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Sánchez, G., Gaikwad, V., Holdsworth, C., Dlugogorski, B., Kennedy, E. and Stockenhuber, M. (2016) Catalytic conversion of glycerol to polymers in the presence of ammonia. *Chemical Engineering Journal*, 291 . pp. 279-286.

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Accepted Manuscript

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PII: S1385-8947(16)30015-8
DOI: <http://dx.doi.org/10.1016/j.cej.2016.01.049>
Reference: CEJ 14666

To appear in: *Chemical Engineering Journal*

Received Date: 29 June 2015
Revised Date: 10 January 2016
Accepted Date: 15 January 2016

Please cite this article as: G. Sanchez, V. Gaikwad, C. Holdsworth, B. Dlugogorski, E. Kennedy, M. Stockenhuber, Catalytic conversion of glycerol to polymers in the presence of ammonia, *Chemical Engineering Journal* (2016), doi: <http://dx.doi.org/10.1016/j.cej.2016.01.049>



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Catalytic conversion of glycerol to polymers in the presence of ammonia

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Abstract

In this contribution, the development of a process for the synthesis of potentially highly valuable polymeric products from the reaction of waste glycerol with ammonia is reported for the first time. The polymers were the result of a single step, continuous gas phase process, catalysed by an alumina-supported iron catalyst, operating under relatively mild reaction conditions. The solid product was characterised using 1D and 2D NMR spectroscopy, FTIR spectroscopy, qualitative chemical tests and elemental analysis. Characterisation revealed building blocks with unsaturated, amido and ester functionalities shaping a mixture of polymers. Nitrogen atoms were present in the main chain of the resultant polymers. NMR analyses of the polymer denotes the formation of structural defects such as unsaturation and branching; while the partial solubility of the polymer in solvents such as CDCl_3 and THF is indicative of the formation of cross-linked structures. Insights into the mechanism of formation of these functional groups were based on the liquid and gas phase product distribution. Polymers with chain structures similar to those synthesised in this work are currently manufactured from fossil fuels and are widely used in biomedical applications not

only because of their architecture but also due to their response to changes in pH and temperature.

Key words: polymers, glycerol conversion, ammonia, iron catalyst

1. Introduction

In the context of glycerol valorisation, oligomers and polymers of glycerol have been investigated at both industrial and laboratory scales [1-3]. Their commercial applications seem to depend strictly on the molecular weight of the synthesised product. While low molecular weight fractions obtained directly from glycerol as monomer are used in food, cosmetic and polymer industries, high molecular weight products from glycidol are of significant interest in the biomedical field due to their resemblance to the polyethylene glycol (PEG) structure [2]. When synthesising di-glycerol (simplest oligomer of glycerol) most of the routes are multi-step processes with very specific and costly starting substances and generation of significant varieties of by-products [1]. Glycerol can also undergo oligomerisation by thermal degradation in an inert atmosphere, however, controlling product selectivity, meeting product specifications and conducting downstream separation procedures remain challenging aspects for commercial application of these reactions [1]. Caesium or magnesium impregnated mesoporous materials have been examined in the selective production of polyglycerol aiming at lowering the rate of formation of acrolein and cyclic polyglycerols [4]. Over iron catalysts, glycerol is converted to acrolein, acetaldehyde, allyl alcohol, hydroxyacetone, carboxylic acids, among others [5-7]. Moreover, these and several other glycerol based chemicals contain functional moieties such as acrylates, vinyl and allyl groups which can also polymerise [8].

With different approaches (i.e. amination or ammoxidation), ammonia has been introduced in processes where glycerol is transformed [9-11]. Amino alcohols, amines, diamines and polyalkylenepolyamines are typical products [9]. These species together with those produced from glycerol conversion could lead to the formation of polymers bearing nitrogen atoms. For instance, polyamides have been previously obtained from amines and carboxylic acids using 3,4,5-trifluorophenylboronic acid as catalyst [12]. Oxazolines have been reported to spontaneously polymerise with α,β -unsaturated acids through a ring opening mechanism via a zwitterion [13]. Likewise, the spontaneous polymerisation of acrylamide has been claimed to occur in glycerol solution [14]. However, to the best of our knowledge, the formation of polymeric products has not been reported directly from glycerol in the presence of ammonia.

In the current study, primary laboratory data has been produced. This data includes a detailed characterisation of the product formed, which is of particular relevance due to the novel character of the work. Insights into the formation of the building blocks present in the polymeric mixture have been developed. From a chemical engineering point of view, information such as this is essential for understanding and optimising the process, which are necessary for commercial exploitation of the studied reaction. It is believed that this communication contributes towards shaping a glycerol value chain by reporting the one-pot synthesis of high value polymeric products at mild conditions over an alumina-supported iron catalyst.

2. Materials and Methods

A 35 wt % glycerol aqueous solution and gas phase ammonia (3 %) were reacted over an alumina-supported iron catalyst. Details on catalyst preparation and composition are provided in previous publications [7, 15]. The reaction was carried out with nitrogen as carrier gas and

with a GHSV of approximately 1190 h^{-1} operating for 180 min at $340 \text{ }^\circ\text{C}$ and atmospheric pressure, in a reactor system described elsewhere [15]. Once the catalytic experiments were terminated, the experimental setup was purged with nitrogen and allowed to cool to room temperature. A mixture of polymeric material was obtained in the lower section of the catalyst support as a solid product. The solid was collected for analysis without further dilution with solvents. Post collection, the solid was dissolved in tetrahydrofuran (THF, ACS-Merck), after which, the soluble and insoluble fractions were separated. The THF-soluble fraction is expected to consist of non cross-linked polymer, while the insoluble fraction will consist predominantly of cross-linked polymer [16]. The THF solvent was allowed to evaporate in a fume cupboard at room temperature. Subsequently, this polymer was dried in a vacuum oven at $40 \text{ }^\circ\text{C}$ for 8 hours to maximise the removal of THF. A concentrated solution of this non cross-linked polymeric mixture was prepared for NMR analyses using CDCl_3 (99.96 atom % D, 0.03 % v/v TMS, Sigma Aldrich). A Bruker Avance 600 nuclear magnetic resonance (NMR) spectrometer was employed for structure determination through 1D and 2D techniques.

A combination of other techniques was used to provide auxiliary data to the NMR characterisation. These consisted of qualitative chemical tests, CHN analysis and infrared spectroscopy.

