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# Characterizations of Aggregation States of Coal Soluble Constituents at Solid State

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Three kinds of pyridine-insoluble fractions (PI) of coal extracts with different solubility in NMP were obtained. Original PI (PI-0), which was obtained by pyridine fractionation of Upper Freeport (UF) coal extracts with carbon disulfide/*N*-methyl-2-pyrrolidinone (CS<sub>2</sub>/NMP) mixed solvent (1:1 by volume), has 53 wt % of solubility in NMP at room temperature. By the addition of a small amount of tetrabutylammonium acetate (TBAA), PI-0 became almost completely soluble in NMP. PI-1 was obtained by the removal of NMP and TBAA from PI-0 solution in NMP containing TBAA, and it has 98 wt % of solubility in NMP. While, PI-2 was obtained from the solvent removal of PI-1 solution in NMP without TBAA, and it has 48 wt % of solubility in NMP. Differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) were employed to characterize the aggregation states of these three solid PIs. The results confirm that the difference in the solubilities of the three PIs was attributed to their different aggregation states. PI-1 has a less aggregated structure compared to PI-0 or PI-2, because it was obtained by the evaporation of NMP with TBAA, which acts as an inhibitor of the aggregation of coal molecules.

## Introduction

Many studies indicate that noncovalent bonds in coal affect strongly the physical properties of coal.<sup>1,2</sup> A *N*-methyl-2-pyrrolidinone/carbon disulfide (CS<sub>2</sub>/NMP) mixed solvent has been found to give high extraction yield more than 50 wt % (daf) for several bituminous coals at room temperature, and no significant chemical reaction was indicated to occur during the extraction.<sup>3,4</sup> This provides a support to the noncovalent network model of coal called as "associated or physical network model" proposed by Nishioka.<sup>5</sup> Larsen et al.<sup>6</sup> observed that soaking four different rank of coals in chlorobenzene at 115 °C for a few days resulted in a significant decrease in pyridine Soxhlet extraction yields, and the heat capacities of the treated coals were also decreased, which indicated a more aggregated structure was formed. Swelling behaviors of the extract fractions obtained from the room-temperature extraction of several bituminous coals suggested that strongly aggregated structures were formed through several noncovalent interactions.<sup>7</sup> In the early study, we have

found<sup>8–10</sup> that when the extracts of coal obtained with a CS<sub>2</sub>/NMP mixed solvent (1:1 by volume) were fractionated into acetone-soluble (AS), pyridine-soluble (PS), and pyridine-insoluble (PI) fractions, a part (33.6 wt %) of PI fractions became insolubles in the CS<sub>2</sub>/NMP mixed solvent. But, the addition of a small amount of tetracyanoethylene (TCNE) to the mixed solvent makes the PI fractions become almost completely soluble again in the mixed solvent. Recently, TCNE was found to convert the salt, i.e., NMP–H<sup>+</sup>1,1,2,3,3-pentacyanopropene (PCNP)<sup>–</sup> and the addition of PCNP salt synthesized was found to increase the extraction yield of coal and solubility of PI. We also confirmed the anion, PCNP<sup>–</sup>, is responsible for the increase in the extraction yield of coal and PI solubility.<sup>11,12</sup> Other salts containing acetate anion (tetrabutylammonium acetate, TBAA) and halide anions (Li or tetrabutylammonium salts of F<sup>–</sup> and Cl<sup>–</sup>) were also effective for the enhancements of the extraction yield of coal and PI solubility.<sup>13,14</sup>

In the previous paper<sup>14</sup> we obtained two kinds of PIs using TBAA with quite different solubility in the CS<sub>2</sub>/NMP mixed solvent. The difference in the solubility of the two PIs was considered to be due to their different aggregation states. But more evidence is needed to confirm this conclusion.

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In this paper, NMP is used as a solvent instead of the CS<sub>2</sub>/NMP mixed solvent. We could prepare three kinds of PIs with different solubility in NMP, and the aggregation states of the three solid PIs are characterized by means of swelling, FTIR, DSC, and TMA.

