

Functional End Group Determination in Photo-degraded Liquid Rubbers

S. S. SOLANKY* AND R. P. SINGH*#

The end functionality of the oligomers of natural rubber determined by acetylation, silylation methods and analysis by ¹H-NMR using trifluoroacetic acid, titration of hydroperoxide determination method etc. is investigated. Attempts were made to estimate the end functionalised groups produced in the chain cleavage during hydrogen peroxide catalysed photo-oxidative degradation of high molecular weight natural rubber which was an initiation of producing liquid natural rubber.

Key words: photo-degraded; end functionality; oligomers; acetylation; silylation; liquid natural rubber; NMR spectroscopy

The term ‘telechelic’ describes^{1,2} the polymers possessing two functional terminal groups. Telechelic oligomers have their applications in surface coatings, adhesives as well as in reactive injection mouldings and extrusion. Currently, they are also used in sealants, adhesives, to make block and graft copolymers and as binder for rocket propellants. Functionality, a very important property of the pre-polymers, is defined as the average number of reactive functional groups per molecule. A number of chemical and spectroscopic methods¹⁻⁷ have been used to determine such as acetylation, acylation, silylation, titrimetric, NMR spectroscopy, gas chromatography, electro-chemical and thermogravimetry. Number-average functionality is defined as the ratio of the number of functional groups to the number of macromolecule⁸. The functionality ranging from

1.9 to 2.6 is estimated in commercial hydroxy terminated polybutadiene. The titrimetric determination⁹ of the esterification with acetic anhydride or phthalic anhydride is a standard method to determine hydroxyl end groups. It can be modified to increase indirectly the enthalpy of this reaction in a calorimeter with excellent accuracy. Schnecko and Angew¹ used IR spectroscopy to determine the carboxylic end groups whereas it is less suitable for hydroxyl group probably because of structural sensitivity. Houwelingen⁹ studied acetylation method using dichloro acetic anhydride (in excess) of dichloro acetic acid.

Gel Permeation Chromatography (GPC) has been used to determine the molecular weight distribution within each functional groups and the inter-relationship between

functionality distribution and molecular weight distribution has been studied¹⁰. Patil *et al.*¹¹ studied the dye interaction test for determination of hydroxyl groups. Chang *et al.*¹² studied in detail the end group determination of hydroxyl telechelic by infra-red spectrometry and described that the IR quantification of the free hydroxyl absorption at 3640 cm^{-1} , is a convenient method for analysis of hydroxyl functionality of linear tri-arm star polyisobutylene. The band of second harmonic valence vibration of O-H at 1420 cm^{-1} can also be used for determination of hydroxyl group¹³. Srecker¹⁴ studied the carboxyl-terminated polybutadiene (CTPB) and established that the gel method is also applicable to hydroxy-terminated butadiene prepolymers (HTPB)-isocyanate systems.

In the present article, the functional end-groups in photo-degraded liquid natural rubbers have been determined by acetylation, silylation and NMR spectroscopy.

EXPERIMENTAL

Materials

Natural rubber (NR) ($\overline{M}_v = 2.82 \times 10^5$) was obtained by the courtesy of Dr. S. Thomas, M.G. University, Kottayam, Kerala. H_2O_2 (30 wt%), acetyl chloride, phenolphthalein, sodium hydroxide, potassium hydrogen phthalate, pyridine (AR Grade) and TiO_2 (anatase) were supplied by M/s. S.D. Fine Chemicals Ltd. Trimethyl chlorosilane and trifluoro acetic acid are Aldrich Chemicals and used as such. Dry toluene was used during experiments. Pyridine, acetone and tetrahydrofuran were of reagent grades and used after distillation.

Determination of End Functionalised Hydroxyl group

In a cylindrical photoreactor, (400 W medium pressure mercury vapour lamp, $\lambda \geq 290\text{ nm}$), natural rubber was photolysed in toluene solution (2.5 wt%) at 30°C under atmospheric air and nitrogen, separately. The natural rubber solution was constantly stirred in the presence of hydrogen peroxide and titanium dioxide. Aliquots were withdrawn at different time intervals and the rubber was precipitated with acetone and dried under vacuum. For photo-controlled degradation, three different experiments were carried out by taking NR solution with H_2O_2 (5 mL) (*Experiment 1*), 1 w/v% TiO_2 (*Experiment 2*) or H_2O_2 (5 mL) + 1 w/v% TiO_2 (*Experiment 3*), respectively. The degradation of natural rubber by FT-IR, ^1H and ^{13}C -NMR spectroscopies, were also studied¹⁵.

