Chemical Modification of Polydienic Elastomers by Organophosphorated Reagents

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ABSTRACT: The synthesis of 1,4-polyisoprenes bearing organophosphorated groups in the side positions of polydiene chains was considered with a chemical modification procedure. The grafting of phosphorated groups along polyisoprene chains was carried out via the reaction of the acid functionality (P—OH) of phosphate or phosphonate acid reagents with oxirane rings previously created on a 1,4-polyisoprene backbone. The reagents considered were dibutylphosphate and 2-chloroethylphosphonic acid. The purpose was to compare the action of these two reagents toward epoxidized units of 1,4-epoxidized polyisoprenes in various media (solvent, bulk, and latex). © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 47–60, 2003

Key words: rubber; modification; latices

INTRODUCTION

The chemical modification of basic polymers is one of the important tools in macromolecular chemistry. The objectives behind chemical modification research are twofold: to improve the behavior and performance of a basic polymer and to prepare new materials for specific uses in areas outside the more traditional ones. For instance, by chemically modifying the rubber backbones of the 1,4-polyisoprene type, we can modify some basic properties (i.e., gas permeability, resistance to oils, and fire resistance) and prepare new rubber derivatives (i.e., photocrosslinkable rubbers and rubber supports for active molecules).[1]

The purpose of this article is to describe how 1,4-polyisoprene (synthetic and natural rubber) can be modified by acid organophosphorated reagents. We used two reagents representative of phosphate [dibutylphosphate (DBP)] and phosphonate [2-chloroethylphosphonic acid (or ethephon)] acid derivatives. We compared the action of these reagents onto epoxidized units of 1,4-epoxidized polyisoprenes in various media (solvent, bulk, and latex).

EXPERIMENTAL

Materials

Benzene (Janssen, Geel, Belgium; 99.5% purity) and 1,4-dioxane (Janssen; 99.0% purity) were used without further purification. Dichloromethane was dried on calcium sulfate, filtered, and then distilled on phosphoric anhydride after 1 h of refluxing. Tetrahydrofuran was distilled on sodium benzophenone under an argon atmosphere and then stored on 4 Å molecular sieves. Methanol was distilled on calcium sulfate after 2 h of refluxing and then stored on 3 Å molecular sieves.

4-Methyloct-4-ene (cis–trans mixtures) was synthesized by the Wittig–Schöllkopf reaction according to the method described by Pinazzi and Reyx.[2] 2-Methyl-2-butene (98% purity) was purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. Sinnopal NP 307 [α-(nonylphenoxy) poly(ethylene oxide)] was purchased from Cognis (Meaux, France). 1,4-Polyisoprene (LIR-30) and synthetic 1,4-polyisoprene latex (LIR-700) were supplied by Siber Hegner Co. (Kuraray, Mirabel, France). LIR-30 was first purified by dissolution and precipitation with benzene/methanol and then dried in vacuo. It contained 90% 1,4-polyisoprene units (64% cis and 36% trans) and 10% 3,4-polyisoprene units. LIR-700 (60% dry rubber content (DRC)) was diluted to 20% DRC.

The epoxidations of 1,4-polyisoprene (20 or 22% epoxidized), 2-methyl-2-butene, and 4-methyloct-4-ene were carried out in dichloromethane with *m*-chloroperbenzoic acid as previously described.[3]

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The epoxidation of synthetic 1,4-polyisoprene latex (22% epoxidized) was carried out as follows. The initial 60% DRC latex was first stabilized with a nonionic surfactant (Sinnopal NP 307). In an Erlenmeyer flask, 40 mL of distilled water was added to 20 g of LIR-700 (to adjust to a 20% DRC latex; 0.176 units of 1,4-polyisoprene). The mixture was magnetically stirred, and then 0.36 g (3 phr) of Sinnopal NP 307 was slowly added. After 30 min of stirring to homogenize the latex, the latter was transferred into a reactor equipped with a condenser. The mixture was magnetically stirred in an oil bath thermostated at 60°C. After the temperature was stabilized to 60°C, 1.8 g (39 mmol) of formic acid (Acros, Noisy-le-Grand, France) was slowly added over the course of 15 min. After 15 min of stirring, 3.78 g (39 mmol) of 35% hydrogen peroxide (Acros) was added to the latex drop by drop (time zero of the reaction was considered to be the moment of the addition of the first drop). At the end of the reaction, a sample of the epoxidized latex was taken, and then the epoxidized 1,4-polyisoprene was isolated by precipitation in methanol to verify the yield of epoxidation. The precipitated polymer was successively squeezed, washed with distilled water, and washed several times with methanol. Finally, it was dried in vacuo until a constant weight was obtained and then was analyzed by NMR.

DBP (Acros Organics; purity 97%) was distilled before use.

2-Chloroethylphosphonic acid was prepared according to a method described previously.[4,5]

Mono(trimethylsilyl) 2-chloroethylphosphonate was prepared by the reaction of ethephon with chlorotrimethylsilane and was isolated by distillation under reduced pressure of the crude mixture obtained.

Di(trimethysilyl) 2-chloroethylphosphonate resulted from the Arbuzov rearrangement of tri(trimethylsilyl)phosphite by action of 1,2-dichloromethane. Tri(trimethylsilyl)phosphite (34 mmol) and 1,2-dichloromethane (50 mmol) were mixed in a 100-mL, round-bottom flask equipped with a magnetic stirrer and a condenser with a guard filled with potassium hydroxide, and a nitrogen atmosphere was maintained throughout the reactor. The mixture was refluxed for 50 h and then distilled under reduced pressure (the yield of the distilled product was 45%).

Reactions carried out first in bulk and then in solution

Reaction of DBP with 4,5-epoxy-4-methyloctane

Equimolecular quantities of 4,5-epoxy-4-methyloctane (1 g) and DBP (1.47 g) were placed in a Pyrex glass tube equipped with a magnetic stirrer and closed with a screwed stopper with a Teflon-cov-

ered sealing joint. The reaction mixture was magnetically stirred for 24 h in an oil bath thermostated at 50°C. After that, the products formed were characterized by NMR.

Reaction of DBP with epoxidized 1,4-polyisoprene

One gram of 22% epoxidized polyisoprene and a stoichiometric quantity of DBP, with respect to epoxidized units, were dissolved in 10 mL of dichloromethane and placed in a Pyrex glass tube equipped with a magnetic stirrer and closed with a screwed stopper with a Teflon-covered sealing joint. The solution was magnetically stirred in an oil bath thermostated at 30°C. Samples were taken at different times and concentrated with a rotary evaporator. The modified polymers were isolated by precipitation into methanol and then purified by successive dissolutions and precipitations with dichloromethane/methanol. Finally, they were dried in vacuo until constant weights were obtained and then were analyzed by NMR.

Reaction of ethephon [or monotrimethylsilyl 2-chloroethylphosphonic acid or di(trimethysilyl) 2-chloroethylphosphonate] with 4,5-epoxy-4-methyloctane (or 2,3-epoxy-2-methylbutane)

Equimolecular quantities of the phosphorated reagent and epoxide (1.38 mmol of each reagent) were placed in a 5-mL Pyrex glass tube equipped with a magnetic stirrer and closed with a screwed stopper with a Teflon-covered sealing joint. The reaction mixtures were stirred at 20°C for 24 h and then analyzed by NMR (for the reactions carried out in a solvent, the latter was previously evaporated in vacuo with a rotary evaporator and then was analyzed by NMR).

Kinetic studies of the addition of ethephon to 2,3-epoxy-2-methylbutane

The reaction conditions have been previously described. Samples were taken at different times and analyzed by ^{31}P-NMR. For the termination of the reaction, the samples were kept in a cold bath maintained at −40°C before the NMR analyses. NMR analyses were also performed at a low temperature (−20°C). The composition changes in the reaction mixture were followed with ^{31}P-NMR by a comparison of the areas of the various peaks characteristic of the phosphorated products present in the mixture.

