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Functionalization at the Double-Bond Region of Jojoba Oil. 9. Solid-State Nuclear Magnetic Resonance Characterization of Substituted Jojoba Wax Chemically Bonded to a Polystyrene Matrix

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ABSTRACT: Solid extractants for metal ions have been prepared by chemical bonding of jojoba wax to a polystyrene backbone, followed by phosphonation or sulfur-chlorination of the jojoba moiety. In this study, the intermediates and final solid products of the reactions were characterized by solid-state ^{13}C and ^{31}P nuclear magnetic resonance spectroscopy. The spectra showed the expected chemical shifts of the atoms involved in the chemical reactions, as well as other parts of the reacting molecules. Thus, the carbonyl carbon of the jojoba chain appears at 175 ppm, the methyl carbons at 15 ppm, the polystyrene backbone at 40–42 ppm (aliphatic carbons) and 128, 137, 143–147 (aromatic carbons). Carbons adjacent to N, S, and P appear at 45–55, 60, and 48 ppm, respectively.
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KEY WORDS: Chemically bonded oil to polystyrene, jojoba oil, phosphonated jojoba oil, solid-state NMR, sulfur-chlorinated jojoba oil.

Solid extractants for metal ions from aqueous solutions have the dual advantage that they can be recycled without loss of material or extraction activity (1,2). Thus, small quantities of such solid matrices can be used to purify large volumes of contaminated aqueous wastes, either to remove the toxic elements or to recover the precious metals. Solid supports of this type were recently prepared by chemical bonding of jojoba wax, a long-chain liquid ester, to a polystyrene backbone, either directly by C–C bond or *via* a "spacer," such as polyamine, by C–N bonds. The double bonds in the jojoba wax molecule were subsequently phosphonated or sulfur-chlorinated to produce the solid extractant for metal ions (3,4). These jojoba-based extractants were found to be efficient and selective for specific ions (5).

Because these new extractants are rich in polystyrene, conventional methods of chemical analysis are not suitable for characterization of the intermediates or the final products. We therefore used solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy as a characterization tool and found that this informative technique lent support to the proposed synthetic pathways outlined in Schemes 1 and 2. We also obtained the ^{31}P NMR spectrum of the phosphonated final product as independent confirmation of the chemical identification of the product.

EXPERIMENTAL PROCEDURES

The solid products were obtained as described in our preceding papers (3,4).

^{13}C NMR and ^{31}P NMR spectra in $CDCl_3$ solution were obtained on a Bruker DMX-500 MHz instrument (Karlsruhe, Germany). Solid-state ^{13}C NMR spectra were obtained with a Bruker DSX-300 MHz spectrometer and a 4-mm MAS probe. All ^{13}C spectra were run on samples spinning at 10,000 ± 2 Hz. The variable amplitude cross polarization-magic angle spinning (VACP-MAS) ^{13}C and ^{31}P spectra were recorded with a proton decoupling power of 85 kHz, a mixing time of 4 ms, and a repetition time of 2 s; 800 scans were accumulated before Fourier transformation. The ^{31}P spectra were measured at a spinning speed of 6,000 ± 2 Hz.

RESULTS AND DISCUSSION

^{13}C NMR of jojoba oil (illustrated as Compound **I** in Scheme 3) in $CDCl_3$ solution revealed 12 types of carbon atoms along the ester chain, as summarized in Table 1.

Although integration was not used to quantify the number of carbon atoms of each type, the height of the sharp signals was proportionally related to the number. Thus, the height of the signals for the carbons designated a, b and c (in **I**, each accounts for two atoms) was twice that of carbons h, i, k, and l (each represents one atom per molecule) and half that of the four allylic carbon atoms (f). The chemical shifts were within the range of values reported in the literature (6). The chemical shifts of the polystyrene matrix were the same as those published previously (7).

