

## Effect of Temperature on a Lignin-based Polymer with Two Types of Microstructures

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A lignin-based polymer (GCL1-JB) was dispersed in solvents with different proportion between 1,4 dioxane and water for forming linear and spherical microstructures. The effects of temperature on the solution behaviors and adsorption characteristics of GCL1-JB with different microstructures were investigated by light scattering, conductivity, zeta potential, UV-Vis spectroscopy, atomic force microscopy (AFM), and contact angle measurements. Results showed that GCL1-JB solutions with different microstructures have different responses to environmental temperature changes, which is related to the movements of charges. For GCL1-JB with a spherical microstructure, as the temperature increases, the degree of ionization does not decrease. However, the surface charges decrease due to the charged groups moving from the surface into the interior because of the charge gradient, which induces a significant decrease in the zeta potential. As the surface charges decrease and the hydrophobic interaction increases, the GCL1-JB aggregates. Therefore, the scattered light intensity increases significantly and the corresponding GCL1-JB adsorbed film has a larger adsorbed amount, a more rough surface, and a larger contact angle. However, for GCL1-JB with a linear microstructure, the surface charges do not obviously change with a temperature increase, even though the charged groups move from side to side. Therefore, the zeta potential and the scattered light intensities of these GCL1-JB solutions are basically independent of temperature, and the corresponding adsorption characteristics do not obviously change.

*Keywords:* Lignin; Microstructure; Temperature effects; Aggregation; Absorption

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### INTRODUCTION

Recently, the effect of temperature on lignin structure was investigated through simulation analysis (Petridis *et al.* 2011). The structure of lignin changes from mobile and extended to glassy and compact states as the temperature is decreased. These simulation results were somehow similar to the behaviors of linear hydrophobic polyelectrolytes (Essafy *et al.* 2011). The linear hydrophobic polyelectrolyte tends to extend at a higher temperature, whereas the linear hydrophilic polyelectrolyte is independent of temperature (Essafy *et al.* 2011). However, lignosulfonates exhibit a spherical structure (Rezanowich and Goring 1960), which may be altered by temperature changes and may be different from those of conventional linear polyelectrolytes. Lignosulfonate in a 0.1 M NaCl aqueous solution loses charges at 40 °C due to its

compact spherical conformation (Kontturi *et al.* 1991, 1992a; Mafé *et al.* 1995). Similar behavior was also observed in the study of cytochrome *c*, another spherical polyelectrolyte, which supported the conclusion that the loss of charge takes place only when the molecule behaves like a compact sphere (Kontturi *et al.* 1992b). For comparison, a linear polyelectrolyte having an unwinding coil conformation has no change at this temperature (Kontturi *et al.* 1992a). In our research group, it was found that sodium lignosulfonate (SL) did not extend but aggregated at a higher temperature due to its spherical microgel conformation and hydrophobic interaction (Qian *et al.* 2014). Qian *et al.* (2014) proposed that the effect of temperature on lignin-based polymer only occurred when the structure was a compact sphere rather than a linear molecule. To date, the mechanism of temperature on the microstructure of polyelectrolytes is still unclear.

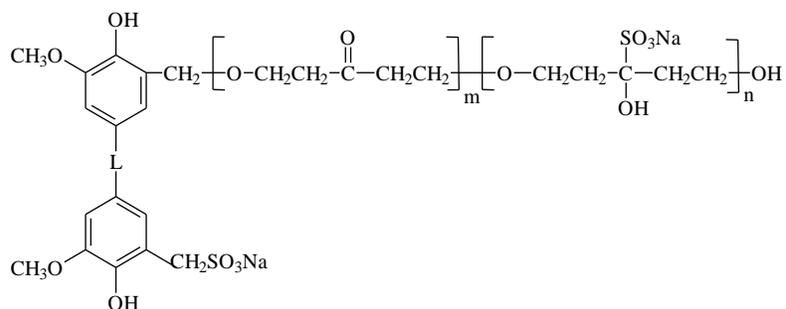
In our previous work, a lignin-based polymer, GCL1-JB, was prepared by graft sulfonation of alkali lignin from the bamboo pulping black liquor obtained from our earlier study (Liu *et al.* 2009). Because of being grafted to carbonyl long aliphatic chains, GCL1-JB has a linear-like molecule structure, which is different from SL with a spherical structure (Deng *et al.* 2012, 2014; Lou *et al.* 2013). Although both GCL1-JB and SL are lignin derivatives, the effect of temperature on GCL1-JB structure is quite different from that of SL structure.