Reaction of ethephon [or monotrimethylsilyl 2-chloroethylphosphonic acid or di(trimethysilyl) 2-chloroethylphosphonate] with epoxidized 1,4-polyisoprene

Twenty percent epoxidized polyisoprene (1.38 mmol in epoxidized units) and a stoichiometric quantity of

ethephon [or monotrimethylsilyl 2-chloroethylphosphonic acid, or di(trimethysilyl) 2-chloroethylphosphonate], with respect to epoxidized units, were placed in a 5-mL Pyrex glass tube equipped with a magnetic stirrer and closed with a screwed stopper with a Teflon-covered sealing joint. The reactions were carried out without a solvent and in various solvents. The reaction mixtures were stirred at room temperature for 24 h and then analyzed by NMR (for the reactions carried out in a solvent, the solvent was previously evaporated in vacuo with a rotary evaporator).

Reactions carried out in a latex medium (or emulsion)

Reaction of DBP with 4,5-epoxy-4-methyloctane

Equimolecular quantities of 4,5-epoxy-4-methyloctane (1 g) and DBP (1.47 g) were dispersed in distilled water containing 3 phr Sinnopal NP 307. The mixture was placed in a Pyrex glass tube equipped with a magnetic stirrer and closed with a screwed stopper with a Teflon-covered sealing joint. It was magnetically stirred for 24 h in an oil bath thermostated at 50°C. The products formed were extracted with dichloromethane, and then the organic layer was dried on anhydrous Na_2SO_4. After filtration of the solution, the dichloromethane was evaporated with a rotary evaporator. Finally, the crude mixture was characterized by NMR.

Reaction of DBP with epoxidized latex

Sixty grams of the 22% epoxidized synthetic latex (DRC 20%; 3 phr Sinnopal NP 307) were placed in a thermostated glass cell equipped with a condenser, a temperature probe, and a magnetic stirrer. The temperature of the magnetically stirred latex was raised to 30°C, and then a stoichiometric quantity of DBP, with respect to epoxidized units, was added at a constant rate of 3.8 mL/min with the dosimeter of a pH meter, which allowed us to follow the latex pH over time. Samples were taken at different times. The modified rubbers contained in the samples were precipitated in methanol and then washed successively with water and methanol. After that, they were purified by successive dissolutions and precipitations with dichloromethane/methanol. Finally, they were dried at 50°C

in vacuo until a constant weight was obtained and then were analyzed.

Measurements

NMR spectra were recorded on a Bruker AC 400 Fourier transform spectrometer at 400.13 MHz for ^{1}H, at 161.98 MHz for ^{31}P, and at 100.61 MHz for [13]C. Samples were analyzed in solution in deuterated chloroform-d (99.8% purity; Spectrométrie Spin et Techniques, Champs-sur-Marne, France) or methanol-d. In ^{1}H-NMR and ^{13}C-NMR, the chemical shifts are expressed in parts per million in the δ scale, in comparison with the singlet of tetramethylsilane as an internal standard. In ^{31}P-NMR, the chemical shifts of various phosphorus atoms are expressed in the δ scale, with reference to the phosphoric acid peak as an external standard.

IR spectra were recorded on a Fourier transform Bruker IFC 66 spectrometer in the $4000–500 \text{ cm}^{-1}$ range (liquid film samples were analyzed between two KBr or NaCl cells, and solid ones were analyzed in KBr pellets).

RESULTS AND DISCUSSION

Here we describe how 1,4-polyisoprene (synthetic and natural rubber) is modified by acid organophosphorated reagents (DBP and ethephon, respectively). Preliminary studies were performed with 2,4-epoxy-2-butane and 4,5-epoxy-4-methyloctane, selected as model molecules of epoxidized 1,4-polyisoprene units to characterize the products obtained after the reaction, to identify the structures formed on the polyisoprene chains. Furthermore, the addition yields were optimized by variations in the reaction parameters, such as the solvent, temperature, and pH of the medium, before generalization of the reactions to the chemical modification of epoxidized 1,4-polyisoprene.

Studies were carried out without an external catalyst. Acid organophosphorated reagents can be added to oxirane rings through P—OH functions without an external catalyst. The reaction is autocatalyzed by the P—OH acid functions of the reagent.[6] The oxirane ring is activated through the formation of a hydrogen-type bond[7] with the acid function of the reagent, which makes the oxirane more electrophilic:
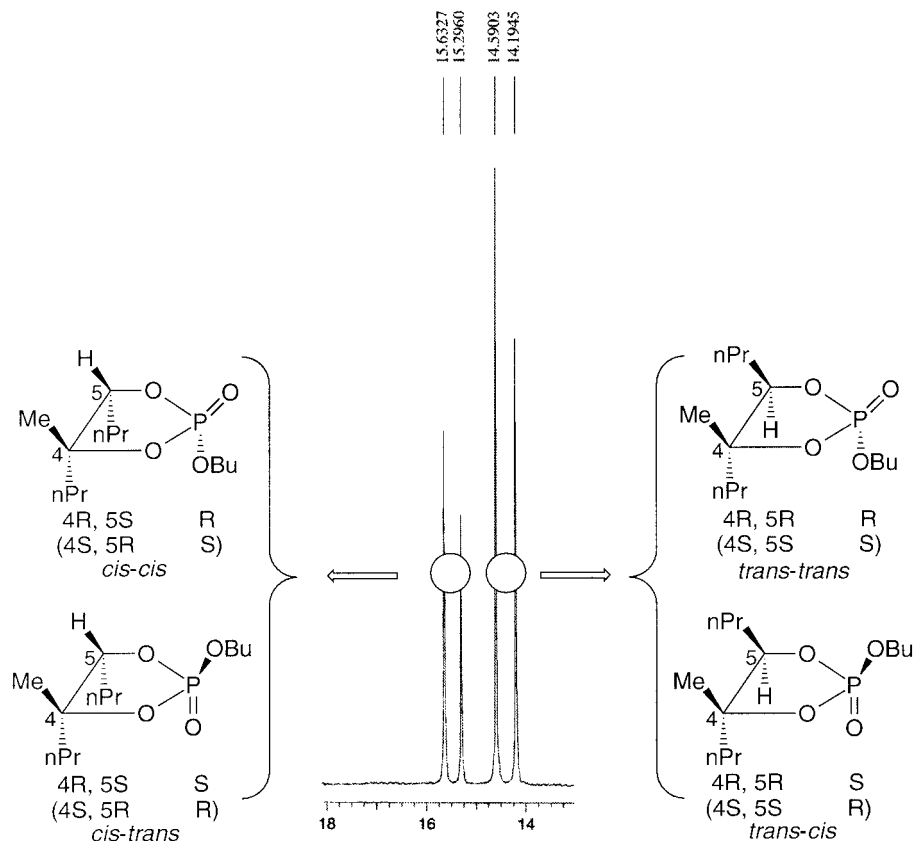

$$(1)$$
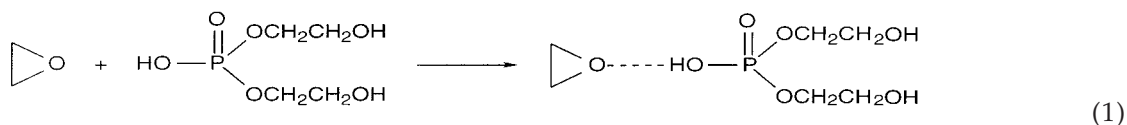
Figure 1 ^{31}P-NMR characterization of the various 2-butoxy-2-oxo-1,3,2-dioxaphospholane diastereomers formed during the reaction in bulk (or in solution) of DBP with 4,5-epoxy-4-methyloctane.

## Chemical modification by DBPs

The flammability of polydienes can be improved after the grafting of dialkyl (or aryl) phosphate groups onto the polydiene chains.[8] The advantage of such grafting is that active species cannot diffuse toward the polymer surface and they remain efficient longer.

The chemical modification of epoxidized 1,4-polyisoprenes by DBP was carried out in bulk, in a solvent, and in latex. In all cases, equimolecular quantities of DBP and epoxidized units were used.

