Production of Hydroxyl-Terminated Liquid Natural Rubber—Mechanism of Photochemical Depolymerization and Hydroxylation

T. RAVINDRAN, M. R. GOPINATHAN NAYAR, and D. JOSEPH FRANCIS,* *Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682 022, India*

Synopsis

Photochemical degradation of natural rubber yielded hydroxyl-terminated liquid natural rubber (HTNR) when carried out in solution in presence of H_2O_2. Ultraviolet radiation from a medium pressure mercury vapor lamp and sunlight were found to be almost equally effective in bringing about the depolymerization and hydroxylation of natural rubber. The variations in the composition of the reagents and exposure time on the extent of depolymerization was conducted, and a suitable procedure for the large scale preparation of HTNR was described. A probable mechanism leading to the formation of HTNR as well as the side products is discussed based on the analytical data.

INTRODUCTION

Degradation of natural rubber (NR) into shorter chain segments with reactive end groups is a prerequisite for the production of new materials such as thermoplastic elastomers based on natural rubber. The earliest attempt to depolymerize NR was carried out by K. V. Hardman in 1923. He succeeded in depolymerizing NR to yield a product which then found use in setting bristles in paint brushes. Several reports appeared later on the depolymerization by thermal, mechanical,[1] chemical, and photochemical degradations. Degradation by mastication is a nonrandom process, where scission occurs only in those molecules possessing greater than a critical chain length,[2-4] which tends to limit the extent of degradation. Thermal breakdown of NR in presence of air or oxygen causes softening.[5] According to Voronenkov et al.,[6] the thermal breakdown of NR proceeds via a cyclic intermediate which is present in small amounts in NR. Prolonged heating of NR solution in chlorobenzene *in vacuo* at temperatures within the range 25–220°C caused degradation.[7] Hydrogenperoxide under pressure and temperature,[8] phenylhydrazine in the presence of ferrous chloride and oxygen,[9] para toluenesulfonic acid and hydrogen peroxide[10] are some of the reagents used for the chemical degradation of NR. Oxidative degradation of 1,4-cis polyisoprene with the help of oxygen in the presence of AIBN at 80°C was reported by Pchelintsev et al.[11] Degradation in solution was effectively carried out using 5–25% of azomethine oxide, nitrile

---

* To whom all correspondence should be addressed.

oxide, nitrile amines, aldehyde–phenyl hydroxylamine reaction products, etc.[12] Ozone is another active scission reagent to NR which yield oligomers with aldehydic and ketonic terminal groups.[13] Redox couples comprising of organic peroxide, perhydrol, and atmospheric oxygen as the oxidizers and aromatic sulphonic acids and aromatic hydrazines as the reducers were successfully employed in the depolymerization of NR.[14]

Degradation in the latex stage was carried out using thionaphthol[7] and nitrobenzene in presence of UV light.[15] Blake and Bruce[16] noticed that unvulcanized rubber becomes sticky in the presence of light. The sensitizing effect of thiobenzophenone in the photodegradation of NR in benzene solutions was studied by Rabek.[17] Use of solar energy to depolymerize dry NR in presence of nitrobenzene and acetylacetonates of iron and cobalt had been reported by Scott et al.[18]

Although the foregoing description presents several methods for the depolymerization of NR, most of them involve cumbersome procedures, and in several cases the products are not suitable for further applications such as chain extension. The methods aimed at the introduction of desired terminal functional groups in the NR oligomers are those reported by Pautrat,[14] Brosse et al.[19] and Gupta et al.[8] According to the first two authors, NR in the latex stage or in an organic solvent was degraded on a large scale by the redox reagent phenylhydrazine and atmospheric oxygen at 50–70°C. The method yielded liquid NR with terminal carbonyl groups which in the presence of excess phenyldrazine were transformed into phenylhydrazones. This terminal functional groups opened several ways to modify the functionality. For example, by reacting with reagentlike diacidchlorides, the hydrazones were transformed into carboxyl groups, controlled oxidation by hypochlorite or hypobromite in alkaline medium generated carboxyl groups, hydrolysis in the presence of acid regenerated the carbonyl groups, etc. Gupta et al.[8] obtained hydroxyl-terminated liquid NR using hydrogen peroxide as the reagent, although the processing conditions, viz., high temperature and pressure, may aggravate side reactions. The efficiency of functionalization reported was very low. A novel method for preparation of hydroxyl-terminated liquid natural rubber (HTNR) was reported from this laboratory in a preliminary communication.[20] Here we report the large scale production of HTNR and the mechanism of depolymerization and hydroxylation of NR. This product will be used in the production of thermoplastic elastomers by copolymerization.

