Functionalization at the Double-Bond Region of Jojoba Oil. 8. Chemical Binding of Jojoba Liquid Wax to a Polymer Matrix *via* an Amine "Spacer"

S. Binman[a], **S. Belfer**[b,*], **and A. Shani**[a]
[a]Department of Chemistry and [b]The Institutes for Applied Research, Ben-Gurion University
of the Negev, Beer-Sheva 84105, Israel

ABSTRACT: Jojoba wax was chemically bonded to a polymer matrix *via* stable C–N covalent bonds. The polymer matrix was prepared by amination of several types of styrene–divinyl benzene or styrene–vinylbenzylchloride–divinylbenzene copolymers with diamines or polyethylene imines (polyamines). The jojoba wax was attached to the aminated polystyrene matrix by reacting an allyl-brominated derivative of jojoba with the matrix to form a C–N bond between the matrix and the jojoba wax. The amount of bound jojoba wax added to the polymer was in the range of 20–70% (w/w), depending on the type of polymer matrix and reaction conditions. The double-bond regions in the jojoba wax bonded to the matrix were preserved, and they were subsequently functionalized by phosphonation and sulfur-chlorination reactions.

JAOCS 73, 1083–1095 (1996).

KEY WORDS: Allyl-brominated jojoba wax derivatives, aminated polystyrene, binding of jojoba wax to polymer, jojoba wax, phosphonation, sulfur-chlorination.

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

$$(Z,Z)\text{-}CH_3(CH_2)_7CH{=}CH(CH_2)_mCOO(CH_2)_nCH{=}CH(CH_2)_7CH_3$$

(I)

$m =$	7,	9,	11,	13	$n = 8,$	10,	12,	14
average composition (%)	11,	71,	14,	1	1,	45,	44,	9

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 (3). In particular, phosphonated and sulfurized jojoba wax derivatives possess good extraction properties compared to the compounds commonly used in solvent extraction for the extraction of metal ions, such as uranium and mercury (4–9). Similarly, polymer matrices, 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 the extraction of mercury and cadmium from acidic solutions (10,11).

The use of impregnated resins in solvent extraction technologies 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 (12–14). To overcome the disadvantages inherent in these technologies, the extractant may be bound to a rigid polymer matrix without damaging its extraction properties. Some of the advantages of using a natural product, such as jojoba wax, as the extractant, bound to a solid polymer support are its lack of toxicity, ready availability, and low cost. In the case of jojoba wax, modification of the double-bond region by phosphonation or sulfur-halogenation has been performed to obtain ion-exchange or chelate groups for the recovery of metal ions from wastewater. The modified jojoba derivatives may have unique properties: the products have a defined structure and size that is regulated by the basic polymer matrix; this will enable their general application without further structural modification.

Polystyrene (PS) matrices were chosen as the substrates for our synthetic procedure for the following reasons: PS is commercially available with a wide range of matrix rigidity or macroporosity; it is mechanically strong and compatible with most organic solvents; and it is chemically stable but easily functionalized. In addition, the hydrocarbon backbone is resistant to attack by most reagents, so various transformations can be carried out without degrading the polymer chain (15–17).

A large number of functional resins have previously been synthesized by chemical modification of cross-linked PS

---

*To whom correspondence should be addressed at the Department of Chemistry, Ben-Gurion University of the Negev, P.O. Box 653, Beer-Sheva 84105, Israel.

(18–21). Functionalized resins have found numerous applications as supports in solid-phase peptide synthesis and as reagents and supports for chromatography and catalysis (22, 23). In each case, the optimal structure of the cross-linked PS depends on the application. In this study, a number of basic copolymer matrices with chloromethyl and sulfochloride functional groups were synthesized to produce a structure that would bind a relatively large organic molecule, such as jojoba wax [molecular weight (MW) ~600].

The overall aim of our ongoing research is to prepare modified jojoba bonded to a solid matrix and to investigate the use of a series of such compounds in the treatment of wastewater and recovery of heavy metal ions. In this paper, we describe the preparation of solid extractants, comprised of jojoba wax derivatives chemically bonded to a PS matrix by stable covalent bonds. The derivatives were prepared by functionalization of the preserved double bonds in the wax by phosphonation or sulfur-chlorination reactions.

EXPERIMENTAL PROCEDURES

Monomers, supplied by Aldrich (Milwaukee, WI), were washed free of inhibitor before use with 1 N NaOH and water, followed by drying over $MgSO_4$ and distillation under reduced pressure. The following amines and polyamines, also supplied by Aldrich, were used without further purification: ethylenediamine (EDA), diaminopropane (DAP), hexamethylenediamine (HDA), diethylenetriamine (DETA), triethylenetetramine (TETA), and tetraethylenepentamine (TEPA). *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was supplied by Merck (Darmstadt, Germany). The AR-grade solvents dioxane, tetrahydrofuran (THF), cyclohexane, and nitrobenzene were dried on a solid drying agent and distilled. All other solvents were AR-grade and used without further purification. Crude jojoba wax was used in all experiments without purification [iodine value (Wijs), 84.0; acid number, 2.7; saponification number, 93]. ^1H Nuclear magnetic resonance (NMR) spectra were determined on a Bruker WP-200SY instrument (Spectrospin AG, Sallanden, Switzerland) in $CDCl_3$ solution. 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. Synthetic polymer beads were sifted before use, and only the 0.2-mm fraction was used in the experiments.

Preparation of polymer supports. A variety of cross-linked PS supports were prepared and functionalized, as described below.

Styrene–2% divinylbenzene (DVB) copolymer. Styrene was copolymerized with 2% DVB by means of suspension polymerization (24). The copolymer was subjected to steam distillation to remove traces of unreacted monomer. To remove surface impurities, the resin was then 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), H_2O, and dimethylformamide. Thereafter, the resin was washed at room temperature with the following solutions: 2 N HCl in methanol, water, methanol, methanol/dichloromethane (1:3), and methanol/dichloromethane (1:10). Finally, the resin designated C5 (Table 1) was dried under vacuum at 70°C.

Styrene–vinylbenzylchloride (VBCl)–DVB copolymer. In a typical run a homogeneous mixture of the monomers styrene, VBCl, and DVB, plus benzoyl peroxide (1%) with or without *n*-heptane, was poured into a 1-L reactor that contained a 1% starch solution preheated to 40°C with vigorous stirring (1000 rpm). The suspension in the reactor was heated to 60, 70, or 85°C over a period of 1 h and maintained at those temperatures for 1 h, followed by 16 h at 90°C. The resulting copolymer beads were filtered off, washed with hot water, cleaned by refluxing in a Soxhlet apparatus with a mixture of methanol/dichloroethane (1:1) for 24 h, and dried under vacuum at 70°C. The characteristics of the copolymers so obtained (C1, C2, C3, C4) are summarized in Table 1.

Functionalization of the styrene–2% DVB copolymer. Two types of functionalization reactions were performed on the styrene–2% DVB copolymer designated C5 (Table 1)—chloromethylation and chlorosulfonation.

Chloromethylation of the copolymer was carried out with a mixture of $ClSO_3H$ and methylal (25). The polymer, 25 g (0.24 eq), was preswollen in 1,1,2-trichloroethylene (CM1) or 1,1,1-trichloroethane (CM2) overnight, excess solvent was filtered off, and a mixture of 75 mL of methylal (1 mol) and 115 mL of $ClSO_3H$ (1 mol), previously cooled in ice, was added. During the addition, the temperature was maintained

TABLE 1
Preparation and Characteristics of the Styrene–Vinylbenzylchloride–Divinylbenzene Copolymers

Matrix		Monomer mixture (%)				Cl (%)		Swelling or solvent uptake (%)		
Designation	Type	St	VBCl	DVB	*n*-heptane[a]	Calc.	Exp.	DCE[b]	Dioxane	Toluene
CI	Macroporous[c]	45	45	10	90	10.4	10.2	120	100	150
C2	Macroporous[c]	20	73	7	90	16.9	16.3	100	100	140
C3	Gel[d]	50	48	2	0	11.1	10.9	150	150	160
C4	Gel[d]	2	96	2	0	22.2	22.1	100	50	100
C5	Gel[d]	98	0	2	0	0	0	200	150	250

[a]Percentage by weight to monomer mixture. [b]DCE, 1,2-dichloroethane. [c]Solvent uptake by weight. [d]Swelling according to volume change.