## Experimental Section

### Preparation of PIs with Different Solubility in NMP.

Original PI (referred as PI-0) was prepared from pyridine fractionation of UF coal extracts with CS<sub>2</sub>/NMP mixed solvent. PI-0 (0.5 g) was dissolved in 60 mL of NMP with an additive, TBAA, under ultrasonic (38 kHz) irradiation for 30 min at room temperature. The amount of TBAA added was 0.25 mmol (0.075 g) per 1 g of PI-0. The mixture was then centrifuged under 29000*g* for 15 min, and immediately filtered through a membrane paper with a pore size of 0.8 μm. After the filtration, NMP was removed from the filtrate by a rotary evaporator at around 90 °C. The precipitated PI was washed exhaustively with water/acetone mixed solvent (4/1 by volume) to remove NMP and TBAA, then dried under vacuum at 80 °C for 12 h. The washing procedure with the water/acetone mixed solvent includes ultrasonic (38 kHz) irradiation for 15 min, centrifugation (29000*g*) for 15 min, and filtration. The washing was usually repeated 6 times to remove completely NMP and TBAA which are strongly retained in PI. The removal of NMP and TBAA from the PI-0 solution in NMP containing TBAA gave PI-1. The PI-1 was completely dissolved in NMP without TBAA and then the removal of NMP from this PI-1 solution gave PI-2. The procedure in detail was described elsewhere.<sup>14</sup>

**Solubility Determination of PI.** PI (0.1 g) was dissolved in 50 mL of NMP under ultrasonic (38 kHz) irradiation for 30 min at room temperature. After the filtration through a membrane paper (0.8 μm) and washing with the water/acetone (4:1 by volume) mixed solvent the residue was dried under vacuum at 80 °C for 12 h. The solubility (wt %) was determined from the weight of the residue:

$$\text{solubility (wt \%, db)} = [1 - \text{residue (g)/PI feed (g)}] \times 100$$

**Swelling Determination of PI.** The swelling ratio (*Q*) was measured by the volumetric method of Green and Larsen.<sup>15</sup> An amount of 0.1 g of PI (under 100 mesh) was placed in a 3 mm i.d. Pyrex tube and centrifuged for 30 min at 1500 rpm. The height of the PI layer was measured as *h*<sub>1</sub>. About 0.6 mL of a solvent was added and mixed thoroughly with the sample using a spatula. The sample was again centrifuged and the height of the PI layer (*h*<sub>2</sub>) was measured. Swelling ratio (*Q*) is defined as *h*<sub>2</sub>/*h*<sub>1</sub>. The swelling and centrifugation were repeated until the height was attained to a constant, equilibrium value. Methanol, tetrahydrofuran (THF), and pyridine were used as a swelling solvent.

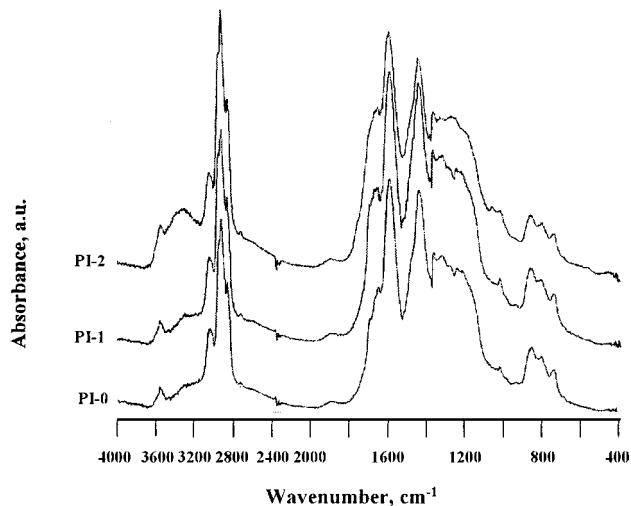
**FTIR Measurement.** Diffuse reflectance FTIR spectra were measured by a JEOL JIR-100 spectrometer at a resolution of 4 cm<sup>-1</sup> by co-adding 200 scans. Samples for FTIR measurement were prepared by diluting 5 mg of PI in 200 mg of KBr.

**DSC Measurement.** Differential scanning calorimetry (DSC) was performed on SHIMADZU DSC-50 equipment. About 8 mg of sample was heated at 8 °C/min to 300 °C. The measurements were carried out under a nitrogen flow of 50 mL/min in order to keep the cell free of oxygen during measurement. An aluminum sample pan with a cover was used in an unsealed mode.<sup>16</sup> The amplitude difference between the blank and the sample heat fluxes at each temperature gives the heat capacity of the sample. After the first scanning,

**Table 1. Solubilities and Elemental Compositions of Various PIs**

sample	solubility (wt %, db)		ultimate analysis (wt %, db)				
	NMP	NMP + TBAA	C	H	N	S	O <sup>a</sup>
PI-0	53	99	83.1	5.2	1.8	1.8	8.1
PI-1	98	100	82.6	5.3	1.8	2.0	8.3
PI-2	48	99	82.2	5.1	1.6	1.8	8.3

<sup>a</sup> By difference.