EXPERIMENTAL

Materials

Natural crumb rubber (ISNR-5, $\overline{M}_n$ = 820,000, intrinsic viscosity in benzene at 30°C: 4.45 dL/g, Wallace plasticity p_0 = 39.0) was supplied by the Rubber Research Institute of India, Kottayam. Hydrogen peroxide (30 wt %) supplied by E. Merck (India) was used. Toluene, methanol, and tetrahydrofuran (THF) were of reagent grade used as such. Hydroquinone from E. Merck (India) was used. Santowhite MK, the nonstaining antioxidant, was obtained from Polyolefins Industries Ltd. (India) and phenyl-β-napthylamine was obtained from Indian Explosives Ltd. (India).

Production of HTNR

(a) By ultraviolet (UV) radiation (Expt 1): Natural crumb rubber was masticated for 30 min at 40°C. One kilogram of it was dissolved in 10 L toluene, and the solution was charged into the photochemical reactor, a glass vessel of 15 L capacity fitted with a water condenser and stirrer. Hydrogen peroxide solution (500 mL) was added and thoroughly mixed with the rubber solution. The mixture was then homogenized to a certain extent by the addition of 1.5 L methyl alcohol or 2.5 L tetrahydrofuran, as the case may be. The 400 W medium pressure mercury vapor lamp in an immersion well is placed in the solution.

After about 50 h irradiation 2 g of hydroquinone (about 0.02% w/v of the reaction mixture) was dispersed in the solution and was allowed to stand for a certain time. A layer of water separated at the bottom along with some white deposits as byproduct. This was removed, and the liquid rubber was recovered from the top toluene layer by distilling off the solvent under low pressure. Finally, the product was washed with methanol, treated with 0.5% w/w Santowhite MK antioxidant and dried in vacuum. The sample for analysis was purified by repeated precipitation by methanol from a toluene solution and dried in a vacuum oven. The byproduct was washed with methyl alcohol and dried in a vacuum oven to get 10% yield of a highly viscid material.

(b) By sunlight (Expt 2): The reactor consisted of a flat-bottomed borosilicate glass flask of 15 L capacity. It was fitted with a water condenser and a mechanical stirrer. The whole assembly, with the material for irradiation having the same composition as in the above method, was placed in sunlight. After 50 h exposure the liquid rubber was recovered by the procedure described above.

Measurements. The molecular weight distribution was measured by a gel permeation chromatograph (GPC) (Waters Associates, Model 6000 A solvent delivery system with differential refractometer R-401). IR spectrum was recorded in a Perkin-Elmer Model 377 IR Spectrometer. The ^{1}H-NMR spectrum of the sample was recorded from a solution in $CDCl_3$ using a JEOL-JNM Spectrometer in the CW mode. The ^{13}C-NMR spectrum (proton decoupled) was recorded under ambient conditions from a solution of $CDCl_3$ using a JEOL-FX 90 Q FTNMR spectrometer, operating at 22–49 MHz. TMS was used as internal standard. Solution viscosity was measured in toluene solvent using the Ubbelhode viscometer.

Hydroxyl, hydroperoxide, carboxyl, and carbonyl groups were estimated using standard methods.[21,22] The depolymerized rubber was compounded in a Brabender Plasticorder (PL-3S), and tensile measurements were done in a Zwick universal testing machine (1445).

RESULTS AND DISCUSSION

The molecular weight measurements at different intervals of time for the depolymerization of NR in UV (Expt 1) and sunlight (Expt 2) are listed in Tables I and II, respectively. Figure 1 represents the GPC traces of the product from Expt 1 and Expt 2. From these data it is clear that sunlight is almost as effective as UV in bringing about degradation of NR in solution. Production cost is very low in this case since sunlight is readily available in

TABLE I
Dependence of Molecular Weight[a] on the Time of Exposure to UV Radiation

Time of irradiation (h)	Homogenizing solvent, tetrahydrofuran					Homogenizing solvent, methanol				
	$\bar{M}_n$	$\bar{M}_v$	$\bar{M}_w$	$\bar{M}_z$	D^b	$\bar{M}_n$	$\bar{M}_v$	$\bar{M}_w$	$\bar{M}_z$	D^b
10	244,200	392,800	441,600	636,900	1.80	301,400	421,000	592,000	714,600	1.96
20	42,500	78,000	89,400	169,800	2.10	94,300	192,100	252,600	479,900	2.67
30	21,000	39,100	46,900	84,400	2.23	44,700	81,200	91,400	163,600	2.04
40	6900	12,400	14,200	24,300	2.06	8400	13,400	15,200	31,900	1.80
50	4100	6900	8300	17,400	2.02	5300	7900	9500	18,000	1.79

[a] Corrected to the nearest hundred.
[b] Molecular weight dispersity.

