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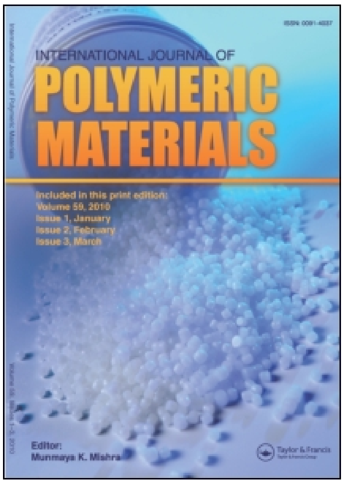

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Chemical Modification of Poly(Vinyl Chloride) with Ethylene Glycol and Its Application in Ion-Chromatography

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Poly(vinyl chloride) (PVC) has been chemically modified through crosslinking with different molar ratios of sodium ethylene glycoxide in ethylene glycol. The crosslinked PVC was used for coating of silica gel 60 particles and the obtained products were impregnated with tetramethylammonium hydroxide (TMAH). The crosslinking reaction as well as the insertion of TMAH were followed up and quantitatively determined with the aid of FT-IR spectroscopic and elemental analyses. The obtained materials were roughly tested for ion chromatographic separation of different ions. Retention time (t_R) was determined for lithium, magnesium, strontium, and calcium cations whereas chloride, nitrate, and sulfate were selected as representatives for anions.

Keywords: poly(vinyl chloride) (PVC), functionalization of polymers, modification, crosslinking, ion chromatography

INTRODUCTION

Chemical modification of polymers is known as a versatile route for production of functionalized polymers that are useful in many applications. This can be achieved through introduction of functional groups [1,2] or replacement of a supported group with another one through chemical reaction [3,4] that may lead to crosslinking [1]. Different

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functionalized polymers were reported for waste water treatment and metal chelating applications either through covalent attachment of the chelating moiety to the polymer support [5,6] or through physical blending of the polymer matrix with the chelating compound [7].

Crosslinking of PVC by use of polyethylene glycol as a catalyst or activator [8] has been reported. Recently, PVC has been modified into polymer-supported alcohol through a sequential chemical modification including the reaction with polyethylene glycol with no detectable crosslinking [9,10].

Also, it has been reported that quaternary ammonium salts can be used as "nonselective" ion-exchangers [11]. Hence, one can support different quaternary ammonium salts on the polymer matrix through chemical bonding [12] or physical mixing. On the other hand, modified silica has been used as a stationary phase in ion chromatography through different modification techniques [13–15] to enhance the separation efficiency [16,17].

Currently, PVC has been crosslinked with ethylene glycol through the formation of ethylenedioxy bridges for coating of silica gel particles. Tetramethylammonium hydroxide (TMAH) was inserted into the modified PVC through physical blending. The obtained PVC-based matrices have been roughly tested as stationary phase for the ion chromatographic separation of different cations and anions. Chemical modification of PVC was followed up through elemental and FT-IR spectroscopic analyses.

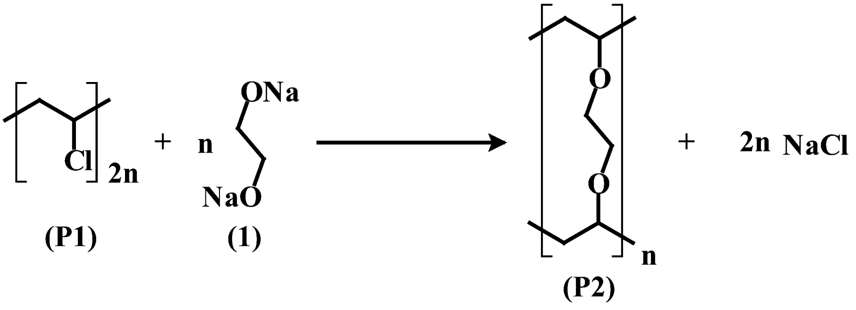
RESULTS AND DISCUSSION

Chemical Modification of PVC

The previously reported techniques for crosslinking of PVC [9,10] may have some drawbacks arising from the multistep nature, in addition to the accompanying cost problems. Moreover, such crosslinks may be flexible to an extent that may lead to high swelling ability of the obtained resin. Such problems may be minimized by using short and/or rigid crosslinks and an ion-exchanging functionality that is easy to be supported by the polymer matrix.

Hence, different crosslinked matrices of PVC (**P2a–e**) were prepared by reaction of the noncrosslinked PVC (**P1**) with sodium ethylene glycoxide (**1**) in ethylene glycol as represented in Equation 1.

