Thermoreversible Gel Lubricants through Universal Supramolecular Assembly of a Nonionic Surfactant in a Variety of Base Lubricating Liquids

Qiangliang Yu,[†,‡] Mingjin Fan,[†] Dongmei Li,[†] Zenghong Song,[†,‡] Meirong Cai,*[,†] Feng Zhou,*[,†] and Weimin Liu*[,†]

[†]State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

[‡]University of Chinese Academy of Sciences, Beijing 100049, China

S Supporting Information

ABSTRACT: The present paper investigates a new type of thermoreversible gel lubricant obtained by supramolecular assembly of low-molecular-weight organic gelator (LMWG) in different base oils. The LMWG is a nonionic surfactant with polar headgroup and hydrophobic tail that can self-assemble through collective noncovalent intermolecular interactions (H-bonding, hydrophobic interaction) to form fibrous structures and trap base oils (mineral oils, synthetic oils, and water) in the as-formed cavities. The gel lubricants are fully thermoreversible upon heating-up and cooling down and exhibit thixotropic characteristics. This makes them semisolid lubricants, but they behave like oils. The tribological test results disclosed that the LMWG could also effectively reduce friction and wear of sliding pairs compared with base oils without gelator. It is expected that when being used in oil-lubricated components, such as gear, rolling bearing, and so on, gel lubricant may effectively avoid base oil leak and evaporation loss and so is a benefit to operation and lubrication failure for a long time.

KEYWORDS: gel lubricant, supramolecular assembly, thermoreversible, lubrication, wear
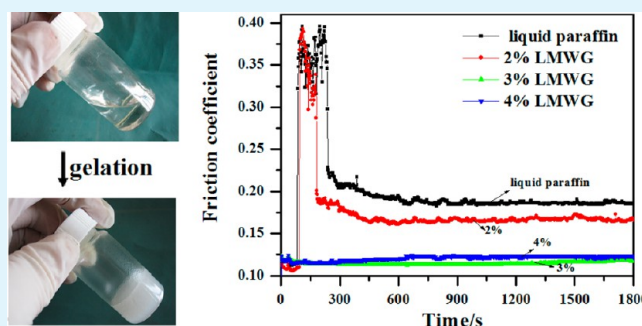
1. INTRODUCTION

The world functions with innumerable moving components and friction between sliding pairs consumes a large portion of energy.[1] Lubrication is the most widespread and effective means to reduce friction and wear and so to save energy. Concurrent with more requirements on energy efficiency and environment protection, the development of green, efficient, and long life lubricant in replacement of conventional recipe is particularly required. Greases are important lubricating materials, but might be problematic in some conditions, such as oil separation, poor lubrication caused by thickener and complex production process, etc.[2] To overcome this problem, the concept of using gel lubricants was developed. Gels can be formed through supramolecular assembly of a small fraction of small molecules in base oils. Gel lubricants are able to reversibly change from gel state to liquid state at the melting point of its gel agent. A thermoreversible gel lubricant was first reported by Takahashi et al.[2] It is shown that thermoreversible gel lubricants have good lubricity, are liable to form strong thick oil film with adhesive, and have long fatigue life. Recently, Our group reported novel ionic liquid (ILs) gelators with special molecular designing that can jelly normal IL through supramolecular assembly to form a gel with fibrous structure.[3] The obtained IL gels have fine anticorrosion ability,

conductivity, thixotropic character, and most importantly good tribological property. Gel-lube may liquefy upon mechanical shearing locally at the sliding interface, and therefore, it behaves like oil. However, it solves the creeping problem of base oils and evaporation loss and so will benefit maintenance and operation. Gelating lubricating oils into semisolid materials makes it easy to transport and store them. These advantages prompt us to develop more and novel gel lubrication system.

The LMWGs can form random three-dimensional networks and cavities in which liquids (lubricant oils) are trapped through H-bonding, π−π stacking, hydrophobic interaction, van der Waals force, London dispersion forces, and electrostatic interaction.[4,5] A variety type of molecules have been used as the LMWGs, for example amino acid,[6,7] fatty acid derivatives,[8] quterary ammonium salts,[9,10] urea,[11,12] anthracene derivatives,[13] organometallic compounds,[14] steroid derivatives,[15] and so on. They can either gelate water or organic solvents and ILs, forming hydrogels, organogels, ionogel, respectively.[16] Anna et al. reported a geminal imidazolium salts as LMWG.[17]

Tatsuo et al. synthesized amino acid compounds as supramolecular gelators,[18] which could gelate different solvents such as aqueous solutions with different pH, common organic solvents, oil and ILs. The design of LMWGs to gelate commonly used lubricating oils is very important, but rarely reported. In the present work, novel thermoreversible gel lubricants formed by supramolecular assembly of a LMWG in base oils are reported. The LMWG can gelate base oils like mineral oil, synthetic oils, and water through collective intermolecular interactions (H-bonding, van der Waals force, hydrophobic interaction) to form a fibrous network.

2. EXPERIMENTAL SECTION

2.1. Materials. All reagents for the synthesis of the gelator including 1-hexadecanol and *p*-toluenesulfonic acid monohydrate, glucono δ-lactone, L-leucine were purchased from J&K. The base oils, polyether (PEG200, PEG400), 150 BS, glycol and glycerol were purchased from Sinopharm chemical reagent Co., Ltd. Polyester (Esterex A51), polyalphaolefin (PAO10 and PAO40), and ultra S8 were purchased from ExxonMobil chemical and Lanzhou petrochemical grease factory, respectively. MACs oil was synthesized by our laboratory. All the other chemicals used in the synthesis were of AR grade.

2.2. Synthesis of the Gelator (LMWG) and Preparation of Gel Lubricants with LMWG. The gelator (LMWG) given in the following was synthesized using a previously reported method.[18] LMWG was dissolved in base oils at given concentrations in a sample vessal (diameter: 25 mm) by heating until complete dissolution, and then the hot mixed solution were slowly cooled to room temperature (RT) to form gels.