TABLE II
Dependence of Molecular Weight[a] on Time of Exposure to Sunlight

Time of irradiation (h)	Homogenizing solvent, tetrahydrofuran					Homogenizing solvent, methanol				
	$\bar{M}_n$	$\bar{M}_v$	$\bar{M}_w$	$\bar{M}_z$	D^b	$\bar{M}_n$	$\bar{M}_v$	$\bar{M}_w$	$\bar{M}_z$	D^b
10	301,500	413,000	521,200	742,400	1.72	394,100	492,700	601,900	812,700	1.52
20	49,600	89,100	94,200	178,300	1.89	114,900	212,500	284,200	596,800	2.47
30	26,000	42,400	48,100	101,000	1.84	61,000	89,100	131,400	233,500	2.15
40	8400	13,200	15,100	28,900	1.79	10,500	18,300	19,600	36,200	1.86
50	4700	8100	9400	24,100	2.00	6200	8900	10,600	18,900	1.70

[a] Corrected to the nearest hundred.
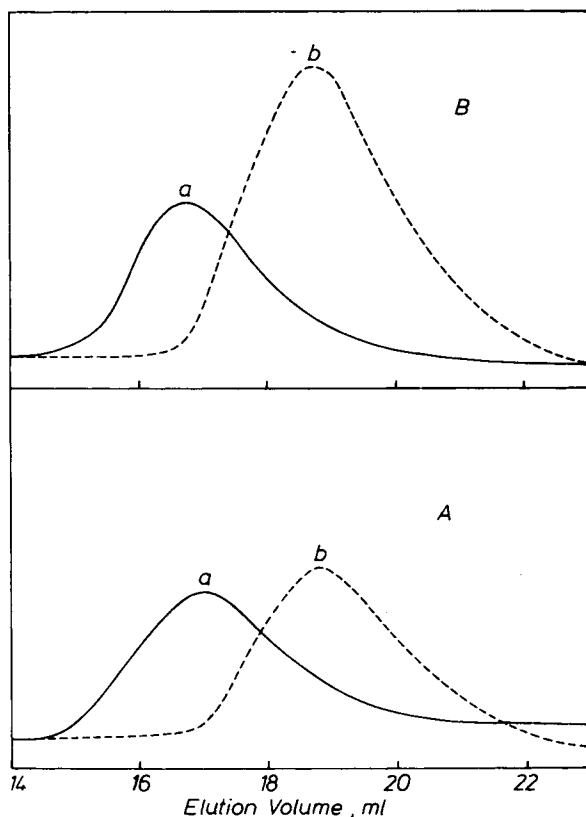[b] Molecular weight dispersity.

Fig. 1. GPC traces of liquid HTNR samples obtained by: (A) sunlight irradiation for (a) 30 h and (b) 50 h; (B) UV irradiation for (a) 30 h and (b) 50 h.

tropical countries like India. The use of masticated rubber in the present processes helped to increase the concentration of the rubber solution. This increased the production rate and also the extent of depolymerization. However, the concentration was limited to 10%, beyond which the solution formed was not workable.

HTNR with any range of molecular weight could be prepared by suitable choice of the composition of the reaction mixture and exposure time. The hydroxyl functionality remained slightly less than 2 (*vide infra*). The extent of depolymerization was found to increase with decreasing concentration of NR, increasing amount of hydrogen peroxide and also by longer exposure time. Varying the amount of homogenizer, i.e., THF or methyl alcohol, beyond the specified amount did not have any effect on depolymerization. The choice of THF rests on the fact that it is miscible with both toluene and aqueous H_2O_2 and at the same time it can dissolve rubber also. Methyl alcohol being a nonsolvent to NR has the advantage that the viscosity of the reaction mixture will be slightly reduced by its addition.[7] The extent of degradation was slightly higher when THF was used. However, on the basis of production cost methyl alcohol is preferred in the large scale production of HTNR.

The liquid NR recovered from the solution after distillation of the solvent under reduced pressure was almost clear and colorless. When this material was

TABLE III
Compounding and Mechanical Properties of HTNR

	Depolymerized rubber $\overline{M}_n - 10,500$	Control sample (crumb rubber)
	Formulation	
Rubber	100	100
ISAF black	50	50
ZnO	5	5
Stearic acid	2	2
Sulfur	2.5	2.5
CBS	0.8	0.8
PBN	1.0	1.0
	Properties	
Tensile strength (MPa)	10.2	28.7
Stress at 200% (MPa)	6.8	6.7
Stress at 300% (MPa)	9.1	8.8
Elongation at break (%)	324	580
Hardness, Shore A	47	62

kept for a few days, its viscosity gradually increased. This drawback entailed processing modifications. Hence after the depolymerization, about 0.2% w/v of hydroquinone was dispersed in the solution for the removal of radical species that may be present in the solution. The recovered material was further modified by adding 0.5% (w/w) of Santowhite MK, a nonstaining antioxidant. These modifications render the HTNR slightly colored, and it could be stored without any appreciable change in viscosity. The addition of phenyl-β-napthylamine caused the material to become profusely colored, and hence it was not used as antioxidant for the HTNR.

