

Pyrolysis GC-MS of Chlorinated Natural Rubber

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ABSTRACT: High-resolution pyrolysis gas chromatography-mass spectrometry (HRPyGC-MS) and Fourier transform infrared spectrometry (FTIR) were used to study the structures of the chlorinated natural rubbers (CNR) prepared by two different processes. The results indicate that the fine structures of CNR prepared from "latex" and "solution" processes are different, whereas their basic structures are similar. The molecule of CNR from the "latex" process contains a few carboxyl and carbonyl groups. The

rings on CNR molecular chains should be hexatomic rings. The optimum pyrolytic temperature for CNR is 445°C, with an available range from 386 to 590°C. The characteristic pyrolytic products are cyclohexane homologues. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 199–204, 2003

Key words: chlorinated natural rubber; structure; FTIR; pyrolysis; GC-MS

INTRODUCTION

Chlorinated natural rubber (CNR), which is prepared by the chlorinated modification of natural rubber (NR) from solution or latex,¹ has properties such as excellent filming-forming ability, adhesiveness, weatherability, abrasive resistance, quick-drying ability, anti-penetrability, corrosion resistance, flame retardancy, good insulation ability, and thermal stability. As a consequence, CNR has been widely used in the production of the raw materials for paints, coatings, adhesives, and ink, etc., and has become one of the most important industrial derivatives of natural rubber. There are mainly two kinds of methods for the production of CNR. In the traditional solution process, chlorination is carried out by passing chlorine gas into the rubber, which is first dissolved in CCl₄. In contrast, in the new latex process, the stabilized natural rubber latex is chlorinated directly with chlorine gas. The studies and applications of CNR can be traced back to the early nineteenth century. But up to the present, no final conclusion has yet been reached on the molecular structure of CNR, which has been one of the focuses in rubber researches over the years. Although a great amount of research work has been done in this field, there are still no reports of pyrolysis gas chromatography-mass spectrometry studies of CNR yet. In this paper, the structures of CNRs prepared by the two different processes just mentioned were studied by using high-resolution pyrolysis gas chromatography-

mass spectrometry (HRPyGC-MS) and Fourier transform infrared spectroscopy (FTIR).

EXPERIMENTAL

Samples

South China Tropical Agricultural Product Processing Research Institute prepared CNR A, a kind of CNR with chlorine content of 64 wt %, by the latex process.

Guangzhou Chemical Industrial Factory of China supplied CNR B, a kind of CNR made by the solution process with a chlorine content of 64 wt %.

Purification of samples

The CNR samples were purified by dissolving them in benzene or toluene, and removing the impurities and insoluble residues by separation. Next, CNR was precipitated from the solution with methanol and dried in a vacuum at 60°C.

FTIR analysis

FTIR analysis was carried out with a Perkin-Elmer Spectrum-GX1 infrared spectrometer. The FTIR spectra were recorded in the wave number range 4000–400 cm⁻¹, and a total of 5 scans was accumulated at 4 cm⁻¹ resolution.

HRPyGC-MS analysis

The HRPyGC-MS experiments were carried out with a JHP-3S Curie point pyrolyzer (Japan Analytical Industry Company) coupled to a HP6890 gas chromato-

