Functionalization at the Double-Bond Region of Jojoba Oil. 7. Chemical Binding of Jojoba Liquid Wax to Polystyrene Resins

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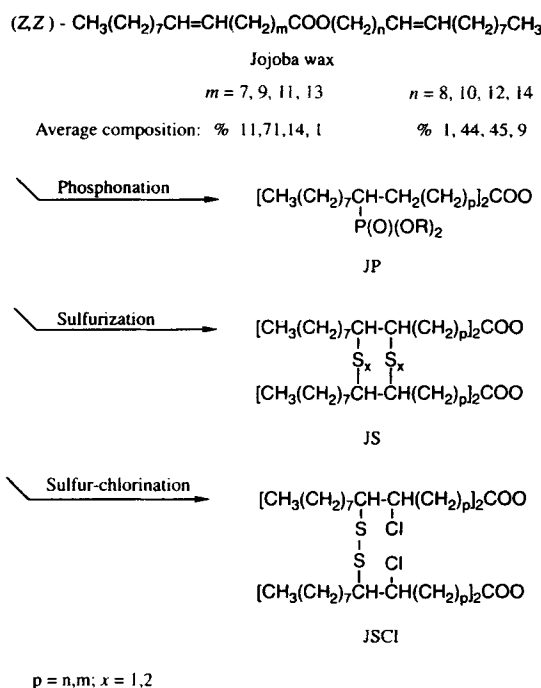Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

ABSTRACT: Jojoba wax was chemically bonded to a polystyrene matrix *via* a stable C-C covalent bond. This was achieved by binding allyl-brominated jojoba derivatives to lithiated crosslinked polystyrene–2% divinylbenzene or XAD-4 polymeric beads *via* a nucleophilic substitution reaction. The double-bond regions in the jojoba wax were preserved. A side reaction that accompanied the nucleophilic substitution was HBr elimination, which produced diene and triene systems in the bound jojoba. Phosphonation and sulfur chlorination at the double bonds of the jojoba wax, bonded to the polystyrene matrix, were also performed. *JAOCS 73*, 1075–1081 (1996).

KEY WORDS: Allyl-brominated jojoba derivative, jojoba wax, polystyrene lithiation, sulfur chlorination.

Jojoba (*Simmondsia chinensis*), a shrub that is native to the Sonoran Desert, is currently being cultivated as an industrial crop in semiarid lands (1). Jojoba nuts contain about 50% (w/w) of a unique liquid wax that differs from common vegetable oils and animal fats in that it is composed mainly of linear wax esters (97%). More than 80% of the esters present are a combination of C_{20} and C_{22} monounsaturated alcohols and acids (I) (Scheme 1).

Although the main application of jojoba wax is currently in cosmetics (2), jojoba wax and its derivatives have many potential commercial uses in a variety of fields. In particular, phosphonated and sulfurized jojoba wax derivatives (Scheme 1) have been shown to possess good extraction properties toward metal ions, such as actinides and mercury, from acidic solutions (3–8). However, the application of these derivatives is limited to highly acidic media, due to difficulties in phase separation at pH values higher than 1.

Previous attempts to improve the efficiency of liquid extractants, which are more versatile than their solid counterparts by elimination of entrainment losses, were based on the technique of impregnating solid resins with extractant in sol-

(Z,Z) - $CH_3(CH_2)_7CH=CH(CH_2)_mCOO(CH_2)_nCH=CH(CH_2)_7CH_3$

Jojoba wax

$m = 7, 9, 11, 13$ $n = 8, 10, 12, 14$

Average composition: % 11,71,14, 1   % 1, 44, 45, 9

Phosphonation →

$[CH_3(CH_2)_7CH-CH_2(CH_2)_p]_2COO$
$\qquad\qquad | $
$\qquad\quad P(O)(OR)_2$

JP

Sulfurization →

$[CH_3(CH_2)_7CH-CH(CH_2)_p]_2COO$
$\qquad\qquad | \quad |$
$\qquad\qquad S_x \; S_x$
$[CH_3(CH_2)_7CH-CH(CH_2)_p]_2COO$

JS

Sulfur-chlorination →

$[CH_3(CH_2)_7CH-CH(CH_2)_p]_2COO$
$\qquad\qquad | \quad |$
$\qquad\qquad S \quad Cl$
$\qquad\qquad |$
$\qquad\qquad S \quad Cl$
$\qquad\qquad | \quad |$
$[CH_3(CH_2)_7CH-CH(CH_2)_p]_2COO$