Scheme 1. Chemical Structure of LMWG
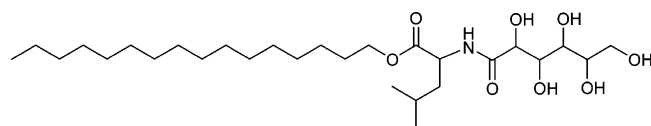
2.3. Characterization. The structure of LMWG was affirmed by proton nuclear magnetic resonance (^{1}H NMR, INOVA-400 Hz,) and carbon nuclear magnetic resonance (^{13}C NMR, INOVA-100 MHz). The spectra and date of nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) are given in the Supporting Information. The thermal properties of the gel lubricants were measured on an STA 449 C Jupiter simultaneous TG-DSC from 25 °C to approximately 800 °C at a heating rate of 10 °C min^{−1} in air. The thermal stability of base oil

gel lubricants were studied through measuring gel-to-sol transition temperature with DSC thermograms (Mettler Toledo DSC822 series). Samples were analyzed in aluminum pans under a steady flow of liquid nitrogen (25 mL min^{−1}) and heated at 2 °C min^{−1} from −20 to 80 °C. To investigate the rheological property of base oil gel, we carried out shear stress and frequency sweeps on a RS6000 Rheometer (Germany) with a cone−plate sensor system (Ti; radius, 17.5 mm; cone angle, 1 °C). The friction track and chemical composition of the worn scars were analyzed according to our previously reported methods[19] by JSM-5600LV SEM and PHI-5702 multifunctional XPS, respectively.

2.4. Tribology Test. The tribological properties of liquid paraffin gel, PAO10 gel, and hydrogel as lubricants were assessed for application in steel/steel contacts using an Optimol SRV-IV oscillating reciprocating friction and wear tester. The experiment and the friction testing parameters were referred to our previously published articles.[20,21] Before the test, a block of the base oil gel was placed in the ball-disk contact area. The friction and wear behavior of the samples were assessed in air at RT. Three repetitive measurements were performed for each sliding process. The corresponding friction curves were recorded automatically with a computer attached to the SRV tester. A MicroXAM 3D noncontact surface mapping profiler was used to measure the wear volume of the lower disk.

3. RESULTS AND DISCUSSION

3.1. Formation of LMWG Supramolecular Gel Lubricant. The gelation process of 5% LMWG in liquid paraffin was recorded by digital camera with ten second interval and the corresponding polarized optical microscopy were obtained on OLYMPUS BX51. The images are shown in Figure 1. We can see that gelation occurs immediately but the gel remains partial transparent at 30s until a dense and stable turbid white gel forms after 1 min (Figure 1a). The rapid process might originate from intermolecular hydrogen bond interaction and intermolecular hydrophobic interaction of the gelator. First, the LMWG assembles to fiberlike aggregates in a small amount and then fibrous bundles that extend further to three-dimensional network (Figure 1b). Figure 1b, c showed that the fibrous network have strongly birefringent effects which verify the crystalline nature (Figure 1c).[3] It was found that the LMWG can solidify a variety of lubricating medium, including water, polyester (A51), 150BS, polyalphaolefin(PAO10, PAO40), Ultra S8, multiple-alkylated cyclopentane (MACS), polyethylenglycol(PEG400), triethylene glycol, glycerin, etc. For different base oils, the gelator will have different optimal
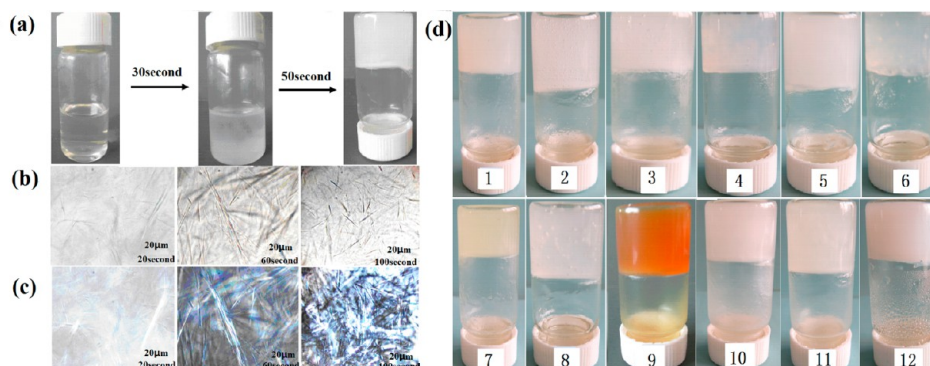
Figure 1. (a) Digital pictures of gelation process in liquid paraffin, (b) optical microscopic images, and (c) polarized light microscopic images of LMWG assemble process in liquid paraffin at different time of the sample. (d) Digital images of the gel lubricants: (1) liquid paraffin+2% LMWG, (2) A51 + 2% LMWG, (3) PAO10 + 2% LMWG, (4) PEG 200 + 2% LMWG, (5) Ultra S8 + 3% LMWG, (6) MACs+3% LMWG, (7) PEG 400 + 2% LMWG, (8) triethylene glycol+2% LMWG, (9) 150BS+3% LMWG, (10) PAO40 + 2% LMWG, (11) glycerin+2% LMWG, and (12) water+1% LMWG.
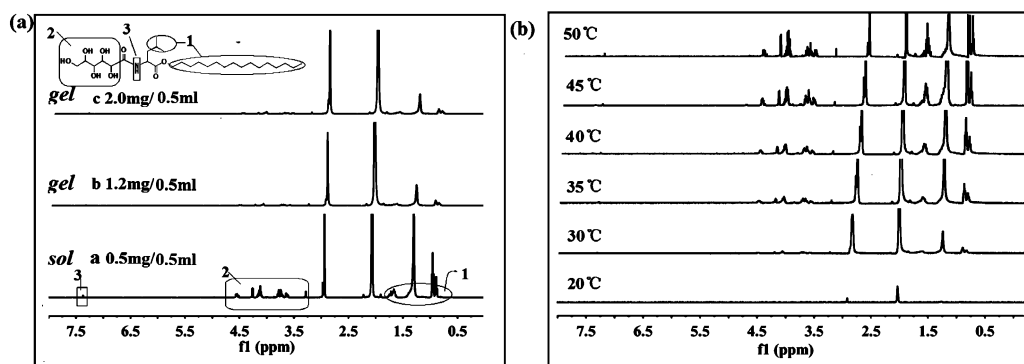
Figure 2. (a) ^{1}H NMR spectra of LMWG in acetone-d_6 at different concentrations and (b) ^{1}H NMR spectra of LMWG in acetone-d_6 at different temperatures (2 mg/0.5 mL).

concentration. Figure 1d shows the solidified base oils under the minimum gelation concentration.