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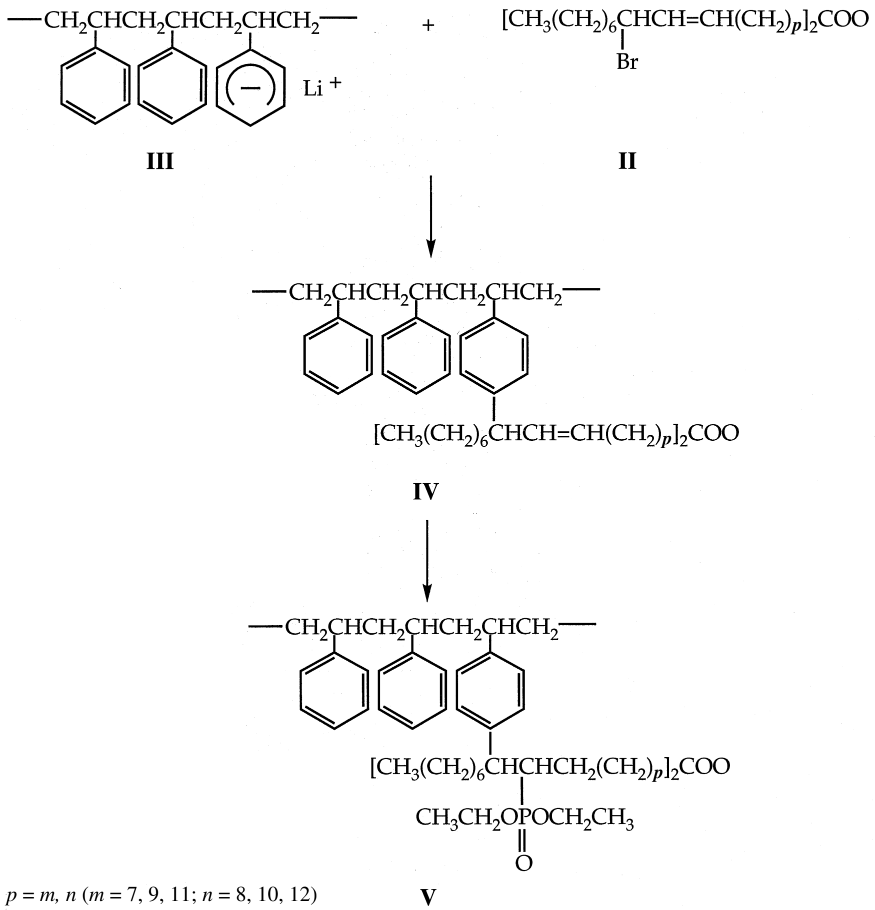


$p = m, n$ ($m = 7, 9, 11$; $n = 8, 10, 12$)

SCHEME 1

TABLE 1
Chemical Shifts[a] of ^{13}C of Jojoba Oil (I) as Liquid Wax and Chemically Bonded to Polystyrene Either Directly (IV) or *via* a Polyamine as a "Spacer" (IX)

Carbon[b]	Number of C atoms	Jojoba wax[c] **I**	XAD-4[d] + Joj **IV**	XAD-4 + Joj + Phosph. **V**	C3[e] + PA[f] + Joj (30%)[g] **IX**	C3 + PA + Joj + Phosph.[h] **X**
a	2	14	15	15	14	14
b	2	22.6				
c	2	31.8	30	30	30	30
d	2	29	(25–35)	(25–35)	(25–35)	
e	18–20	29–30				
f	4	27.1				
g	4	129.7	[i]	48[j]	[i]	[k]
h	1	24.9	30[l]	30[l]	30[l]	30[l]
i	1	34.3				
j	1	173.8	175	175	175	175
k	1	64.3	65	65	66	66
l	1	25.9	30[l]	30[l]	30 [l]	30[l]

[a] δ in ppm downfield from tetramethylsilane as standard; Joj, jojoba; Phosph., phosphonate.

[b] Assignment of carbon atoms in **I**:

$$^{a}CH_3{}^{b}CH_2{}^{c}CH_2{}^{d}CH_2({}^{e}CH_2)_3{}^{f}CH_2{}^{g}CH{=}{}^{g}CH{}^{f}CH_2({}^{e}CH_2)_x{}^{h}CH_2{}^{i}CH_2{}^{j}COO{}^{k}CH_2{}^{l}CH_2({}^{e}CH_2)_y{}^{f}CH_2{}^{g}CH{=}{}^{g}CH{}^{f}CH_2({}^{e}CH_2)_3{}^{d}CH_2{}^{c}CH_2{}^{b}CH_2{}^{a}CH_3$$

Polymers **IV** and **V** and polymers **IX** and **X** are illustrated in Schemes 1 and 2, respectively.

