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Chemical Degradation of Natural Rubber Latex in Acidic Medium Catalysed by $CoCl_2$ and $(NH_4)_2Fe(SO_4)_2$

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Liquid natural rubber (LNR) is a derivative of natural rubber (NR) which has a molecular weight of less than 50, 000 g/mol. In this study, LNR was prepared via *chemical degradation reaction using hydrogen peroxide and sodium nitrite as reagents in latex solution. Compared to the reaction without catalyst, molecular weight of LNR obtained was found to decrease approximately three and two times in the presence of cobalt chloride ($CoCl_2$) and ferrous ammonium sulphate ($(NH_4)_2Fe(SO_4)_2$), respectively. Using the method described, the degradation reaction generates functional groups such as hydroxyl and carbonyl in the LNR chains. In the presence of these catalysts, the hydroxyl groups are decreased and contrarily carbonyl groups in the LNR chains are increased.*

Keywords: Liquid natural rubber (LNR), cobalt chloride, ferrous ammonium sulphate, redox reaction.

Liquid natural rubber (LNR) is a derivative of natural rubber (NR) with molecular weight less than 50,000 g/mol[1], and behaves as a fluid at room temperature. LNR can be prepared in many ways, for instance *via* degradation of NR either in latex[2–7] or solution[8–10]. It has been used as a raw material for adhesives[11], reactive plasticiser[12,13] and as a precursor for further reaction to form new materials[14–24].

The efficiency of degradation reaction depends on various factors such as reaction method, reaction condition, type of NR, reagent used, additives, *etc*. These factors not only affect the molecular weight of LNR obtained, but also influence the type of functional groups formed on the LNR chains. The ability of obtaining a wide range of rubber with narrow molecular weight distribution offers large number of applications, whilst the reactive functional groups can be exploited for further reactions.

Titanium dioxide (TiO_2) in the presence of hydrogen peroxide was reported to catalyse photo degradation of NR and produced LNR functionalised by hydroxyl groups[7,8,25]. Degradation of NR either in latex using phenylhydrazine and $FeCl_2$ as catalyst was reported to yield LNR with

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hydroxyl, carbonyl, carboxylic, C=N and phenylhydrazone groups[2]. Sakdapipanich *et al*.[26] degraded DPNR using UV-irradiation in the presence of hydrogen peroxide. However, the degree of degradation was found to be very low without iron and cobalt metal as catalysts. Use of hydrogen peroxide and sodium nitrite to degrade the NR latex has been explored and iron content was claimed to increase the NR chain breakage, hence, lower molecular weight of LNR was obtained[27].

In our recent work, the degradation reaction was carried out in an acidic medium using a combination of hydrogen peroxide and sodium nitrite to yield LNR with hydroxyl groups. In this present report, degradation of NR latex in acidic medium was found to be accelerated by $CoCl_2$ and $(NH_4)_2Fe(SO_4)_2$.

EXPERIMENTAL

Materials

Low ammonia latex (LATZ) of NR with 60% dry rubber content (DRC) was supplied by Lee Rubber Sdn Bhd. Analytical grade sodium nitrite, hydrogen peroxide, $CoCl_2$ and $(NH_4)_2Fe(SO_4)_2$ were supplied by Merck (Malaysia) and were used as received. Sodium dodecyl sulphate (SDS), toluene and methanol were supplied by Sigma Aldrich (Malaysia) and were used without further purification.

Chemical Degradation of NR Latex

One mol of NR latex (number average molecular weight (Mn) ≈ 657 × 10^{-3} g/mol; molar mass of isoprene unit = 68.11 g/mol) was diluted with distilled water to 20% DRC and stabilised with 2% (w/w) SDS. The solution was then poured in a reaction flask and placed in a water bath. The solution was heated to 70ºC before 0.2 mol of sodium nitrite (molar mass = 68.99 g/mol) and hydrogen peroxide (molar mass = 34.01 g/mol) were added. The reaction was carried out for 8 h and terminated with sodium hydroxide (NaOH). The LNR obtained was coagulated using methanol and washed a few times with water and subsequently dried in a vacuum oven at 60ºC. Further purification of the LNR was conducted by dissolving in toluene and re-precipitated using methanol and further dried in a vacuum oven at 60ºC to a constant weight.

