

Synthesis and Crosslinking Polymerization of some Vinyl-Benzyl-*N*-Quaternary Salts

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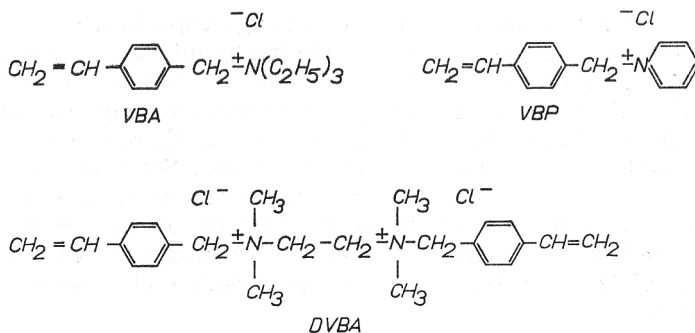
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The reaction of 4-chloromethylstyrene with triethylamine, pyridine, or tetramethylethylenediamine gave 76% 4-vinylbenzyl-triethylammonium chloride (VBA) 72% *N*-(4-vinylbenzyl)pyridinium chloride (VBP), and 62% *N,N'*-di(4-vinylbenzyl)-*N,N,N',N'*-tetramethylethylenediammonium dichloride (DVBA), respectively.

The polymerization reactions of VBA and VBP with crosslinking agents (DVBA, divinylbenzene) were performed in aqueous solutions (for DVBA) or water-dioxane solutions (for divinylbenzene) using $K_2S_2O_8$ as initiator. The anion exchange capacities of the resins obtained were determined.

The preparation and study of cationic polyelectrolytes has been an area of increased interest in recent years^{1,2}. These polymers are normally prepared either by the quaternization of preformed polymers or by the polymerization of charged vinyl monomers. In addition, when a difunctional monomer is present in the latter systems, intermolecular reactions give rise to crosslinking and formation of strongly basic anionic exchange network resins³. The crosslinking reaction can be accomplished by various means and a typical anion exchange resin is usually made by chloromethylation and subsequent amination of a styrene-divinylbenzene copolymer⁴.

In this communication we report the synthesis, crosslinking polymerization and some properties of anionic exchange resins obtained from 4-vinylbenzyl-triethylammonium chloride (VBA) or *N*-(4-vinylbenzyl)pyridinium chloride (VBP) as monomers and *N,N'*-di(4-vinylbenzyl)-*N,N,N',N'*-tetramethylethylenediammonium dichloride (DVBA) or divinylbenzene (DVB) as crosslinking agents.



Although mention has been made, particularly in the patent literature, of the preparation and polymerization of vinylbenzylquaternaryammonium chlorides^{5,6}, these monomers do not appear to have been well characterized. Besides, the compound DVBA, as far as we know, is not synthesized before. The monomers used VBA, VBP and DVBA, were prepared as a crystalline solids by reaction of 4-chloromethylstyrene and corresponding amines and were characterized by elemental analysis and by NMR spectroscopy. The NMR spectra were conducted in D₂O and were compared with spectra of reported imidazolium salts⁷. The prepared salts readily polymerized and copolymerized in the presence of DVBA or DVB forming crosslinked polymers with appreciable anion exchange capacity. The results of the polymerization reactions and some polymer properties are summarized in Table I. The polymerization reactions were performed in aqueous solution using potassium persulfate as initiator at 50 °C. When DVB was used as a crosslinking agent, the polymerization was carried out in a water-dioxane mixture. The compositions of the copolymers were estimated by nitrogen content determined by Kjeldahl's method.

TABLE I

Crosslinking Polymerization Conditions and Polymer Properties of Vinyl-benzyl-N-quaternary salts

Exp. No.	Polymerization ^a			Polymer properties		
	Monomer-1 %	Monomer-2 %	Yield %	N/% Found	Exchang capacity mg-equiv./g of resin	
					Calc'd ^b	Found ^c
1.	VBA, 90.0	DVBA, 10.0	95.0	5.57	3.99	3.82
2.	VBA, 80.0	DVBA, 20.0	92.5	5.61	4.01	3.88
3.	VBA, 50.0	DVBA, 50.0	88.5	5.90	4.21	3.82
4.	VBA, 95.0	DVB, 5.0	65.6	5.01	3.58	3.42
5.	VBA, 80.0	DVB, 20.0	58.8	3.82	2.73	2.21
6.	VBP, 90.0	DVBA, 10.0	88.0	6.00	4.28	4.14
7.	VBP, 50.0	DVBA, 50.0	89.0	6.27	4.48	4.23
8.	VBP, 90.0	DVB, 10.0	72.0	5.55	3.96	3.77

^a Polymerization was conducted in water at 50 °C in the presence of 1% K₂S₂O₈.

^b Estimated from the composition of the copolymer.

^c Determined through displacement of chloride ion by nitrate in neutral solutions.