TABLE 2
Chloromethylation and Chlorosulfonation of Styrene–2% Divinylbenzene Copolymers[a]

Matrix designation	Preswelling solvent	Reaction mixture C5 (g)	$ClSO_3H$ (mL)	Methylal (mL)	Exp. (%) S	Cl	Swelling (%) DCE	Dioxane	Methylal	Toluene
CM1[b]	1,1,2-TCE	25	115	75	>0.1	25.7	50	20	70	70
CM2[b]	1,1,1-TCE	25	115	75	0.7	23.5	100	50	110	120
CS	DCE	10	70	0	12.0	11.5	250	—	—	250

[a]See Table 1 for abbreviation. [b]The maximum calculated Cl% for PS-CH_2Cl is 23%: the higher Cl content probably resulted from double substitution of CH_2Cl group on several phenyl rings.

at 10–15°C, and thereafter the temperature was increased to 30°C. After 2 h, the resin was filtered off. The chloromethylated polystyrene was washed with 1,2-dichloroethane (DCE), methanol/toluene (1:1), and methanol, cleaned by refluxing in a Soxhlet apparatus with DCE and then with acetone, and dried under vacuum at 60°C. The chloromethylated PS was characterized in terms of elemental analysis and swelling capacity (Table 2).

Chlorosulfonation of the copolymer was carried out with $ClSO_3H$ (CS, see Table 2). Ten grams (95 meq) of copolymer, preswollen in DCE, was added to 70 g (0.61 mol) of chlorosulfonic acid. The reaction mixture was maintained at room temperature for 1 h, and then at 40°C for 4 h. The copolymer was filtered off and washed with DCE, cleaned by refluxing in a Soxhlet apparatus with DCE for 24 h, and dried in air overnight.

Amination of the chloromethylated styrene–DVB or styrene–VBCl–DVB copolymer. A sample of the copolymer was allowed to swell in a mixture of dioxane and the relevant diamine for 3 h at room temperature, after which time a further quantity of the same diamine was added. In a typical experimental run, 10 g (31 mmol Cl) of the chloromethylated styrene–DVB copolymer was preswollen in a mixture of 9.6 g (93 mmol) of diethylenetriamine in 20 mL of dioxane. After preswelling at room temperature, another portion of the diamine–dioxane mixture was added to bring the final copolymer-to-diamine molar ratio to 1:6. The reaction mixture was then maintained at 70°C for 16 h with mechanical stirring. The suspension was filtered off, and the aminated copolymer was washed with dioxane, dioxane/1 N HCl (1:1), 2 N HCl, and water until the washing water was free of chlorides. The weak anion exchanger prepared in this way was then shaken overnight with 1 N NaOH and washed with water until the washing water was neutral. The iodine number of the animated PS was determined as described below (Table 3). The total ion-exchange capacity of the aminated copolymers was determined, and potentiometric titration and elemental analysis were performed (Tables 4–6).

Amination of the chlorosulfonated styrene–DVB copolymer. In a typical experimental run, 19.2 g (192 mmol) of diethylentriamine in 40 mL of dioxane was added to 10 g (32 mmol Cl) of the chlorosulfonated styrene–DVB copolymer (CS in Table 2). The reaction mixture was maintained at room temperature for 16 h with mechanical stirring. The suspension was filtered off, and the product was washed and characterized as described above for aminated chloromethyl PS.

A cross-linked aminomethyl PS PS-CH_2NH_2 resin was also synthesized from the chloromethylated matrices by a Gabriel-type alkylation with potassium phthalimide (26).

Preparation of allyl-dibrominated derivatives of jojoba wax (J-2Br). Allylic bromination of the crude jojoba wax (**I**) was carried out with *N*-bromosuccinimide (NBS) in CCl_4 as previously reported (27). The dibromo allyl derivative of jojoba wax (J-2Br) was produced at a molar ratio of 2:1 of NBS to jojoba wax. The J-2Br derivative contained 21.7% Br (calc. 21.05%) and had an iodine number of 60.0 (mg I/100 g) (calc. 66.8).

Binding of jojoba wax to the polymer matrix. J-2Br were bound to the polymer matrix by reacting them with aminated PS, as described below.

Binding of J-2Br to aminated copolymers. Ten grams of aminated copolymer were preswollen overnight in 60 mL of a solution of 30% J-2Br in dioxane (w/w) at room temperature. The reaction mixture was maintained at 60–65°C for 24 h. The product was filtered off, washed with dioxane and methanol, cleaned by refluxing in a Soxhlet apparatus with CCl_4, and then washed again with methanol, methanol/water (1:1), 10% $NaHCO_3$, water, methanol/water (1:1), and acetone. The product was dried under vacuum at 60–70°C. The amount of jojoba wax bound to the polymer matrix was calculated from differences in weights. The nature of the binding and the composition of the product were determined from elemental analysis and iodine number (Tables 7–9).

TABLE 3
Iodine Number of Aminated Polystyrene Matrices[a]

Aminated matrix designation	Amino group	No. nitrogen atoms	Iodine number (mg I/100 mg)
AM-1	EDA	2	11.0 ± 0.5
AM-2	DAP	2	11.5 ± 0.5
AM-3	DETA	3	28.0 ± 1.0
AM-4	TETA	4	36.0 ± 1.0
AM-5	TEPA	5	44.0 ± 2.0

[a]AM, aminomethyl polystryene; EDA, ethylenediamine; DAP, diaminopropane; DETA, diethylenetriamine; TETA, triethylenetetraamine; TEPA, tetraethylenepentamine.

TABLE 4
Amination of Chloromethylated Polystyrene Matrices with Tetraethylenepentamine (TEPA)

Aminated polymer designation	Polymer matrix[a]		Amination				$-CH_2Cl$ reacted groups (%)	Amine attachment[d]		IEC (meq/g)[e]	
	Designation	mmol Cl/g	Solvent	TEPA[b] (%)	mmol Cl left/g[c]	mmol amine introduced/g[c]		Single (%)	Double (%)	Q_{H^+}	Q_{Cl^-}
AMT-1	C3	3.07	Dioxane	20	0.46	1.19	85	45	55	2.40	2.21
AMT-2	C3	3.07	DMF[f]	20	1.33	0.72	57	42	58	1.85	1.57
AMT-3	C3	3.07	Dioxane	30	1.75	1.09	43	82	18	2.38	2.48
AMT-4	C3	3.07	Dioxane	50	1.10	1.42	64	72	28	4.43	4.50
AMT-5	CM2	6.62	Dioxane	50	3.80	1.57	43	56	44	4.30	4.32
AMT-6	C1	2.87	THF[f]	50	0.30	1.15	90	87	13	1.92	1.87
AMT-7	C2	4.60	THF	50	1.85	0.72	60	25	75	1.35	1.21
AMT-8[g]	CS	3.24	Dioxane	50	0.50	0.53	85[h]	18	82	1.25	0.05

[a] From Tables 1 and 2. [b] % TEPA in solvent; molar ratio of amine to polymer of 6:1; reaction at 60°C, 24 h. [c] Calculated values on the basis of experimental elemental analysis of Cl% and N% in aminated polystyrene. [d] Calculated value on the basis of mmol introduced amine/g and mmol reacted Cl/g. [e] Ion exchange capacity. [f] DMF, dimethylformamide; THF, tetrahydrofuran. [g] Amination at room temperature. [h] SO_2Cl reacted group (%).

Reactions of the double-bond region in jojoba wax bonded to the polymer matrix (PS–Joj): phosphonation. Five grams of polymer matrix with 20–40% (w/w) of bonded jojoba wax were allowed to swell in a reaction mixture that contained 10 g (72 mmol) of diethylphosphite, 0.5 g (2.6 mmol) of butyl perbenzoate, and 20 mL of toluene for 4 h at room temperature. After addition of a further 0.5 g of initiator, the reaction mixture was maintained at 110°C under agitation and an Ar blanket for 6 h. The reaction was monitored by sampling and analyzing for phosphite content by the addition of 0.2 N NaOH and back titration with 0.2 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 (Table 10).

Sulfur-halogenation. The polymer matrix with the bonded jojoba wax (1.76–3.4 mmol) was preswollen in 10 mL of nitrobenzene for several hours. A mixture of 0.2–0.6 mL of S_2Cl_2 in 5 mL of 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 (Table 11).

Properties of the polymer matrices: swelling. Substituted polymer matrix (1 mL) was placed in a 5-mL volumetric flask, which was then filled with solvent, and the polymer was allowed to swell for 48 h. The degree of swelling was calculated from the difference in volume between the swollen and dry polymer.

Properties of the polymer matrix: capacity determination. The ion-exchange capacity of the weak anion exchangers obtained after amination of the styrene–VBCl–DVB copolymer with diamines was determined as follows: 1 g of polymer in the OH^- form was shaken for 24 h at room temperature with 100 mL of 0.1 N HCl. Concentrations of H^+ and Cl^- ions in the solution were determined by potentiometric and argentometric titration. From the differences in the concentrations, Q_{H^+} and Q_{Cl^-} (meq/g) were calculated.

