ELSEVIER

Polymer 41 (2000) 2359–2365

polymer

Ozonolysis of natural rubber in chloroform solution
Part 1. A study by GPC and FTIR spectroscopy

H.M. Nor[a], J.R. Ebdon[b,*]

[a]*Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, Karung Berkunci 791, 80990 Johor Baharu, Malaysia*
[b]*The Polymer Centre, School of Physics and Chemistry, Lancaster University, Lancaster, LA1 4YA, UK*

Received 6 October 1998; received in revised form 10 June 1999; accepted 15 June 1999

Abstract

The kinetics of chain scission and major changes in functional groups of natural rubber (NR) during ozonolysis in chloroform at 0°C have been followed by gel permeation chromatography (GPC) and Fourier transform infrared (FTIR) spectroscopy. Reduction in molecular weight occurs most noticeably in the first minute of ozonolysis to give products with a bimodal distribution of molecular weight and then more gradually. After 20 min of ozonolysis, the number average molecular weight ($\overline{M}_n$) falls to less than 900 and the molecular weight distribution becomes close to unimodal again. These findings are interpreted in terms of an initial, rapid, diffusion-controlled process of ozonolysis, during which polymeric ozonides and peroxides (and possibly also hydroperoxides) are formed, followed by a slower second stage during which the ozonides and peroxides are cleaved, possibly by reaction with further ozone, to give oligomers with various oxygenated end groups. There may also be a minor competing crosslinking reaction initiated by radical intermediates from the breakdown of peroxides and hydroperoxides. Examining the products of ozonolysis at various times by FTIR spectroscopy allows changes in the relative concentrations of the oxygenated functional groups, such as carbonyl, ozonide, hydroxyl and/or hydroperoxide, introduced during ozonolysis and accompanying the reductions in molecular weight, to be monitored. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Natural rubber; Ozonolysis; Oligomers

1. Introduction

Plaumann and Ho used gel permeation chromatography (GPC) to follow reductions in molecular weight of *cis*-1,4-polyisoprene during ozonolysis in hexane at 25°C for reaction times of up to 6 min [1]. They found that ozonolysis produced products with a bimodal distribution of molecular weight. However, no observations of what happened to the bimodal distribution at ozonolysis times of greater than 6 min were reported. In an early study, Allison and Stanley described the use of IR spectroscopy to follow the ozonolysis of natural rubber (NR) in ethylene dichloride at room temperature [2]. Another early study utilizing IR spectroscopy to follow ozonolysis of NR was reported briefly by Salomon and van der Schee [3]. Both groups noted that increases in the intensities of bands arising from carbonyl (1720 cm^{-1}) and hydroxyl groups (3450 cm^{-1}) were accompanied by a reduction in the intensity of a band arising from carbon–carbon double bonds (835 cm^{-1}). Other peaks at 874, 1025 and 1090 cm^{-1} were also detected and assigned to epoxide, –O–O–, and –O– groups, respectively. Neither report mentioned the presence of ozonide groups in the ozonolysed NR. The work reported here extends the scope of these earlier studies of the ozonolysis of NR and also forms a part of our programme of work on using ozonolysis of polymers to produce telechelic oligomers (a process we call "constructive degradation") with potential uses in reactive processing and in the synthesis of novel copolymers [4–10]. Judging from the available literature on the degradation of natural rubber, it would seem that only redox and photochemical methods have been exploited to any significant extent so far to produce telechelic derivatives, although ozonolysis of synthetic *cis*-1,4- and *trans*-1,4-polyisoprenes, followed by reduction of the intermediate ozonides, appears to have been used to some extent in the former USSR to prepare low molecular weight α, ω-glycols [11–16]. Ozonolysis, if it can be controlled to give telechelic products with reproducible chain lengths, chain length distributions and end-groups, would obviously be a useful additional route to such materials. The literature to date on methods of synthesizing telechelic natural rubber derivatives and on ozonolysis of

---

* Corresponding author. Tel.: +44-01524-593655; fax: +44-01524-844037.