[c] In $CDCl_3$ solution.

[d] XAD-4, commercial copolymer of styrene and divinylbenzene.

[e] C3, terpolymer of styrene (48%), vinylbenzyl chloride (50%), and divinylbenzene (2%).

[f] PA, polyamine.

[g] 30% of jojoba per gram of matrix.

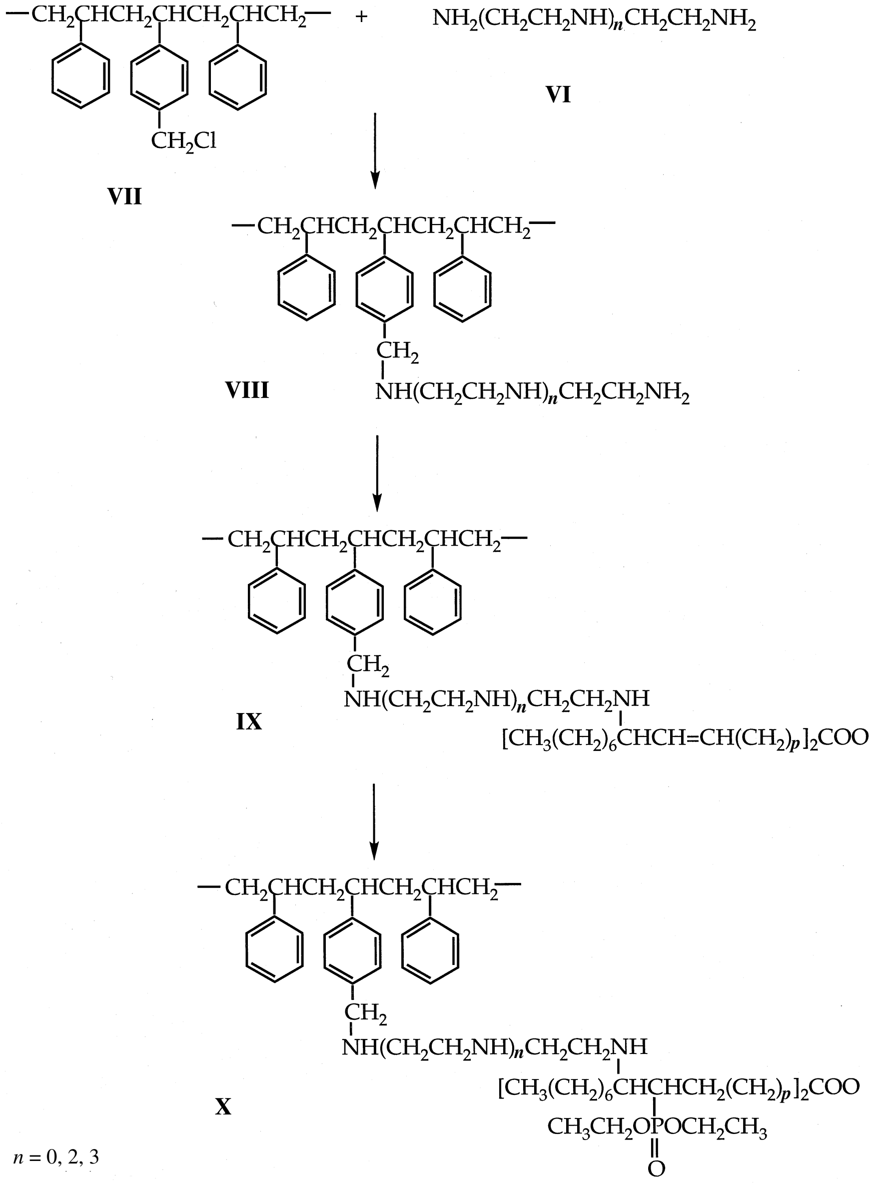
[h] Diethyl jojobylphosphonate as shown in Table 3.