Determination of the iodine number of the polymer matrices. CCl_4 (20 mL) and 20 mL of Wijs solution (0.1 N ICl in acetic acid) were added to 100–150 mg of the dry polymer matrix. The mixture was shaken and then left to stand in the dark for 1 h. Then, 20 mL of 15% aqueous KI solution and 100 mL of distilled water were added, and the mixture was stirred with a magnetic stirrer for a few minutes. In this method, excess I^+ reacts with I^- and I_3^- to form I_2, which is then titrated with 0.1 N thiosulfate solution; toward the end of the titration 1% starch solution is added and the color

TABLE 5
Amination of Chloromethylated Polystyrene Matrices with Ethylenediamine (EDA)

Aminated polymer designation	Polymer matrix		Amination				$-CH_2Cl$ reacted groups (%)	Amine attachment (%)[c]		IEC (meq/g)[d]	
	Designation	mmol Cl/g	Solvent	EDA[a] (%)	mmol Cl left/g[b]	mmol amine introduced/g[b]		Single (%)	Double (%)	Q_{H^+}	Q_{Cl^-}
AME-1	C3	3.07	Dioxane	30	0.18	1.43	94	50	50	2.01	2.03
AME-2	C3	3.07	Dioxane	50	0.16	2.11	94	80	20	2.80	2.60
AME-3	CM2	6.62	Dioxane	50	3.10	2.85	53	46	54	2.43	2.40
AME-4	C1	2.87	THF	50	0.71	1.85	75	79	21	2.40	2.37
AME-5[e]	CS	3.24	Dioxane	50	0.10	1.92	97[f]	59	41	1.65	0

[a] % EDA in solvent; molar ratio of amine to polymer of 6:1; reaction at 60°C, 24 h; see Tables 3 and 4 for abbreviations. [b] Calculated values on the basis of experimental elemental analysis of C1% and N% in aminated polystyrene. [c] Calculated value on the basis of mmol introduced amine/g and mmol reacted Cl/g. [d] Ion exchange capacity. [e] Amination at room temperature. [f] SO_2Cl reacted group (%).

TABLE 6
Amination of the Chloromethylated Polystyrene (PS) Copolymer (C3) with Different Diamines

Aminated polymer designation	Amine[a]	Functional group	mmol Cl left/g	mmol N introduced/g[b]	mmol amine introduced/g[b]	Reacted $-CH_2Cl$ groups (%)	Amine attachment[c]		pKa[d]	IEC (meq/g)[e]	
							Single (%)	Double (%)		Q_{H^+} (meq/g)	Q_{Cl^-} (meq/g)
C3	—	$PS-CH_2Cl$	3.07	—	—	—	—	—	—	—	—
AM-1	Phthalimide	$PS-CH_2NH_2$	0.48	2.64	2.64	84	100	0	—	1.50	1.60
AM-2	EDA	$PS-CH_2NH(CH_2)_2NH_2$	0.16	4.22	2.13	94	73	27	8.4	2.01	2.03
AM-3	DAP	$PS-CH_2NH(CH_2)_3NH_2$	0.09	3.86	1.93	97	72	28	8.2	2.71	2.79
AM-4	HDA	$PS-CH_2NH(CH_2)_6NH_2$	1.83	2.14	1.01	49	86	14	7.5	1.20	1.09
AM-5	DETA	$PS-CH_2(NHCH_2CH_2)_2NH_2$	0.21	5.64	1.88	93	66	34	7.8	4.50	4.50
AM-6	TETA	$PS-CH_2(NHCH_2CH_2)_3NH_2$	0.16	5.61	1.40	95	48	52	7.9	4.70	4.71
AM-7	TEPA	$PS-CH_2(NHCH_2CH_2)_4NH_2$	1.10	7.09	1.42	64	72	28	6.7	4.42	4.50

[a] Amines: HDA, hexamethylenediamine; other abbreviations as in Table 3. [b] Calculated values on the bases of experimental elemental analysis of Cl% and N% in aminated polystyrene. [c] Calculated value on the basis of mmol introduced amine/g and mmol reacted Cl/g. [d] Experimental results. [e] Ion exchange capacity.

changes from dark blue to white. The iodine number is calculated as follows:

$$\text{iodine number (mg I / 100 mg)} = \frac{(B-V)N \times 12.69}{S} \quad [1]$$

where $B = 0.1$ N $Na_2S_2O_3$ (mL) added to the blank, $V = 0.1$ N $Na_2S_2O_3$ (mL) added to the sample, N = concentration of thiosulfate solution (eq/L), and S = sample weight (g).

For the aminated polymer matrices with bonded jojoba wax, the iodine number was higher than expected from HBr elimination, even if a high degree of HBr elimination occurred. The color of the white polymer during iodine number determination turned to brown, which led us to assume that I_3^- was adsorbed onto the polymer matrix, attaching itself to the protonated amino groups. This would lead to less I_2 being detected, and as a result a higher iodine number would be obtained. We found that this iodine could be eluted from the polymer by addition of thiosulfate or sodium hydroxide solution. Thus, the real value of the iodine number in aminated matrices to which jojoba was bonded was much lower than the measured value. Correction of the measured iodine number was made as follows:

$$C\ (\text{mg I / 100 mg}) = \frac{M - A \cdot D}{100} \quad [2]$$

where C = corrected iodine number, M = measured iodine number of the polymer matrix (mg I/100 mg), A = aminated fraction in the polymer (%), and D = iodine number of the aminated polymer (mg I/100 mg).

Aminated polymer matrices were tested for iodine capacity by the iodine number test, and the results were expressed in mg I/100 mg polymer (Table 3). A correlation was found between the iodine number and the number of nitrogen atoms.

Potentiometric titration. The experimental pKa of the aminated matrices was calculated from the potentiometric titration curve of the resins (28).

RESULTS AND DISCUSSION

Scheme 2 summarizes the process of preparation of the solid extractants, comprising phosphonated or sulfur-chlorinated jojoba wax derivatives chemically bonded to a PS-type matrix *via* an amine "spacer" in the following order: selection of the solid polymer matrix; attachment of the amine spacer; chemical bonding of jojoba wax to the matrix *via* the amine spacer; and functionalization of the double bond in jojoba wax by phosphonation or sulfur-chlorination.

Polymer matrices. The first step in our research was the selection of suitable polymeric matrices because the structure

TABLE 7
Binding of Allylic Dibromojojoba Derivatives to Different Polystyrene Matrices Aminated with TEPA (AMT) or EDA (AME)[a]

Exp. no.	Basic CM-PS matrix	Aminated polystyrene		Increase in weight (%)	Br left (%)	Jojoba wax in product (%)	mmol Jojoba/g product
		Designation	mmol amine/g				
J-1	C3	AMT-4	1.42	39	0.9	27	0.46
J-2	CM2	AMT-5	1.57	18	0.3	15	0.26
J-3	C1	AMT-6	1.15	32	0.3	24	0.41
J-4	C2	AMT-7	0.72	17	0.5	10	0.17
J-5	C3	AME-2	2.11	74	4.2	38	0.65
J-6	CM2	AME-3	2.85	14	0.8	12	0.20
J-7	C1	AME-4	1.85	41	1.7	28	0.48
J-8	PAN	Lewatite E304/88®[b]	5.85	14	0.5	12	0.20

[a] See Tables 3 and 6 for abbreviations. PAN, polyacrylonitrile; CM–PS, chloromethylated-PS.
[b] Bayer Company, Levelkusen, Germany.

TABLE 8
Binding of Allylic Dibromojojoba Derivatives to the Chloromethylated-PS Copolymer Designated C3 That Had Been Aminated with Different Diamines

Exp. no.	Aminated matrix no.	Amine[a]	Increase in weight (%)	Jojoba wax in product (%)	Br left (%)	Iodine no. (Wijs)[b]	mmol Jojoba/g product	mmol Br/g product	mmol DB[c]/ mmol jojoba	IEC (meq/g)[d] Q_{H^+} (meq/g)	Q_{Cl^-} (meq/g)
J-10	AM-1	$-NH_2$	6	5	0.1	5.0	0.09	0	2.31		
J-11	AM-2	EDA	74	38	4.2	34.0	0.65	0.53	2.07	0.52	0.53
J-12	AM-3	DAP	62	34	3.6	38.1	0.58	0.45	2.61	0.56	0.57
J-13	AM-4	HDA	28	20	2.2	25.1	0.34	0.28	2.91	0.63	0.63
J-14	AM-5	DETA	66	40	0.1	43.2	0.68	0	2.51	0.54	0.54
J-15	AM-6	TETA	64	38	1.0	37.8	0.64	0.13	2.31	0.85	0.76
J-16	AM-7	TEPA	39	27	0.9	24.8	0.46	0.12	2.13	1.70	1.41

[a]See Tables 3 and 6 for abbreviations. [b]Corrected iodine number. [c]DB, double bond. [d]Ion-exchange capacity.

of the matrix influences the success of binding the jojoba wax. Both gel and macroporous types of PS were used. Introduction of chloromethyl groups was achieved by direct copolymerization of VBCl, styrene, and DVB with or without porogen or by chloromethylation of the PS matrix with a mixture of chlorosulfonic acid and methylal.

