Chemical Modifications of Polydiene Elastomers: A Survey and Some Recent Results

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ABSTRACT: By chemical modification of natural rubber, it is possible to modify its basic properties (for instance, improvement of gas permeability, resistance to oils or fire resistance) or to prepare new polymeric materials for specific applications (for instance, photocrosslinkable rubbers and rubbers support of active molecules). The purpose of the present paper is to give an overview of recent works carried out in the field of new rubber derivatives for specific applications, especially dealing with natural rubber degradation and products derived from liquid rubbers of type 1,4-polyisoprene (liquid natural rubbers, synthetic polyisoprenes) and/or their epoxidized forms. A reflexion on the perspectives of researches on natural rubber or its derivatives is given in conclusion. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1461–1477, 2000

Key words: natural rubber; degradation; chemical modification

INTRODUCTION

Chemical modifications of natural rubber (NR) have been, for many years, an interesting method for producing new polymeric materials. The first commercially successful modified NRs (hydrochlorinated, chlorinated, and cyclized rubbers) were produced some fifty years ago. A more recent modified form, the epoxidized rubber,[1–5] presently finds several applications, especially in the tyre field. Liquid natural rubber (LNR) is another important derivative that can be easily produced by oxidative degradation of NR by different processes: from the coagulated rubber by mechanical (mastication) or radiation process, or from the latex phase by action of phenylhydrazine/oxygen system. LNR presents an industrial interest especially in two areas: first as a reactive plasticizer, especially in tire processing and high hardness compounds, and second in the production of easier processing NR by blending LNR and conventional rubber in the latex phase. Concerning its epoxidized form, the presence of epoxidized functions gives a possibility of adjusting the damping amount, decreasing gas permeability and improving resistance to oils. The product is of some interest in the adhesives and sealants industry.

Numerous new natural rubber derivatives have been developed during the last decades. The purpose of the present paper is to give an overview of recent works carried out in the field of new natural rubber derivatives for specific applications, especially dealing with natural rubber degradation and new products derived from LNR and/or its epoxidized form.

DEGRADATION

The transformation of high molecular weight polymers into well-defined oligomers by chain cleavage reaction can be considered as a step in a synthetic scheme.

When they are uncontrolled and lead to loss of the required properties for the concerned application, polymer chain cleavages are considered with respect to the degradation of properties resulting from the molecular weight decrease. However, for high molecular weight polymers, molecular weight decrease can be of interest because of the molecular weight/viscosity and viscosity/processability relationships. In this point of view, controlled chain cleavages can be considered with respect to the improvement of the material properties.[6,7]

Controlled chain cleavages of high molecular weight natural or industrial polydienes in order to obtain telechelic polymers were described. Two kinds of cleavages can be considered: oxidative cleavages and metathetical cleavages involving functional olefins. On a preparative point of view, several aspects can be taken into account:

- The control of the average molecular weights in relation with the cleavage reaction yield.
- The control of the molecular weight distributions in relation with the random or nonrandom cleavages.
- The control of the chain-end microstructure in relation with the specificity of the cleaving reaction.
- The possibility to perform the chain cleavage in a latex phase rather than in an organic solution

Oxidative Chain Scission

Telechelic oligomers with terminal ketone and/or carboxylic groups depending on the double bond structure can be obtained by specific oxidative double-bond cleavages of 1,4-butadiene, 1,4-isoprene, or other unsaturated units in homopolymers and copolymers (Fig. 1).

Carbon–carbon double bond cleavages by ozonolysis at first performed with an analytical purpose on butyl rubber[8] were recently applied, with a preparative purpose, to copolymers containing a controlled amount of 1,4-polydienic or polyacetylenic units.[9–11] Specific cleavages by the action of specific oxidizing agent such as ruthenium tetroxides[12,13] have also been shown efficient.

Telechelic oligomers with terminal hydroxy groups were more difficult to obtain specifically by direct oxidative chain cleavages.

Oxidative photodegradation of natural rubber with hydrogen peroxide[14,15] and oxidative degra-
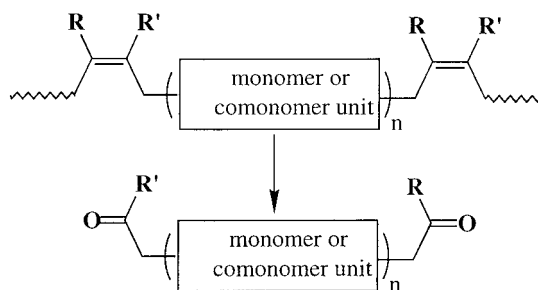

Figure 1 Synthesis of telechelic oligomers by specific oxidative double bond cleavages of 1,4-butadiene, 1,4-isoprene, or other unsaturated units.

dation with periodic acid were described. Functionalities around 2 were observed[16] but explicit mechanisms were not described. To get hydroxy-terminated polydienes, the reduction of higher oxidized terminal group can be considered. On this basis, we can mention the specific ozonolysis of high molecular weight *cis*-1,4-polybutadiene followed by specific reduction of the intermediary polymeric ozonide.[17] The hydroxy terminated liquid polybutadienes obtained are highly *cis*-1,4, be known difficult to be prepared by direct telomerization.

On the other hand, considering the rubber latex as a biological source of materials, the controlled oxidative degradation of the high molecular weight polyisoprenes contained in rubber latex has been considered through two main ways:

- the degradation process patented by IRCA.[18,19] In this degradation process, the oxidative degradation is accelerated by using air/phenylhydrazine redox system. The polyisoprenic oligomers molecular weights can be controlled by the phenylhydrazine ratios until an appreciable low floor limit. The mechanism and the terminal group determination were approached by studies on molecular polyisoprenic models.
- the possibility to drive epoxidation and specific epoxide cleavages in the latex medium.

Phenylhydrazine Accelerated Oxidation

Liquid polymer with 1,4-*cis* polyisoprene structure can be obtained from the degradation of natural rubber latex by action of phenylhydrazine with oxygen (Fig. 2). The decomposition is expected to arise by random cleavages and the macromolecular weight, controlled by phenylhydrazine ratios. Nevertheless, degradation limitation
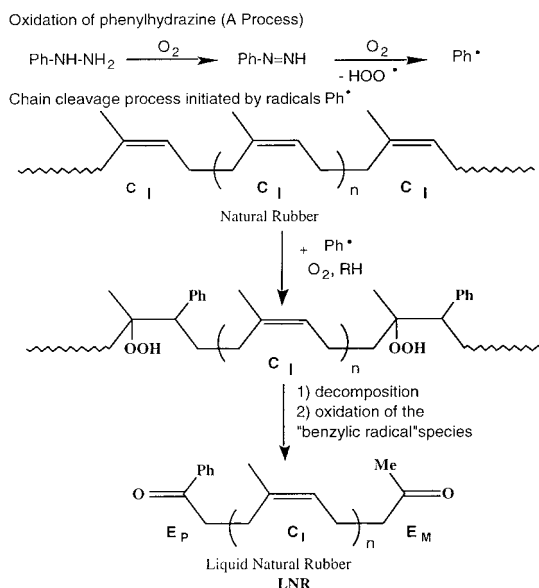
Figure 2 Degradation of natural rubber latex by action of phenylhydrazine with oxygen.