E-mail address: j.ebdon@lancaster.ac.uk (J.R. Ebdon)

PII: S0032-3861(99)00417-6

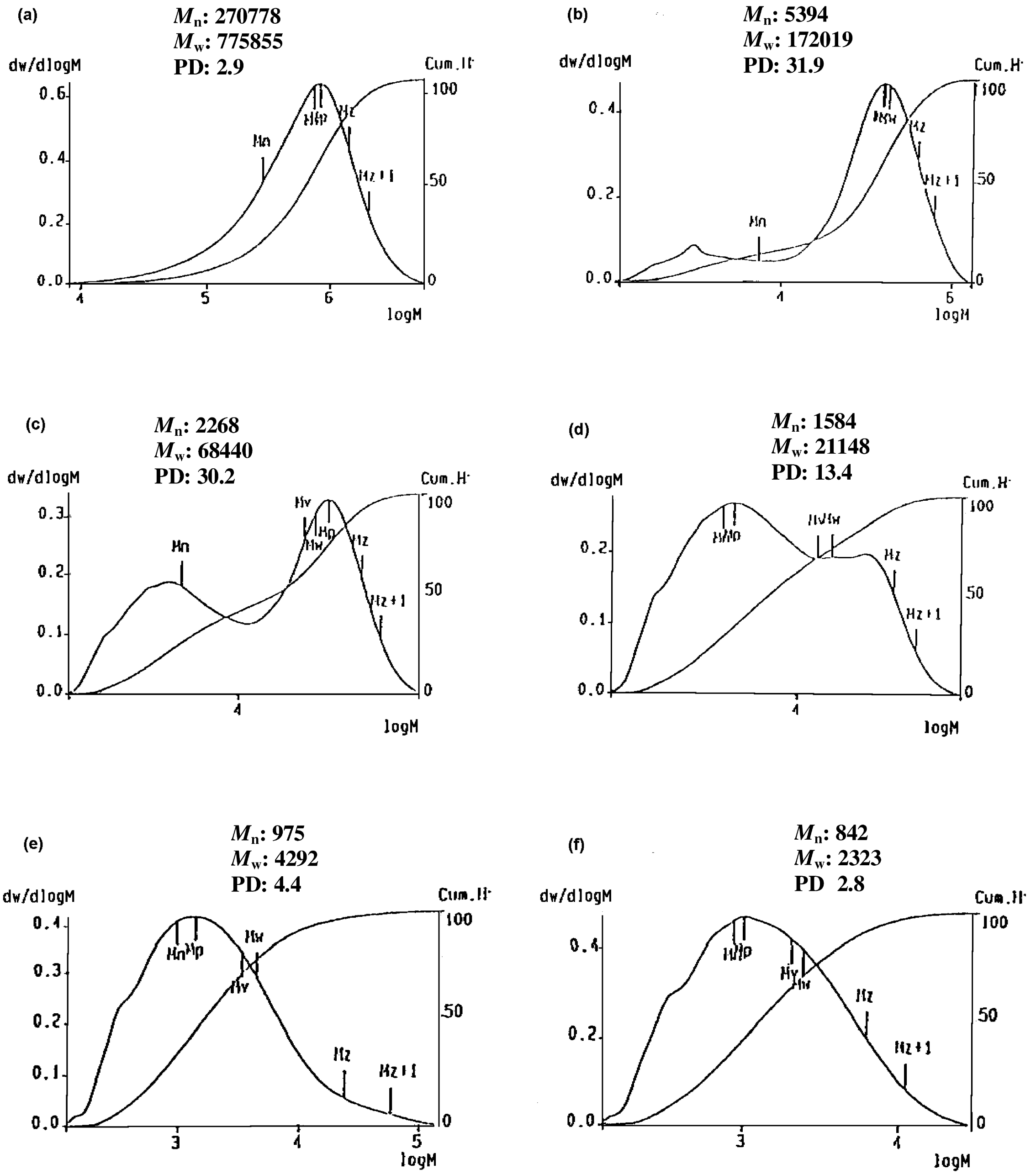


Fig. 1. Molecular weight distribution curves of ozonolysed NR recorded at various times during ozonolysis at 0°C in chloroform: (a) 0 min; (b) 1 min; (c) 5 min; (d) 10 min; (e) 15 min and (f) 20 min.

natural rubber has recently been comprehensively reviewed by us and hence will not be presented again here [17].

2. Experimental

2.1. Materials

The NR sample employed in this work was supplied in latex form by Revertex Limited, Essex. The latex was described as *low protein unvulcanised, centrifuged latex* and as having the following properties: total solids content: 60.79%: alkalinity: 420 meq. KOH per 100 g water; volatile fatty acid number: 0.023. A solid sample was prepared by drying the latex first under a stream of air in a fume cupboard to remove the bulk of the water and then in a vacuum oven at room temperature. It was purified by dissolution in hexane, filtration to remove any undissolved material, precipitation in excess methanol and then drying again in the vacuum oven (to constant weight). The sample was kept in the dark at room temperature (ca. 20°C) prior to use to prevent photodegradation.