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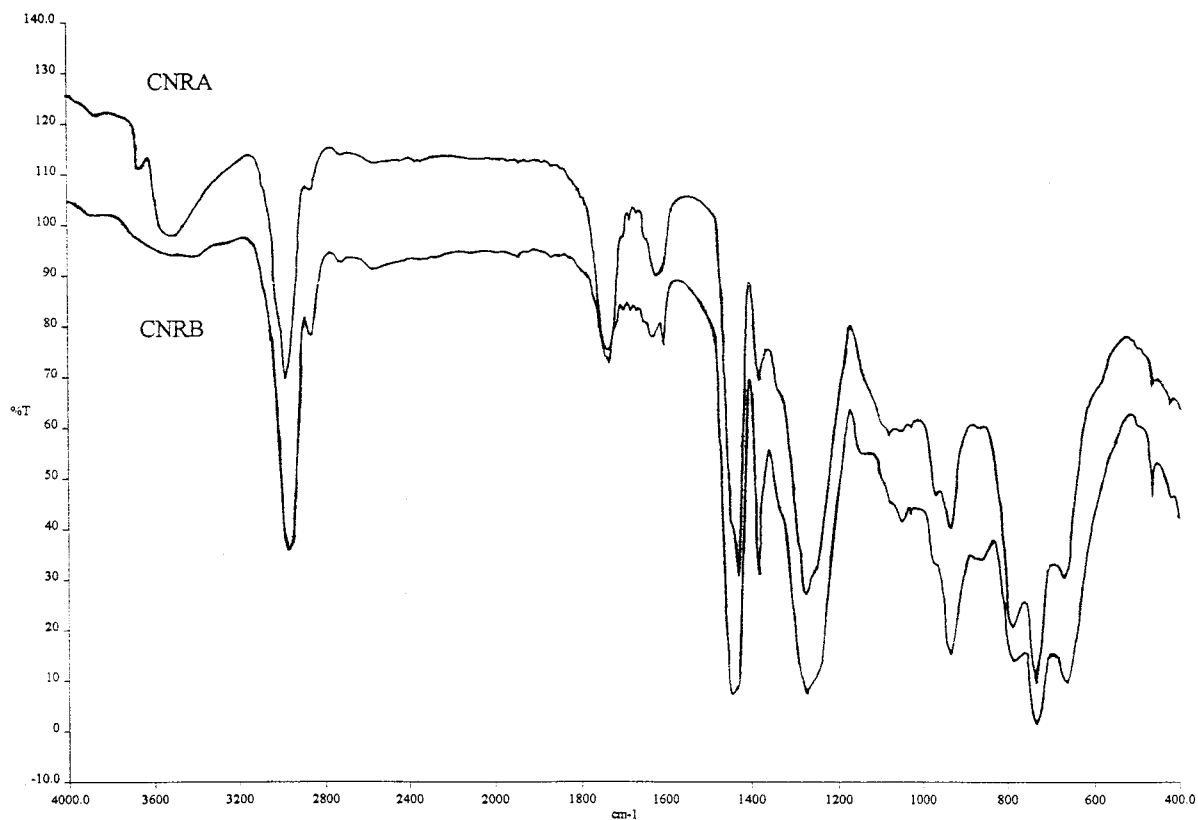


Figure 1 FTIR spectra of CNRA and CNR B

graph linked to a 5973 quadrupole mass spectrometer. Each sample (0.20–0.30 mg) was wrapped in a pyrofoil container ($8 \times 23 \times 0.05$ mm) in a manner ensuring good contact between the sample and the foil. The pyrofoil container was loaded into a quartz pyrolysis chamber (40×4 mm i.d.) maintained at 250°C and

then it was heated inductively for 5 s under conditions that generated sample temperatures of 315 , 386 , 445 , 590 , and 764°C . Pyrolysis was accomplished with a carrier gas of nitrogen in high purity at a flow rate of 50 mL/min. The GC column was a HP-5 fused silica capillary column (30 m \times 0.25 mm i.d.). The GC