Spectral Analysis

^1H -NMR spectra were recorded using Bruker AC 200 MHz spectrometer (time acquisition: 22.048 sec, temperature: 24°C , number of transient: 512) where CDCl_3 (Aldrich 99.8% D) was used as solvent. Thin films were obtained by evaporating 1.0% w/v solution of the oxidized rubber by drying till constant weight. FT-IR spectra were recorded by PERKIN ELMER 16 PC spectrophotometer at room temperature.

Acetylating Method

The acetylation reagent was prepared by mixing acetyl chloride in dry toluene (1.5 mole/L). The ice cold 5 mL acetylation reagent was added in a dry round bottom flask, containing 1 mL pyridine in natural rubber.

The pyridine was added in NR in such a quantity that acetyl chloride was in excess (0.5 mole) against alcohol. The round bottom flask was stoppered and shaken and put in a thermostatic bath at 60°C, loosening the stopper momentarily to expel air and then stoppered tightly for 45 min with occasional shaking. The remaining pyridinium salt was hydrolysed (unused reagent) by addition of 15 mL of distilled water after cooling. The formed acetic acid was titrated by N/2 NaOH solution using phenolphthalein as an indicator. The number of hydroxyl groups were obtained by the difference between the OH content measured in the sample and the blank experiment.

$$\text{Hydroxyl number per repeating unit} = \frac{(\text{Blank} - \text{sample reading of burette}) \times [\text{N}] \text{ NaOH} \times 40}{\text{Wt of polymer (g)} / 68.12} \quad 1$$

Functionality

The functionality of the telechelic oligomers has a greater significance by itself. Properties such as viscosity of the fine solids loaded mixture and the strength of the cured propellant are greatly affected by the functionality of the polymer. Probably, it is the most important single parameter which determines the nature of the oligomeric chains. Number average molecular weight (\bar{M}_n) was determined by Vapour Pressure Osmometer, and functionality was calculated.

$$F_n = \frac{\bar{M}_n \times \text{Hydroxyl number}}{40,000} \quad 2$$

where hydroxyl number is equal to NaOH (mg)/polymer (g)

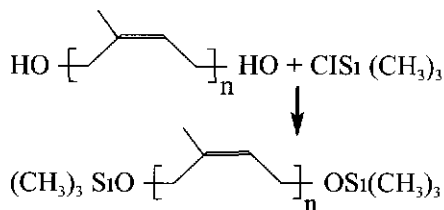
Silylation Method

The degraded natural rubber sample (50 mg) was dissolved in benzene (3.33 mL) with trimethyl chlorosilane and pyridine (1 mL), refluxed for 1 h under argon atmosphere. The remaining trimethyl chlorosilane (0.6319 mL or 1.5 mole/L) and the assumed secondary products were discarded by vacuum drying. Benzene and pyridine were also removed under reduced pressure. The $^1\text{H-NMR}$ analysis was performed in CDCl_3 without TMS. Hydroxyl functionality of the polymer was replaced by trimethoxysilane group where the presence of methyl proton shift at $\delta = 0$ ppm proves the presence of hydroxyl group in the degraded sample (Figures 3 and 4) and the functionality was calculated.

$$F_n = \frac{[\text{Intensity of } -\text{OSi}(\text{Me})_3 / 9] \times \bar{M}_n}{\text{Intensity of diene chain} / [(2x+y) \times 68.12]} \quad 3$$

where $(2x+y) = 1$,

x and y can be determined in the vinylic region of $^1\text{H-NMR}$ spectra, $y = 1,4$ structure where $\delta = 5.1$ ppm



Hydroxyl Group Determination by Using Trifluoro Acetic Acid

The measure of the intensity of the signal corresponding to the proton of the hydroxyl displaced by addition of trifluoroacetic acid led to good results in the case of oligomers. This

signal was not detected for the polymers having \bar{M}_n more than 3000. The functionality may be calculated by:

$$F_n = \frac{[\text{Intensity of } -\text{CH}_2\text{O}/2] \times \bar{M}_n}{\text{Intensity of } \text{CH}=\text{CH}/[(2x+y) \times 68.12]} \quad \dots 4$$

Hydroperoxy Group Determination by Titrimetric Method

The titration method was used as reported by Brosse and co-workers¹⁶. The degraded natural rubber sample (1 g) was dissolved in toluene (20 mL) with 2-propanol (80 mL), acetic acid (10 mL) and potassium iodide solution (3%), refluxed for 1 h. On addition of thiosulphate, no colour change was observed at the end of titration which indicated that these degraded natural rubber samples did not contain hydroperoxides.