Copolymerization. Details of the suspension copolymerization of VBCl, styrene, and DVB are summarized in Table 1 and Scheme 3. The two gel-type copolymers C3 and C4 were synthesized with different amounts of VBCl in the initial reaction mixture. The percentage of active chloromethyl groups in copolymer C4 was 96%, a value twice that in C3. Both copolymers contained low amounts of cross-linking agent (2%). The two macroporous-type cross-linked copolymers C1 and C2 were obtained by the addition of *n*-heptane (as a porogen) during the course of the copolymerization of the same vinyl monomers. The solvent uptake by these two matrices was almost the same, being independent of the amount of chloromethyl groups. The conversion of VBCl in the copolymerization reaction was high, as can be seen from the agreement between the experimental and calculated Cl contents (Table 1). Because the commercial VBCl monomer is a mixture of two isomers, in which the $-CH_2Cl$ group is substituted at the *meta* and *para* positions on the styrene ring in a 2:1 ratio, we can assume that both *meta* and *para* isomers of VBCl were incorporated into the copolymer structure. Table 1 shows that the swelling of the copolymers decreased as the amount of the incorporated chloromethyl groups increased. Because of its cross-linked structure, C4 was dropped from the program, and we decided to concentrate on the macroporous C1 and C2 and the gel-type C3 matrix.

Chloromethylation. Chloromethylated polystyrene (CM–PS) gel-type beads were also prepared (Scheme 4). Chloromethylation was performed by reaction of the styrene–DVB (2%) copolymer designated C5 (Table 1) with a mixture of $ClSO_3H$ and methylal (Table 2). The high amount of chlorine incorporated into the copolymer (25.7 and 23.5% for CM1 and CM2, respectively) probably resulted from double substitution of the $-CH_2Cl$ group on certain phenyl rings (the maximum calculated percentage of Cl for CM–PS is 23%).

The swelling of the CM1 matrix was half that of CM2, evidently due to some cross-linking *via* $-CH_2-$ bridges between PS rings during the chloromethylation reaction (29). This matrix was therefore not included in subsequent experiments. The chloromethylated copolymers (all with a high Cl content), obtained by the two different synthetic routes showed low swelling in the same solvents. In the chloromethylation route, the $-CH_2Cl$ groups substituted mainly in the *para* position on the phenyl rings, in contrast to the copolymerization procedure (23,24).

Chlorosulfonation. Chlorosulfonation of polystyrene (CS–PS) with chlorosulfonic acid was also carried out to ob-

TABLE 9
Nature of Jojoba Wax Bonding to Aminated Polystyrene (PS) (C3)

Matrix designation	Amine	Jojoba wax in product (%)	mmol Br/g product	Composition (%)[a] Allylic Br[b]	Diene formation[c]	Bound to polymer[d]
J-10	$-NH_2$	5	—	—	—	—
J-11	EDA	38	0.53	81	4	15
J-12	DAP	34	0.45	78	22	0
J-13	HDA	20	0.28	81	19	0
J-14	DETA	40	0	0	20	80
J-15	TETA	38	0.13	19	14	67
J-16	TEPA	27	0.12	26	15	59

[a]Composition of the far side of the jojoba wax molecule bound on the near side to aminated PS. See Tables 3 and 6 for abbreviations. [b]Based on Br analysis. [c]Based on iodine number. [d]Calculated value.

TABLE 10
Phosphonation with Diethyl Phosphite of Jojoba Wax Bound to Polystyrene (C3) *via* Amine Spacers

Phosphonated matrix designation	Reagent					Phosphonated product		
	Matrix	Functional group	mmol Jojoba/g product	mmol DB[a]/g product	Q_{Cl^-} (meq/g)	P (%)	P mmol/g product	Yield[b]
JP-1	C3[c]	PS-CH_2Cl	—	0	0	1.13	0.35	—
JP-2	AM-7[d]	PS-CH_2–TEPA	—	0	4.50	2.13	0.67	—
JP-3	J-16[e]	PS-CH_2–TEPA-Jojoba	0.46	0.98	1.41	1.98	0.62	64
JP-4	J-15[e]	PS-CH_2–TETA-Jojoba	0.64	1.49	0.76	3.17	0.99	66
JP-5	J-14[e]	PS-CH_2–DETA-Jojoba	0.68	1.70	0.54	4.16	1.30	77
JP-6	J-12	PS-CH_2–DAP–Jojoba	0.58	1.51	0.57	3.22	1.04	69

[a]DB, double bond; see Tables 3 and 6 for other abbreviations. [b]Efficiency of double-bond phosphonation. [c]Table 1. [d]Table 6. [e]Table 8.

tain a resin with active $-SO_2Cl$ groups (CS in Table 2).

Introduction of amine spacers. The amination of chloromethylstyrene by a variety of diamines has been reported (30–33). However, the wide range of possible reaction conditions during our amination reaction resulted in each case in aminated PS with different structural variations. The aim of the second stage of our study was to attach amine spacers to the polymer, which would subsequently be used to bind jojoba wax to the solid matrix. The experiments described below were carried out to study the effects of the following parameters on the efficiency of the amination reaction of the CM–PS (C1, C2, C3, and CM2) and CS–PS matrices: diamine and polyamine concentrations in the reaction solution; type of solvent; and type of polymer matrix. In most experiments, the C3 matrix (the best swollen gel-type matrix, see Table 1) was selected to react with the different amines. The amination reactions are presented schematically in Schemes 5 and 6, and the results are summarized in Tables 4–6.

Diamine concentration in reaction solution. The influence of amine concentration on the course of the amination reaction was tested in the C3 polymer matrix. Increasing the concentration of TEPA in dioxane [aminated polystyrene with TEPA (AMT)-1,3 and 4 in Table 4] and EDA [aminated polystyrene with EDA (AME)-1,2 in Table 5], but keeping a constant molar ratio of 6:1 of the amine to chloromethyl groups in the polymer, resulted in a higher amount of introduced amine. At the same time, the CH_2Cl conversion was reduced with TEPA (from 85% to 43–64%), while with EDA it remained high (94%).

However, Tables 4 and 5 show that the conversion (percentage or mmol of reacted chloromethyl groups) of $-CH_2Cl$ groups was higher than the degree of amination (mmol of attached amine), and this leads us to the conclusion that the amination was accompanied by an additional chemical cross-linking side reaction in the copolymer. It seems that, after the first primary amine in EDA or TEPA reacted, the second primary amine and/or the secondary amine (CH_2CH_2NH) in the multifunctional polyamine reacted with another $-CH_2Cl$ group, which increased the cross-linking in the matrix. The reaction of the $-CH_2Cl$ group with secondary amines is possible, although less probable, and it has been reported that the degree of amination with –NH groups in multifunctional polyamines of the type used by us is low (34).

The percentage of double ($PS-CH_2NH{\sim\sim}NHCH_2PS$) and single ($PS-CH_2NH{\sim\sim}NH_2$) attachment of the diamine was evaluated (Tables 4 and 5). It is clear that, at higher amine concentrations, monoamination prevails, as expected in an amine alkylation reaction. This result was also reflected in the higher ion-exchange capacity of the aminated PS matrices.

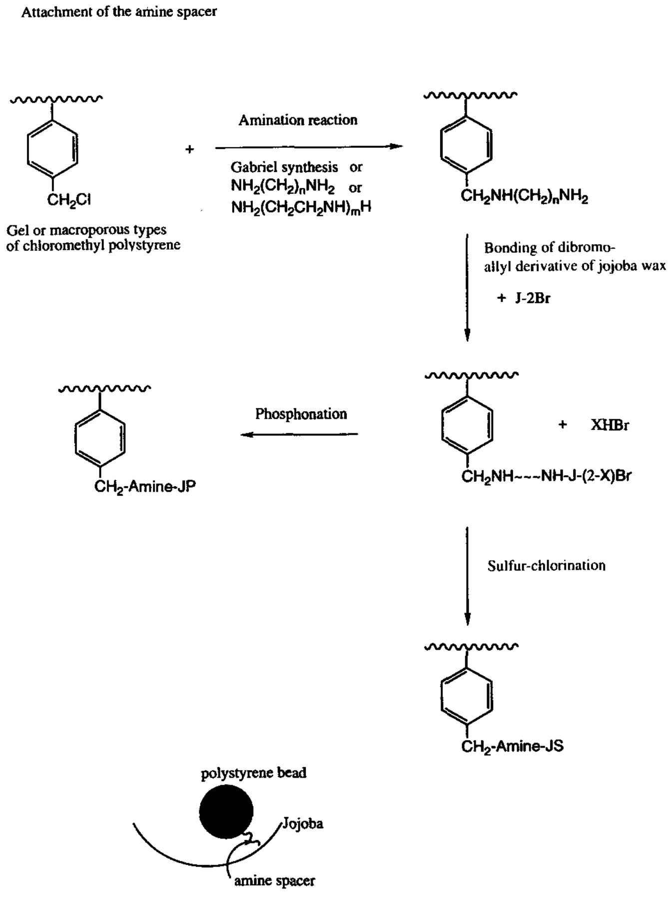
Nature of the polymer matrix. To explore the influence of the nature of the CM–PS matrix on the course of amination reaction, a number of different PS matrices with chloromethyl functional groups were aminated with TEPA and EDA under the same conditions (Tables 4 and 5).