Study first in bulk and then in a solvent

The reaction carried out in bulk at 50°C with 4,5-epoxy-4-methyloctane showed a total consumption of the epoxide after 24 h and the formation of two categories of 1:1 phosphorated adducts: five-membered cyclic adducts [2-butoxy-2-oxo-1,3,2-dioxaphospholane] and 1:1 β-hydroxyphosphate adducts:
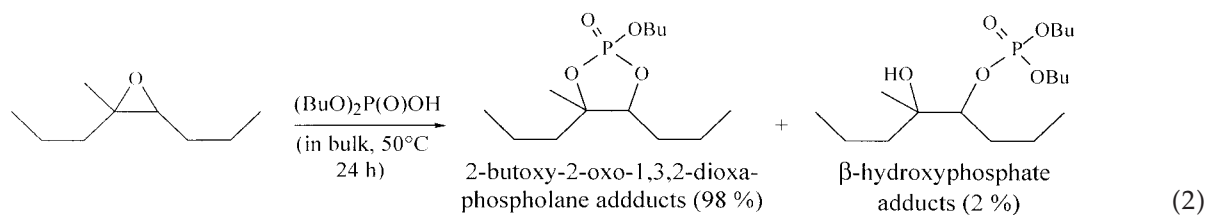
The 2-oxo-1,3,2-dioxaphospholane adduct that results from an internal condensation reaction between a butylphosphate function and the tertiary alcohol function of the initial 1:1 adduct formed is characterized in ^{31}P-NMR by four peaks between 14 and 18 ppm, a zone characteristic of phosphorus of the 2-alkoxy-2-oxo-1,3,2-dioxaphospholane type. Each peak corresponds to a specific isomer of the molecule. Consequently, the latter, which has three asymmetry centers (two asymmetrical carbons and
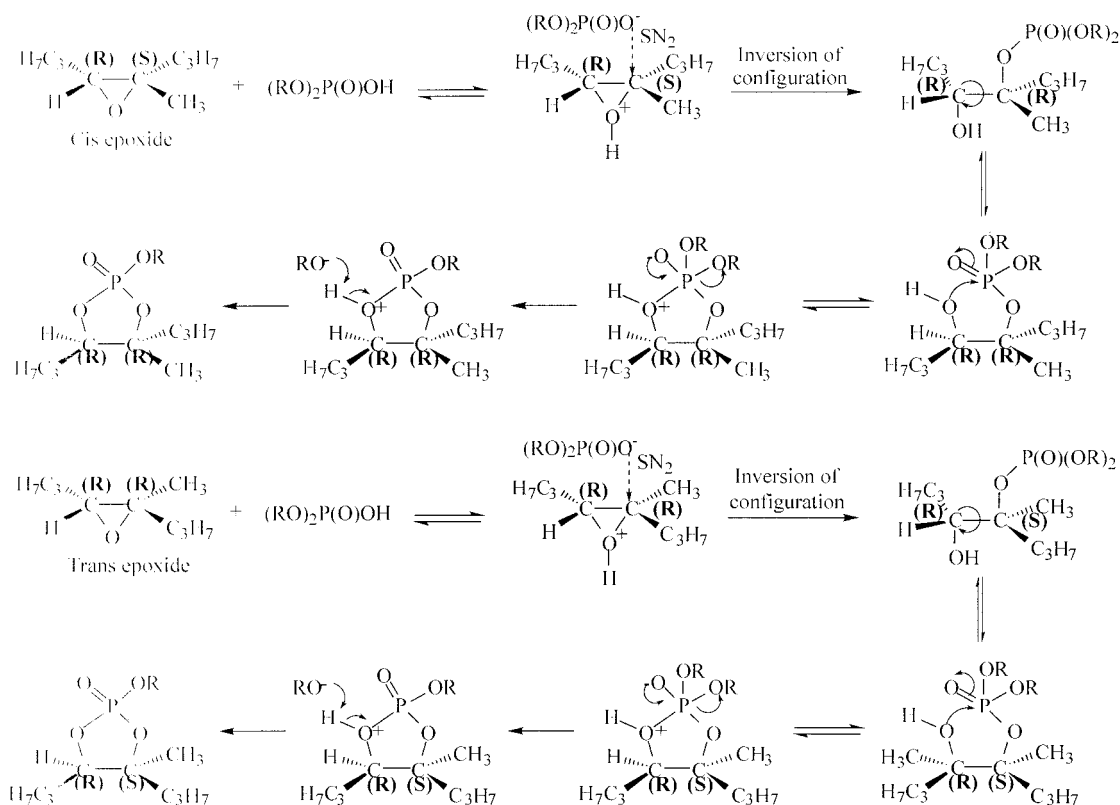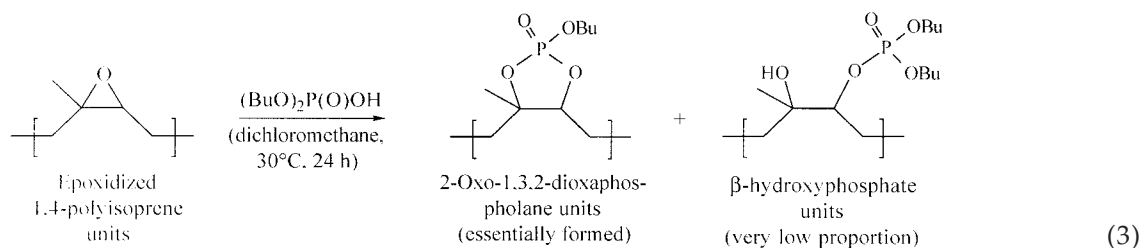
Figure 2 Mechanisms of the formation of the various 2-butoxy-2-oxo-1,3,2-dioxaphospholanes from *cis*- and *trans*-4,5-epoxy-4-methyloctane.

the phosphorus), is composed of four diastereomers (Fig. 1).

As has been demonstrated previously, a cis epoxide is transformed into *trans*-2-oxo-1,3,2-dioxaphospholane, and vice versa (Fig. 2),[3] so each diastereomer formed can be precisely identified in ^{31}P-NMR. By taking into account that 4,5-epoxy-4-methyloctane was composed of 62% cis epoxides and 38% trans epoxides and that [area sum of signals at $\delta = 14.19$ and 14.59 ppm]/[area sum of signals at $\delta = 15.30$ and 15.63 ppm] = 62/38, we attributed the respective signals at $\delta = 14.19$ and 14.59 ppm to the trans–cis and trans–trans dioxaphospholane diastereomers and those at $\delta = 15.30$ and 15.63 ppm to the cis–trans and cis–cis ones.

Whatever the reaction conditions were (in bulk or in a solvent), the reaction of DBP with epoxidized units of a 22% epoxidized 1,4-polyisoprene occurred in a way very similar to that observed for the model molecule:

$$\tag{3}$$

Epoxidized 1,4-polyisoprene units → (BuO)$_2$P(O)OH (dichloromethane, 30°C, 24 h) → 2-Oxo-1,3,2-dioxaphospholane units (essentially formed) + β-hydroxyphosphate units (very low proportion)