3.2. Mechanism Analysis of Gel Lubricants. NMR was used as a complementary tool for the investigation of LMWG[22] through chemical shifts, intensity of the NMR signals with concentration, solvent composition, or temperature.[22-24] In the present study, the formation of intermolecular hydrogen-bonds of the gelator molecules is verified by the results from concentration- and temperature-dependent ^{1}H NMR studies of LMWG-acetone-d_6 systems. The results of this experiment are shown in Figure 2. The signals at 0.85–1.5, 3.3–4.8, and 7.4 ppm detected for the acetone-d_6 solution of LMWG (0.5 mg/0.5 mL) can be assigned to the alkyl groups, OH and NH groups of LMWG, respectively. With increasing concentration of LMWG, the three signals reduce gradually and aggregation takes place, indicating the formation of hydrogen bonds. When concentration of LMWG reaches 2 mg/0.5 mL, large and NMR-silent assemblies are formed indicating complete gel formation. Beatriu et al.[22] and Sajid Iqbal et al.[25] have also reported similar results on supramolecular gels. Temperature-dependent NMR analysis of supramolecular gels will give more information. The ^{1}H NMR spectra of the LMWG-acetone-d_6 system (2 mg/0.5 mL) were recorded at different temperatures (Figure 2b). As anticipated, with increasing temperature, the intensities of the three group signals increase gradually. When temperature reaches 50 °C, the split of all the three group signals on ^{1}H NMR spectra (2 mg/0.5 mL) becomes clear, which suggests the breaking of the intermolecular interaction. Similar results have been also observed by Bhattacharya.[26] The result indicated that intermolecular H-bonding at the head-group and hydrophobic van der Waals interaction as indicated in Scheme 2 synergistically act as a driving force for aggregation of the molecules.

3.3. Gel–Sol Transition Temperature (T_g) and Thermal Properties of Gel Lubricants. The T_g of the gel lubricants were determined by DSC and the results were listed in Figure 3 and Table S1 in the Supporting Information. The results showed that the gelation was largely affected by the concentration of gelator and types of base oils (Figure 3a). For example, an increase in the concentration of LMWG in all base oils led to an increase in the gelation rate. Of course, increase of the gelator concentration in base oils also led to an increase of the T_g. Taken liquid paraffin as an example, when the concentration of gelator increased from 2% and 5% to 10%, the T_g of the system increased from 57.78 and 60.73 °C to 61.30 °C (Figure 3b).

**Scheme 2. Proposed Supermolecular Assembly Mode of Gelator in Base Oil**
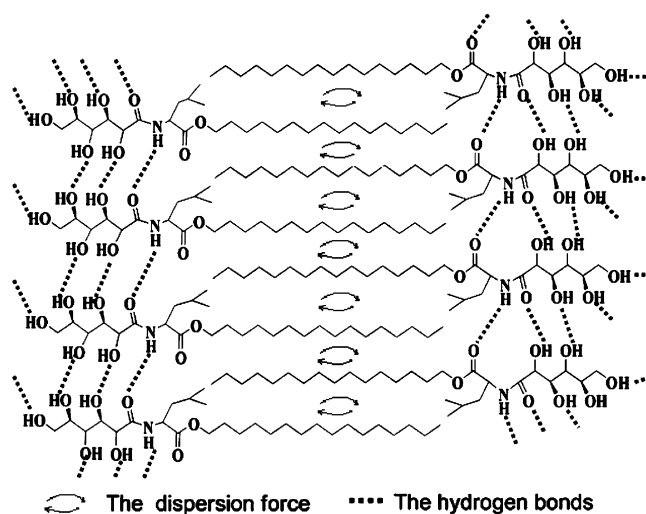
The thermal stability of the oil gels was evaluated by TGA in air atmosphere (Figure 4). Figure 4a shows that the thermo-decomposition temperature of all the gel lubricants is higher than 200 °C, which indicates its good thermal stability. Figure 4b shows the thermo-decomposition temperature of liquid paraffin with various mass percent of LMWG. We can see that the thermo-decomposition temperature of the liquid paraffin gel increased with the increase in concentration of LMWG. It is obvious seen that the thermo-decomposition temperature of liquid paraffin+10% LMWG is much higher than neat liquid paraffin, implying that LMWG can enhance the decomposition temperatures of base oils during the lubrication processes.