Molecular Weight Determination

Number average molecular weight of the LNR was determined by using Viscotex Multi-Detector Gel Permeation Chromatography (GPC) with tetrahydrofuran (THF) as a solvent and also an eluent. The molecular weight was determined from an internal standardised molecular weight curve which was prior obtained using polyisoprene molecular weight standard.

Qualitative Spectroscopy Analysis

The Fourier transform infrared spectroscopy (FTIR) spectrum of LNR was recorded on a Perkin Elmer Spectrum BX spectrophotometer and the attenuated total reflection (ATR) technique was employed for the analysis. Proton nuclear magnetic resonance (^{1}H NMR) spectrum was recorded using Bruker 400 spectrometer, with deuterated chloroform ($CDCl_3$) as the solvent. Tetramethylsilane (TMS) was used as the internal standard for zero axis calibration.

Thermal Characterisation

The thermal stability of LNR prepared was studied using a Mettler Toledo TGA/SDTA 518. The sample was heated at a temperature

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range of 40ºC to 800ºC with heating rate of 20ºC/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Cobalt chloride is an inorganic compound of cobalt and chloride. Due to its chemical properties and ability of changing colour, it has major uses in petrochemicals and plastic industries, as both a hetero and homogeneous catalyst. Ferrous ammonium sulphate $(NH_4)_2Fe(SO_4)_2$ is a double salt inorganic compound commonly known as Mohr's Salt. Cobalt and iron were used in this reaction due to their strong characteristic of degrading rubber[26].

Our recent work[28] showed that the degradation of NR by hydrogen peroxide and sodium nitrite has different profiling when carried out in acidic or alkaline media. In alkaline medium, the cleavage of NR chain occurs through a redox reaction and yields LNR with carbonyl groups. However, degradation reaction in acidic medium is dominated by hydroxyl radicals. This is due to the formation of peroxynitrite acid as a result of chemical interaction between hydrogen peroxide and sodium nitrite in acidic medium (pKa = 6.8)[29]. LNRs obtained from reactions were analysed using GPC to determine the molecular weight. In this work, molecular weight can be used as an indication of reaction efficiency when lower molecular weight of LNR indicates greater degradation or reaction.

Reaction Catalysed by $CoCl_2$

Table 1 shows the decrease of Mn of LNRs prepared in the presence of $CoCl_2$. The Mn of LNR reduced significantly from 36.66×10^3 g/mol without $CoCl_2$ to 9.22×10^3 g/mol when 0.05 mmol of $CoCl_2$ was used in the reaction. Increasing the $CoCl_2$ concentration led to further but smaller reduction in Mn, down 5.87×10^3 g/mol with 0.5 mmol $CoCl_2$. However, the polydispersity was found to be with no specific trend, in the range of 2.28 to 3.07 in the presence of $CoCl_2$ as catalyst in the degradation reaction.

Figure 1 illustrates the IR spectra of LNRs prepared with various amount of $CoCl_2$. Without $CoCl_2$, there are peaks at 3400 and 1089 cm^{-1}, corresponding to hydroxyl groups, and only a very small peak was observed at 1719 cm^{-1}, corresponding to carbonyl groups. The presence of hydroxyl groups on the LNR chain is a result of chain breaking[28,30]. However, the spectra of LNRs prepared with $CoCl_2$ showed an increasing absorbance at 1719 cm^{-1}, and decreasing absorbance at

TABLE 1. MOLECULAR WEIGHT OF LNRS PREPARED WITH $CoCl_2$

Amount of $CoCl_2$ (mmol)	Mn × 1000 (g/mol)	Polydispersity (P)
NR latex	657	7.80
0	36.66	2.74
0.05	9.22	2.75
0.1	9.38	2.28
0.2	8.51	2.32
0.3	8.26	2.28
0.4	7.62	2.60
0.5	5.87	3.07

