

Mechanism of Organogel Formation from Mixed-Ligand Silver (I) Carboxylates

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Ag(I) carboxylate gelators with mixed-ligands were systemically investigated to understand the mechanism of the organic gel formation. The gelators constructed 3-D networks of nanometer-sized thin fibers which facilitated gel formation in various aromatic organic solvents, even at very low concentrations. The loss of reflection peaks in the X-ray diffraction data indicated the reduction of strong interactions between the long alkyl chains as the Ag(I) carboxylates formed gels by maximizing their interactions with the organic solvents. The gelation temperature (T_{gel}) was measured to explore the interaction between the gelator molecules and solvents depending on their composition and concentration. Based on the gelation phenomena, a dissociation/re-association mechanism was proposed.

Key Words : Gel, Coordination polymer, Solubility, Gel transition temperature

Introduction

It is of great importance to understand the thermodynamics of polymer-solvent systems, because the competitive interactions between polymer-polymer and polymer-solvent determine the conformations of polymer chains in solution affecting their physical and chemical properties. The interactions of polymer chains in solvents have been intensively studied based on the well-known Flory-Huggins theory of polymer solution.¹⁻⁵ Modifying the structure and chemical nature of the side chains has been a typical approach to alter the interactions of polymer chains especially in the areas of organic polymers.

On the other hand, coordination polymers, in which the repeating units are coordination complexes, have been less studied in their interaction with solvent compared to typical organic polymers. The poor solubility of the polymer chains in common solvent makes it difficult to study the interaction between coordination polymer and solvent.⁶⁻⁹ Up to now, only few soluble coordination polymers have been synthesized through the introduction of bulky substituent on the backbone, with adamant or dendron side chains, to prevent chain aggregation and improve polymer-solvent interactions.¹⁰⁻¹³ The conformations and self-assembly of soluble coordination polymers are greatly influenced by the properties of the bulky side-chains, solvent polarity and temperature.

Recently, the importance of coordination polymers have been emphasized due to their versatile intriguing architectures and topologies, and the potential applications in, for example, magnetism, sensing, and biomimetic materials.¹⁴⁻¹⁷ Further understanding of coordination polymers can come from systematic study of their interactions with solvents which could affect their chain architecture. For this, it is

important to choose a model system of simpler composition and structure than the abovementioned soluble coordination polymers.

Ag(I) carboxylates, so-called silver soaps, have been used in thermographic and photothermographic imaging for several decades and are good candidates for coordination polymer-solvent interaction studies.¹⁸⁻²¹ Ag(I) carboxylates have well-defined crystalline structures, composed of layers of polymeric silver carboxylate.²²⁻²⁶ (Figure 1(a)) These structures arise from the strong interactions of regularly-oriented, long alkyl chains, which give poor solubility of Ag(I) carboxylates in most non-coordinating solvents at

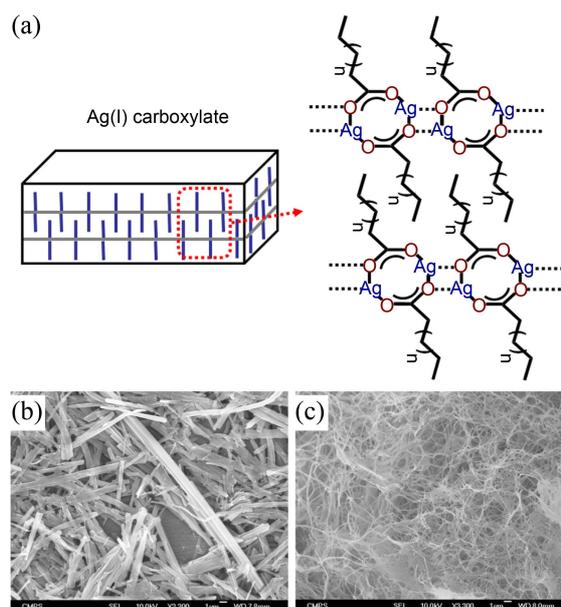


Figure 1. Crystalline structure (a) and SEM images of Ag16 (b) and the xerogel of Ag16/Ag6 (c).

ambient temperature.²⁷⁻²⁹ Previously, we investigated the polymer-solvent interactions of Ag(I) carboxylates through a mixture of different chain length carboxylates.³⁰ Mixtures of Ag(I) hexanoate and Ag(I) palmitate in toluene formed organic gels at substantially diluted concentrations. The mixed-ligands reduced the interactions between side chains and increased polymer-solvent interactions by breaking the surface regularity of the Ag(I) carboxylate polymeric chains.

