

Layer-structured Metallopolymers with Pendant Carbazole Groups

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Organic polymers with spatially ordered functional groups often exhibit enhanced physical properties compared to amorphous polymers with randomly orientated functional groups.¹⁻⁷ Many crystalline and mesophase polymers have been developed in order to achieve supramolecular ordering of functional groups and/or the polymer backbone.¹⁻⁷ For example, a wholly aromatic polyester consisting of a rigid poly(*p*-phenylene terephthalate) (PPT) backbone based on 2,5-disubstituted terephthalic acid and large-sized hole-transporting groups exhibited either layered or nematic-like mesophase structure.⁷⁻¹⁰ The spatial ordering in the mesophase structure has shown excellent photorefractive responses for transmission and reflection grating geometries.⁷⁻¹⁰

We have recently synthesized series of one-dimensional (1D) and three-dimensional (3D) coordinated metallopolymers^{11,12} by using a nonconventional polymerization method, the solvothermal reaction.¹³⁻¹⁵ The metallopolymers synthesized with zinc salts and 2,5-disubstituted terephthalic acid bearing flexible side chains exhibited either layered mesophase or isorecticular metal-organic framework (IRMOF) structures,¹⁶ depending on the lengths and flexibilities of the side chains.¹³⁻¹⁵ However, in metallopolymers synthesized using the solvothermal reaction, the influences of large-sized pendant groups on their mesophase behavior and resulting physical properties have not been fully understood yet.

Here we report on the design and synthesis of a series of mesophase metallopolymers with pendant groups. New metallopolymers were synthesized using the solvothermal reaction of zinc nitrate and 2,5-disubstituted terephthalic acids bearing oxyalkyl-9*H*-carbazole groups with various length of alkyl spacers (see Figure 1(a)). Despite the large size of the pendant carbazole groups, the metallopolymers exhibit layer-structured mesophase, and their layer distances and glass transition temperatures vary systematically with the length of the oxyalkyl spacers. The layer distances of the metallopolymers with oxyalkyl-9*H*-carbazole groups are larger than those of previously reported wholly aromatic polyesters with identical oxyalkyl-9*H*-carbazole groups.

In order to investigate the influence of large-sized pendant groups on the mesophase characteristics in metallopolymers, a carbazole (CZ) group was introduced into the terephthalic acid. The chemical structure of the organic linkers, CZ*m*-acid bearing oxyalkyl-9*H*-carbazole groups, is shown in

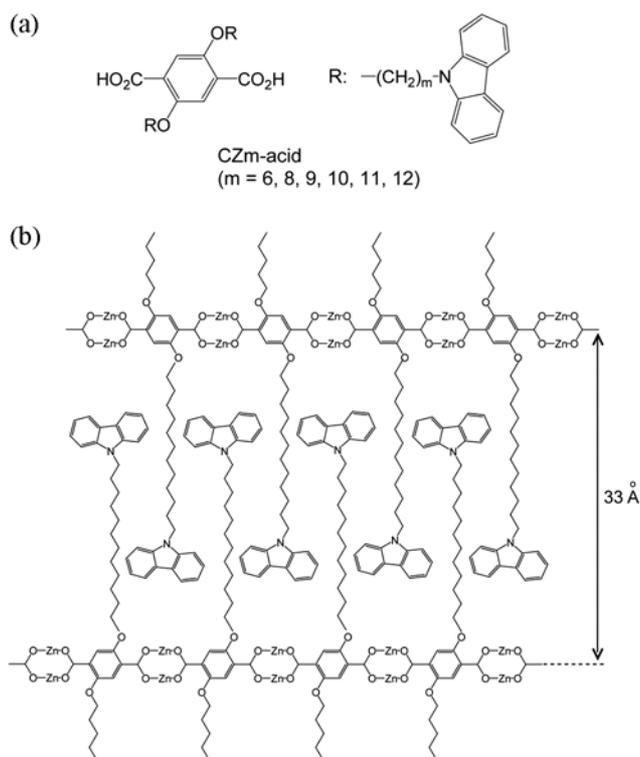


Figure 1. (a) Chemical structures of 2,5-disubstituted terephthalic acid derivatives, CZ*m*-acid. (b) Schematic illustration of layered mesophase structure of ZnCZ12 metallopolymers.