In the current work, the GCL1-JB with a linear-like structure was used to prepare a spherical microstructure by adding a poor solvent to the GCL1-JB aqueous solution. To demonstrate that only spherical microstructure can cause a significant change at an elevated temperature, the effects of temperature on the GCL1-JB with two types of microstructures were investigated by techniques such as laser light scattering (LLS), conductivity, zeta potential, UV-Vis spectroscopy, atomic force microscopy (AFM), and contact-angle measurements. This work clarified the mechanism of temperature effects caused by different microstructures for the first time and provided significant insight into the basic structure of lignin-based polymers.

## EXPERIMENTAL

### Materials

The lignin-based polymer (GCL1-JB) was obtained by graft sulfonation of alkali lignin from the bamboo pulping black liquor as described by Liu *et al.* (2009). The possible structure of GCL1-JB is shown in Fig. 1. GCL1-JB has a weight-averaged molecular weight of 24038Da with a polydispersity of 2.33 (by GPC), and a sulfonate group content of 2.99 mmol/g.



**Fig. 1.** Structural representation of GCL1-JB

Sodium lignosulfonate (SL) was obtained from Shixian Papermaking Co. Ltd. (China). Both GCL1-JB and SL were purified by filtration and ultrafiltration through an ultrafiltration apparatus (Wuxi Membrane Science and Technology Co., China) with a 2500 Dalton cut-off membrane. Poly(diallyldimethylammonium chloride) (PDAC) with molecular weights ( $M_w$ ) from 20,000 to 35,000, (20% solution; Sigma-Aldrich, USA) was diluted to a concentration of 0.1 mmol/L (repeated unit) and was used as a polycation. The 1,4-Dioxane from Lingfeng Chemical Reagent Co. Ltd (China) was of analytical grade. Ultrapure water (electrical resistivity higher than 18  $M\Omega \cdot \text{cm}$ ) was obtained from a water purification system (Millipore Co., USA) and used for all experiments.

## Methods

### *Self-assembled films*

The self-assembled films were fabricated by dipping a quartz slide (4 cm  $\times$  1 cm) alternately into the GCL1-JB and the PDAC solutions. The GCL1-JB solutions were kept at temperature ranging from 10 to 60  $^{\circ}\text{C}$  by the use of a water bath. Prior to deposition, the quartz slides were sonicated in a 98%  $\text{H}_2\text{SO}_4$ / 30%  $\text{H}_2\text{O}_2$  bath (piranha solution) for 1 h, then sonicated in a 25%  $\text{NH}_4\text{OH}$ /30%  $\text{H}_2\text{O}_2$ /  $\text{H}_2\text{O}$  (1:1:5) bath for 1 h, followed by a thorough rinse with ultrapure water, and finally dried with an air stream. The construction of the self-assembled films is described as follows. The quartz slide was first immersed into the PDAC solution for 10 min, rinsed with ultrapure water, dried with air steam, and transferred into GCL1-JB solution for 10 min. After being rinsed by dipping into three beakers with the corresponding solvent for 1 min each and dried with an air steam, the self-assembled films were obtained by repeating the above steps in a cyclic fashion. The GCL1-JB films mentioned in the following section refer to self-assembled 10-layer films, which were prepared by alternately depositing of GCL1-JB and PDAC for 10 cycles.

### *Characterization of films*

Since the characteristic absorbance wavelength of GCL1-JB is 280 nm, and PDAC has no absorption at this wavelength, the self-assembly process of GCL1-JB was monitored by a UV-Vis spectrophotometer (UV-2550; Shimadzu Co., Japan) at  $\lambda_{280\text{nm}}$ . The surface morphological images of self-assembled films were obtained with an atomic

force microscope (Park XE-100, Park Systems Co., South Korea) operating in non-contact mode.

