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Synthesis of Photo-crosslinkable Elastomers by Chemical Modification of Liquid Natural Rubber

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Photo-crosslinkable elastomers were synthesised by addition of photo-sensitive alcohols to the alkylsuccinic ring of liquid natural rubber (LNR) and synthetic liquid 1,4-polyisoprene (LIR) was modified for the first time by reaction with maleic anhydride. Two reagents were used: 2-hydroxyethyl cinnamate (HEC) and 2-hydroxyethyl acrylate (HEA). The fixation proceeded by succinic ring opening by the action of the alcohol function of the photo-reactive molecule and led to a hemi-ester adduct. At moderate temperature (about 70°C), the reaction on succinic anhydride functions of maleinisated LIR was fast and quantitative when it was catalysed by pyridine and led to polymers which were completely soluble in organic solvents. On the other hand, under the same conditions, yields of HEC addition on succinic rings of maleinisated LNR were less significant (~ 60%) than on maleinisated LIR, and in the case of the acrylate reagent, the reaction was affected by the formation of gel structures. The relationship between the polymer structure and its photo-sensitivity is presented. The effects of photo-reactive group contents on the photo-crosslinking kinetics were investigated for each category of prepared polymers. Flexible films with good adherence on metal were prepared by using formulations including LIR or LNR carrying cinnamate groups.

The constant search for more sensitive resins that can photo-polymerise 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[1], mainly as photo-resists 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 photo-reactivity, the performances of new photo-sensitive elastomers with polyisoprene backbone were examined. The aim was to prepare new photo-reactive polymers able to lead, after photo-crosslinking, to flexible and damping materials having the properties of polydienes, *i.e.* elasticity and good adherence to metals.

A new material is produced with the development of a patented process[2,3] of depolymerisation of natural rubber. It is prepared by controlled degradation of natural rubber in the latex phase according to a redox reaction using the phenylhydrazine/oxygen system[2]. By controlling the reaction conditions, it is possible to obtain liquid compounds called liquid natural rubber (LNR) with low viscosity and the structure of *cis*-1,4-polyisoprene. The feasibility of industrial production of LNR has been demonstrated with the establishment of a semi-industrial pilot plant at the IRCA (Institut de Recherche sur le Caoutchouc) Bimbresso Station in the Ivory Coast.

If LNR can be compared to synthetic liquid 1,4-polyisoprene and used in the same field of applications, it may be useful as a starting

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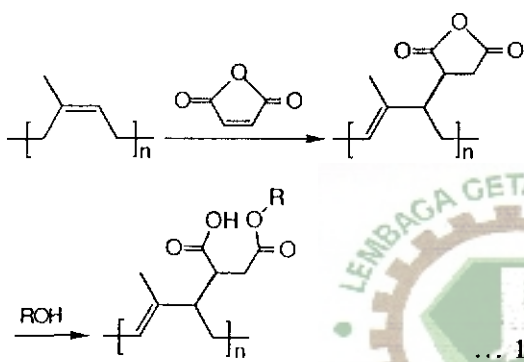
product for the preparation of specific polymers for highly technical applications through judicious chemical modification of its structure. In this way, its transformation into a photo-sensitive product similar to synthetic 1,4-polyisoprene (LIR) was carried out by a two-step process. In the first step, maleic anhydride was added to polyisoprene units to obtain functionalised intermediate polydiene with pendent succinic anhydride functions. The second step of the chemical modification was the introduction of the photo-sensitive graft, using the known reactivity of the succinic rings towards alcohol functions, by reaction of the succinic anhydride groups with photo-reactive alcohols, such as 2-hydroxyethyl acrylate (HEA) and 2-hydroxyethyl cinnamate (HEC) *(Equation 1)*:



$R = -CH_2-CH_2-O-CO-CH=CH-C_6H_5$
(cinnamate group)

$-CH_2-CH_2-O-CO-CH=CH_2$
(acrylate group)

This paper describes the synthesis of the photo-sensitive polydienes derived from LIR and LNR, and compares their photo-reactivity. The photo-reactivities of the different prepared polymers were evaluated by comparison of the kinetics of photo-crosslinking reactions. Some orientation tests were also carried out on the use of modified LNR or LIR in UV formulations of industrial character to obtain flexible and damping films.

EXPERIMENTAL

Purification of Solvents and Reagents

Solvents were commercial products. Benzene and toluene (99.5% purity) were used as received. Hexane was distilled on $LiAlH_4$ and kept on a 3 Å molecular sieve. Pyridine was distilled on potassium hydroxide before it was used. Chloroform was distilled on phosphoric anhydride. Methanol was dried by distillation on $Mg(OMe)_2$ prepared *in situ*. Ethanol was dried on activated lime for several days, distilled and kept on a 3 Å molecular sieve. Methyl ethyl ketone (MEC) was distilled.

Maleic anhydride was recrystallised from benzene. 0.5 *N* solution of tetrabutylammonium hydroxide in methanol was supplied by Janssen. Ethylene glycol (Janssen) was further dried by azeotropic distillation of benzene. Cinnamoyl chloride (Janssen, 97% purity) was used as received. HEA (Aldrich product) was distilled at low pressure immediately before it was used.

HEC was synthesised in pyridine by reaction[4] between molten cinnamoyl chloride and ethylene glycol at a temperature below 25°C. The ester was used after purification by distillation. Its purity was verified by ^1H NMR.

Synthetic liquid *cis*-1,4-polyisoprene (LIR 30) was supplied by the Japan Kuraray Company. It was purified by re-precipitation from toluene into methanol and dried *in vacuo*. The average molecular weights of LIR were: $\overline{M}_n$ = 12 400, $\overline{M}_v$ = 12 700, $\overline{M}_w$ = 27 600. It consists of 92% of −1,4 and 8% of −3,4 structures.

LNR is a derivative of natural rubber obtained by depolymerisation in the latex phase by a chemical method using the phenylhydrazine/oxygen system[2,3]. It was supplied by the Institute of Applied Research on Polymers of Le Mans. The average molecular weights of LNR were: $\overline{M}_n$ = 7700, $\overline{M}_v$ = 8900, $\overline{M}_w$ = 26 100. It consists of 100% *cis*-1,4 structure.

Reaction of Maleic Anhydride to Polyisoprene Structures

Addition of maleic anhydride to polyisoprene structures was carried out by using thermal initiation. Polyisoprene in toluene solution (200 g of polyisoprene for 1 litre of toluene), maleic anhydride and cupric acetylacetonate (0.1 g for 100 g of polyisoprene) used as anti-gel additive, were introduced under nitrogen atmosphere in a 30 ml stainless steel Mecabar autoclave. The reaction mixture was heated to 200°C in a metallic bath (wood alloy). After 24 h, the reaction was stopped. The resulting mixture was poured into excess cold ethanol. The precipitated product which was the maleinisated polyisoprene, was immediately recovered and purified by re-precipitation from toluene into hexane. It was stored in toluene solution.

