Fluorescence Spectroscopic and Atomic Force Microscopic Studies on the Microstructure of Polyimide/Silica-Titania Ternary Hybrid Composites

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Abstract: Biphenyltetracarboximide-phenylene diamine polyimide/silica-titania ternary hybrid composites were prepared by thermal imidization and sol-gel reaction. Fluorescence spectroscopic, scanning electron microscopy, and atomic force microscopy studies revealed that the addition of small amount of titania showed profound effects on the microstructure and photophysical behaviors of polyimide/silica hybrid composites, when the content of silica-titania mixture was small or when the ratio of silica to titania in the mixture was high.

Keywords: polyimide, silica, titania, hybrid composite, microstructure.

Introduction

Aromatic polyimides have attracted much interest in microelectronic industries because of their good solvent and water resistance, low thermal expansion coefficient, low dielectric constant, low residual stress and high tensile strength and modulus.[1-4] Since polyimide (PI) is, however, originated from organic materials, there exists a limit for far higher performance applications in which inorganic materials are used.

Silica (Si) has been most extensively investigated as an inorganic compound for the hybrid composites because of the expected interesting catalytic and electronic applications.[5] Since the first work of Nandi *et al.*[6], several authors reported on the structure and properties of the PI/Si composites.[7-10] Recently, works on the PI/Si hybrid composites have been well reviewed by Ahmad and Mark.[11] Meanwhile, titania (Ti) is one of promising partner of polymer in hybrid composites for photonic applications because of its high refractive index. When TiO_2 is obtained by sol-gel method, however, it is not easy to prepare hybrid composite thin films of Ti with a polymer because of very fast hydrolysis reaction and thus extremely fast gellation of titanium alkoxide. Thus, only a

few works have been reported on the polymer/Ti composites.[12] Instead, composites of a polymer with the mixture of Si and Ti have been attempted.[13-15] For instance, Yoshida and Prasad[14] studied on the sol-gel-processed Si/Ti/poly (vinylpyrrolidone) composites for optical waveguides.

To the best of our knowledge, however, no paper has been published with the investigation of the microstructure of the PI/Si-Ti ternary hybrid composites. In this work, the effect of small amounts of Ti on the microstructure of the PI/Si hybrid systems was investigated using a fluorescence spectroscopy, scanning electron microscopy (SEM), and an atomic force microscopy (AFM). We believe that the investigation will give insight to the future application of the PI/Si-Ti ternary systems in a certain way especially for photonic or electronic devices.

Experimental

Raw Materials. 3,3,4,4-Biphenyl tetracarboxylic dianhydride (BPDA, TCI Chemicals) was recrystallized and vacuum-dried at 200 °C for 24 h before use. A sublimed *p*-phenylene diamine (PDA), anhydrous *N*-methyl pyrrolidinone (NMP), tetraethylorthosilicate (TEOS) and titanium iso-propoxide [Ti(OPr)₄] were purchased from Aldrich and were used as received.

Preparation of PI/Si-Ti Ternary Hybrid Composite Films.

The poly(amic acid) (PAA) was polymerized by adding an equimolar amount of BPDA powder into the NMP solution of PDA with continuous stirring at room temperature for several hours. First, various quantities of TEOS and Ti(OPr)$_4$ with water and HCl as a catalyst were added into the PAA solution (15 wt%). The weight ratio of TEOS/Ti(OPr)$_4$ mixture to PAA varied from 0.05 to 0.75 (see Table I for notation). After stirring for several days, the resulting homogeneous mixtures were spun on glass plates or quartz wafers to prepare the PAA as-spun hybrid films. The PAA as-spun films after drying at 80 °C for 30 min were heated at 200 °C for 30 min followed by 350 °C for 1 h in an oven under nitrogen purge to prepare the PI/Si-Ti ternary hybrid composite films. The films were cooled to room temperature at a rate of 10 °C/min. The chemistry of thermal imidization in this work is illustrated in Figure 1. For comparison, the PI/Si binary hybrid film of 10 wt% of Si was also prepared in a similar way as described above. The only difference is that only TEOS was used not with Ti(OPr)$_4$.