In this paper, we report a systematic investigation of the mixed-ligand effect on the polymer-solvent interactions of coordination polymers in terms of their gelation properties. Influences of composition, concentration and molar ratios of the Ag(I) carboxylates mixtures in various solvents were analyzed by measuring the morphologies, crystallinities and gel-sol transition temperatures (T_{gel}). A mechanism of gel formation is proposed and used to explain the gels' unique thermal stabilities.

Experimental Section

Chemicals and Methods. AgNO₃ (99.9%), hexanoic acid (99%), octanoic acid (98%), decanoic acid (98%), dodecanoic acid (99%), myristic acid (99%), and palmitic acid (95%) were purchased from Sigma-Aldrich and used as received. The morphologies of xerogels were characterized by scanning electron microscopy (SEM) (JEOL JSM 7401F, Japan). Powder XRD data were collected at room temperature in the angular range of $2.5^\circ \leq 2\theta \leq 30^\circ$ with step width of 0.016671° and a total measurement time duration of 1 hour on a Bragg-Brentano diffractometer (Bruker-AXS Advance D8) with a Cu X-ray tube ($\lambda = 1.5406 \text{ \AA}$).

Synthesis of Ag(I) Carboxylate. Ag(I) hexanoate (Ag6), Ag(I) octanoate (Ag8), Ag(I) decanoate (Ag10), Ag(I) dodecanoate (Ag12), Ag(I) myristate (Ag14) and Ag(I) palmitate (Ag16) were synthesized from elsewhere-described reactions between sodium carboxylate and AgNO₃.³¹ Briefly, 1 equiv. of the corresponding carboxylic acid was dissolved in aqueous NaOH at 80 °C. 1 equiv. of aqueous AgNO₃ (10 mL, 2.5 M) was added drop-wise to the carboxylate solution under vigorous stirring. White precipitate was filtered and washed twice with de-ionized water and dried under reduced pressure.

Gel Formation and T_{gel} Measurements. Two Ag(I) carboxylates of different chain length were added to small vials containing various organic solvents. Samples were capped and sonicated for several minutes, followed by heating at 130 °C until the white solid dissolved. Solutions were then cooled in ice baths and stored at room temperature. Gelling was confirmed by the inverted test tube method. T_{gel} was found by the falling ball method.^{32,33} Shortly, a glass bead ($d = 4.0 \pm 0.3 \text{ mm}$ and density = 1.5 g/cm^3) was placed on the gel in a test tube ($d = 10 \text{ mm}$). The test tube was heated in an oil bath at 1 °C increments. The distance the glass bead fell during 2 min was measured at each temperature. T_{gel} was assumed as the temperature at which the glass bead abruptly dropped to the bottom of the test tube.

Results and Discussion

Morphology and Crystalline Structure of the Gel. The competitive interactions between polymer-polymer and polymer-solvent would determine the behavior of the polymer chains in a solvent. Ag(I) carboxylate could not be fully dissolved in toluene and formed a turbid suspension. However, a mixture of Ag16 and Ag6 (Ag16/Ag6) produced a transparent gel in toluene, as previously reported.³⁰ This great change of solubility with single and mixed-ligand Ag(I) carboxylates indicates great differences of polymer-polymer and polymer-solvent interactions. These interactions were compared through investigation of the morphological and crystalline structures of the typical and mixed Ag(I) carboxylates.

The SEM image of Ag16 shows a sub-micro sized wire structure (Figure 1(b)). In contrast, the Ag16/Ag6 xerogel freeze-dried from toluene gel clearly exhibits 3-D networks of interlocked nanometer-sized thin fibers (Figure 1(c)). The morphological change from micro-wire to nano-sized strands is possibly imputable to the destruction of the regular Ag(I) carboxylate crystalline structure; the regularity of the polymer's side chain determines its degree of crystallinity, and further greatly influences its solubility.