JSCl

$p = n,m; x = 1,2$

SCHEME 1

vent (wet process) or without it. For example, commercially available polymer supports, such as XAD-2, XAD-4, and XAD-8 (Rohm and Haas Company, Philadelphia, PA), impregnated with a sulfurized jojoba wax derivative, have been used for extraction of mercury ions from acidic media (9). The use of impregnated resins, containing an absorbed liquid extractant, in solvent extraction for metal ions has a number of advantages, but the problems of the loss of expensive extractants and the contamination of aqueous solutions have yet to be solved (10). To overcome the disadvantages inherent in these technologies, the liquid extractant may be chemically bound to a rigid polymer support in the form of beads. The polymer networks to which the extractants are covalently bonded as ion-exchange ligands can be used in a packed-column technology for the removal of metal ions from aqueous solutions.

Such solid–liquid extractions may also suffer from disadvantages, such as the higher initial cost associated with the synthesis of the polymer, lower rates of extraction as a result of diffusional limitations, and possible changes in the extraction properties of extractant (selectivity, capacity). Despite these limitations, polymeric systems enjoy some important advantages: extractant loss through solubility and entrainment is clearly eliminated; the polymer support serves as the diluent, so that no additional solvent is required; and the system is readily adaptable to long-term continuous operation, which is most appropriate for metal ion recovery from dilute solutions (11).

In addition to their use as ion exchangers, functionalized polystyrene resins are currently used as supports in solid-phase synthesis, enzyme immobilization, chromatography, and catalysis, and as reagents or protecting groups in organic syntheses (12). Although there is a wide range of chelating and coordinating polymers of organic or inorganic origin, research efforts are being directed to the development of new synthetic ion-exchange resins.

The polystyrene matrix was chosen as the backbone for our extractant because it is commercially available or can be easily synthesized with a wide range of matrix rigidity or macroporosity (13) and because it is chemically resistant to degradation under the conditions of our applications. In the present investigation, the chemical binding of jojoba wax to polystyrene beads via stable C-C covalent bonds was studied.

EXPERIMENTAL PROCEDURES

Materials. Crude jojoba wax was used in all experiments without purification [iodine value (Wijs), 84; acid number, 2.7; saponification number, 93]. All solvents were obtained from Aldrich, (Milwaukee, WI). AR-grade cyclohexane was dried over CaH_2 and nitrobenzene over $CaCl_2$. All other solvents were AR grade and used without further purification. Styrene and divinylbenzene (DVB) were supplied by Aldrich and were washed free of inhibitor with 1 N NaOH and water, followed by drying over $MgSO_4$ and distillation under reduced pressure. Benzoyl peroxide (BDH), reagent-grade, was recrystallized from a mixture of chloroform/methanol. All other chemicals (supplied by Aldrich) were reagent-grade and were used without further purification. N,N,N,N-tetramethylethylenediamine (TMEDA) was supplied by Merck (Darmstadt, Germany). The macroreticular resin XAD-4 (BDH) was washed clean of surface impurities before use (14).

Elemental analysis. Elemental analyses, based on ASTM methods, were performed in the Analytical Laboratory of the Institutes for Applied Research, Ben-Gurion University of the Negev, Israel.

Surface area. The N_2 adsorption isotherms of the polymer samples were performed in a standard, high-vacuum, volumetric adsorption system (Pyrex, Corning Glass Works, New York, NY). The system was comprised of an oil-diffusion pump backed by a rotary van pump. Pressure was measured with a 100-kPa absolute-pressure transducer (Validyne Co.,

Validyne Engineering Corp., Northridge, CA). The sample weights were 1–3 g. The surface area of the polymers, in m^2/g, was evaluated from the Brunaur-Emmet-Teller isotherm.

Allylic bromination of jojoba wax. Allylic bromination of crude jojoba wax (I) was carried out with N-bromosuccinimide (NBS) in CCl_4, as previously reported (15).

Styrene–2% DVB copolymer. Styrene was copolymerized with 2% DVB by suspension polymerization (16,17). Synthetic polymer beads were sieved before use, and only the 0.5-mm fraction was used in the experiments. The copolymer, designated PS in the tables, was subjected to steam distillation to remove residual monomers. To remove surface impurities, the resin was brought into contact with each of the following solutions in the following order for 1 h at 60–80°C: 1 N NaOH, 1 N HCl, 2 N NaOH/dioxane (1:2), 2 N HCl/dioxane (1:2), water, and dimethylformamide. Thereafter, the resin was washed at room temperature with the following solutions: 2 N HCl in methanol, water, methanol, methanol/dichloro-methane (1:3), and methanol/dichloromethane (1:10). Finally the resin was dried under vacuum at 70°C (14). The iodine number of the copolymer was 2.0 (mg I/100 mg).