Reaction of Maleinisated Polyisoprenes with Photo-sensitive Hydroxyethyl Structures

Addition of 2-hydroxyethyl cinnamate. The addition of 2-hydroxyethyl cinnamate to maleinisated polyisoprene was carried out in toluene solution, in the presence of pyridine as a catalyst. 10 g portion of a maleinisated polyisoprene free of maleic anhydride[5] in 100 ml of toluene and 2-hydroxyethyl cinnamate in the molar ratio [2-hydroxyethyl cinnamate]/[succinic anhydride function] = 2.3 and pyridine in [pyridine]/[succinic anhydride function] = 0.5 were placed in a round-bottomed flask fitted with a reflux condenser carrying a calcium chloride guard tube. The mixture was heated while being stirred to 75°C in a thermostated oil bath for 24 h. At the end of the reaction which was controlled by infra-red spectroscopy, by following the disappearance of the succinic bands at 1780 and 1860 cm^{-1}, the resulting mixture was poured into excess methanol (or hexane when the degree of modification by maleic anhydride was too high) and the precipitate was obtained as the product. The product was collected, purified by re-precipitation from chloroform into methanol and stored in chloroform solution under nitrogen atmosphere and sheltered from light.

Addition of 2-hydroxyethyl acrylate. The reaction was conducted in the same manner as for HEC. Maleinisated polyisoprene concentration was fixed at 7.5 g portion of polymer in 100 ml of toluene. The reaction was carried out in the presence of hydroquinone (0.3 g for 100 g of maleinisated polyisoprene), as the polymerisation inhibitor.

Photo-crosslinking of Photo-sensitive LNR and LIR

Photo-crosslinking kinetics. Photo-sensitive elastomers were dissolved in chloroform at a concentration of 150 g/litre. Film specimens for UV irradiation were prepared by casting the chloroform solution on quartz cell for UV analysis, with a 6 μm Conway bar. After removing solvent under reduced pressure, the film thickness was estimated to be about 1 μm. The UV irradiation was carried out at ambient temperature at a distance of 9 cm from an ultra-high pressure mercury lamp (PCG 9G-1 model from Ultraviolet Products Inc.; 2.5 watts). The principal beams of the used UV lamp are 253.7 (80% of the energy), 312.5 and 365 nm, the others being visible. The photo-crosslinking rate of the synthesised photo-sensitive rubbers was determined by the intensity change of the UV absorption at λ = 278 nm due to the carbon-carbon double bond of cinnamate groups for polyisoprene modified with HEC and at λ = 200 nm due to the carbon-carbon double bond of acrylate groups for polyisoprene modified with HEA.

Photo-crosslinking of UV formulations. The selected UV formulation for the present study has been perfected by the Institute of Applied Research on Polymers of Le Mans to obtain a film having properties of adherence on painted steel (used in the car industry), flexibility and good resistance to solvents and shocks. The formulations used were:

- Approximately 50% by weight of photo-sensitive polyisoprene (LIR-HEC or LNR-HEC)
- Mono-functional monomers:
  - — glycidyl methacrylate
  - — urethane derivative (M 200, Rahn)

- Multi-functional monomers:
  - — 1,6-hexanediol diacrylate
  - — triacrylate derivative (OTA 480, Union Chimique Belge)
- Photo-initiator: 651 Irgacure (2,2-dimethoxy-2-phenyl acetophenone) (Ciba Geigy)

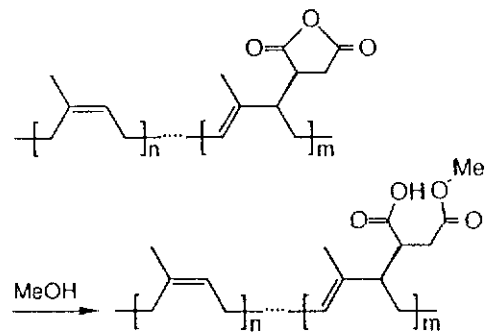
The mixture was dissolved in chloroform and the films were prepared by casting the chloroform solution on metallic plates. After removing the solvent under reduced pressure, the film was exposed under UV irradiation supplied by a high powerful medium pressure mercury lamp (Aric 8200; 80 watts/cm) from Aric Company, for short periods (3-5 s). The crosslinking test was carried out to control the solubility of the film in chloroform. Qualitative adherence tests were conducted as follows: squaring of the film with a cutter, then estimation of the adherence by peeling with adhesive tape.

Characterisation of Products

The products were characterised by infra-red, UV and NMR spectroscopy. UV spectra were recorded on a UV/visible Varian DMS 100 spectrometer. Infra-red analyses were carried out on film samples of the polymers on NaCl cells, using a Fourier transform Perkin-Elmer 1750 spectrometer ^{13}C NMR and ^{1}H NMR measurements were carried out on deuterated chloroform solutions containing tetramethylsilane as the internal standard by using respectively Varian FT 80A (20 MHz) and Varian EM 90 spectrometers.

Molecular weights were determined by gel permeation chromatography (GPC) in THF on a Waters 1500 instrument fitted with 5 μ Styragel columns (0.7 × 120 cm) of different pore sizes (100, 3 × 500 and 1000 Å), calibrated with polystyrene standards.

After maleinisation, the contents of succinic groups in the polyisoprenes were determined by titration using a Metrohm potentiometer (Impulsomat 614; Dosigraph 625; pH-meter 632, Dosimat 655) as described earlier[5]. It consists of titrating the carboxylic acid functions formed after opening of the succinic rings obtained by reaction of an alcohol with a known quantity of maleinisated polymer *(Equation 2)*:



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After maleinisation, a portion of the toluene polymer solution was refluxed in the presence of pure MeOH (2 mol for one polymer constitutive unit) for a few hours. The reaction was stopped after complete disappearance of the infra-red bands at 1780 and 1860 cm^{-1}, characteristic of the succinic ring. The esterified product was poured into excess methanol to eliminate the residual reagents and the polymer precipitate obtained was dissolved in toluene and stored in this form.

The contents of photo-sensitive groups in the prepared polymers were estimated according to a previous paper[4]. For the photo-sensitive polymers derived from LIR, it was admitted that the photo-reactive group content was equal to the initial succinic anhydride content. In the case of photo-crosslinkable elastomers prepared from LNR, the usual method cannot be applied because, at the start of the addition of photo-reactive alcohol, some succinic functions were opened by secondary processes which occurred during maleinisation. The amount of incorporated cinnamoyl substrates on maleinisated LNR was determined from high performance liquid chromatography (HPLC) by using the standard calibration procedure. The method is based on the measurement of the quantity of residual 2-hydroxyethyl cinnamate contained in the solution[4].

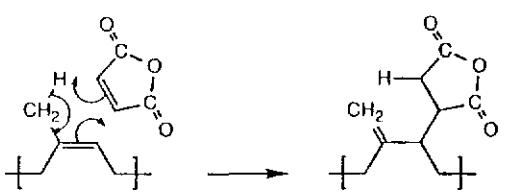
RESULTS AND DISCUSSION

Two products from different origins: a synthetic, 1,4-polyisoprene (92% of 1,4-units; 8% of 3,4-units) (LIR 30) with $\overline{M}_n$ = 12 400 and a liquid natural rubber (100% of *cis* 1,4-units) (LNR) with $\overline{M}_n$ = 7700 were studied.