The contact angles of water on the film surfaces were measured with a sessile drop method using a contact angle tester JC2000C1 (Zhongchen Digital Technic Apparatus Co. Ltd., China). The contact angles reported in this paper are static contact angles. A water drop was made on the tip of a syringe and placed on a surface by moving the sample stage vertically until contact was made between the water drop and the surface. An image of the droplet was taken through a CCD camera and enlarged on computer screen. Contact angles were obtained by using the equipped software based on Young-Laplace fitting method. The contact angles reported in this paper are static contact angles. Experimental errors were estimated from the measurements on 10 droplets placed at different sample locations.

The formation process of GCL1-JB with a spherical microstructure was monitored using a ALV/CGS-3 LLS (ALV GmbH, Germany) equipped with a multi- $\tau$  digital time correlator (ALV-7004, ALV, Germany) and a 22-mW Uniphase He-Ne laser (JDS-Uniphase,  $\lambda_0 = 632$  nm). To eliminate the effect of fluorescence emission and polarization, a high performance laser-line bandpass filter (NT47-494) and Glan-Thompson interferometer was placed between the sample solution and the photomultiplier. The scattered light intensities of GCL1-JB dispersions under different temperatures were determined with a detector angle relative to the laser of  $90^\circ$ .

The conductivity (Orion 3-Star, Thermo, USA), pH (PB-10, Sartorius, Germany), and zeta potential (NanoBrook 90Plus, Brookhaven Instruments Co., USA) of GCL1-JB with two types of microstructures and of SL at different temperatures were determined to detect the temperature effect on solution behaviors. Experimental errors were estimated from measurements based on 5 samples.

## RESULTS AND DISCUSSION

### Preparation of GCL1-JB with a Spherical Microstructure

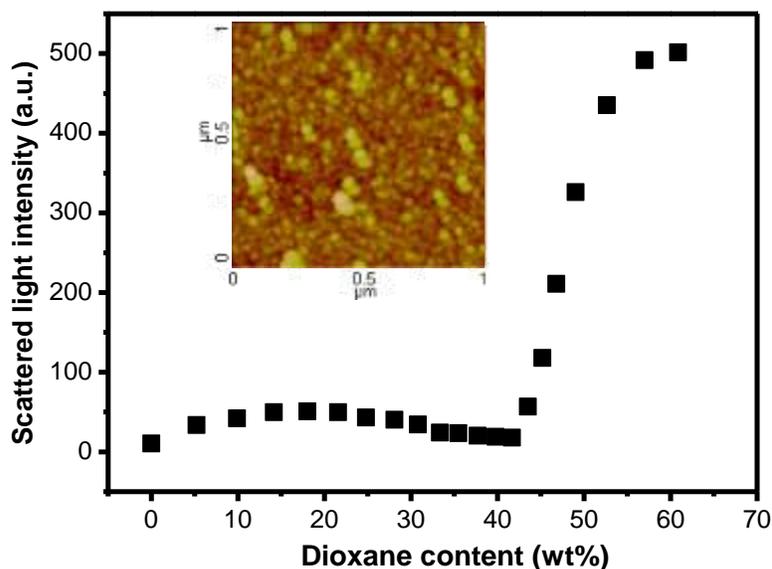
The microstructure of the amphiphilic polymers in solution can be changed by adding selected solvents (Halperin *et al.* 1992). The lignin-based polymer GCL1-JB, which was modified from alkali lignin, is a linear-like amphiphilic polymer that has a number of hydrophilic chains and few hydrophobic phenylpropanoid backbones (Liu *et al.* 2009; Deng *et al.* 2012; Lou *et al.* 2013). Thus, the GCL1-JB is soluble in water and insoluble in organic solvent. Here, two types of GCL1-JB with different microstructures were prepared. One was GCL1-JB dissolved in a good solvent (water), and the GCL1-JB molecules were presented as linear microstructure. The other was GCL1-JB dissolved in water with the addition of a poor solvent (1,4-dioxane), and the GCL1-JB molecules were presented as coiled molecules in spherical aggregate structures. The aggregation process for GCL1-JB was monitored by DLS, and the GCL1-JB with a spherical microstructure was observed by AFM.