Hydroxyl Group Determination by NMR Method

The ¹H-NMR spectra (Figure 6) presented the *cis* 1,4-polyisoprene signals in CDCl₃ at 24°C, ¹H-NMR δ = 1.63 p.p.m. (-CH₃, 3 H); δ = 2.05 p.p.m. (-CH₂-C=C, 4 H); δ = 5.1 p.p.m. (vinyl proton). The signal due to hydroxy

proton in the hydroxymethyl group is observed at ~ 4.15 p.p.m.¹⁸ but in our studies, this peak was quite clear at 3.5 p.p.m. – 4.0 p.p.m. under air as well as nitrogen atmosphere.

Molecular Weight Determination

\bar{M}_n of the controlled degraded rubbers were determined in dried toluene (0.016 wt%) at 25 ± 0.1°C using vapour pressure osmometer as shown in Tables 1 and 2.

RESULTS AND DISCUSSION

The functionality and reproducibility of the end groups depend on the photocatalytic and/or oxidizing agents. A high value of functionality and randomness was observed in case of photo-degradation of neat natural rubber (Table 3). The addition of oxidizing agent and co-catalyst may constitute an essential feature for more accurate functionality.

Functionality was estimated ~ 2 in *Experiment Number 3*, as shown in Figures 1 and 2. It was proposed that hydrogen peroxide and/or allylic hydroperoxides act as photo-initiators and produce hydroxy radicals and/or alkoxy radicals. Addition of titanium dioxide is a new approach in combination of H₂O₂ in the chain cleavage of NR in the solution form. The TiO₂ catalyzed photo-oxidation generates hydroxy

TABLE 1. \bar{M}_n OF PHOTO-DEGRADED NATURAL RUBBER (IN AIR)

| Irradiation time (h) | Number average molecular weight ($\times 10^3$) | | | |
|----------------------|---|----------------------------------|---------------------|--|
| | NR | NR+H ₂ O ₂ | NR+TiO ₂ | NR+H ₂ O ₂ +TiO ₂ |
| 0 | 282 | 282 | 282 | 282 |
| 36 | 8.3 | 1.11 | 2.37 | 2.19 |
| 63 | 7.2 | 1.02 | 1.86 | 1.58 |

TABLE 2. \bar{M}_n OF PHOTO-DEGRADED NATURAL RUBBER
(IN NITROGEN ATMOSPHERE)

| Irradiation time (h) | Number average molecular weight ($\times 10^{-3}$) | | | |
|-------------------------|--|----------------------------------|---------------------|--|
| | NR | NR+H ₂ O ₂ | NR+TiO ₂ | NR+H ₂ O ₂ +TiO ₂ |
| 0 | 282 | 282 | 282 | 282 |
| 36 | 9.9 | 6.3 | 4.63 | 5.67 |
| 63 | 6.1 | 3.26 | 4.21 | 5.03 |

TABLE 3. DETERMINATION OF HYDROXYL NUMBER IN THE
PHOTO-DEGRADED NATURAL RUBBER

| Samples | Irradiation time (h) | Hydroxyl number | |
|--|-------------------------|-----------------|-------------|
| | | In air | In nitrogen |
| NR | Neat | 0.015 | 0.015 |
| | 36 | 11.71 | 4.96 |
| | 63 | 13 | 16.32 |
| NR+H ₂ O ₂ | 36 | 68.1 | 11.17 |
| | 63 | 74.5 | — |
| NR+TiO ₂ | 36 | 20.59 | 12.52 |
| | 63 | 38.49 | — |
| NR+H ₂ O ₂ +TiO ₂ | 36 | 32.14 | 11.8 |
| | 63 | 49.87 | 14.2 |

radicals^{18, 19} on its surface which produces hydroxy-terminated end groups. The absorbed U.V. radiation < 370 nm releases electrons and positive holes in the TiO₂ crystals, some of which diffuse into the surface, resulting in the production of free radicals, which can attack the polymer causing the classical oxidative degradation. Under nitrogen atmosphere, it was observed that continuous increase in hydroxyl region which may be due to the accumulation of hydroxyl groups onto TiO₂, as they were not decomposed due to lack of free hydroxy groups formed in the presence of air as shown in *Figure 1*. The results show that functionality ~ 2 was achieved after 63 h of photo-irradiation of natural rubber

(*Figures 2 and 3*) while in initial irradiation hours, it was very low.