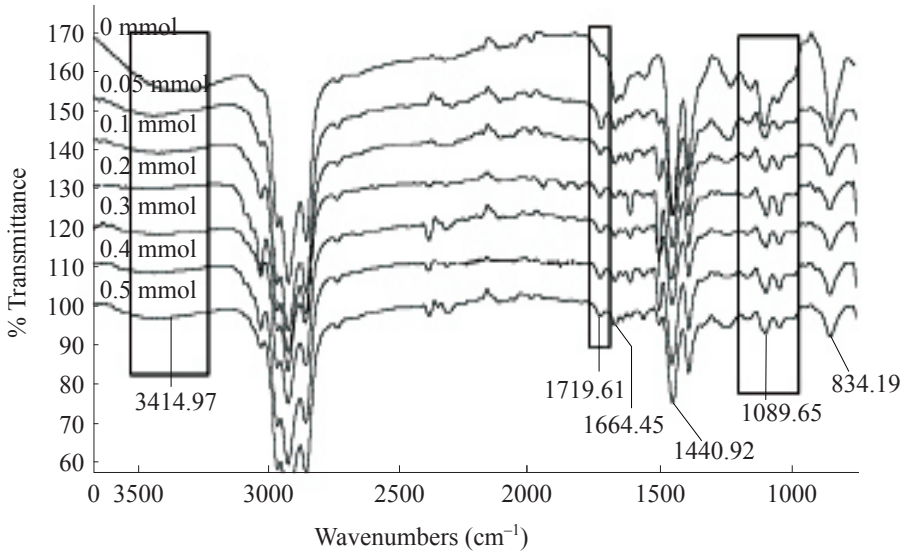

Figure 1. IR spectra of LNRs prepared with various amount of $CoCl_2$.

3400 and 1089 cm^{-1}, suggesting that $CoCl_2$ has reduced the number of hydroxyl groups in LNR chains whilst increasing the carbonyl groups. Peaks at 1664, 834 and 1440 cm^{-1} which represent vibration of C=C, =CH and C-C, respectively, were decreased when $CoCl_2$ was used, indicating that the chain breakage occurred at both C=C and C-C bonds. These results are in agreement with the ^{1}H NMR spectra as shown in *Figure 2*.

Figure 2 shows the ^{1}H NMR spectra of LNRs prepared using 0, 0.1 and 0.5 mmol of $CoCl_2$ as the catalyst for the degradation reaction. In addition to the main chain *cis*-1,4-polyisoprene peaks, small peaks appeared at chemical shift between 2 and 5 ppm which is normally indication of the presence of hydroxyl protons[31]. The peak broadening effect is due to the rapid chemical exchange of protons between the α carbon and hydroxyl. The peaks around 3.2–3.8 ppm are resonance effect caused by protons that belong to hydroxylated methylene and methine protons[7,31,32]. Peaks of LNR samples prepared in the degradation reaction catalysed by $CoCl_2$ were either less intense or disappeared. It is worthy to note that a peak emerged at 2.17 ppm when 0.5 mmol $CoCl_2$ was used and the peak corresponded to ketone groups[7].

As the colour of LNRs obtained became darker with the increasing amount of $CoCl_2$, some components of LNR formed a complex with cobalt[26] as shown in the thermogravimetric analyser (TGA) result. The degradation temperature of LNR prepared without $CoCl_2$ occurred at 396ºC (*Figure 3*) with only one curve as shown by DTG plot, whilst LNR prepared with 0.5 mmol $CoCl_2$ showed two curves, indicating two step degradation have occurred (*Figure 4*). The first step of degradation began at an onset temperature similar to the control LNR, but a small peak appeared later. The second degradation curve is believed to come from the complex of cobalt with LNR.

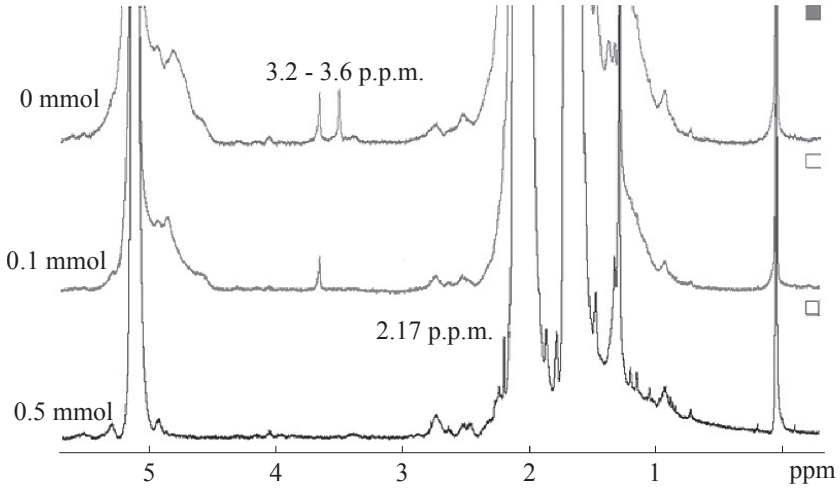

Figure 2. ^{1}H NMR spectra of LNRs prepared with 0, 0.1 and 0.5 mmol of $CoCl_2$.