[i] Covered by the polystyrene broad signal.

[j] See Table 3.

[k] Covered by carbons of the polyamine ($-HNCH_2CH_2NH-$).

[l] Under the broad signal of carbons b–e.



SCHEME 2

Bonding of jojoba wax directly to the polystyrene matrix (**II** and **III** to form **V** in Scheme 1) did not have a large effect on the chemical shifts of the chain carbon atoms, some of them being covered by the broad peaks of the polystyrene backbone (Table 2). The broadening of the peaks was due to nonhomogeneity in the polymer structure as well as to the large number of slightly different carbon atoms along the aliphatic polymer chain and the aromatic carbons in the substituted benzene rings. The major change, resulting from binding the polyamine "spacer" to the C3 matrix (**VI** and **VII** to form **VIII** in Scheme 2), was the shift in the signal attributed to the $-CH_2Cl$ group (carbon s) and in that attributed to the phenyl-ring carbon atom bearing this group (carbon r) (footnote *b* in Table 2). The separated signal at δ137 for the carbon assigned r in the C3 matrix (structure **VII** in Table 2) was replaced by a broad band at δ143–145;

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

I

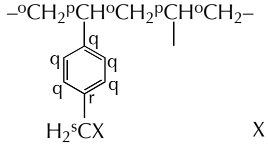
$m = 7$ (11%), 9 (71%), 11 (14%); $n = 10$ (44%), 12 (45%), 14 (9%)

SCHEME 3

TABLE 2
Chemical Shifts[a] of ^{13}C of Polystyrene Before and After Bonding of Jojoba Wax Either Directly or *via* a Polyamine as a "Spacer"

Carbon	XAD-4[c] **III**	Polystyrene matrix (C3)[d] **VII**	C3 + PA[e] **VIII**	C3 + PA Joj (30%)[f] **IX**	C3 + PA Joj + Phosph.[g] **X**
o	{ 40	{ 40	{ 40	{ 40	{ 40
p	40–42	40–42	40–42	40–42	40–42
q	128, 148	128, 147	128, 147	128, 147	128, 147
r	—	137	143–145	143–145	143–145
s	—	47	45–55	45–55	45–55
t	—	—	60–62	60–62	50–62

[a] δ in ppm downfield from tetramethylsilane as standard. Brackets indicate no separation, overlap.
[b] Assignment of carbon atoms in polymers **VII** and **VIII** (see Scheme 2):



X = Cl, $–HN^{t}CH_2{}^{t}CH_2NH$

Polymer **III** is illustrated in Scheme 1, and polymers **IX** and **X** are in Scheme 2.
[c] XAO-4, commercial copolymer of styrene and divinylbenzene.
[d] C3, terpolymer of styrene (48%), vinylbenzyl chloride (50%), and divinylbenzene (2%).
[e] PA, polyamine.
[f] 30% of jojoba per gram of matrix.
[g] Diethyl jojobylphosphonate, as shown in Table 3.

and the signal at δ47, attributed to carbon s, was changed to a broad shoulder (δ45–55) on the major signal of the $–CH_2–CH(C_6H_5)–CH_2–CH(C_6H_5)–CH_2–$ polymer chain at δ40-42.

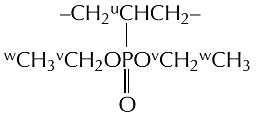
The appearance of the small, but detectable, peak of the carboxy carbon j (Table 1) at δ175 was an indication of the bonding of the intact jojoba molecule to the polymer matrix. If hydrolysis had occurred, we would have found an upfield shift of carbon k to δ60–62 (6).

The concentration of the jojoba wax bound to the polystyrene matrix affected the height of the signal of the $-CH_2-$ groups as compared to those in the aliphatic backbone of the polymer. Thus, when 20% jojoba wax was bound (20% of wax in the matrix), the height of the ester chain signal at δ30 was about 65% of that of the polymer chain at δ40–42; whereas at a 30% concentration, the ratio was 5:4 in favor of the jojoba chain (the base of each broad signal was about the same in all these signals).