With a view to study the change in mechanical properties caused by the depolymerization process, the liquid NR was compounded as per a conventional recipe. The properties of the vulcanized material are listed in Table III. Considerable loss in properties was observed which is due to the reduction in chain length of the rubber molecule caused by depolymerization.

The hydroxyl-terminated liquid NR obtained by the irradiation of NR by UV light was characterized previously using the spectral and chemical analyses and was reported in our earlier communication.[20] The product presently obtained by the sunlight irradiation was analyzed by the IR, ^{1}H-NMR, ^{13}C-NMR, and the other chemical methods.[21,22] The results obtained were comparable to the earlier data[22] for the UV-irradiated sample. This is quite evident from the IR spectra [Figs. 2(b, c), ^{1}H-NMR [Figs. 3(a, b)], and ^{13}C-NMR [Fig. 4(a, b)] of the samples from Expts 1 and 2, respectively. The broad OH stretching band at 3600–3400 cm^{-1} in the IR spectra and the peaks at $\delta = 60.72$ and 63.51 characteristic of the α-carbon of allylalcohol in the ^{13}C-NMR spectra suggest the terminal hydroxyl groups in the product. In both cases the signals due to the allylic hydroxyl protons in the ^{1}H-NMR spectra are masked by the multiplets at $\delta = 5.1$ of the
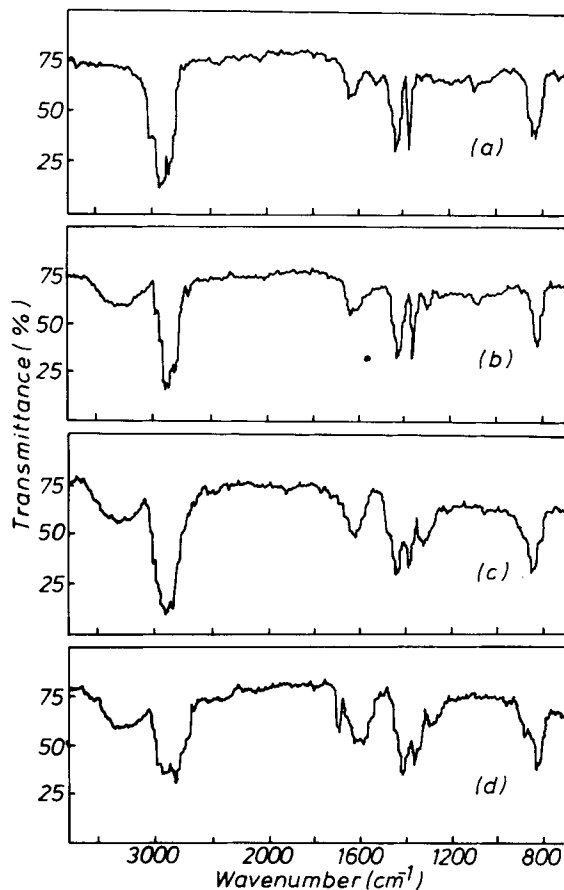
$$\text{C}=\text{C}_{\text{H}}$$
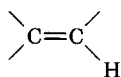
protons.

Fig. 2.   Infrared spectra of: (a) raw natural rubber; (b) HTNR by sunlight irradiation; (c) HTNR by UV irradiation; (d) the byproduct.

The main absorption bands characteristics of NR are preserved in the spectra, indicating that the 1, 4-cispolyisoprene configuration was not disturbed during the depolymerization process. The hydroxyl values estimated for products from Expts 1 and 2 after 50 h irradiation are 26.95 mg of KOH/g and 23.04 mg of KOH/g, which gave functionalities 1.97 and 1.93, respectively, when THF was used as the homogenizing solvent, and 19.3 mg of KOH/g and 16.35 of KOH/g, which give functionalities 1.82 and 1.80, respectively, when methanol was used as the homogenizer. The products readily reacted with diisocyanates such as toluene diisocyanate, leading to chain extention. Rapid reaction with the isocyanate is characteristic of primary hydroxyl groups. The reactivity of the hydroxyl group towards diisocyanate decreases in the order pri > sec > ter. This observation along with the aforementioned findings corroborate the presence of primary hydroxyl groups at the chain ends of the liquid rubber from both the experiments.