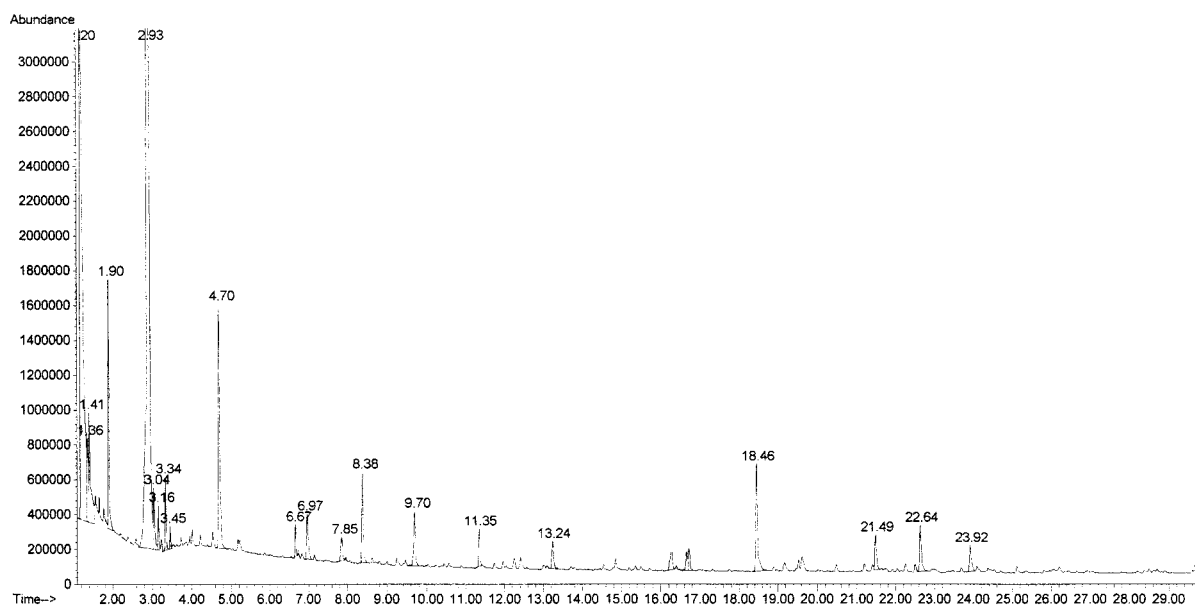
















Figure 2 HRPyGC-MS spectra of CNR B at 590°C

TABLE I
The Main Fragment Peaks of CNRB and Their Relative Amount of Area (%)

Retention Time (min)	Compound	Structure	<i>m/z</i>	Relative Amount, (area %)
1.41	CH ₂ Cl ₂	CH ₂ Cl ₂	85	5.5
1.66	CHCl ₃	CHCl ₃	119.5	1.4
1.90	Benzene		78	7.2
2.93	Toluene		92	100.0
3.04–3.86	DiMe-Cyclohexane		112	5.0
3.23	1-Et-2-Me-Cyclopentane		112	0.4
3.34	Octane	CH ₃ (CH ₂) ₆ CH ₃	114	2.2
3.95	Et-Cyclohexane		112	0.7
4.01	1,1,3-TriMe-Cyclohexane		126	1.1
4.54	Et-Benzene		106	1.2
4.70–5.23	Xylene		106	10.9
4.22	Cl-Benzene		112.5	1.0
6.67–6.83	Cl-Toluene		126.5	1.6
6.96–7.96	Et-Me-Benzene		120	4.4
8.39	Cl-Benzyl		126.5	3.9
9.70	Cl-Xylene		140.5	2.5
11.35	ClMe-Toluene		140.5	1.8
13.24–18.46	DiCl-Benzene and homologues			9.4
21.49–25.12	TriCl-Benzene and homologues			5.2
9.25–15.36	Indane and homologues			1.4
16.27–22.26	Biphenyl, Naphthalene, Fluorene and homologues			9.5

column temperature initially was held at 50°C for 2 min, then was programmed to 280° C at 5 °C/min and held for 30 min. The GC/MS interface was set at 230°C. Mass spectra were recorded under electron impact ionization energy at 70 eV, and the total flow was split at ratio of 50 to 1.

RESULTS AND DISCUSSION

FTIR analysis of CNR

The FTIR spectra of CNR A and CNR B are shown in Figure 1. It can be seen that the wave numbers of IR absorption peaks for CNR A and CNR B are similar

except for the difference in the absorption intensities, indicating that the basic structures of CNR prepared by the two processes are similar, but their fine structures are different. The absorption peaks for both CNR A and CNR B at $930\text{--}670\text{ cm}^{-1}$, which are attributed to the stretching vibrations of the C—Cl bond, are similar in wave numbers and intensities, indicating that the configurations and conformations of C—Cl bonds and chlorine contents are similar. By taking the relative intensity of the C—Cl peak as a reference, the absorption peaks at other wave numbers can be compared. The strong absorption peaks for CNR A and CNR B at 1275 cm^{-1} , which is attributed to the wagging vibration of ClC—H, also have similar intensities. The absorption intensity for CNR A at 1380 cm^{-1} , which is attributed to the symmetric wagging vibration of C—H in $\text{CH}_3\text{—}$, is weaker than that for CNR B, demonstrating that the content of $\text{CH}_3\text{—}$ in CNR A is less than that in CNR B. The absorption that is attributed to the asymmetric wagging vibration of C—H is shifted from 1470 to $1430\text{--}1440\text{ cm}^{-1}$ because of the Cl^- adjacent to C—H, and the intensities for both CNR A and CNR B are similar. From the spectrum of CNR B, it can be seen there is a weak absorption peak at 1733 cm^{-1} but no absorption peak at 3500 cm^{-1} , indicating there are a few carboxyl groups on CNR B molecular chain. The appearance of a strong absorption peak at 1742 cm^{-1} together with the absorption peak at $\sim 3500\text{ cm}^{-1}$ indicates there are certain numbers of carboxyl and carbonyl groups on the molecular chain of CNR A that are much higher than those on CNR B. The strong absorption peak at $2800\text{--}3000\text{ cm}^{-1}$ is due to the stretching vibration of saturated C—H, indicating there are no unsaturated bonds on CNR molecular chain.

