Depolymerisation of Highly Purified Natural Rubber. I. Metal-catalysed Oxidation of Deproteinised Natural Rubber

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An attempt was made to establish a method to prepare liquid rubber by chain-scission of highly-purified natural rubber (NR) using UV-irradiation and catalytic thermal degradation by shaking at 65°C. The NRs used for the study were both in latex and solution forms. The rubber in toluene solution was more susceptible to degradation than the latex form. The structural characterisation of degraded rubber was carried out by FTIR, ^1H- and ^{13}C-NMR analysis. Acetone extracted deproteinised NR in the presence of 1 p.h.r. Co(acac)$_2$ was the most effective material for producing liquid NR by shaking at 65°C for 24 h.

Low molecular-weight NR of $\overline{M}_w$ value about 10^3–10^4 obtained by depolymerisation is called liquid rubber. It has been used widely as a raw material for adhesives and reactive plasticiser for improving processing properties of compounded rubber for tyres. Nowadays, liquid rubber has attractive attention in various fields because of advantages in the production of various products from the viewpoint that the use of liquid rubber could make the rubber softer and therefore easier to mix with and disperse the compounding chemicals during the mixing process.

In general, a depolymerised NR can be obtained by mechanical, chemical or thermal degradations[1]. However, some side reactions such as epoxidation and isomerisation of the main-chain occur easily, and are difficult to control[2]. In addition to the depolymerisation method, the purity of raw material, *i.e.* non-rubber components in NR[3] are regarded as important factors affecting the above problem. This paper will present the effect of non-rubber components and depolymerisation method such as shaking and UV-irradiation of NR latex and NR solution. The deproteinised NR (DPNR) and

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acetone-extracted NR (NR-AE) were also studied to ascertain the effect of protein-free and fatty acid-free rubbers to explain the effect of non-rubbers on degradation. The purpose of this study is to elucidate the appropriate condition to prepare and characterise liquid NR from highly purified NR.

EXPERIMENTAL

Materials

Fresh NR latex (FL-NR) was preserved with 0.5% NH_3 before use. The FL-NR was incubated at 37°C overnight in the presence of 0.04% proteolytic enzyme and 1% sodium dodecyl sulphate (SDS) as a surfactant and then subjected twice to centrifugation at 12 000 r.p.m. for 30 min to prepare deproteinised NR (DPNR) latex[4]. The DPNR latex was stabilised with 1% SDS. The solid rubber from FL-NR and DPNR latex was obtained by coagulating latex with acetone and dried up *in vacuo* at 50°C. Both the solid FL-NR and DPNR were then subjected to acetone-extraction to remove free fatty acids, which are referred to as FL-NR-AE and DPNR-AE, respectively. Pale crepe rubber (PC) was also used as commercial grade rubber. All the chemical reagents are analytical grades.

Degradation of Rubber by UV-irradiation

10 ml of 30% H_2O_2 was added into 200 ml of DPNR latex at dry rubber content (DRC) of 5% or 200 ml of 5% w/v DPNR-AE in toluene solution. This reaction mixture was subjected to UV-irradiation using a high-pressure mercury lamp for 24 h. Excess amount of methanol was added to stop the reaction. The coagulated rubber was reprecipitated three times from toluene solution with methanol.

Degradation of Latex Using Catalyst under Oxygen Atmosphere

50 ml DPNR latex with a DRC of 5% was added to 30% H_2O_2 (1 p.h.r.) and catalyst, *i.e.* cobalt chloride ($CoCl_2$), cobalt-*bis*-acetyl acetonate ($Co(acac)_2$), iron (II) sulphate ($FeSO_4$) and iron (II) chloride ($FeCl_2$). The degradation was carried out at 65°C; the reaction time was 24 h. The reaction in a flask was carried out by using a shaker with 135 r.p.m. at 65°C. The degraded latex was coagulated with $CaCl_2$ and then the rubber obtained was purified by reprecipitating the solution in toluene with methanol for three times.