3.4. Rheological Characterization and Thixotropic Behavior of Base Oil Gels. To evaluate the viscoelastic and mechanical properties of gel lubricants, we measured liquid paraffin gel with 2, 3, and 4% LMWG (Figure 5a, b), PAO10 gel with 2, 3, and 4% of LMWG (Figure 5c, d), and hydrogel with 1, 2, 3, and 4% LMWG (Figure 5e,5f), respectively. Figure 5a shows that both the storage moduli (G') and loss moduli (G'') as a function of strain. G' shows a substantial elastic response, which is larger than G'' in measurement strain range.[3] It is found that G' and G'' of liquid paraffin with different concentration of LMWG decreases gradually with the increasing strain, indicating the shear thinning property. A frequency sweep can testify the tolerance of a material to external forces,.[27] It is seen that G' is significantly larger than
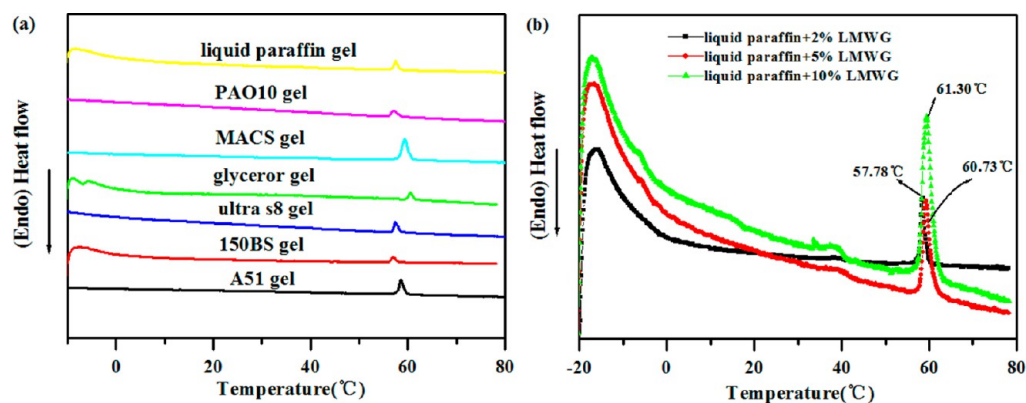
Figure 3. (a) DSC curves of different base oil gels, (b) changes in phase transition temperature when concentration of LMWG in liquid paraffin increased form 2 to 5 and 10%.
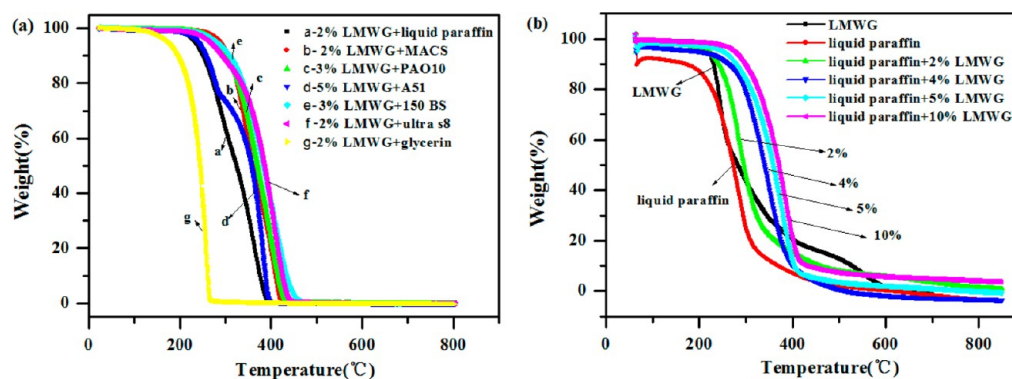

Figure 4. (a) TGA curve of base oil gels and (b) liquid paraffin with various mass percent of LMWG.

G'', and both moduli exhibit dependence on frequency. implying a more elastic nature than the viscous property throughout the entire frequency region. The rheological property of the PAO10 gel (Figure 5c, d) consisting of LMWG is shown in Figure 5c, d. Figure 5c shows stress sweeps of the PAO10 gel. Increasing the gelator concentration from 2 to 4% the storage modulus G' increases from 2.64 to 22.8 kPa. This indicates that the viscoelastic properties and mechanical stability of the gel network increases with the gelator concentration. In Figure 5d shows G' and G'' as a function of frequency for three different concentrations of LMWG. We can see that both G' and G'' slightly increase with frequency and the G' is higher than G'' in almost all the frequency range, demonstrating the dominant of elastic behavior of the system. Figure 5e, f presents the rheological data of hydrogel at stress sweep (Figure 5e) from $\sigma = 0.01$ to 500 and frequency sweep (Figure 5f) from $f = 0.01$ to 100. The G' and G'' increase with the concentration of LMWG, suggesting the enhanced mechanical stability of the hydrogel gels with the concentration of LMWG. This experiment is consistent with liquid paraffin gel and PAO10 gel. For three gel lubricants the G' and G'' increases with the gelator concentration. The rheological behavior of the gel lubricant was beneficial for special lubrication as a succedaneum for lubricating grease.

Interestingly, rapid shaking led to gel-to-sol phase transition and resting some time the solution results in gelation again (Figure 6). As stated before, in the system, a large number of nanofibers are formed by supramolecular noncovalent interaction between gelator molecules and build up an abundant of cavities in which oil is trapped. However, the noncovalent interaction (H-bonding at gelator head and van der Waals interaction along hydrophobic tail) is relative weak and can be destroyed under shearing or drastic shaking so that the trapped base oil can be released. Upon waiting for some time, the LMWG can self-assemble to form gel once again. The reversible process is characteristic of the thixotropy effect, which can be further quantitatively demonstrated from the rheological data as shown in Figure 5. The both elastic modulus and loss modulus of liquid paraffin gel decreased with increasing shear stress, while the PAO and hydrogel show some threshold shear stress, after which both G' and G'' decrease sharply. Both G' and G'' become instable at high shear frequency.