TABLE 3
Chemical Shifts[a] of ^{13}C of Diethyl jojobylphosphonate (XI) in Solution and Bonded to Polystyrene Matrix

Carbon[b]	Jojoba wax[c] **I**	**XI**[c]	XAD-4[d] + Joj **IV**	XAD-4 + Joj + Phosph. **V**	C3[e] + PA[f] + Joj (30%)[g] + Phosph. **X**
a	14	13.9	14	14	14
g	129.7	—	—	—	—
u		35.2, 36.3	-	48[h]	[i]
v		61.3	—	62–65	62--65
w		16.3	—	22	17

[a] δ in ppm downfield from tetramethylsilane as standard.
[b] Assignment of carbon atoms in **I** (see Table 1, footnote *b*) and **XI**

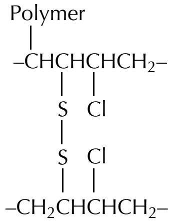


$$\begin{array}{c} –CH_2{}^{u}CHCH_2– \\ | \\ {}^{w}CH_3{}^{v}CH_2OPO^{v}CH_2{}^{w}CH_3 \\ \| \\ O \end{array}$$

[c] In $CDCl_3$ solution.
[d] XAD-4, commercial copolymer of styrene and divinylbenzene.
[e] C3, terpolymer of styrene (48%), vinylbenzyl chloride (50%), and divinylbenzene (2%).
[f] PA, polyamine.
[g] 30% of jojoba per gram of matrix.
[h] See Table 1, footnote *j*.
[i] Covered by carbons of the polyamine ($–HNCH_2CH_2NH–$).

Phosphonation of the double bonds with diethylphosphite in the jojoba molecule (**V** in Scheme 1, **X** in Scheme 2, and **XI** in Table 3) is reflected in the NMR spectrum as shown in Table 3. The two major changes were the appearance of new CH_3 signals at δ17 and 22 in the C3 matrix and in XAD-4 [a commercial macroporous polymer of styrene and divinylbenzene (4%)], respectively, and the new signal of -CH_2OP at δ62–65. The olefinic carbons g (in **I**, Table 1) were detected (as carbon u in **XI**, Table 3) at δ48 for the XAD-4 matrix, in which no amines are present to mask this signal, as found in the C3 matrix bonded *via* the polyamine "spacer."

The sulfur-chlorinated product (Scheme 4) exhibited a similar ^{13}C spectrum to **V** and showed no CH_3 peaks of the phosphonate at δ17 or 22. The ^{13}C signals of carbons bonded to sulfur appeared as a broad-low signal at δ60.



SCHEME 4

The ^{31}P signal of diethyl jojobylphosphonate **XI** (Table 3) in solution appeared at δ32.5, downfield from 85% H_3PO_4 as the internal standard (8). In the solid-state VACP-MAS NMR spectrum of **V** (Scheme 1), three ^{31}P signals could be distinguished with chemical shift parameters (with respect to the phosphor line in 85% H_3PO_4): {δ_{11} = 65.7 ppm, δ_{22} = 18.0 ppm, δ_{33} = –77.5 ppm}, {δ_{11} = 63.8 ppm, δ_{22} = 45.3 ppm, δ_{33} = –56.5 ppm}, and {δ_{11} = 64.6 ppm, δ_{22} = 64.6 ppm, δ_{33} = –55.6 ppm} (9).

The isotropic chemical shift values of these MAS sideband patterns were 1.8, 17.5, and 24.5 ppm, respectively, with line widths of about 10 ppm and relative intensities about equal to 2:1:1. The ^{31}P spectrum of **X** (Scheme 2, $n = 2$) contained similar sideband patterns to the **V** spectrum, the only differences being a significant reduction of the chemical shift anisotropy of the first pattern and an increase of the widths of the center and sidebands of the second and third patterns by a factor of about two. One of the three ^{31}P peaks was that of the diethyl jojobylphosphonate moiety in the matrix. The two others were probably phosphonate derivatives that resulted from a reaction of the diethyl phosphite with residual double bonds in the backbone of the polymer.

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