Degradation of Rubber Solution Using Catalyst under Oxygen Atmosphere

FL-NR, FL-NR-AE, DPNR, DPNR-AE and PC rubbers were used as 2% w/v solution in toluene. The rubber solution of 50 ml was mixed with catalyst $Co(acac)_2$ or $CoCl_2$ by shaking at the same condition as mentioned above. The reaction was terminated with methanol-HCl and then subjected to the above reprecipitation procedure.

Molecular Weight and Structural Analyses

Intrinsic viscosity [η] was determined using an Ubbelhode viscometer at 0.1 g/dl–0.4 g/dl in toluene solution at 30°C. Number-average molecular weight was obtained from vapour pressure osmometry at 35°C. The Fourier-Transform Infrared (FTIR) analysis was done using JASCO 5300 FTIR Spectrometer. The ^1H- and ^{13}C-NMR measurements were performed on JEOL GX-270 in deuterated chloroform at 270 MHz and 67.5 MHz, respectively.

RESULTS AND DISCUSSION

It is known that NR latex contains many kinds of non-rubber components. These components cause difficulties in identifying the structure of degraded rubbers. Some of these non-rubber substances like tocotrienol[5,6], proteins[6] and amino acids[7] have been shown to have a positive relationship with the resistance of NR towards oxidation. Therefore, rubber latex containing low non-rubber content or highly purified NR will be a suitable material used for preparing liquid NR.

Five kinds of NR were used in this study, *i.e.* FLNR, PC, FLNR-AE, DPNR and DPNR-AE. The FLNR and PC are regarded as raw rubbers; the former was obtained after tapping and the latter is a commercial grade rubber. The nitrogen content of FLNR, FLNR-AE and PC was 0.50%, 0.49% and 0.45%; while that of DPNR and DPNR-AE was 0.02% and 0.018%, respectively. The ester content of rubber was reduced from 14.8 to 4.6 m mol/kg rubber after acetone-extraction, as in the FLNR-AE and DPNR-AE. Thus, DPNR and DPNR-AE were used as the highly purified rubbers to study the structure of the degraded rubber.

Degradation of the highly purified NR latex or DPNR-AE in toluene solution was carried out in three ways (*Appendix 1*) as follows:

- Rubber was reacted with 30% H_2O_2 using UV-irradiation[8];

- Rubber in toluene solution was reacted with 30% H_2O_2 and metal catalyst[9] by shaking at 65°C;

- Rubber in toluene solution was reacted with Co(acac)$_2$ by shaking at 65°C.

Firstly the degradation of NR by using UV-irradiation was carried out using a mixture of DPNR latex and DPNR or DPNR-AE in toluene solution by the addition of 10 ml of 30% H_2O_2 for each. After 30 h of irradiation time, the degradation of DPNR latex was not clearly observed and the resulting rubber was still solid rubber with [η] of 5.8. On the other hand, liquid rubber with [η] of 1.5 and 1.2 was obtained when DPNR and DPNR-AE in toluene solution were used, respectively. These lower [η] values of the rubber obtained in toluene solution indicates that the degree of degradation is affected by the form of rubber used, *i.e.* NR in the latex form is difficult to degrade and *vice versa*. This may be due to the difficulty of the reagent and UV-light to pass through the membrane of rubber particles as latex form, as well as the scattering of UV-light by colloidal particles in latex. However, after the removal of free fatty acid including naturally occurring antioxidants as given in DPNR-AE would make the rubber more feasible to degrade. However, only slight difference was observed in the extent of degradation between DPNR and DPNR-AE, compared with the difference between the [η] value of the resulting rubber from latex. This indicates the effect of acetone extraction on the extent of degradation in toluene solution.