A THF solution of the soluble fraction was examined by Gel Permeation Chromatography (GPC).

Liquid phase products were analysed by GC-FID and GC-MS following dilution in methanol using 99.8 % cyclohexanone from Sigma Aldrich as internal standard.

3. Results and Discussion

3.1. Polymer characterisation

Results from CHN analysis of the polymeric mixture, including both cross-linked and non cross-linked fractions, confirmed the presence of nitrogen in the polymeric product, as listed in Table 1. The polymer was not formed when the aqueous glycerol solution was reacted over the iron catalyst in the absence of ammonia with nitrogen as gas carrier. This suggests that the source of nitrogen in the polymer is from feed ammonia. Considering our reactants, the other possible element is oxygen which would be in balance to the ones listed. Oxygen containing groups were identified by NMR and FTIR. The presence of C=O was also confirmed by qualitative chemical tests (i.e. hydroxamic acid test)

The soluble, non cross-linked polymer fraction was analysed by GPC, NMR and FTIR spectroscopy, while the insoluble cross-linked polymer fraction was examined by ATR FTIR. The molecular weights of the soluble fraction were M_n : 1536 g · mol⁻¹ and M_w : 2239 g · mol⁻¹ as determined by GPC, which implies a polydispersity index of 1.5.

3.1.1. NMR analysis

NMR analysis is directed towards identifying the functional groups in the polymer and postulating probable chain structures. Due to the nature of the experimental process and the chemistry involved, the polymer obtained is most likely to be composed of more than one chain structure and will also possess several structural defects. This complicates the NMR analysis and makes unequivocal identification of functional groups and chain structures extremely difficult. The analysis presented in the subsequent sections of this manuscript is based on 1-D and 2-D NMR experiments as well as the data available in literature. The ¹³C

spectrum from Heteronuclear Multiple-Quantum Correlation (HMQC) experiment was used for structure elucidation due to its better resolution.

In order to differentiate CH_2 and CH_3 from quaternary C and CH groups, DEPTQ 135 (distortionless enhancement by polarisation transfer retaining quaternary centres using a 135 degree decoupler pulse) and DEPT 135 (distortionless enhancement by polarisation transfer using a 135 degree decoupler pulse) experiments were conducted. Their spectra are disclosed in figures 1 and 2, respectively. Tetramethylsilane (TMS) was used for chemical shift referencing (its signal is negative), therefore, negative peaks were attributed to CH and CH_3 groups, while signals above the axis (i.e. positive) were assigned to CH_2 , in both DEPT spectra, and quaternary carbons in the DEPTQ. The peaks at 176 and 178 ppm have been attributed to the presence of the C=O functional group in the polymeric mixture. Peaks in the range of 63 - 68 ppm were assigned to the methylene carbon in $-\text{CH}_2\text{OC}=\text{O}$, which suggests then presence of ester linkages [13, 17]. These assignments were confirmed by chemical tests: while the same solution analysed by NMR tested negative to the 2,4-dinitrophenylhydrazine (DNPH) test (where a yellow/orange precipitate was absent), a positive result was obtained for the hydroxamic acid test suggesting that the carbonyl group observed on the ^{13}C NMR spectrum is not from a ketone nor an aldehyde but from an ester and/or amide. Peaks in the range of 68 – 71 ppm were attributed to the methine carbon in the $>\text{CHOC}=\text{O}$ [18]. Signals at 62 and 72 ppm were assigned to methylene and methine carbons, respectively, in the CH_2NHCH group as observed for products of the polymerisation of unsaturated aldehydes and aliphatic amines [19]. Signals at approximately 30 ppm were associated with methylene carbons which are the repeating unit in one of the structures present in the polymeric mixture. The signal at approximately 34 ppm was attributed to the methylene carbon in $\text{NHC}=\text{OCH}_2$ groups [17]. Peaks between 9 – 22 ppm can be attributed to CH_3 groups from side chains present in the polymer [20]. Signals at 19 and 27 ppm are most

likely due to $\text{CH}_2\text{-CH}_2$ type carbons. The peak observed in the ^{13}C NMR at approximately 43 ppm (Figure S1 of the Electronic Supplementary Information (ESI)) was assigned to the methine carbon in CHC=ONH groups in which the nitrogen atom is part of a pendant unit [21]. Likewise from HMQC, signals at 124 and 139 ppm were assigned to carbons in $\text{CH}_2=\text{CH}$ type structures in the polymer (Point E Figure S2 of the ESI) [13]. This is in agreement with chemical tests with bromine water that resulted in a discoloration of the bromine due to the presence of unsaturation in the sample.

Based on the information described previously and data from the HMQC NMR spectrum (available as Figure S2 of the ESI), the chemical shifts between 1.8 and 2.3 ppm in the ^1H NMR spectrum (figure 3) were attributed to protons in one of the backbone chains ($\text{CH}_2\text{-CH}_2$ repeating unit). The signal at 0.9 ppm was assigned to CH_3 side chain groups, while the peak at 1.15 ppm was attributed to protons in both CH_2 and CH_3 groups, which again are a part of the branching in the polymer. Region between 3.4 and 4.2 ppm is characteristic of overlap between protons from CH_2 and CH moieties. Protons in $>\text{CH}_2\text{OC=O}$ and $-\text{CHOC=O}$ groups exhibit their signature between 3.9 and 4.2 ppm, while peaks at approximately 3.4 and 3.7 ppm correspond to protons from methine and methylene carbons, respectively, in the CH_2NHCH group. The chemical shifts between 6.6 and 7.3 ppm were assigned to protons in a $\text{CH}_2=\text{CH}$ type group. No signals corresponding to the proton present in OH groups (at approximately 5 ppm) were observed. Signals between 7.5 and 8.0 ppm were assigned to NH type protons in NHC=OCH_2 groups.