Other chemicals used were calcium chloride (BDH, GPR, anhydrous), oxygen gas (BOC, 99%), oxygen free nitrogen gas (BOC, 99%), hexane (Prolabo, 99%), methanol (Fisons, 99.5%), chloroform (Fisons, >99%, stabilised with 100 ppm amylene, contains <0.1% water), and tetrahydrofuran (Fisons, GPC grade).

2.2. GPC measurements

GPC data were obtained at room temperature (ca. 20°C) on a Waters model 510 gel permeation chromatograph equipped with a differential refractometer, model 410 and a Rheodyne injector, model 7125. The chromatograph was fitted with a set of three 30 cm columns packed with 10 μm diameter PLgel™ beads with mixed pore sizes. The column set was calibrated using polystyrene standards. Tetrahydrofuran was used as the solvent with a flow rate of 1 ml per min. The GPC data were collated and processed using Polymer Laboratories Caliber™ software, version 5.11.

2.3. IR measurements

IR spectra were recorded on thin films cast onto rock salt plates using a Perkin–Elmer FTIR spectrometer, model 1720-X. All the spectra were recorded in absorbance mode and were the result of 20 scans with a 2 cm^{-1} resolution.

2.4. Ozonolysis procedure

The ozonizer used in this work was a Type BA 023012, manufactured by Wallace and Tiernan, Tonbridge, England. The reactor consisted of a five-necked, round-bottomed flask equipped with a drying tube containing anhydrous calcium chloride, a thermometer, a gas inlet and a motor-driven stirrer.

About 1.0 g of NR was charged into the reactor and dissolved in sufficient chloroform with stirring to give a concentration of 1% (w/v) and then cooled to 0°C. An oxygen–ozone stream from the ozonizer was passed into the rapidly stirred NR solution through a fritted glass disk (to break up the gas into a stream of fine bubbles) at a rate of 45 $l\ h^{-1}$ giving a rate of delivery of O_3 of 1.73 $g\ h^{-1}$. The delivery rate of ozone was determined in a separate experiment by passing the oxygen/ozone stream into an aqueous potassium iodide solution for a set time and then titrating the iodine released with standard sodium thiosulphate solution. Samples of the ozonolysed NR solution were withdrawn after 1, 5, 10, 15 and 20 min from the start of reaction. IR spectra of films cast from these samples were recorded immediately. GPC data for the samples were recorded after the samples had first been freed from chloroform by blowing with nitrogen, followed by pumping overnight in a vacuum oven at room temperature. Yields of oligomeric products recovered from ozonolysed solutions of natural rubber in this way varied from about 90 to 110% by weight of the starting rubber, reflecting the balance between the increase in weight brought about by oxidation and the loss of some very small fragments during the prolonged removal of solvent.

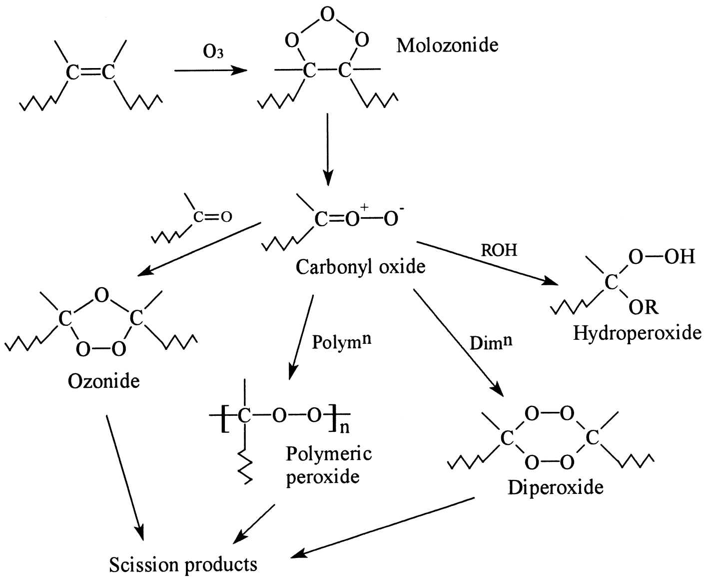
3. Results and discussion

3.1. GPC analysis

Fig. 1(a)–(f) shows the molecular weight distribution curves of NR and ozonolysed NR after 1, 5, 10, 15 and 20 min of ozonolysis, respectively, derived from GPC traces.