The structural information of the single and mixed Ag(I) carboxylates was explored based on X-ray diffraction data. The XRD curves of Ag16, Ag14, Ag10 and Ag6 differed much from those of xerogels from Ag16/Ag14, Ag16/Ag10 and Ag16/Ag6 (Figure 2). The XRD patterns of Ag16, Ag14, Ag10 and Ag6 show well-developed intense ($0k0$) reflection peaks attributable to the regularly stacked Ag(I) carboxylate layers. The average interlayer spacings calculated from the Bragg equation (eq. 1) were 4.40 nm, 3.91 nm, 2.96 nm and 1.97 nm, respectively, slightly smaller than the twice length of the corresponding carboxylate chain. This may arise from the interdigitation of alkyl chains of neighboring layers,

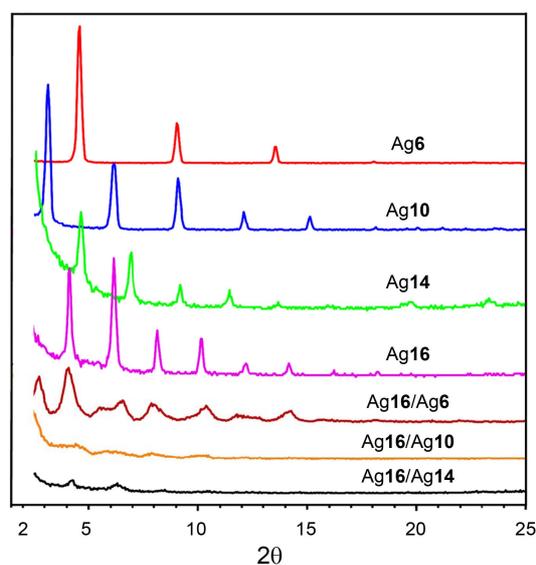


Figure 2. XRD patterns of Ag6, Ag10, Ag14, Ag16, Ag16/Ag6, Ag16/Ag10 and Ag16/Ag14.

implying strong interaction between polymer chains.^{25,26} Crystalline domain sizes calculated from the Scherrer formula (eq. 2) of the (010) peak were 127 nm, 41 nm, 88 nm and 127 nm, respectively, indicating that the Ag(I) carboxylates had crystalline domains much larger than their unit cells. However, the Ag16/Ag14 and Ag16/Ag10 xerogels did not have the intense reflection peaks that the single Ag(I) carboxylates had, indicating the break down of the regular crystalline structure. Most of reflection peaks were too weak to calculate crystalline domains. Ag16/Ag6 showed several broad reflection peaks, much broader than those of Ag16 or Ag6, but sharper than those of Ag16/Ag14 and Ag16/Ag10. Interestingly, the XRD pattern of Ag16/Ag6 cannot be attributed to a simple mixing of Ag16 and Ag6.

$$2d\sin\theta = n\lambda \quad (1)$$

where d is the average interlayer spacing, $n = k$, λ is the wavelength of the X-rays (1.5406 Å for CuK α radiation), and θ is the peak position.

$$\text{domain size} = \lambda/(\beta\cos\theta) \quad (2)$$

where, β is the half-width of the (010) peak in radians.

The SEM and XRD data on the single and mixed-ligand Ag(I) carboxylates suggest severe changes of morphology and crystallinity which arise from different polymer segments interactions. The polymer-polymer interactions in the mixed-ligand Ag(I) carboxylates were greatly reduced by the loss of regularity in the side chains. Without strong interlayer interactions, the coordination polymer became single chains, resulting in a great increase in polymer-solvent interactions. These strong polymer-solvent interactions constructed a 3D-network that could immobilize a sufficiency organic solvent to form a gel: the organic gel contained as little as 0.2% mixed-ligand Ag(I) carboxylates polymer.³⁰

Gel-formation in Diverse Solvents. Gels came about from the reduction of polymer-polymer interactions and the increase of polymer-solvent interactions. Therefore gelation highly depends on the solvent. The solvent interactions of organic polymer chains can be expressed by the polymer-solvent interaction parameter, χ , originally introduced in Flory-Huggins theory.¹⁻⁵ It can be estimated by the equilibrium swelling ratio of the cross linked polymer gel.⁴ Based on few previous studies about this parameter for coordination polymers, it depends on the complex interactions of the coordination polymer chain with the solvent, which not only depend on the conformations of the back-bones and side chains but also the coordination interaction between the metal centers and solvent.