Figure 3 Oxidation of phenylhydrazine (B process).

was observed when relative phenylhydrazine ratios and reaction time increase. The first studies driven on 4,8-dimethyldodeca-4,8-diene and on squalene in organic or aqueous medium have allowed us to propose a new chain cleavage mechanism.[20]

The results were explained by the, namely, *A Process* (Fig. 2) of phenylhydrazine oxidation by direct reaction with oxygen. This process leads to the formation of phenyl radicals. The addition of phenyl radical on carbon–carbon double bonds and the decomposition of the derived peroxides lead to the formation of methylketone and phenylketone terminal groups (Fig. 2). Further studies on γ,δ-ethylenic methylketone and γ,δ-ethylenic phenylketone models have led to propose reactions involving ketones, phenylhydrazine and oxygen.[21]

These results correspond to a *B Process* (Fig. 3) of phenylhydrazine oxidation by a repetitive reaction cycle in which the carbonyl groups act as a catalyst in the oxidative decomposition of phenylhydrazine.[22,23]

This repetitive cycle was shown to control the chain-scission/crosslinking competition,[23] probably through the α-azohydroperoxide chain-end ($\mathbf{E_A}$) decomposition (Fig. 3).[24–26]

Periodic Acid Cleavages in Epoxidized Polydiene

Many studies were performed on epoxidized natural rubber and related compounds because of

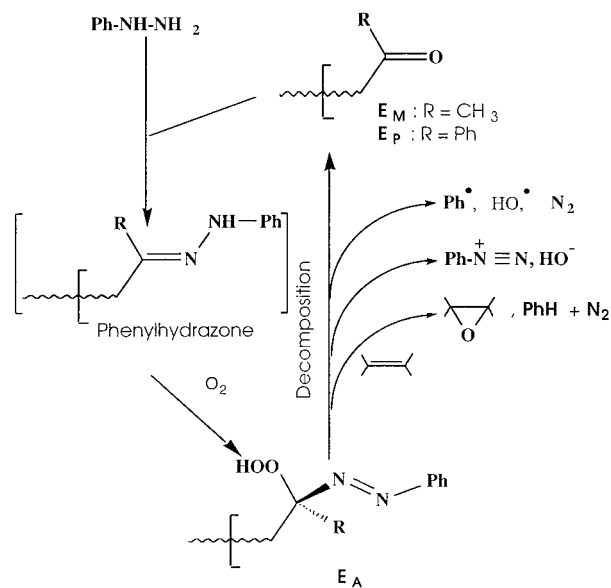their improved properties. Epoxidized polymers can also be used to cleave selectively the epoxidized units with suitable oxidative reagents in order to prepare, according to the epoxy structure and to the oxidative reagent specificity, heterotelechelic or homotelechelic oligomers.

Moreover, the possibility to run epoxidation directly in the latex[28–30] makes possible a direct production of telechelic oligomers on the rubber production site.
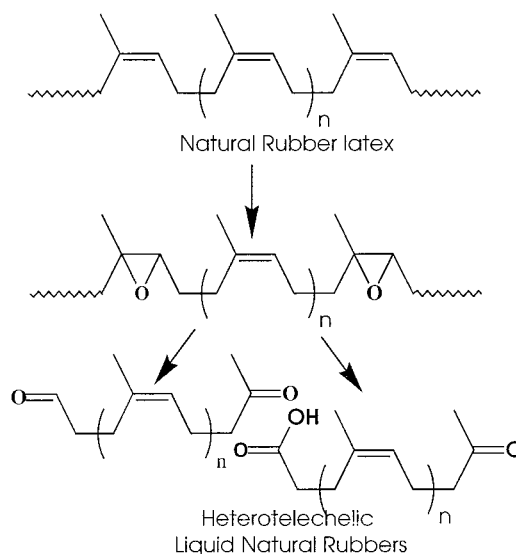

Figure 4 Cleavages by action of periodic acid upon epoxidized polydienes.
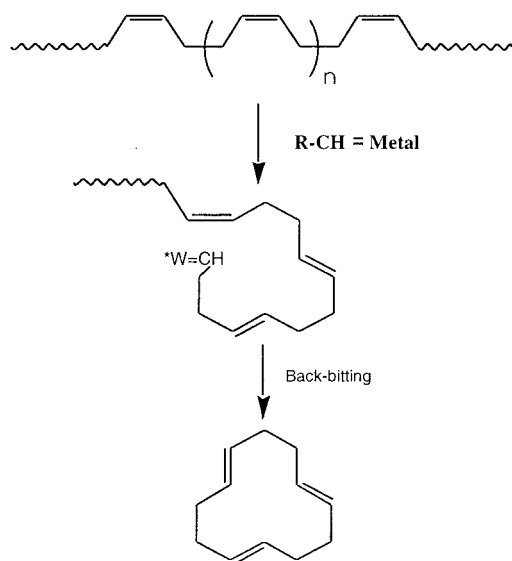
Figure 5 Metathesis by a carbene mechanism.

A first feasibility test was performed on a natural rubber latex stabilized by Berol.[31] Epoxidation was achieved with performic acid (formed *in situ* by reaction of formic acid with hydrogen peroxide) and oxirane cleavages with periodic acid.

The interpretation referring to the molecular weight control has to take into account the cleavage yields, the epoxy cleavable unit amounts, and their distribution. The epoxide furanization makes higher the length of uncleavable units block since the furanic structures are insensitive to the cleaving reagent. Further stabilization of natural rubber latex by Berol and convenient stirring to perform both epoxidation and chain cleavage in the latex phase were carried out. Good results were obtained by using $HCOOH/H_2O_2/C_5H_8 = 1/1/25$ molecular ratios with dry rubber content = 20, and performing the chain cleavage stage by use of $IO_4 - K$ in a $IO_4/C_5H_8O = 1/1$ rather than IO_4H, which induces coalescence of the latex. However, while the molecular weights and polydispersity are higher than expected in the hypothesis of a random distribution of the epoxidized units, molecular weight of the liquid rubbers decreases as the epoxy content increases.

These preliminary results lead to the consideration of the influence of the biphasic reaction medium on the distribution of the epoxidized units along the chain. Further investigations on the possibility to control this cleaving procedure on rubber latex and on synthetic polydiene latex are in progress.

Metathetical Chain Scissions

Metathesis of unsaturated polymers can induce degradations by two processes:

- By metathesis catalysis (especially by metal-lacarbenes) (Fig. 5). The carbene species are transferred to the polymer and induce molecular weight redistribution. In adequate conditions, a back bitting-like mechanism can occur. Such back-bitting reactions induce the formations of cyclic oligomers and bimodal molecular weight distributions as in ring-opening metathesis polymerizations (ROMP) and in acyclic diene metathesis (AD-MET).[32–35]

- By cross metathesis with a symmetric alkene R—CH=CH—R (Fig. 6). The formation of cyclic oligomers competes with the formation of linear oligomers in which polymer units are inserted between the alkylidene groups R—CH= of the alkene.

When R consists of reactive functional group, linear oligomers can be considered as telechelic (i.e. terminally functionalized) oligomers.

The metathetical preparations of telechelic oligomers were first investigated for the preparation of diesters telechelic oligobutadienes. WCl_6/Me_4Sn catalyzed cross-metathesis of polybutadiene with the symmetrical dimethyl-3-hexene-1,6-dioate[36] (Fig. 6, $R = CH_2—COOMe$) was considered at the same level as cross-metathesis telomerization of cyclooctadiene by the same unsaturated diester.[37–39] The limitations for a complete control of the molecular weight decrease[40] would not be the result of a low yield in the cleaving metathesis reaction. They are explained by a selective unproductive metathesis at the chain end (Fig. 7) because of interactions between the active carbene species and the chain-end ester
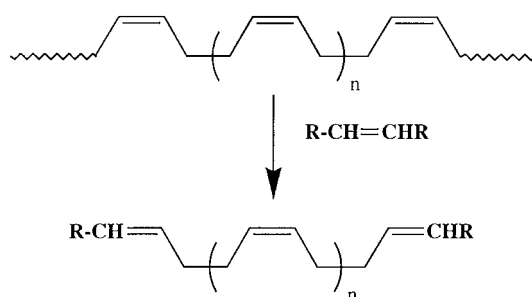

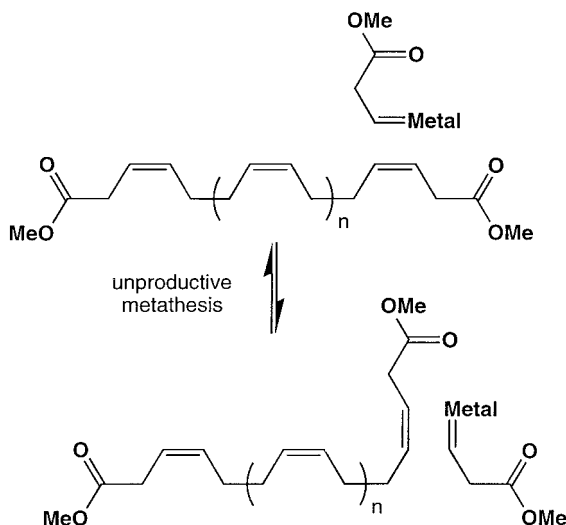**Figure 6** Cross-metathesis with a symmetric alkene.

