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A novel thermal degradation mechanism of phenol–formaldehyde type resins

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ABSTRACT

The thermal degradation of phenol–formaldehyde resins (PFR) was studied using thermogravimetry analysis (TG) technique. The structural changes of thermal degradation of synthetical and commercial PFR were investigated by Fourier-transform infrared rays (FTIR) and solid-state ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy. The experimental results show that the degradation of PFR can be divided into three stages. Additional cross-links are formed and small exposed groups of the cured resin are removed in the first stage. In the second stage, methylene bridges decompose into methyl groups then both phenol and cresol homolog appear. The degradation of phenol group occurs in the third stage. According to these results, a novel degradation mechanism of phenol–formaldehyde type resins is proposed: the mainly degradation process of PFR is the decomposition reaction of methylene bridges in this mechanism instead of auto-oxidation of the methylene bridges in the prevenient mechanism.

1. Introduction

During the past three decades, many efforts have been made to study the main thermal degradation behavior of phenol–formaldehyde resins (PFR) in relation to their structure [1–14]. Three typical mechanisms of PFR thermal degraded under inert gases are concluded as follows.

Ouchi and Hond [11] proposes a mechanism of degradation consisting of three stages. In the first stage, additional cross-links are formed as a result of two condensation reactions between functional groups of the cured PFR. One reaction involves the two phenol groups and results in an ether cross-link. The second condensation reaction involves a phenol group and a methylene group forms a carbon–hydrogen cross-link. In the second reaction stage, cross-links are broken, and the evolution of methane, hydrogen and carbon monoxide occurs. In the third stage, hydrogen atoms are removed from the ring structure and hydrogen gas is evolved. Jackson and coworkers [12] proposed a mechanism oxidation degradation. Although degradation occurs in inert environment, the decomposition products provide a source of oxygen. The oxidation reaction results in the formation of a carbonyl cross-link. Jackson specifically disputes with the formation of an ether link as described by Ouchi. Parker and Winkler [13] proposed a mechanism involving the formation of thermal cross-linked intermediate structure with the elimination of pendant aromatic rings and retention of all aromatic carbons that are multiple-bonded in the initial polymer structure. The mechanism predicts the evolution of phenol and cresol from the scission of the pendant aromatic rings. The mechanism cannot explain the evolutions of water until the final stage of degradation.

Although these mechanisms are incomplete or contradictious to one another, some details of thermal degradation of PFR under inert atmosphere can be still identified with them. For example (1): above 350 °C, the evolution of water and unreacted oligomers can be observed. The evolution of water has been attributed to the condensation reaction between residual methylol groups and phenolic OH···OH groups [3]. The starting temperature of this reaction depends on the nature of the PFR, such as number of residual methylol groups, dimethylene ether. (2): At 500 °C, carbonyl groups can be detected in the resin although the degradation was taking place in an inert atmosphere. The polymer itself can be thought to contribute to the oxidation through producing either OH radicals or water, which may act as an oxidizing agent, leading to the formation of oxidized exposed groups such as aldehydes and carboxylic acids, followed by the evolution of CO_2 [14]. (3): Up to 500 °C, the polymer network remains essentially intact, whereas above 500 °C dramatic changes are noticed in the FTIR spectra of PFR due to the collapse of the network to form polyaromatic domains [14].

Thus it can be concluded that a process of auto-oxidation of the methylene bridges during the thermal degradation of cured PFR, of which the structure is primarily cross-linked by methylene bridge units. And these conclusions are mainly based on the FTIR experiments. Although relatively much information is available for thermal degradation using FTIR technique, while the peaks of var-