The aim was to study the partial modification of 1,4-polyisoprene structures because only a small proportion of photo-reactive functions is sufficient to permit a good crosslinking reaction. For these reasons, it was decided to limit the modification yield to a maximum of 20% ([maleic anhydride]/[polyisoprene units] < 0.2 mol.mol^{-1}).

Fixation of Maleic Anhydride on LIR and LNR

The addition of maleic anhydride[5,6] to 1,4-polyisoprene can be carried out by heating to moderate temperature in the presence of free-radical catalysts, or in the absence of catalysts by heating to significantly higher temperatures of 180°C to 230°C. The latter was achieved by thermal processes in the presence of cupric acetylacetonate as the anti-gel additive to prevent the polydiene crosslinking. The thermal reaction which requires high activation temperatures (of about 200°C), proceeds by an electronic 'ene' mechanism as shown in *Equations 3* and *4:*



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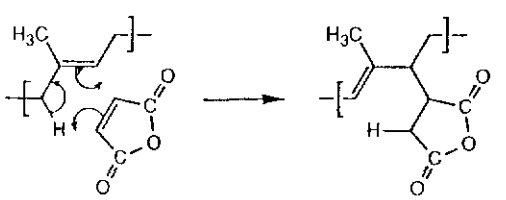

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According to the 'ene' synthesis, five polyisoprenes containing respectively 3%, 7%, 10%, 11% and 15% maleinisated units were prepared from LIR, and three with 5%, 9% and 15% maleinisated units from LNR *(Table 1)*. After maleinisation, each prepared maleinisated polymer was systematically controlled under infra-red spectroscopy to verify the eventual existence of some ring opening secondary reactions. With LIR, the yields from the maleinisation reaction were about 70% and the maleinisated units were totally in the succinic anhydride form. With LNR, it was necessary to keep the maleinisated LNR in solution because they are non-soluble after drying, which can be explained by the existence of hydrogen bond interactions between the chains. The differences in the results obtained with LIR are probably due to the presence of some acid or basic compounds in the initial liquid rubber, which result in the ring opening reaction.

Structural characterisation of maleinisated polyisoprenes. The maleinisated polyisoprenes derived from LIR or LNR have the same characteristics in ^{1}H NMR and infra-red spectroscopy.

In ^{1}H NMR, fixation of maleic anhydride is characterised by a chemical shift at δH = 2.3 - 2.8 p.p.m characteristic of the protons on the succinic rings. The presence of two isomer structures, has also been reported[5]. Analysis of polymers derived from LNR which are only composed of 1,4-units, reveals the presence of an another signal at δ_H = 4.8 p.p.m. characteristic of protons on 'exo' methylenic carbon-carbon double bonds.

In infra-red spectroscopy, the succinic anhydride function is readily identified by means of two strong absorption bands at 1780 and 1860 cm^{-1}. Products derived from LNR were also present on another absorption band of weak intensity at 1700 cm^{-1}, which characterises the partial succinic ring opening with formation of carboxylic acid functions. As they did not occur during the chemical modification of LIR, it is probable that they are induced by the non-rubber constituents initially present in the LNR which can initiate

TABLE 1. CHARACTERISTICS OF THE PHOTO-REACTIVE POLYISOPRENES OBTAINED AFTER CHEMICAL MODIFICATION OF LIR AND LNR, BY MALEINISATION WITH MALEIC ANHYDRIDE FOLLOWED BY ESTERIFICATION OF THE FORMED SUCCINIC ANHYDRIDE FUNCTIONS BY SELECTED PHOTO-SENSITIVE ALCOHOLS HEC AND HEA

Sample		Modification yield	
from HEC	from HEA	After maleinisation (% of maleinisated units)	After addition of the photo-reactive alcohol (% of photo-reactive units)
LIR-HEC-3		3[a]	3[b]
LIR-HEC-7		7[a]	7[b]
LIR-HEC-10		10[a]	10[b]
LIR-HEC-11		11[a]	10[c]
LIR-HEC-15		15[a]	15[b]
	LIR-HEA-15	15[a]	15[b]
LNR-HEC-5		10[a]	5[c]
LNR-HEC-9		15[a]	9[c]
LNR-HEC-15		27[a]	15[c]

[a] Determinated by titration
[b] Equal to the modification yield by maleic anhydride
[c] Determinated from HPLC measurement of the residual HEC

decarboxylation or esterification of some succinic rings.

Addition of Photo-polymerisable Alcohols on Maleinisated LIR and LNR

Photo-polymerisable alcohols were added to maleinisated LIR or LNR in the presence of pyridine as the catalyst[4]. The studies were conducted in toluene (10 g of maleinisated polymer in 100 ml of toluene) at 75°C. A slight excess of photo-reactive alcohol compared with succinic anhydride functions was used: [photo-reactive alcohol]/[succinic anhydride group] = 2.3 mol.mol^{-1}.

The progress of the succinic anhydride chemical modification reaction was controlled by following the disappearance of the infra-red absorption bands at 1780 cm^{-1} and 1860 cm^{-1} characteristic of the succinic anhydride function.

Addition of 2-hydroxyethyl cinnamate. Addition of HEC to the previously prepared maleinisated LIR and LNR was quantitative at moderated temperature after only 24 h of reaction when it was conducted in the presence of pyridine[4]. No side-reaction occurred during maleinisation of LIR, therefore, starting with LIR, the percentages of constitutive units having the cinnamate group were identical *(Table 1)*. Alternatively, for the photo-sensitive polyisoprene derived from maleinisated LNR, such extrapolation was not possible owing to the partial succinic ring opening noted during maleinisation of LNR and, in this case, it was necessary to find a solution to the problem of determination of the percentage of photo-sensitive units. It was achieved by using the HPLC technique which permits the monitoring each time of the quantity of residual HEC. The results summarised in *Table 1* show that, for all the maleinisated LNR, the proportion of maleinisated constitutive units really modified by HEC corresponds to about half of the initial one, which by ignoring the ring openings noted during maleinisation, placed the esterification yield at about 60%. This value is

in fact the minimum since the calculation was based on the maleinisation yield which includes all the maleic anhydride modified constitutive units without making a distinction between the closed succinic rings and the opened ones.

Structural characterisation of the cinnamate photo-sensitive polyisoprenes. In GPC, no significant change was noted between the chromatogram of the initial LIR or LNR and those of the correspondent modified products.

The chemical structures of the modified polymers were characterised by ^{1}H NMR, infra-red and UV spectroscopy. In infra-red spectroscopy, the absorption bands characteristic of the cinnamic ester function appeared at 1713 cm^{-1} (C=O ester and carboxylic acid, stretching), 1638 cm^{-1} and 893 cm^{-1} (C=C cinnamate, stretching). In ^{1}H NMR, the 2-hydroxyethyl cinnamate addition to maleinisated 1,4-polyisoprene structures was verified by a singlet at δ_H = 4.4 p.p.m. characteristic of the methylenic protons -O-CH_2-CH_2-O-. In UV spectroscopy, the two important absorption bands noted at λ = 278 nm and λ = 200 nm characterised respectively the cinnamate functions and the polyisoprene carbon-carbon double bonds.