Figure 1(a). The carbazole groups are linked by oxyalkyl spacers ($m = 6, 8, 9, 10, 11,$ and 12), where m is the number of methylene units in the flexible oxyalkyl chains. New ZnCZ*m* metallopolymers were synthesized using a solvothermal reaction of zinc nitrate and CZ*m*-acid. In the newly synthesized ZnCZ*m* metallopolymers, the coordination between zinc metal and carboxylate groups (see Figure 1(b)) was determined using thermogravimetric analysis (TGA) from the amount of ZnO ash remaining after combustion at high temperature (> 500 °C) under a mixture of O₂ and air. In infrared (IR) absorption spectra, the vibrational peaks of carboxylate are also shifted to lower wavenumbers due to the metal-carboxylate coordination.^{13,14}

Figures 2(a) and 2(b) show the powder X-ray diffraction patterns of ZnCZ*m* metallopolymers bearing oxyalkyl-9*H*-carbazole groups. Despite the large size of the pendant carbazole groups, all ZnCZ*m* metallopolymers exhibited layered mesophase structures. The X-ray diffraction peaks in

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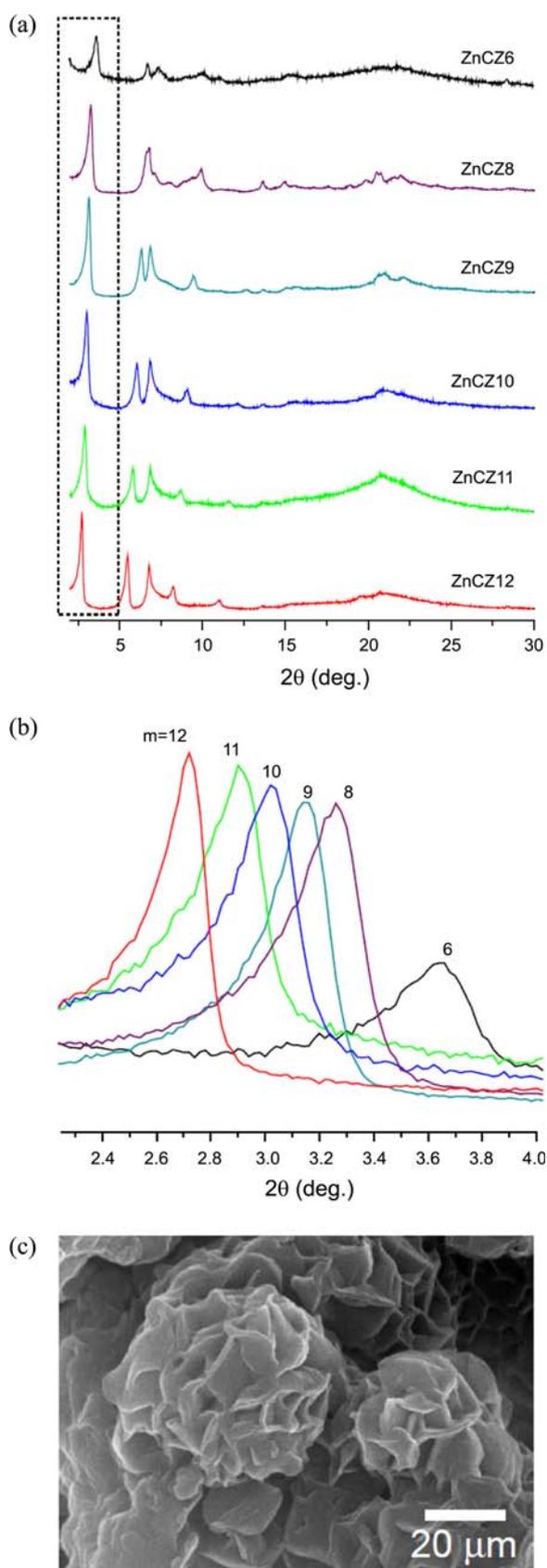


Figure 2. (a) Powder X-ray diffraction patterns of ZnCZ m metallopolymers. (b) Powder X-ray diffraction patterns of the area framed in Figure 2(a). (c) SEM image of ZnCZ12.