The identical nature of the products suggested that the course of degradation process follows the same path. In the light of the analytical data obtained in the present studies and the theories of the earlier investigators, a mechanism of chain scission and hydroxylation is discussed here. The most probable point of attack on the NR molecule is at the α-methylene carbon atom is
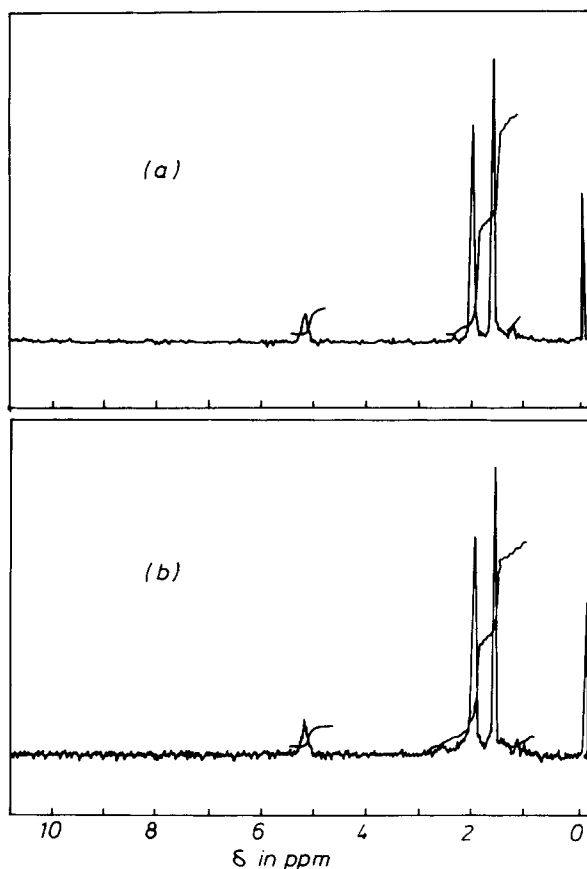
Fig. 3. ^{1}H-NMR spectra/CDCl$_3$/25°C of: (a) HTNR by sunlight irradiation; (b) HTNR by UV irradiation.

supported by the fact that, in oxidation processes, the initial product is a hydroperoxide and that there is no change in the degree of saturation.[23] The presence of a CH$_3$ group attached to the ethylenic carbon atom in polyisoprene tends to reduce the C—H dissociation energy by hyperconjunction, facilitating substitution at the α-methylenic carbon atom.[24] The studies on light aging of NR has established that the double bonds in the chains were not affected in the initial stages, and they disappeared slowly only after prolonged exposure to light.[25-27]

Based on the foregoing discussion it is inferred that whether it is degradation by chemical species or by radiation, the point of attack is not the double bond in the chain but the C^α—H bond. It is further evidenced by the fact that there is no change observed in the absorption band of the isoprene unit,

$$
\begin{array}{c}
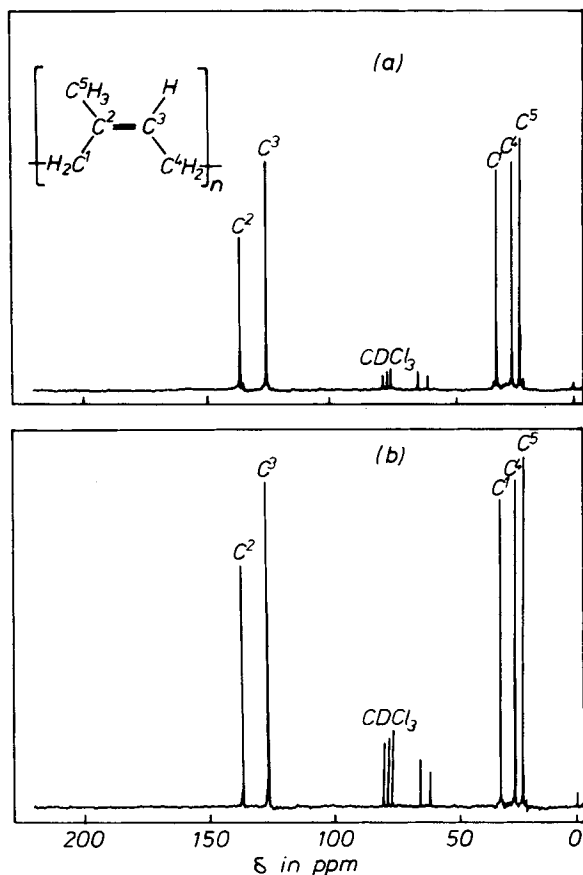\text{CH}_3 \\
| \\
\text{—CH}_2\text{—C}\text{=}\text{CH—CH}_2\text{—}
\end{array}
\qquad\qquad \text{(viz. 835 cm}^{-1}\text{)}
$$

in the IR spectra (Fig. 2).

Fig. 4. ^{13}C-NMR {H} Spectra/CDCl$_3$/25°C of: (a) HTNR by sunlight irradiation; (b) HTNR by UV irradiation.