From the results just presented it can be concluded that the main difference in the structures of CNR A and CNR B is the existence of more carboxyl and carbonyl groups on the molecular chains of CNR A. The reason for this difference is that the chlorination of natural rubber in latex is a “water-oil-gas” heterogeneous reaction with a longer chlorination time, during which a few C=C bonds have been oxidized into carboxyl and carbonyl groups in the presence of hypochlorous acid.¹ In contrast, the preparation of CNR by dissolving natural rubber in CCl_4 is a very homogeneous system.

HRPyGC-MS analysis

The pyrolysis spectrum of CNR B at 590°C is shown in Figure 2, and the relative peak area ratios (toluene as criteria) are presented in Table I. It can be seen that a great amount of HCl (retention time of 1.20 min) was released during the pyrolysis of CNR. The main fragments from the main chain are toluene (retention time of 1.90 min) and then benzene (retention time of 2.90

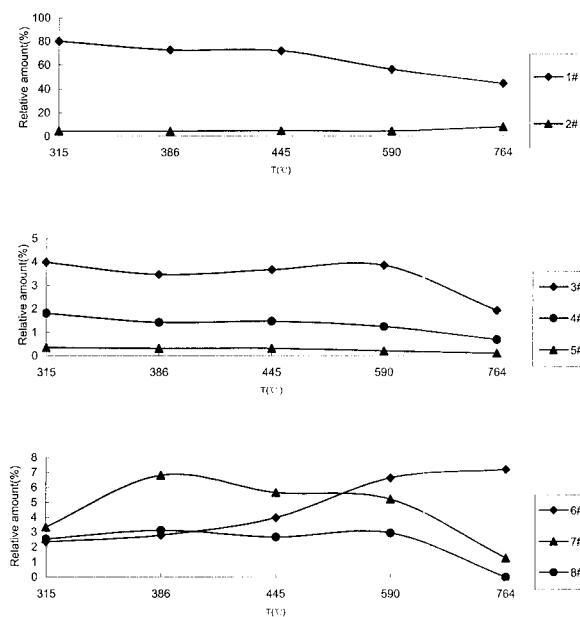
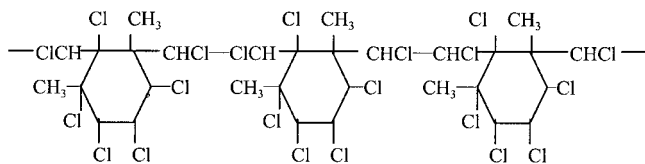


Figure 3 The variation of area of the main fragment peaks of CNR B with temperature from 315 to 764°C : (1) toluene, (2) benzene, (3) cyclohexane, (4) octane, (5) cyclopentane, (6) Cl-benzene and homologues, (7) diCl-benzene and homologues, (8) triCl-benzene and homologues. Vertical axis as a percentage of relative amount and horizontal axis as temperature ($^\circ\text{C}$).

min). Therefore, the pyrolysis of CNR is similar to those of PVC and chloroprene rubber (CR).² However, the appearance of the characteristic fragments of cyclohexane homologues (retention time of 3.04–3.45 min) in CNR is different from those of PVC and CR because there are no such fragments in the latter two materials. According to the structure, the pyrolytic fragments from the main chain of CNR could be approximately classified as monocyclic aromatics, cyclohexane (including a very little amount of cyclopentane), *n*-octane, and monochloride, dichloride, trichloride, and multiring aromatics.

The variation with temperature in ratio (compared with the total area of the peaks of the main fragments) of the peak areas of the fragments from the main chain of CNR B pyrolyzed from $315\text{--}764^\circ\text{C}$ are shown in Figure 3. The amount of toluene is the highest and decreases along with the increment of temperature. When the temperature was raised from 315 to 764°C , the amount of toluene decreases from 80.09% to 44.14% . The amounts of all the other fragments are lower than that of toluene. The amounts of benzene and monochloride aromatics increase, whereas the others decrease with the increasing of temperature. The most noticeable result is that there are almost no changes for the fragment peak of cyclohexane from 315 to 590°C , but it begins to decrease at 764°C , indicating that the rings do exist on the main chain structures. Many researchers have affirmed the existence of the



Scheme 1 The hexatomic rings of CNR proposed by Bloomfield.³

ring structures on CNR molecular chains, however, there are two viewpoints as to the type; that is, hexatomic³ and pentatomic rings.⁴ The hexatomic rings of CNR proposed by Bloomfield³ are shown in Scheme 1.