The dissolved NR at the outset of the experiment (Fig. 1(a)) has a $\overline{M}_n$ of 271 000 and a polydispersity of 2.9. Upon ozonolysis, the molecular weight of NR decreases dramatically, initially with the production of a bimodal distribution (in accordance with the findings of Plaumann and Ho [1]), but becoming nearly unimodal again after 20 min (Fig. 1(b)–(f)). After 1 min of ozonolysis, the molecular weight distribution of the ozonolysed NR is bimodal with a small peak representing a low molecular weight fraction and a larger peak representing a higher molecular weight fraction (Fig. 1(b)). After 5 min ozonolysis, the concentration of the lower molecular weight fraction of the ozonolysed NR has increased markedly with a corresponding decrease in concentration of the higher molecular weight fraction (Fig. 1(c)). After 10 min ozonolysis, the lower molecular weight fraction of degraded NR is larger than the higher molecular weight fraction (Fig. 1(d)). Close comparison of the molecular weight distribution curves at 1, 5 and 10 min ozonolysis reveals that the peak molecular weight of the higher molecular weight fraction is declining more rapidly than the peak molecular weight of the lower molecular weight fraction. After 15 min ozonolysis, the peak representing the higher molecular weight fraction has disappeared leaving the peak representing the low molecular weight fraction dominant in the molecular weight distribution curve (Fig. 1(e)), suggesting that the ozonolysed NR is now made up almost entirely of low molecular weight oligomers. Finally, after 20 min ozonolysis, the molecular weight distribution curve of ozonolysed NR becomes essentially unimodal with a $\overline{M}_n$ of 840 and PD of 2.8 (Fig. 1(f)).

The results from this study suggest that 20 min ozonolysis is required in order to obtain a unimodal distribution of low molecular weight ozonolysed NR under the present experimental conditions. It is worthwhile to note here that in the molecular weight distribution curves in Fig. 1(c)–(f), a small shoulder, which corresponds to a very low molecular weight fraction such as levulinaldehyde or levulinic acid, starts to develop after as little as 5 min ozonolysis and becomes slightly more apparent after 20 min. This suggests that ozonolysis of NR in solution can lead to the direct formation from high molecular weight chains of some very low molecular weight fractions. This finding is consistent with a rapid, diffusion-controlled, ozonolysis process in



Scheme 1. Possible reactions following ozonolysis of a diene-containing polymer.

which some chains, when in close proximity to the point of entry of ozone to the reactor, are extensively ozonolysed.

The reason why NR should be ozonolysed to give products having initially a bimodal distribution of molecular weights is not immediately clear. However, a possible reason is that the relatively stable, polymeric, ozonides and peroxides formed during an initial, fast, diffusion-controlled reaction between the NR and ozone undergo scission only in a second, slower, stage, and possibly only after reaction with further ozone, to form oligomers with functional, oxygenated end-groups. Ho has reported that the number of chain scissions during the ozonolysis of polybutadiene and polyisoprene in both hexane and chloroform depend on the square of the amount of ozone absorbed suggesting that two molecules of ozone are involved in the breaking of each double bond [18]. Furthermore, Razumovskii et al. have reported that the time of formation of cracks on the surfaces of solid polyisoprene samples exposed to ozone is inversely related to the square of the ozone concentration, again implying the involvement of two molecules of ozone in every scission event [19].

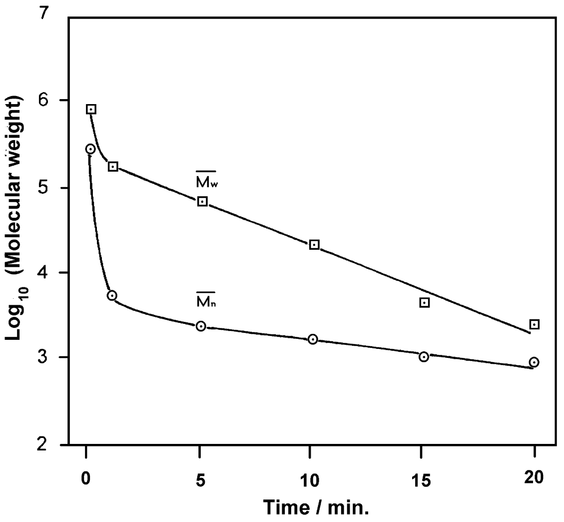


Fig. 2. Average molecular weights of ozonolysed NR as a function of ozonolysis time.