In all the earlier proposals free radical mechanism has been suggested for the degradation of NR. The chemical reagents used in the process are free radical generators such as thiols, peroxides, etc.[28-31] These free radicals interact with the labile C$^\alpha$—H bond abstracting the proton and leaving behind the macroradicals.[32,33,24] In a similar manner in the photochemical degradation the photons remove the C$^\alpha$—H r⁻ ʾon, giving rise to macroradicals.[25] The peroxides formed by the interacı ᶠ these radicals with oxygen decompose to yield the various degradation products containing the carbonyl, carboxyl, and hydroxyl groups at the chain ends.[18,25,32] The estimation of hydroperoxide groups and the identification of carbonyl and carboxyl group were given as proof of participation of oxygen in the degradation process.

However, analysis of the main product obtained in the present studies did not show any indication of the presence of peroxide, carbonyl, and carboxyl groups. The hydroxyl functionality of very nearly 2 and the absence of the other oxygen bearing groups suggest that a mechanism other than the conventional one is to be sought in the present processes. In our earlier studies,[20] with the aid of spectral data, we could clearly establish the existence of

structures I and II in the depolymeterized products:
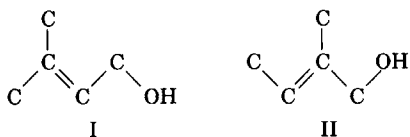
The generation of such structural entities entails the cleavage of the original rubber molecule in between the α-carbon atoms. In the case of NR the σ bond between α-methylenic groups which connect the isoprene units are not in the same plane with the double bonds. This is because there is a tendency of coiling up of the rubber segments due to its cis configuration.
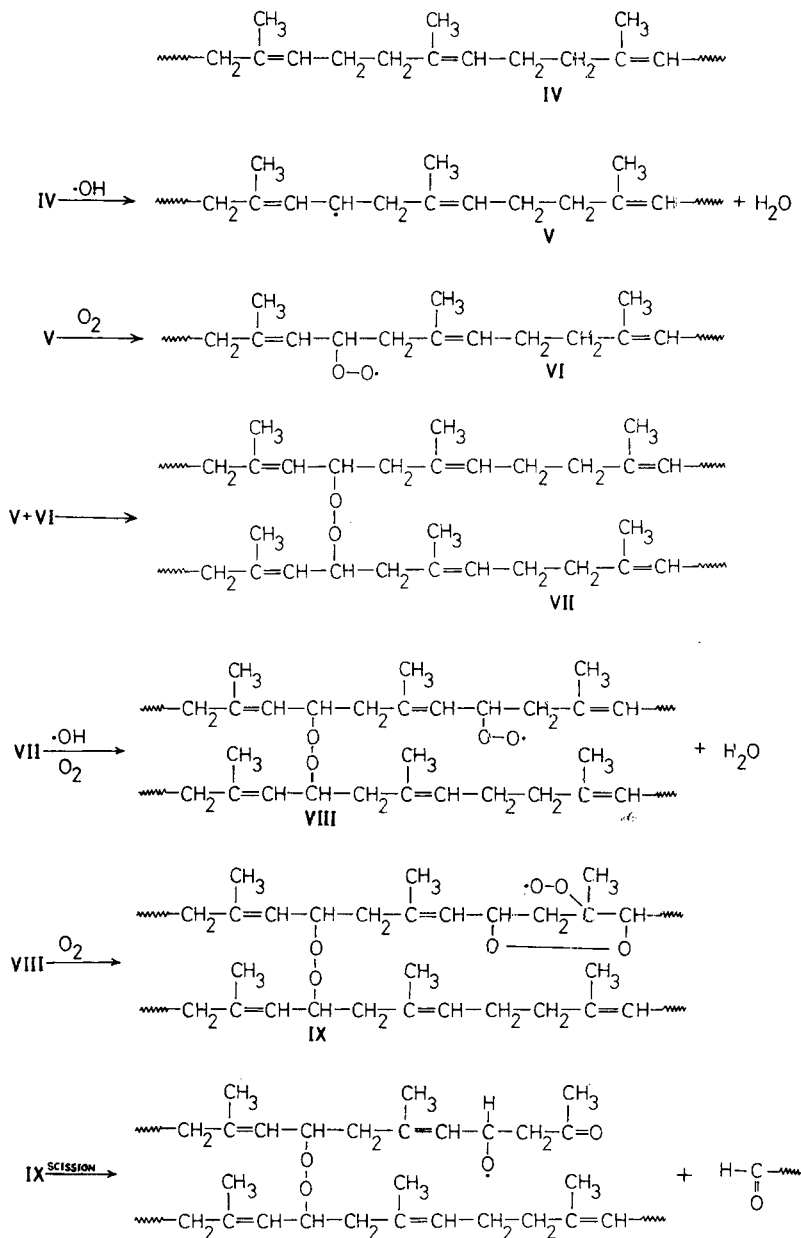

