area of styrene-DVB copolymer with low initial specific surface area was obviously increased after amination.

Table 11 Effect of solvent on amination reaction

Solvent	Weight ratio of <i>di-n</i> -butylamine/ substrate	Reaction time (h)	Reaction temp. (°C)	Acid value of product (meq./g)	Nitrogen content of product (%)		Extent of reaction (%)
					Calcu- lated value	Experi- mental value	
Tetrahydro- furan	10	10	40	0.49	3.74	2.75	73.5
Dioxane	10	10	40	1.66	3.74	1.75	46.8
Petroleum ether	10	10	40	2.59	3.74	1.46	39.0

Table 12 Effect of temperature on amination reaction

Temp. (°C)	Weight ratio <i>di-n</i> -butylamine/ substrate	Solvent	Reaction time (h)	Acid value of product (meq./g)	Nitrogen content of product (%)		Extent of reaction (%)
					Calcu- lated value	Experi- mental value	
20	10	Dioxane	10	1.76	3.74	1.76	47.1
40	10	Dioxane	10	1.66	3.74	1.75	46.8
60	10	Dioxane	10	1.49	3.74	1.46	39.0

Table 13 Effect of time on amination reaction

Reaction time (h)	Weight ratio of <i>di-n</i> -butylamine/ substrate	Solvent	Reaction temp. (°C)	Acid value of product (meq./g)	Nitrogen content of product (%)		Extent of reaction (%)
					Calcu- lated value	Experi- mental value	
5	10	Dioxane	40	1.66	3.74	1.66	44.4
10	10	Dioxane	40	1.66	3.74	1.75	46.8
15	10	Dioxane	40	1.34	3.74	1.85	49.5
20	10	Dioxane	40	1.63	3.74	1.76	47.1

Table 14 Change of physical structures of macroporous polystyrene resin after phosphonylating reaction

Type of resin	Specific surface (M ² /g)	Apparent density (g/ml)	True density (g/ml)	Porosity (ml/g)	Pore size (Å)
Cop I×20 ₁₀₀	99.89	0.4206	1.1292	1.4920	299
PAM I×20 ₁₀₀	52.69	0.5253	1.1549	1.0378	394
Cop I×10 ₁₀₀	68.92	0.5601	1.0849	0.8636	251
PAM I×10 ₁₀₀	32.33	0.6083	1.1576	0.7801	483
Cop I×10 ₁₅₀	8.64	0.3564	1.1188	1.9120	4426
PAM I×10 ₁₅₀	18.60	0.3425	1.3524	2.1803	2344
Cop I×10 ₅₀	0.38	0.8643	1.0748	0.2266	~0
PAM I×10 ₅₀	7.42	0.7395	—	—	—
Cop I×5 ₁₀₀	47.84	0.5947	1.0845	0.7594	317
PAM I×5 ₁₀₀	27.62	0.6770	1.1667	0.6200	449
Cop K×6 ₁₀₀	60.79	0.4812	0.9931	0.806	267
Carb K×6 ₁₀₀	51.30	0.6044	1.1108	0.571	152
PAM K×6 ₁₀₀	17.13	0.9635	1.2469	0.320	232

Where Cop is copolymer of styrene-divinylbenzene.
 Carb is crosslinked acetopolystyrene.
 PAM is phosphonyl amide resin.

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