The effect of thixotropic behavior has important implications in lubrication, in which solid-like lubricants are liquefied under high shear strength (high load and lateral shear) and take part in lubrication like oils, while lubricants in solid state not only make them easy to transport but also can effectively avoid oil creeping and evaporating loss and so benefit to maintenance.[3] On the basis of this consideration, the gel lubricant 5% LMWG in PAO10 and its base oils PAO10 are exposed to the ground simulated atomic oxygen. As shown in Figure 7, after 2.5 h of atomic oxygen irradiation, PAO10 on the surface of steel block spread to all the surface because of the increased surface energy of both the oil and steel surface, whereas the PAO10 gel covered area does not change, indicating no creeping at all. One can imagine that the sealing problem will be less of a concerned when using gel lubricant, the application of which we will pay more attention to in future work.
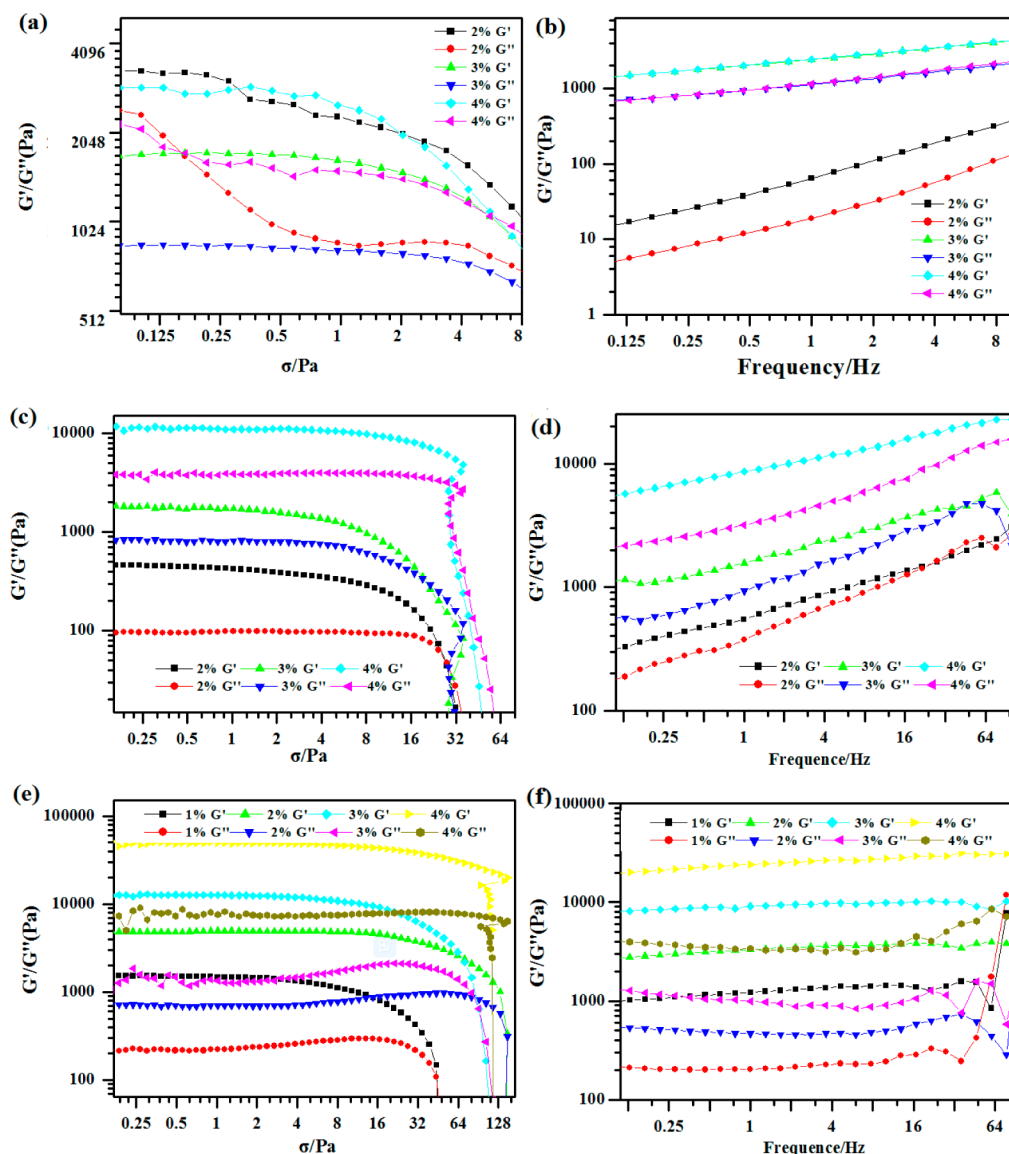
Figure 5. Oscillation mode rheological data of different gel lubricants with different gelator concentrations. The evolution of G' and G'' as a function of the applied shear stress ($\sigma = 0.1-100$ Pa) of (a) liquid paraffin gel, (c) PAO10 gel, and (e) hydrogel, respectively, and the frequency from 0.01 to 100 Hz at $\sigma = 5$ Pa, (b) liquid paraffin gel, (d) PAO10 gel, and (f) hydrogel, respectively.

3.5. Tribological Properties of the Gel Lubricants. The tribological properties of the liquid paraffin gel, PAO10 gel, and hydrogel at RT were investigated. It was found that gel lubricants have better lubricating properties than the base oils. The friction coefficient (COF) evolution and wear volume losses of lower disks under lubrication of liquid paraffin gel, PAO10 gel and water gel are shown in Figures 8−10, respectively. Panels a and b in Figure 8 display the evolution of COF and wear volumes of sliding discs under lubrication of liquid paraffin and liquid paraffin gel with different concentrations of LMWG at RT. We can see that the COF increase in the following sequence: 3% LMWG+liquid paraffin gel < 4% LMWG+liquid paraffin gel < 2% LMWG+liquid paraffin gel < liquid paraffin (Figure 8a). The wear volumes of the discs increase in the following sequence: 4% LMWG+liquid paraffin < 3% LMWG+liquid paraffin gel < 2% LMWG+liquid paraffin gel < liquid paraffin gel (Figure 8b). It means that the concentration of LMWG has a significant impact on the tribological properties. The addition of 3% LMWG can

significantly reduce friction and wear of sliding pairs lubricated by liquid paraffin. From the inset photographs in Figure 8a, it is seen that before and after the test, liquid paraffin gel remained in a good gel state with appropriate viscosity. This means LMWG can not only gelate base oils to gels but also act as friction-reduction and AW additive.

We have investigated the effect of the frequency on triobological propertites of liquid paraffin and its gel. A frequency ramp test from 15 up to 40 Hz by 5 Hz interval at a load of 100 N at 25 °C is shown in Figure 8c. The test duration for each frequency was 5 min. It is seen that liquid paraffin has a larger COF. The addition of 2, 3, and 4 wt % LMWG, gels have low COF compared with liquid paraffins. Increasing the concentration of LMWG leads to a decrease of the COF. Upon shearing, the gel at interface liquefies and more and more LMWG molecule will adsorb onto metal surface to form protective film. So the gel lubricant displays better lubrication property than neat liquid paraffin and strengthen its perform-ance when increasing concentration. The similar result was
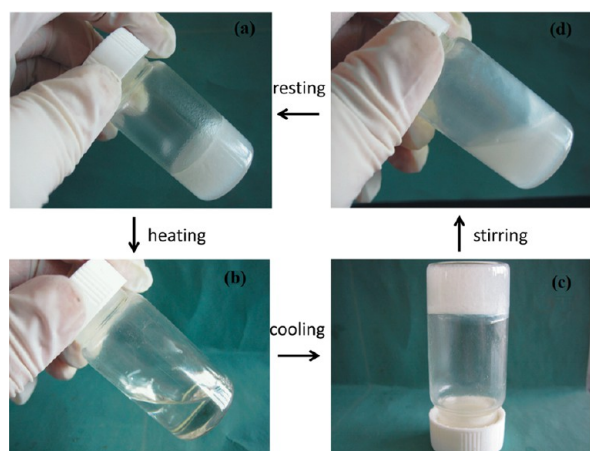
Figure 6. Thixotropic behavior of the base oil gel: (a) liquid paraffin +3% LMWG gel, (b) heat dissolution of liquid paraffin+3% LMWG gel, (c) reform of liquid paraffin+3% LMWG, (d) shear thinning of liquid paraffin+3% LMWG gel.
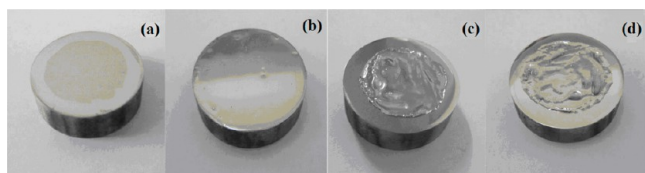
Figure 7. Creeping behavior of PAO10 and PAO10 with 5% LMWG gel on the surface of the steel pieces before and after atomic irradiation: (a) PAO10 before irradiation experiment, (b) PAO10 after irradiation experiment; (c) PAO10 gel before irradiation experiment, (d) PAO10 gel after irradiation experiment.