Figure 7 Selective unproductive metathesis reaction at the chain end.

functions[41] (the resulting unproductive metathesis can be considered as not-random unproductive chain-end cleavages).

The development of this procedure to the preparation of perfectly difunctional telechelic polybutadienes with various functional groups (silanes, esters, silylether, imides, boranes) was made possible[42–44] by using the selective and specific metallacarbene catalysts[35] activities of which are compatible with many functional groups.

In conclusion, the controlled degradation of polymers can be considered as an alternative way in the strategy for the synthesis of well-defined oligomers. In this respect, tailor-made high molecular weight polymers takes place as intermediate in the synthesis schemes. In another point of view, polymers (and eventually crosslinked polymers) from recovery can be considered as raw material to be cleaved in valuable fragmented products for an efficient recycling.

CHEMICAL MODIFICATION

More recently, it has been shown that LNR and ELNR oxidized liquid natural rubber can be good starting products for the synthesis of higher value added materials with specific properties in relation with the expected application. They are basic compounds able to be subjected to subsequent chemical modifications, thereby leading to new products with various useful applications. Their chemical structure offers many possibilities of

chemical transformations involving the highly reactive carbon–carbon unsaturations or epoxidized groups. The purpose here is to expose recent technological applications possibilities of compounds derivated from LNR and ELNR, and on the other hand, to examine and discuss the perspectives of chemical modification of these basic products (NR, ENR, LNR, ELNR) in the future.

LNR and ELNR, as Starting Products for the Synthesis of New Materials

The polymer chemical modification is one of the first tools in macromolecular chemistry. The objectives behind chemical modification research are twofold: on one hand, to improve the behavior and the performances of a basic polymer, on the other, to prepare new materials for specific uses in areas outside its traditional ones.

The development of chemical modification for unsaturated polymers is concerned mainly with the synthetic polyisoprenes and polybutadienes.[46,47] As far as we are concerned, a great deal of studies have been realized in our laboratory: hydroboration, epoxidation, maleinization, carbenization, chlorophosphonylation, phosphorylation, silylation, and metallation are some examples (Fig. 8).

Among the described reactions, some of them have been recently extended to NR and/or its derivatives, especially LNR and ELNR, which can be easily prepared in latex phase by NR degradation[48,49] (Fig. 9). The possibility to obtain directly the epoxidized form by the action of performic acid (prepared *in situ* from the hydrogen peroxide–formic acid couple) on the latex mixture obtained after the degradation step is a great advantage.[50]

The synthesis of polymer-supported active molecules by chemical modification needs the use of specific reactions in order to avoid secondary reactions. In some cases, intermediate functionalization may be necessary to attach an active molecule on the hydrocarbon polymer. In this field, LNR and ELNR are the starting products and their chemical modification may allow new properties and technological interests. Indeed, the presence of carbon–carbon double bonds, or oxirane rings on the rubber backbone is of great interest because of the number of chemical reactions that can be used to add reagents. If LNR can be compared to synthetic liquid 1,4-polyisoprene and used in the same field of applications, it may be useful to use LNR as starting product for preparation of specific polymers for highly technical
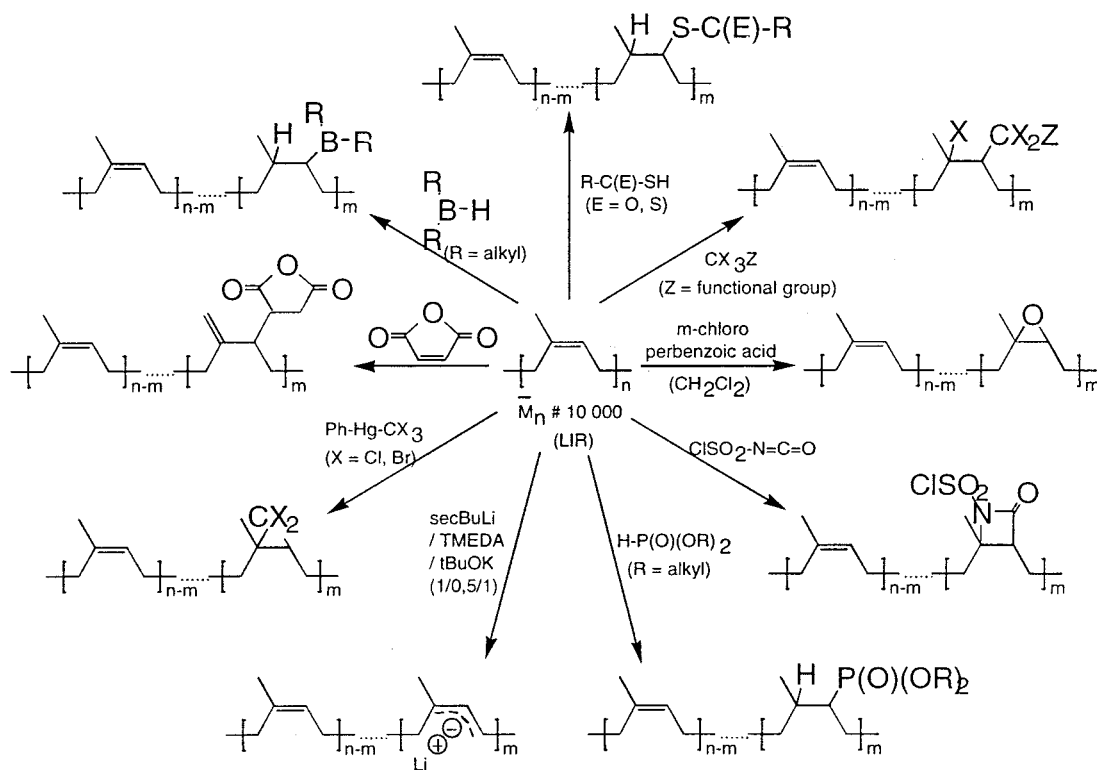
Figure 8 Examples of first-degree chemical modification of 1,4-polyisoprenes.