Alternatively, it may be that small quantities of hydroperoxidic groups introduced during ozonolysis, perhaps by reaction of intermediate carbonyl oxides with adventitious water, decompose giving polymeric radicals which subsequently are involved in slight crosslinking in competition with the major chain scission. It should be noted that, on standing, the oligomers tended to separate into an overtly liquid fraction and a gel-like (but still soluble fraction) which suggests that there may have been some slight crosslinking. Scheme 1 summarises the various possible reactions that can take place during ozonolysis of natural rubber based on the generally accepted (Criegee) mechanism involving the formation of an intermediate carbonyl oxide which can then react further to give primary and secondary ozonides and various peroxidic species depending on solvent polarity and on the presence or absence of other potential reactants [20].

Graphs representing the trends in the reduction of both $\overline{M}_n$ and $\overline{M}_w$ (for the overall sample) with ozonolysis time are shown in Fig. 2.

The graphs make clear that the average molecular weights of NR reduce very markedly in the first minute of ozonolysis and then more gradually over the subsequent 19 min. From $\overline{M}_n$ values obtained by GPC, it is possible to calculate the average number of chain scissions, S, of the ozonolysed NR using the equation:

$$S = \frac{(\overline{M}_n)_0}{\overline{M}_n} - 1$$

Table 1
The average number of chain scissions, *S*, based on $\overline{M}_n$ values obtained by GPC

Time (min)	$\overline{M}_n$	*S*
0	271 000 ± 1000	0
1	5390 ± 50	49 ± 1
5	2270 ± 20	118 ± 1
10	1580 ± 10	170 ± 2
15	980 ± 5	275 ± 3
20	840 ± 5	321 ± 4

in which $(\overline{M}_n)_0$ and $\overline{M}_n$ are the number average molecular weights before and after ozonolysis [21,22]. The results of these calculations are listed in Table 1.

A graph of the average number of chain scissions, *S*, versus ozonolysis time is shown in Fig. 3.

The graph, which is not a straight line passing through the 0,0 origin within experimental error, confirms that the rate of chain scission is at its most rapid during the first minute of ozonolysis and then declines, becoming roughly constant for the remainder of the reaction time. This suggests that it is the longer chains that are most susceptible to ozonolysis, a fact which may be connected with the lower translational mobility of long chains compared with short chains leading to the longer chains having longer times of exposure to ozone when in the vicinity of the point of entry of ozone to the reactor.

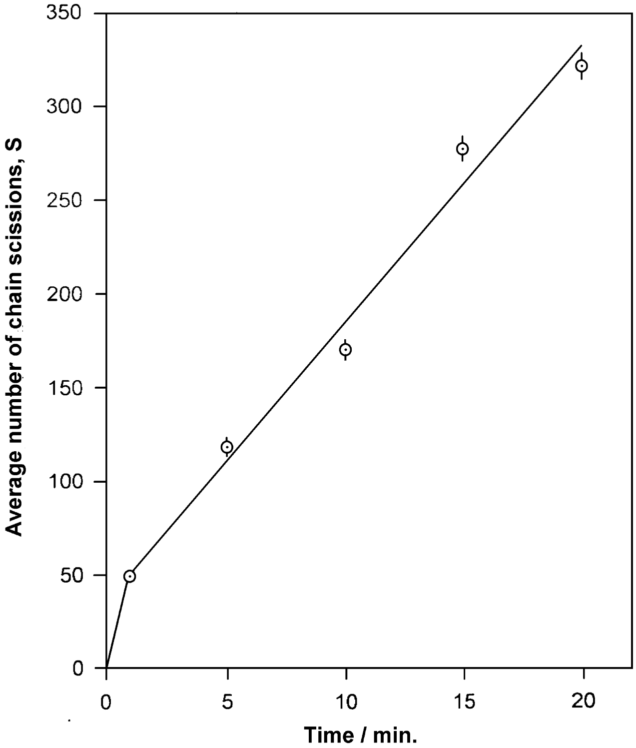


Fig. 3. Average number of scissions per chain, *S*, with time during ozonolysis of NR. Straight lines have been added merely to indicate the general trend in the data.

3.2. IR analysis

Fig. 4(a) shows the IR spectrum of NR, which contains seven principal peaks, characteristic of the well-known structural features of NR.