Such interactions between gelator and solvent were investigated, with gelation of various organic solutions of 0.5 wt % 1:1 molar ratio Ag16/Ag6 being monitored (Table 1). Only aromatic solvents, such as toluene, benzene, xylene and chlorobenzene generated the clear gels indicative of maximized polymer-solvent interactions. The solubility of silver soaps in aromatic solvents has been reported to increase rapidly at high temperature due to the occurrence of

Table 1. Gelation properties of 0.5 wt % 1:1 molar ratio Ag16/Ag6 solutions

Solvents	Appearance ^a (T _{gel})	NP ^b
benzene	CG (77 °C)	X
toluene	CG (89 °C)	X
xylene	CG (87 °C)	X
chlorobenzene	CG	O
<i>n</i> -octane	P	X
<i>n</i> -dodecane	PG	X
THF	PG	X
CCl ₄	P	X
CHCl ₃	PG	O
DMF	P	O
butanol	P	O
isopropyl alcohol	P	O
DMSO	TG	O

^aCG, clear gel; P, precipitate; PG, partial gel; TG, turbid gel. ^bNP means the formation of nanoparticles.

Ag(I)- π interactions.^{28,29} These strong interactions between mixed-ligand silver soaps and aromatic solvents swelled the soaps sufficiently to generate clear gels. In contrast, gels were not formed in hydrocarbons and other organic solvents such as THF and CCl₄, with only partial gels (*n*-dodecane, THF) or precipitations (*n*-octane, CCl₄) being produced. The occurrence of partial gels with much lower equilibrium swelling ratios than the clear gels, likely results from weak polymer-solvent interaction. *n*-Octane and CCl₄ had insufficient interaction with the inorganic polymer to create a gel and so merely formed precipitates.

The Ag(I) carboxylates in alcoholic solvents heated to 130 °C became yellow, indicating the formation of Ag nanoparticles rather than gel: the origin of the yellow color (ca. 420 nm) is assigned to the surface plasmon peak of Ag nanoparticles.³⁴ It has been often reported that Ag nanoparticles have been obtained through the decomposition of Ag(I) complexes in the presence of reductants such as triethylamine.³⁵⁻³⁸ They have also been observed in some other solvents, such as DMSO, CHCl₃ and DMF. Chlorobenzene, with both aromatic and reducing properties, formed a yellowish, clear gel indicating the production of Ag nanoparticles within the gel.

These results show that mixed-ligand Ag(I) carboxylates can generate clear solutions upon heating with subsequent gel formation during cooling only in the solvents with π -electrons. The strong interaction between Ag(I) carboxylate and an organic solvent, capable of Ag(I)- interaction without reducing it, is responsible for the gel formation.

Thermal Stability of the Gel. Gels' thermal stabilities reflect the strength of the thermodynamic interaction between polymer and solvent. Therefore, it is worthwhile to study the gels' thermal stabilities by monitoring their destruction with temperature. T_{gel} is defined as the temperature at which gel breaks down and was measured by finding the temperature at which a floated ball could fall through the solution. T_{gel} of mixed-ligand Ag(I) carboxylates in toluene

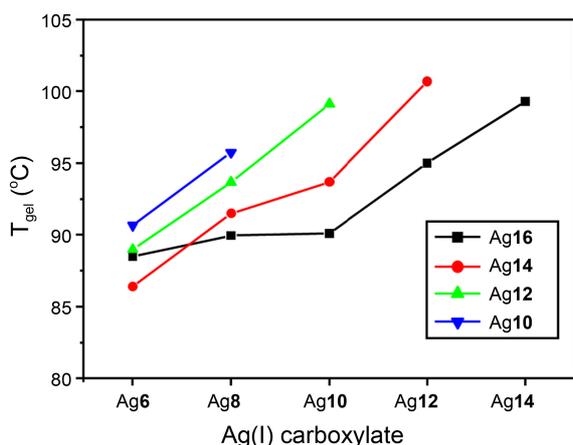


Figure 3. Relationship between the T_{gel} and chain length of carboxylate ligand.

was systemically analyzed with respect to composition and concentration.