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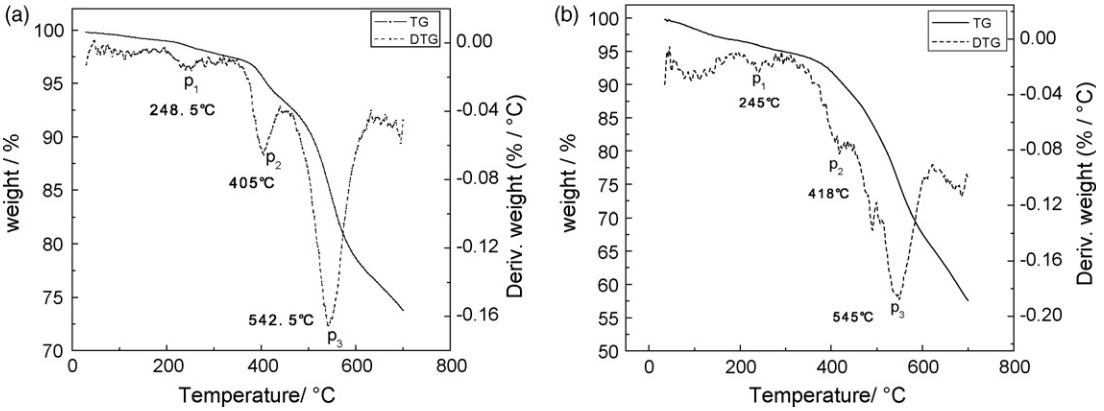


Fig. 1. TG and DTG curves: *Note*: (a) synthetical resin and (b) commercial resin, heating rate 10 °C/min under nitrogen flow.

ious organic components in the FTIR spectra always overlap with one another and the quantitative analysis of them is very difficult. The solid-state nuclear magnetic resonance (^{13}C NMR) technique is adapted to quantitative analysis and has excellent precision. However, there are no reports using solid-state ^{13}C NMR technique to study the degradation of PFR. Therefore, besides using FTIR, we also used ^{13}C NMR technique to study the degradation of PFR.

2. Experimental

2.1. Materials

Two resol-type resins with different moral ratios were used: phenol–formaldehyde molar ratios are 1.2 (PFS) and 1.5 (PFC). These were either laboratory samples (PFS) which was synthesized with ammonia as catalyst by ourselves or commercially available PFR$_{2130}$ (PFC) which was synthesized by using catalyst sodium carbonate.

2.2. Methods

Two fresh resins were put in an oven and cured stepwise at 90 °C for 2 h, then at 140 °C for 4 h, and at 170 °C for 1 h in the end. Thermogravimetry analysis of cured samples (about 10 mg) was investigated by the NETZSCH STA449C thermal analyzer with alumina sample holder, at a heating rate of 10 °C/min to 700 °C under nitrogen. Cured resins were heat-treated to 300, 450 and 600 °C under inert atmosphere, then the residues heat treated under different temperatures were characterized using FTIR and solid-state ^{13}C NMR technique. The term of the solid residue after pyrolysis to 700 °C is used to compare their thermal stability.

Solid-state ^{13}C NMR spectra (CP/MAS) were obtained with a Varian Infinity plus 300WB spectrometer. Samples (ground to be fine powder) were placed in a boron nitride sample holder. Contact time was 1.100 min, phase resolution $\leq$0.25°, frequency resolution $\leq$0.1, acquisition speed $\geq$8 MHz and spin rate was 3 kHz.

FTIR absorption spectra were recorded with a WQF-410 spectrometer and acquisition conditions were spectral with a width of 4000–400 cm^{-1}, 32 accumulations, and 4 cm^{-1} resolution. All the pellet samples were prepared with mixing KBr.

3. Results and discussion

3.1. Thermogravimetry analysis

The thermogravimetry (TG) curves along with the derivative thermogravimetry (DTG) curves of two resins are shown in Fig. 1a and b (PFS) and (PFC), respectively.

Their DTG curves consist of three overlapped peaks which are marked with P$_1$, P$_2$ and P$_3$. According to the three peaks of DTG curves, the degradation process of the PFR can be divided into three stages. However, there are some differences in an amount of solid residue after pyrolysis. After being heated to 700 °C, the PFS leaves