Figure 2 shows the scattered light intensity of the GCL1-JB in water/1,4-dioxane dispersion relative to the 1,4-dioxane content. When 1,4-dioxane was gradually added to the GCL1-JB aqueous solution, the GCL1-JB molecules tended to coil. While the 1,4-dioxane content reached a critical value of 43 wt%, the scattered light intensity sharply

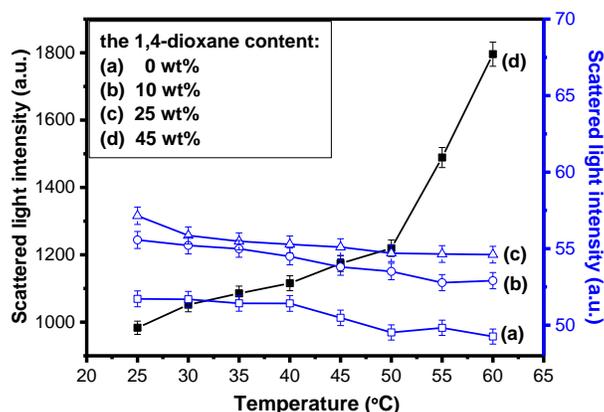
increased to indicate that the GCL1-JB started to form aggregates in the solution. These aggregates are spherical colloids, as shown in Fig. 1 (insert).

Figure 3 shows the scattered light intensities of GCL1-JB in mixed solvents with different 1,4-dioxane content as a function of temperature. The scattered light intensity of GCL1-JB slightly decreased with increasing temperatures when the 1,4-dioxane content was below 43 wt%. However, when the 1,4-dioxane content was above 43 wt%, the scattered light intensity of GCL1-JB increased with elevated temperatures, and the rate increase became faster at temperatures above 50 °C. This observation indicated that only the GCL1-JB with a spherical microstructure became more aggregated with increasing temperature, whereas the GCL1-JB with a linear microstructure did not exhibit this effect.

It was obvious that GCL1-JB with different microstructures had different responses to environmental temperature changes. To further explore this phenomenon, the adsorption behaviors of GCL1-JB with different microstructures at various temperatures were investigated in the following sections. Here, the GCL1-JB in water was selected as the typical sample with a linear microstructure, whereas the GCL1-JB in the water/1,4-dioxane co-solvent with 45 wt% 1,4-dioxane was selected as the typical sample with a spherical microstructure.



**Fig. 2.** Scattered light intensity vs. 1,4-dioxane content of the GCL1-JB in the polymer co-solvent mixture of water and 1,4-dioxane. The initial concentration of GCL1-JB in water was 1.0 g/L. Insert image: AFM image of GCL1-JB when the 1,4-dioxane content was 45 wt%; scan size 5  $\mu\text{m}$   $\times$  5  $\mu\text{m}$

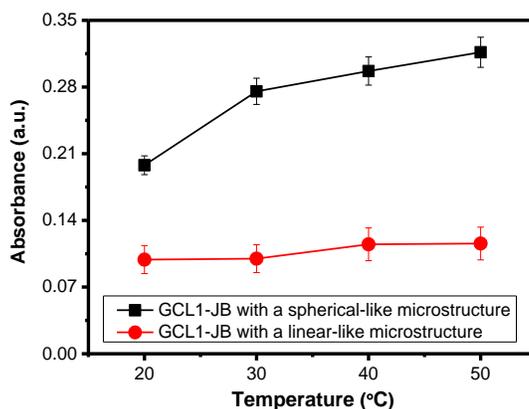


**Fig. 3.** Scattered light intensity vs. temperature of GCL1-JB with different 1,4-dioxane contents in mixture of water and 1,4-dioxane. The vertical axis on the left is for sample (d), and the vertical axis on the right is for sample (a),(b), (c).