Secondly, we applied a combination of H_2O_2 and iron or cobalt metal catalyst to the degradation of DPNR latex. Iron and cobalt metal were chosen due to the strong effect they have on the deterioration of rubber[7]. The degraded rubbers in the presence of 1 p.h.r. $FeSO_4$ or $FeCl_2$ by shaking at 65°C for 24 h were still solid rubbers with [η] of 6.1 and 5.9, respectively. However, rubbers obtained from the reaction at the same condition as above in the presence of 1 p.h.r. $CoCl_2$ or Co(acac)$_2$ were soft rubbers with [η] of 3.2 and 2.9, respectively. The reason why the liquid NR could not be obtained from DPNR latex under the above conditions is probably due to the interference of non-rubber components or surfactant on the rubber particles to the

3

reactivity of catalyst and oxygen which make it difficult to pass through the membrane of the rubber particle. It should be noted that the products obtained from DPNR and DPNR-AE in toluene solution with 1 p.h.r. $Co(acac)_2$, which was shaken at 65°C, became liquid rubber with [η] of 1.2 and 0.7 after 24 h of reaction time, respectively. In this case, DPNR-AE was much more subject to oxidative degradation than DPNR, judging from the viscosity of resulting rubbers. This result was almost the same as that obtained by using UV-irradiation. Thus, this is a strong evidence to show that the removal of lipid from DPNR-AE could facilitate the degradation of rubber in toluene.

At the present stage, the liquid NR can be obtained easily by shaking DPNR or DPNR-AE solution with $Co(acac)_2$ at 65°C for 24 h. However, the degraded product from DPNR-AE and $Co(acac)_2$ was green-yellow in colour, even after purification with reprecipitation from toluene solution into methanol for several times. This indicates that the catalyst could not be removed completely from rubber, which may be due to the occurrence of complexation between Co^{2+} and some components in rubber. This will lower the purity of the resulting liquid NR. Therefore, another type of Co^{2+}; *i.e.* $CoCl_2$, was applied as a catalyst instead of $Co(acac)_2$, because it is expected to be removed easily by reprecipitation of the rubber in toluene solution by methanol. As it was anticipated, the resulting rubber from DPNR-AE in toluene solution with 1 p.h.r. $CoCl_2$ by shaking at 65°C for 24 h was a colourless and transparent sticky rubber with [η] of 1.8. From the resulting rubber $CoCl_2$ was able to be removed easily. This may be due to $CoCl_2$ which does not dissolve completely in toluene as in the case of $Co(acac)_2$, thus reactivity of $CoCl_2$ was reduced and led to the low extent of degradation.

The finding mentioned above indicates that we have to consider the effect of purity of NR
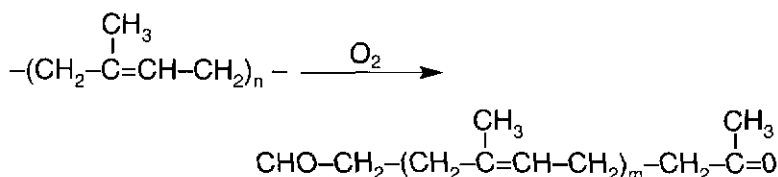
on oxidative degradation. The rubbers used in this experiment were FLNR, FLNR-AE, PC, DPNR and DPNR-AE. All the rubbers in toluene solution at concentration 2% w/v were mixed with 1 p.h.r. $Co(acac)_2$ and then were subjected to shaking at 65°C for 24 h. The resulting rubbers from FLNR, FLNR-AE and PC were still solid rubbers with [η] of 5.9, 5.0 and 5.2, respectively, while the rubber from DPNR and DPNR-AE were liquid rubbers with [η] of 1.20 and 0.8, respectively. The non-rubber contents in FLNR-AE and PC were slightly less than those in FLNR. Therefore, it seems reasonable to assume that the [η] value of the former was slightly lower than that of the latter. However, the resulting rubbers from these three kinds of rubbers were not liquid but solid rubbers. This implies that there was not much of a difference on the efficiency of degradation among FLNR, FLNR-AE and PC. However, after the removal of proteins as in DPNR and DPNR-AE, the [η] value of the resulting rubbers reduced remarkably. This result is compatible with the finding that most of the naturally occurring antioxidants in NR are removed during preparation of DPNR and a synthetic antioxidant has to be added to DPNR at the final stage of concentrated latex formation. This may be the reason why DPNR rubber is more susceptible to oxidise and degrade than the other rubbers. Furthermore, if the free fatty acid is removed from DPNR, *i.e.* DPNR-AE, these are very subject to oxidative degradation.