At the same TEPA concentration of 50% in dioxane or THF (Table 4), more amine was introduced with C3 and CM2 (AMT-4, AMT-5) gel-type matrices than with macroporous C1 and C2 matrices (AMT-6, AMT-7). Consequently, the re-

TABLE 11
Sulfur-Chlorination of Bonded Jojoba Wax to AM-PS (C3) Matrices[a]

Sulfur-chlorinated matrix designation	Reagent						Sulfur-chlorinated matrices					
	Basic matrix	Functional group	mmol Jojoba/g product	mmol D.B./g product	Cl (%)	Br (%)	S (%)	Cl (%)	mmol S/g product	mmol Cl/g product	mmol Cl/ mmol S	Yield[b] (%)
JS-1	C3[c]	PS-CH_2Cl	0	—	10.2	0	1.9	9.8	0.620	2.760	—	0
JS-2	AM-7[d]	PS-CH_2–TEPA	0	—	3.9	0	8.3	2.0	2.594	0.563	0.22	0
JS-3	J-16[e]	PS-CH_2–TEPA–Jojoba	0.46	0.98	2.0	1.0	4.7	2.7	1.484	0.775	0.52	79
JS-4	J-15[e]	PS-CH_2–TETA–Jojpba	0.64	1.49	0.2	1.0	6.1	7.7	1.922	2.169	1.13	100
JS-5	J-14[e]	PS-CH_2–DETA–Jojoba	0.68	1.70	0.5	0.1	5.0	6.1	1.563	1.718	1.10	100
JS-6	J-12[e]	PS-CH–DAP–Jojoba	0.58	1.51	0.5	0.1	5.3	5.9	1.656	1.661	1.00	100

[a]See Tables 3, 6, and 8 for abbreviations. [b]Efficiency of double-bond sulfur-chlorination. [c]Table 1. [d]Table 6. [e]Table 8.

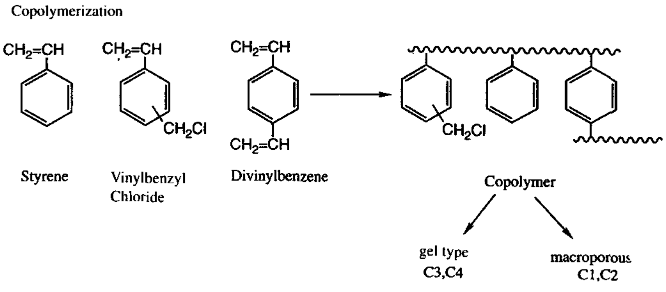


SCHEME 2

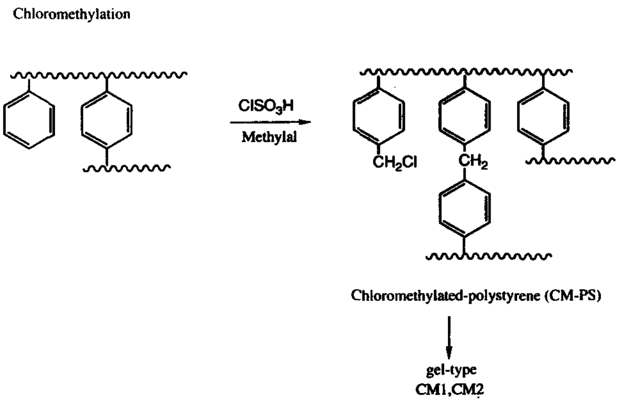
sulting weak anion-exchange resins of the macroporous type also showed poor ion-exchange properties.

The same behavior was observed for amination with EDA (Table 5). The gel-type matrices C3 and CM2 (AME-2 and AME-3) yielded aminated PS that contained 2.11 and 2.85 mmol amine/g, while in the macroporous Cl matrix (AME-4) 1.85 mmol amine per gram was introduced.

In the copolymer C3, in which half of the matrix is chloromethyl styrene, only 64% of the $-CH_2Cl$ groups reacted with TEPA (AMT-4), whereas 94% reacted with EDA (AME-2). In the CM–PS CM2 polymer, whose $-CH_2Cl$ group content was twice that of the C3 matrix, a higher degree of double diamine attachment was observed (AMT-5 vs. AMT-4 in Table 4 and AME-3 vs. AME-2 in Table 5). This picture repeated itself for the macroporous copolymers, but to an even greater extent (AMT-6 vs. AMT-7 in Table 4). These results confirm the previous findings (typical of amine alkylation) that a higher chlorine content (a higher concentration of electrophile) leads to increased substitution, and hence to increased double attachment (Scheme 5).

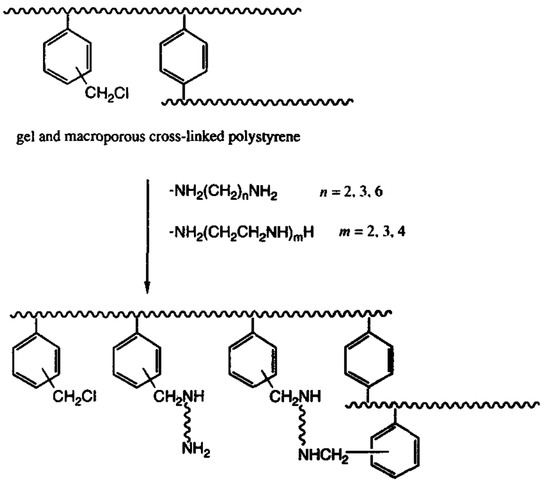


SCHEME 3



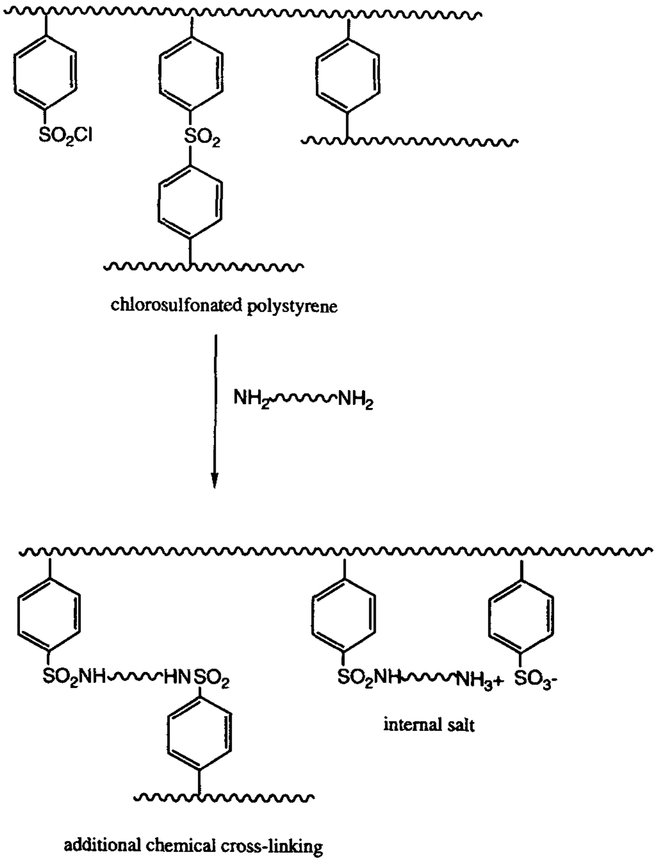
SCHEME 4

Amination of CS–PS with the same amines was carried out at room temperature (Scheme 6). The CS–PS, which had the same amount of $-SO_2Cl$ reactive groups as C3 had $-CH_2Cl$ groups, underwent solely a cross-linking reaction with TEPA (AMT-8 in Table 4) and EDA (AME-5 in Table 5), leading to a product with bisulfonamide groups ($PS-SO_2NH\sim\sim NHSO_2-PS$) (Scheme 6). These matrices did not exhibit anion exchange capacity ($Q_{Cl^-} = 0$) and did not



relative ratio:	unreacted chloromethyl groups	aminated polystyrene	additional chemical cross-linking
simple diamines:	0	4 (80%)	1 (20%)
multifunctional: amines	2 (33%)	3 (50%)	1 (17%)

SCHEME 5



SCHEME 6

swell in water. As a result, the polymers cannot bind jojoba wax and were dropped from subsequent studies.