applications through judicious chemical modification.[50] It is the same for ELNR, whose reactivity of the epoxide groups toward carboxylic acids,[51,52] amines,[53,54] phosphoric acid derivatives,[55] and al-

cohols[56] is well known (Fig. 10). Some recent studies have shown the importance of these compounds in the synthesis of higher value added materials.
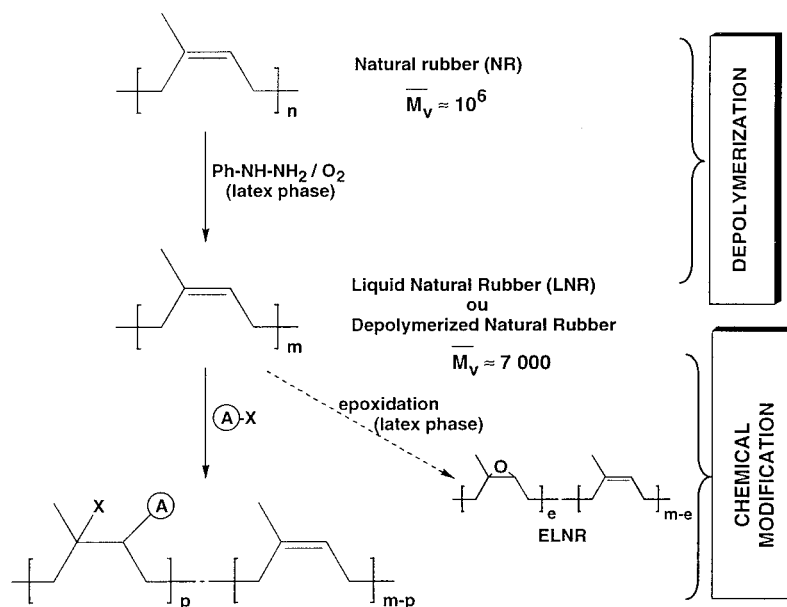

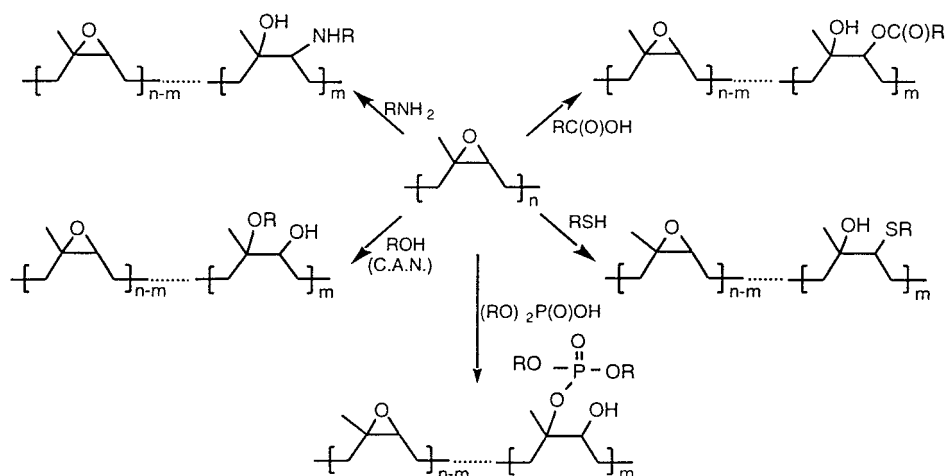**Figure 9** Synthesis of LNR and ELNR derivatives.

Figure 10 Examples of second-degree chemical modification of epoxidized polyisoprene.

An example of second-degree chemical modification is the alcoholysis of epoxidized polyisoprenes by direct opening of oxirane rings with alcohol derivatives (Fig. 11). This modification reaction was reported only recently, probably owing to the missing of an available procedure for carrying the reaction. Indeed, in practice, most epoxide rings are cleaved under acidic conditions that leads to side reactions such as ring opening polymerization of the epoxides, intramolecular rearrangements of epoxide units,[1–5,57,58] and cyclization of polydiene chains. Consequently, mild conditions must be used in order to avoid the undesirable side reactions that generate unsatisfactory yields in β-alkoxyalcohols. In order to achieve the ring opening process of epoxides by alcohols under mild and neutral conditions, a solution was found with the use of cerium ammonium nitrate as catalyst (CAN).[56]
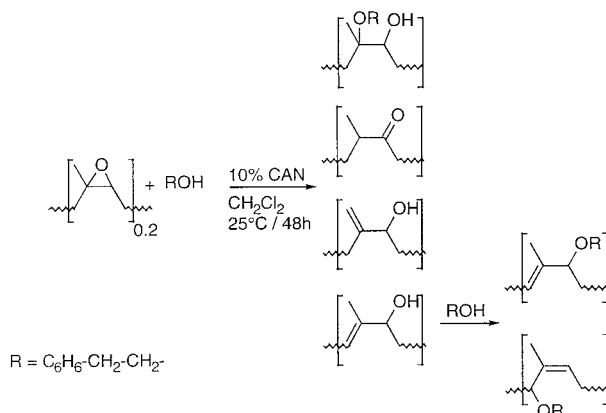

Figure 11 Alcoholysis of epoxidized polyisoprene.

The reaction led in bulk or in solvent medium can be carried out with different type of alcohols. In all cases, the yields of β-alkoxyalcohols were satisfactory (50–70%) and the alcoholysis does not generate any crosslinking or cyclization reactions.

Synthesis of Photocrosslinkable Varnishes

The constant search for new sensitive resins that can be photopolymerized instantly under UV radiation has led to the development of highly reactive functional liquid polymers. As a consequence, UV-curable systems have found widespread applications in various industrial sectors,[59] mainly as photoresists for the production of printing plates and integrated circuits, and as fast-drying resins for varnishes, printing inks, adhesives, and composites.

In an attempt to further improve their photoreactivity, polymers able to lead, after photocrosslinking, to flexible and damping materials having the polydiene properties, i.e., elasticity and good adherence on metals, can be prepared from LNR or ELNR:

Photosensitive Elastomers from LNR

In the same manner as for low molecular weight synthetic 1,4-polyisoprene, LNR can be used as starting product to lead in two-step chemical modification (eq. 1) to photosensitive elastomer able to rapidly crosslink under UV irradiation.[60–62] In a first time, the LNR is maleinizated by thermal "ene" addition of maleic anhydride on
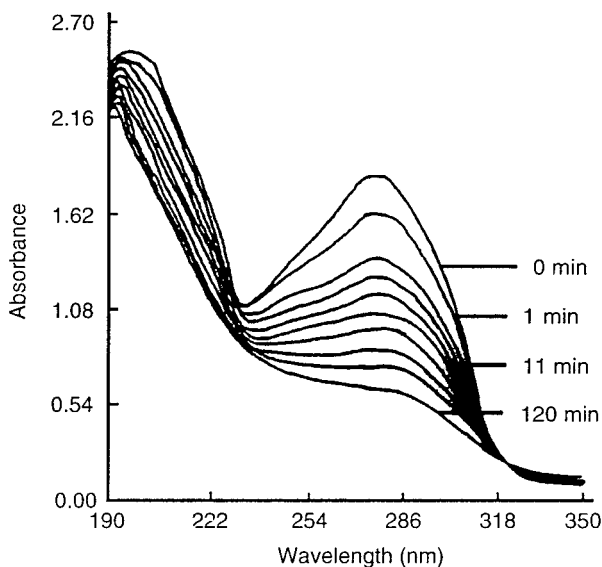
Figure 12 Changes in UV spectra of LNR carrying cinnamate groups (15% of photosensitive units) in terms of UV irradiation time.

polyisoprene unsaturations, and after, the resulting maleinized elastomer is transformed into photosensitive polymer by reaction of photopolymerizable alcohols, such as 2-hydroxyethyl cinnamate and 2-hydroxyethyl acrylate, on the succinic anhydride functions.

$$R = -CH_2-CH_2-O-CO-CH=CH-C_6H_5 \text{ (cinnamate group)}$$
$$-CH_2-CH_2-O-CO-CH=CH_2 \text{ (acrylate group)} \quad (1)$$
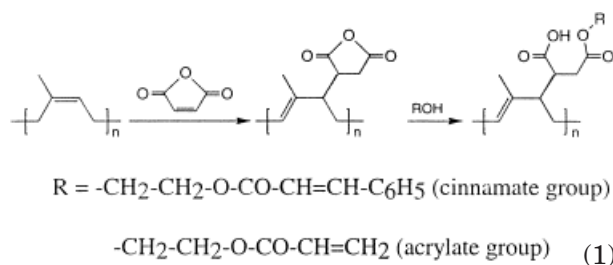
These LNRs carrying cinnamate group are quite soluble in most of the organic solvents. They are more stable than those bearing acrylate pendent groups, which can easily crosslink during the synthetic process. With LNRs carrying cinnamate groups, the maximum efficiency of the photocrosslinking rate is obtained with a LNR having less than 10% of photosensitive units (Fig. 12).