According to the published work by Mayo[10], the structure of oxidative degraded rubber is presented as shown in *Scheme 1*.
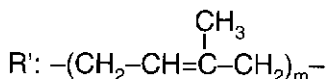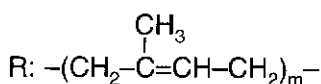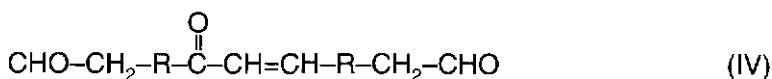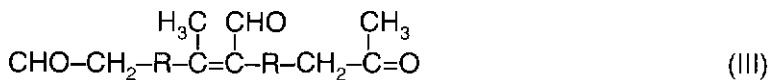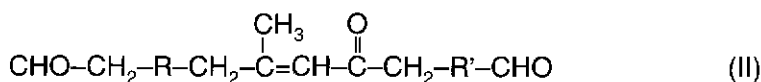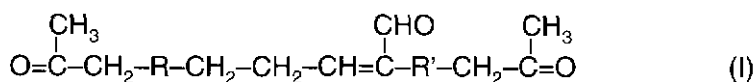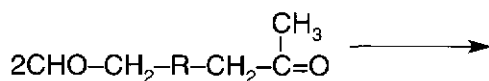
The degraded rubbers by using UV-irradiation or shaking at 65°C from the present work were subjected to structural analysis. *Figures 1 (A)* and *(B)* show the FTIR spectra of DPNR and liquid NR from DPNR-AE in toluene solution using

UV-irradiation, respectively. The characteristic bands of ketone and aldehyde are clearly observed at 1720 cm⁻¹ and 1740 cm⁻¹ in *Figure 1 (B)*. NMR signals characteristic of functional groups such as carbonyl groups could not be detected in both ^{1}H- and ^{13}C-NMR spectra of this rubber, except for the epoxide groups and isomerisation of *cis*-1,4-isoprene unit to *trans*-

$$
\underset{\text{CH}_3}{-(\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2)_n}- \xrightarrow{\text{O}_2}
$$

$$
\text{CHO}-\text{CH}_2-(\text{CH}_2-\underset{\text{CH}_3}{\text{C}}=\text{CH}-\text{CH}_2)_m-\text{CH}_2-\underset{\text{CH}_3}{\text{C}}=0
$$

Scheme 1

$$
2\text{CHO}-\text{CH}_2-\text{R}-\text{CH}_2-\underset{\text{CH}_3}{\text{C}}=\text{O} \longrightarrow
$$

$$
\text{O}=\underset{\text{CH}_3}{\text{C}}-\text{CH}_2-\text{R}-\text{CH}_2-\text{CH}_2-\text{CH}=\underset{\text{CHO}}{\text{C}}-\text{R'}-\text{CH}_2-\underset{\text{CH}_3}{\text{C}}=\text{O} \qquad \text{(I)}
$$

$$
\text{CHO}-\text{CH}_2-\text{R}-\text{CH}_2-\underset{\text{CH}_3}{\text{C}}=\text{CH}-\overset{\text{O}}{\text{C}}-\text{CH}_2-\text{R'}-\text{CHO} \qquad \text{(II)}
$$

$$
\text{CHO}-\text{CH}_2-\text{R}-\underset{\text{H}_3\text{C}}{\text{C}}=\underset{\text{CHO}}{\text{C}}-\text{R}-\text{CH}_2-\underset{\text{CH}_3}{\text{C}}=\text{O} \qquad \text{(III)}
$$

$$
\text{CHO}-\text{CH}_2-\text{R}-\overset{\text{O}}{\text{C}}-\text{CH}=\text{CH}-\text{R}-\text{CH}_2-\text{CHO} \qquad \text{(IV)}
$$

$$
\text{R:}\ -(\text{CH}_2-\underset{\text{CH}_3}{\text{C}}=\text{CH}-\text{CH}_2)_m-
$$

$$
\text{R':}\ -(\text{CH}_2-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{CH}_2)_m-
$$