A total disappearance of the signal characteristic of the oxirane hydrogens ($\delta = 2.70$ ppm) was noted on the ^{1}H-NMR spectra of the polymers obtained in bulk and in solution. The formation of 2-butoxy-2-oxo-1,3,2-dioxaphospholane units is confirmed by ^{31}P-NMR by the presence of four peaks at 14.12, 14.53, 15.30, and 15.53 ppm that characterize the presence of four diaste-

reomers, as previously noted during the study achieved with 4,5-epoxy-4-methyloctane. β-Hydroxyphosphate units were also characterized on the ^{31}P-NMR spectra ($\delta = 1.38$ ppm), but in very low proportions with respect to the dioxaphospholane units (3% after 3 h). No side structures were characterized. The best addition yields were observed when the reaction was carried out in bulk.
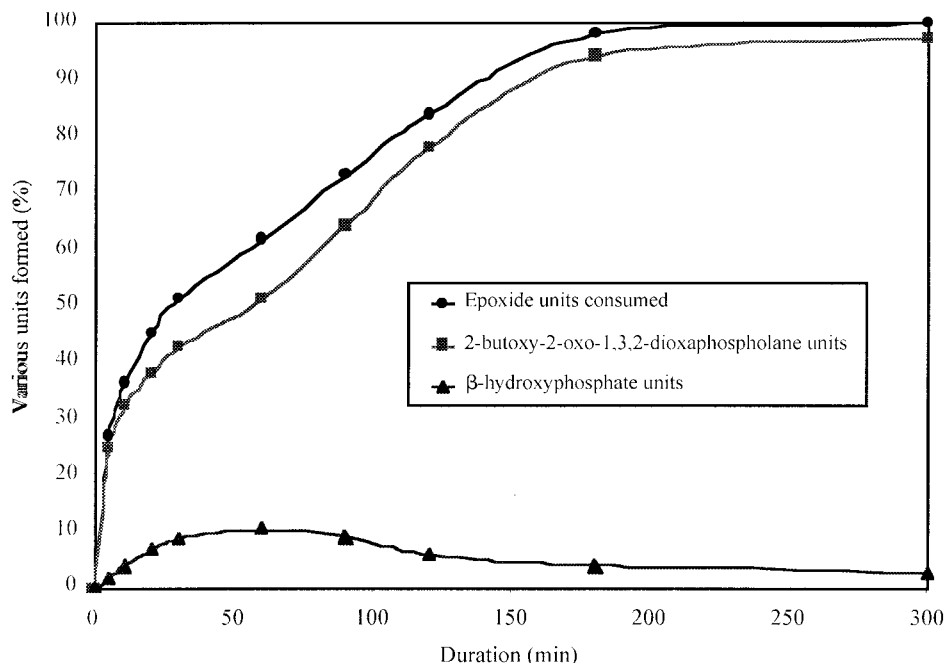
Figure 3 Reaction of DBP with 22% epoxidized polyisoprene in dichloromethane (20% epoxidized polyisoprene in dichloromethane; [DBP]/[epoxidized units] = 1 mol mol^{-1}; temperature = 30°C; rate of DBP addition = 3.8 mL/min).

The reaction of DBP with 22% epoxidized 1,4-polyisoprene is fast, as demonstrated by a kinetic study performed in dichloromethane (Fig. 3). Epoxidized units were totally consumed after 3 h, and the formation of 2-oxo-1,3,2-dioxaphospholane and β-hydroxyphosphate units was noted right at the start of the reaction. Moreover, it was observed that the proportion of β-hydroxyphosphate units reached a maximum and then decreased. By taking into account previous results, particularly the kinetics of the addition of 2-chloroethylphosphonic acid to 2,3-epoxy-2-methybutane, which showed that α addition was highly favored in comparison with β addition,[9] and the fact that the ratio of α/β-ring opening was the same whatever the structure of the P—OH acid used was,[10] we suggest that the α addition of DBP groups to epoxidized units is probably highly favored.

From these results, a scheme was proposed to explain the reaction carried out in dichloromethane (Fig. 4). First, the acid adds itself to the oxirane ring, especially according to an α addition, to lead to a β-hydroxyphosphate structure. Because of their very high

reactivity, the β-hydroxyphosphates resulting from the α addition are immediately transformed into 2-butoxy-2-oxo-1,3,2-dioxaphospholane (they could not be identified on the NMR spectra of the various samples taken because of their very short lifetime). The transformation of β-hydroxyphosphates resulting from a β addition (minority) is much slower, explaining why they are characterized in the ^{31}P-NMR spectra.

Study in a latex medium

The chemical modification in a latex medium was carried out on two types of rubber latex stabilized with 3 phr Sinnopal NP 307: a 22% epoxidized synthetic 1,4-polyisoprene (DRC 20%) and a 6% epoxidized natural rubber latex (DRC 5%).

The addition of DBP was first carried out with an emulsion of 4,5-epoxy-4-methyloctane stabilized by 3 phr Sinnopal NP 307 (at 50°C for 24 h). Under these conditions, 4,5-epoxy-4-methyloctane was essentially transformed into 2-hydroxy-4-methyl-4,5-di-n-propyl-2-oxo-1,3,2-dioxaphospholane:
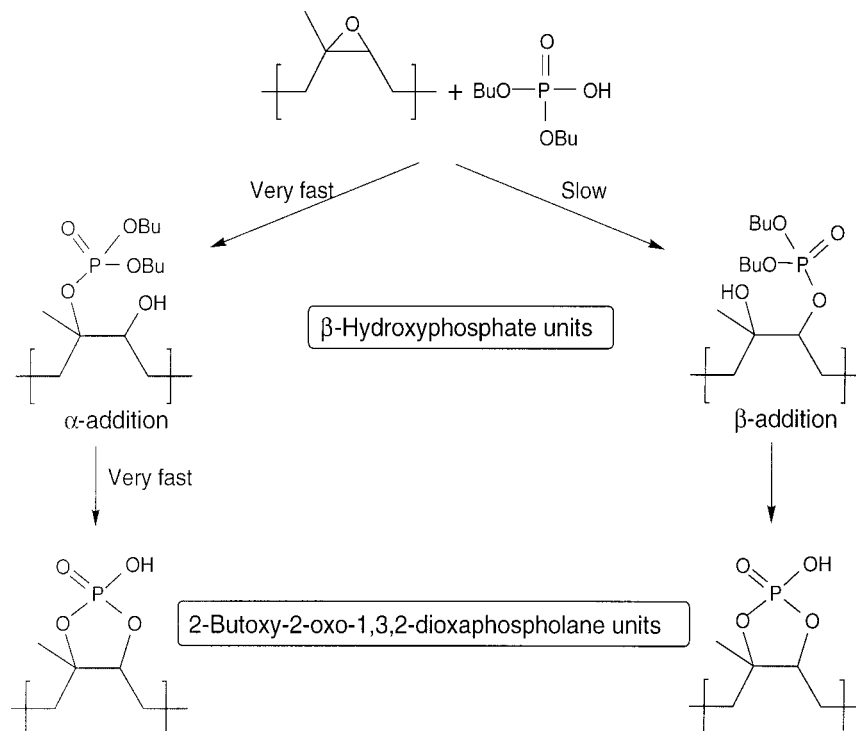

(4)
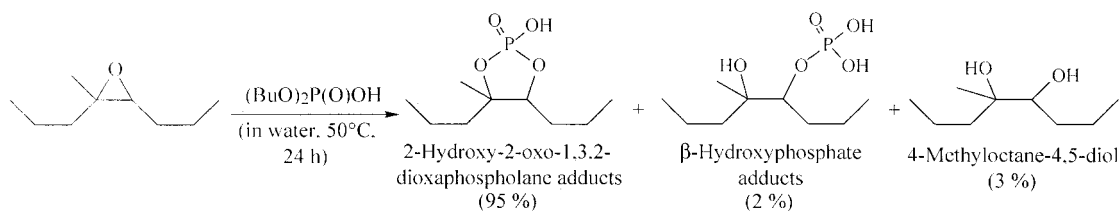
Figure 4 Schematic representation of the addition of DBP to epoxidized 1,4-polyisoprene in dichloromethane.
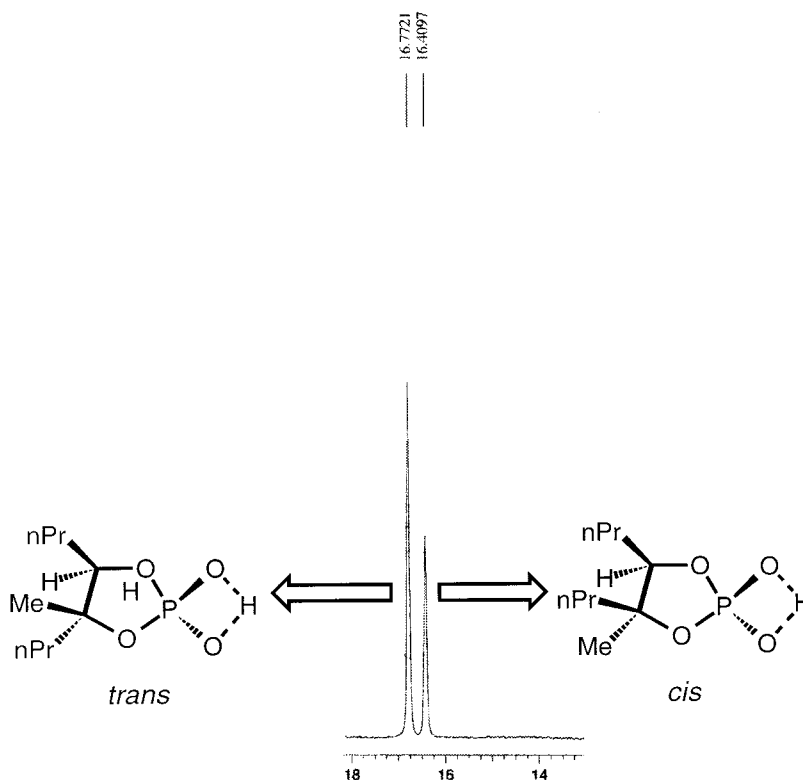
Figure 5 ^{31}P-NMR characterization of the various 2-butoxy-2-oxo-1,3,2-dioxaphospholane diastereomers formed during the reaction in the emulsion of DBP with 4,5-epoxy-4-methyloctane.