**Figure 1.** FT-IR spectra of PI-0, PI-1, and PI-2.

the sample was cooled under the nitrogen flow to room temperature, then the second scanning was made at the same conditions.

**TMA Measurement.** Thermomechanical analysis (TMA) was carried out on SHIMADZU TMA-50 equipment. 45–50 mg of a sample was pressed into a cylindrical pellet using a steel mold and hydraulic press. The diameter and length of the cylindrical pellet are 4.4 mm and 2.8 mm, respectively. Pressure up to 645 MPa was used to make the pellet. Pressurizing and depressurizing were done at a very slow rate. Rapid pressure variation can result in a cracked sample pellet. The sample pellet thus obtained was placed into the quartz reference tube. The glass push rod was inserted into the quartz tube until it rested on the middle of the sample. A constant load of 10 g was applied on the sample pellet through the expansion probe to ensure the proper contact of the probe and the sample. The sample was heated at 8 °C/min from room temperature to 300 °C under nitrogen flow of 50 mL/min. The change in the length, (*L*<sub>T</sub> – *L*<sub>0</sub>)/*L*<sub>0</sub>, where *L*<sub>0</sub> and *L*<sub>T</sub> are the length of a sample at room temperature and *T*, respectively, was plotted as a function of *T*.

**TG Analysis.** Thermo gravimetric (TG) analysis was carried out on a TG/DTA 32 analyzer (SII, Seiko Instruments). About 6 mg of sample was placed in an aluminum pan and heated from 25 °C to 300 °C at a rate of 8 °C/min under 60 mL/min helium gas flow.

## Results and Discussion

**Solubility and Swelling of PIs.** Table 1 shows the solubility in NMP and ultimate analysis of three PIs (PI-0, PI-1, and PI-2). Table 1 shows that PI-0 and PI-2 have a lower solubility (48, 53%), compared to that (98%) of PI-1. This tendency is in agreement with the result for PIs obtained using the CS<sub>2</sub>/NMP mixed solvent in the previous paper.<sup>14</sup> PI-0, PI-1, and PI-2 have similar elemental compositions (Table 1) and FTIR spectra (Figure 1) and also little mass loss from PI-0 to

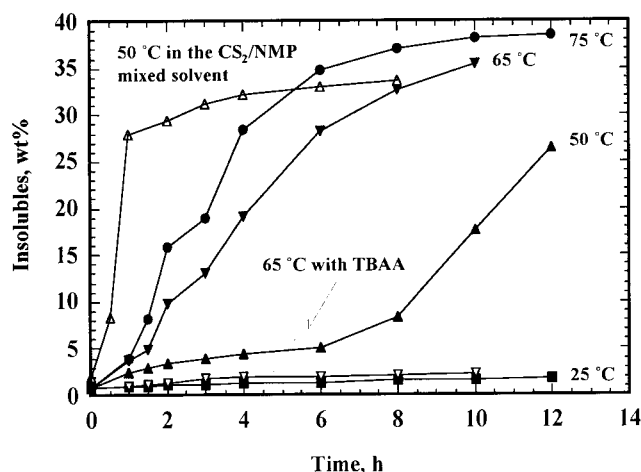
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**Table 2. Swelling Ratios ( $Q$ ) for PI-0 and PI-1**

solvent	methanol ( $Q$ )	THF ( $Q$ )	pyridine <sup>a</sup>
PI-0	1.2	1.8	1.8
PI-1	1.2	1.8	2.0

<sup>a</sup> About 30 wt % of PI-1 was dissolved in pyridine and almost no dissolution was observed for PI-0.



**Figure 2.** Change of the amount of the insolubles in PI-1 solution in NMP with time at 25 °C (■), 50 °C (▲), 65 °C (▼), and 75 °C (●) without TBAA and at 65 °C with TBAA (▽), together with the result in the CS<sub>2</sub>/NMP mixed solvent at 50 °C (Δ) with TBAA.<sup>14</sup>

PI-1 and from PI-1 to PI-2, indicating that they have the same chemical compositions.