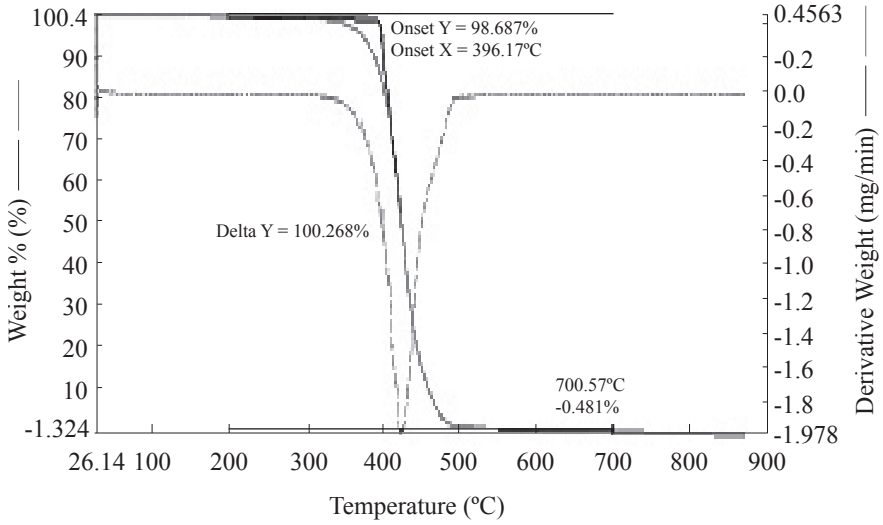

Figure 3. TGA thermogram of LNR prepared without $CoCl_2$.

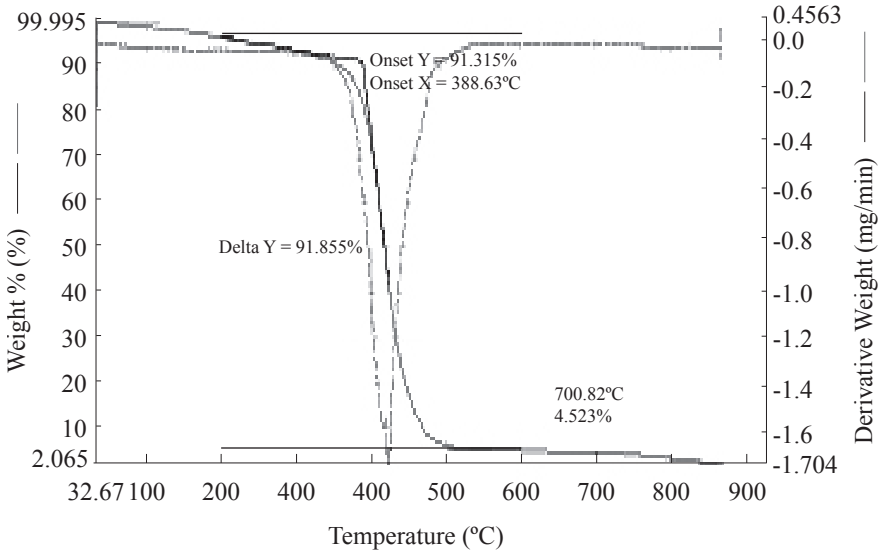

Figure 4. TGA thermogram of LNR prepared with 0.5 mmol $CoCl_2$.

LNRs prepared with 0.5 mmol $CoCl_2$ were analysed *via* x-ray diffraction analysis (XRD) to determine the existence of $CoCl_2$ residue that may be associated with some components in rubber. However, due to the detection limit of the XRD instrumentation, the XRD spectrum obtained (*Figure 5*) showed no indication of any crystal existence in the sample tested.