Lithiation. All lithiation reactions and the reactions involving lithiated resin intermediates were carried out under an inert atmosphere (Ar) in a specially designed flask, fitted with a coarse-porosity, fritted-glass filter. This one-piece reaction vessel facilitated the addition or removal of solvents and excess reagents or by-products and the washing of the resin without transfer to other reactors without exposure to the atmosphere.

Direct lithiation of polystyrene resins. Fifty mL of 2.5 M n-BuLi in hexane were added with stirring to washed styrene–2% DVB copolymer (10 g, 95 meq) or XAD-4 (10 g), suspended in 60 mL of dry cyclohexane containing 9.3 g (78 mmol) of TMEDA under an Ar blanket. The reaction mixture gradually turned brown during 5 h of heating at 65°C. After the liquid phase was removed, the resin was rinsed twice with dry cyclohexane to yield the lithiated resin. The lithiation reaction was quenched by the addition of a slurry of dry ice in tetrahydrofuran (THF). After filtration, the polymer was washed with THF, methanol, THF/water (2:1), water, THF/water (2:1), THF, and finally methanol. The carboxylated polymers then were dried under reduced pressure at 60°C, and the products were characterized in terms of the weak cation-exchange capacity of -COOH groups.

Binding of allyl bromide derivatives of jojoba wax (J-xBr) to lithiated resins. One of the following allyl brominated jojoba wax derivatives, dissolved in 10 mL of dry cyclohexane (J-1Br, 10.7 g, 16 mmol; J-2Br, 12 g, 16 mmol; or J-4Br, 15 g, 16.4 mmol) was added to the lithiated resin, prepared as described above. The suspension was stirred for 2 h at 60°C, and then an additional 16 h at room temperature. The resin was collected on a filter and washed with cyclohexane, toluene, dioxane, dioxane/water (1:1), water, dioxane/water (1:1), dioxane, and methanol. The resin then was extracted in a Soxhlet apparatus with CCl_4, filtered, washed with methanol and acetone, and dried under vacuum at 60°C.

Reactions of the double bond in jojoba wax bonded to the

polymer matrix. Bromination was performed as follows: to 2 g of the J-2 or J-4 polymers (see tables for explanation of the product number), preswollen in CCl_4, 0.23 g (1.44 mmol) or 0.14 g (0.88 mmol) of Br_2 in CCl_4 was added dropwise over a period of 1 h. After the reaction mixture had been maintained for a further 2 h at room temperature, the resin was filtered off, washed with CCl_4, methanol, saturated $NaHSO_3$ solution, water and acetone, and dried under vacuum at 60°C.

Phosphonation was performed as follows: 5 g of polymer matrix J-2 or J-4, containing 24 or 13% (w/w) of bonded jojoba wax, was allowed to swell in a reaction mixture containing 5 g (36 mmol) or 2.5 g (18 mmol) of diethylphosphite, 0.25 g (1.3 mmol) of *tert*-butyl perbenzoate, and 20 mL of toluene for 4 h at room temperature. After addition of a further 0.25 g of initiator, the reaction mixture was agitated at 110°C under an Ar blanket for 6 h. The reaction was monitored by sampling and analyzing for phosphite content by the addition of 0.1 N NaOH and back titration with 0.1 N HCl. Thereafter, the suspension was filtered off, and the resin was washed with toluene, methanol, 10% $NaHCO_3$ (×4), water (until the washing water was neutral), methanol, and acetone. After drying under vacuum, the resin was weighed, and the composition was determined by elemental analysis.