Characterization. The emission spectra of the hybrid composite films were measured using a fluorescence spectrometer (FS 900CDT spectrometer, Edinburgh Instruments). All measurements were made at room temperature using 1 mm slit widths. Films were excited in a front-face arrangement to minimize self-absorption. Fluorescence intensity was corrected to account for variations in PMT sensitivity and absorption using a rhodamine B standard solution. Seven measurements were performed and signal averaged. For AFM (Digital Instruments, Nanoscope III)) measurements, the cantilever used in the present study was a V-shaped one mounted a quadrangular pyramid silicon nitride (Si$_3$N$_4$) microtip at the end (Olympus, Co. Ltd., Japan) with a bending spring constant of 0.022 N/m. In the AFM observations, a feedback loop kept the vertical position of the tip constant by moving the sample surface up and down with the piezo-
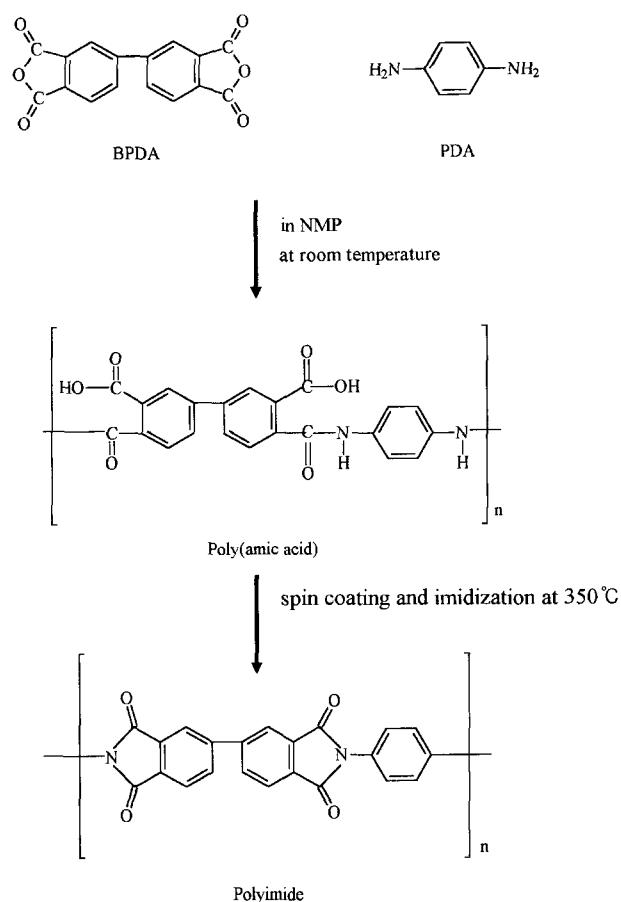

Figure 1. Chemistry of thermal imidization of BPDA-PDA PI from the PAA precursor.

electric scanner. The images were taken with 2 μm × 2 μm scanners. The morphology of the composite samples was also observed with Scanning Electron Microscope (JEOL

Table I. Preparation of BPDA-PDA PI/Silica-Titania Hybrid Films

Sample Notation[a]	PAA[b] (mg)	TEOS (mg)	Ti(OPr)$_4$ (mg)	TEOS/Ti(OPr)$_4$ Ratio	Silica/Titania (wt%[c])
ST(41)-0.05 g	300	8.0	2.0	4	0.7/0.15
ST(31)-0.05 g	300	7.20	2.4	3	0.7/0.18
ST(21)-0.05 g	300	7.66	3.83	2	0.7/0.28
ST(21)-0.1 g	300	15.4	7.7	2	1.4/0.56
ST(21)-0.5 g	300	76.6	38.3	2	6.8/2.7
ST(11)-0.05 g	300	4.17	4.17	1	0.4/0.3
ST(11)-0.1 g	300	8.34	8.34	1	0.8/0.6
ST(11)-0.5 g	300	41.7	41.7	1	3.7/2.9

[a]Samples are denoted as ST(ij)- k g, where i and j are the compositions of silica and titania in the silica/titania mixture respectively and k is the amount of the mixture based on 6.667 g of PAA according to our previous work.[16] For instance, ST(11)-0.05 g denotes that 8.34 mg of 1/1 (by weight) ratio of TEOS/Ti(OPr)$_4$ mixture was added to 300 mg of PAA solution, which corresponds to 0.05 g of the mixture in 6.667 g of PAA.
[b]15wt% PAA solid content solution in NMP.
[c]Calcuated silica and titania content(by wt%) in the hybrid films assuming that the gel reaction was completed.