### Adsorption Behaviors of GCL1-JB with Different Microstructures

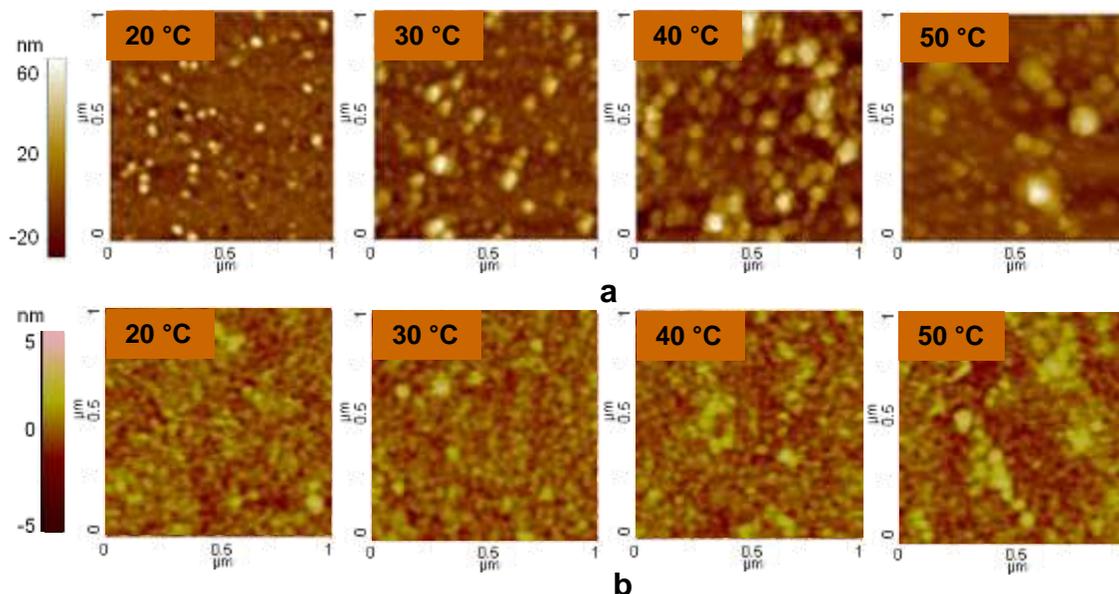
It was hard to accurately detect the temperature effect on the adsorption behavior of GCL1-JB because the GCL1-JB monolayer film is very thin. To investigate the impact of temperature on GCL1-JB with different microstructures, GCL1-JB solutions with different microstructures were used as polyanions to prepare layer-by-layer self-assembled multilayer films with PDAC as a polycation under different temperature conditions.

Temperature plays an important role in the self-assembly (Dubas and Schlenoff 1999). Figure 4 shows the absorbance at  $\lambda_{280\text{nm}}$  of GCL1-JB multilayer films obtained from different microstructures as a function of temperature. Obviously, GCL1-JB film obtained from the spherical microstructure had a larger UV absorbance with increasing temperature, which indicated that it has a larger adsorbed amount. However, the adsorbed amount of the GCL1-JB film obtained from the linear microstructure exhibited no obvious change with temperature.



**Fig. 4.** UV absorbance at  $\lambda_{280\text{nm}}$  vs. temperature for GCL1-JB films obtained from two types of microstructures. Multilayer films were prepared from GCL1-JB with different microstructures at different solution temperatures. The linear microstructures of GCL1-JB were obtained from GCL1-JB dissolved in water; the spherical microstructures of GCL1-JB were obtained from GCL1-JB dissolved in a co-mixture of water and 1,4-dioxane with a 1,4-dioxane content of 45 wt%.

The morphologies of the GCL1-JB films obtained from different microstructures were characterized by AFM, as shown in Fig. 5. When the temperature rose, the surface roughness of the GCL1-JB film obtained from the spherical microstructure increased significantly, whereas the GCL1-JB film obtained from the linear microstructure only increased slightly.



**Fig. 5.** AFM images of GCL1-JB films prepared from (a) GCL1-JB with a spherical microstructure at various temperatures, and (b) GCL1-JB with a linear microstructure at various temperatures; scan size: 1  $\mu\text{m}$   $\times$  1  $\mu\text{m}$

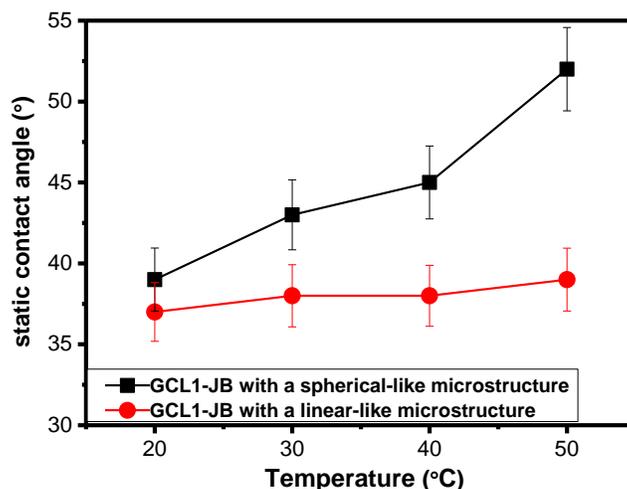
This phenomenon can be explained as follows. Since only GCL1-JB with a spherical microstructure became more aggregated with an increase in temperature, the corresponding GCL1-JB adsorbed film had a larger adsorbed amount and greater surface roughness when increasing the temperature.