Reaction Catalysed by Ammonium Iron(II) Sulphate Hexahydrate $(NH_4)_2Fe(SO_4)_2$

The LNRs prepared with $(NH_4)_2Fe(SO_4)_2$ were yellowish gold in colour and TGA thermograms showed similar characteristic to the control LNR sample. $(NH_4)_2Fe(SO_4)_2$ was found to have catalytic effect on degradation of NR latex as the Mn of LNRs obtained was significantly reduced (*Table 2*). The Mn of LNRs reduced from 36.66×10^3 g/mol (without $(NH_4)_2Fe(SO_4)_2$) to 20.08×10^3 g/mol when 0.05 mmol of $(NH_4)_2Fe(SO_4)_2$ was used as catalyst in the degradation reaction. Increasing the $(NH_4)_2Fe(SO_4)_2$) concentration led to further reduction, down to 10.33×10^3 g/mol with 0.5 mmol $(NH_4)_2Fe(SO_4)_2$). However, the polydispersity of the LNRs was found to increase slightly when the amount of $(NH_4)_2Fe(SO_4)_2$ used was more than 0.3 mmol.

Figure 6 illustrates the IR spectra of LNRs prepared with various amount of $(NH_4)_2Fe(SO_4)_2$. Without $(NH_4)_2Fe(SO_4)_2$, there are peaks at 3400 and 1093 cm^{-1}, indicating the existence of hydroxyl groups. However, the spectra of LNRs prepared with $(NH_4)_2Fe(SO_4)_2$ showed an increasing absorbance at 1722 cm^{-1} corresponding to carbonyl groups, and decreasing absorbance at 3400 cm^{-1} 1093 cm^{-1}. This indicates that the $(NH_4)_2Fe(SO_4)_2$ reduced the number of hydroxyl groups in the LNR chains whilst increasing the carbonyl groups. With $(NH_4)_2Fe(SO_4)_2$ the peak of 1722 cm^{-1} appears

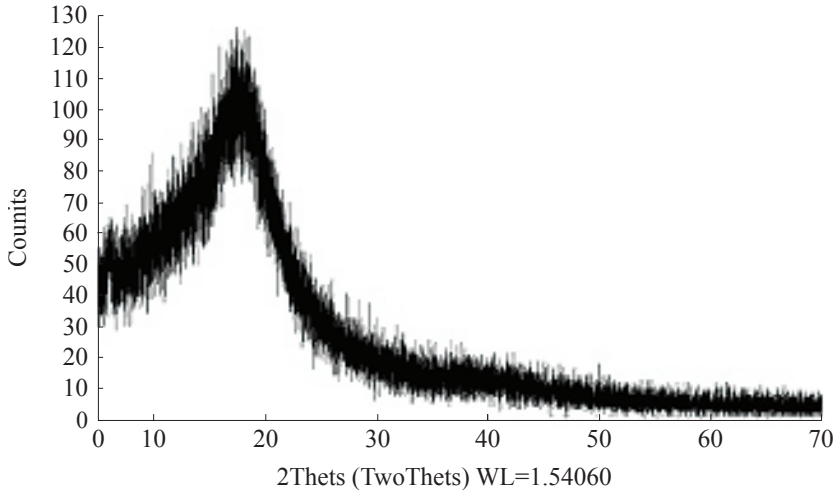

Figure 5. XRD spectrum of LNR prepared with 0.5 mmol $CoCl_2$.

TABLE 2. GPC RESULT OF LNRS PREPARED WITH $(NH_4)_2Fe(SO_4)_2$

Amount (mmol)	Mn × 1000 (g/mol)	Polydispersity (P)
NR latex	657	7.8
0	36.66	2.74
0.05	20.08	2.16
0.1	16.78	2.31
0.2	13.69	2.14
0.3	12.01	2.15
0.4	10.45	2.55
0.5	10.33	2.65

weaker compared to $CoCl_2$. Peaks at 1662, 835 and 1445 cm^{-1} that represent vibration of C=C, =CH and C-C, respectively, decreased when $(NH_4)_2Fe(SO_4)_2$ was used, indicating that the chain breakage occurred at both C=C and C-C bonds. These results are in agreement with the ^1H NMR spectra shown in *Figure 7*.

^1H NMR spectra of LNRs prepared using $(NH_4)_2Fe(SO_4)_2$ as the catalyst in the degradation reaction is shown in *Figure 7*. A decrease in peak intensity is observed for the small peaks in the range of 3-5 ppm compared to LNR prepared without $(NH_4)_2Fe(SO_4)_2$. This explains the disappearance of hydroxyl groups in the LNR chains. On the other hand, a small peak that represents ketone group was detected at 2.17 ppm. This result is similar to the $CoCl_2$ catalysed degradation reaction mentioned above and thus, the mechanism of chain breaking reaction with and without the catalysts may differ.