Addition of 2-hydroxyethyl acrylate. Contrary to HEC, the addition of HEA to maleinisated LIR or LNR was carried out in the presence of hydroquinone to prevent all risks of polymerisation by the intermediate acrylic groups, very sensitive towards heat. The reaction on 15% maleinisated LIR went to completion, *i.e.* complete disappearance of the infra-red absorption bands characteristic of the succinic anhydride functions was observed after 9 h of reaction and no gel formation was noted in the medium. It was not possible to fractionate HEA from hydroquinone by HPLC and so, to measure HEA residual quantity each time[4], it was assumed that the percentage of photo-sensitive acrylate units was, as in the case of the study with HEC, identical to that of maleinisation, *i.e.* with the 15% maleinisated LIR *(Table 1)*. With maleinisated LNR, the addition of HEA was disturbed by gel formation after only 4 h of reaction, *i.e.* before complete transformation of the succinic rings by HEA, which was verified in infra-red spectroscopy by the presence of absorption bands at 1860 cm^{-1} and 1780 cm^{-1}.

Structural characterisation of the acrylate photo-sensitive polyisoprenes. The fixation of acrylate groups is confirmed in ^{1}H NMR by the presence of a singlet at δ_H = 4.4 p.p.m. due to the -O-CH_2-CH_2-O- protons. In infra-red spectroscopy, the principal absorption bands are noted at 1734 cm^{-1} (C=O ester, stretching), 1713 cm^{-1} (C=O acid, stretching), 1666 cm^{-1} (C=C polyisoprene, stretching), 810 cm^{-1} and 1640 cm^{-1} (C=C acrylate, stretching). The UV spectrum presents two adsorption bands at λ = 200 nm and λ = 250 nm which characterise respectively the polyisoprene carbon-carbon double bonds and the acrylate groups.

Photo-crosslinking

Polymers bearing cinnamate groups are well known for their ability to be photo-crosslinked *via* 2 + 2 cyclo-addition involving the carbon-carbon double bond of the cinnamate function, resulting in the formation of a cyclobutane ring[7]. However, the photo-chemistry of these polymers cannot be explained by the only cyclobutane structure formation. Nakumura and Kikuchi[8] have proposed, according to ESR data, the intervention of two different kinds of radical intermediates, one of them being produced by hydrogen abstraction from the main chain of the polymer. It is possible that these radical forms can occur in the cross-linking process. Reiser[9] analysed the products obtained after UV irradiation of poly(vinyl cinnamate) in the solid state and concluded that at least 65% of the total of the formed structures are cyclobutane dimers, the others being derivatives resulting from combinations between radical species generated along the chain during the irradiation. We have tried to photo-crosslink a film of 15% maleinisated LIR and established that photo-crosslinking can occur in the absence of photo-polymerisable graft *(Figure 1)*, which seems to prove that the thesis of a propagation *via* radical species is credible. The time decrease of the UV

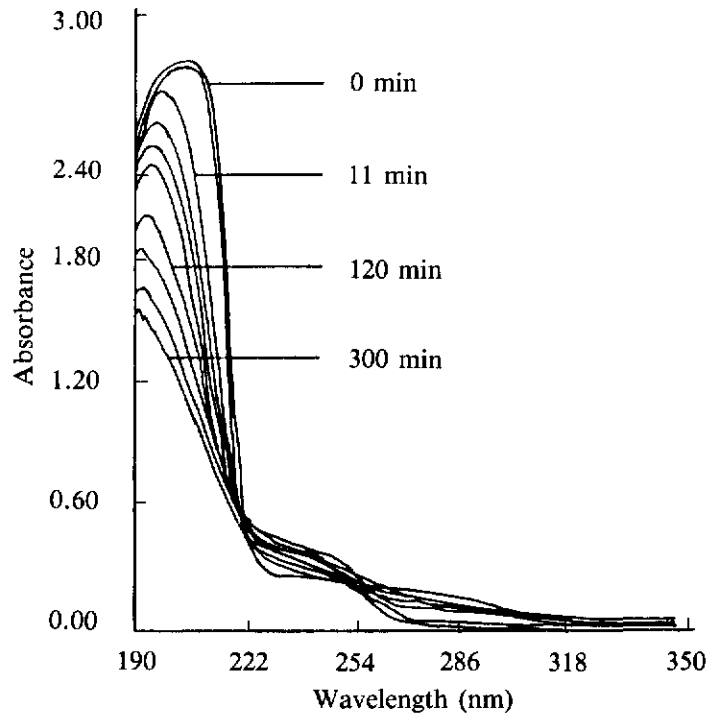

Figure 1. Changes in UV spectrum of 15% maleinisated LIR in terms of UV irradiation time.

absorption bands characteristic of the polyisoprene carbon-carbon double bonds at $\lambda = 200$ nm and the gradual insolubilisation of the sample prove the intervention of the polyisoprene unsaturations in the photo-crosslinking process. It is not rejected that the succinic anhydride groups present along the chain can also act as a photo-initiator. Under UV irradiation, radicals can be generated by homolytic cleavage of the bonds in the α position from carbonyl group and initiated propagation involving polyisoprene unsaturations.

For polymers containing the photo-reactive acrylate or methacrylate groups, photo-dimerisation is not expected to play a role in crosslinking. The photo-crosslinking mechanism is essentially a radical chain propagation.

Photo-crosslinking kinetics of the photo-sensitive LIR and LNR. During all the studies on photo-reactivity of the prepared polymers, the tests were carried out in the solid state and the thickness of the films were measured as the same for each sample (around 1 μm after drying).

The UV irradiation tests on the prepared photo-reactive polyisoprenes were carried out on samples prepared according to the method described above.

Kinetic studies of the photo-crosslinking of polyisoprenes bearing pendent cinnamate groups derived from LIR and LNR. In the case of polyisoprene carrying cinnamate groups, *Figure 2* shows a slight decrease of intensity of the absorption band around $\lambda = 200 - 210$ nm which corresponds to the polyisoprene carbon-carbon double bond, compared to the absorption band shown in *Figure 1* at the same irradiation time. But a significant change in the intensity of the cinnamate absorption band