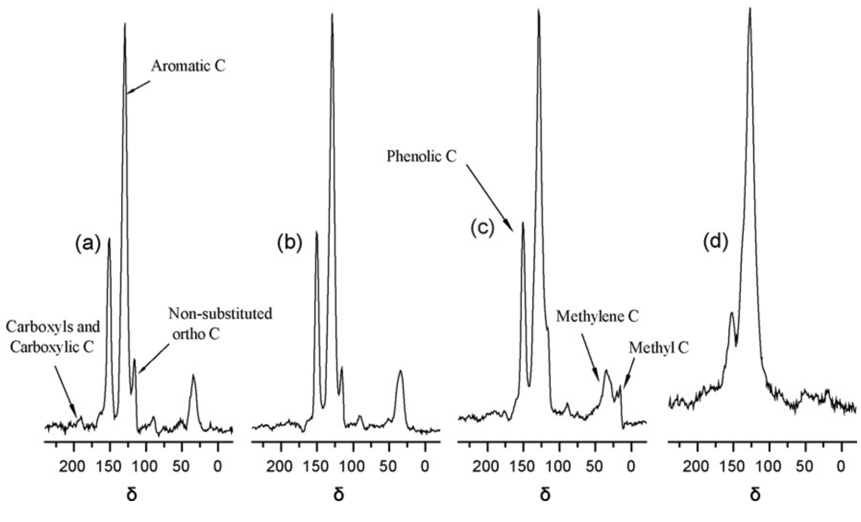
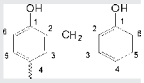


Fig. 2. ^{13}C NMR spectra of PFS: (a) cured, (b) 300 °C, (c) 450 °C and (d) 600 °C.

Table 1
CP/MAS ^{13}C NMR chemical shifts of resin [15,16]

Resin	Carbon chemical shifts δ								
	C=O, COOH	C_1	C_2, C_3, C_4, C_5	C_6	$H_2C–O–CH_2$	CH_2OH	CH_2	CH_3	Note
PFS	190	151	129	116	–	–	35	20, 16	
PFC	190	150	129	116	74	65	35	20, 16	

large amount of residue (74%), while the PFC leaves less residue (57%). Three peaks in the DTG curves correspond to three kinds of degradation reactions. Therefore two resins were heat-treated separately to 300, 450 and 600 °C which correspond to the peaks P_1, P_2 and P_3, respectively. The cured resins (170 °C) and the residues heat-treated to different temperatures were analyzed with ^{13}C NMR and FTIR.

3.2. Solid-state ^{13}C NMR spectra analysis

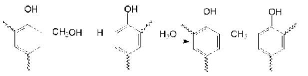
3.2.1. Solid-state ^{13}C NMR spectra analysis of PFS

The ^{13}C NMR spectra of PFS residues heat treated to 300, 450 and 600 °C are shown in Fig. 2(b), (c) and (d), respectively, when compared with the spectrum of cured resin (Fig. 2a).

Following recognized peaks identification of ^{13}C NMR spectra of organic compounds, the functional groups correspond to the major peaks of the spectra have been identified as listed in Table 1.

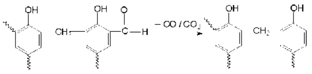
The broad band around δ160–150 is a characteristic of all C_1 carbons bearing a hydroxyl group in the aromatic. The band around δ140–120 contain the simultaneous resonance of aromatic *meta*-carbons (C_3, C_5), *ortho*-(C_2) and *para*-substituted aromatic carbons (C_4) and non-substituted *para*-aromatic carbons (C_4), while the shoulder around δ120–110 is a characteristic of non-substituted aromatic *ortho*-carbons (C_6). The weak band at δ90 indicates the presence of polyoxymethylene chains. The band at δ75 is attributable to dimethylene ether bridges ($–CH_2–O–CH_2$) and the band at δ65 is attributable to hydroxymethyl groups ($–CH_2OH$). The broad band around δ45–25 is a characteristic of methylene bridges ($–CH_2–$), and the band around δ20–15 is attributable to methyl ($–CH_3$) groups.

Fig. 2(a) shows that cured resin has a high number of non-substituted *ortho*-sites, few residual hydroxymethyl groups and a high proportion of methylene links. Resin heat treated to 300 °C has fewer free *ortho*-carbons. It can be explained by additional condensation reaction:



(1)

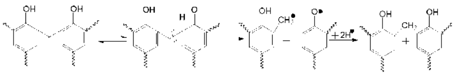
Aldehyde carbonyl C=O groups decreases in intensity can be explained by reaction:



(2)

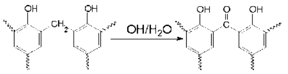
These reactions result in the peak (P_1) in Fig. 1(a). Methylene and other groups almost keep unchanged at this temperature.