reported by Pro. Mori using other gel lubricants.[28] The fact that when we change the frequency the COF remains very stable and that the applying load is rather high (more than 2 GPa) and the friction coefficient is around 0.1 may suggest that the lubrication lies in the boundary regime.

Figure 8d displays the tribological properties of liquid paraffins at lower contact pressures and at longer testing times. We can see that the liquid paraffin has higher COF about 0.20 at a load of 100N and instable during friction test. When the concentration of LMWG is merely 2%, the gel lubricant has very low and stable COF. As the concentration of LMWG increased, the lubrication property of lubricant could not be improved further. Even at 2% gelator concentration, the thermoreversible gel lubricant exhibits long fatigue life. This contrast also demonstrates the significant role of gelator in friction-reduction and AW, probably because of the strong absorption of gelator through its polar headgroup.[28,29]

The effect of the temperature on the tribological properties of liquid paraffin gel lubricant were also investigated and the results are shown in Figure 8e. Figure 8e displays the results of a temperature ramp test from 20 up to 120 °C stepped by 20 °C at 300 N for liquid paraffin and liquid paraffin gel (3% concentration and 4% concentration, respectively). The test duration at each temperature was 5 min. During the test, For liquid paraffin gel with 3% and 4% LMWG, it is found that the friction coefficient maintains steady at temperature below 40 °C, while it increases dramatically (to about 0.17 for 3%), but still smaller than the value of liquid paraffin when the temperature is increased to 60 °C, a temperature that gel structure is damaged. Friction reduction property of liquid

paraffin gel lubricant decreases as temperature increases after the phase transition temperature. This result indicates that gelation of the base oil is beneficial to the tribological properties of the oil because of the increased viscosity through the supramolecular assembly of gelator and gelator molecule absorption on the metal sliding surface.[30]

The tribological properties of gel lubricant can be explained by both chemical and physical effects.[19] The gelator can easily and strongly absorb on metal surface with its polar head-group.[19] The absorbed film plays a role as an oiliness agent and significantly decreases the friction and wear. From the viewpoint of a physical effect, thermoreversible gel lube might become solid under high pressure; therefore, a solid-like film might be formed in the Hertzian area and protects sliding pairs from direct metal-to-metal contact.[31] Further work is still required to clarify the mechanism of thermoreversible gel lube in detail.[29,31]

Synthetic oils are commonly used lubricants, especially for combustion engines. The present gelator LMWG can also gelate synthetic oils, like polyalphaolefin (PAO). After gelation, the tribological property of PAO10 was significantly improved. The COF evolution and wear volume losses of sliding discs are shown in Figure 9. The results show that pure PAO10 as neat lubricant oil can form continuous lubrication oil protective films to reduce friction within the first 10 min (approximately 700 s), but at the high load (about 3 GPa) the boundary lubrication oil film is not firm enough under thermal and mechanical stress and is easily worn out. Therefore, the COF bumps up to 0.6 and afterward levels off to a high value of about 0.3. The gelator concentration of 2% is not enough to provide sufficient friction reduction and AW. The concentration of gelator reaches to 3%, the bump up of COF almost disappears and COF decreases to a very low level. No significant improvement can be observed after 4% concentration of LMWG. PAO10 is usually used as synthetic lubricant with high molecular weight and so fairly large viscosity, which makes it load-bearing capacity due to physical absorption to form viscous film at sliding interface. However, the physically absorbed film is not strong enough, and may break down under continuous thermal stress, leading to lubrication failure. This was altered when adding gelator to form friction-reduction and AW adsorbed layers and further tribochemical reaction protective films on the sliding metallic surfaces.[32] The antiwear property of PAO gel lubricants is much better than pure PAO10. The wear volume of the lower discs is reduced by about 20 times as compared with that lubricated with pure PAO 10 when the concentration of LMWG increases to 4% (Figure 9b).