3.1.2. FTIR spectroscopy

Figure 4 shows the ATR/FTIR spectra of both the insoluble cross-linked polymer and the soluble non cross-linked polymer after the samples were exhaustively dried at 40 °C for 8 hours. The main difference between the spectra is the absorbance at approximately 1720 cm^{-1}

(C=O stretching vibration) as well as a more defined band with maximum at 1240 cm^{-1} , characteristic of the C-O stretching of an ester [22], present in the soluble fraction but absent in the insoluble fraction. These differences between both spectra were thought to be consequences of the solubility in CHCl_3 of the building blocks present in the polymeric mixture. For instance, polyesters such as polyester 6,10 and polyester 12,10 are soluble in CHCl_3 while nylon 6,10 and nylon 12,10 are insoluble in the same solvent [17]. Differences in the frequency of absorption at high wavenumbers were observed between cross-linked and non cross-linked fractions. While the insoluble product exhibited a broad band between 3200 and 3600 cm^{-1} , a comparatively narrow signal between 3300 and 3500 cm^{-1} was evident in the spectrum of the soluble fraction. The latter was attributed to N-H stretching and the former also to N-H stretching that overlaps with the stretching vibration of OH groups. This finding was in agreement with ^1H NMR results of the non cross-linked fraction that did not show peaks at chemical shifts as high as 5.2 ppm typical of the proton in the hydroxyl group. This functional group therefore corresponds to the cross-linked fraction of the polymer. It is worthwhile mentioning that the polymer samples were free from water following preparation for NMR and FTIR analyses.

In both spectra, a high intensity band observed at 1038 cm^{-1} was assigned to C-O stretching vibrations [23, 24]. Absorptions at 2876 cm^{-1} and 2930 cm^{-1} correspond to C-H stretching vibrations and the signal at 1114 cm^{-1} was assigned to C-O-C stretching vibrations [23, 24]. In the spectral region of 1564 cm^{-1} and 1651 cm^{-1} , bands were assigned to N-H deformation and C=O stretching vibrations, respectively. At lower wavenumbers, the signals were identified as follows: 920 cm^{-1} due to C-OH stretching vibration, 1380 cm^{-1} (present in the spectrum of the cross-linked fraction) attributable to CH_3 symmetric deformation, 1408 cm^{-1} due to C-OH bending vibration (also present in the spectrum of the cross-linked

fraction) and 1460 cm^{-1} attributable to CH_3 antisymmetric deformation. The functional group responsible for the signal at 1408 cm^{-1} was only found in the insoluble fraction.

CHN analysis, chemical and solubility tests, NMR spectroscopy and FTIR measurements conducted on both cross-linked and non cross-linked fractions of the polymeric product formed from the reaction of ammonia and glycerol enabled further characterisation of the polymeric mixture. One of the components is likely to be a polymer chain with $-(\text{CH}_2-\text{CH}_2)-$ as repeating unit and CH_2 , CH , $\text{OC}=\text{O}$ and CH_3 as part of the side chains. Another possibility is a polymer chain with $-(\text{CH}_2-\text{CHC}=\text{ONHCH}(\text{CH}_3)_2)-$ as backbone with $-\text{C}=\text{ONHCH}(\text{CH}_3)_2$ as pendant group. Nitrogen atoms were also thought to be present in a chain consisting of NHCOCH_2 and $\text{CH}_2\text{OC}=\text{O}$ groups, although another alternative structure is a polymer with $-(\text{CH}_2-\text{CH})-$ as repeating unit and NHCH_2 as part of the side chain. Olefinic carbons were most likely in proximity of carbonyl groups. The proposed polymer structures are represented in figure 5.

Along with the previously discussed defects, it is likely that the polymer will consist of additional structural defects, such as branching. The absence of signals at approximately 5 ppm on the ^1H NMR spectrum was in agreement with FTIR analyses of vacuum dried samples, which suggested that hydroxyl groups are part of the cross-linked polymer.

3.2. Insights on the mechanism of formation of the building blocks present in the polymer mixture

Our research group has recently published on the use of ammonia enhancing the formation of allyl alcohol from glycerol over an iron catalyst [15]. Product distribution in the liquid phase consists predominantly of allyl alcohol, acrolein, acetaldehyde, hydroxyacetone, carboxylic acids, 2,4-dimethyl-2-oxazoline-4-methanol, 2-(aminooxy)propanoic acid among others, with carbon dioxide, carbon monoxide, acrolein and acetaldehyde in the gas phase

[15]. The formation of a solid product did not occur when ammonia was absent operating at the same reaction conditions, which suggests the involvement of the reactant gas in the polymerisation mechanism. Additional tests were conducted operating at the same conditions in an uncatalysed process. In a separate set of experiments, alumina was used as for the iron catalyst. Solid products were collected and prepared for NMR analyses in both tests.

Polyglycerols are in general highly branched structures of dendritic architectures and important end group functionalities [25]. Salehpour et al. reported glycerol polymerisation through a step growth mechanism either base or acid catalysed [2]. At high temperatures, both routes involved glycidol as an intermediate in the reaction [2]. Moreover, polyglycerols can be formed from glycidol and primary amines as core and/or initiators [26]. Glycidol was not detected in the liquid phase using GC-MS analysis when reacting glycerol over the iron catalyst, nor was it detected when ammonia was present over the same catalyst and operating conditions. Even if glycidol was formed in the presence of ammonia, it is likely to be unstable as ring opening of the epoxide is expected to occur when amines are present. Other than the glycidol intermediate pathway, self-condensation of glycerol has been reported to take place with sulfuric acid as catalyst or on a base catalysed process via the formation of alkoxide, however, the rate of polymerisation of the latter is slow [2]. The reaction order was determined adopting the integral method approach. It was found that the rate of glycerol self-condensation into polyglycerols is independent of the reactant concentration (i.e. zero order reaction). These calculations were carried out under the assumption that glycerol self-condensation is the main reaction taking place, operating at the current reaction conditions. However, as detailed in section 3.1, amido and unsaturated functionalities are present in the final product in addition to ester groups. The former functional groups are evidence of the involvement of some products of glycerol conversion in the polymerisation reaction over iron catalysts. As previously reported, graphical methods based on the integral of the rate equation

apply to those cases where reaction products have no influence on the course of the polymerisation [27]. The formation of different structures in the current investigation when comparing to those glycerol polymerisation studies could be explained based on the reaction temperature which favours the formation of acrolein and other products in contrast to previously reported processes where this parameter does not exceed 180 °C [2].