JSM-35CF). Samples were cryogenically fractured in liquid nitrogen. The fractured surface of the specimens was directly observed by gold coating.

Results and Discussion

Though fluorescence spectroscopy has been also used to investigate the interfacial interaction or miscibility in polymer blends as well as the dynamics and structure of solid polymers,[16-22] very little has been published on the fluorescence spectroscopic studies of organic/inorganic hybrid composites. Recently, we reported that the fluorescence spectroscopy can provide insight into how the state of organization of the PI matrix is altered by the presence of Si in the PI/Si hybrid composite films.[16]

Hasegawa, *et al.*[18,19] reported that for BPDA-PDA PI film a broad emission peak was observed around 540 nm with 350 nm excitation. Similar emission spectrum was also observed in our work. It is generally accepted that PI fluorescence usually arises from charge transfer complex (CTC) that is formed by electron donor (diamine) and electron acceptor (diimide) segment pairs in the fully cured PI,[20] even though there is still controversy whether the CTCs are intermolecular or intramolecular (Figures 2 and 3).

Figure 2 shows the emission spectra of the PI/Si-Ti ternary hybrid composite films with two different contents of the Si-Ti mixture (nominally, 0.1 and 0.5 g) of two different ratios of Si to Ti [ST(11) and ST(21)]. The peak intensity of the emission spectra of BPDA-PDA PI decreases as the content of ST(11) or ST(21) increases. For both the ST(21)-0.5 g and the ST(11)-0.5 g films, broad and structureless spectra were observed as for the BPDA-PDA PI film. We note, however, that the emission spectra of ST(11)-0.1 g and ST(21)-0.1 g films show several separated peaks at around 450-650 nm wavelength region, whereas spectra of other ST(11)-0.5 g and ST(21)-0.5 g films do not.

The more interesting point is that three separated peaks were observed in the emission spectrum of the ST(21)-0.1 g film around 510-580 nm wavelength region, i.e. at approximately 512, 539, and 570 nm whereas only two separated peaks were observed at approximately at 522 and 557 nm in the emission spectrum of the ST(11)-0.1 g film over the same wavelength region. Other several peaks around approximately 465, 494, 595, and 649 nm were overlapped for the emission spectra of both ST(21)-0.1 g and ST(11)-0.1 g films. The peak separation behaviors in the emission spectra were also clearly observed when the contents of the Si-Ti mixture (ST) were very small (here, ST(*ij*)-0.05 g) and the ratio of Si to Ti content was 2/1 or higher, as shown in Figure 3.

The results of Figures 2 and 3 suggest that the microstructures of PI/Si-Ti ternary hybrid composite films with smaller Si-Ti mixture (ST) content or with the ratio of Si to Ti of 2/1 and higher are not identical to that with higher ST
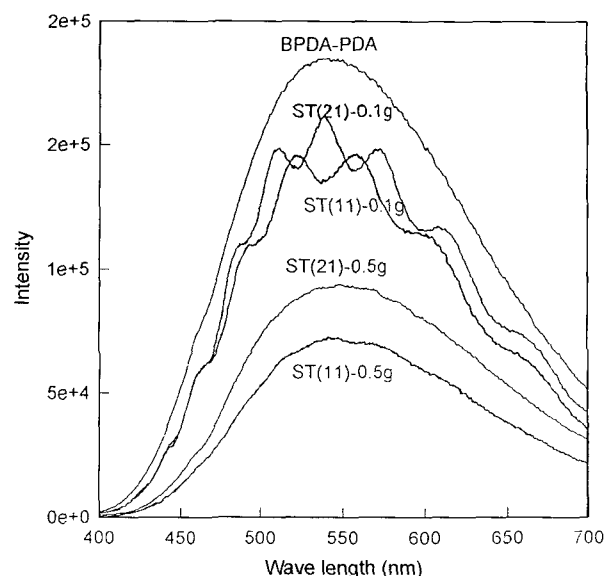