The results from the HRPyGC-MS of this study support the hypothesis of Bloomfield.^{5,6} When CNR was pyrolyzed at high temperature, the C—Cl and C—C bonds were broken down at first; therefore, there are great amounts of free radicals, such as Cl·, CH₃· carbon chain fragments, and hexatomic ring radicals existing in the system. Cl· is very active and can abstract the H· from the other fragments to form HCl. HCl is also unstable at high temperature and can be dissociated into H· and Cl·, so there are many kinds of radicals in the system. The carbon chain fragments can be easily rearranged to monocycle aromatics whose stability is very high, which is the reason why there are great amounts toluene and benzene produced in the fragments. This is also the case of the pyrolysis of polyvinylchloride (PVC) and chloroprene rubber (CR).² From the dissociation of the C—Cl of the hexatomic ring radical, the monocycle aromatics can be formed as well as by the combination of the adjacent radicals. Because CH₃— can form a σ - π hyperconjugation with a benzene ring when a π -conjugation has been formed, the amount of toluene in the frag-

ments is much higher than that of benzene and there are three kinds of xyloles formed. Although C—Cl is not stable because of its low bond energy, the stability of C—Cl can be greatly reinforced by forming p - π conjugation with benzene ring when it is attached to benzene ring. Therefore, there are all kinds of chlorinated monocycle aromatics in the fragments but no chlorinated cyclohexanes. In addition, because the α -H of CH₃— attached to toluene is very active and is very easy to be dissociated, the monochloride, dichloride, and trichloride methylbenzenes can be formed. The cyclohexane and its homologues are formed by the combination of all sorts of hexatomic ring radicals with H·, CH₃·, and other free radicals. The n -octane and a very little amount of cyclopentane should also be the structures existing in the main chain, and their amounts are not changeable along with the temperature. At higher temperature, because of the breaking down of the hexatomic ring, the amounts of toluene and cyclohexanes decrease and the fragments are rearranged into multiring aromatics. At 764°C, multiring aromatics with more than three rings are produced, but at 445°C, there are almost no multiring aromatics evident. From the distribution of the peaks of the fragments in the pyrolysis of CNR, the optimum pyrolytic temperature for CNR is 445°C, with an acceptable range of 386 to 590°C.

The pyrolysis spectrum of CNR A at 590°C is shown in Figure 4, and the variation in ratios (comparing with the total area of peaks of the main fragments) with temperature of the peak areas of the fragments from the main chain of CNR A pyrolyzed from 315 to 764°C are shown in Figure 5. The peaks of several kind of fragments of CNR appear on the pyrolysis spectrum of CNR A, which corresponds to their IR spectra,