the area framed in Figure 2(a) ($2\theta = 2.0\text{--}4.0^\circ$) are corresponding to the layer distance of ZnCZ m metallopolymers and their high ordered diffraction peaks are observed; for example, ZnCZ12 with a layer distance of 33 Å ($2\theta = 2.7^\circ$) shows high ordered diffraction peaks at $2\theta = 5.4, 8.2, 10.9$ and 13.6° . Moreover, all ZnCZ m metallopolymers show a diffraction peak at $2\theta \approx 6.8^\circ$ as similarly in analogous metallopolymers bearing oxyalkyl groups.¹³ Figure 1(b) shows a schematic illustration of the layered mesophase of ZnCZ12 metallopolymer. A scanning electron microscope (SEM) image of ZnCZ12 shows the typical morphology of a layered mesophase structure in metallopolymers (see Figure 2(c)). As shown in Figure 2(b), the X-ray diffraction peaks corresponding to the layer distance shift to lower angles as the length of the oxyalkyl spacers increases. It is noted that the layer distance of ZnCZ m increases with increasing oxyalkyl spacer lengths.

The layer distance of the ZnCZ m metallopolymers bearing oxyalkyl-9H-carbazole groups is larger than that of metallopolymers bearing only oxyalkyl groups reported previously.¹³ For example, the layer distance is 33 Å for ZnCZ12 and 29 Å for ZnCZ10, while it is 23 Å and 20 Å for analogous metallopolymers bearing only oxydodecyl groups ($m = 12$) and oxydecyl groups ($m = 10$), respectively.¹³ The difference (about 10 Å) in the layer distance between the ZnCZ m bearing oxyalkyl-9H-carbazole groups and metallopolymers bearing oxyalkyl groups with the same number of methylene units is larger than the size of CZ groups (< 3 Å). This result is attributed to the fact that the packing of CZ groups in the layered structure provide more steric hindrance to the metallopolymer backbone than the packing of alkyl chains.

Figure 3 shows the layer distances and glass transition temperatures of ZnCZ m metallopolymers. For comparison, those of analogous polyesters bearing identical oxyalkyl-9H-carbazole groups synthesized by conventional condensation polymerization with CZ m -acid and hydroquinone, obtained from Ref. [7], are also shown in Figure 3. These analogous polyesters, called PPT-CZ m , consist of rigid wholly aromatic poly(*p*-phenyleneterephthalate) (PPT) backbones and flexible oxyalkyl-9H-carbazole groups and exhibit a layered mesophase structure.⁷ As shown in Figure 3(a), the layer distances of the ZnCZ m metallopolymers increase with increasing oxyalkyl spacer lengths, and the layer distances are larger than those of the PPT-CZ m analogues with identical side chains. The bigger spaces between the polymer backbones in the layered structure may allow a larger amount of guest molecules to be present in polymeric composites, which is an advantage for achieving a high concentration of guest molecules.^{7,8}

In addition, compared to those of PPT-CZ m polyester,⁸ the X-ray diffraction peaks of ZnCZ m are much sharper and larger (see Figure 2(a)). It is noted that the ZnCZ m metallopolymers exhibit better crystalline perfection and a higher degree of crystallinity (*i.e.*, better spatial ordering of functional groups).