Such crosslinks are short enough to be more rigid relative to other long crosslinks used before [8]. As a result, the obtained polymeric matrix has lower swelling ability and this will, more or less, keep the free volume of the polymer matrix unchanged even with repeated

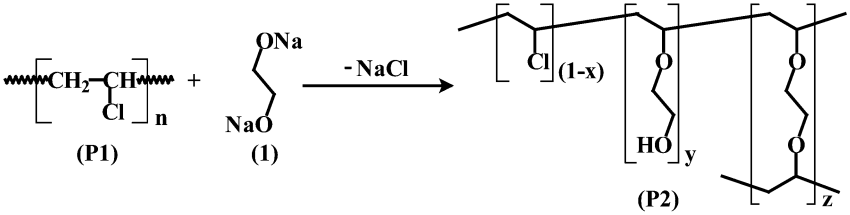


EQUATION 1 Crosslinking of PVC (**P1**) with sodium ethylene glycoxide.

swelling process. Such free volume will contain TMAH that will be inserted through immersion of the polymer matrix in an aqueous solution of TMAH. Consequently, the entrapped TMAH in the polymeric matrix will be difficult to be leached during the repeated exchange process.

The obtained products are of different crosslink density according to the theoretically calculated molar ratio of sodium ethylene glycoxide used for crosslinking, namely 10, 20, 25, 50, and 100% in addition to the blank sample without crosslinking. In addition to the possibility for reaction of PVC (**P1**) with ethylene glycol from both sides leading to crosslinking, there is a possibility for PVC (**P1**) to react only with one side of sodium ethylene glycoxide forming hydroxyethoxy functionality that will be supported to the PVC matrix as represented in Scheme 1.

The formation of ethylenedioxy crosslinks and the hydroxyethoxy pendant functionalities may be followed up by using FT-IR



where: n = number of repeating units
x = total mole fraction of the reacted units = y + z
y = mole fraction of the reacted units into pendant hydroxyethoxy units
z = mole fraction of the crosslinked units via ethylenedioxy bonding
1-x = mole fraction of the unreacted PVC units

SCHEME 1 Reaction of PVC (**P1**) with sodium ethylene glycoxide.

spectroscopy while elemental analysis was used to quantitatively determine the fraction of vinyl chloride units involved in crosslinking and the pendant hydroxyethoxy functionality according the mole fraction concept [1]. The crosslinking reaction of PVC (**P1**) with sodium ethylene glycoxide was conducted with the exclusion of oxygen to inhibit the possible dehydrohalogenation reaction of **P1** leading to formation of unsaturation centers along PVC molecular chains. Such unsaturation has been detected as small and weak absorption at $\nu = 1675\ \text{cm}^{-1}$. This absorption was detected only in the 10% crosslinked PVC sample (**P2a**). Also, there is no significant correlation between the data of elemental analysis and the presence of significant unsaturation. The extent of unsaturation can be neglected on this basis.

Table 1 shows the elemental analysis data and the percentage of crosslinking as well as the pendant hydroxyethoxy functionalities for the products **P2a–e** obtained from the reaction of PVC (**P1**) with sodium ethylene glycoxide. From these results, one can conclude that the utilized sodium ethylene glycoxide has not been quantitatively reacted with PVC as the percentage of crosslinks calculated on the basis of the added amount of sodium ethylene glycoxide was different from that calculated from the elemental analysis data. Also, the elemental analysis calculations proved that the reacted sodium ethylene glycoxide was almost consumed to form crosslinks only. This conclusion has been supported by the negative percentage of the hydroxyethoxy functionality based on the calculation according to the mole fraction concept.