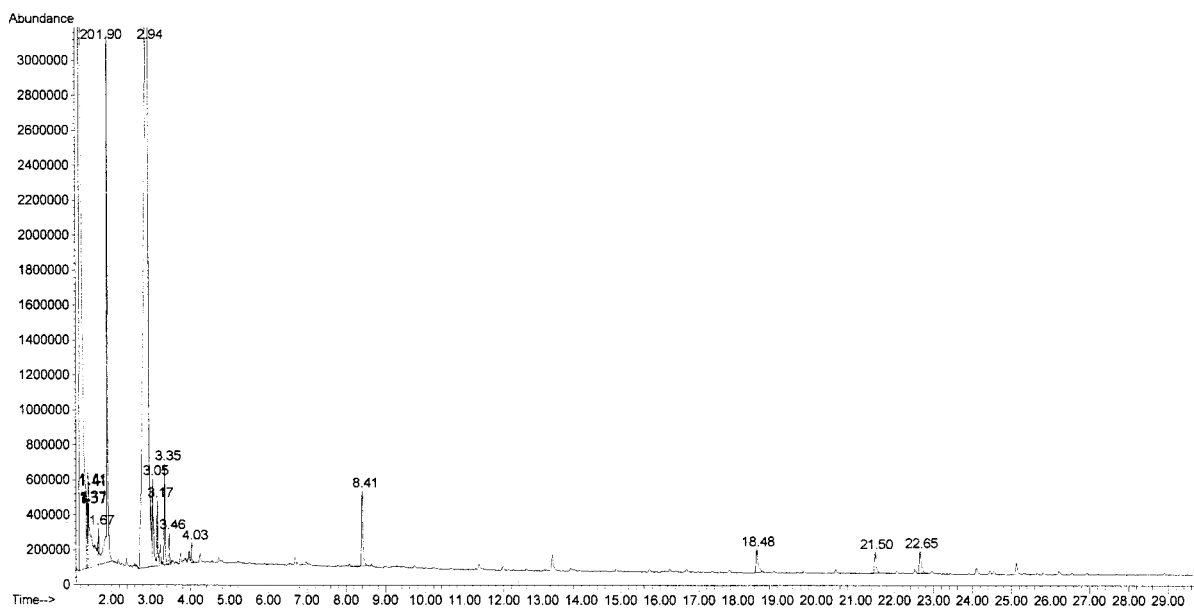


Figure 4 HRPyGC-MS spectra of CNR A at 590°C

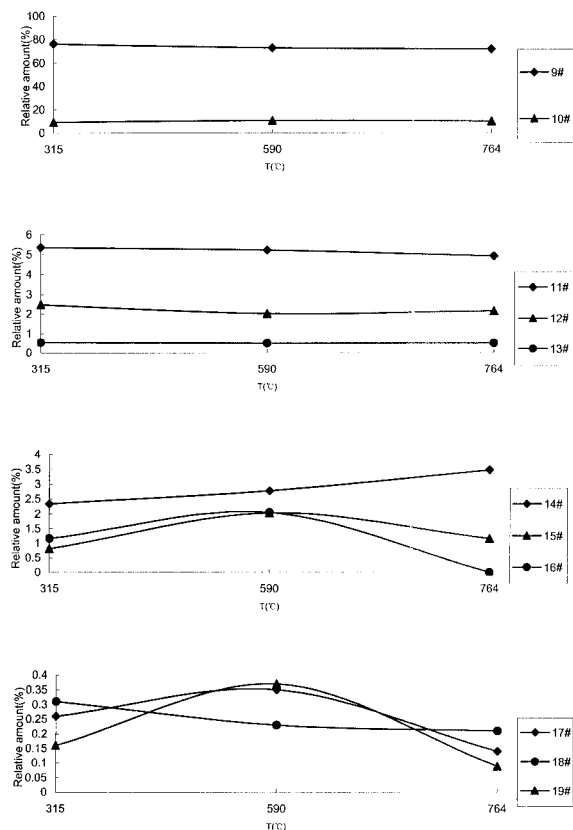


Figure 5 The variation of the area of the main fragment peaks of CNR A with temperature from 315 to 764°C: (9) toluene, (10) benzene, (11) cyclohexane, (12) octane, (13) cyclopentane, (14) Cl-benzene and homologues, (15) DiCl-benzene and homologues, (16) triCl-benzene and homologues, (17) triCl-benzaldehyde, (18) triCl-benzoic acid, (19) triCl-phenyl-ethanone. Vertical axis as a percentage of relative amount and horizontal axis as temperature (°C).

indicating the basic in structures of CNR from the two processes are similar. By comparison with the spectra of CNR B obtained at the same temperatures, the numbers of peaks on the CNR A spectra are fewer. There are almost no multiring aromatics in the spectrum of CNR A at 590°C. The multiring aromatics only appear on the spectrum of CNR A at 764°C, and the peak areas of all the fragments do not changed greatly with the temperature, indicating that the structures and stabilities of the two samples are different. In addition, a small amount of acetophenone trichloride (retention time of 24.10 min), trichloride benzoic acid (retention time of 24.45 min), and benzaldehyde tri-

chloride (retention time of 25.14 min) are detectable at all the pyrolytic temperatures. This result corresponds to the IR spectra and also indicates the existence of carboxyl and carbonyl groups on the main chain of CNR A molecule.

CONCLUSIONS

1. The fine structures of CNRs prepared from "latex" and "solution" processes are different, although their basic structures are similar.
2. The rings on the CNR molecule should be hexatomic rings with certain amount of linear structures and a very few pentatomic ring structures. The molecule of CNR made by the "latex" process contains more carboxyl and carbonyl groups than that of CNR made by the "solution" process.
3. The optimum pyrolytic temperature for CNR is 445°C, with an acceptable range of 386 to 590°C. The characteristic pyrolytic products are cyclohexane homologues.

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