Sulfur halogenation was carried out as follows: 4 g of polymer matrix J-4 or J-2 was preswollen in 10 mL of nitrobenzene for several hours. A solution of 0.2–0.4 mL S_2Cl_2 in 5 mL nitrobenzene was added with mechanical stirring to the suspension. After 24 h at room temperature, the polymer was filtered off, washed with nitrobenzene, toluene, THF, acetone, 5% $NaHCO_3$, water, ethanol, and acetone, and dried at 40°C under vacuum for two days.
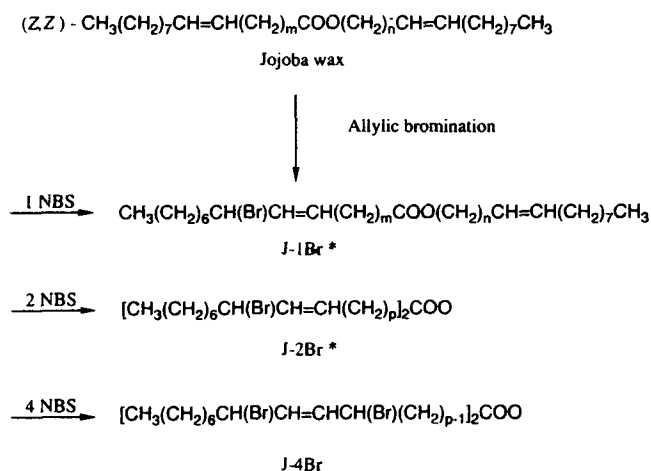
RESULTS AND DISCUSSION

Two types of cross-linked polystyrene beads—solvent-swellable polystyrene–2% DVB and macroreticular resin XAD-4—were functionalized by direct lithiation (14). Allyl-brominated derivatives of jojoba wax (J-xBr) were reacted with lithiated polystyrene beads to create a product in which the double-bond region in the bound jojoba wax was preserved. Further modification of the double bonds by phosphonation or sulfur chlorination produced matrix-bound ligands with an extraction ability equivalent to that of liquid jojoba extractants.

Direct lithiation of polystyrene. Chemical modification of two insoluble cross-linked polystyrene matrixes, polystyrene–2% DVB and XAD-4, was accomplished *via* a direct lithiation reaction. Fast quenching of the lithiated polystyrene with dry ice enabled us to estimate the actual amount of lithiated phenyl rings in the polystyrene, in terms of the acidic carboxyl groups that were formed. Characterization of these acidic polymers in terms of ion-exchange capacity (see the Experimental Procedures section) showed that their capacities depended on the type of initial polymer matrix. The resin obtained from polystyrene–2% DVB had a slightly higher capacity (1.1 meq/g) than that based on XAD-4 (0.95 meq/g), apparently as a result of the higher swelling of the former ma-

trix. Thus, the direct lithiation reaction yielded about 10% lithiated phenyl rings in the polystyrene matrix.

Binding of jojoba wax to lithiated polystyrene. Three allyl-brominated derivatives (Scheme 2) were obtained by changing the molar ratio of NBS to jojoba wax. Tetrabromojojoba wax (J-4Br), dibromojojoba wax (J-2Br), and crude monobromojojoba wax (J-1Br) were produced at ratios of 1:4, 1:2, and 1:1 of jojoba wax to NBS, respectively. The products were characterized in terms of % Br and iodine number (Table 1). The difference between the experimental and calculated values of iodine number is probably due to some bromine addition to the double bonds during the allylic bromination of the wax (discussed later in the text).

The two types of lithiated resin, polystyrene–2% DVB and XAD-4, were allowed to react with the previously-described bromoallyl derivatives (J-xBr) to produce a series of "substituted" polymers (Table 2 and Scheme 3). The products, which contained bound jojoba wax and a few percentage of residual bromine, were characterized in terms of iodine number. The gel-type matrix, polystyrene–2% DVB, reacted with all three bromoallyl derivatives of jojoba (J-1Br, J-2Br, and J-4Br), and it was evident that the higher the amount of active allyl bromine sites in the J-xBr, the higher the percentage of bonded jojoba in the J-1, J-2, and J-3 products (Table 2).

$(Z,Z) - CH_3(CH_2)_7CH=CH(CH_2)_mCOO(CH_2)_nCH=CH(CH_2)_7CH_3$

Jojoba wax

Allylic bromination

I NBS → $CH_3(CH_2)_6CH(Br)CH=CH(CH_2)_mCOO(CH_2)_nCH=CH(CH_2)_7CH_3$

J-1Br *

2 NBS → $[CH_3(CH_2)_6CH(Br)CH=CH(CH_2)_p]_2COO$

J-2Br *

4 NBS → $[CH_3(CH_2)_6CH(Br)CH=CHCH(Br)(CH_2)_{p-1}]_2COO$

J-4Br

* - one of several possible isomers

SCHEME 2

TABLE 1
**Characterization of Allyl-Brominated Derivatives of Jojoba Wax (J-xBr)**

J-xBr	Bromine (%)		Iodine no. (Wijs)	
	Found	Calc.	Experimental value	Calc. value
J-0Br	0	0	84.0	84.7
J-1Br	12.1	11.8	69.6	74.7
J-2Br	21.7	21.05	60.0	66.8
J-4Br	35.9	34.8	54.3	55.2