Its formation was confirmed with ^{31}P-NMR (two peaks at 16.41 and 16.77 ppm; Fig. 5) by comparison with the ^{31}P-NMR spectrum of the compound obtained after the hydrolysis of 2-butoxy-4-methyl-4,5-di-*n*-propyl-2-oxo-1,3,2-dioxaphospholane.[3] The presence of only two peaks is explained by the formation of a hydrogen bond between P=O and P—OH functions, which cancels the chirality of the phosphorus atom. On the basis of a comparison of the respective areas of the ^{31}P-NMR signals with the composition of initial 4,5-epoxy-4-methyloctane (62% cis and 38% trans), the highest signal at $\delta = 16.77$ ppm was attributed to *trans*-dioxaphospholane, and the other at $\delta = 16.41$ ppm was attributed to the cis one. The pres-

ence of β-hydroxyphosphate acid structures was equally noted on the ^{31}P-NMR spectrum at $\delta = 1.65$ ppm, but in a low quantity. Moreover, about 3% 4-methyloctane-4,5-diol was also formed during the reaction; it was identified with ^{1}H-NMR [the signal at $\delta = 3.40$ ppm is characteristic of —**CH**(OH)— protons].

Performed under the same conditions used for the organic medium, the reaction of DBP with 22% epoxidized latex (DRC 20%, 3 phr Sinnopal NP 307, 30°C) occurred with slight differences. With respect to the results obtained in an organic medium, β-hydroxyphosphate and 2-oxo-1,3,2-dioxaphospholane units were really formed, but in their acidic form:

(5)
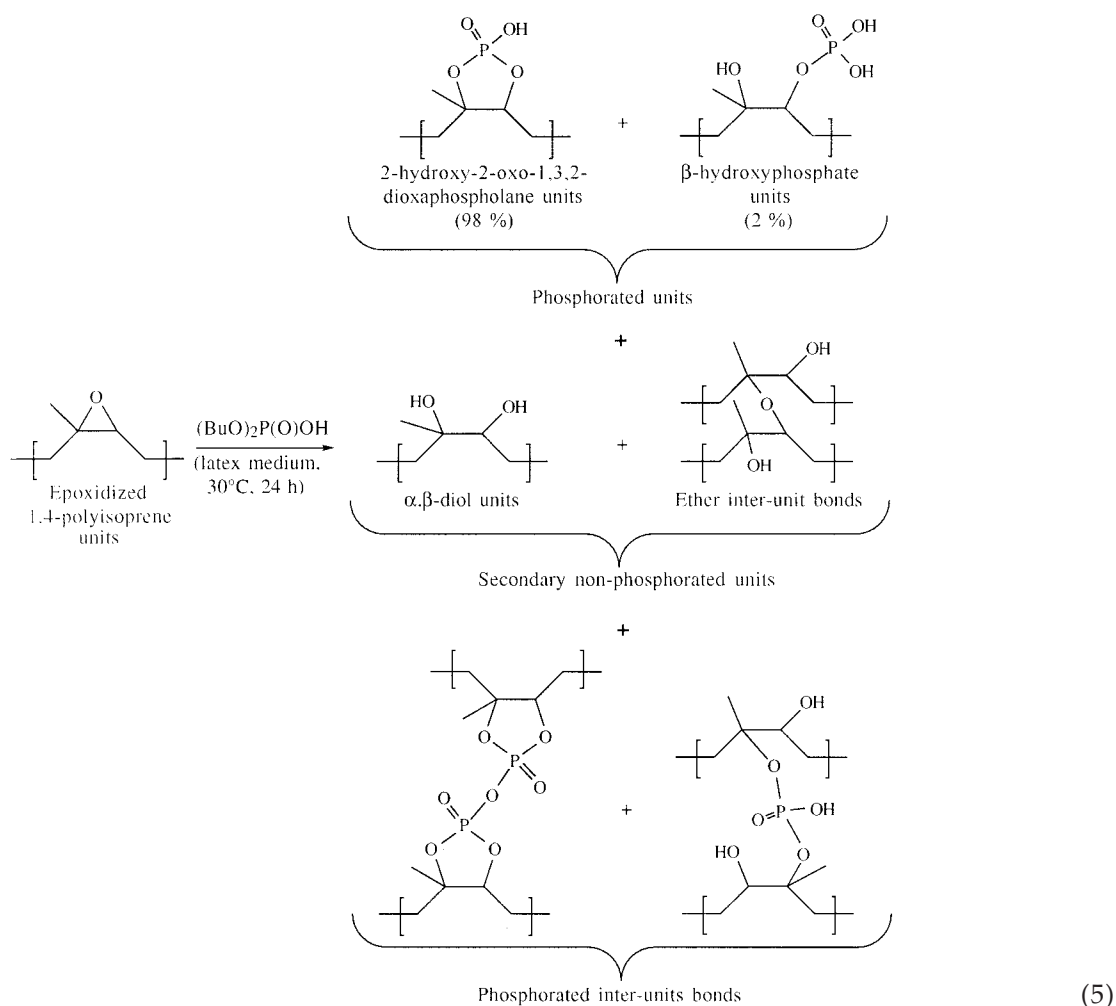
In ^{31}P-NMR, —O—P(O)(OH)$_2$ groups of β-hydroxyphosphate units were characterized at $\delta = 1.62$ ppm, and the 2-hydroxy-2-oxo-1,3,2-dioxaphospholane microstructures were characterized at $\delta = 16.00$ and 16.34 ppm. The most important signal at $\delta = 16.00$ ppm was attributed to *trans*-dioxaphospholane (it came from the cis-epoxidized units, whose proportion