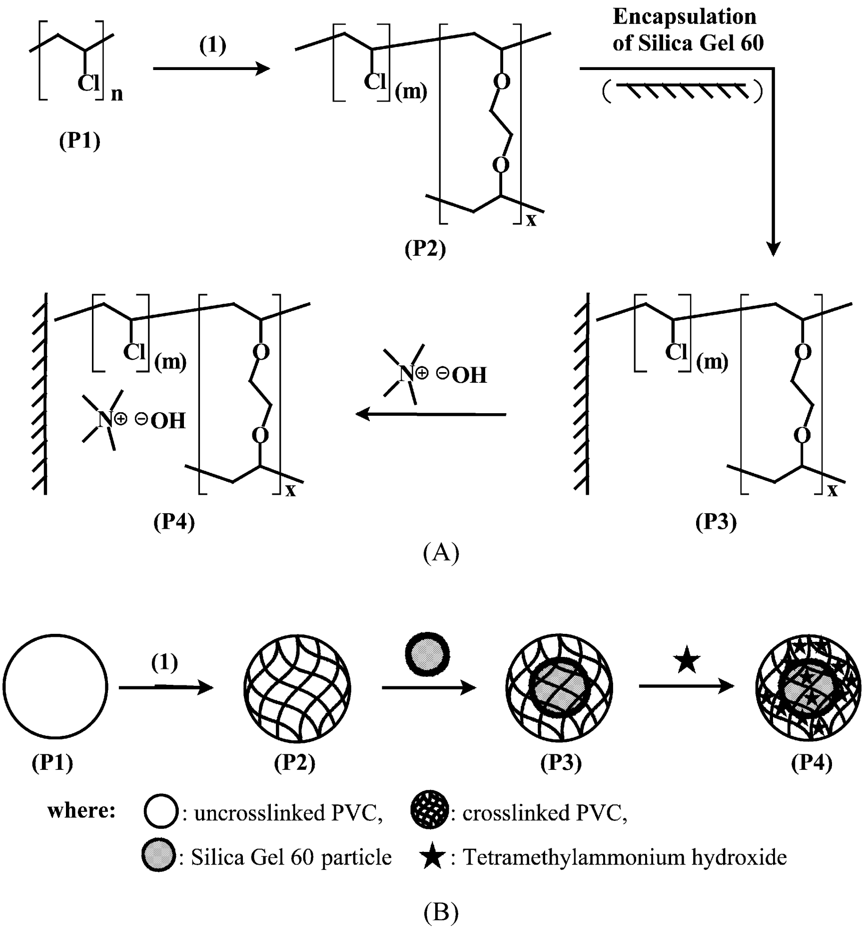
On the other hand, FT-IR spectroscopic analysis of **P2a–e** showed marked absorption at $\nu = 1096\ \text{cm}^{-1}$ corresponding to C–O–C ether bonding for all samples, except the blank sample that has no

TABLE 1 Elemental Analysis Data and the Percentage of Crosslinking for the Products **P2a–e**

	Elemental analysis data		Percentage of crosslinking	
Sample no.	C (%)	H (%)	Theoretical*	Actual**
P1	38.41	4.82	0	0
P2a	39.76	5.52	10	6.0
P2b	40.33	5.80	20	8.5
P2c	41.07	6.20	25	11.7
P2d	45.89	8.67	50	32.2
P2e	53.95	12.78	100	64.9

*Based on the added mole fraction of sodium ethylene glycoxide.

**Based on the mole fraction calculations from the elemental analysis data.



SCHEME 2 Preparation of silica gel particles encapsulated in crosslinked PVC and loaded with tetramethylammonium hydroxide (TMAH).

crosslinking, although no absorption for the alcoholic functionality was present. This supports in another way the findings from the elemental analysis calculations.

After silica gel particles have been encapsulated in crosslinked PVC, the obtained particles (**P3a–e**) were immersed in a solution of TMAH to enhance the ion exchange capacity. FT-IR spectroscopic analysis proved the insertion of TMAH into the polymer matrix. The final products (**P4a–e**) showed absorption at $\nu = 1600\ \mathrm{cm}^{-1}$ and $2350\ \mathrm{cm}^{-1}$ corresponding to the quaternary ammonium nitrogen. The intensity of such absorption increases relatively with the crosslinking density. This means that the higher the crosslinking density, the lower the swelling ability and consequently the lower the leaching ability of TMAH from the matrix and the more effective in ion exchanging applications. Preparation of PVC-coated silica gel and impregnated with TMAH is outlined in Scheme 2.

Chromatographic Separation

The prepared PVC-based ion-exchange resins have been roughly tested toward the ability for ion-chromatographic separation of different ions. Li^+, Mg^{2+}, Sr^{2+}, and Ca^{2+} were selected as representative cations whereas Cl^-, NO_3^-, and SO_4^{2-} were used as representative anions. Retention time (**t_R**) for cations was determined by using buffered solution eluent at $pH = 6.6$, and **t_R** values were 11.633, 22.412, 23.277, and 27.086 min for Li^+, Mg^{2+}, Sr^{2+}, and Ca^{2+} cations, respectively.