Characterisation of the polymeric product suggested the presence of $(\text{CH}_2\text{-CH})\text{C}=\text{ONHCH}(\text{CH}_3)_2$ groups as a part of the mixture where the amide corresponds to the pendant group. In previous reports, the polymerisation of acrolein and amines was claimed to proceed via a step growth mechanism in which the degree of functionalisation of the starting monomers generated cross-linked polymeric products [19]. The reactivity of the carbonyl group in acrolein was evident by the absence of signals at 9.5 ppm in the ^1H NMR spectrum corresponding to CHO groups as well as chemical tests which suggested that the carbonyl group typical of an aldehyde was not present in the polymer. Acrolein was present in the liquid phase in yields in the range of 0.3 % to 0.9 % as determined by GC-FID when the reaction of glycerol and ammonia was conducted over the iron catalyst or operating at the same conditions in an uncatalysed process. However, using alumina as for the iron catalyst, acrolein yields of up to 4 % were obtained. For the uncatalysed reaction, the conversion of glycerol was relatively low (4 – 17 %) which can explain the low acrolein yields, nevertheless that was not the case for the iron catalysed reactions, where conversion was close to 100 %. One possible explanation for this observation is that over the iron catalyst, acrolein is oxidised to acrylic acid, which was detected in low concentrations in liquid samples by GC-MS. In the uncatalysed process and in the reaction catalysed by the alumina support, the organic acid was not detected. When reacting with ammonia, acrylic acid yields acrylamide [28], which can polymerise with aliphatic aldehydes as initiators and/or cross-linking agents [29]. In the current system, acetaldehyde is present and formaldehyde is a

possible product but under reaction conditions is likely to decompose into hydrogen and carbon monoxide [7]. Other authors have reported the chain growth polymerisation of acrylamide without termination in the absence of initiator and in the presence of glycerol [14]. This is in agreement with NMR analyses of the polymeric products from the uncatalysed, Al₂O₃ and Al₂O₃/Fe catalysed reactions of glycerol and ammonia, where unsaturated compounds were significant only when alumina was catalysing the reaction. This coincides with conditions where the highest selectivity in the liquid phase to unsaturated aldehydes (such as acrolein and acetaldehyde) and the formation of phenol (which was not present in any of the other two experiments) was observed. Such observations are based on peaks at approximately 115, 120 and 129 ppm in the ¹³C NMR spectrum of the alumina catalysed polymeric product (Figure S3 of the ESI) as well as peaks at 6.8 ppm and 7.2 in the ¹H NMR spectrum of the same sample (Figure S4 of the ESI). The absence of signals at 176 and 178 ppm in the ¹³C NMR spectra for polymeric products obtained in the absence of the iron catalyst (Figure S3 and Figure S5 of the ESI) suggests that acrylic acid is required for the formation of (CH₂-CH)C=ONHCH(CH₃)₂ groups.

Nitrogen atoms were also identified as part of a chain where NHCOCH₂ and CH₂OC=O groups were present. In the presence of ammonia, cyclic imidates such as 2,4-dimethyl-2-oxazoline-4-methanol were detected in the liquid phase. This species was thought to result from the reaction of an aldehyde (possibly acetaldehyde or acrolein) with an amino alcohol. Even though alkanolamines were not identified through GC-MS analyses of liquid samples, the presence of products such as 2-(aminoxy)propanoic acid were confirmed. Carboxylic acids produced from glycerol over the iron catalyst (acetic, acrylic or propanoic acid) could have also been involved in the formation of the oxazoline [30]. Oxazolines have been reported as nucleophilic monomers that spontaneously polymerise with α,β -unsaturated acids (i.e. electrophilic monomers) through a ring opening mechanism via a zwitterion [13].

Acrylic acid present in the liquid phase as determined by GC-MS, could have reacted with the oxazoline to form a copolymer. This reaction could explain the signals in the ^{13}C NMR spectrum at 117 and 124 ppm as well as the positive result to the bromine test.

The synthesis of polyesters from glycerol has been reported in the presence of a dicarboxylic acid [31, 32] in catalysed or uncatalysed processes through a condensation reaction where water is formed in stoichiometric quantities for every ester unit [33]. Polymer characterisation revealed that not only ester linkages but amide groups were present in the main chain. One of the possible routes for the formation of structures similar to poly(ester amide)s is via oxazolinium, when an aldehyde is present, proceeding also through a ring opening polymerisation [34]. As mentioned previously, oxazolines as well as acrolein and acetaldehyde were detected in the liquid phase.

A detailed study of the kinetics of the polymerisation reaction of glycerol in the presence of ammonia over alumina-supported iron catalysts is very complicated, when taking into account the number of reactions occurring under the current conditions and the influence of some products on the reaction. For amido functionalities, no kinetic data for this reaction is available considering that acrolein formation is a side reaction in the current process. Data collection reacting neat acrolein over the iron catalyst may not provide reliable results since glycerol and aldehydes (required for acrylamide polymerisation) will not be present under these conditions. Similar limitations apply for the formation of unsaturated chains.

4. Conclusions

Potentially valuable polymers are synthesised in a single step gas phase reaction under an inert atmosphere from glycerol and ammonia over an alumina-supported iron catalyst. NMR and FTIR spectroscopy techniques allowed characterisation of the products as a mixture

containing both ester and amide functional groups. Specifically, $\text{CH}_2\text{OC}=\text{O}$, $\text{CHOC}=\text{O}$, CH_2NHCH , $\text{NHC}=\text{OCH}_2$, $\text{CHC}=\text{ONH}$ and $\text{CH}_2=\text{CH}$ type structures were confirmed to be present in the polymeric mixture. A polymerisation mechanism different to glycerol self-condensation was explained by the presence of acrolein and acetaldehyde from glycerol dehydration at 340 °C, their subsequent oxidation yielding carboxylic acids and the interaction of the latter with amino derivatives that starts the polymerisation reaction.

5. Acknowledgements

Gizelle Sanchez and Vaibhav Gaikwad would like to thank the University of Newcastle for their post graduate research scholarships. Funding by African Explosives Ltd. is gratefully acknowledged. Authors thank Mr. Sazal Kundu and Dr Monica Rossignoli for their help with preliminary NMR analyses.

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Figure Captions

Figure 1. DEPTQ 135 NMR spectrum for polymeric product from the reaction of glycerol and ammonia over an alumina-supported iron catalyst. The peak at 78 ppm is attributed to the CDCl_3 solvent.

Figure 2. DEPT 135 NMR spectrum for polymeric product from the reaction of glycerol and ammonia over an alumina-supported iron catalyst. The peak at 78 ppm is attributed to traces of impurities of CHCl_3 in the CDCl_3 solvent.