The relationship between T_{gel} and chain length of mixed-ligand Ag(I) carboxylates is shown in Figure 3. The T_{gel} of Ag14/Ag12 (100 °C) was the highest followed by Ag16/Ag14 (99 °C), compared with the one of Ag14/Ag6 having the lowest (86 °C). T_{gel} appears to be influenced less by absolute chain length than by the length difference of the carboxylates. For example, the mixtures of Ag16/Ag14, Ag14/Ag12 and Ag12/Ag10 with two carbon atoms difference had similar T_{gel} (at ca. 99 °C), as did other similarly matched pairs, the mixtures of Ag16/Ag12, Ag14/Ag10 and Ag12/Ag8 with four carbon atoms difference let the ball fall at 95, 94 and 94 °C, respectively. When the difference exceeded six carbon atoms, T_{gel} was in the range of 87 to 91 °C. The short chain lengths, e.g. Ag8/Ag6, produced mixtures barely soluble in hot toluene, with only partial gel being produced, implying higher interaction between the polymer chains than between the polymer and solvent. So, the precise measurement of T_{gel} was difficult and the data wasn't included in Figure 3.

The influence of gelator concentration on T_{gel} is shown in Figure 4. The T_{gel} of Ag16/Ag14 increased slightly from 99 °C to 102 °C, when its concentration increased from 0.5 wt % to 2.0 wt %, indicating that the gelator concentration only slightly affected the melting of the gel. Ag16/Ag6 showed a similar trend, but at lower temperatures. It clearly indicates that T_{gel} was affected more by chain length disparity rather than gelator concentration.

T_{gel} was measured of Ag16/Ag14 and Ag16/Ag6 with the carboxylates at various molar ratios (Figure 5). Interestingly, Ag16/Ag14 had largely similar T_{gel} for molar ratios between 1:2 and 4:1, and decreased slightly only when Ag14 content was very high (1:3). In contrast, T_{gel} of Ag16/Ag6 increased continually with increasing Ag16 content. When Ag6 content was high, i.e. Ag16/Ag6 molar ratio of 1:1.5, only a turbid gel was obtained and the precise measurement of T_{gel} became difficult. Detailed discussion of the gels' thermal stabilities, including effect of molar ratio follows.

Gelation Mechanism. Low molecular weight gelators

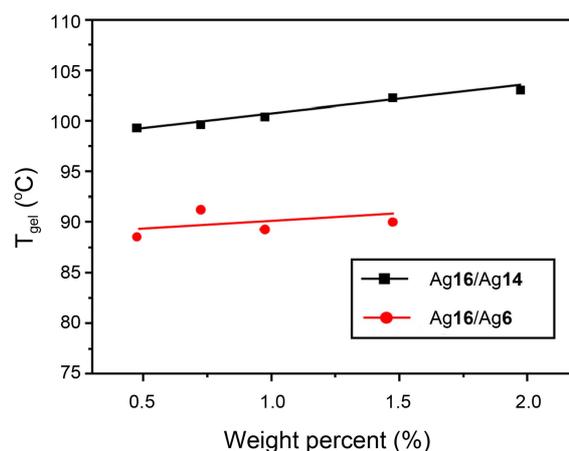


Figure 4. Relationship between the T_{gel} and weight percent of Ag16/Ag14 and Ag16/Ag6.

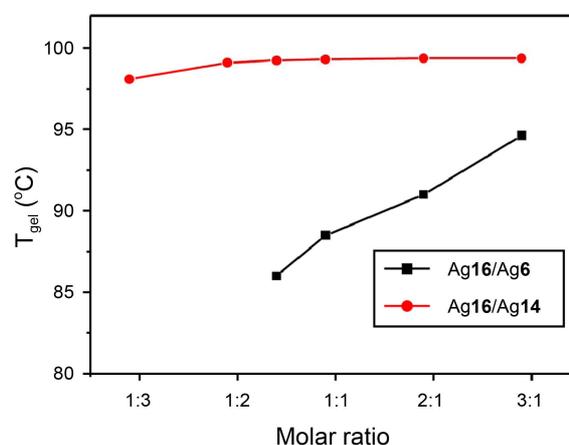
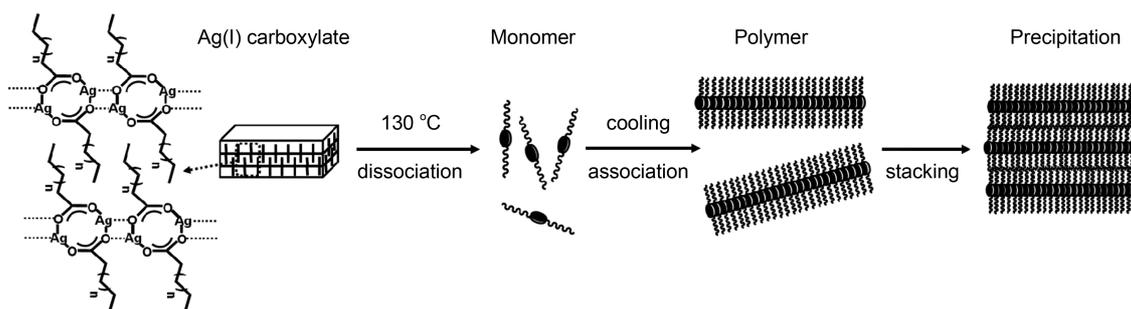