When the sample heat-treated at 450 °C, methylene bridges decompose into methyl groups like reaction:



(3)

then both phenol and cresol homolog appears. The new peak appears at δ20 is characterized as chemical shift of methyl groups' carbon atom. But there still reserve quantity of methylene bridges in the residue. It indicated that the PFS resin has a good thermal property, which has been proved in Section 3.1. Even heat-treated to 450 °C, the intensity of C_1 bands at δ150 (corresponding to phenol) does not decrease. These phenomena show that the degradation temperature of phenolic OH groups is higher than that of the methylene groups. And the other groups such as aldehyde and hydroxymethyl which contained oxygen were stripped in the first degradation stage. Being shortage of OH radicals or water, which may act as an oxidizing agent, the oxidation reaction:



(4)

described in the prevenient mechanism is difficult to occur. The carbonyl band (C=O, the produces of oxidation) scarcely be found in these ^{13}C NMR spectra (C=O absorption peak at δ190). Therefore, a new mechanism was tentatively put forward: the degradation of methylene bridges was a decomposition reaction (3) instead of an auto-oxidation reaction (4).

When heat-treated to 600 °C, the residue has few residual hydroxyl-substituted in phenol ring (δ151). This phenomenon shows that the degradation of phenol group occurred in the third stage.

3.2.2. Solid-state ^{13}C NMR spectra analysis of PFC

The ^{13}C NMR CP/MAS spectra of PFC residues heat treated to 300, 450 and 600 °C are shown in Fig. 3(b), (c) and (d), respectively, when compared with the spectrum of cured resin (Fig. 3a).

The spectra changes in the residues of commercial resin are similar to those already described for the residues of synthetic resin. However, the band at δ20 appeared in the residue heat treated to 300 °C (Fig. 3b). This change indicates that methylene bridges decomposed in a lower temperature. When heat-treated to 450 °C, the changes around δ20–40 of the PFC are acute comparing with the PFS. It indicates that the thermal stability of commercial resin is worse than synthetic resin. Therefore, its carbon yield was also lower than synthetic resin as described in Section 3.1. The intensity of C_1 bands at δ150 (corresponding to phenol) still keeps fixedness. The carboxyl bands still scarcely be found in all residues spectra of PFC heat treated to different temperatures. These results also indicate that auto-oxidation of the methylene bridges does not represent an important reaction pathway in the pyrolysis of PFC. These evidences uniformly prove that the main degradation of PFR is that: methylene bridges, the main cross-link structure of PFR, are directly broken into methyl groups.

3.3. FTIR analysis

3.3.1. FTIR analysis of PFS

The FTIR spectra of PFS residues heat treated to 300, 450 and 600 °C are shown in Fig. 4(b), (c) and (d), respectively, when compared with the spectrum of cured resin (Fig. 4a).

Following recognized peaks identification of infrared spectrum of organic compounds, functional groups correspond to the major peaks of the spectra have been identified as listed in Table 2.

It can be noticed that the peak appearing at 1650 cm^{-1}, ascribing to carbonyl C=O groups as a weak shoulder on the 1600 cm^{-1},

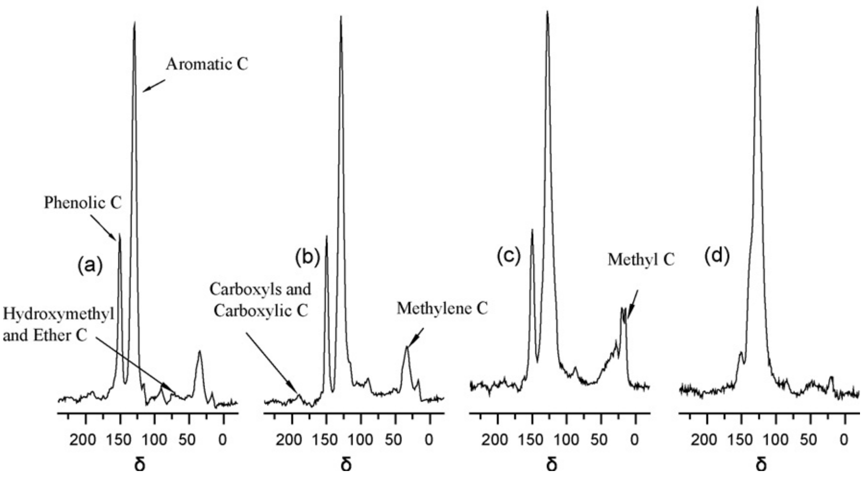


Fig. 3. ^{13}C NMR spectra of PFC: (a) cured, (b) 300 °C, (c) 450 °C and (d) 600 °C.