Fig. 4(b)–(f) show IR spectra of ozonolysed NR recorded after 1, 5, 10, 15, and 20 min ozonolysis, respectively. As can be seen clearly from those spectra, major changes have occurred relative to the original spectrum of NR (Fig. 4(a)) upon ozonolysis. Six of the seven characteristic peaks (2962, 2928, 2855, 1720, 1664, 1450 and 838 cm^{-1}) decrease in intensity with time, three of them (2962, 2928 and 2855 cm^{-1}) markedly. However, a peak at 1378 cm^{-1} remains unchanged in intensity. This is a possibly because the group ($-CH_3$) and this particular vibrational mode (C–H asymmetric bend) are not significantly affected by ozonolysis. Besides the reductions in intensity of the original IR peaks, three new major peaks (3440, 1720 and 1084 cm^{-1}) appear in the spectra of ozonolysed NR with two of them (1720 and 1084 cm^{-1}) being particularly prominent. In order to see more clearly the trends in the changes of the functional groups to which the various IR peaks relate, the ratios of the absorbances of the peaks that change in intensity to the absorbance of the one that does not (1378 cm^{-1}), are plotted in Fig. 5. It can be seen from Fig. 5 that the main IR peaks characteristic of NR decrease in intensity relative to the peak at 1378 cm^{-1} confirming that the NR has undergone profound structural changes in the course of ozonolysis as expected.

There are four major structural changes that can be recognised in the IR data (Figs. 4 and 5). One is the appearance of carbonyl groups indicated by the peak at 1720 cm^{-1}. The relative intensity of the peak increases rapidly over the first 5 min, then more gradually, levelling off after 20 min. The peak is relatively broad at the bottom indicating that more than one type of carbonyl group may be present in the ozonolysed NR. Three types of carbonyl groups are in fact possible: aldehyde, ketone, and/or carboxylic acid. The types of carbonyl compound present in the oligomeric products from ozonolysed NR will be discussed in more detail in a subsequent paper.

The second major change to the IR spectrum on ozonolysis is the appearance of a rather broad peak at 1084 cm^{-1} which has a shoulder at 1107 cm^{-1}. This peak is assigned to ozonides in line with conclusions drawn from previous work reported in the literature [23–25]. The appearance of bands assignable to ozonide groups is also an evidence of relatively slow scission of the ozonides following their initial rapid formation.

The third major change involves the C–H and C=C bonds of the isoprene repeat units. Three peaks at 2962, 2928 and 2855 cm^{-1} which arise from C–H asymmetric stretch in CH_3, C–H asymmetric stretch in $-CH_2-$, and C–H symmetric stretch in both $-CH_2-$ and $-CH_3$, respectively, reduce in intensity markedly on ozonolysis. A rather weak peak associated with C=C bonds is also reduced in intensity.