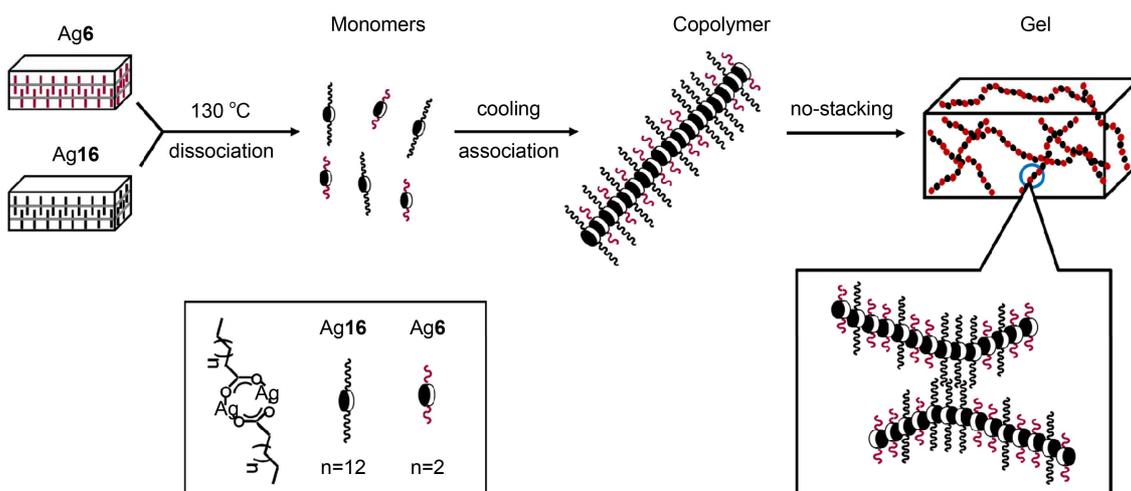
Figure 5. The influence of the molar ratio of Ag16/Ag14 and Ag16/Ag6 on T_{gel} .

generally form gels through their self-assembly.³⁹⁻⁴⁸ They self-assemble into high aspect ratio superstructures through van der Waal's interactions, coordination, hydrogen bonding, and π - π interactions, forming a 3-D network. In contrast, the mixed-ligand Ag(I) carboxylates formed gels in organic solvents through de-assembly. The introduction of the second carboxylate ligand broke the regular structure of the Ag(I) carboxylate, reducing the strong interactions between ligands. Tightly stacked Ag(I) carboxylate coordination polymer precipitates were split into individual chains which then constructed a 3-D network. This unique gelation mechanism might be responsible for the gels' exceptional thermal stabilities. A gelation mechanism is proposed which could explain the phenomena observed here.

Ag(I) carboxylate coordination polymers are dynamic; their morphologies change upon heat treatment in toluene, as previously reported.³⁰ This is the result of the polymer's dissociation into dimeric units, $[\text{Ag}_2(\text{carboxylate})_2]$, which can re-associate to polymeric chains upon cooling. The polymers are stacked in multilayered structures through the strong interaction of the carboxylate ligands, resulting in sub micron-sized units that precipitate from solution (Scheme 1).



Scheme 1. Dissociation and re-association of Ag16.