Figure 2. Emission spectra of the BPDA-PDA PI/Si-Ti ternary hybrid composite films with two different contents of the Si-Ti mixture(0.1 and 0.5 g) of two different ratios of Si to Ti (ST(11) and ST(21)). For details of the sample notation, see Table I.
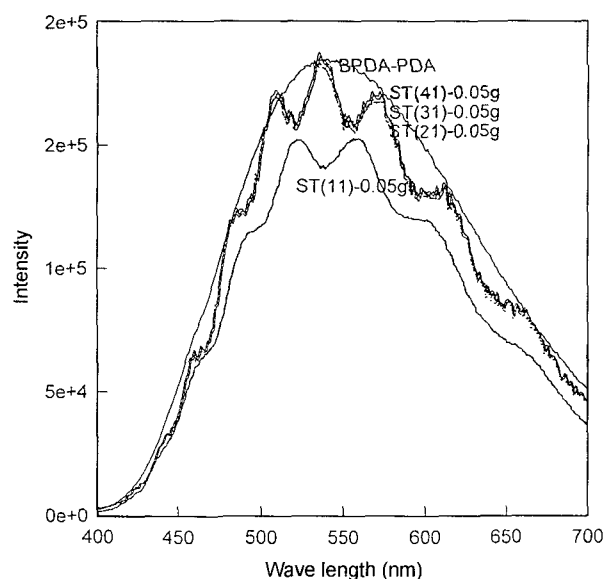

Figure 3. Effects of the different ratios of Si to Ti in the Si-Ti mixture of constant contents (0.05 g) on the emission spectra for BPDA-PDA PI/Si-Ti ternary hybrid composite films. For details of the sample notation, see Table I.

content or the 1/1 ratio of Si to Ti. The results also suggest that the PI/Si-Ti ternary hybrid composite systems have different environments for the chromophores depending on the content of the Si-Ti mixture and the ratio of Si to Ti in the mixture, though the exact assignment of each peak is not

easy at this moment.

It may be assumed that the results in Figures 2 and 3 are due to the change in local structural environment in the systems. For the PI/Si systems, we can find only Si dispersed in PI matrx, giving only one kind of morphology in the system. Thus, only one broad emission peak was observed for PI itself. For the PI/Si-Ti ternary hybrid composite systems, however, the morphology in the final matrix is more complex than the PI/Si binary hybrid composite systems depending on the content of the Si-Ti mixture and the ratio of Si to Ti content in the mixture. In this regard, AFM can be used to examine the size of inorganic particles of hybrid materials.[12,23]

Figure 4 shows the 3-D AFM images of the PI/Si10 binary hybrid composite and the PI/Si-Ti ternary hybrid composites (ST(11)-0.1 g and ST(21)-0.1 g). It is seen that Si particles with diameter of around 30-80 nm were observed in the PI/Si hybrid films when the Si contents was 10 wt%, while the size of the Si-Ti particles was significantly reduced to the diameter less than around 10 nm in the PI/Si-Ti hybrid films, although Si and Ti particles are not discernible each other. Such fine morphology of the PI/Si-Ti ternary hybrid composites means the formation of 'nanocomposites', as often stated for the composites of nanometer scale inorganic clusters. Careful inspection of Figure 4 shows that the microstructure of PI/Si-Ti ternary hybrid composite film containing 2/1 ratio of Si to Ti content is finer than that of the composite film containing 1/1 ratio of Si to Ti content. The result implies that the nanocomposite formation is more preferential when the amounts of Ti in the presence of a given amount of Si are smaller in the ternary hybrid composites.

In the case of the AFM images, however, one may not know exactly whether the true size of Si was significantly decreased with the addition of small amounts of Ti or smaller particles were migrated to the surface and larger particles were buried under the surface. Therefore, SEM observation was made to prove the reduction of the particle size in the bulk. Figure 5 shows the SEM micrographs of the fractured surface of the PI/Si10 and PI/ST(21)-0.1 and PI/ST(11)-0.1 composites. It is clearly seen that the particle