Figure 3. ^1H NMR spectrum for polymeric product from the reaction of glycerol and ammonia over an alumina-supported iron catalyst.

Figure 4. a. ATR-FTIR spectrum for cross-linked polymeric product from the reaction of glycerol and ammonia over an alumina-supported iron catalyst. b. FTIR spectrum for non cross-linked polymeric product from the reaction of glycerol and ammonia over an alumina-supported iron catalyst.

Figure 5. Probable chain structures of polymeric products present in the soluble fraction.

Figure 6. a. 2,4-dimethyl-2-oxazoline-4-methanol detected in liquid products of the conversion of glycerol in the presence of ammonia. b. Zwitterion proposed as intermediate in the polymerisation of 2-methyl-2-oxazoline and acrylic acid [13].

Figure S1. ^{13}C NMR spectrum from HMQC experiment of polymeric product from the reaction of glycerol and ammonia over an alumina supported iron catalyst.

Figure S2. HMQC NMR spectrum of polymeric product from the reaction of glycerol and ammonia over an alumina supported iron catalyst.

Figure S3. ^{13}C NMR spectrum of polymeric product from the reaction of glycerol and ammonia over an alumina catalyst.

Figure S4. ^1H NMR spectrum of polymeric product from the reaction of glycerol and ammonia over an alumina catalyst.

Figure S5. ^{13}C NMR spectrum of polymeric product from the uncatalysed reaction of glycerol and ammonia.

Table 1. CHN analyses for polymeric product from the reaction of glycerol and ammonia over an alumina-supported iron catalyst.