While conventional polymers with flexible polymer back-

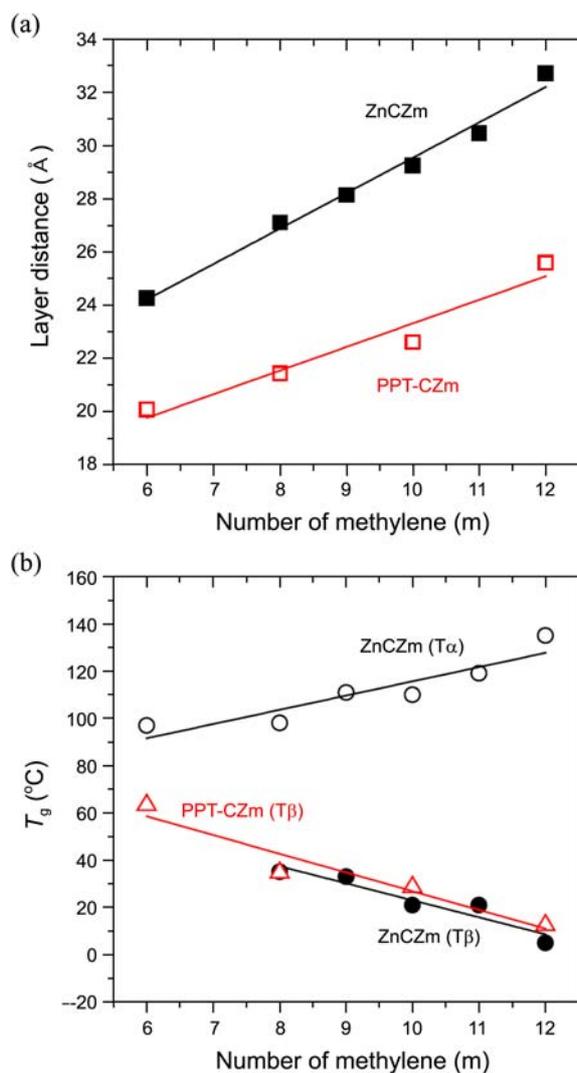


Figure 3. (a) Layer distances and (b) glass transition temperatures of ZnCZm and PPT-CZm, obtained from Ref. [7], as a function of the number of methylene units.

bones exhibit only one glass transition temperature T_g , polymers with rigid polymer backbones and flexible side chains often exhibit two glass transition temperatures, the α glass transition temperature T_α and the β glass transition temperature T_β , which correspond to the motions of the rigid backbone and the flexible side chains, respectively.^{17,18} Figure 3(b) shows the glass transition temperatures of ZnCZm metallopolymers and PPT-CZm polymers.⁷ As the length of the alkyl spacers in ZnCZm increases, the α glass transition temperature T_α increases, while the β glass transition temperature T_β decreases. Interestingly, despite the better crystallinity of the ZnCZm metallopolymers compared to the PPT-CZm polymers discussed above, the β glass transition temperature T_β is practically identical in both polymers. It is noted that the β glass transition temperature T_β results solely from motion of the flexible oxyalkyl-9H-carbazole groups. Such polymeric systems with two glass transition temperatures are very useful for preparing highly stable polymeric composites, because a low β glass transi-

tion temperature T_β allows for high mobility of guest molecules, while a high α glass transition temperature T_α provides temporal stability of the composites without phase separation of the guest molecules.⁷ These newly synthesized ZnCZm metallopolymers maintain the advantages of the PPT-CZm polymers, in that they form a layered mesophase and have two glass transition temperatures, but they also show better crystalline perfection and have a higher degree of crystallinity at a larger layer distance.

In summary, we have reported on the design and synthesis of a series of mesophase metallopolymers, ZnCZm. The metallopolymers ZnCZm were synthesized using the solvothermal reaction of zinc nitrate and CZm-acid bearing oxyalkyl-9H-carbazole groups. Despite the large size of the pendant carbazole groups at the end of the alkyl spacers, the ZnCZm metallopolymers exhibit a layered mesophase structure. Their layer distances and glass transition temperatures vary systematically with the length of the oxyalkyl spacers. The layer distances of the ZnCZm metallopolymers with oxyalkyl-9H-carbazole groups are larger than those of the previously reported wholly aromatic polyesters, PPT-CZm, with identical oxyalkyl-9H-carbazole groups. Moreover, the ZnCZm metallopolymers had better quality and a higher degree of crystallinity than their PPT-CZm analogues.

Experimental Section

The monomers, CZm-acids bearing oxyalkyl-9H-carbazole groups with different alkyl spacers ($m = 6, 8, 9, 10, 11$, and 12) were synthesized according to the literature.⁷ The ZnCZm metallopolymers were synthesized using the solvothermal reaction of 2,5-disubstituted terephthalic acid, CZm-acid and zinc nitrate.^{13,14} For synthesis of ZnCZ12, CZ12-acid (0.25 mmol, 0.2163 g) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.5 mmol, 0.1487 g) were added to 8 mL of DEF in a capped vial and heated to 80 °C for 3 days. The final solid product was filtered and washed with DEF and acetone. DEF can be replaced by cheaper DMF solvent to produce the same product. The metallopolymers ZnCZ6, ZnCZ8, ZnCZ9, ZnCZ10, and ZnCZ11 were obtained in a similar synthetic manner to that used for the ZnCZ12 metallopolymer.

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