For industrial applications, the direct use of photosensitive polymers without other component cannot be performed because some problems arise during processing due to its high viscosity. So, for these reasons, they are always incorpo-

rated in formulations that are generally composed of different diluent reactive monomers with varied chemical structure nature, associated with a photoinitiator.[63] The studies of formulations including LNRs carrying cinnamate groups among the different components have shown that flexible films with good adherence on metal and good resistance toward solvent action can be prepared. Example of complete UV formulations prepared with the 2-hydroxyethyl cinnamate modified polyisoprenes is given in the Figure 13: the obtained films after 3 s of irradiation do not swell in chloroform, and show good adherence on the support and good flexibility.

Photosensitive Elastomers from ELNR

Another photosensitive elastomers derivated from NR is the methacrylic acid grafted ELNR.[64] The addition reaction between the ELNR, via the epoxide functions, and methacrylic acid leads to methacrylic acid grafted ELNR (eq. 2), where the presence of polymerizable unsaturated groups on the methacrylic acid part enable them to be crosslinked by means of UV radiation, thereby making them useful in paints and varnish industry.

$$(2)$$
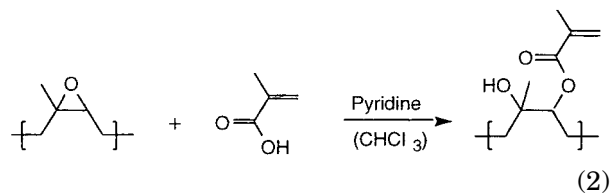
ELNR as Support of Biologically Active Compounds

As for the synthetic polymers,[65] ELNR can be used to prepare systems allowing the control of biologically active compound release, such as drugs, herbicides, pesticides, and plant growth

- **Photocrosslinkable elastomer** :
    2-hydroxyethyl cinnamate modified ELNR (50 % w/w)
- **Monofunctional monomers**:
        - glycidyl metacrylate
        - urethane derivative
- **Multifunctional monomers**:
        - 1,6-hexanedioldiacrylate
        - triacrylate derivative
- **Photoinitiator** : Irgacure 651 (dimethoxyacetophenone)

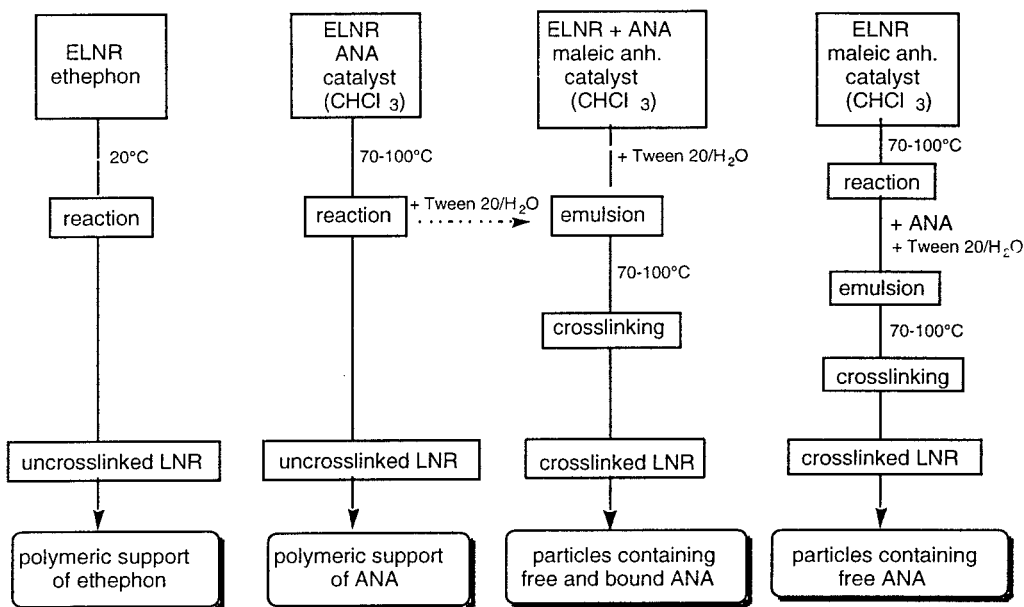**Figure 13** Example of UV formulation for industrial applications.

Figure 14 General diagram of processes used to prepare systems containing free and/or linked plant growth stimulator molecules in rubber matrix.

stimulators, in order to improve the duration of their efficiency. Recent researches involving ELNR have been led in the last field. Among plant growth stimulators, some molecules can improve the latex production of the *Hevea brasiliensis*—for instance 2-chloroethylphosphonic acid (ethephon), 2,4-dichlorophenoxy acetic acid (2,4-D), and naphthylacetic acid (ANA). The problem is, when these stimulators are applied on the trees, that they are generally rapidly washed by rain, or destroyed by other surrounding factors, before developing their action totally. Several systems have been tested from ELNR for the controlled liberation of plant growth stimulator molecules (Fig. 14).

Naphthylacetic Acid

- Chemical bonding of ANA molecules to a ELNR substrate by addition on oxirane rings, via carboxylic function, in the presence of ANA tetamethylammonium salt as a catalyst (eq. 3), with the possibility to control its liberation versus time.[66,67]
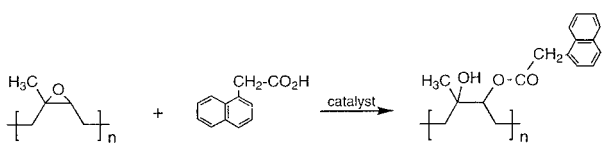
- catalyst : tetramethylammonium salt of naphtylacetic acid   (3)

- Dispersion of free and/or linked ANA into ELNR gel,[66,67] the crosslinked ELNR being obtained in emulsion under mild conditions by the action of either diacids or anhydrides, in the presence of the tetrabutylammonium salt of the corresponding diacids as a catalyst (eq. 4), so as to obtain particles whose size is controlled by the emulsion parameters.[68]
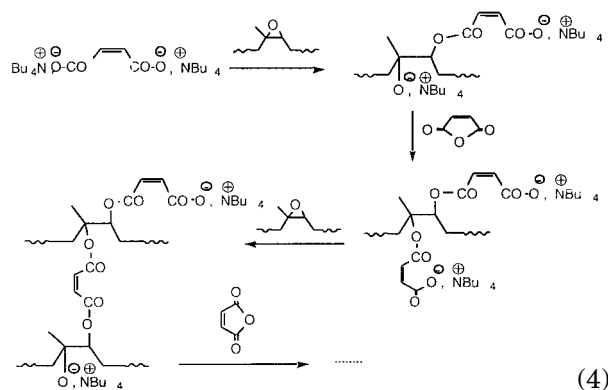
(4)

When active species are dispersed in a polymer matrix, the release is controlled by diffusion through the support, dissolution, or degradation (hydrolysis) of the support. If the active species is linked to the matrix by a chemical bond, hydrolysis must also be considered.