TABLE 2
**Characterization of Products of Binding of Jojoba Wax to Lithiated Polystyrene–2% Divinylbenzene (PS) and XAD-4**

Product no.	Polymer matrix	J-*x*Br	Increase in weight (%)	Bound jojoba wax[a] (%)	Product Br (%)	Product Iodine no.
J-1	PS	J-1Br	15	12	>0.1	11.8
J-2	PS	J-2Br	33	24	0.4	35.9
J-3	PS	J-4Br	43	26	4.4	41.4
J-4	XAD-4	J-2Br	17	13	1.9	18.5
J-5	XAD-4	J-4Br	25	18	3.1	33.4

[a]Calculated from the difference between percentage of increase in weight of polymer and bromine content. See Table 1 for other abbreviation.

Direct lithiation of polystyrene
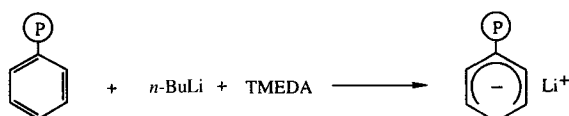
General synthetic strategy
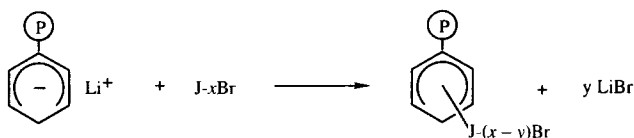
SCHEME 3

The macroporous XAD-4 polystyrene bound less jojoba than the gel-type resin, 13 and 18% for the diallyl (J-2Br) and tetraallyl (J-4Br) bromine derivatives of jojoba wax (J-4 and J-5), respectively (Table 2).

In general, the degree of the substitution reaction depended on the type of polystyrene matrix and the extent of allyl bromination sites of the J-*x*Br derivative of jojoba wax.

Table 3 shows that the bonded jojoba wax still contained some bromine. This finding implies that some active sites of allyl-brominated jojoba did not react, despite the reactive phenylcarban ion in the polymer. Another reason is the presence of vicinal bromine atoms, bonded to saturated carbon atoms as the result of some addition of bromine to the double bonds of the wax. Two competitive reactions took place: (i) nucleophilic substitution and (ii) HBr elimination, as follows: (i)

The powerful phenylcarban ion in the lithiated polystyrene beads attacked the allylic position in the allyl-brominated derivatives of jojoba wax. This nucleophilic substitution reaction yielded products that contained jojoba bound directly to the phenyl rings in the polystyrene backbone *via* a stable C-C covalent bond. (ii) The theoretical ratio of mmol double bond per mmol of jojoba wax is ~2. The increase in the amount of double bonds in our products (molar ratio of 3–4) was apparently due to the formation of new double bonds (Table 3). This was possibly due to attack by a phenylcarban ion as a strong base on the homoallylic hydrogen, with the consequent formation of diene and triene systems in the bound jojoba due to a competitive HBr elimination reaction (Scheme 4). It seems that the competitive HBr elimination reaction was preferred over the nucleophilic substitution reaction in our systems. This can be seen from high degree of double bond formation, while unreactive allylbromide sites (1.08–1.28 mmol/mmol jojoba) remained in the bound jojoba (Tables 2 and 3).

The conclusion that may be drawn from these results is that, out of two bromine atoms in J-2, one reacted in the nucleophilic substitution reaction and the other was eliminated to form a diene system (J-2 in Table 3). With four bromine atoms, again only one was substituted, two were eliminated to yield a diene or a triene, and one remained unreacted (J-3 and J-5 in Table 3).

Modification of jojoba wax bound to polystyrene. To test the reactivity of the double-bond regions in our new products and to explore their application in the preparation of resins that contained various functional groups, we brominated the products. The polymers J-2 and J-4 were chosen because they were both obtained from the J-2Br derivative. J-2, which was based on the gel polystyrene matrix, contained twice as much bound jojoba as the macroporous J-4 polymer, and the amounts of double bonds in the two matrixes were 3.47 and 3.31 mmol double bonds per mmol jojoba, respectively. The degree of bromine addition was estimated by elemental analysis of bromine (Table 4).

Based on the reactivity of the double bonds in J-2 and J-4 during the bromine addition reaction, we functionalized the double bonds by phosphonation and sulfur chlorination reactions, as shown in Scheme 5 and Tables 5 and 6.