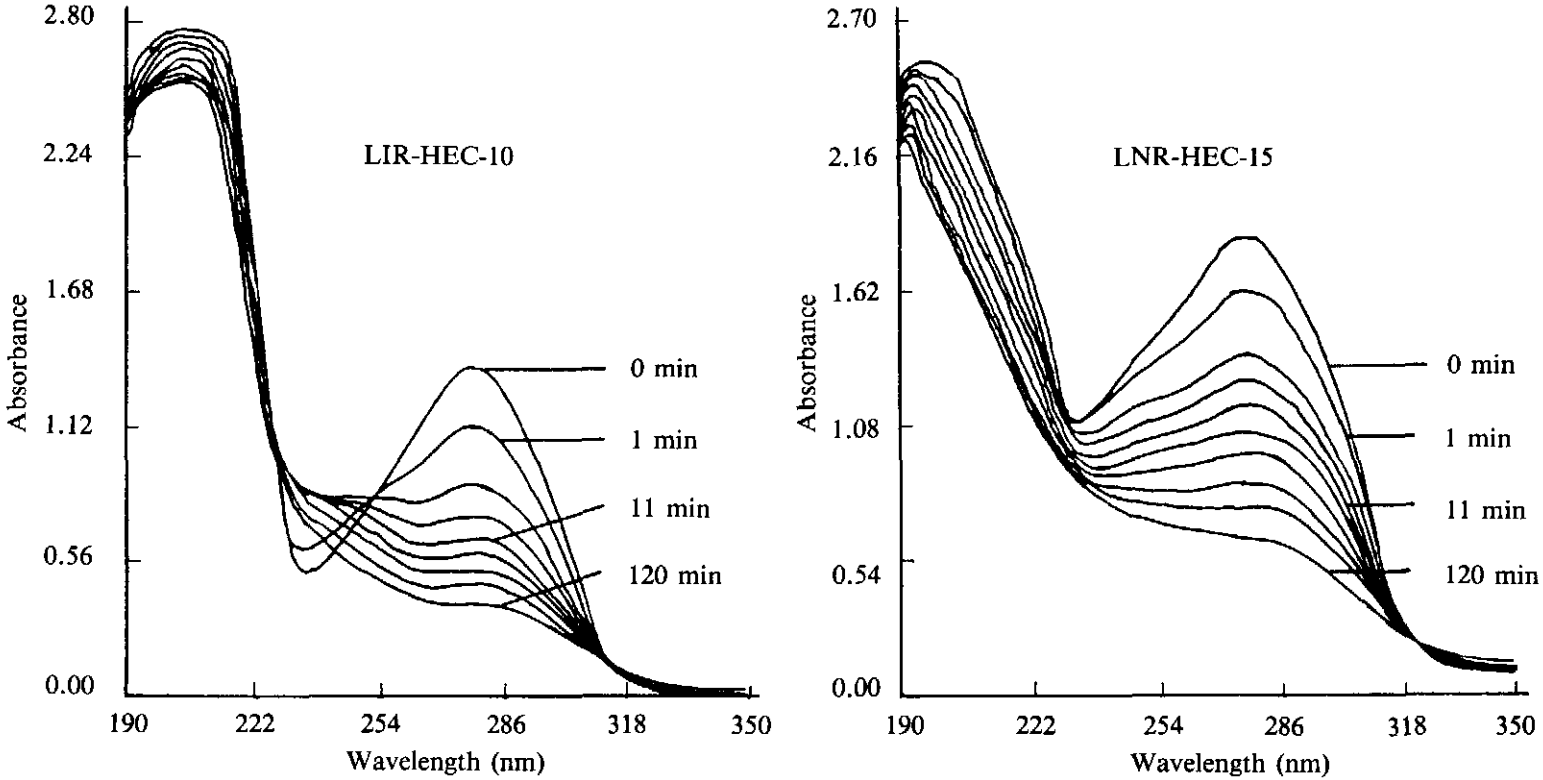

Figure 2. Changes in UV spectra of LIR-HEC-10 and LNR-HEC-15 in terms of UV irradiation time.

at λ = 278 nm is observed, especially at irradiation time of less than 11 min. Therefore, the photo-sensitivity of the polyisoprene carrying cinnamate groups can be considered principally as a reaction of photo-dimerisation of the cinnamate group as shown earlier.

There are detailed reports by Azuma *et al.*[10,11] on the photo-dimerisation of cinnamate groups in polydienes or polypentenamers with pendent cinnamoyl ester groups, in which the kinetic equations of the reaction have been expressed.

By considering that the photo-dimerisation of cinnamate groups is finally summarised by four basic reaction paths *(Figure 3)* according to the previous work of Tsuda[12], and by assuming the steady state of the excited species and the isomerisation of the cinnamate groups does not take place in a solid film, the photo-dimerisation rate is expressed by Azuma *et al.* as follows:

$$-\frac{d[C]}{dt} = 2\frac{d[C-C]}{dt} = 2\alpha l_{abs}\, k_2\, [C]/lk_4$$

where l and l_{abs} denote film thickness of a specimen and light intensity absorbed by the sample, and α denoted the reciprocal of Einstein:

$$\alpha = (6.023 \times 10^{23}\, h\, \nu)^{-1}$$

This expression is formulated in two forms depending on the conditions of the absorbed light intensity:

- In the case where the absorbed light is less than the incident light intensity ($l_{abs} < l_o$), the photo-dimerisation rate is represented as a second-order reaction rate equation based on the concentration of the cinnamate groups and independent of the film thickness, as follows:

$$\frac{1}{[C_t]} - \frac{1}{[C_o]} = k_{obs}t \qquad \ldots 5$$

- If the absorbed light is nearly equal to the incident light intensity ($l_{abs} \sim l_0$), the photo-dimerisation rate is represented as a pseudo first-order reaction rate equation and the film thickness term is included in the observed rate constant, as follows:

$$\mathrm{Ln}\frac{[C_o]}{[C_t]} = k_{obs}t \qquad \ldots 6$$

In our study, we have verified that the photo-crosslinking rate depends on the film thickness. Consequently, the second expression was retained to express the photo-polymerisation rates.

When a film specimen of polyisoprene carrying pendent cinnamate groups is irradiated with UV light, the absorption intensity of the UV spectrum due to the cinnamate group at λ = 278 nm decreases.

The consumption of the cinnamate groups was estimated by using the UV spectral change

A. Excitation $\quad C \xrightarrow{h\nu,\ k_1} C^*$

B. Dimerisation $\quad C^* + C \xrightarrow{k_2} C{-}C^* \longrightarrow C{-}C$

C. Isomerisation $\quad C^* \xrightarrow{k_3} C^{isomer}$

D. De-activation $\quad C^* \xrightarrow{k_4} C$

C and C* denote the cinnamate groups at the ground singlet state and the lowest excited state consisting of the singlet or triplet state, respectively.

Figure 3. Basic reaction paths in photo-lysis of cinnamate groups.

at $\lambda = 278$ nm which is an effective wavelength for the dimerisation of cinnamate groups.

Since measurements were always made on films of the same thickness (about 1 μm), *Equation 6* can be written, according to Beer-Lambert's equation, as follows:

$$\text{Ln}\ \frac{[C_o]}{[C_t]} = \text{Ln}\ \frac{[A_o]}{[A_t]} = k_{obs}t \qquad \ldots 7$$

where $[A_o]$ and $[A_t]$ are respectively light intensity absorbed by the film sample at the times t_o and t.