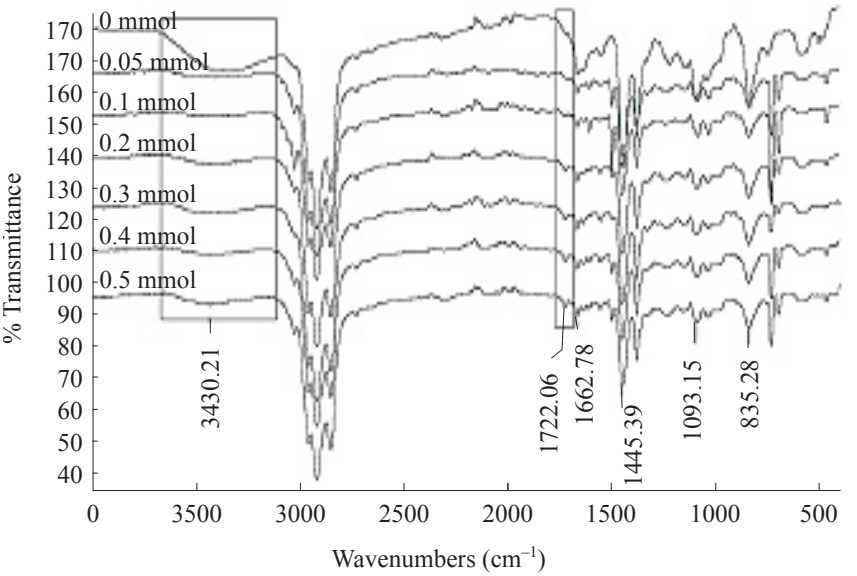

Figure 6. IR spectra of LNRs prepared with various amount of $(NH_4)_2Fe(SO_4)_2$.

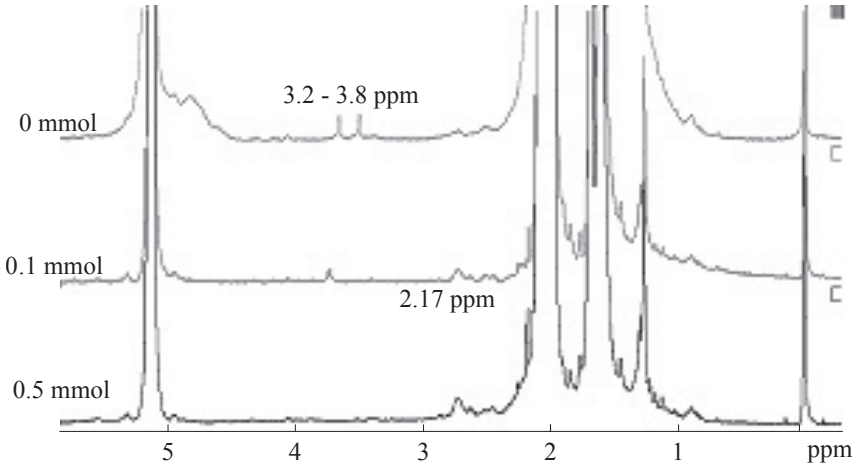

Figure 7. ^1H NMR spectra of LNRs prepared with 0, 0.1 and 0.5 mmol of $(NH_4)_2Fe(SO_4)_2$.

CONCLUSION

Degradation of NR latex using sodium nitrite and hydrogen peroxide was successfully carried out where the molecular weight (Mn) of NR was reduced from 657×10^3 g/mol to 36.66×10^3 g/mol. The reaction was found to be more efficient in the presence of $CoCl_2$ and $(NH_4)_2Fe(SO_4)_2$ as catalysts. $CoCl_2$ performed better as a catalyst for degradation of NR than $(NH_4)_2Fe(SO_4)_2$ where the Mn of LNR was as low as 5.87×10^3 g/mol and 10.33×10^3 g/mol respectively. The reactions catalysed by both $CoCl_2$ and $(NH_4)_2Fe(SO_4)_2$ yielded LNRs with lower C=C and hydroxyl groups, but higher level of carbonyl group compared to LNR prepared without catalyst.

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