III
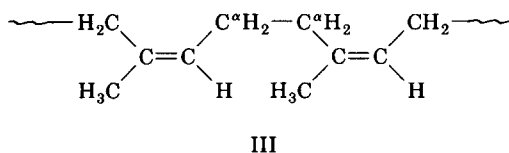
The steric hinderance caused by such an unbalanced structure with pendent methyl groups weakens the CH_2—CH_2 bond, leading to its rupture under favorable conditions which are provided by thermal energy[34,8] or the chain modifications caused by radical species[35,32] or by radiation.[36,37,25] The radical reagent used in the degradation process, namely hydrogen peroxide, is susceptible to decomposition under the influence of radiation. Although hydrogen peroxide has an absorption maximum at 254 nm, it interacts with radiation up to 370 nm, yielding hydroxyl radicals.[38]

Based on the above discussion, the following mechanism is suggested for the depolymerization and hydroxylation of NR:

$$H_2O_2 \overset{h\nu}{\rightleftharpoons} H_2O_2^*$$

$$H_2O_2^* \rightarrow 2\,\dot{O}H$$
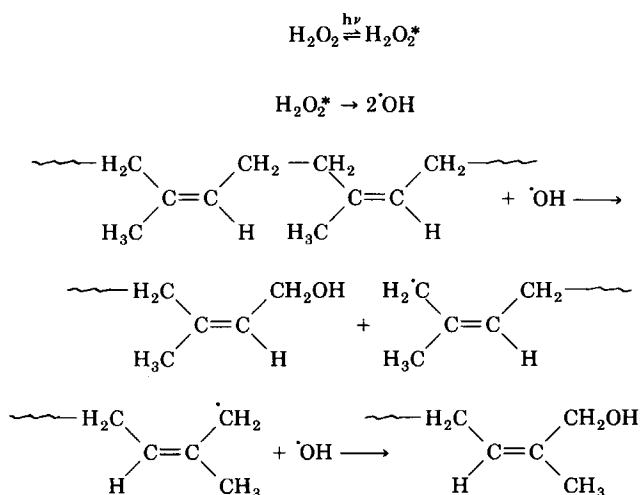
The byproduct isolated from the reaction mixture was found to contain carbonyl group [IR peak at 1710 cm^{-1} in Fig. 2(d)]. Chemical analysis of the

material gave hydroxyl value of 18.46, mg of KOH/g carbonyl value 5.94 mg of KOH/g, and carboxyl value of 12.29 mg of KOH/g. The formation of these groups may be through side reaction with free O_2, giving peroxide radicals and its subsequent decomposition. The low solubility of the byproduct and the observation that its yield increased with increase in rubber concentration, hydrogen peroxide and exposure time, show that crosslinking plays an important role in its formation. Based on the above the following mechanism in which the macroperoxide crosslink and also decompose to yield carbonyl and carboxyl groups is proposed:

$$\text{~~~}CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_2-\underset{\underset{CH_3}{|}}{C}=CH\text{~~~}$$
$$\textbf{IV}$$

$$\textbf{IV} \xrightarrow{\cdot OH} \text{~~~}CH_2-\underset{\underset{CH_3}{|}}{C}=CH-\overset{\cdot}{C}H-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_2-\underset{\underset{CH_3}{|}}{C}=CH\text{~~~} + H_2O$$
$$\textbf{V}$$

$$\textbf{V} \xrightarrow{O_2} \text{~~~}CH_2-\underset{\underset{CH_3}{|}}{C}=CH-\underset{\underset{O-O\cdot}{|}}{C}H-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_2-\underset{\underset{CH_3}{|}}{C}=CH\text{~~~}$$
$$\textbf{VI}$$

$$\textbf{V+VI} \longrightarrow$$

[Structure VII: two crosslinked chains connected through an O–O bridge]

$$\textbf{VII}$$

$$\textbf{VII} \xrightarrow[O_2]{\cdot OH} \quad + H_2O$$

[Structure VIII: crosslinked chains with O–O· peroxide radical]

$$\textbf{VIII}$$

$$\textbf{VIII} \xrightarrow{O_2}$$

[Structure IX: crosslinked chains with cyclic peroxide ·O–O]

$$\textbf{IX}$$

$$\textbf{IX} \xrightarrow{\text{SCISSION}} \quad + \; H-\underset{\underset{O}{\|}}{C}\text{~~~}$$

[Scission products with carbonyl and carboxyl groups]

Scheme 1

CONCLUSION

The photochemical degradation of natural rubber in solution, described above, is an efficient and economical method for the preparation of HTNR, since the labor and machinery requirements are low and also it utilizes solar energy. The high clarity and processability are added advantages to the material. Two products are obtained in the degradation process. The main product is HTNR and the byproduct in 10% yield is a lightly crosslinked liquid rubber with carbonyl, carboxyl, and hydroxyl functional groups which can be easily separated from the main product.