The results were not very much satisfactory by silylation method. Functionality determined was 1.66 (*Figure 4*) and 1.72 (*Figure 5*).

The determination of the functionality of the degraded natural rubber using trifluoroacetic acid method was a simple and reliable technique where x and y were the molar ratio of 1,2 and 1,4 units (molecular weight of a unit = 68.12). Since the peak intensity was very weak in this analysis as shown in *Figure 6*, the exact functionality could not be detected in the degraded natural rubber samples.

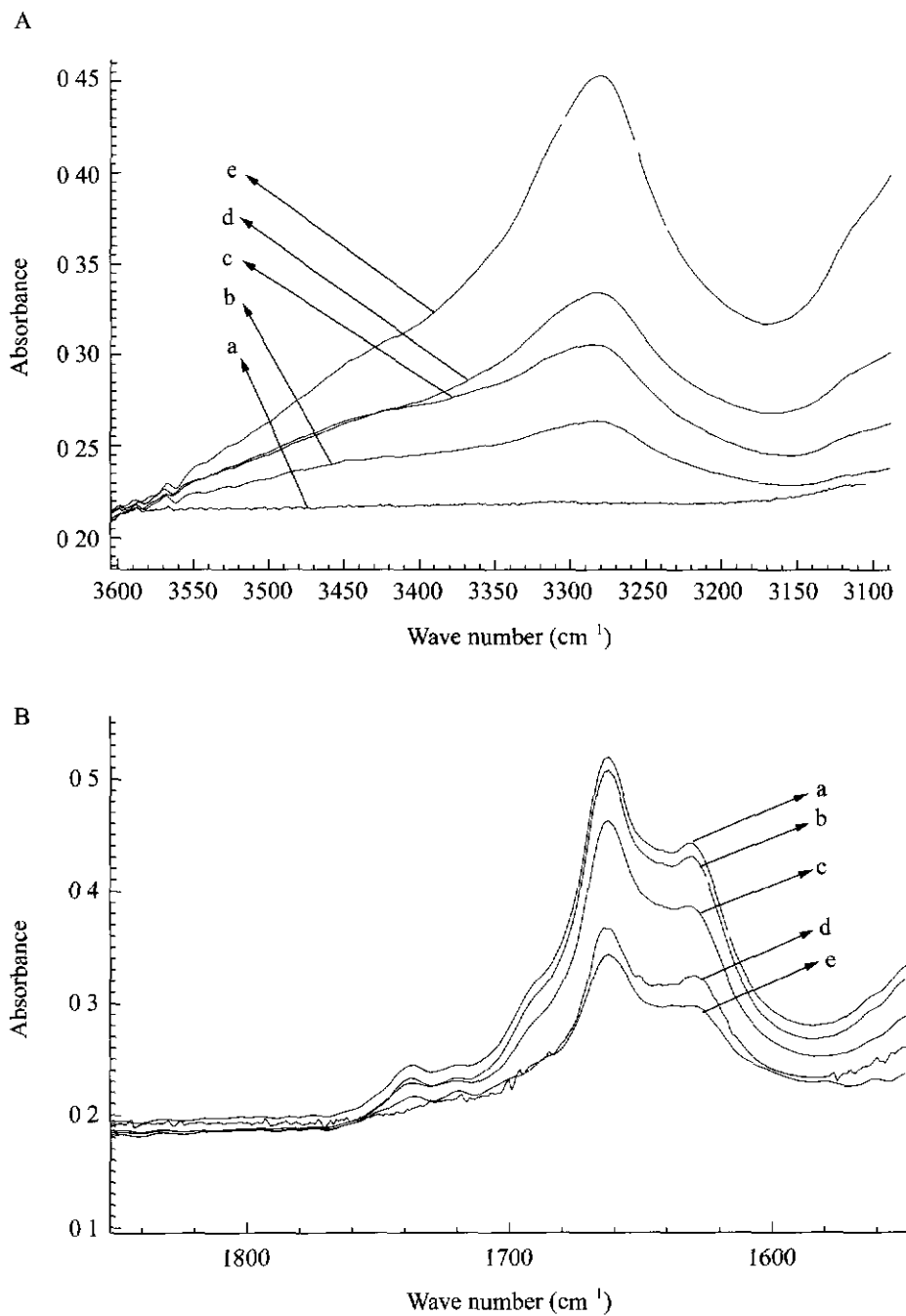


Figure 1 FT-IR spectral changes in the (A) hydroxy and (B) carbonyl region of UV irradiated natural rubber in the presence of titanium dioxide (under nitrogen atmosphere)
a Control, b 12 h, c 36 h, d 48 h and e 63 h

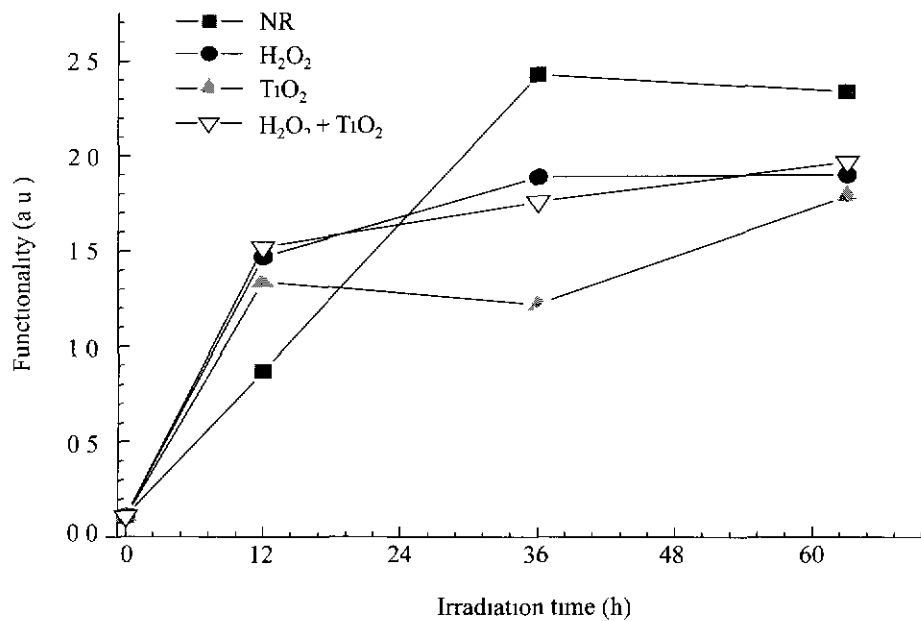


Figure 2 Rate of functionality in degraded natural rubber with irradiation time (in air)

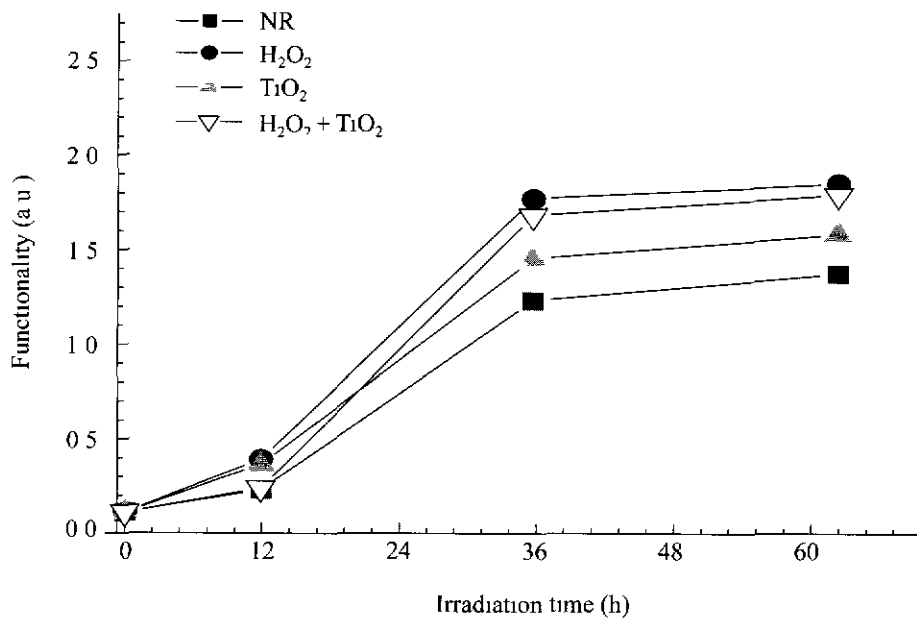


Figure 3 Rate of functionality in degraded natural rubber with irradiation time (in nitrogen atmosphere)