Element	Concentration (wt %)
N	6.9
C	50.2
H	9.3

Figure 1

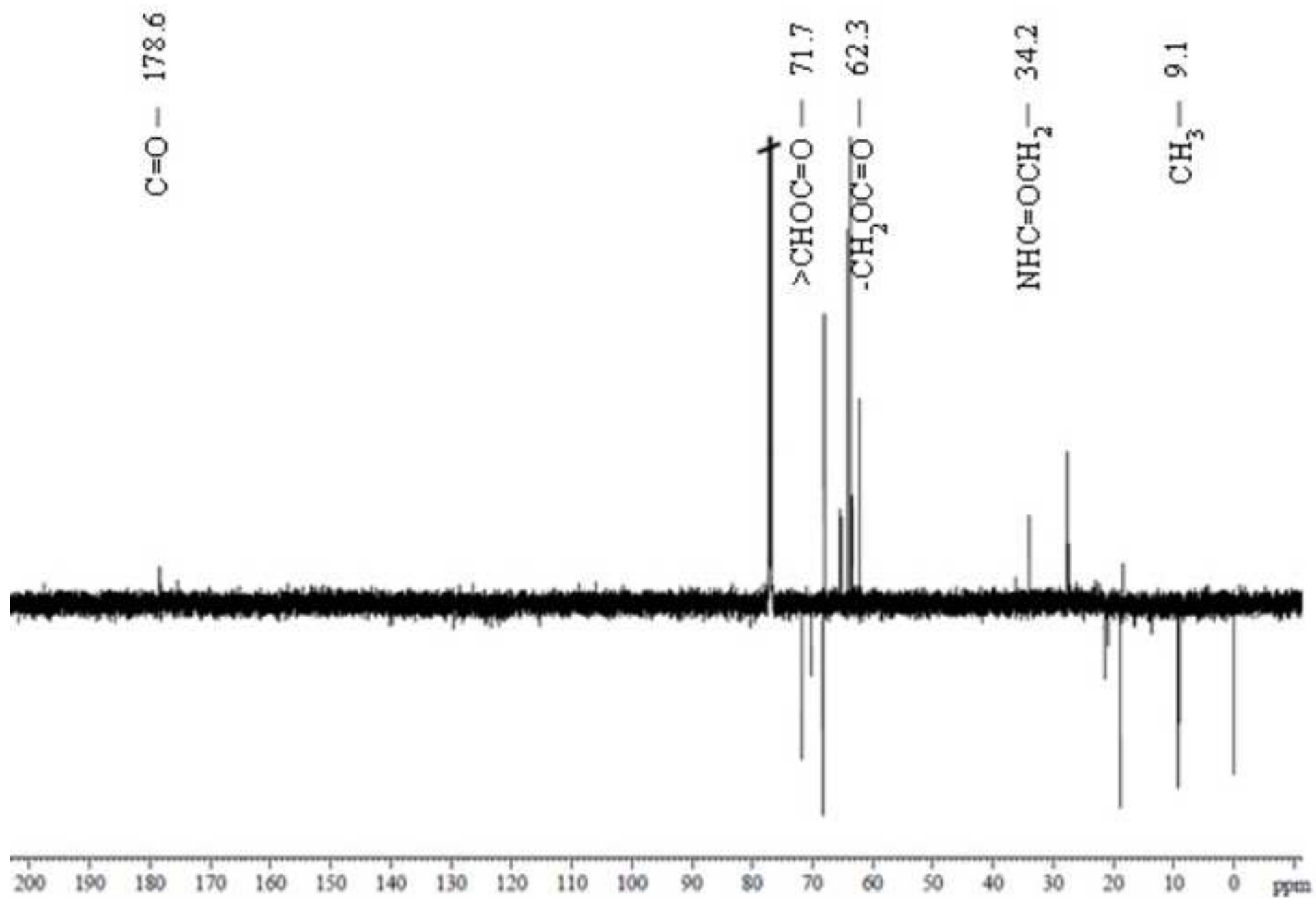


Figure 2

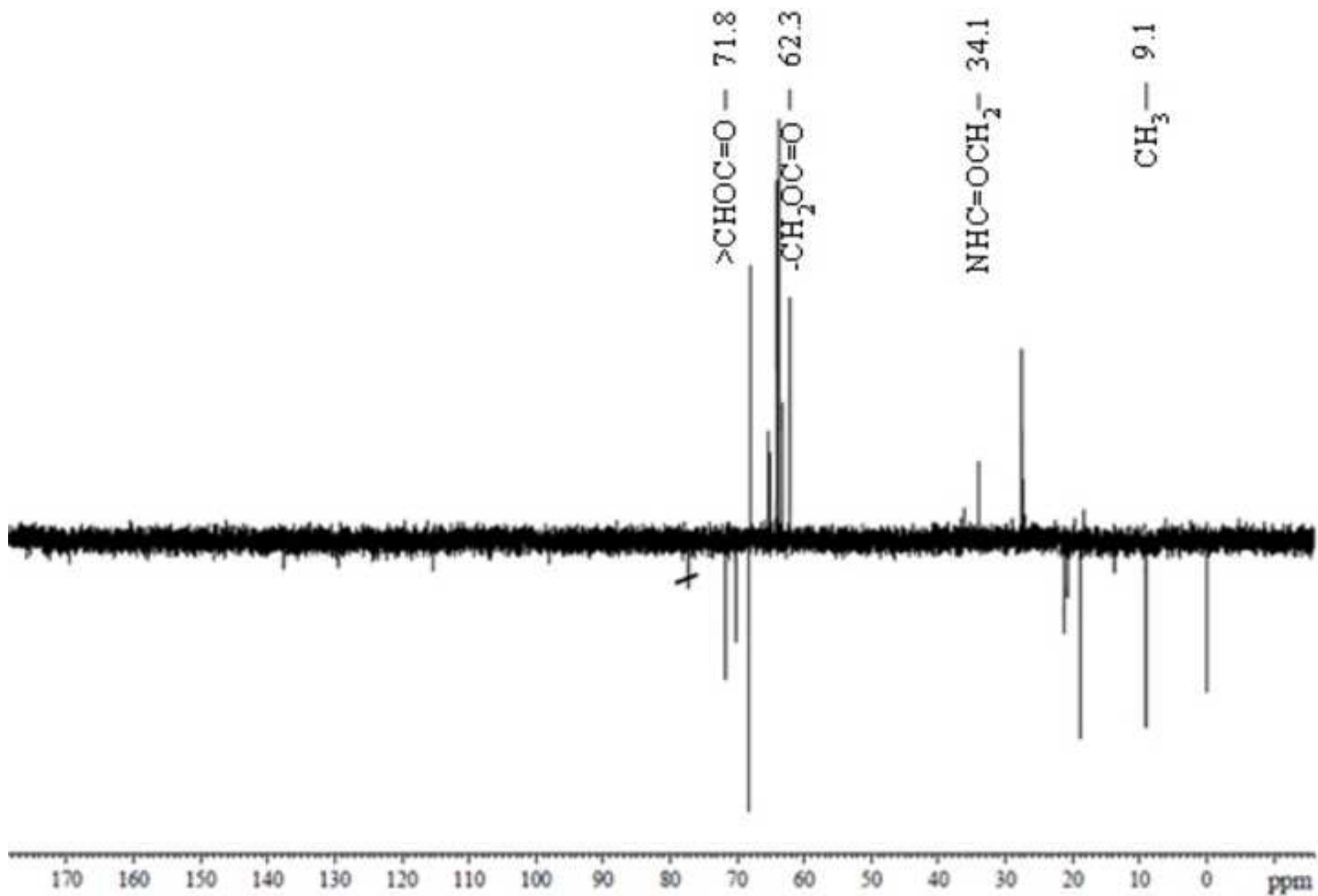
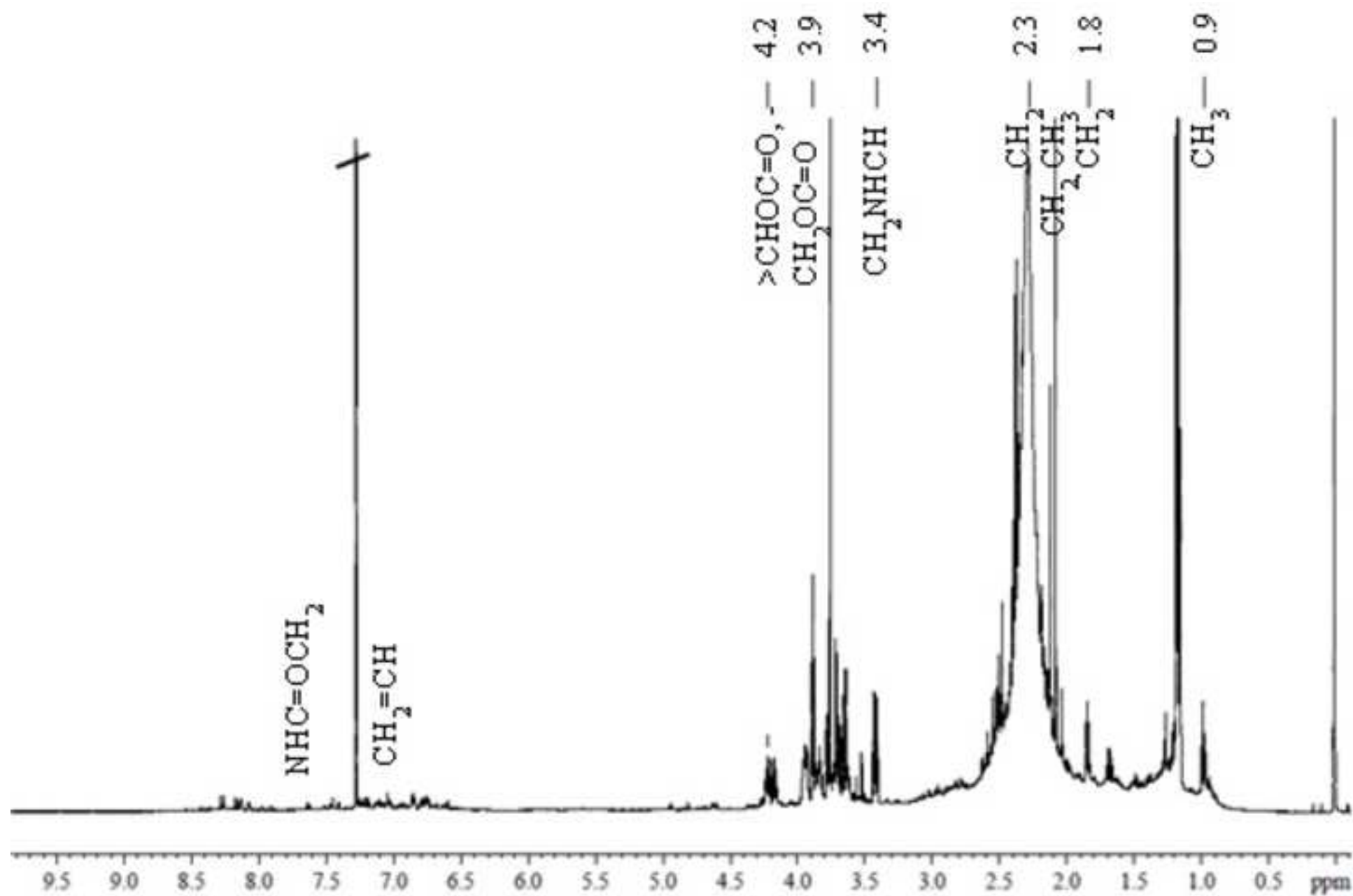