References

1. W. F. Watson and M. Pike, *J. Polym. Sci.*, **9**, 229 (1952).
2. D. J. Angier et al., *J. Polym. Sci.*, **25**, 129 (1957).
3. F. Boche, *J. Appl. Polym. Sci.*, **4**, 101 (1960).
4. G. M. Brislow, *J. Polym. Sci.*, **A1**, 2261 (1963).
5. H. Hagen, *Kautschuk*, **14**, 203 (1938).
6. V. V. Voronenkov, G. V. Bobykina, Yu. F. Shapiro, and E. A. Lazurin, *Vysokomol. Soedin.*, **20**, 724 (1978).
7. G. Foxley, *Rubber Chem. Technol.*, **34**, 1212 (1961).
8. S. K. Gupta, M. R. Kurup, E. Devadoss, Rm. Muthiah, and S. Thomas, *J. Appl. Polym. Sci.*, **30**, 1095 (1985).
9. K. Mori and T. Fuji, Japan Kokai, 7664585 (1976); *Chem. Abstr.*, **85**, 109801 t (1976).
10. R. Pautrat and J. Marteau, Belg. Pat. 824,654; *Chem. Abstr.*, **84**, 45773e (1976).
11. V. V. Pchelintsev, L. M. Ivanova, K. B. Piotroviskii, and T. V. Dykina, *Zh. Prikl. Khim.*, **51**, 2367 (1978).
12. G. I. Illarinova, G. I. Kogan, V. A. Krol, Yu. A. Patrushin, and K. Salnis, *U.S.S.R. Pat.* 626097 (1978); Chem. Abstr., **90**, 24534m (1979).
13. D. P. Stephens, R. C. M. C. Intrsh, and O. Taylor, *J. Polym. Sci. A-1*, **6**, 1037 (1968).
14. R. Pautrat, *Rev. Gen. Caoutch. Plast.*, **600**, 91 (1980).
15. D. Barnard, *Proceedings of a UNIDO Sponsored Symposium*, Phuket, Thailand, May 1981, p. 79.
16. J. T. Blake and P. L. Bruce, *Ind. Eng. Chem.*, **33**, 1198 (1941).
17. J. F. Rabek, *Polymery*, **11**(6), 266 (1966).
18. L. M. K. Tillekeratne, P. V. A. G. Perera, M. S. C. DeSilva, and G. Scott, *J. Rubber Res. Inst. Sri Lanka*, **52**(2), 501 (1977).
19. J. C. Brosse, R. Pautrat, and G. Boccaccio, *Proceedings of a UNIDO Sponsored Symposium*, Phuket, Thailand, May 1981, p. 195.
20. T. Ravindran, M. R. G. Nayar, and J. D. Francis, *Makromol Chem. Rapid Commun.*, **7**, 159 (1986).
21. A. Krause, A. Lange, and M. Erzin, *Plastics Analysis Guide*, Macmillan, New York, 1983, p. 29, 32–34.
22. J. C. Brosse, M. Bonnier, and G. Legeay, *Makromol. Chem.*, **183**, 303 (1982).
23. J. L. Bolland and C. Gee, *Rubber Chem. Technol.*, **20**, 609 (1947).
24. J. Cortyl-Lacau, *Rubber Chem. Technol.*, **28**, 746 (1955).
25. A. Tkač and V. Kellö, *Rubber Chem. Technol.*, **28**, 383 (1955).
26. A. Tkač and V. Kellö, *Rubber Chem. Technol.*, **28**, 968 (1955).
27. A. Tkač, V. Kellö, and J. Hrivikova, *Rubber Chem. Technol.*, **28**, 989 (1955).
28. C. G. Moore and J. Scanlan, *Rubber Chem. Technol.*, **34**, 309 (1961).
29. M. Montu, *Rev. Gen. Caoutch.*, **29**, 506 (1952).
30. G. Gromandi, *Kautschuk*, **6**, 177 (1930).

31. P. Campagnon and A. Delande, *Rev. Gen. Caoutch*, **24**, 4 (1947).

32. P. M. Norling, T. C. P. Lee, and A. V. Tobolsky, *Rubber Chem. Technol.*, **38**, 1198 (1965).

33. E. M. Bevilacqua, *Rubber Chem. Technol.*, **29**, 583 (1956).

34. S. K. Gupta, B. John, and M. R. Kurup, *Proceedings of International Rubber Conference*, Rubber Res. Inst., Kottayam, India, November 1980.

35. M. Imoto and S. Kiriyama, *J. Polym. Sci.*, **18**, 309 (1955).

36. L. Bateman, *Trans. Inst. Rubber Ind.*, **21**, 118 (1945).

37. Bondy, *Rev. Gen Caoutch.*, **11**, 6 (1934).

38. D. K. Tang and S. Y. Ho, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1357 (1984).