In general, the results show that the double-bond regions in the bound jojoba wax were active in three different addition reactions. Higher yields were obtained in the modification of the J-2 polymer than in that of the J-4 polymeric ma-
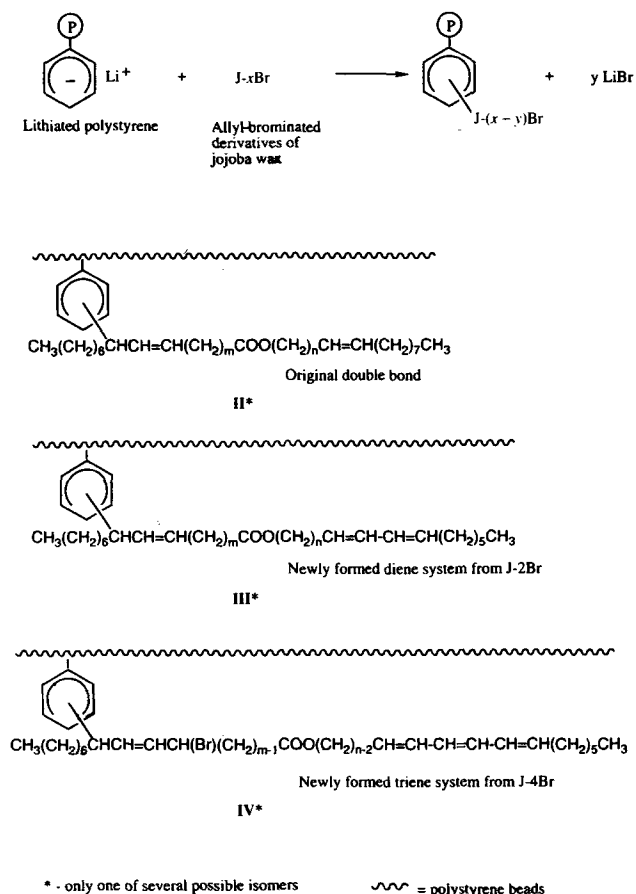
TABLE 3
Calculated Composition of Jojoba Wax Bound to Polystyrene Matrixes PS and XAD-4[a]

Product no.	mmol Jojoba/g	mmol Br/g	mmol DB[b]/g	mmol DB / mmol jojoba	mmol Br / mmol jojoba
J-1	0.203	0	0.465	2.29	0
J-2	0.407	0.050	1.413	3.47	0.12
J-3	0.441	0.550	1.630	3.70	1.25
J-4	0.220	0.238	0.728	3.31	1.08
J-5	0.302	0.388	1.315	4.35	1.28
Jojoba wax	1.610	0	3.220[c]	2.00	0

[a]See Table 2 for abbreviation.
[b]DB, double bond.
[c]Calculated value on basis of experimental iodine number.

SCHEME 4

SCHEME 5

TABLE 4
Bromination of the Double-Bond Region in Jojoba Wax Bound to Polystyrene (PS or XAD-4)[a]

Polymer			Bromination		
no.	mmol Jojoba/g	mmol DB/g	Br (%)	mmol Br/g	Yield[b]
J-2	0.407	1.413	18.3	2.29	81
J-4	0.220	0.728	11.2	1.03	60

[a]See Tables 2 and 3 for abbreviation.
[b]Yield calculated from elemental analyses of the derivative (mmol Br per mmol DB).

TABLE 5
Phosphonation of the Double-Bond Region in Jojoba Wax Bound to Polystyrene (PS or XAD-4)[a]
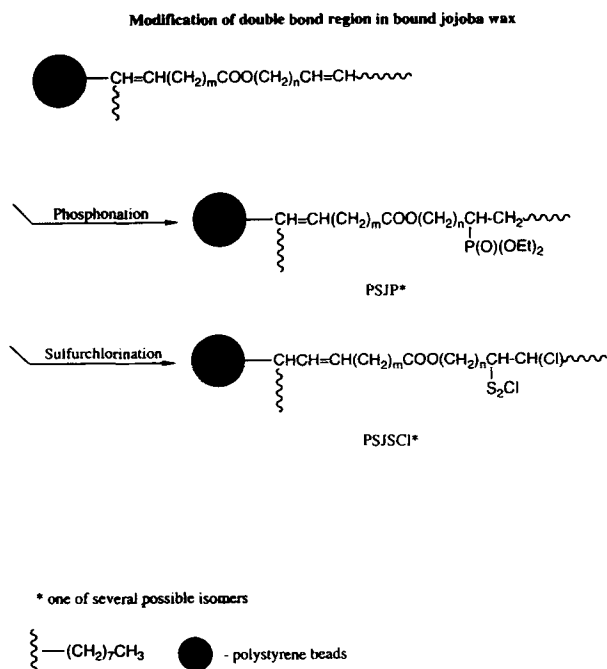
Polymer			Phosphonation		
no.	mmol Jojoba/g	mmol DB/g	P (%)	mmol P/g	Yield[b]
J-2	0.407	1.413	3.00	0.94	71
J-4	0.220	0.728	1.41	0.44	52

[a]See Tables 2 and 3 for abbreviation.
[b]Yield calculated from elemental analyses of the derivative (mmol P per mmol DB).