Aqueous lubrication is attractive in the tribological field because of the desire to understand and potentially mimic how biotribological contacts lubricate in nature.[33] It is well-known that water is the most common lubricating medium with high cooling capability. However, it is unconventional lubricant for most tribological applications in long run because of the high corrosivity, liable to evaporation and high fluidity(low viscosity). These problems might be weakened by forming hydrogels. Figure 10 shows that the addition of 1 and 2% LMWG can greatly reduce friction and wear of sliding pairs water at RT. When the concentration increases to 3 wt %, the COF reduces from above ∼0.5 to a very low level (∼0.15). These results demonstrate that the hydrogels have good lubricating properties for steel/steel contacts as compared with pure water. When the content of gelator is above 4 wt %, no
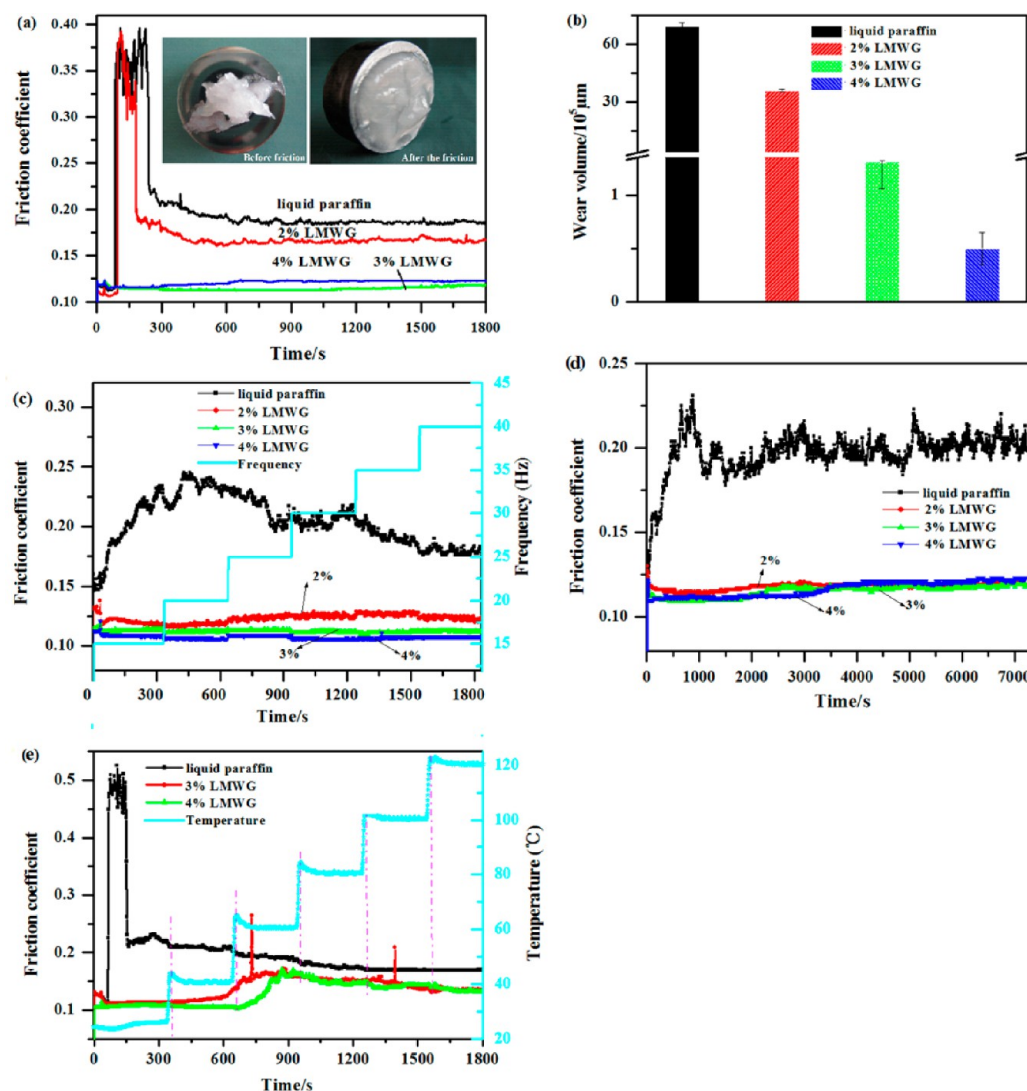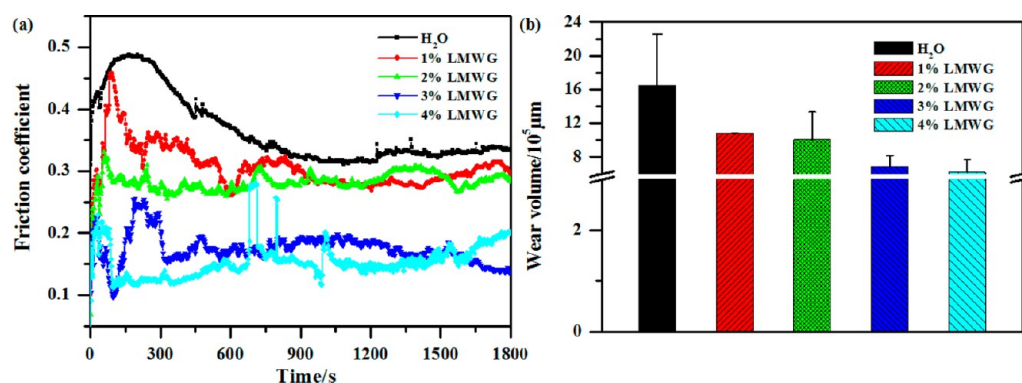
Figure 8. (a, b) Evolution of COF/time and wear volume losses for the steel disks lubricated by different concentrations of LMWG in liquid paraffin at RT. (c) Evolution of COF with time during a frequency ramp test from 15 to 40 Hz for liquid paraffin and gel with different concentration of LMWG at 25 °C (SRV load, 100 N; stroke, 1 mm; duration, 30 min). (d) Evolution of COF of long time testing of liquid paraffin and liquid paraffin gel with different LMWG at 25 °C (SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz; duration, 120 min). (e) Evolution of COF with time during a temperature ramp test from 20 to 120 °C for liquid paraffin and liquid paraffin gel with 3% LMWG and 4% LMWG (SRV load, 300 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min.).
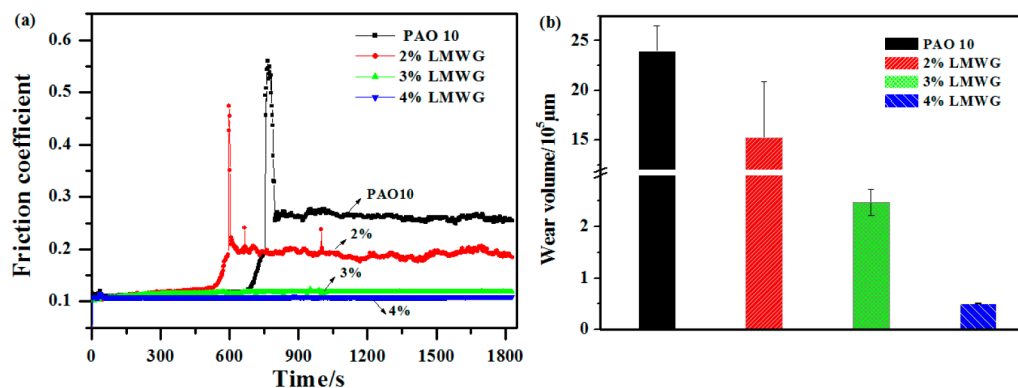

Figure 9. (a) Evolution of COF/time and (b) wear volume of the lower disks lubricated by different concentrations of LMWG in PAO10 gel at RT (SRV load, 200 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min.).

further improvement in the friction-reducing and AW can be observed.