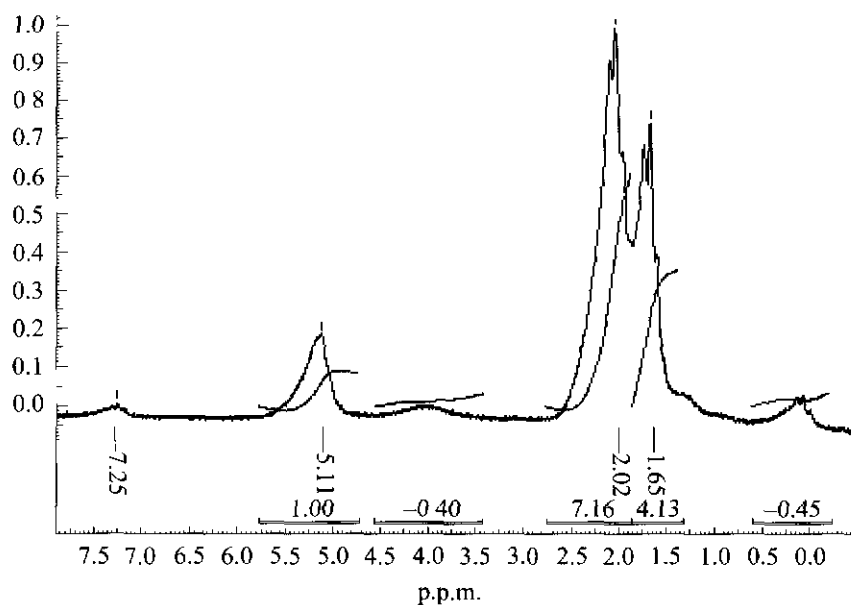


Figure 4 ^1H -NMR spectra of degraded natural rubber to determine the functionality.

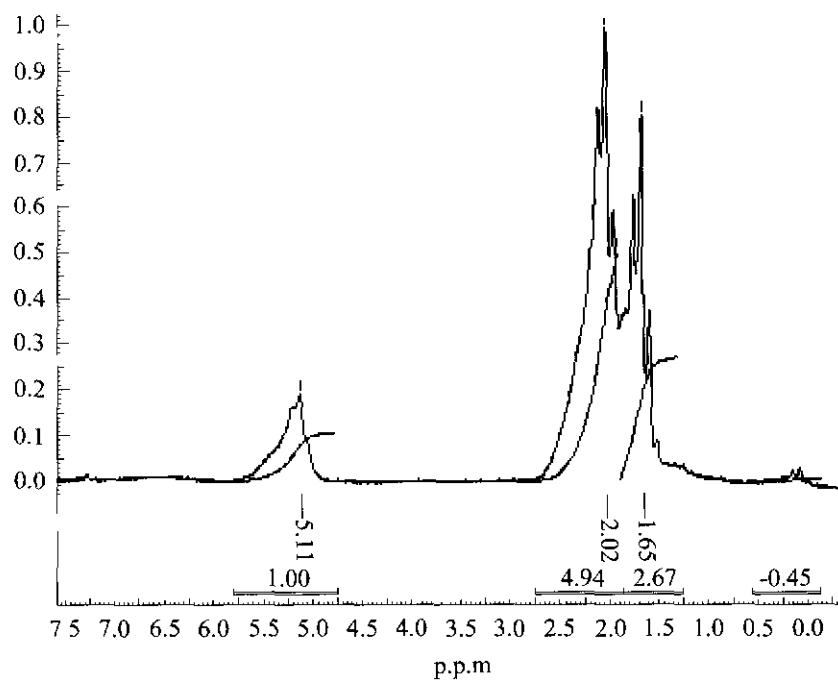


Figure 5 ^1H -NMR spectra of degraded natural rubber to determine the functionality.