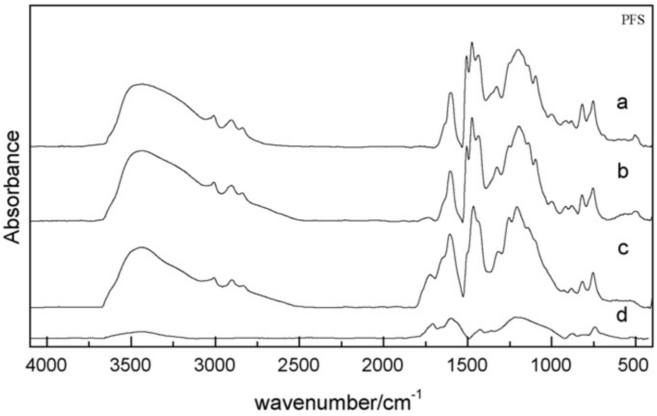


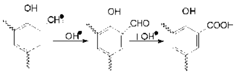
Fig. 4. FTIR spectra of PFS: (a) cured, (b) 300 °C, (c) 450 °C and (d) 600 °C.

becomes weaker when the temperature increases to 300 °C. This change can be explained by the reaction (2) as mentioned in Section 3.2.1. Together with the condensation reaction (1), the intensity of aliphatic CH_2 (asymmetric bending, 1480–1450 cm^{-1}) has a little enhancement compared with the original resin (Fig. 4a). All these changes result in the peak (P_1) in Fig. 1(a).

Table 2
Infrared bands and assignments for PF resin [7,17,18]

Wavenumbers (cm^{-1})	Assignments
3300	Phenolic O–H stretch
3300–3100	Aromatic C–H stretch
2950–2800	Aliphatic C–H stretch
1740	Tetra-substitute benzene ring C–C stretch
1680–1650	Carbonyl C=O stretch
1610, 1590, 1514	Aromatic C–C stretch
1480–1450	CH_2 deformation
1437	Aliphatic CH_3 asymmetric bending
1360, 1340	Phenolic O–H in-plane deformation
1260	Biphenyl ether C–O stretch
1220, 1160	Alkyl-phenolic C–O stretch
1060	Dimethylene ether C–O deformation
1010	Hydroxymethyl C–O deformation
890–690	Out-of-plane substituted rings C–H deformation

When the resin heat treated to 450 °C (Fig. 4c), two weak peaks appearing at 1650 cm^{-1} and at 1740 cm^{-1} were found in this spectrum. They are assigned as carbonyl (1650 cm^{-1}) and carboxylic (1740 cm^{-1}) in the literature [3,14], which were produced by oxidized reaction. Thus it was concluded that a process of auto-oxidation of the methylene bridges occurred in the thermal degradation of cured PFR as described as reaction (4). While carboxyl and carboxylic mean the same group (COOH). More, it is a mistake to assign the 1740 cm^{-1} as C=O of carboxylic acids, the 1740 cm^{-1} should be assigned as tetra-substituted benzene ring according to Ref. [9]. Furthermore, the peak of carbonyl at 1650 cm^{-1} is appeared as a shoulder peak on the 1600 cm^{-1}, the intensity of the groups is very low. Thus, according to the FTIR results, the oxidation reaction (4) described in the prevenient mechanism is difficult to occur. Combined with the ^{13}C NMR spectra analysis we infer that the little carbonyl peak is produced by reaction:



(5)

instead of reaction (4). The reaction (5) occurred subsequently the methylene decomposition reaction (3). Although aliphatic CH_3 is obtained by rupturing the methylene bridges CH_2 as the reaction (3), the peak at 1437 cm^{-1}, ascribing to its asymmetric bending, is hidden by the methylene bridges (CH_2, 1450–1480 cm^{-1}) peak in this spectrum.When the temperature is to 600 °C, the phenolic O–H intensity decreases sharply and all other functional groups of PFR disappear in the spectrum (Fig. 4d). These changes illustrate that the structure of resin is destroyed. Dehydrogenation and carbonization reactions are occurred in this stage.