was higher than that of the trans ones, in the initial epoxidized polyisoprene). This characterization was confirmed by reference to the results obtained with epoxidized natural rubber latex (entirely composed of cis-epoxidized units). In this case, the dioxaphospholane units formed were characterized in ^{31}P-NMR by only one peak at $\delta = 16.00$ ppm. However, the butanol
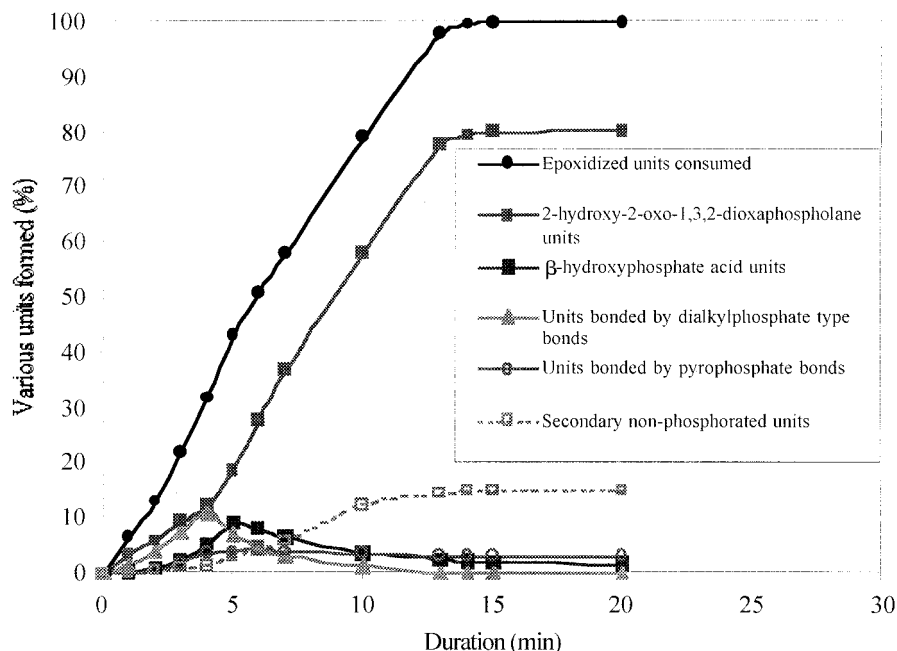
Figure 6 Reaction of DBP with 22% epoxidized synthetic latex (20% DRC; 3 phr Sinnopal NP 307; [DBP]/[epoxidized units] = 1 mol mol^{-1}; temperature = 30°C; rate of DBP addition = 3.8 mL/min).

released during the reaction (during the formation of dioxaphospholanes or by the hydrolysis of butylphosphate bonds) was characterized by ^{1}H and ^{13}C-NMR.

Contrary to the reaction carried out in a solvent or in bulk, secondary processes occur in a latex medium, leading essentially to the formation of phosphorated and nonphosphorated interunit bonds. By taking into account the bibliographic data[11] and the results obtained with a latex of epoxidized squalene (totally trans), we deduced that the new peaks observed in the ^{31}P-NMR spectrum at δ = −3.84 and −4.20 ppm were characteristic of pyrophosphate interunit bonds formed between two 2-hydroxy-2-oxo-1,3,2-dioxaphospholanes groups. The signal at δ = −2.00 ppm corresponded to dialkylphosphate-type bonds formed by reactions between the residual epoxides and the β-hydroxyphosphates coming from an α addition.

The kinetic study of the reaction (Fig. 6) showed that the rate of epoxide consumption was much higher than that observed in the organic medium (totally consumed after 15 min as opposed to 3 h in the organic medium), demonstrating a higher reactivity of DBP toward oxirane rings in a latex medium. Moreover, as for the reaction performed in solution, the addition of DBP groups could occur in the α or β positions of the oxirane, the addition in the α position being highly favored.[9,10] The maximum observed on the curve giving the variation of the proportion of β-hydroxyphosphate acid units coming from a β addition demonstrates that the transformation of these forms into 2-hydroxy-2-oxo-1,3,2-dioxaphospholane units is slow.

However, at the beginning of the reaction, the rates of formation of 2-hydroxy-2-oxo-1,3,2-dioxaphospholane units and dialkylphosphate-type bonds between two epoxidized units are similar but higher than that of the formation of β-hydroxyphosphate acid units coming from a β addition. This shows that, during this first step, the cyclization of β-hydroxyphosphate structures in 2-oxo-1,2,3-dixoaphospholanes competes with its addition on another oxirane ring through the dihydroxyphosphate function. Moreover, the maximum observed on the curve giving the variation of the proportion of units bonded by dialkylphosphate-type bonds proves the instability of these structures: they rearrange to form 2-hydroxy-2-oxo-1,3,2-dioxaphospholane and α,β-diol units, as demonstrated on the graph by the increase in the proportions of these last structures. With respect to the pyrophosphate bonds (ca. 3% of the epoxidized units transformed), they are essentially formed at the beginning of the reaction. Finally, after total consumption of the epoxidized units, the global composition of the modified rubber remains unchanged with time.

On the basis of these different remarks, a scheme of the reaction of DBP with the synthetic latex of epoxidized polyisoprene was proposed to explain the formation of the various units characterized (Fig. 7). The β-hydroxyphosphate formed by α addition is quickly hydrolyzed in its diacid form, which can immediately react with itself to form a 2-hydroxy-2-oxo-1,3,2-dioxaphospholane unit or with a neighboring epoxidized
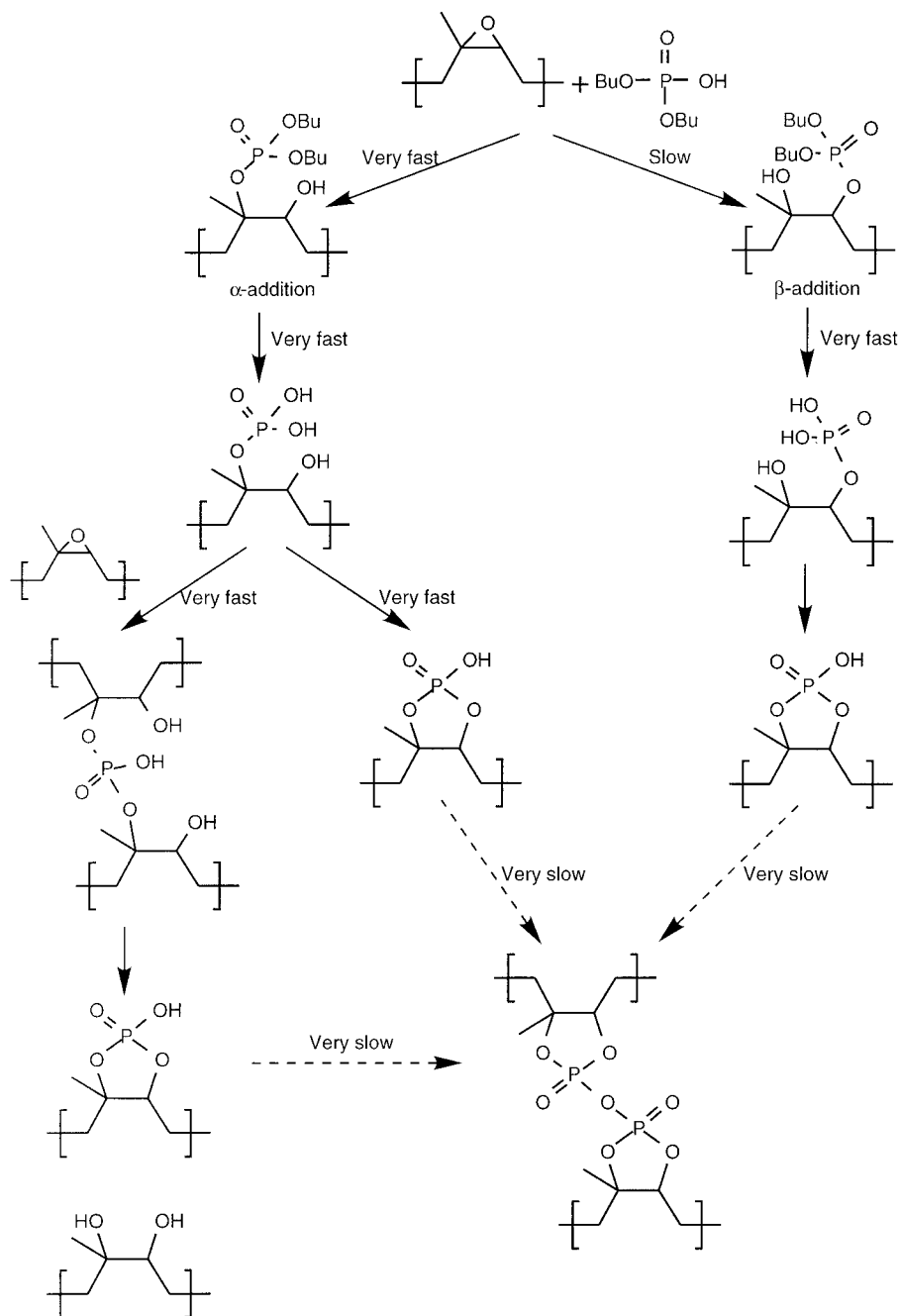
Figure 7 Schematic representation of the addition of DBP to epoxidized 1,4-polyisoprene in a latex medium.

unit of the same (or other) polymer chain to create a dialkylphosphate-type bond that afterward rearranges into 2-hydroxy-2-oxo-1,3,2-dioxaphospholane and α,β-diol units. The β-hydroxyphosphate units formed by β addition are quickly hydrolyzed into their diacid form and then slowly transformed into 2-hydroxy-2-oxo-1,3,2-dioxaphospholane units. Pyrophosphate bonds result from a condensation reaction between two neighboring 2-hydroxy-2-oxo-1,3,2-dioxaphospholane units.