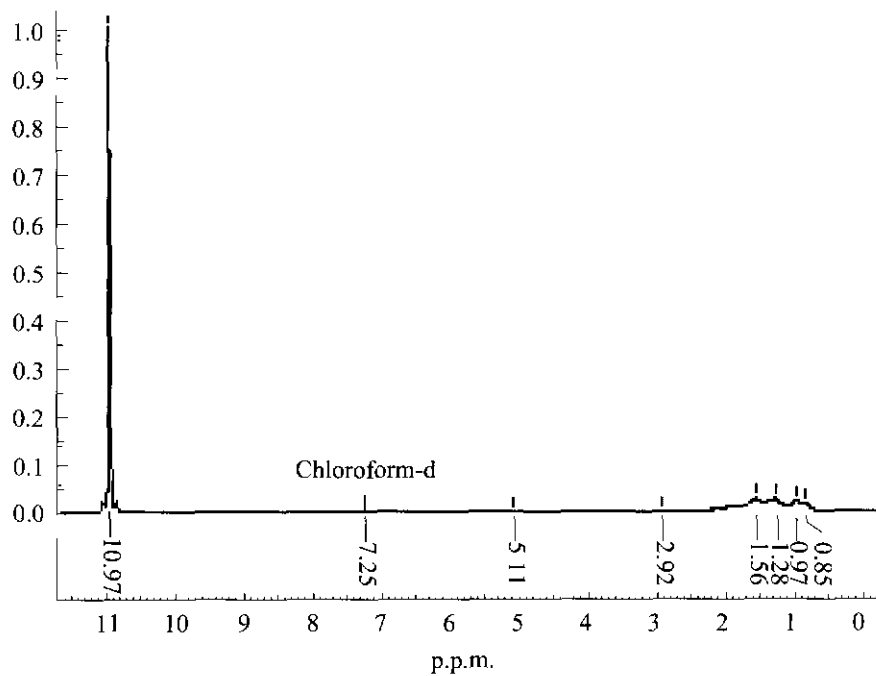


Figure 6. ^1H -NMR spectra of degraded natural rubber to determine the functionality using trifluoro acetic acid.

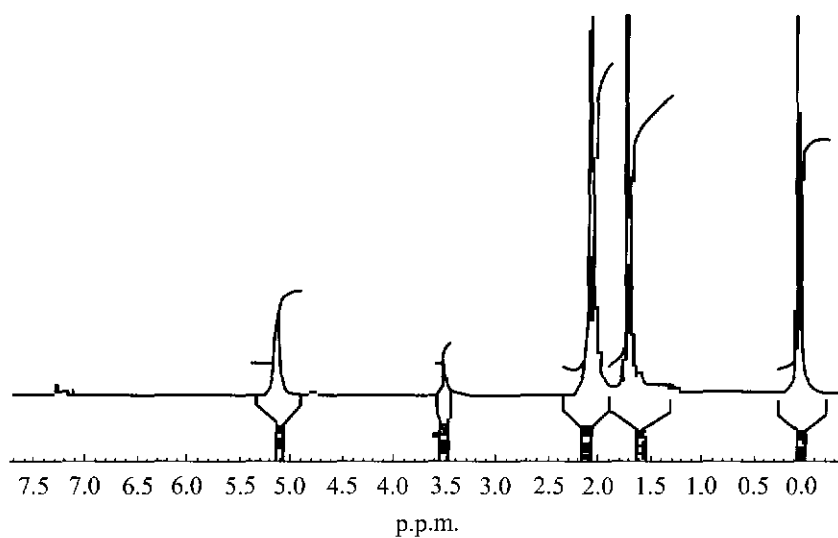


Figure 7. ^1H -NMR spectra of functionalised photo-degraded rubber.

The photolysis in the presence of hydrogen peroxide causes hydroxy radical-induced chain cleavage^{20, 21} and therefore was implied to characterise the resulting allylic alcohol chain ends. The proton adjacent to the oxygen at the end groups could be detected at $\delta = 3.4$ p.p.m. – 3.8 p.p.m. in natural rubber and latexes (Figure 7). Errors are, however, conceivable if more than one OCH_2 - group was present at the chain end.

ACKNOWLEDGEMENT

The authors would like to thank Indo-French Centre for the Promotion of Advanced Research (Centre Franco-Indian Pour la Promotion de la Recherche Avancee), New Delhi for financial support (Grant No. 1708-2). The authors are grateful to Dr. S. Sivaram, Director, National Chemical Laboratory, Pune for fruitful discussions and encouragement.