Conversion of cinnamate groups can be expressed as follows:

$$\text{Conversion}\ (\%) = \frac{[C_o] - [C_t]}{[C_o]}\ 100 \qquad \ldots 8$$

According to Beer-Lambert's law, *Equation 8* can be written as follows:

$$\text{Conversion}\ (\%) = \frac{[A_o] - [A_t]}{[A_o]} 100 \qquad \ldots 9$$

There is little difference between the photo-crosslinking kinetics of photo-sensitive LIR and LNR, as shown in *Figures 4* and *5* which represent the time conversions of the cinnamate groups in the different cinnamate polyisoprenes prepared respectively from LIR and LNR and the pseudo first-order kinetics. In all the cases, the rate of conversion was observed to decrease with increasing reaction time, and crosslinking yields after 120 min of irradiation time were generally about 60%. This result is easily explained by the decrease of mobility of the chains, due to the three dimensional network formation which reduces the probability of meeting between the cinnamate groups and/or can probably enhance the intervention of the polyisoprene unsaturations in the photo-crosslinking process. *Figure 2* shows, at long periods of irradiation, an increasingly comparable change of intensity of absorption band at $\lambda = 278$ nm and $\lambda = 200 - 210$ nm. This information again supports the fact that at the initial irradiation time, the photo-crosslinking reaction occurs almost exclusively from cinnamate groups. Furthermore, the rate conversion is not influenced by the content of cinnamate groups on the polyisoprene when it is lower than 10%. The observed rate constants obtained as the initial slope of the pseudo first-order kinetics, owing to the fact that the slopes decrease with reaction duration, are identical when the considered cinnamate polyisoprene result from the same initial polyisoprene (LIR or LNR) *(Table 2)*. At equal cinnamate contents, the observed rate constant is always slightly lower with the LNR derivative than with the LIR derivative. On the other hand, it is surprising that the rate conversion slows down when the cinnamate content exceeds 10%. A possible explanation for this phenomenon is that increasing the carboxylic acid group concentration on the backbone polyisoprene can induce an initial increase of the medium viscosity owing to hydrogen bond interactions, which will increase with the cinnamate proportion.

Because the photo-crosslinking rate of cinnamate derivatives is significantly increased in the presence of photo-initiator compounds[13], a series of tests of photo-crosslinking of polyisoprenes carrying pendent cinnamate groups was carried out with 2,2-dimethyl-2-hydroxy acetophenone (Darocur 1173), as the photo-initiator. The results obtained with LIR HEC 7 and LNR HEC 9 mixed with a portion of 4 g for 100 g of photo-sensitive polymer were compared with those obtained without photo-initiator. No notable photo-crosslinking rate increase was noted. This may be due to incompatibility between the chemical nature of the two ingredients of the mixture.

Kinetic study of the photo-crosslinking of polyisoprenes bearing pendent acrylate groups derived from LIR. The study was carried out with only one sample: 15% acrylate modified LIR (LIR-HEA-15). Two tests were carried out, with and without photo-initiator (Darocur 1173).

Figure 6 shows the changes in UV spectrum of LIR-HEA-15 in terms of UV irradiation time. Contrary to photo-crosslinking of polyisoprenes carrying cinnamate groups

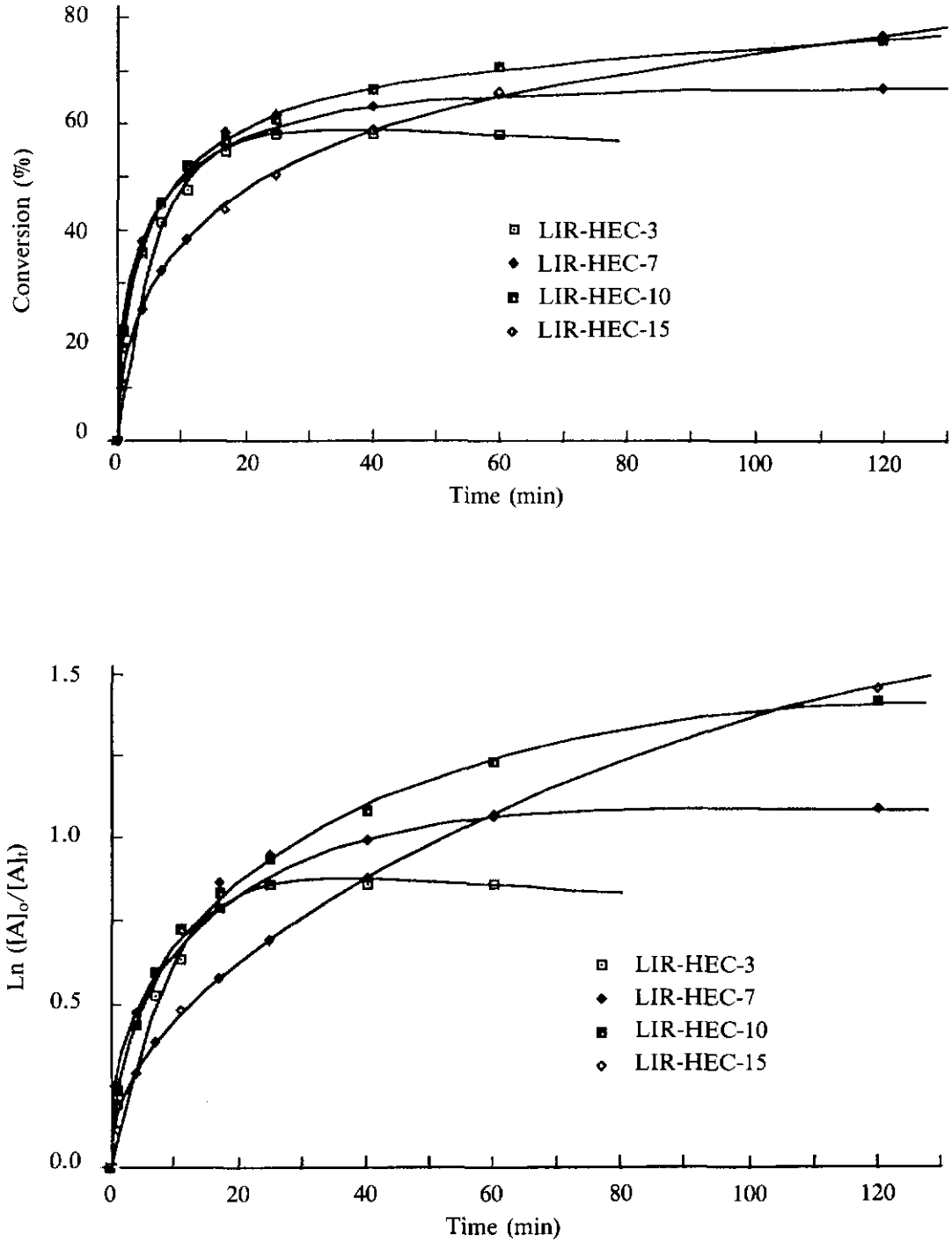

Figure 4. Conversion of cinnamate groups in LIR-HEC in terms of UV irradiation time and the relationship between Ln $([A]_o/[A]_t)$ and UV irradiation time.