Amination of the chloromethylated (C3) copolymer with diamines and polyamines. The aim of these experiments was to study the effect of the length of the amine on the amination reaction and to produce PS beads with amine spacers of different lengths. To this end, the chloromethylated copolymer C3 was aminated with amines of the type NH_2-$(CH_2)_n$-NH_2 (n = 2, 3, 6) and multifunctional polyamines NH_2-$(CH_2CH_2NH)_m$-H (m = 2, 3, 4) (Table 6). The substitution of $-CH_2Cl$ groups with diamines and multifunctional polyamines was high (93–97%), with the exception of the longest amines in each series—HDA [aminated PS (AM)-4] and TEPA (AM-7)—for which the conversion (reacted chloromethyl groups) was 49 and 64%, respectively. The amount of introduced amine decreased as the length of the amine increased. In general, the degree of additional chemical cross-linking during amination with the simple diamines was lower (14–28%) than with multifunctional polyamines (28–52%). The amines with the longest aliphatic chains, HDA (AM-4) and TEPA (AM-7), gave products with a lower degree of cross-linking in each series but also with a lower degree of first substitution due to their relatively low reactivity, which stemmed from the steric factor.

Aminated polystyrene matrices are, in fact, weak anion exchangers that may be characterized in terms of ion-exchange capacity of Q_{H^+} and Q_{Cl^-}. The superior ion-exchange capacities in the aminated matrices, prepared from the polyamines DETA, TETA, and TEPA (AM-5, AM-6, and AM-7), are a function of the presence of free secondary amino groups ($-NHCH_2CH_2-$) [which is not true for simple diamines EDA, DAP, and HDA (AM-2, AM-3, and AM-4)].

The pKa values of aminated matrices were determined from potentiometric titrations of the resins (Table 6). The results show that the basicity of the amino groups attached to solid PS was reduced as the length of the diamine increased.

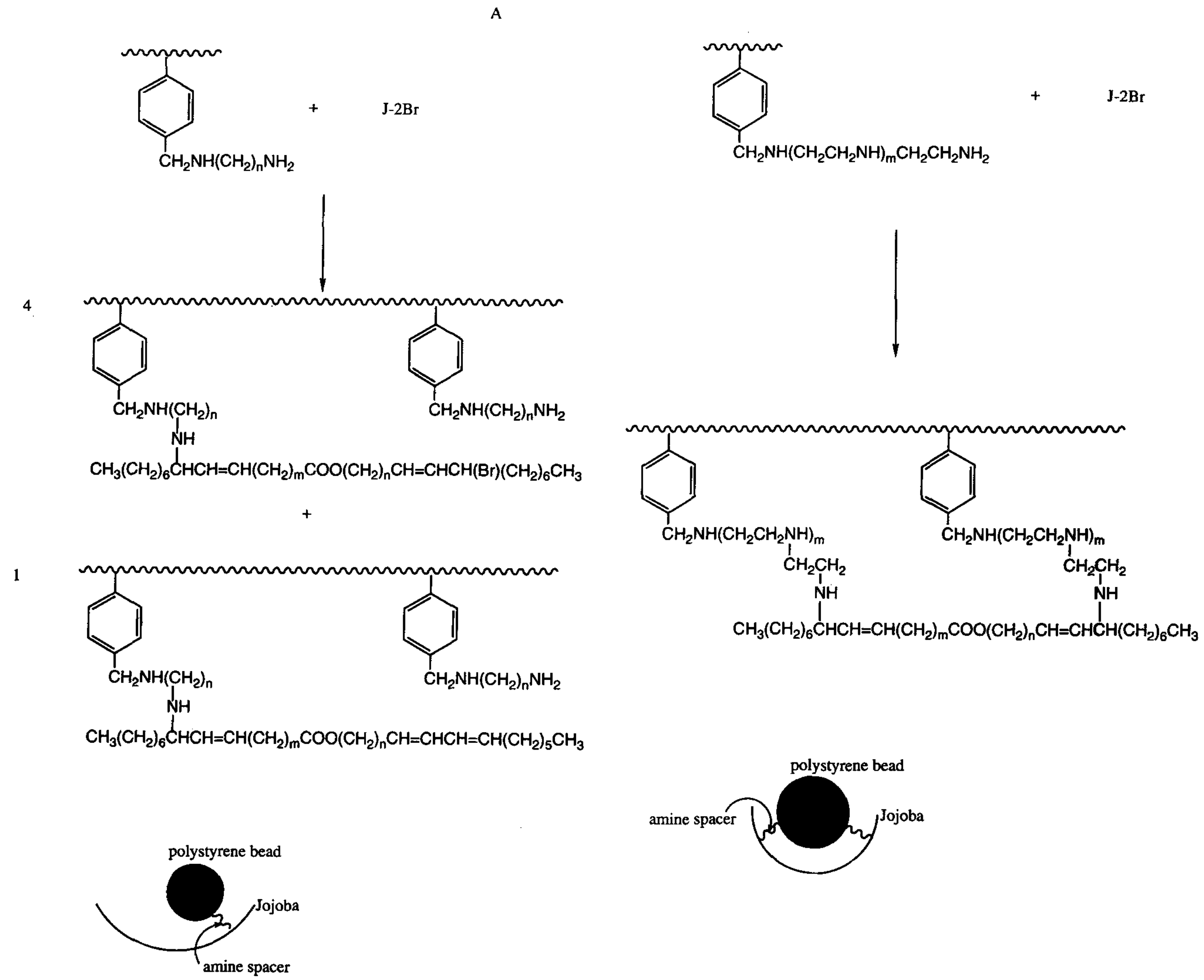
AM-1 with 2.64 mmol amine/g was obtained by means of Gabriel synthesis and has the shortest "spacer" for jojoba binding.

The following conclusions may be drawn from the experiments described above. The PS gel-type matrices yielded aminated products with higher amine contents than the macroporous polystyrene. The gel-type copolymer type (C3) yielded mainly monoaminated products (70–80%) (Scheme 5 and Tables 4 and 5), while the chloromethylated matrix (CM2) was less reactive [only 50% of its CH_2Cl reacted with the amines (Scheme 5 and Tables 4 and 5)], and the ratio of single to double bonding was about 1:1, which indicates less free primary amines for the reaction with brominated jojoba. A higher concentration of CH_2Cl on the polymer matrix resulted in increased double attachment. The higher the concentration of the amine in solution, the higher the amount of monoamination, leaving the second primary amine free (less double attachment). Even though shorter amines gave rise to higher substitution than longer amines, the amount of double attachment was higher with the shorter amines. The optimal conditions for monoamination were: a gel-type matrix, less CH_2Cl groups, and a high concentration of amine in solution.

Bonding of J-2Br to aminated PS via *amine groups.* The crucial step in the synthesis of the final products was the binding of jojoba wax to the amine spacer by nucleophilic substitution of the primary amino group to the bromo allyl derivative of jojoba wax (Scheme 7), as described below.

Different aminated resins. Aminated PS polymers (AM–PS) with TEPA functional amino groups (series AMT in Table 4) or EDA functional amino groups (series AME in Table 5) were reacted with the J-2Br. These two series differ in their basic polymeric matrices (C3 and CM2, gel type; and C1 and C2, macroporous type) and their degree of amination. Only those matrices that exhibited high degrees of single amino attachment were used for this stage. In addition, the commercial weak anion exchange resin Lewatite E304/88® (Bayer Company, Levelkusen, Germany), which is based on a polyacrylonitrile (PAN) matrix and has multifunctional amino active groups, was used for comparison. The amounts of chemically bonded jojoba wax in the resins are summarized in Table 7.

The percentage of total increase in weight of the starting AM–PS matrices after J-2Br bonding fell in a wide range of values, from 14 up to 74%, while the commercial resin based on PAN with a higher content of similar amino groups bound only 14% jojoba wax (J-8).



SCHEME 7

The AM–PS polymer with EDA (PS–EDA), produced on the basis of the gel type CM–PS copolymer designated C3 (AME-2), yielded a product that contained the maximum amount of bound jojoba wax—38% (J-5)—while the PS–EDA resin (AME-3), based on the CM2 matrix, gave a product with only 12% of bound jojoba wax (J-6).

The same picture repeated itself with PS aminated with TEPA (PS–TEPA). The percentage of jojoba wax in the product based on the C3 matrix (AMT-4) was 27% (J-1), whereas only 15% (J-2) jojoba wax was present in AMT-5, which was based on CM2 matrix.