TABLE 6.
Sulfur-Chlorination of the Double-Bond Region in Jojoba Wax Bound to Polystyrene (PS and XAD-4)[a]

| Polymer	Sulfur-chlorination					
no.	S (%)	Cl (%)	mmol S/g	mmol Cl/g	Yield[b]	Yield[c]
J-2	4.19	4.25	1.31	1.20	46	93
J-4	1.75	1.93	0.55	0.54	32	64

[a]See Table 2 for abbreviation.
[b]Yield calculated from elemental analyses for structure V (mmol S_2Cl_2 per mmol DB).
[c]Yield calculated from element analyses for structure VI (mmol S_2Cl_2 per 2 mmol DB).

trix. This finding can be attributed to the better swelling properties of the J-2 gel-type polystyrene in the reaction medium. The final products were comprised of a phosphorus or sulfur-chlorinated jojoba wax ligand, bound chemically to the poly-

styrene matrix, which then contained 0.94–1.31 (for J-2) and 0.44–0.55 (for J-4) mmol of functional groups per gram in the gel and macroporous-types polystyrene, respectively (Scheme 5 and Tables 5 and 6).

Sulfur-chlorination. The structure of sulfur-halogenated jojoba has been previously studied (3), and the mechanism proposed for the sulfurization of jojoba wax is:
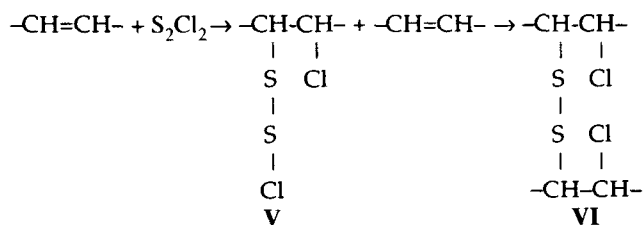
A two-stage reaction between jojoba wax and S_2Cl_2 was assumed to occur by ionic addition to the double bond. In the first stage, the product **V** is obtained, and in the second stage, **V** may react with a second double bond to form **VI**. Cross-linking by intermolecular sulfur bridges takes place, which leads to an increase in viscosity and molecular weight.

It is not clear on the basis of elemental analysis whether the addition of sulfur chloride to the double bonds in the different matrixes produced the intermediate structure **V** or structure **VI**, in which cross-linking by intermolecular sulfur bridges occurred.