Table 2 shows equilibrium swelling ratios ( $Q$ ) of PI-0 and PI-1. Swelling is considered to be a reflection of cross-link density. Generally, a decreased swelling ratio indicates an increase in cross-link density of a network structure of a sample, and vice versa.<sup>17</sup> Table 2 shows that  $Q$  (2.0) of PI-1 in pyridine was higher than that (1.8) of PI-0, suggesting that PI-1 has a less cross-link density compared to PI-0. However, the different solubilities in pyridine, i.e., about 30 wt % for PI-1 and few wt % for PI-0 are possible to affect  $Q$  and obscure the above conclusion. Table 2 also indicates that PI-0 and PI-1 have the same swelling ratio in methanol and THF and the swelling ratios in THF are larger than in methanol for both PIs.

**Effect of Temperature on the Aggregation of PI-1 in NMP Solution.** It was found that the insolubles (precipitates) were formed in the CS<sub>2</sub>/NMP mixed solvent solution of PI-1 by standing the solution at 50 °C.<sup>14</sup> The insolubilization of PI-1 was also observed in NMP solution, as shown in Figure 2. Figure 2 shows that the rate of the insolubles formation from PI-1 solution in NMP increased with increasing temperature from 25 °C to 75 °C, and the rate at 65 °C decreased dramatically in the presence of TBAA. These observations can explain why PI-2 became partially insoluble. PI-2 was obtained from the evaporation of NMP from NMP solution of PI-1 at about 90 °C for 1–2 h without the presence of TBAA, which are enough time and temperature to induce the insolubilization. While, the evaporation of NMP from PI-0 solution was carried out with TBAA which prevents the aggregation, as the result at 65 °C with TBAA is shown in Figure 2.

The possible role of TBAA in prevention of aggregation is that TBAA anion interacts with PI-0 molecules in some active sites where the aggregation of coal molecules will be easy to carry out by hydrogen bonds,  $\pi$ – $\pi$  interaction between aromatic rings or some other noncovalent bonds, resulting in PI molecules more stable in solution because of the loss of active sites. Figure 2 suggests that PI-1 solution in NMP got to an equilibrium state after standing the solution at 75 °C for 10 h. A similar result (open triangle in Figure 2) was observed for PI-1 solution in the CS<sub>2</sub>/NMP mixed solvent at 50 °C after 4 h. Figure 2 also shows that the insolubles formation in NMP at 50 °C was slow compared to that in the CS<sub>2</sub>/NMP mixed solvent at the same temperature. The reason may be the lower diffusibility (mobility) of coal molecules in NMP, compared to that in the CS<sub>2</sub>/NMP mixed solvent, because of higher viscosity ( $1.69 \times 10^{-3}$  Pa·s) of NMP compared to  $6.15 \times 10^{-4}$  Pa·s of the 1:1 CS<sub>2</sub>/NMP mixed solvent at 25 °C.<sup>3</sup>

**Characterizations of PIs at Solid State. FTIR.** FTIR can provide structural information of coal in detail. The FTIR spectra for the three PIs shown in Figure 1 are similar, indicating that they have the same chemical structure. No peak appeared at 2950 cm<sup>-1</sup> for PI-1, suggesting almost all the TBAA was removed by washing with acetone/water mixed solvent in PI-1.<sup>14</sup> The peaks at 1670 cm<sup>-1</sup> for the three PIs, which is due to the C=O group of NMP,<sup>3,18</sup> are very small, suggesting that little amount of NMP existed in the PIs.

**DSC.** DSC is one of powerful tools to characterize the aggregation state of coal molecules at solid state, since heat capacity is affected by the change in aggregation states. It is generally admitted that heat capacity decreases when the stiffness of macromolecular chains increases by increasing cross-linkages or molecular interactions.<sup>19,20</sup> Figure 3 shows the heat capacities of the three PIs. The first scanning of DSC indicates that PI-1 has a larger heat capacity than those of PI-0 and PI-2. However, some peaks appeared in the profiles indicate the existence of a small amount of water and NMP in the PIs (Figure 3a) and this may influence the accuracy of heat capacity obtained. Three peaks at around 80 °C, 130 °C, and 220 °C for PI-0 may be attributed to water, pyridine, and NMP, respectively. For PI-1, a small broad peak appeared at 280 °C, and this may be due to NMP interacting strongly with PI-1 molecules.<sup>21</sup> The TG profiles in Figure 4 indicate that NMP retained in PIs is less than 5 wt %, and the heat treatment by the first DSC scanning (heating at a rate of 8 °C/min to 300 °C under nitrogen flow of 50 mL/min) can remove the retained solvents almost completely as seen from no weight loss TG patterns for the three heat-treated PIs in Figure 4. Thus, the second scanning of DSC may be more informative because water and NMP can be removed by the first scanning. Figure 3b shows that in the second scanning PI-1 has a larger heat capacity than those of PI-0 and PI-2 with lower solubility. PI-1, which has larger heat capacity