In vitro hydrolysis of naphthylacetic acid ELNR derivatives has been performed in buffer solutions. In all cases, it is favored in basic media:
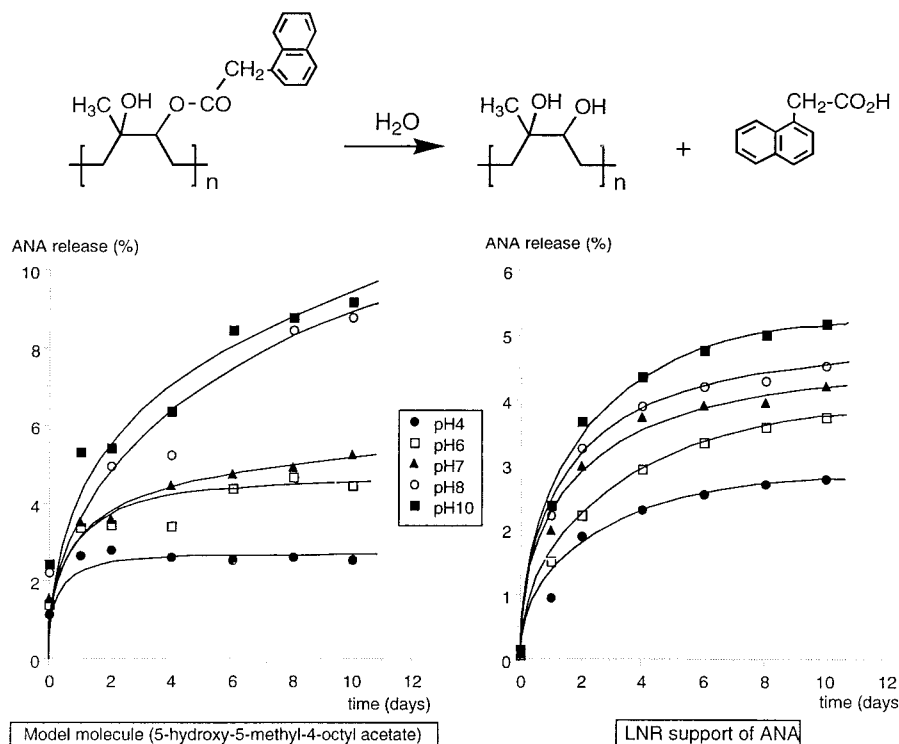
Figure 15   Hydrolysis of polymeric derivatives of ANA in buffer solutions at 25°C [ANA-LNR] = 4 g/L.

- Rate of acid release from ANA chemically linked to the ELNR backbone is lower than that from the model molecule (5-hydroxy-5-methyl-4-octylacetate), which is explained by the better accessibility of the model ester groups (Fig. 15).
- Compared to the crosslinked ELNR particles containing only free ANA where all ANA is rapidly released at the beginning of the hydrolysis, those incorporating free and linked ANA show a rapid release of free ANA at the beginning of the hydrolysis and a slower release of the linked ANA versus time (Fig. 16).

In vivo stimulation studies have shown that the ANA modified ELNR form has the same activity as the free ANA.

Chloroethylphosphonic Acid

The addition of 2-chloroethylphosphonic acid[69,70] on epoxidized polyisoprene was carried out at 20°C, with solvent or in bulk (Fig. 17). This reaction allows the formation of two types of structures: one including phosphorous adducts derivatives as regioisomers 1:1 and dioxaphospholane, and the other containing no phosphorous compounds such as allylic alcohols by rearrangement of oxirane and diol from hydrolysis of units including ethephon.[71]

The stimulation by ethephon is due to a release of ethylene from this molecule. Therefore, the efficiency of the stimulation depends on the ethene production. Consequently, ethephon-supported polyisoprene derivatives have been submitted to *in vitro* tests that were carried out at constant pH and temperature, then the ethene release was plotted against time. However, the velocity of release at 25°C and pH maintained at 8 is lower than that from the ethephon decomposition[72] (Fig. 18).

Attempts of *in vivo* activity have been performed unsuccessfully and have led to synthesize more sophisticated molecules whose interesting behavior was shown.[72]

Synthesis of Flame-Retardant Rubbers

As synthetic rubbers, NR has one important setback: it is combustible. The problem of controlling the fire hazard of polymeric materials has become a subject of worldwide concern in recent years due to increased usage of these products. One way to improve the flammability of polymer materials is
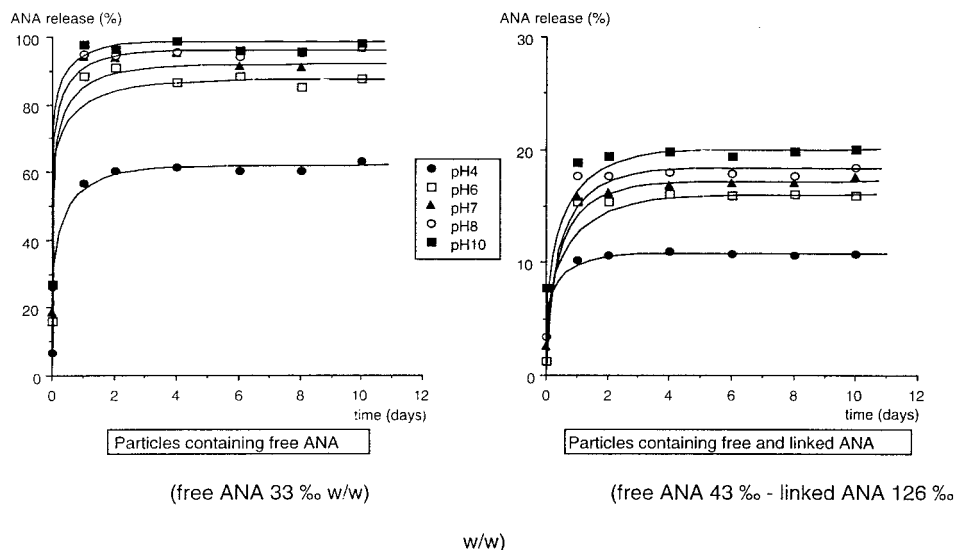
Figure 16 Release of ANA from ELNR particles in buffer solutions at 25°C. [particles] = 2 g/L.

chemical modification by using phosphorus-containing reagents or monomers.[73,74] The advantage of this method is the inclusion of active species in the polymer structure. So, they cannot diffuse toward the polymeric material surface and remain effective for longer period. Another way of improvement is to introduce a flame-retardant additive, a phosphorus-containing oligomer having a good compatibility with the flame-sensitive material.[74,75]

In this way, modification of ELNR by fixing phosphorus atoms on NR backbone was attempted to prepare a flame-retardant polymer additive for rubber vulcanization by sulfur-vulcanizing agent.[77] By reacting ELNR oxirane rings with di(alkyl or aryl)phosphate, it is possible to chemically modify the polymer (eq. 5).

The chemical modification of liquid epoxidized polyisoprene or ELNR by di(alkyl or aryl) phosphate, carried out in bulk or in solvent medium, allowed the ring opening of oxirane to take place.[56] In the case of diethylphosphate, the reaction led to the gel formation. The reaction of diphenylphosphate with epoxidized polyisoprene in bulk produced mainly the formation of 2-oxo-1,3, 2-dioxphospholane structures.
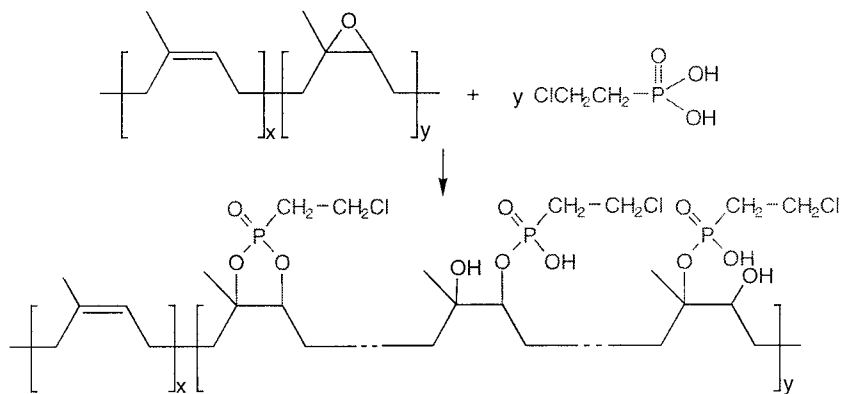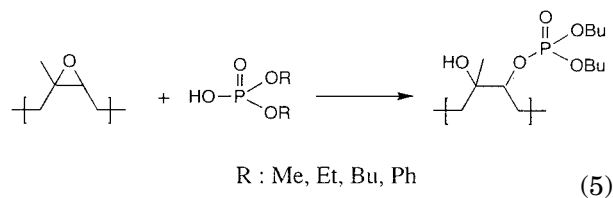