**Table 1.** Surface Roughness of GCL1-JB Films Obtained from Two Types of Microstructures at Various Temperatures

GCL1-JB with spherical microstructure		GCL1-JB with linear microstructure	
Temperature ( $^{\circ}\text{C}$ )	Roughness (nm)	Temperature ( $^{\circ}\text{C}$ )	Roughness (nm)
20	5.198	20	0.950
30	15.565	30	0.975
40	16.834	40	1.109
50	22.168	50	1.115

The wettability of GCL1-JB multilayer films with different microstructures as a function of temperatures was estimated by contact angle measurement. As shown in Fig. 6, for the GCL1-JB film obtained from a spherical microstructure, the contact angle increased from  $39^{\circ}$  to  $52^{\circ}$  as the temperature was increased. However, the GCL1-JB film

obtained from a linear microstructure had no obvious change when increasing the temperature. This phenomenon can be explained in this way. Firstly, only GCL1-JB with a spherical microstructure became more aggregated with increasing temperature, and then the corresponding GCL1-JB film had a larger surface roughness at a higher temperature. Secondly, it was reported that the surface wettability of films is related to the roughness and the hydrophilicity of the surface (Cassie and Baxter 1944; Chen *et al.* 1999).

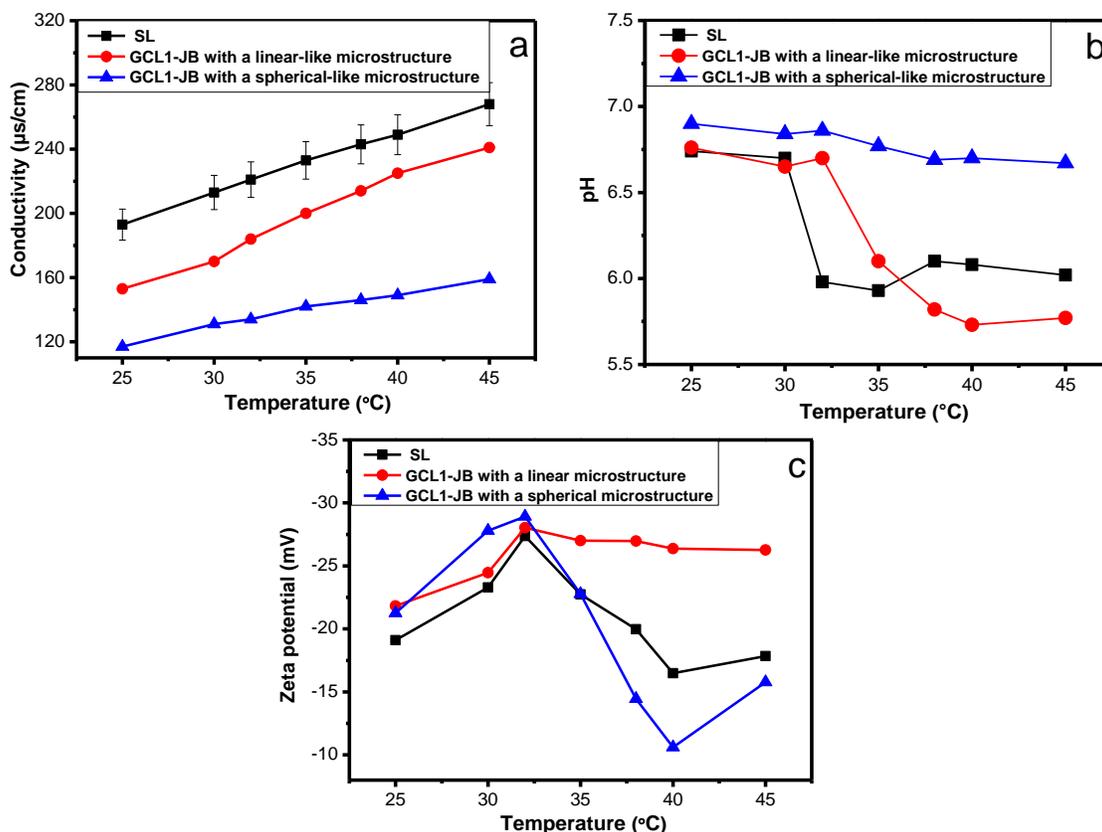


**Fig. 6.** Static contact angle vs. temperature for GCL1-JB films obtained from two types of microstructures. The linear microstructures of GCL1-JB was obtained from GCL1-JB dissolved in water; the spherical microstructures of GCL1-JB was obtained from GCL1-JB dissolved in a co-mixture of water and 1,4-dioxane with a 1,4-dioxane content of 45 wt%.