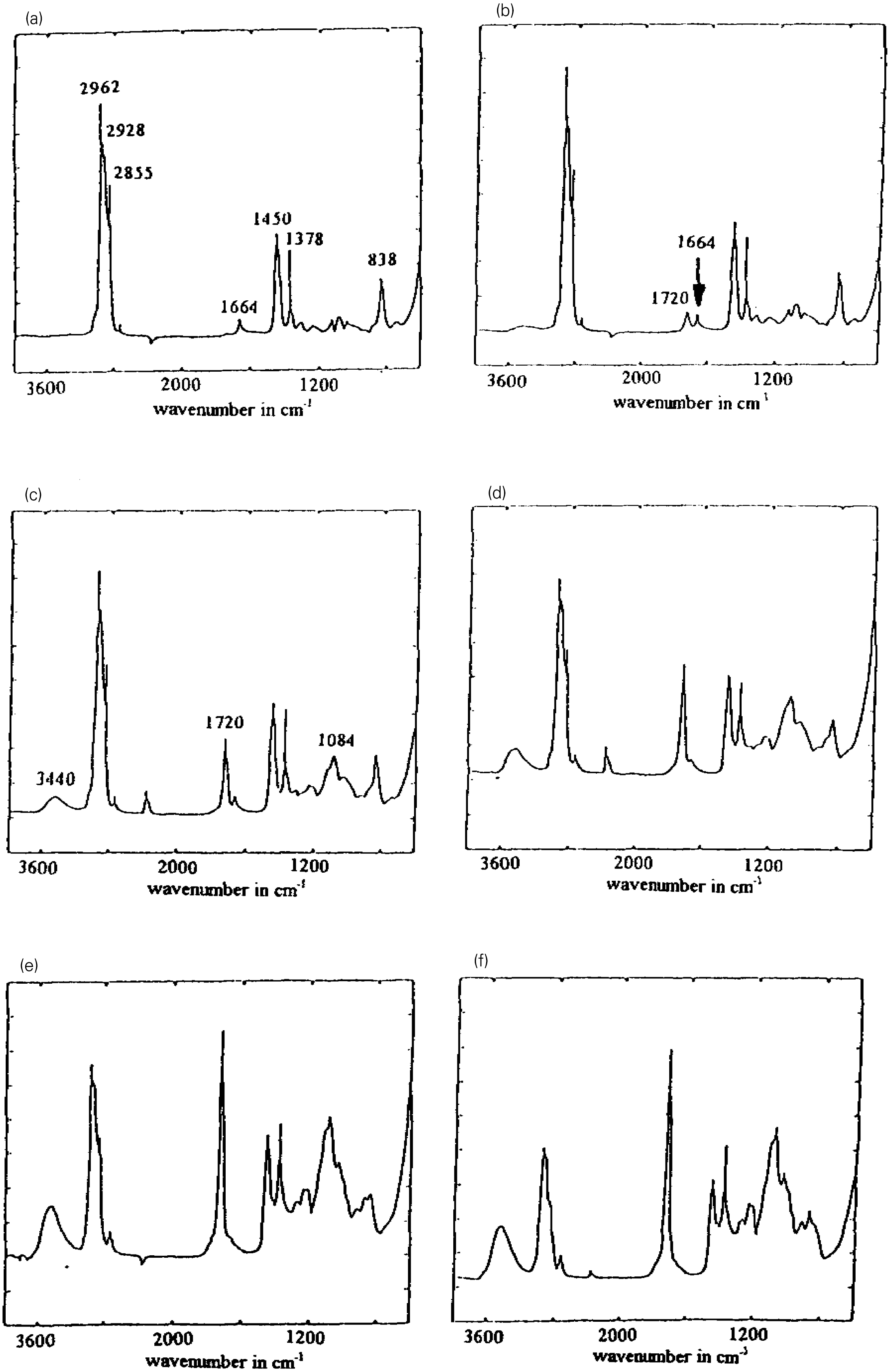


Fig. 4. IR spectra of ozonolysed NR recorded at various times during ozonolysis at 0°C in chloroform: (a) 0 min; (b) 1 min; (c) 5 min; (d) 10 min; (e) 15 min and (f) 20 min.

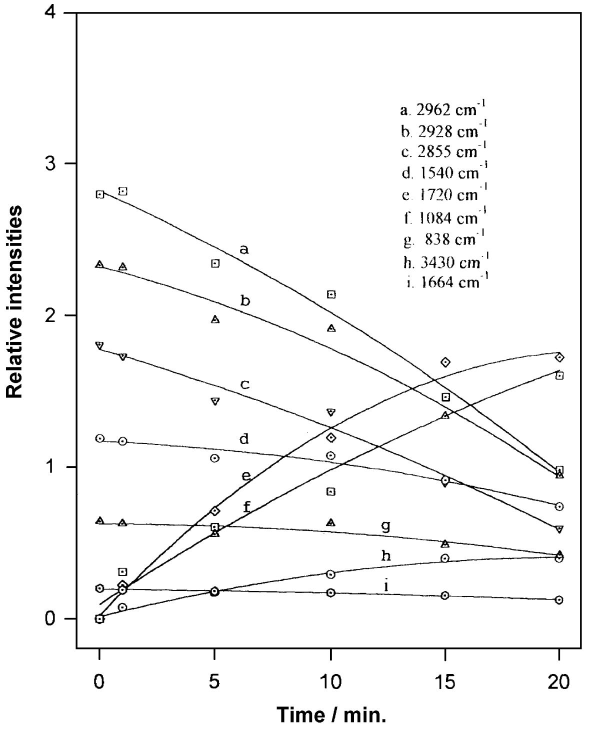


Fig. 5. Ratios of IR peak intensities at various frequencies to that at 1378 cm^{-1} against ozonolysis time for NR ozonolysed in chloroform.

These reductions in peak intensity are due to the expected ozonolytic chain scissions at C=C bonds of isoprene repeat units.

The last major change that can be found in the spectra is the appearance of a broad peak between 3300 and 3600 cm^{-1}, with a maximum at 3440 cm^{-1}. This peak indicates the presence of OH groups in the ozonolysed NR. Several types of OH group are possible, viz., hydroxyl, hydroperoxide, carboxylic acid or a mixture of them.