Scheme 2. Possible structures of degraded rubber after aldol condensation.

-CHO
1736

C
|
-C=O
1722

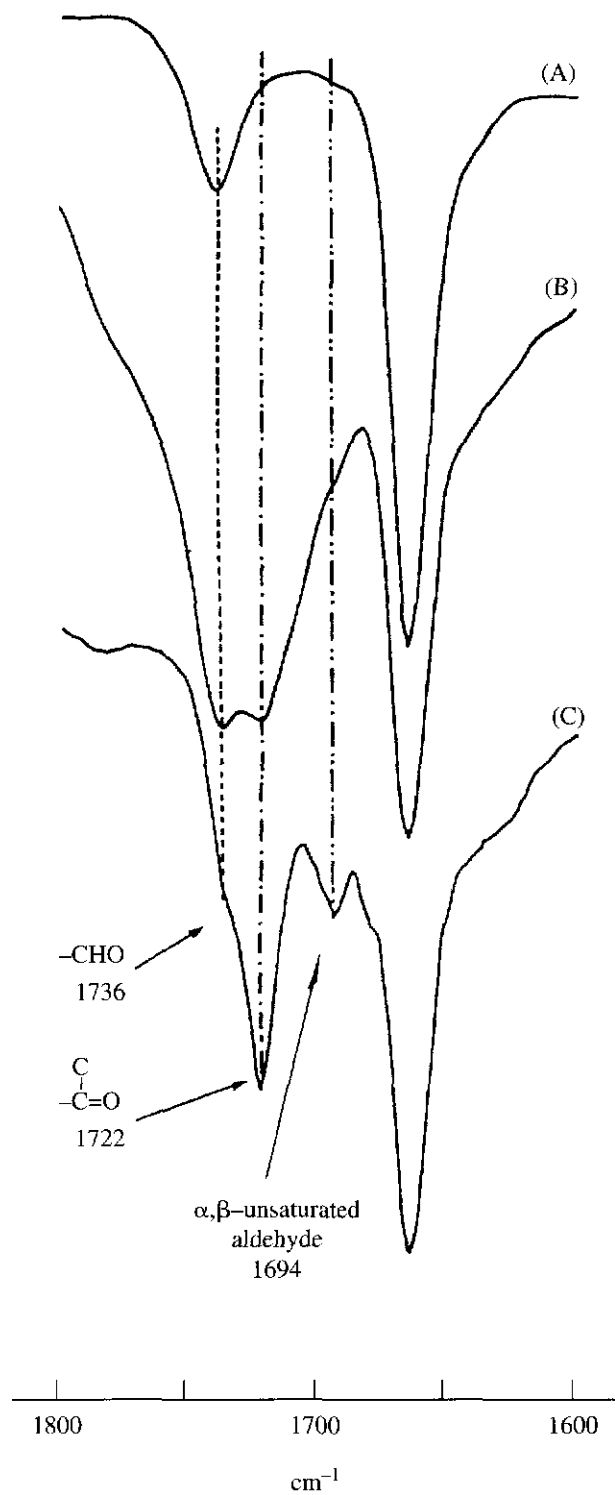α,β–unsaturated
aldehyde
1694

1800   1700   1600

cm⁻¹

Figure 1. FTIR spectra of (A) DPNR and the degraded products from DPNR-AE by (B)