Usually, the contact angle decreases with increasing surface roughness when the contact angle is less than 90°. Therefore, the increase in the contact angle for the GCL1-JB film obtained from a spherical microstructure was not caused by surface roughness, but by surface hydrophobicity. This observation indicated that only the GCL1-JB with a spherical microstructure became more hydrophobic as the temperature was increased.

### Analysis of Temperature Effects

The GCL1-JB with different microstructures has different responses to environmental temperature changes, but the mechanism is still unknown. As discussed above, when the temperature increased, the GCL1-JB adsorption film obtained from a spherical microstructure had a higher adsorbed amount, a larger surface roughness, and a higher contact angle because it became more aggregated at elevated temperature; however, the GCL1-JB adsorption film obtained from a linear microstructure did not exhibit this behavior.



**Fig. 7.** (a) Conductivity, (b) pH value, and (c) zeta potential of three samples with different microstructures. The three samples are 1.0 g/L sodium lignosulfonate (SL) in water, 1.0 g/L GCL1-JB in water, and 1.0 g/L GCL1-JB in a co-mixture of water and 1,4-dioxane with a 1,4-dioxane content of 45 wt%

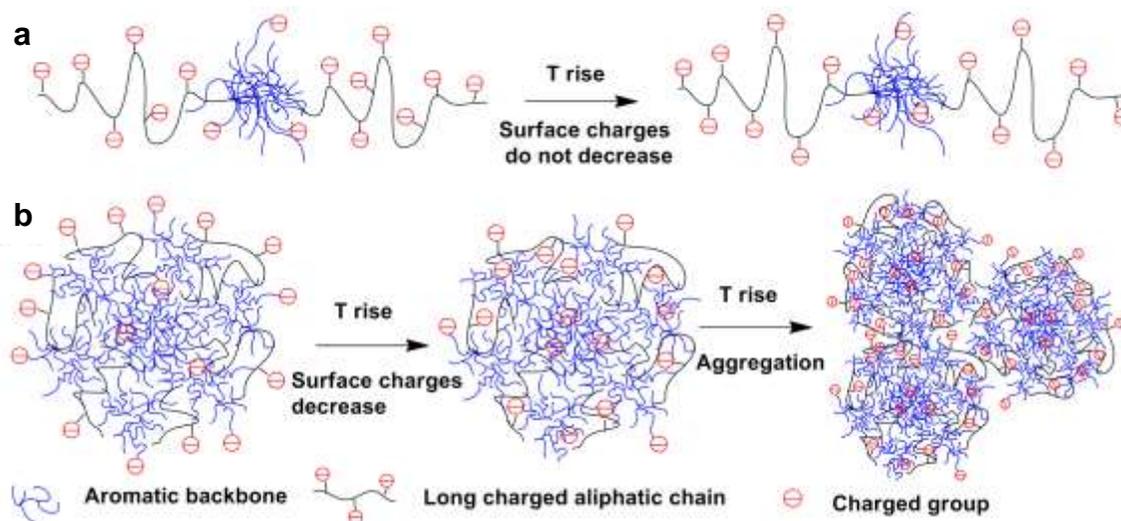
To confirm that the spherical microstructure was the only reason for GCL1-JB to aggregate with increasing temperature, the conductivity, pH value, and zeta potential of GCL1-JB with different microstructures were examined at various temperatures. For comparison, the same characteristics of SL with a spherical structure were examined at various temperatures.