R : Me, Et, Bu, Ph   (5)

Figure 17 Reaction of 2-chloroethylphosphonic acid upon epoxidized polyisoprene.
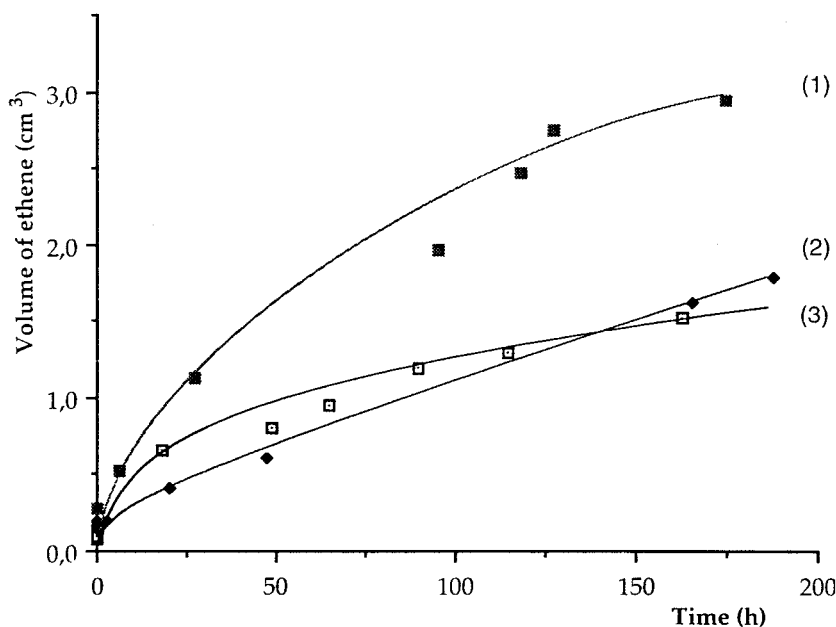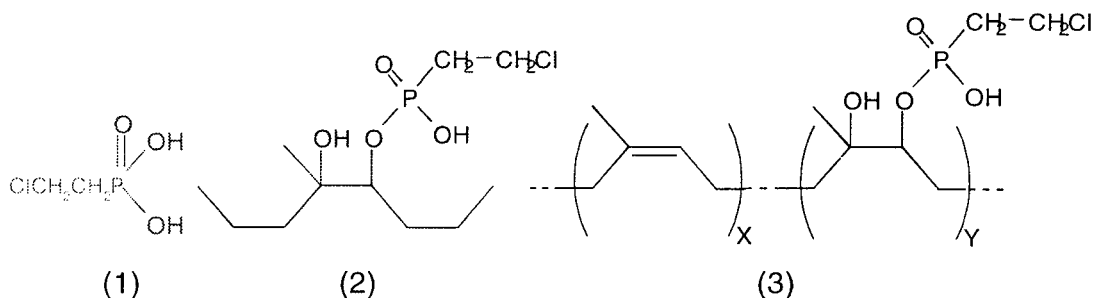
Figure 18 "Ethenogene" properties of the various products.

The efficiency of flame resistance of the various rubbers, including chemically bonded di(alkyl or aryl)phosphate groups along the polydiene chains, was estimated by the determination of the limiting oxygen index (LOI). The specimens used to determine the relative flammability of materials were prepared on two stages. At first, the chemical modification was realized by mixing liquid epoxidized polydiene and di(alkyl or aryl) phosphate, and second, crosslinking was achieved by using methylnadic anhydride. The best fire-resistance behavior was obtained in rubber network incorporating diphenylphosphate groups (Fig. 19).

Modification of ELNR by fixing phosphorous atoms on the natural rubber backbone using dibutylphosphate reaction was attempted to prepare a flame-retardant polymer additive for rubber vulcanization by a sulfur-vulcanizing agent.[77] Incorporation of the phosphorus-modified liquid rubbers in a NR formulation decreases the flammability behavior of the vulcanizates (Fig. 20), but decreases also the mechanical properties because vulcanization is greatly affected by phosphorus units.

New Perspectives of Research on NR and Its Derivatives

The results over the last decades show that fundamental and applied research on NR chemistry is essentially distributed in five main themes:[78,79]

- The research of new form of NR (liquid rubbers, stabilized latex concentrates, prevulcanized latex, blends with thermoplastics).
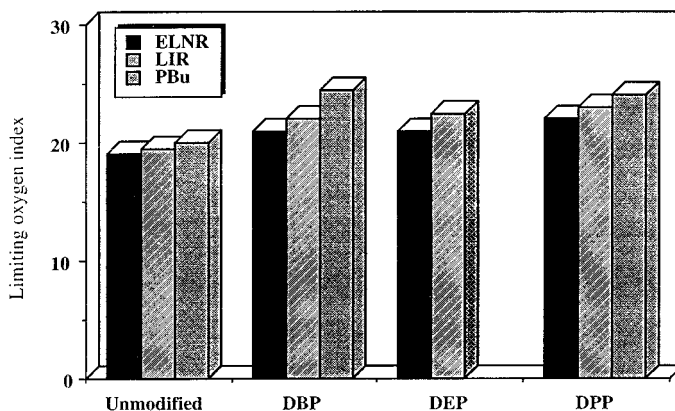- The chemistry of functionalization (chlorina-

Figure 19 Limiting oxygen index of specimens, unmodified and modified by dialkyl(or aryl) phosphates.

tion, epoxidation, isomerization), which is in agreement with the reactivity of alkene function.
- The chemistry of grafting: graft copolymers derived from NR.
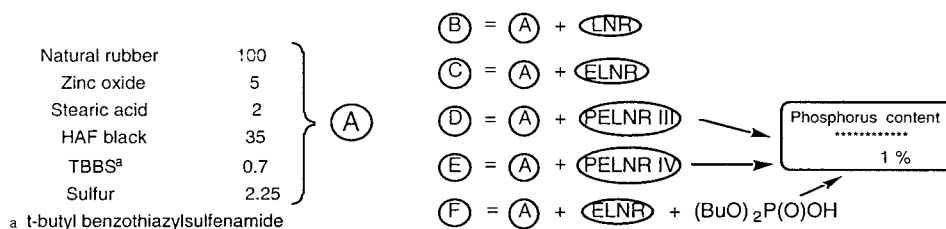- The chemistry of oxygen aging.

- The chemistry of vulcanization.