We therefore calculated the efficiency of sulfur monochloride addition to the double bonds (Table 6). If the intermediate **V** was formed, then yields of 46 and 32% would be obtained for the J-2 and J-4 polymers, respectively. However, if structure **VI** was formed, then high yields of 93 and 64% would be obtained for the J-2 and J-4 polymers, respectively.
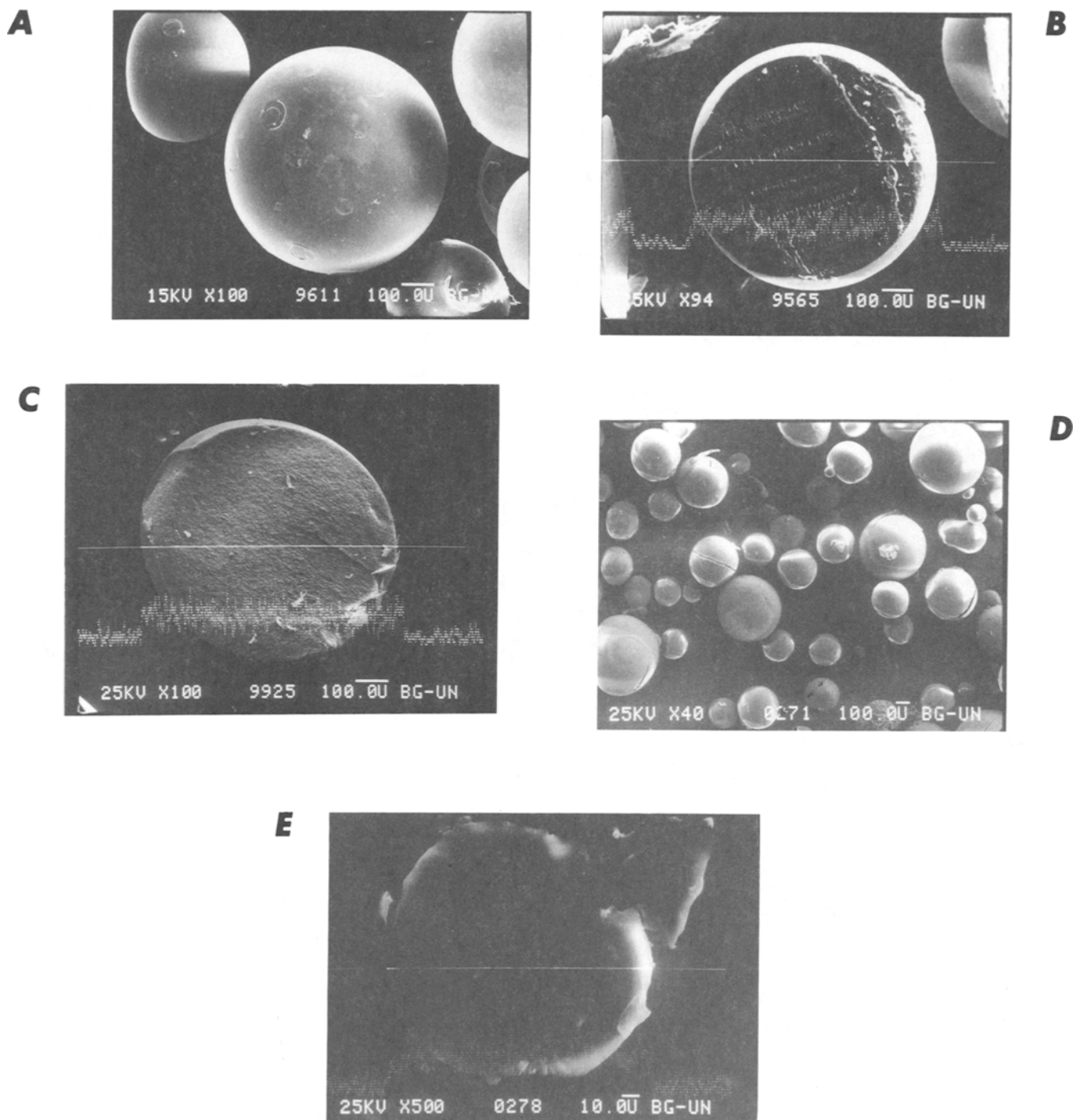
FIG. 1. A: Surface area of J-4 polymer; B, inner section of J-4 after phosphonation [Line Scanning Profile of phosphorus (LSP-P)]; C, inner section of J-4 after sulfur-chlorination [Line Scanning Profile of chloride (LSP-Cl)]; D, surface area of J-2 polymer; and E, inner section of J-2 after phosphonation (LSP-P).

Structure. Scanning electron microscopy was used to determine the distribution of the functional groups. Cross-sections of the polymer beads after modification of the double-bond region were examined (Fig. 1). The distribution of P and Cl was recorded by X-ray probe analysis. The results show that the distribution of the functional group along the inner section of the bead was quite homogeneous (Fig. 1).

The following data—styrene–2% DVB, 0.90; J-2, 0.76; XAD-4, 750; and J-4, 727—show that the surface area of the products to which modified jojoba wax was bonded remained the same as that of starting polystyrene polymers, within the limits of experimental error. Because the jojoba wax content in the products was as high as 12–26%, it seems that jojoba chains reacted with and penetrated into the resin—rather than forming a (mono) layer on the pore surface area—and were homogeneously distributed throughout the volume of the polymer beads.

In conclusion, allyl-brominated jojoba was reacted with lithiated polystyrene to bind jojoba directly *via* a C-C bond to polymer matrix. The formation of new double bonds during the substitution reaction was observed due to a competitive HBr elimination reaction. Modification at the double-bond region of the bound jojoba wax produced products that contained phosphonate or sulfur chlorine groups as ligands bound to an insoluble polymeric carrier. The solid metal-ion extractants prepared in this way are now being tested for their ability to extract metal ions from aqueous solutions.

ACKNOWLEDGMENT

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