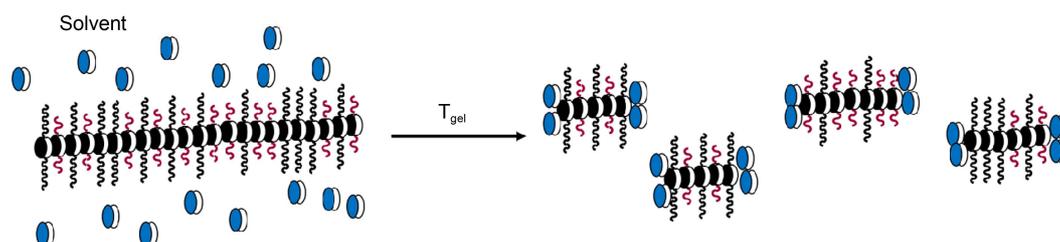


Scheme 2. Gelation of Ag16/Ag6.

In mixtures of Ag(I) carboxylates of different chain lengths, two kinds of dimeric units, $[\text{Ag}_2 (\text{long chain carboxylate})_2]$ and $[\text{Ag}_2 (\text{short chain carboxylate})_2]$ were produced upon heating. The dimeric units then re-associate into a random copolymer (Scheme 2). Copolymer composition has been confirmed in previous work by differential scanning calorimetry (DSC): copolymers had broad endothermic peaks, whereas homopolymers had sharp ones.³⁰ The disappearance of the sharp peaks in XRD analysis in Figure 2 also supported this conclusion. The random composition of the copolymer hinders the interdigitation of the long alkyl chains of the carboxylate ligands, disturbing copolymers' efficient stacking, resulting in isolated single copolymer chains. The isolated copolymer chains cross-link through their matching parts and create 3-D networks (inset of Scheme 2). Accordingly, the strength of the interaction between the copolymer chains is related to the copolymer's

surface roughness.

The thermal destruction of gels' 3-D networks is also related to the randomness of the side chains. With sufficient polymer-solvent interaction, solvent molecules can intervene in the Ag(I) carboxylate strands breaking them apart (Scheme 3). Therefore, T_{gel} is lowered by greater polymer-solvent interactions. This was confirmed by the tests of T_{gel} that compared chain length difference. The copolymers with small chain length differences, like Ag16/Ag14, Ag14/Ag12, Ag12/Ag10 had a higher T_{gel} than the copolymers composed of chains greatly difference in length. The lower chain length differences lead to weaker interactions of the polymer with the solvent than polymers with large chain length differences. Therefore, roughness of ligand chains, arising from differences of chain length, greatly determines polymer-solvent interactions. The concentration of gelator has negligible effect on T_{gel} as copolymer surface rough-



Scheme 3. Destruction of the mixed ligand Ag(I) carboxylate gel.

ness is independent of concentration. Molar ratio the Ag(I) carboxylates with high chain length differences greatly affect copolymer surface roughness and hence T_{gel} . In contrast, molar ratios of Ag16/Ag14, with small chain length difference and low surface roughness, had only minor effect on T_{gel} .

The compounds synthesized herein are rare examples of organogels from silver complexes.⁴⁹ They open a new avenue for converting non-gelling coordination polymers into efficient gelators by simply changing the properties of the side chains. The morphologies and conformations of silver soaps in solution can be greatly influenced by modifying the interaction of the coordination polymer chains and solvent. This could also be useful in work with other coordination polymers.

Conclusion

Gelling and its detailed mechanism were investigated for Ag(I) carboxylate gelators with mixed ligands. Gels formed in aromatic organic solvents, such as benzene, toluene, xylene and chlorobenzene, whereas only partial gels were obtained from aliphatic solvents. Ag nanoparticles were produced in organic solvents that could reduce the Ag(I) carboxylate. SEM and XRD analyses of xerogels showed that the gels were composed of 3-D networks of nanometer-sized thin fibers that resulted from the weakening of the strong interactions between the long alkyl chains of the carboxylate ligands. T_{gel} was greatly influenced by ligands' chain length difference, whereas concentration of gelator had negligible effect. Molar ratios of the Ag(I) carboxylates also influenced the T_{gel} , although its impact depends on the chain length difference. The unique thermal stabilities of the gels may be related to the copolymers' surface roughness.

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