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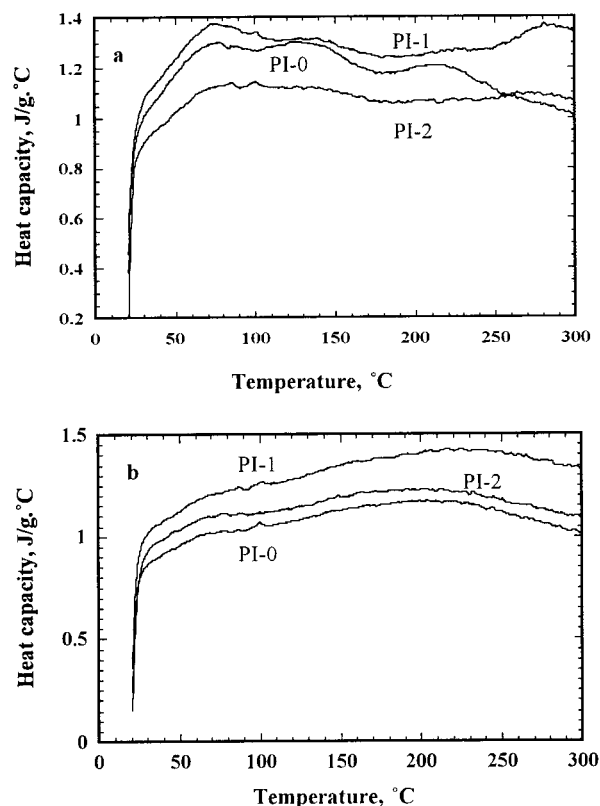
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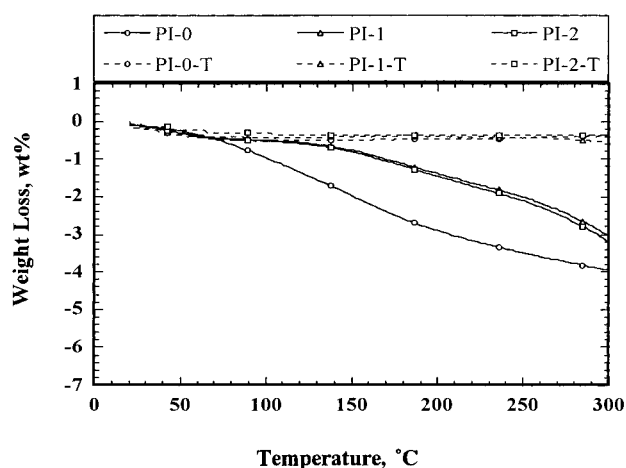
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**Figure 3.** Heat capacities of the three PIs from the first DSC scanning (a) and the second DSC scanning (b).



**Figure 4.** Mass losses of the three PIs vs temperature before and after heat treatment (the first DSC scanning). PI-0-T, PI-1-T, and PI-2-T are the heat-treated samples of PI-0, PI-1, and PI-2 at a heating rate of 8 °C to 300 °C under a nitrogen flow of 50 mL/min, respectively.

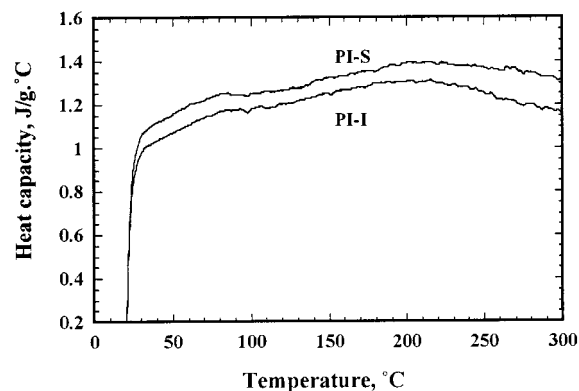
and high solubility, surely has a less aggregated structure compared to PI-0 or PI-2.