3.3.2. *FTIR analysis of PFC*

The FTIR spectra of PFC residues heat treated to 300, 450 and 600 °C are shown in Fig. 5(b), (c) and (d), respectively, when compared with the spectrum of cured resin (Fig. 5).

It can be noticed that all functional groups and their intensity changes in this instance are similar to PFS (Fig. 4). The intense OH stretching band is obviously split into a broad peak reveals that there are two different types of OH group: phenolic and alcoholic. When the temperature increase to 300 °C, evidence can be found that the OH stretching band at 3350 cm^{-1} shifts toward higher wavenumbers. The alcoholic OH group is decomposed or oxide to

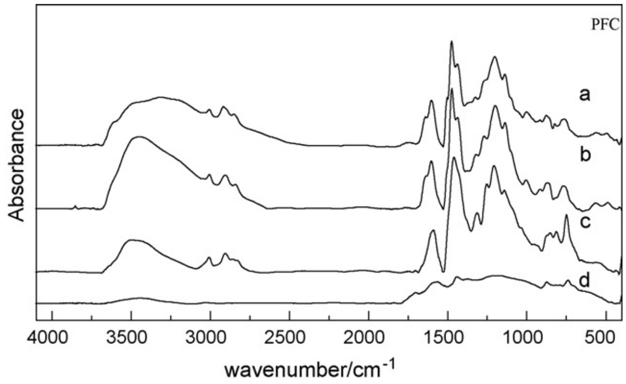
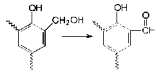


Fig. 5. FTIR spectra of PFC: (a) cured, (b) 300 °C, (c) 450 °C and (d) 600 °C.

carbonyl C=O groups (aldehyde) as reaction:



(6)

in low temperature. The peak appears at 1650 cm^{-1} as a shoulder peak on the 1600 cm^{-1} was characterized as aldehyde C=O groups (Fig. 5b).When being heated to 450 °C, the intensity of CH_2 bridges at 1450–1480 cm^{-1} decrease sharply, while the intensity of aliphatic CH_3 at 1437 cm^{-1} increases at the same time. But the CH_3 absorption peak is still hidden or overlapped by the aliphatic CH_2 absorbance peak in this instance. This change shows that the thermal stability of the commercial resin is lower than synthetic resin. Phenol and cresol homolog yield and removed from the resin's body when methylene bridges are decomposed. Therefore, the char yield of PFC was lower (Fig. 1b) than synthetic resin.

The OH bands at 3350 and 1360 cm^{-1} decrease obviously after heat-treated to 600 °C. This change also indicates that the phenolic OH degradation occurred subsequently upon the methylene bridge's decomposition. Above this temperature, all the bands become more complex; the main structure of the polymer is changing to form a polyaromatic structure.

All these evidences show that the degradation of PFR is the CH_2 break into CH_3 showed as reaction (3), but not auto-oxidation of the methylene bridges showed as reaction (4). In another word, auto-oxidation is not considered as an important reaction pathway in the degradation of resin. While the peak of aliphatic CH_3 is always hidden or overlapped by the peak of CH_2 in all instances in FTIR spectra, the degradation had better analyzed combined with solid-state ^{13}C NMR, in which spectrum the peaks of CH_2 and CH_3 can be obviously separated.

4. Conclusions

1. The thermal behavior is similar for both the synthetic and commercial resin. The DTG curves consist of three overlapped peaks. However, there are some differences in the stability of two resin. The PFS sample is more stable, leaving the higher amount of residue (74%), the PFC is worse stable with the less residue (57%) after heated to 700 °C under N_2 atmosphere.
2. The degradation of PFR can be divided into three stages. Small terminal groups of the cured resin are removed and additional cross-links are formed as a result of condensation reactions in the first stage. In the second degradation stage, the methylene bridges are decomposed into methyl groups then yield both phenol and cresol homologe. The degradation of phenol groups occurred in the third stage.
3. Although the peak of aliphatic CH_3 appears during resin's degradation, its absorption peak was hidden or overlapped by the aliphatic CH_2 absorbance peak in the FTIR spectra. The^{13}C NMR investigations obviously show that the oxidation only can occur subsequently the methylene decomposition. The ^{13}C NMR results were consistent with FTIR investigations and more distinctly show that the main degradation of PFR was decomposed instead of auto-oxidation of the methylene bridges.

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