Date of receipt: June 2002

Date of acceptance: January 2003

REFERENCES

1. SCHNECKO, H. AND DIE ANGEW (1978) Synthesis and Characterization of Functional Dene Oligomers in View of Their Practical Applications. *Makromolekulare Chemie*, **70**, 9.
2. VEIBEL, S. (1972) *The Determination of Hydroxy Groups*. London: Academic Press p 69.
3. RAMEY, K. C. HAYES, M. W. AND ALTENAU, A. G. (1973) ^{13}C , ^{19}F , and ^1H Nuclear Magnetic Resonance Studies of Hydroxy-Terminated Polybutadienes. *Macromolecules*, **6**, 795.
4. MUNEKER, H. (1969) *J. Macromol. Sci.-Chem.*, **A-3**, 1465.
5. STUBBS, W. H., GORE, C. R. AND MARVEL, C. S. (1966) α , ω -Glycols from Butadiene. *J. Polym. Sci. A*, **14**, 1898.
6. ANDERSON, J. N., BACZEK, S. K., ADAMS H. E. AND VESCELIUS, L. E. (1975) Functionality Distribution of Hydroxyl-Terminated Polybutadienes Using Gel Permeation Chromatography. I. The Method and Calibration Procedure. *J. Appl. Polym. Sci.*, **19**, 2255.
7. TOMPA, S. (1972) Infrared Determination of Carboxyl and Hydroxyl Contents of Functionally Terminated Polybutadienes. *Anal. Chem.*, **44**, 628.
8. SMITH, D. M. (1935) Rapid Determination of Hydroxyl by Means of Acetyl Chloride and Pyridine. *J. Am. Chem. Soc.*, **57**, 61.
9. VAN HOUWELINGEN, G. D. B. (1981) Various Applications of Functional Group Analysis. *Analyst*, **106**, 1057.
10. LAW, R. D. (1971) Application of Gel Permeation Chromatography to Studied of Functionality Distribution of Carboxy- and Hydroxy- Polybutadienes. *J. Polym. Sci.*, **A-1**, **9**, 589.
11. PATIL S. R. AND MUKHERJEE, A. R. (1962) Formation of Hydroxyl Endgroups in Polymers and Their Detection by Dye Tests. *J. Polym. Sci.*, **58**, 1243
12. CHANG AND KANEDY (1983) *Polym. Bull.*, **9**, 518.
13. FAL'KOVA O. S. *et al.* (1974) *Vysokomol. Soedin.*, **A 16**, 2230.
14. STRECKER, R. A. H. AND FRENCH, D. M. (1968). The Determination of Reactive-Group Functionality from Gel Point

- Measurements. *J. Appl. Polym. Sci.*, **12**, 1697.
15. SOLANKY, S. S. SINGH, R. P., REYX D. AND CAMPISTRON, I. (2000) Photo-controlled Degradation of Natural Rubber *J. Rubber Res.*, **3**(2), 76–94.
16. BROSSE, J. C BONNIER M. AND LEGEAY, G. (1982) Synthese par Voie Radiclaire, de Polymers a Extremités Hydroxylees, Synthese de Polybutadienes: Etude des Microstructures. *Makromol. Chem.*, **183**, 303.
17. GAN, S. N. AND HAMID, Z. A. (1997) Partial Conversion of Epoxide Groups to Diols in Epoxidized Natural Rubber. *Polymer*, **8**, 1953.
18. PAPPAS, S. P. AND KAHHRIST, W. (1979) *J. Paint Technol.*, **47**, 42.
19. DJEGHRI, D., FORMENTI, M., JUILLET F. AND TEICHNER, S. J. (1974) *Faraday Diss. Chem. Soc.* (London), **58**, 185.
20. RAVINDRAN, T., GOPINATHAN NAYAR, M. R. AND FRANCIS, J. D. (1986) A Novel Method for the Preparation of Hydroxyl Terminated Liquid Natural Rubber. *Makromol. Chem., Rapid Commun.*, **7**, 159.
21. RAVINDRAN, T., GOPINATHAN NAYAR, M. R. AND FRANCIS, D. J. (1988) Production of Hydroxyl-Terminated Liquid Natural Rubber — Mechanism of Photochemical Depolymerization and Hydroxylation. *J. Appl. Polym. Sci.*, **35**, 1227.