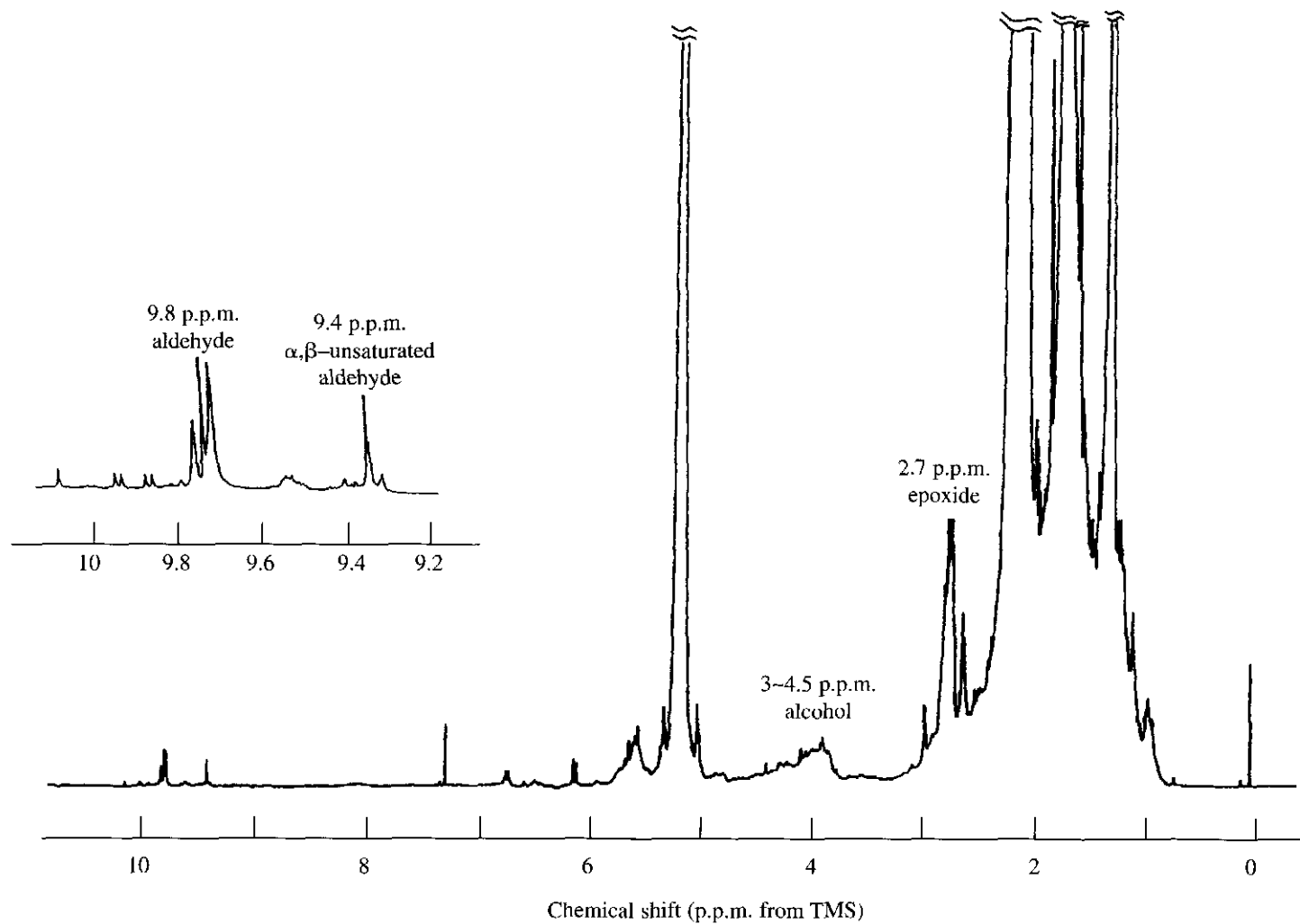*UV-irradiation, (C) shaking in the presence of Co(acac)₂.*

Figure 2. ^{1}H-NMR spectrum of product from degradation of DPNR-AE in toluene solution with 1 p.h.r. Co(acac)$_2$ by shaking at 65°C for 24 h.