Chemical modification by 2-chloroethylphosphonic acid (ethephon)

The reaction of 2-chloroethylphosphonic acid (or ethephon), a well-known stimulating molecule for the production of latex by *Hevea brasiliensis*, with epoxidized polyisoprenes was investigated for the preparation of systems able to allow a controlled release of ethephon with time (ethephon is bonded to the polymer backbone by a hydrolyzable bond), with the aim
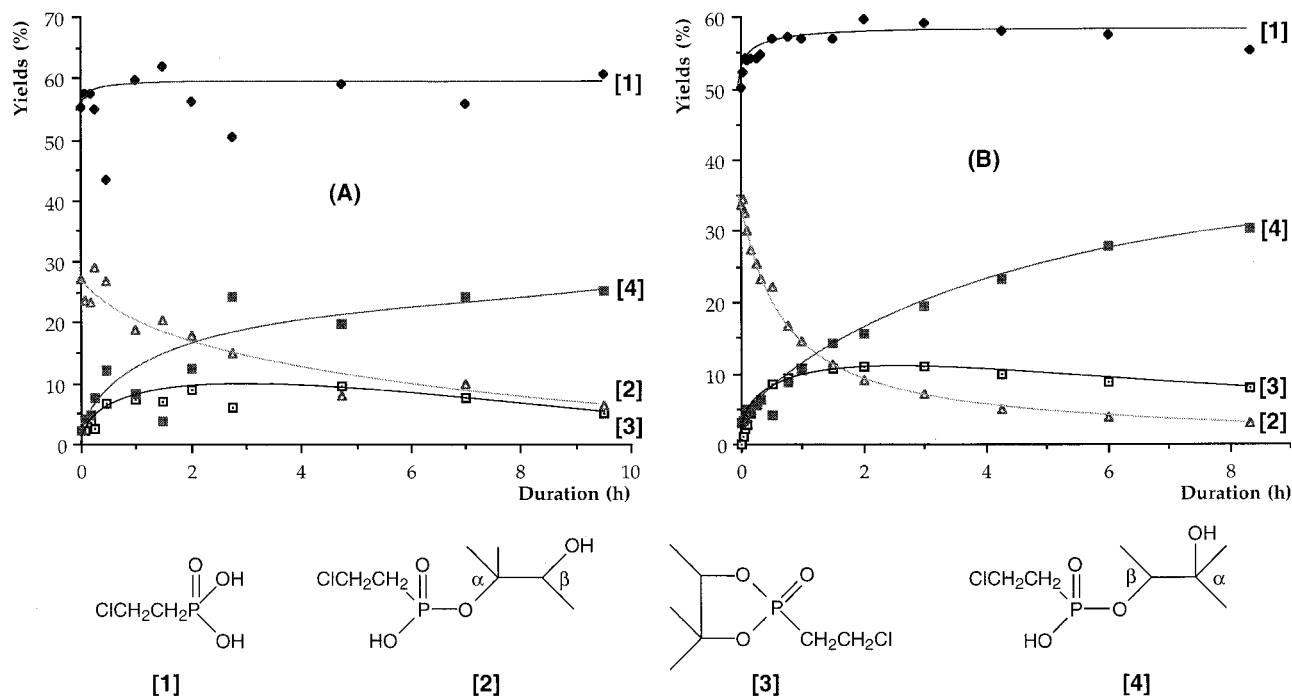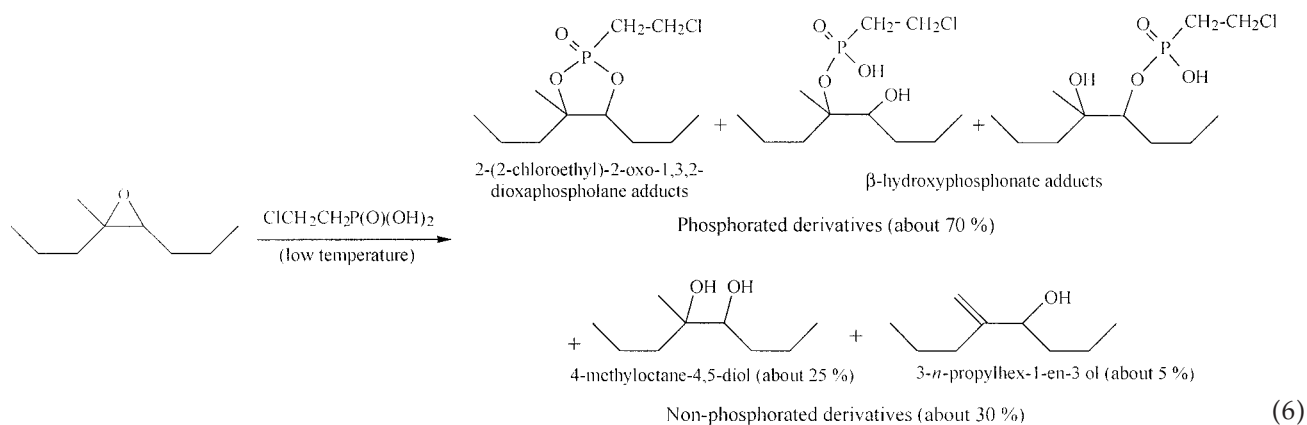
Figure 8 Addition of ethephon to 2,3-epoxy-2-methylbutane (A) without a solvent and (B) in CDCl₃.

being to prolong the activity of stimulation for latex production by *Hevea brasiliensis*.[12–16]

The addition of ethephon to a stoichiometric quantity of 4,5-epoxy-4-methyloctane occurs similarly to that of DBP:

(6)

Whatever the reaction conditions were (at a low temperature in a solvent or without a solvent), the following derivatives were characterized:

- Various phosphorated adducts distributed in β-hydroxyphosphonate adducts, whose phosphorated group was bonded in the α position of the oxirane ring (on the most substituted carbon) or in the β position, and cyclic 2-oxo-1,3,2-dioxaphospholane adducts composed of four diastereomers.
- Several nonphosphorated compounds derived from 4,5-epoxy-4-methyloctane (ca. 30% of the compounds obtained), including α,β-diols coming from the oxidative opening of the oxirane rings (or the hydrolysis of the phosphorated adducts) and allylic alcohols formed by rearrangement of the epoxide. The secondary processes were greatly favored in the acidic medium.