The following experiment was done to show that heat capacity is really related with aggregation state. PI-0 was separated into two parts, which were insolubles (PI-I) and solubles (PI-S) in NMP. The solubilities in NMP and the elemental compositions of PI-I and PI-S were shown in Table 3. About 15 wt % of PI-S become insoluble in NMP, probably because the aggregation proceeded during the evaporation of NMP from the solution. It is reasonable to believe that PI-I has a more aggregated structure compared to PI-S, because the solubility of PI-I in NMP increases from 5 to 96 wt %

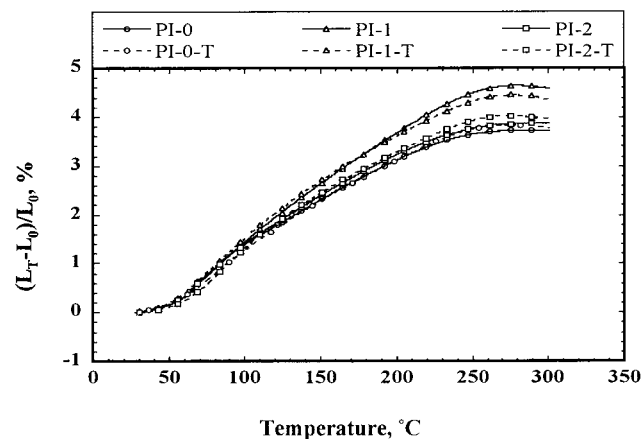
**Table 3.** Solubilities and Elemental Compositions of PI-S and PI-I

sample	solubility (wt %, db)		ultimate analysis (wt %, db)			
	NMP	NMP + TBAA	C	H	N	S + O <sup>a</sup>
PI-S	85	100	85.2	5.1	1.6	8.1
PI-I	5	96	84.2	5.2	1.3	9.3

<sup>a</sup> By difference.



**Figure 5.** Heat capacities of PI-S (NMP-solubles of PI-0) and PI-I (NMP-insolubles of PI-0) from the second DSC scanning.



**Figure 6.** Thermal expansions of the three PIs as a function of temperature before and after heat treatment (the first DSC scanning). PI-0-T, PI-1-T, and PI-2-T are the heat-treated samples of PI-0, PI-1, and PI-2 at a heating rate of 8 °C/min to 300 °C under a nitrogen flow of 50 mL/min, respectively.

by the addition of a small amount of “aggregation inhibitor”, TBAA (0.25 mmol/g-PI-I) in NMP solution. The heat capacities of PI-I and PI-S from the second DSC scanning are shown in Figure 5. PI-S has a larger heat capacity than PI-I due to its less aggregated state.

**TMA.** TMA can be used to get the information about thermal expansion of the sample. The thermal expansion coefficient (TEC) is sensitive to the microstructural characteristics of the material.<sup>22</sup> It is well-known that for the less flexible, more rigid structural materials, the resistance to deformation increases as the temperature increases, thereby, they have a smaller TEC compared to that of the loose structural materials.<sup>23</sup> Figure 6 shows the thermal expansions of the three PIs. PI-0 and PI-2 have similar thermal expansion, and the thermal expansion of PI-1 is larger than that of PI-0 and PI-2,

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suggesting that PI-1 has a more flexible, i.e., less aggregated structure compared to PI-0 or PI-2. Figure 6 shows that PI-0-T, PI-1-T, and PI-2-T, in which water and NMP were removed by the heat treatment from the first DSC scanning, gave the same results as the nontreated ones. This may indicate that the irreversible structural relaxation by the heat treatment of the first DSC scanning was negligible. The TMA results also support that PI-1 is a less aggregated structure compared to PI-0 and PI-2, resulting in its high solubility in NMP.

### Conclusions

Three kinds of PIs solid with different solubility in NMP were obtained, i.e., the solubilities are 53, 98, and 48% for PI-0, PI-1, and PI-2, respectively. The difference

of the three PIs in solubility was attributed to their different aggregation states. The physical properties of the three solid PIs were examined by DSC and TMA. PI-1 has a larger heat capacity and thermal expansion compared to PI-0 or PI-2. FTIR suggests that the three PIs have the same chemical structure. The results obtained here confirm that PI-1 is a less aggregated structure compared to PI-0 and PI-2, resulting in its high solubility in NMP.

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