The aminated resins based on chloromethylated gel-type matrix CM2, which were cross-linked during chloromethylation by $-CH_2-$ bridges (CM2) and later on during amination (AMT-5 and AME-3), were not able to swell sufficiently to allow the jojoba to penetrate into the matrix to react with the active groups (J-2 and J-6). In contrast, the solvent-swollen aminated resins (AMT-4 and AME-2) based on copolymer C3 (styrene–VBCl–DVB), in which the degree of additional chemical cross-linking during amination of CM-PS matrix was low, contained the highest amounts of bound jojoba wax (J-1 and J-5). The macroporous aminated PS resins (AMT-6 and AME-4) based on copolymer C1, in which the degree of additional chemical cross-linking was also low (J-3 and J-7), still bound a high percentage of jojoba, but less than the gel-type C3. This is probably due to the lower amount of functional amino groups in these resin obtained after amination.

To summarize, the percentage of jojoba wax that was bound to the polymer strongly depended on the nature of the polymer matrix. The final products contained about 10–38% of bound jojoba wax. This was achieved due to a nucleophilic substitution reaction, in which the functional amino groups in the AM-PS resins were active as nucleophiles that attacked the bromoallyl electrophilic sites in the J-2Br derivative of jojoba wax. As a result, the jojoba wax was chemically bound to aminated polystyrene matrices *via* stable C-N covalent bonds:

$$\text{PS}{\sim\sim}\text{NH}_2 + \text{J-2Br} \rightarrow \text{PS}{\sim\sim}\text{NH-J-(2-n)Br} + \text{nHBr} \qquad [3]$$

Different amino groups as spacers. In the next series of experiments, the gel-type PS matrix, C3, was aminated with different simple diamines of the type $NH_2(CH_2)_nNH_2$, (n = 2, 3, 6) and multifunctional polyamines of the type $NH_2(CH_2CH_2NH)_mH$ (m = 2, 3, 4) under the same conditions, and was then reacted with bromojojoba. The amount of J-2Br bound to the aminated matrices and characterization of the products are presented in Table 8.

The smallest amount of bound jojoba wax, ~5%, was found when the aminomethyl ($-CH_2NH_2$) group was attached directly to the polystyrene (J-10). When aliphatic diamines EDA, DAP, and HDA (J-11, J-12, and J-13) were used as the spacer group, the amount of bound jojoba decreased as the amount of attached amino groups decreased and the length of the aliphatic chain in AM-PS resins increased.

AM-PS that contained the multifunctional amines DETA, TETA, and TEPA (J-14, J-15, and J-16) bound jojoba wax to the same extent as the aliphatic α,ω-diamines, and the amount of bound jojoba decreased as the length of the amine spacer increased.

Nature of bonding of jojoba wax. On the basis of our experimental observations, a mechanism for the bonding of jojoba wax bonding can be proposed. The allyl brominated jojoba wax derivative J-2Br has two reactive allyl bromines, one on each side of the ester group. During nucleophilic substitution by the amino groups on the AM-PS resins at the allylic position, one side of the jojoba molecule will be bound to the polymer *via* a C–N bond. There are three possible paths for the second bromine (Scheme 7): the allyl bromine may remain unreacted; a competitive HBr elimination reaction may take place, followed by diene formation; or another nucleophilic substitution of allylbromine may occur to create an additional new C-N bond. Thus, the wax will be bound at two sites to the polymer.

The nature of the J-2Br bonding to the aminated PS was calculated on the basis of the analytical results given in Table 9. One side of the jojoba molecule is bound to the AM-PS resin, while the structure on the second side of the molecule could be the product of one of the three possible pathways mentioned previously.

It is clear that the bonding of jojoba to resins aminated with simple diamines differs from that of those aminated with multifunctional polyamines. The AM-PS resins that contained the simple diamines DAP or HDA (J-12 or J-13) reacted with J-2Br only on one side of the molecule, while on the other side of the chain, ~80% of allyl bromine sites were left unreacted and 20% diene formation occurred due to HBr elimination. Only in product J-11, obtained from the resin aminated with EDA, 15% jojoba wax was bound at two sites to polystyrene matrix *via* amine spacer.

In the AM-PS resins aminated with multifunctional polyamines, 59–80% of the jojoba wax was bound at two sites to the polymer (J-14, J-15, and J-16) due to a high degree of substitution on the second side of the bound jojoba (Scheme 7B). The degree of additional bonding at the second site decreased as the length and number of –NH– groups in the multifunctional animo spacer increased. This indicates that steric effects were the predominant factors dictating the type of reactions involved. The main substitution reaction was accompanied by diene formation (15–20%). The amount of unreacted allyl bromine sites increased slightly as the length of amine spacer increased. In all cases except one (J-11), the main substitution reaction was accompanied by diene formation (14–22%).

The chemical C–N bond between the jojoba wax and the polymer matrix is stable. No losses in weight were observed after washing and cleaning of the final products obtained in further modifications. The double bonds in jojoba wax were preserved during the bonding, which enabled further functionalization of the jojoba moiety.

The solvent remaining after the reaction of J-2Br with aminated polystyrene was evaporated, and the residue was analyzed by ^1H NMR spectroscopy. The oily residue contained the unreacted J-2Br derivative in admixture with a diene derivative of jojoba wax. No traces of jojoba wax alcohol were detected. These findings indicate that there was no competitive aminolysis reaction of the ester group in J-2Br during bonding to the polymer.

The final products contained 20–40% of jojoba wax (w/w) per gram of product. Our new polymers contain free $-NH_2$ and/or –NH ion-exchange hydrophilic groups, as well as the bound jojoba wax, which is hydrophobic in nature. This is probably the reason why there was no difference in swelling of the products between polar or nonpolar solvents, the value being in the range of 40–60%.

Functionalization of the double-bond region of jojoba wax bound to the PS matrix. The double-bond region in the bound jojoba was functionalized by two different addition reactions: phosphonation (JP) and sulfur-chlorination (JS). The reactions were carried out with the aminated gel-type C3 matrix, which contained the minimum amount of allylic bromine (see above).

Phosphonation. The phosphonate derivative of liquid jojoba wax (JP) (**II**) was obtained in a radical reaction between jojoba wax and dialkyl phosphite in the presence of an initiator:

$$-CH{=}CH- + (RO)_2P(O)H \rightarrow -CH_2\text{-}CH\text{-}P(O)(OR)_2- \quad [4]$$

(II)

When two equivalents of phosphite were used, both double bonds of jojoba wax were phosphonated (10).

The same phosphonation reaction was carried out on a number of our PS carrier polymers with jojoba wax bound to the matrix *via* an amine spacer (PS-Amine-Joj). In addition, the stabilities of the basic CM-PS matrix $PS\text{-}CH_2Cl$ (C3), and its aminated derivative PS-TEPA (AM-7), were tested in the phosphonation reaction (Table 10). Table 10 shows that both the chloromethyl (JP-1) and amino (JP-2) functional groups reacted with dialkylphosphite, resulting in the insertion of P into the copolymer C3 (1.13% P) and aminated resin AM-7 (2.13% P). The phosphite radical probably reacted with the chloromethyl group in C3 and amino groups in AM-7 according to the following competitive reactions:

$$(RO)_2POH + PS\text{–}CH_2Cl \rightarrow PS\text{–}CH_2OP(OR)_2 + HCl \qquad [5]$$

$$(RO)_2POH + PS\text{–}CH_2(NHCH_2CH_2)_nCH_2CH_2NH_2 \rightarrow PS\text{–}CH_2(NHCH_2CH_2)_nCH_2CH_2NH\text{-}P(OR)_2 \qquad [6]$$

In the series of PS–Amine–Joj with different amine spacers, the content of phosphorus increased as the amount of jojoba wax and double bonds in the polymer increased (Table 10). The yield of double-bond phosphonation in jojoba wax bound *via* polyamines (64-77%) was similar to that in jojoba wax bound *via* simple diamines (69%).

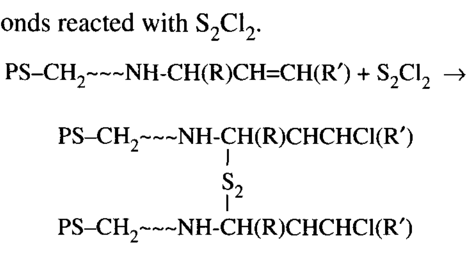
From earlier results, we know that, as the length of the amine spacer decreased, the amounts of free $-CH_2Cl$ and $-NH_2$ groups in the polymer decreased. Thus, even if the two previously described competitive reactions to the radical competitive phosphonation of double bonds occur during modification of PS–Amine–Joj polymers, their efficiency will be considerably reduced.