Figure 7a shows the temperature effect on the conductivity of GCL1-JB with the two different microstructures, and of SL. The value of conductivity defines the conductive property of solutions, which is related to the ionic strength. Because the solvents exhibited slight temperature effects, the data in Fig. 6a excluded the temperature effect on solvents. The conductivities of GCL1-JB and SL increased with increasing temperature, indicating that the degrees of ionization of GCL1-JB and SL increased at the higher temperatures. This phenomenon was further confirmed by pH measurement, as shown in Fig. 7b. As the pH of solvents was decreased at the higher temperature, the data in Fig. 7b excluded the temperature effect on solvents. The pH values of all samples tended to decrease at the higher temperatures, suggesting that the  $H^+$  obtained by the ionization of charged groups increased when the temperature was increased.

The zeta potentials of GCL1-JB and SL were measured at various temperatures. As shown in Fig. 7c, when the temperature was increased from 32 to 40 °C, the absolute value of the zeta potential for GCL1-JB with a linear microstructure was nearly constant, whereas that for GCL1-JB with a spherical microstructure suddenly decreased, similar to

that for SL. There were two possibilities that may have caused this observed phenomenon. One was that the degree of ionization of the charged groups declined; the other was that charged groups moved from the surface to the interior because of spherical microstructure. The temperature effects on the conductivity and the pH of GCL1-JB and SL suggested that the degree of ionization of charged groups did not decline with increasing temperature. Therefore, the zeta potential decreased at elevated temperature because the charged groups moved from the surface to the interior because of the spherical microstructure. Above 40 °C, the absolute value of the zeta potential increased slightly due to the adjustment of aggregation and microstructure. However, the zeta potential of GCL1-JB with a linear microstructure did not decrease with increasing temperature.

Temperature effects on the two different microstructures of GCL1-JB are illustrated in Fig. 8.



**Fig. 8.** Scheme for the temperature effects of GCL1-JB with two types of microstructures: (a) GCL1-JB with a linear microstructure was obtained from GCL1-JB dissolved in water; and (b) GCL1-JB with a spherical microstructure was obtained from GCL1-JB dissolved in a co-mixture of water and 1,4-dioxane with a 1,4-dioxane content of 45 wt%

For the GCL1-JB with a spherical microstructure, the charged groups transferred from the surface to the interior with increasing temperature, so the GCL1-JB tended to further aggregate due to increasing hydrophobic interaction and weakening of electrostatic repulsion. As a result, the scattered light intensity of GCL1-JB solution with a spherical microstructure increased significantly at the higher temperatures, and the corresponding GCL1-JB adsorbed film had a larger adsorbed amount, a rougher surface, and a larger contact angle. However, most of charged groups of GCL1-JB with a linear microstructure are distributed on both sides of the aliphatic chains, so the loss of surface charges was not obvious, even though the charged groups keep moving. Therefore, the scattered light intensity of the GCL1-JB solution with a linear microstructure and the corresponding adsorption behaviors were almost independent of temperature.

## CONCLUSIONS

1. GCL1-JB has a linear microstructure in water, but forms a spherical microstructure in water/1,4-dioxane co-mixture when the 1,4-dioxane content is above 43 wt%.
2. The zeta potential of GCL1-JB with a linear microstructure is basically independent of temperature, whereas that with a spherical microstructure decreases with increasing temperature.
3. GCL1-JB with a spherical microstructure aggregates more with increasing temperature, so the scattered light intensity increases significantly and the corresponding GCL1-JB adsorbed films have a larger adsorbed amount, a rougher surface, and a larger contact angle. However, the GCL1-JB with a linear microstructure does not aggregate at this condition, so the scattered light intensity does not increase and the corresponding GCL1-JB adsorbed films exhibit no obvious changes.
4. For GCL1-JB with a spherical microstructure, as the temperature increases, the degree of ionization does not decrease, but the surface charges decrease because of charged groups moving from the surface into the interior because of a charge gradient. Nonetheless, the charge groups of GCL1-JB with a linear microstructure are distributed on both sides of the aliphatic chains, which cannot cause any decrease in surface charges with increasing temperature. Therefore, only spherical microstructures can exhibit the observed phenomena with increasing temperature.

## ACKNOWLEDGMENTS

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