Figure 3



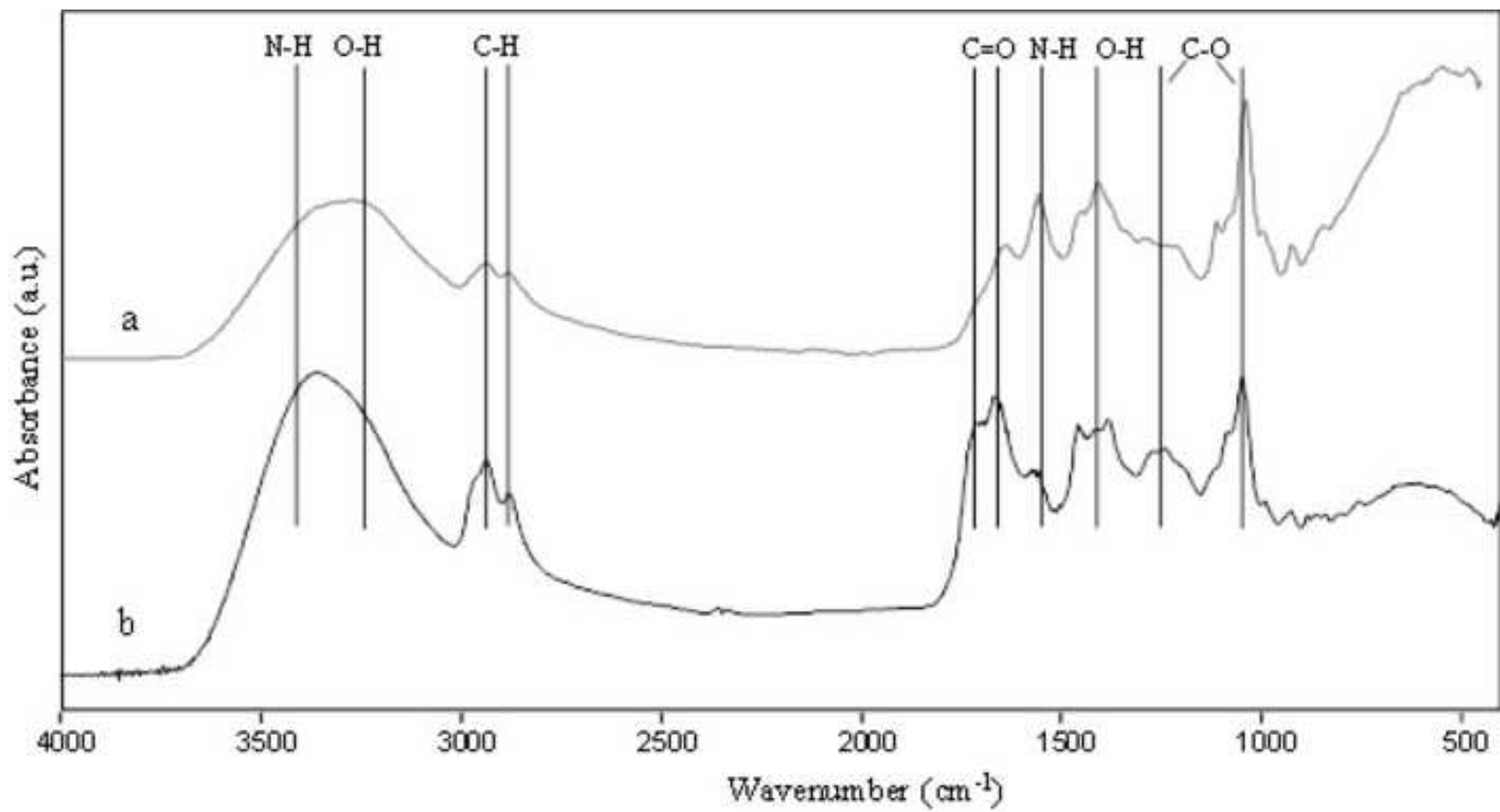
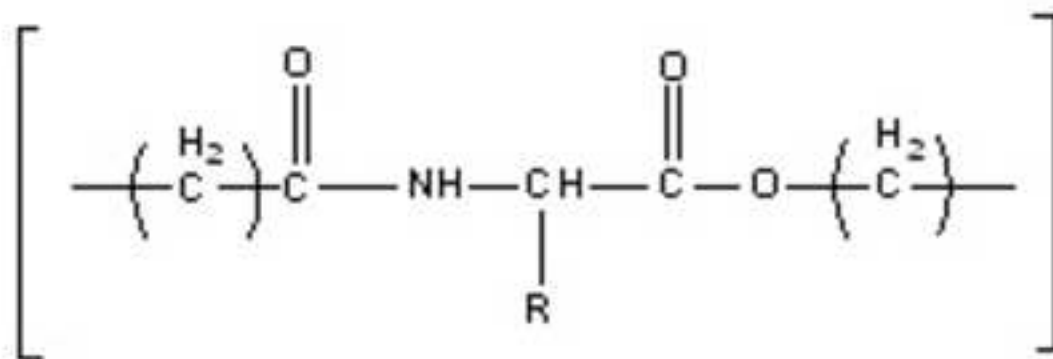
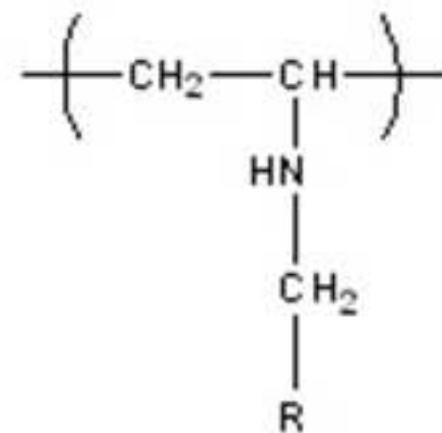
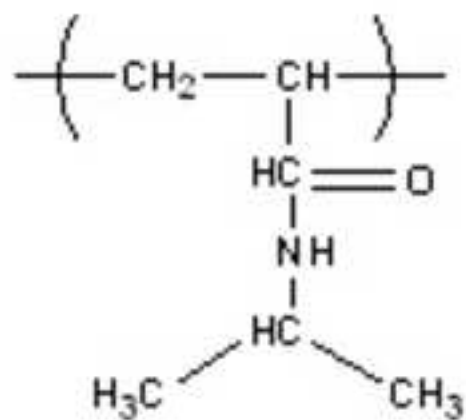
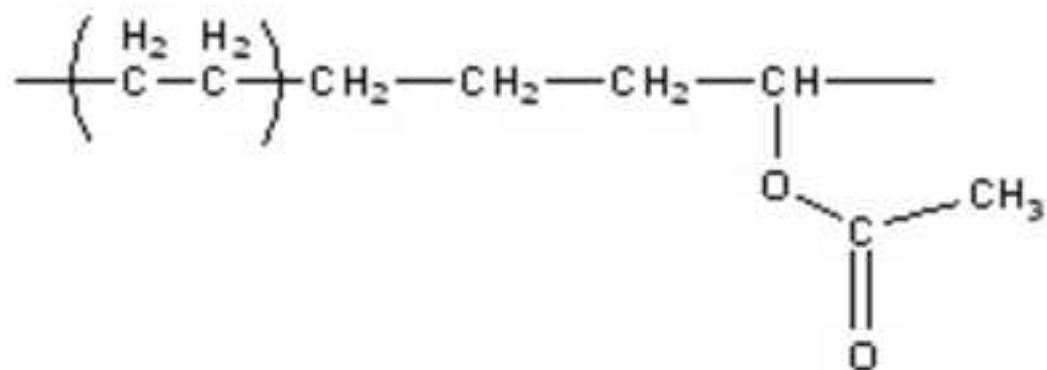
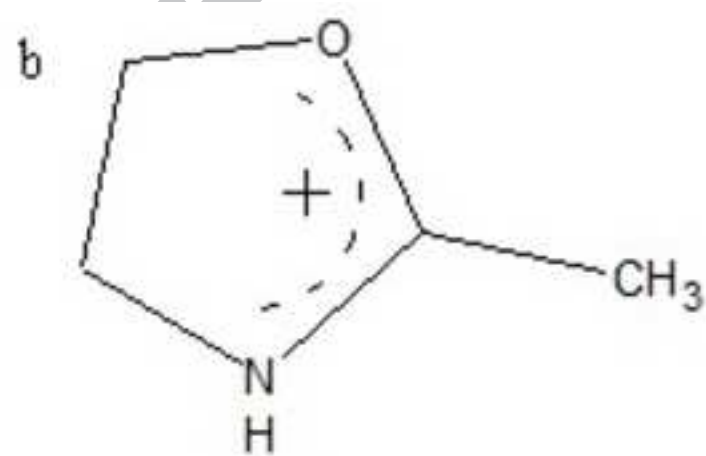
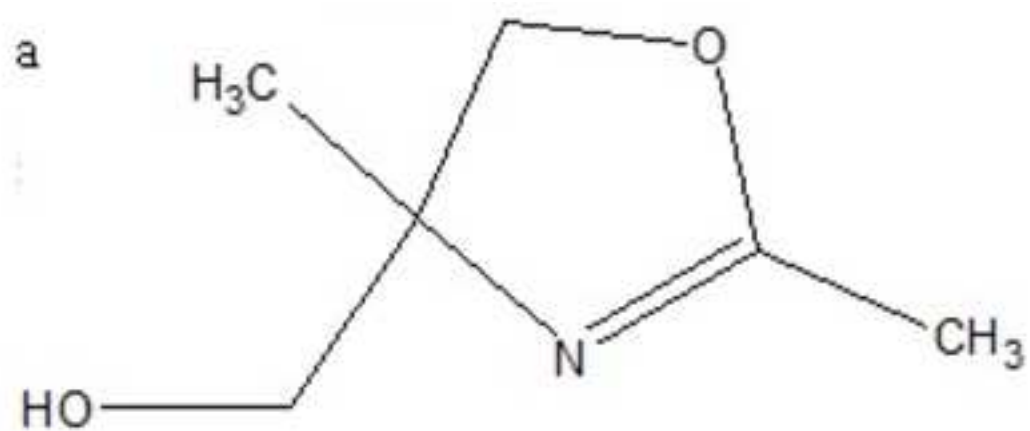
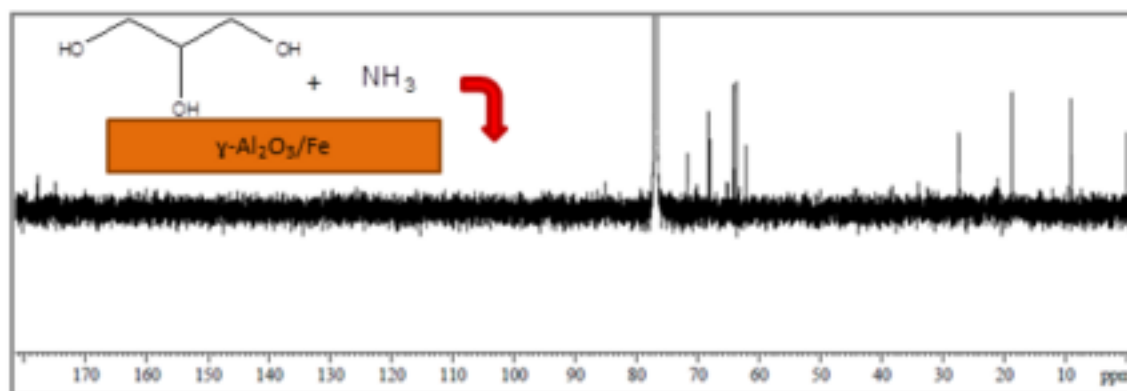


Figure 5







Highlights

- First synthesis of polymers from glycerol and ammonia over an iron catalyst;
- Characterisation revealed unsaturated, amido and ester functionalities;
- Unsaturated, branched and cross-linked structures were present in the polymer;
- Oxidation of glycerol dehydration products is required for the polymerisation.

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