PI/Si10
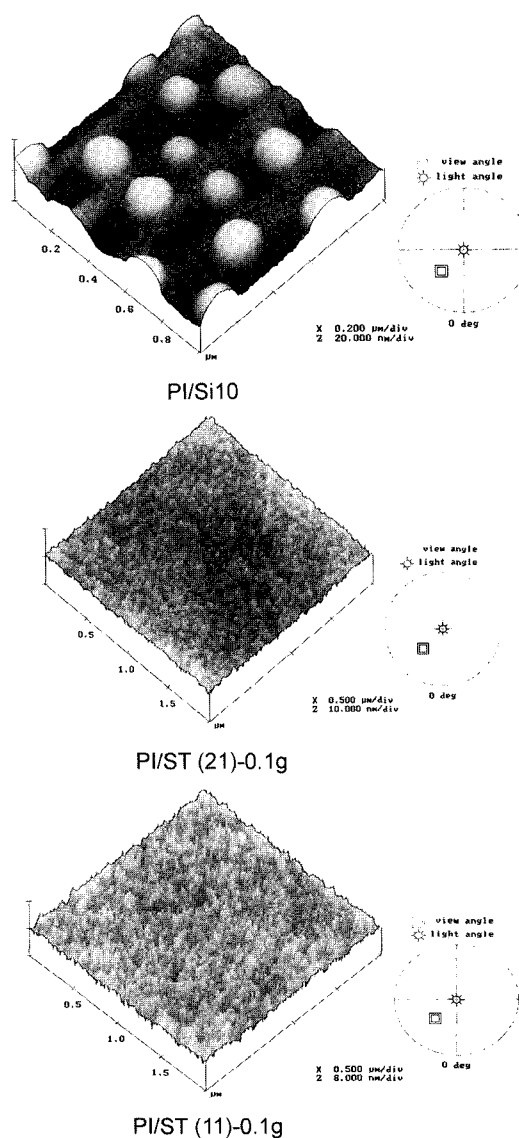
PI/ST (21)-0.1g

PI/ST (11)-0.1g

Figure 4. AFM 3-D image of PI/Si10 and PI/Si-Ti ternary hybrid composite films with two different ratios of Si to Ti (ST(11) and ST(21)) at constant contents (0.1 g) of the Si-Ti mixture. For details of the sample notation, see Table I.

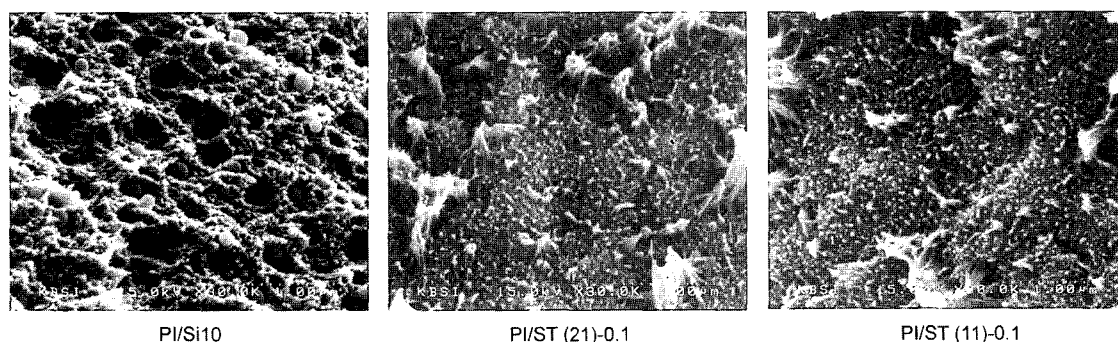PI/Si10   PI/ST (21)-0.1   PI/ST (11)-0.1

Figure 5. SEM micrographs of PI/Si10 and PI/Si-Ti ternary hybrid composite films with two different ratios of Si to Ti (ST(11) and ST(21)) at constant contents (0.1 g) of the Si-Ti mixture. For details of the sample notation, see Table I.

size of the Si was significantly reduced for the ternary hybrid composites in comparison to the PI/Si10 binary hybrid composite, indicating the formation of nanocomposites for the case of the ternary composites. It is also noteworthy that the matrix morphology was also slightly different in that the morphology of the ternary hybrid composites show somewhat ductile matrix nature due to the interfacial interaction between the domains and the matrix, whereas the PI/Si10 shows a typical brittle matrix nature.