1,4-isoprene unit. This shows that many side reactions occurred during degradation. Thus, it is difficult to get liquid NR of well-defined structure by using UV-irradiation.

The liquid NR obtained by degradation of DPNR-AE in toluene solution and $Co(acac)_2$ by shaking at 65°C showed different structural characteristics. The FTIR spectrum of this rubber is shown in *Figure 1 (C)*. In addition to the characteristic bonds of ketone and aldehyde at 1720 cm^{-1} and 1740 cm^{-1}, another band due to α,β-unsaturated aldehyde group was detected. This result supports the proposed structure of *Scheme 1*. The ^{1}H- and ^{13}C-NMR spectra in *Figures 2* and *3* also confirmed the presence of those functional groups, as can be seen in the assignment of characteristic signals given in the spectra.

If two molecules of the degraded rubber are reacted together *via* aldol condensation as shown in structure of *Scheme 1*, the possible structures can be written as given in *Scheme 2*. The ^{13}C-NMR chemical shifts were calculated for the anticipated structures (I) – (IV), according to the HOSE method[11]. Only the calculated chemical shifts for the structure (I) fits well in the observed value. The degree of polymerisation (DP_n) of this liquid NR was estimated to be 83 from the intensity ratio between the ^{1}H-NMR signals of rubber main-chain at 5.2 p.p.m. and the signals due to ketone and aldehyde at 9.2 and 9.8 p.p.m., respectively. This value is in good agreement with the DP_n value obtained by vapour pressure osmometer (VPO), $\overline{M}_n = 6.6 \times 10^3$ or $DP_n \approx 97$. About one epoxide group per chain was also found in liquid NR molecule. These results indicate the formation of functional carbonyl groups in liquid NR prepared by shaking the DPNR-AE solution with 1 p.h.r. $Co(acac)_2$, although it contains epoxide group.

CONCLUSION

Highly purified liquid NR was prepared by shaking DPNR or DPNR-AE in toluene solution with 1 p.h.r. $Co(acac)_2$ at 65°C for 24 h. The DP_n of this liquid NR estimated from characteristic signals of ketone and aldehyde functional groups in ^{1}H-NMR spectrum corresponded to DP_n obtained from VPO, indicating that the liquid NR prepared by this method had well-defined structure.