The experimental determination of exchange capacities of the resins obtained involved the displacement of chloride ion by nitrate in neutral solutions⁸ and the calculated values were estimated from the nitrogen content of the copolymer. The table gives the nitrogen content and exchange capacities of the dry chloride forms of the resins and it is evident that there is a good agreement between calculated and found exchange capacities. Some differences appear when very high concentrations of crosslinking agent were used probably due to high crosslinking density of the resin obtained. As expected, the higher exchange capacities were obtained when DVBA was used as a crosslinking agent instead of DVB, as the former resins possess higher quaternary group concentrations.

EXPERIMENTAL

All the solvents and chemicals were purified by conventional methods. DVB, pract. grade, as a mixture of isomers (~50%) in ethyl vinylbenzene. 4-Chloromethylstyrene was prepared as described earlier⁹. The infrared spectra were taken on Perkin-Elmer Model 137 spectrophotometer in KBr pellets. The NMR measurements were done with an A-60 Varian instrument in D₂O with DSS as the internal standard.

4-Vinylbenzyltriethylammonium chloride (VBA)

A cold mixture of 7.63 g (0.05 mol) of freshly distilled 4-chloromethylstyrene and 6.06 g (0.06 mol) of anhydrous triethylamine was left overnight at 0 °C with intermittent shaking. The formed solid crystallized from iso-amyl alcohol yielding 9.64 g (76.0%) long white prismatic crystals. NMR spectrum centered at δ 1.49 (6H, ethyl CH₃), δ 3.22 (4H, ethyl CH₂), δ 4.42 (2H, benzyl CH₂), δ 5.57–6.02 (2H, vinyl CH₂), δ 6.86 (H, vinylidene CH), δ , 7.59 (4H, ring protons).

Anal. C₁₅H₂₄ClN (253.18) calc'd.: C 70.98; H 9.58; Cl 13.97; N 5.52%
found: C 70.71; H 9.41; Cl 13.82; N 5.28%

N-(4-Vinylbenzyl)pyridinium chloride (VBP)

The compound was obtained in the same way as described above for VBA, using pyridine and 4-chloromethylstyrene, in 72.0% yield. NMR spectrum centered at δ 5.56–6.0 (2H, vinyl CH₂), δ 6.18 (2H, benzyl CH₂), δ 6.76 (H, vinylidene CH), δ 7.71 (4H, benzene ring protons), δ 8.21–9.45 (pyridine ring protons).

Anal. C₁₄H₁₄ClN (231.72) calc'd.: C 72.56; H 6.09; Cl 15.30; N 6.04%
found: C 72.34; H 5.96; Cl 15.32; N 6.16%

N,N'-Di(4-vinylbenzyl)-N,N,N',N'-tetramethylethylenediammonium dichloride (DVBA)

The compound was prepared from 4-chloromethylstyrene and tetramethylethylenediamine in a similar way as described above in 62% yield.

NMR spectrum centered at δ 3.38 (12H, N—CH₃), δ 4.33 (4H, N—CH₂), δ 4.84 (4H, benzyl CH₂), δ 5.52 (2H, vinyl, trans to phenyl, dd, J_{cis} 10.5 Hz, J_{gem} 1.5 Hz), δ 5.99 (2H, vinyl, cis to phenyl, dd, J_{trans} 17.0 Hz, J_{gem} 1.5 Hz), δ 6.86 (2H, vinylidene, dd, J_{cis} 10.5 Hz, J_{trans} 17.0 Hz), δ 7.65 (8H, ring protons).

Anal. C₂₄H₃₄Cl₂N₂ (421.46) calc'd.: C 68.39; H 8.13; Cl 16.82; N 6.65%
found: C 68.07; H 8.00; Cl 16.35; N 6.88%

Polymerization procedures

A mixture of 10 ml of water, 0.02 g K₂S₂O₈ and 2 g of the monomers was placed into a double-jacketed 30 ml glass reactor. The reactor was connected to a thermostat and under a constant stream of nitrogen was kept for 24 hours at 50 °C under vigorous stirring with a magnetic stirrer. The swollen polymer was filtered off, washed with water and dried under vacuum. When divinylbenzene was used as a comonomer, the polymerization was conducted in a water-dioxane (1 : 2) solution.

Exchange capacities⁸

The polymers were dried to constant weight in a presence of sodium hydroxide pellets and phosphoric oxide in vacuo. About 0.2 g of dried resin was shaken overnight with 50 ml of 5 M sodium nitrate solution, and the displaced chloride ion was determined gravimetrically.

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SAŽETAK

Umreženi polimeri na osnovi vinil-benzil-*N*-kvarternih soli

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Opisana je sinteza 4-vinilbenzil-trietil-amonijeva klorida (VBA), 4-vinilbenzil-piridinijeva klorida (VBP) i 4,4'-di(vinil-benzil)-tetrametil-etilendiamonijeva klorida (DVBA). Polimerizacijom monomera (VBA odnosno VBP) u prisutnosti DVBA ili divinilbenzena u vodenom mediju uz $K_2S_2O_8$ kao inicijator dobiveni su umreženi polimeri sa svojstvima anionskih izmjenjivača. Istražen je utjecaj sastava polimera na veličinu izmjene NO_3^- -iona.

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