Sulfur chlorination. Sulfur-chlorination of the double bond region in the jojoba wax bound through an amine spacer to the polymer was carried out with sulfur monochloride S_2Cl_2 in nitrobenzene (Table 11). Reaction of S_2Cl_2 with a polystyrene containing TEPA (AM-7) as the spacer yielded a product with a high content of S (JS-2). It is known that secondary and primary amines can react with sulfur monochloride to give stable *N,N*-thiobisamines (35).

$$R_2NH + S_2Cl_2 \rightarrow R_2N\text{-}S_2\text{-}NR_2 + 2R_2NH \cdot HCl \qquad [7]$$

Even when jojoba wax is bound to the PS by a TEPA spacer (J-16), the sulfur monochloride reacts with the double bonds of jojoba as well as with the free amino groups, even though to a lesser extent (JS-3).

When the amino spacer DETA or TETA is shorter than TEPA and there is a smaller number of free amino groups (J-14 and J-15), the main reaction is addition of S_2Cl_2 to the double bond: the molar ratio Cl:S ~1 is the same as that in the sulfur monochloride. The reactivity of the double bond in bound jojoba wax in the sulfur-chlorination reaction was high—all double bonds reacted with S_2Cl_2.



$$\begin{array}{l} PS\text{–}CH_2\text{---}NH\text{-}CH(R)CH{=}CH(R') + S_2Cl_2 \rightarrow \\ PS\text{–}CH_2\text{---}NH\text{-}CH(R)CHCHCl(R') \\ \qquad\qquad\quad | \\ \qquad\qquad\quad S_2 \\ \qquad\qquad\quad | \\ PS\text{–}CH_2\text{---}NH\text{-}CH(R)CHCHCl(R') \end{array} \qquad [8]$$

In conclusion the results presented in this work clearly show that the gel-type matrix, which produces a better swollen polymer, is the matrix of choice for binding jojoba wax *via* an amine spacer, as well as for functionalization of the double bonds in the wax. At present, phosphonated and sulfur-halogenated derivatives of jojoba wax bound to polymer matrices are being tested for metal ion recovery from aqueous solutions.

REFERENCES

1. *Jojoba: New Crop for Arid Lands, New Raw Material for Industry*, edited by F.R. Ruskin, Report to the National Research Council, National Academy Press, Washington, D.C., 1985.
2. Shani, A., *CHEMTECH 25*:49–54 (1995).
3. Wisniak, J., Potential Uses of Jojoba Oil and Meal—A Review, *Ind. Crops and Prod. 3*:43–68 (1994).
4. Wisniak, J., and H. Benajahu, Sulfurization of Jojoba Oil, *Ind. Eng. Chem., Prod. Res. Dev. 14*:247–258 (1975).
5. Wisniak, J., and H. Benajahu, *Ind. Eng. Chem. Prod. Res. Dev. 17*:247–258 (1975).
6. Wisniak, J., Phosphonation of Jojoba Oil, in *3rd International Conference on Jojoba and Its Uses*, edited by D.M. Yermanos, Riverside, University of California, 1978, pp. 113–119.
7. Shorr, G., Extraction of Hg(II) by Sulfurized Jojoba Oil, Undergraduate Project, Ben-Gurion University, Beer-Sheva, 1987.
8. Wisniak, J., U.S. Patent 4,587,107 (1986).
9. Wisniak, J., Recent Advances in the Chemistry and Properties of Jojoba Oil, in *7th International Conference on Jojoba and Its Uses*, edited by A.R. Baldwin, Phoenix, 1988, pp. 222–245.
10. Wisniak, J., G. Schorr, D. Zocovsky, and S. Belfer, Extraction of Hg(II) with Sulfurized Jojoba Oil, *Ind. Eng. Chem. 29*:1907–1916 (1990).
11. Wisniak, J., G. Schorr, and S. Belfer, Extraction of Hg(II) with Sulfurized Jojoba Oil, in *8th International Conference on Jojoba and Its Uses*, Asuncion, Paraguay, 1990, pp. 1–20.
12. Alexandratos, S.D., M.A. Strand, D.R. Quillen, and A.J. Walder, Synthesis and Characterization of Bifunctional Phosphinic Acid Resins, *Macromolecules 18*:829–834 (1985).
13. Kauczor, H.W., and A. Meyer, Structure and Properties of Levextrel Resins, *Hydrometallurgy 3*:65–73 (1978).
14. Belfer, S., S. Binman, Y. Lati, and Z. Zolotov, Immobilized Resins and Liquid Extractants for Potassium Extraction from Concentrated Brines, *React. Polym. 14*:81–84 (1991).
15. Daly, H.D., Influence of Support Structure on Preparation and Utilization of Polymeric Reagents, *Macromol. Chem. Suppl. 2*:3–25 (1979).
16. Leznoff, C.C., and W. Sywanyk, Use of Insoluble Polymer Supports in Organic Synthesis. IX. Synthesis of Unsymmetrical Carotenoids on Solid Phases, *J. Org. Chem. 42*:3203–3208 (1977).
17. Qureshi, A.E., and W.T. Ford, Halogenation of Poly(*p*-methylstyrene), *React. Polym. 10*:279–285 (1989).
18. Soutif, J.C., and J.C. Brosse, Chemical Modification of Polymers: I. Applications and Synthetic Strategies, *React. Polym. 12*:3–29 (1990).
19. Sherrington, D.C., Preparation, Functionalization and Characteristics of Polymer Supports, in *Polymer-Supported Reactions in Organic Synthesis*, edited by P. Hodge and D.C. Sherrington, John Wiley & Sons, New York, 1980, pp. 1–82.
20. Seildl, J., K. Malinsky, K. Dusek, and W. Heitz, Makroporose Styrol–Divinylbenzol–Copolymere in ihre Verwendung in der Chromatographie und zur Darstellung von Ionenaustauschern, *Adv. Polym. Sci. 5*:113–128 (1967).
21. Warshawsky, A., Chelating Ion Resins, in *Ion Exchange and Sorption Processes in Hydrometallurgy* (critical reports on Applied Chemistry; v. 19), edited by M. Streat and D. Naden, John Wiley & Sons, Great Britain, 1987, pp. 166–226.
22. Merrifield, R.B., Solid-Phase Peptide Synthesis. The Synthesis of a Tetrapeptide, *J. Am. Chem. Soc. 85*:2149–2153 (1963).
23. Kraus, M.A., and A. Patchornic, Polymeric Reagents, *J. Polym. Sci., Macromol. Rev. 15*:55–67 (1980).

24. Gregoriev, A.P., and O.I. Fedotova, Laboratoniu practicum po texnolugue plastizeckix macc., *Vyshaya Shkola*, Moscow, 1977, pp. 69–73.
25. Belfer, S., and R. Glozman, Anion Exchange Resins Prepared from Polystyrene Crosslinked *via* a Friedel-Crafts Reaction, *J. Appl. Polym. Sci. 24*:2147–2157 (1979).
26. Sparrow, J.T., An Improved Polystyrene Support for Solid Phase Peptide Synthesis, *J. Org. Chem. 41*:1350–1356 (1976).
27. Shani, A., A Functionalization at the Double Bond Region of Jojoba Oil: I. Bromine Derivatives, *J. Am. Oil. Chem. Soc. 58*:845–850 (1981).
28. Gustafson, R.L., H.F. Fillius, and R. Kunin, Basicities of Weak Base Ion Exchange Resins, *Ind. Eng. Chem. Fundam. 9*:221–229 (1970).
29. Belfer, S., R. Glozman, A. Deshe, and A. Warshawsky, Structural Transformations During Chloromethylation of Flexible Polystyrene Networks, *J. Appl. Polym. Sci. 25*:2241–2263 (1980).
30. Egawa, H., and H. Saeki, Selective Absorption Resins. I. Metallic Ion Absorptivity of Low Cross-Linked Anion Exchange Resins, *Kogyo Kagaku Zasshi 74*:772–775 (1971).
31. Kirk-Othmer, *Encyclopedia of Chemical Technology*, 2nd edn., Vol. 11, John Wiley & Sons, New York, 1966, pp. 871–875.
32. Bachman, R., and H. Reuter, British Patent 1,058,625, 1967.
33. Warshawsky, A., A. Deshe, G. Rosey, and A. Patchornik, Functionalization of Polystyrene. II. Synthesis of Chelating Polymers by Alkylation of 4-Aminomethylpolystyrene, *React. Polym. 2*:301–314 (1984).
34. Tashiro, T., Removal of Polyethylene Glycol Mono-*p*-Nonylphenyl Ether and Dodecylbenzene-Sulfonate by Chloromethylated Polystyrene-Polyethylpolyamines and -Polyethyleneimines, *J. Appl. Polym. Sci. 32*:3791–3808 (1986)
35. Thompson, Q.E., The Chemistry of Thiobisamines, *Quarterly Reports on Sulfur Chemistry 5*:245–250 (1970).

[Received August 9, 1996; accepted April 2, 1996]