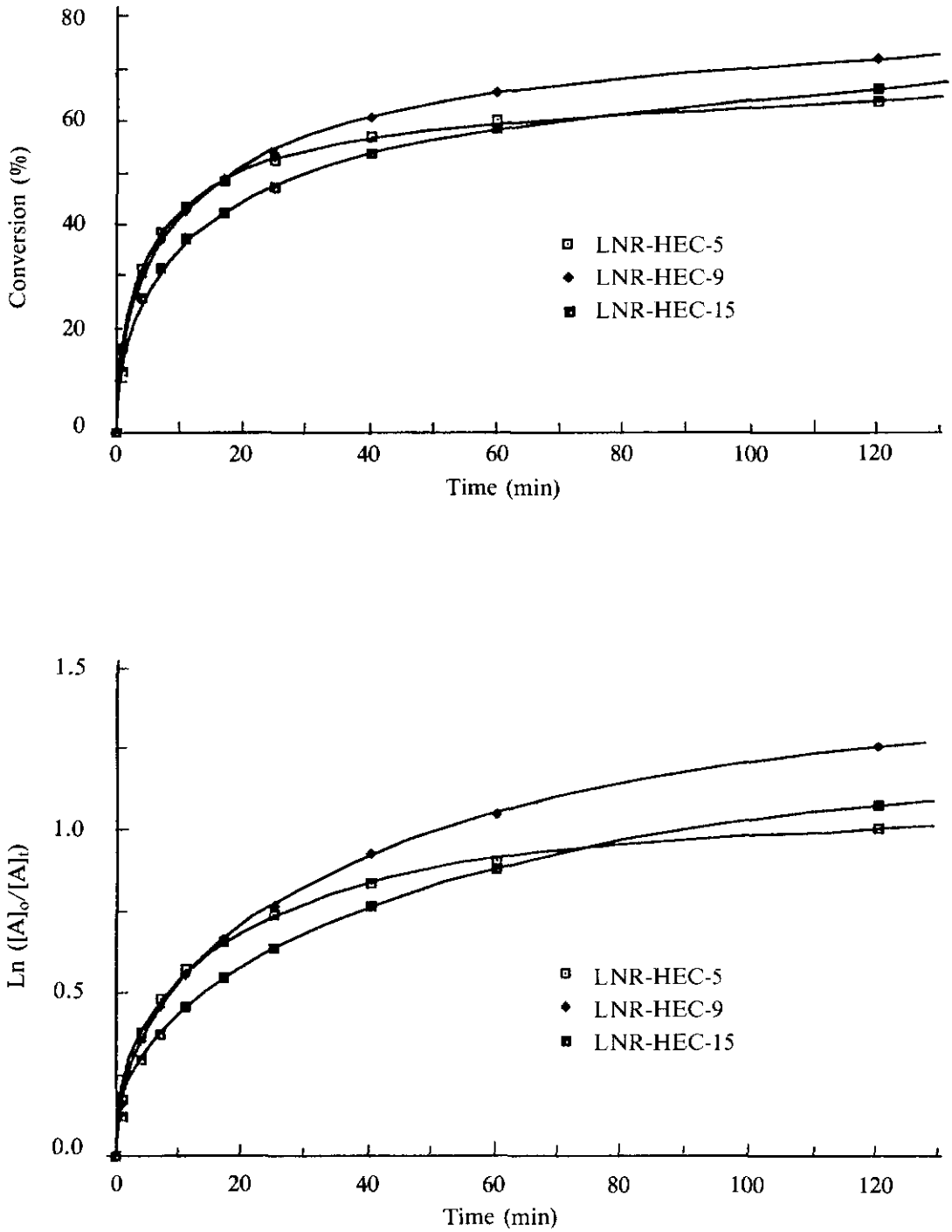

Figure 5. Conversion of cinnamate groups in LNR-HEC in terms of UV irradiation time and the relationship between Ln ($[A]_o/[A]_t$) and UV irradiation time.

TABLE 2. PHOTO-CROSSLINKING OF LIR AND LNR CARRYING CINNAMATE GROUPS: OBSERVED RATE CONSTANTS, k_{obs}, OBTAINED AS THE INITIAL SLOPE OF THE PSEUDO FIRST-ORDER KINETICS

Sample	k_{obs}
LIR-HEC-3	0.25
LIR-HEC-7	0.25
LIR-HEC-10	0.25
LIR-HEC-15	0.11
LNR-HEC-5	0.18
LNR-HEC-9	0.18
LNR-HEC-15	0.09

(Figure 2) but in agreement with those of 15% maleinisated polyisoprene *(Figure 1),* a large decrease of the intensity of the polyisoprene unsaturation absorption band at λ = 200 nm which apparently denotes a simultaneous consumption of polyisoprene carbon-carbon double bonds and acrylate groups, was noted. However, this decrease was more rapid than for the 15% maleinisated polyisoprene. These observations confirm a mechanism different from that observed in the case of the polyisoprene carrying cinnamate groups.

The time conversion of the acrylate groups in LIR-HEA-15 is shown in *Figure 7.* The positive action of the photo-initiator appeared only after 15 min of exposure. A gradual rate acceleration in function of the duration was then noted.

Photo-crosslinking of a few UV formulations for industrial applications. For industrial applications, the direct use of photo-sensitive polymers without other ingredients cannot be contemplated because its high viscosity sets some problems for its processing. So, for these reasons, they are always incorporated in formulations which are generally composed of different diluent reactive monomers of varied chemical nature, associated to a photo-initiator.

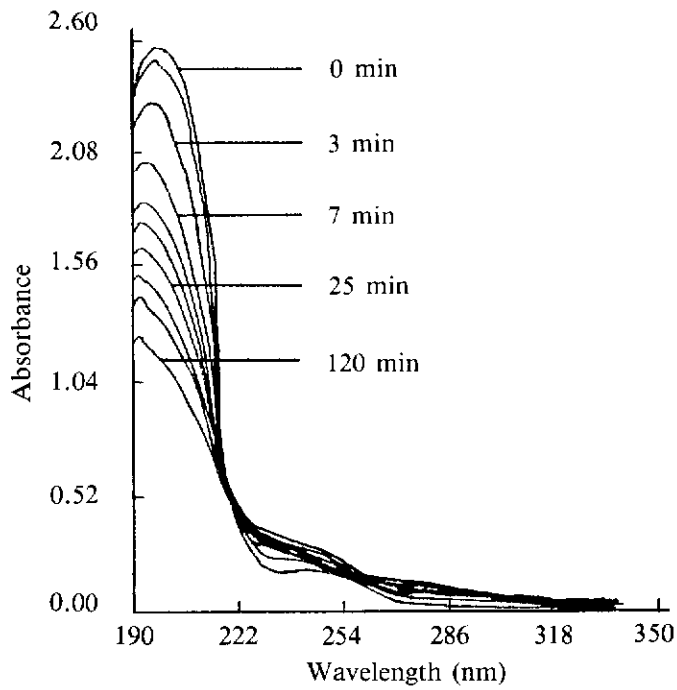

Figure 6. Changes in UV spectrum of LIR-HEA-15 in terms of UV irradiation time.

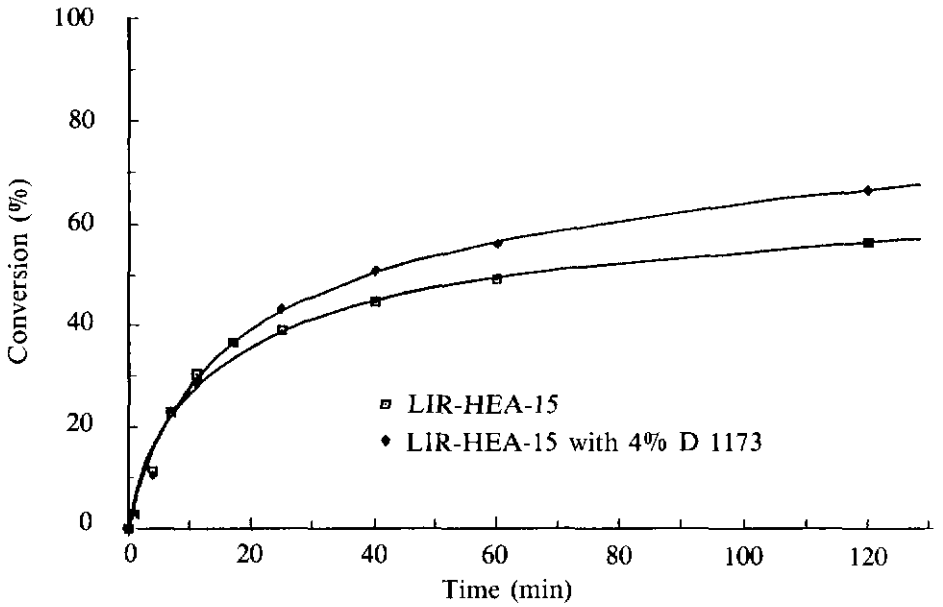

Figure 7. Conversion of acrylate groups in LIR-HEA in terms of UV irradiation time.