When small amount of $Ti(OPr)_4$ are added to TEOS, they are transformed to Ti and Si, respectively, by sol-gel reaction. Then, small amount of TiO_2 particles exist together with SiO_2 as well as possibly covalent Si-O-Ti-O-Si network particles during molecular alignment or orientation of PAA to PI as a matrix. Thus, such a variety of local structure environment may give several different characteristic emission peaks. As the amount of Ti is increased, however, the system contains more complex particle systems. Some structure is overlapped with other structure, while some structure persists its own characteristics, depending on the reactivity (relative rate of hydrolysis and condensation during sol-gel reaction) of Si-O-Si, Ti-O-Ti and Si-O-Ti-O-Si bonding as well as the interaction between PI matrix and the inorganic particles. The homo- and hetero- condensation reactions of Si-alkoxide and/or Ti-alkoxide during sol-gel processing were systematically investigated by Hoebbel, *et al.*[24,25]

As the amount of Ti is increased in the Si-Ti system, any of the structures due to lots of different kinds of particles affect competitively and cooperatively on the photophysical behavior of the composite systems. Then, it may be considered that no peculiar structure is predominant and instead the local structure environment combines a variety of complex morphology, which gives a single broad and structureless emission peak. Similar photophysical behavior was observed when the contents of total inorganic particles (Si and Ti) were higher. The complex local structure for the composites of higher Ti content yields, however, a little bit lower emission intensity.

The question why the addition of small amount of Ti gives such a profound effect on the microstructure of PI/Si hybrid composites is very difficult to explain properly. The presence of Ti nanoparticles may be one of the possible explanations. It should be noted that an important advantage of the sol-gel synthesis route for PI/Si and PI/Si-Ti composites is that the PAA organic matrix acts to prevent agglomeration of the Si, which can lead to nanometer scale Si and Ti clusters in the composites. The effect of preventing the agglomeration of inorganic particles seems to be more significant when small amounts of Ti are present together with Si.[12,26] The very fast hydrolysis rate of titanium isopropoxide can be also another possible reason (the titanium isopropoxide can form Ti particles within a few seconds, while any Si precursor can form Si powders in a few hrs.) The formation of fast hydrolyzed-and-condensed Ti particles may hinder the growth of the

slow hydrolyzed-and-condensed Si powders during the sol-gel reaction in comparison to the PI/Si hybrid composites in the absence of Ti. More detailed studies on this matter should be done in our future work.

It may be assumed that the formation of new peaks at lower wavelength (i.e. 465 and 494 nm) in the case of PI/Si-Ti hybrids of lower Ti amounts relative to Si contents or those of smaller amounts of Si/Ti mixture in Figures 2 and 3 is related to the formation of clusters of nanometer-sized TiO_2 powders, i.e. Ti "nanoparticles". On the other hand, the new peaks at higher wavelength (i.e. 595 and 645 nm) in addition to the inherent emission peak of PI may be ascribed in part to surface states resulting from oxygen defects or the absorption of impurities such as surface-organic species, H_2O chemisorbed and OH groups bonded with Ti, which always exist on nanosized particles.[26] Such quantum size effect of Ti nanoparticles may be diminished and a broad structureless peak is observed with the disappearance of the peaks at lower wavelength and high wavelength when the amount of Ti is increased and the size of Ti particles are larger due to the agglomeration, for instance, as for the PI/ST(11)-0.5 g and the PI/ST(21)-0.5 g systems. Further systematic studies on the exact cause of such a profound effect of Ti addition on the microstructure of PI/Si hybrid composites are now underway in order to address more clearly for some speculative explanations in this work. Moreover, the difference on the fluorescence spectra reported in this work might have been the results of the different status of curing of PI if the Ti and Si alkoxides affects the curing reaction. Thus, further experimental works should be also taken in order to check the extent of the curing reaction by Fourier-transform infrared spectroscopy or other methods.

Conclusions

It was observed by AFM and SEM that for all the BPDA-PDA PI/Si-Ti ternary hybrid composites very fine particles, almost in nanometer scale, are uniformly distributed in PI matrix, regardless of the relative amount of Si and Ti as well as the total amounts of inorganic materials. Furthermore, the AFM and SEM studies showed that the microstructure of PI/Si-Ti ternary hybrid composite films is much finer as the content of Si-Ti mixture (ST) is smaller or when the ratio of Si/Ti content is higher. Different fluorescence behavior was observed depending on the ratio of Si and Ti in the Si-Ti mixture and the total amounts of Si-Ti mixture. The result was interpreted as being due to the formation of different local structural environment as Ti content increases. When the Ti content relative to Si is small, the emission spectra showed several separated peaks representing each chemical structural environment.

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