On the other hand, mixed solution of 0.05 mM EDTA-2Na and 2 nM HNO_3 was used as an eluent at $pH = 4$ for the determination of **t_R** values for $MgCl_2$, $Mg(NO_3)_2$, and $MgSO_4$. It was noticed that **t_R** was constant for Mg^{2+} at 9.70 min whereas it was 4.24, 4.75, and 4.80 min for Cl^-, NO_3^-, and SO_4^{2-} anions. On increasing pH up to 5 by addition of NaOH, **t_R** raised up to 19.2 min for Mg^{2+} and up to 8.9 min for SO_4^{2-} anions. The dependence of **t_R** for anions on pH may indicate the presence of two possible active exchange positions for both cations and anions and this means that the investigated PVC-based ion exchange resins have dual activity toward separation of cations and anions.

EXPERIMENTAL

Materials

PVC was used as white powder of average molecular weight 10000 and supplied by Fluka. All reagents and solvents were supplied by Aldrich and used as supplied without further purification. Milli Q deionized water was used for preparation of solutions.

FT-IR spectroscopic measurements have been performed using Perkin Elmer FT-IR spectrophotometer whereas elemental analysis was performed at the Micro-analytical Unit, King Abdulaziz University, Saudi Arabia.

The Waters ion chromatography system consists of a Pump (Waters 1515), Pulse Dampener, Conductivity Detector (Waters 432), and Injection Valve (Rhyodyne) coupled with 20 μL Loop. These components are controlled by a microprocessor-driven System Controller. Ion Chromatograph was used to roughly test the ability of the ion exchange resins to be used for ion separation.

Crosslinking of PVC with Ethylene Glycol

To an excess of dried amount of ethylene glycol, 36.8 mg of clean sodium metal was added cautiously to prepare sodium ethylene glycoxide (**1**) solution in ethylene glycol. The obtained solution was added to a solution of 1 g PVC (**P1**) in 100 ml THF under stirring for 2–3 h in inert atmosphere and in presence of traces of potassium iodide. The crosslinked PVC (**P2a**) was then filtered off and washed successively with water, acetone, and ether and finally dried overnight at 50°C and subjected for analysis by elemental analysis and IR-spectroscopy. This procedure has been repeated to prepare different samples of crosslinked PVC (**P2b–e**) by using different amounts of sodium ethylene glycoxide as shown in Table 2.

Preparation of PVC-Based Ion Exchange Resin

Silica gel particles with grain size <0.063 mm (5 g) were heated at 150°C for 2 h and left to cool in desiccators. A known amount of crosslinked PVC (**P2a–e**) was added to 25 ml of THF and stirred until equilibrium swelling. Dried silica gel particles were then added to the crosslinked PVC (**P2a–e**); stirred for about 30 min and filtered off. The mechanical coating of silica gel particles with crosslinked PVC was completed by repeating this process and evaporation of the utilized solvent (THF) by using a Rotating Evaporator. The dried PVC-coated silica gel particles (**P3a–e**) were then sieved through a 400 mesh standard sieve and treated with aqueous solution of 2% tetramethylammonium hydroxide (TMAH) in 40/60 of water/acetonitrile mixture. The obtained resins (**P4a–e**) were washed with

TABLE 2 Amounts of Ethylene Glycol and Sodium Metal used in the Crosslinking Reaction of 1 g PVC

Sample no.	Wt. of ethylene glycol (mg)	Wt. of sodium metal (mg)	Percentage of glycoxide (%)
a	49.5	36.8	10
b	99.0	73.6	20
c	123.8	92.0	25
d	247.5	184.0	50
e	495.0	368.0	100

distilled water, dried overnight at 50°C, and subjected to FT-IR spectroscopic analysis.

Chromatographic Separation

Ion separation was achieved and Retention time ($\mathbf{t_R}$) of the investigated ions was determined parallel to that previously reported [18] by using Waters LCI instrument in its ion chromatography configuration with a separation column of 10 cm length and 4 mm diameter. The separation column was manually packed with the 25% theoretically crosslinked PVC product (**P4c**). Buffered solution at $pH = 6.6$ was prepared by mixing solutions of sodium gluconate, boric acid, and sodium tetraborate according to the operation manual for cation separation. Also, buffered solution at $pH = 4$ was used for anions and prepared by mixing 0.05 mM ethylenediamine tetraacetic acid disodium salt (EDTA-2Na) with 2 mM nitric acid (HNO_3). Li^+, Mg^{2+}, Sr^{2+}, and Ca^{2+} were selected as representative cations whereas Cl^-, NO_3^-, and SO_4^{2-} were selected for anions.

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