Although attempts to transform NR into other useful materials predated the chemical modification of synthetic polymers by some fifty years, it is important to emphasize that, in this field, the

Preparation of natural rubber vulcanizates
Choice of the formulations

Mix	A	B	C	D	E	F
LNR	-	13.3	-	-	-	-
ELNR	-	-	13.3	-	-	13.3
PLNR III (bulk)	-	-	-	25	-	-
PLNR IV(solution)	-	-	-	-	25	-
Dibutylphosphate	-	-	-	-	-	11.3

Natural rubber	100
Zinc oxide	5
Stearic acid	2
HAF black	35
TBBS[a]	0.7
Sulfur	2.25

a t-butyl benzothiazylsulfenamide

$\text{B} = \text{A} + \text{LNR}$

$\text{C} = \text{A} + \text{ELNR}$

$\text{D} = \text{A} + \text{PELNR III}$

$\text{E} = \text{A} + \text{PELNR IV}$

$\text{F} = \text{A} + \text{ELNR} + (BuO)_2 P(O)OH$

Phosphorus content
1 %

Burning times (sec) of the samples

% of oxygen	A	B	C	D	E	F
21	80	84.5	86	102	101	103
19.5	102	106	108	138	137	139
19	123	125	128	180	175	178
18.5	164	166	170	187	190	195
18	180	190	192	230	225	230
17.5	217	219	218	270	280	extinguished

Figure 20 Dibutylphosphate modified ELNR as flame-retardant additive for vulcanized natural rubber.
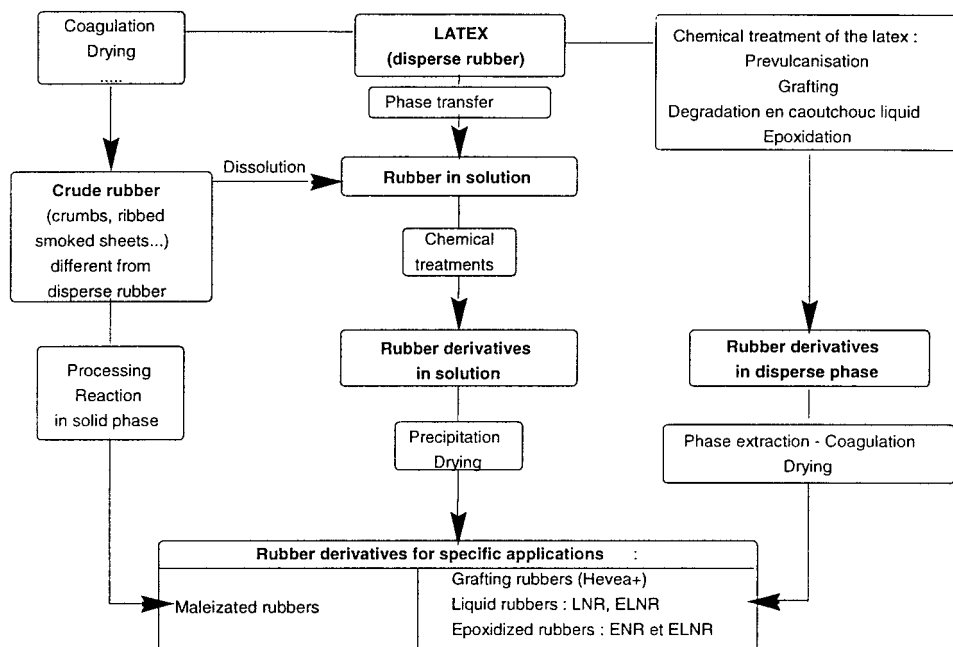
Figure 21 Processes that can be used to modify NR (in solid phase, in solution, and in latex phase).

research have greatly competed with the work realized on synthetic rubbers (polyisoprenes, polybutadienes, diene copolymers, . . .). This can be explained by the nature of the chemistry performed on NR, which was not always clear due to the lack of fundamental knowledge about the nature of rubber composition, and its behavior and reactivity. In spite of some chemical modification studies carried out in its liquid form (see, part above), of all the gross modification examined to date, epoxidation is the only one that results in improved physical properties to fulfill application requirements and is economically attractive. These differences are principally explained by the poor knowledge of the physics and physiological characteristics of NR, and also by the low quality of the raw material (latex, sheet).

For the chemistry of NR (Fig. 21), reactions should be capable of being carried out with high efficiency in latex phase or during conventional dry rubber mixing or curing processes, and should not induce change in the NR structure (e.g., crosslinking, cyclization, *cis–trans* isomerization) other than those intended, the all with the objective to find the most economical process.

According to these principles, it is possible to define the great orientations in the future developments of NR:

NR Derivatives as Higher Value Added Rubbers

As stated before, chemical modification of rubber concerns principally the synthetic rubbers because of the higher purity of the product. The reason is that NR is a biological elastomer that contains secondary nonrubber compounds *which* can disturb the chemical processes. Up to date, most of the examples concern chemical transformations in organic solution. The main future developments expected in the field of NR chemical modification can be predicted in three directions:

Chemistry in Latex Phase

Compared to a reaction performed in solution, its realization in latex phase is a great process simplification whose interest, especially on economical viewpoint, is evident (the controlled degradation of NR that leads to LNR[20,50] and the epoxidation[1–5] are two significant examples of chemical modification of NR in latex phase (Fig. 9).

Chemical modification of NR in latex phase, compared with synthetic polymer, is more difficult due to an uncomplete understanding of the NR latex composition and properties. This is especially true for the nature and composition of nonrubber materials, and for the causes of variability in processing behavior. Composition of la-

tex is extremely complex, rendering the chemical analysis very difficult, and the particle–serum interface is extremely difficult to study. The recent development of the analytical methods in the fields of fractionation (development of new specific column packings, use of supercritical fluids in chromatography and extraction, electrophoresis development, coupling of chromatography with mass and IRTF spectroscopies), spectroscopy, and surface analytical examination (microscopy coupled with IRTF) would bring further clarification in the determination of the role of the adsorbed layers on the particles in latex stabilization. Progresses in chemical modification in latex phase include systematically a better knowledge of the latex emulsion and improvements in NR purification technics (extraction of nonrubber compounds).

Chemistry in Biphasic Systems

The developments in the field of NR chemical modification also will be able to lean on the new physicochemical knowledges of dispersed media. Recently, it has been shown that the direct solubilization of the latex rubber part in an organic solvent is possible without the passage by the coagulation and/or drying steps.[80,81] The possibility to transform the latex mixture in a liquid–liquid biphasic system can be associated with the well-known reactions performed in biphasic systems (with or without the use of phase transfer catalysts), which would enable a better control of the reaction. Principle of synthesis using phase transfer catalysts is that the reaction is carried out in a system of two phases (liquid–liquid); one can select a phase transfer agent that, in catalytic quantities, can bring one reactant from its "normal" phase into the phase of the second reagent, such that reaction between the two can occur with reasonable rate.[82]

The coupling of the rubber transfer process in the organic phase with the use of a phase transfer reaction is attractive because it is a way to avoid the number of manipulations, with a great effect on the cost.

Chemistry in Solid Phase

Chemical transformations in solid phase can also be possible. Maleinization is one of the reactions that set no problem.

Blends and Composites Including NR

During the past twenty years, blends incorporating NR or modified NR with thermoplastics have been developed that combine some of the properties of conventional NR and thermoplastics. The interest to develop these materials is that they can possess the properties of each one of the polymer components that explain their commercial advantages over the conventional rubbers. For example, for the blends including NR and thermoplastics, the advantage is that they can be processed on thermoplastics machinery without requiring vulcanization. However, the first problem in the blend technology is to obtain a good compatibility between the different polymers.

NR chemical modification can be a mean to improve the compatibility of NR with other polymers included in the formulation of polymer blends. Among the known polymers, there are little ones that, in a limited area of concentration and temperature, can show a real compatibility with NR (miscibility at molecular scale), and generally, it is necessary to introduce a compatibiliser (additive or an interpolymer of the blend of basic polymers) that ensures the high bond strength of the contacting polymers. The incorporation of ELNR into polymer blend including NR has led to positive results.[83,84] The objective of compatibilization of NR with polymers different by their nature and properties, would lead to the elaboration of new functionalized derivatives of NR or its derivatives in which the functionalized units would associate to the NR. So, the development in this field is closely dependent on the progresses noted in the chemistry on NR.

These perspectives on the research concerning the chemistry of NR can also automatically benefit from the new potentialities of organic chemistry (in organic chemistry, the chemistry carried out in aqueous phase constitutes henceforth one of the challenges of the beginning of the 21th century).

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