A more detailed analysis of the microstructures of the oligomeric products of ozonolysis of natural rubber clearly requires a technique more able than infrared spectroscopy to discriminate between groups of similar structure. Such discrimination is possible with the aid of ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. An examination of the oligomeric products of ozonolysis of natural rubber by NMR has recently been completed and will be reported in a subsequent paper.

4. Conclusions

Ozonolysis of NR in dilute chloroform solution at 0°C is shown to be a rapid method for the production of low molecular weight NR oligomers with a broad, but close to unimodal, molecular weight distribution. In this work, a number-average molecular weight, $\overline{M}_{\mathrm{n}}$, of less than 900 has been obtained after 20 min of ozonolysis. The reduction in molecular weight of NR during ozonolysis is accompanied by the introduction of a variety of oxygenated functional groups. The precise natures and amounts of these functional groups will be the subject of a subsequent paper.

Acknowledgements

The authors are grateful to Universiti Teknologi Malaysia for the provision of a scholarship and study leave to HMN and to Revertex Limited, Essex, for the gift of the sample of natural rubber latex.

References

[1] Plaumann HP, Ho KW. J Macromol Sci Chem 1987;A24:1175.
[2] Allison AR, Stanley IJ. Anal Chem 1952;24:630.
[3] Salomon G, van der Schee AChr. J Polym Sci 1954;14:181.
[4] Ebdon JR, Flint NJ, Rimmer S. Macromolec Rep 1995;A32(5–6):603 and references cited therein.
[5] Rimmer S, Ebdon JR, Shepherd MJ. React Funct Polym 1995;26:145.
[6] Ebdon JR, Flint NJ. Europ Polym J 1996;32:289.
[7] Rimmer S, Ebdon JR. J Polym Sci, Polym Chem 1996;34:3573.
[8] Rimmer S, Ebdon JR. J Polym Sci, Polym Chem 1996;34:3591.
[9] Ebdon JR, Rimmer S. J Chem Res (S) 1997;408.
[10] Ebdon JR, Rimmer S. J Polym Sci, Part A, Polym Chem 1997;35:3255.
[11] Odinokov VN, Ignatyuk VK, Tolstikov GA, Monakov YuB, Berg AA, Shakirova AM, Rafikov SR, Berlin AA. Izv Akad Nauk SSSR, Ser Khim 1976;7:1552 Chem Abstr 85:125414z.
[12] Odinokov VN, Tolstikov GA, Ignatyuk VK, Kukovinets OS, Akhunova VR, Rafikov SR. Dokl Akad Nauk SSSR 1981;259:123 Chem Abstr 95:149871d.
[13] Timirova RG. Khim Vysokomol Soedin Neftekhim 1973:69 Chem Abstr 81:38056h (1974).
[14] Gordienko VI, Valuev VI, Shlyakhter RA, Petrov GN. Kauch Rezina 1978;2:5 Chem Abstr 88:122427g.
[15] Odinokov VN, Timirova RG, Tolstikov GA, Monakov YuB. USSR 1976;498:285 Chem Abstr 84:90943w.
[16] Beresnev VV, Grigorjev EI. Kauch Rezina 1993;4:10 Chem Abstr 121:59422j.
[17] Nor HM, Ebdon JR. Progress in Polym Sci 1998;2:143.
[18] Ho KW. J Polym Sci, Part A, Polym Chem 1986;24:2467.
[19] Razumovskii SD, Kefeli AA, Vinitskaya EA, Zaikov GE. Dokl Akad Nauk SSSR 1980;253:1173 Chem Abstr 94:16854h.
[20] Criegee R. Angew Chem Int Ed Engl 1975;14:745.
[21] Guillet JE, Norrish RGW. Proc R Soc (London), Ser 1955;A233:153.
[22] Guillet JE. Polymer photophysics and photochemistry; an introduction to the study of photoprocesses in macromolecules, 1. Cambridge: Cambridge University Press, 1985 p. 77.
[23] Kendall FH, Mann J. J Polym Sci 1956;19:503.
[24] Andries JC, Diem HE. J Polym Sci Polym Lett Ed 1974;12:281.
[25] Anachkov MP, Rakovsky SK, Shopov DM, Razumovskii SD, Kefely AA, Zaikov GE. Polym Degrad Stab 1985;10:25.