Kinetic studies of the addition of ethephon to 2,3-epoxy-4-methylbutane were performed without a solvent [Fig. 8(A)] and in CDCl₃ [Fig. 8(B)].[9] These kinetic studies showed an instantaneous reaction between ethephon and the epoxide. A significant ethephon consumption (ca. 50%) was observed immediately af-
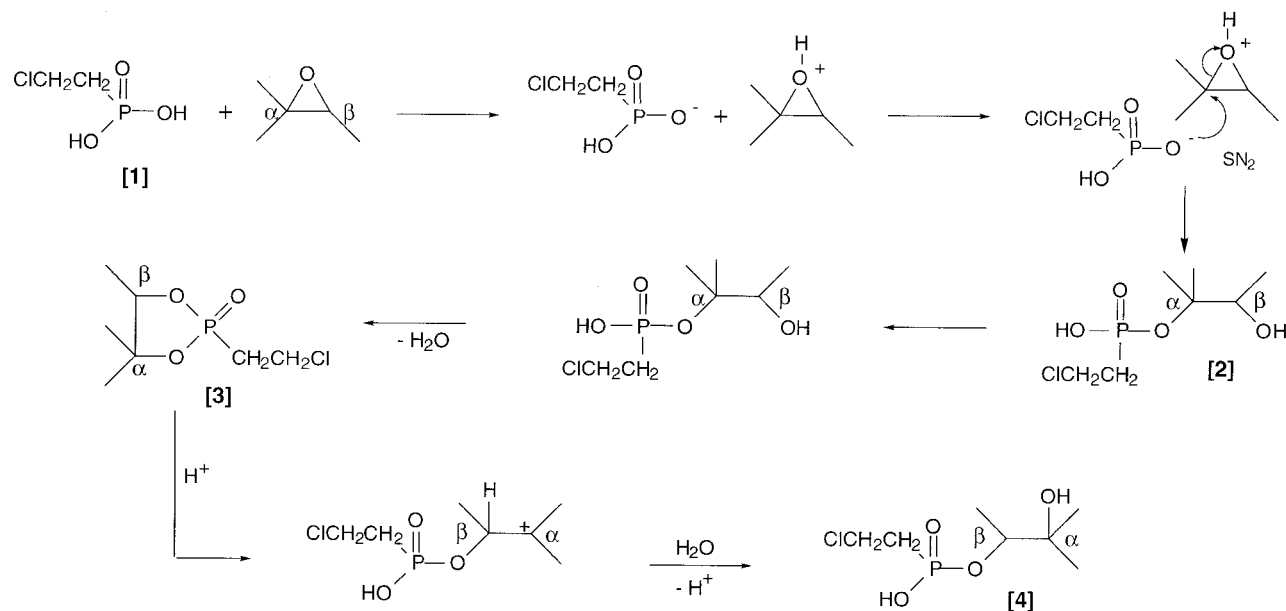
Figure 9 Mechanism of the addition of ethephon to trialkyl-substituted epoxides.

ter the start of the reaction, as well as the formation of the β-hydroxyphosphonate regioisomer with the phosphorated group bonded to the most substituted carbon of the oxirane (α addition). Simultaneously, a total consumption of the epoxide was noted.

Thereafter, the ethephon proportion did not progress any more, at which point changes in the composition of the 1:1 phosphorated adduct mixtures were noted as the reaction duration increased. The initially formed β-hydroxyphosphonate disappeared gradually to reach a final proportion of 5%. In return, the 2-oxo-1,3,2-dioxaphospholane adduct, and the β-hydroxyphosphonate adduct with the phosphorated group bonded to the least substituted carbon of the initial oxirane, appeared slowly within the first seconds of the reaction, and afterward, their respective proportions increased. However, as the global proportion in 2-oxo-1,3,2-dioxaphospholane increased during the first 2 h and then decreased, that of the β-hydroxyphosphonate followed a constant increase with time. Consequently, the formation of the 2-oxo-1,3,2-dioxaphospholane adduct and, afterward, that of β-hydroxyphosphonate with the phosphonated group bonded on the least substituted carbon of the oxirane ring were the result of several successive conversions from the β-hydroxyphosphonate adduct initially formed, as shown in Figure 9.

A good result was achieved by the replacement of ethephon with its trimethylsilylated derivatives [monotrimethylsilyl 2-chloroethylphosphonic acid or di(trimethysilyl) 2-chloroethylphosphonate]. Addition could also occur through a trimethylsilyl phosphonate bond, which led to high yields in phosphorated ad-

ducts, especially when di(trimethysilyl) 2-chloroethylphosphonate was used (Table I). The highest yields obtained when the reaction was carried out with the trimethylsilylated derivatives of ethephon were explained by the low acidity of the reaction medium, which unfavorably affected rearrangements and oxidative openings of the epoxides catalyzed by acids.

The generalization of the reaction to a 20% epoxidized 1,4-polyisoprene led to results comparable to those obtained with the model molecules, in that 2-oxo-1,3,2-dioxaphospholane and β-hydroxyphosphonated units were formed (Table II). Optimized conditions of reaction with epoxidized polyisoprene were achieved with di(trimethysilyl) 2-chloroethylphosphonate as a reagent. Under these conditions, the yields in phosphorated units, essentially composed of 2-oxo-1,3,2-dioxaphospholane units, were greater than 60%.

CONCLUSIONS

In conclusion, phosphate acid and phosphonate acid derivatives add to trisubstituted oxirane structures in the same manner. In the first step, an SN_2 nucleophilic substitution with ring opening of the oxirane occurs principally at the most substituted carbon of the oxirane structure, leading to the formation of a β-hydroxyphosphate (or phosphonate) intermediate that is immediately transformed into a 2-oxo-1,2,3-dioxaphospholane structure. This orientation of the reaction is favored by the electrodonor effect of the methyl. The mechanisms, however, differ after the

TABLE I
Addition of Ethephon-[or Monotrimethylsilyl 2-Chloroethylphosphonic Acid or Di(trimethylsilyl) 2-Chloroethylphosphonate] on 4,5-Epoxy-4-methyloctane

Phosphorated reagent	Residual phosphorated reagent[a] (%)	Total phosphorated adducts formed (%)	Phosphorated adducts[a] (%) Distribution (%)	
			2-Oxo-1,3,2-dioxa-phosphalane adducts	1:1 Adducts
$ClCH_2CH_2P(=O)(OH)(OH)$	58.4	41.6	86.3	13.7
$ClCH_2CH_2P(=O)(OH)(O\text{-}SiMe_3)$	30.8	69.2	93.9	6.1
$ClCH_2CH_2P(=O)(O\text{-}SiMe_3)(O\text{-}SiMe_3)$ (SnCl₂ as catalyst)	17.3	82.7	100	0

Reaction conditions: without solvent, 20°C, 24 h, (Phosphorated reagent)/(Epoxide) = 1 mol mol⁻¹
[a] Calculated from ³¹P-NMR spectra.

2-oxo-1,2,3-dioxaphospholane formation. When the SN₂ substitution occurs in the β position of the oxirane, the cyclization reaction leading to the formation of 2-oxo-1,3,2-dioxaphospholane is lower.

Two noteworthy findings are that phosphonate derivatives can be added to epoxide functions via trimethylsilyl phosphonate bonds and that the kinetics of DBP addition to epoxidized polyisoprene units are

TABLE II.
Addition of Ethephon [or Monotrimethylsilyl 2-Chloroethylphosphonic Acid or Di(trimethysilyl) 2-Chloroethylphosphonate] on 20% Epoxidized 1.4-Polyisoprene.

Phosphorated reagent	Solvent ($\varepsilon;\mu$)	Residual phosphorated reagent[a] (%)	Residual epoxidized units[b] (%)	Total phosphorated units formed[c] (%)	Phosphorated units[a] (%) Distribution (%) 2-Oxo-1,3,2-dioxaphospholane units	β-hydroxy-phosphonate units
$ClCH_2CH_2P(=O)(OH)(OH)$	Without	42.5	0	57.5	24	76
	dioxane (2:2; 0.45)	59.5	—	40.5	80	20
	tetrahydrofurane (7.6; 1.75)	78	9	22	100	0
$ClCH_2CH_2P(=O)(OH)(O\text{-}SiMe_3)$	Without	53.5	0	46.5	38	62
	dioxane	45	—	55	68	32
	tetrahydrofuran	60	32	40	100	0
$ClCH_2CH_2P(=O)(O\text{-}SiMe_3)(O\text{-}SiMe_3)$	Without	38	0	62	100	0
	dioxane	95	—	5	100	0
	tetrahydrofurane	62	0	38	100	0

Reaction conditions: 20°C, 24 h, (Phosphorated reagent)/(Epoxidized units) = 1 mol mol⁻¹
[a] Determined from ³¹P-NMR spectra.
[b] Determined from ¹H-NMR spectra.
[c] Global proportions of epoxidized units transformed in phosphorated units (2-oxo-1,3,2-dioxaphospholane plus β-hydroxyphosphonate units).

much higher in a latex medium than in organic solvents.

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