Three of the synthesised photo-sensitive polyisoprenes were selected to verify the possibility of obtaining flexible films by their incorporation into formulations: LIR-HEC-7, LIR-HEC-15 and LNR-HEC-9. It was noted that without diluent, after 5 s of irradiation, the polyisoprene carrying cinnamate groups led to partially crosslinked films (the swelling test in chloroform showed swelling with some deterioration of the film due to partial dissolution of it in the solvent). On the other hand, in the presence of a photo-initiator, no damage of the films was observed after 5 s of irradiation; only its swelling in the chloroform was noted. Contrary to the former results obtained with the PCG 9G-1 UV lamp, these results demonstrate the positive influence of the photo-initiator on photo-crosslinking.

In complete UV formulations prepared with the HEC modified polyisoprenes, films having the mechanical and chemical properties with no swelling in chloroform, a good adherence on the support and a good flexibility were obtained after 3 s of irradiation.

CONCLUSION

The aim of the present study was to synthesise photo-sensitive elastomers from liquid natural rubber (LNR) obtained by depolymerisation of natural rubber in the latex phase with the phenylhydrazine/oxygen system. It was demonstrated that LNR, in the same manner as low molecular weight synthetic 1,4-polyisoprene (LIR), can be used as the starting product in the two-step chemical modification to obtain a photo-sensitive elastomer with the ability to rapidly crosslink under UV irradiation. For the first time, the LNR (or LIR) was maleinisated by thermal 'ene' addition of maleic anhydride on polyisoprene unsaturations, and the resulting maleinisated elastomer was transformed into the photo-sensitive polymer by reaction of photo-polymerisable alcohols, such as 2-hydroxyethyl cinnamate and 2-hydroxyethyl acrylate, on the succinic anhydride functions.

It was noted that polyisoprenes carrying cinnamate groups were more stable than those bearing acrylate pendent groups which can easily crosslink during the synthetic process.

The former are easily prepared from LNR according to the selected process and are quite soluble in most of the organic solvents, whereas preparation of the latter presented some problems because, generally, gel formation occurred rapidly during the esterification step. The photo-crosslinking studies have shown that in the case of polyisoprene carrying cinnamate groups, the maximum efficiency of the photo-crosslinking rate is obtained with a polymer having less than 10% of photo-sensitive units. Polyisoprene bearing cinnamate grafts are principally photo-crosslinked *via* 2+2 cyclo-addition involving the carbon-carbon double bond of the cinnamate functions with formation of cyclobutane rings, which explains the retention of elastic properties of the initial polydiene.

The difficulties encountered during the synthesis of LNR bearing pendent acrylate groups have prevented a study with this family of polymers. A single polymer derived from LIR was tested. It was shown that, with this acrylate LIR category, the polyisoprene carbon-carbon double bonds are involved in the photo-crosslinking process.

The study of formulations including LNR (or LIR) among the different ingredients has shown that these photo-sensitive elastomers can be used to prepare flexible films with good adherence on metal and good resistance to solvent action.

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REFERENCES

1. ROFFEY, C.G. (1982) *Photopolymerization of Surface Coatings.* Chichester, UK: John Wiley & Sons.

2. PAUTRAT, R. AND MARTEAU, J.(1974) Method for the Preparation of Rubbers with Low Molecular Weight through Degradation of Macromolecular Polyenes and the Products thus Obtained. *Fr. 74 03 052 (Chem. Abstr. 84: 45773e).*

3. PAUTRAT, R.(1980) Liquid Rubbers from Natural Polyisoprenes. Preparation and Properties. *Rev. Gen. Caoutch. Plast.*, **600**, 91.

4. DEROUET, D., PHINYOCHEEP, P., BROSSE, J.C. AND BOCCACCIO, G. Synthesis of Photocrosslinkable Elastomers by Chemical Modification of Liquid Natural Rubber. II. Study of the Succinic Ring Opening by Reaction with Photopolymerizable Alcohols. *Eur. Polym. J.*, in press

5. DEROUET, D., PHINYOCHEEP, P., BROSSE, J.C. AND BOCCACCIO G. Synthesis of Photocross-linkable Elastomers by Chemical Modification of Liquid Natural Rubber. I. Maleic Anhydride Introduction onto Polyisoprene Structures. *Eur. Polym. J.*, in press.

6. PINAZZI, C., DANJARD, J.C. AND PAUTRAT, R. (1963) Addition of Unsaturated Monomers to Rubber and Similar Polymers. *Rubb. Chem. Technol.*, **36**, 282.

7. CREED, D., GRIFFIN, A.C., GROSS, J.R.D. HOYLE, C.E. AND VENKATARAM, K. (1988) Photochemical Crosslinking of Novel Poly-cinnamate Main-chain Mesogens. *Mol. Cryst. Liq. Cryst.*, **155** (Part. B), 57.

8. NAKAMURA, K. AND KIKUCHI, S. (1967) Photosensitive Resins. II. The Electron Spin Resonance Spectra of Light-irradiated Poly(vinyl cinnamate). *Bull. Chem. Soc. Jpn.*, **40**, 2684.

9. EGERTON, P.L., PITTS, E. AND REISER, A. (1981) Photocycloaddition in Solid Poly(vinyl cinnamate). The Photoreactive Polymer Matrix as an Ensemble of Chromophore Sites. *Macromolecules*, **14**, 95.

10. AZUMA, C., SANUI, K. AND OGATA, N.(1982) Synthesis and Properties of Photosensitive Polymers. IV. Photosensitivity of Cyclized Polydienes and Polypentenamer with Pendent Cinnamate Groups. *J. appl. Polym. Sci.*, **27**, 2065.

11. AZUMA, C., HASHIZUME, N., SANUI, K. AND OGATA, N. (1983) Synthesis and Properties of Photosensitive Polymers. IV. Photosensitive Rubbers from Hydroxyethyl Cinnamate and Polyisoprene Modified with Maleic Anhydride. *J. appl. Polym. Sci.*, **28**, 543.

12. TSUDA, M. (1972) Photochemical Reaction Mechanism of Photosensitive Polymers. *Yuki Gosei Kagaku Kyokai Shi*, **30**, 589 (Chem. Abstr. 78: 44305t).

13. BROSSE, J.C., REMMAS, M. AND SOUTIF, J.C. (1990) Polymeres photoreticulables à unités cinnamiques. 3) Photoreticulation. *Makromol. Chem.*, in press.