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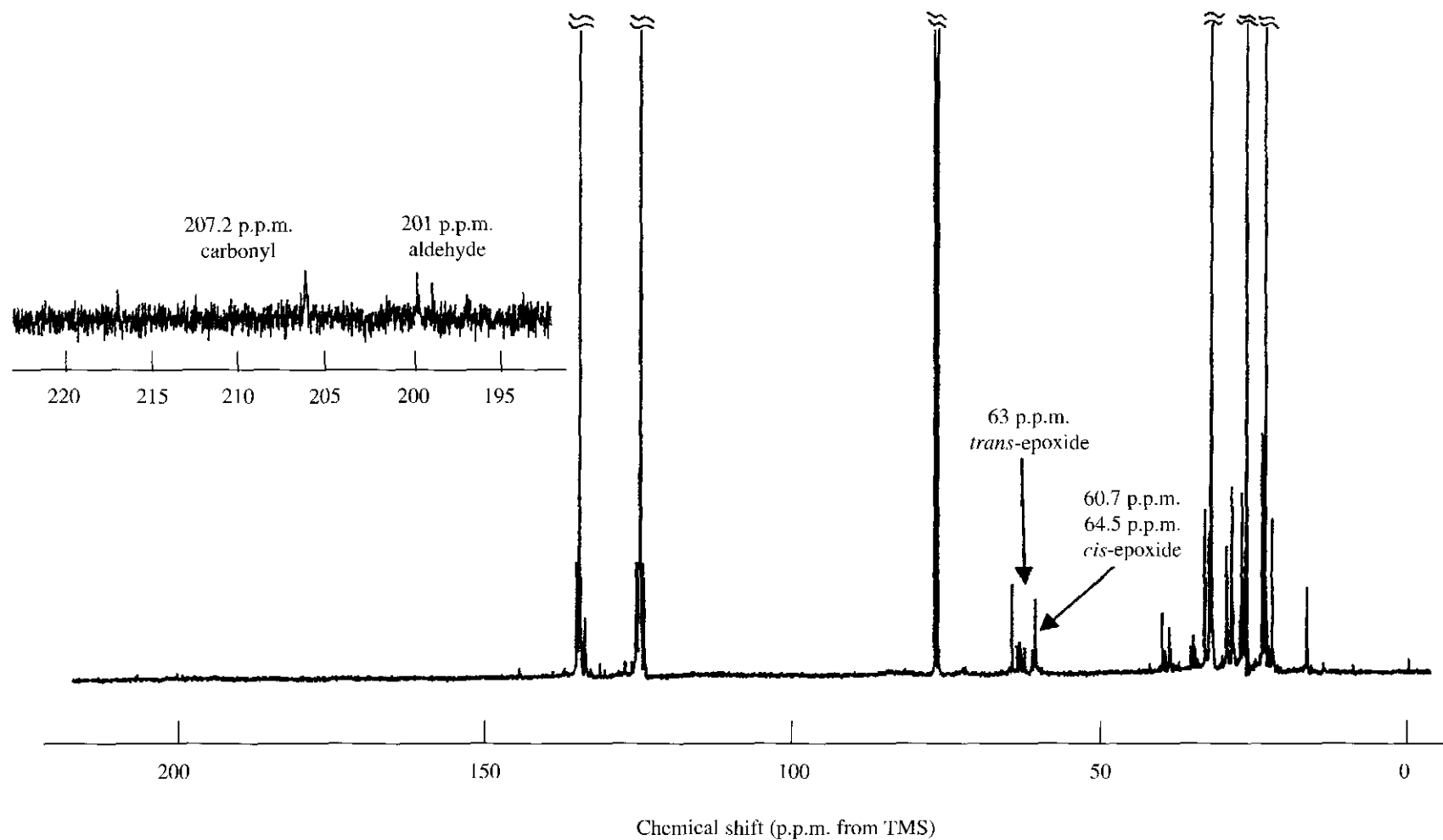
Figure 3. ^{13}C-NMR spectrum of degraded product from DPNR-AE in toluene solution with 1 p.h.r. Co(acac)$_2$ by shaking at 65°C for 24 h.

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APPENDIX 1.

THE INTRINSIC VISCOSITY OF DEGRADED RUBBER FROM VARIOUS METHODS

Method	$[\eta]$
UV-irradiation for 24 h (+10 ml 30% H_2O_2)	
DPNR latex	5 8
DPNR solution	1 5
DPNR-AE solution	1 2
Shaking at 65°C for 24 h (H_2O_2 + 1 p h r metal catalyst)	
DPNR latex + H_2O_2 + 1 p h r $FeSO_4$	6 1
DPNR latex + H_2O_2 + 1 p h r $FeCl_2$	5 9
DPNR latex + H_2O_2 + 1 p h r $CoCl_2$	3 2
DPNR latex + H_2O_2 + 1 p h r Co (acac)$_2$	2 9
DPNR-AE solution + 1 p h r $CoCl_2$	1 8
DPNR-AE solution + 1 p h r Co (acac)$_2$	0 7
DPNR solution + 1 p h r Co (acac)$_2$	1 2
Shaking at 65°C for 24 h [+ 1 p h r Co (acac)$_2$]	
FLNR solution	5 9
FLNR-AE solution	5 0
PC solution	5 2
DPNR solution	1 2
DPNR-AE solution	0 7