3.6. Surface Analysis. Figure 11 presents the SEM micrographs of the worn steel surfaces lubricated by pure

Figure 10. (a) Evolution of COF/time and (b) wear volume of the lower disks lubricated by different concentrations of LMWG in hydrogel at RT (SRV load, 100 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min.).
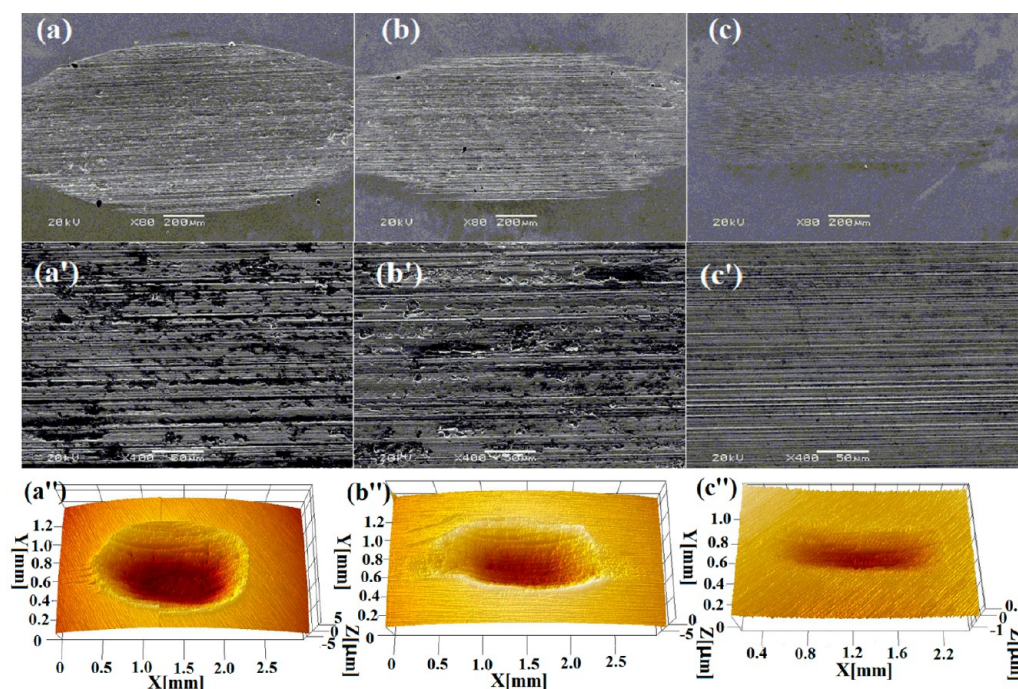

Figure 11. SEM and 3D optical microscopic morphology of worn surfaces lubricated by liquid paraffin and gels with different LMWG concentration: (a, a′, a″) Liquid paraffin, (b, b′, b″) 2% LMWG, and (c, c′, c″) 4% LMWG, (magnification on the above is 80×, and on the below is 400×; load, 300 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min; temperature, 25 °C).
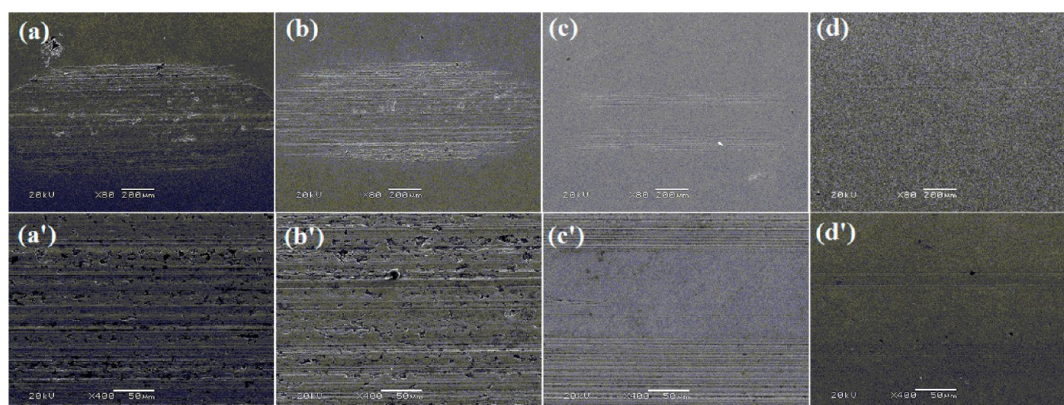
Figure 12. SEM morphology of worn surfaces lubricated by PAO10 and gels with different LMWG concentration: (a, a′) PAO10, (b, b′) 2% LMWG, (c, c′) 3% LMWG, and (d, d′) 4% LMWG (magnification on the above is 80×, and on the below is 400×; load, 200 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min; temperature, 25 °C).
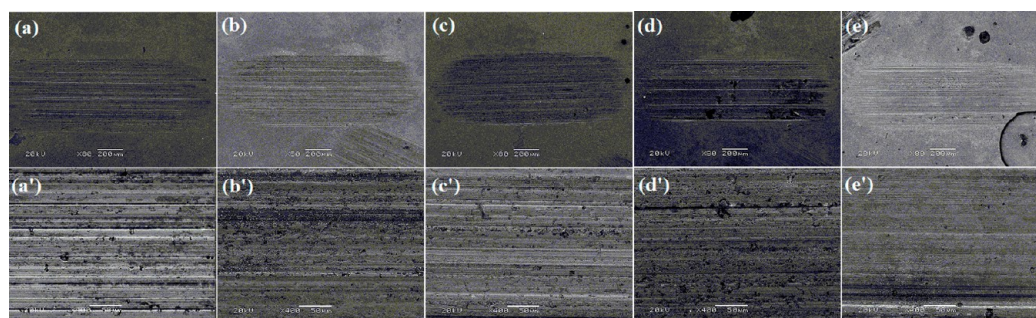
Figure 13. SEM morphologies of worn surfaces lubricated by H_2O and hydrogel with different LMWG concentration: (a, a′) H_2O, (b, b′) 1% LMWG, (c, c′) 2% LMWG, (d, d′) 3% LMWG, and (e, e′) 4% LMWG (magnification on the above is 80×, and on the below is 400×; load, 200 N; stroke, 1 mm; frequency, 25 Hz; duration, 30 min; temperature, 25 °C).
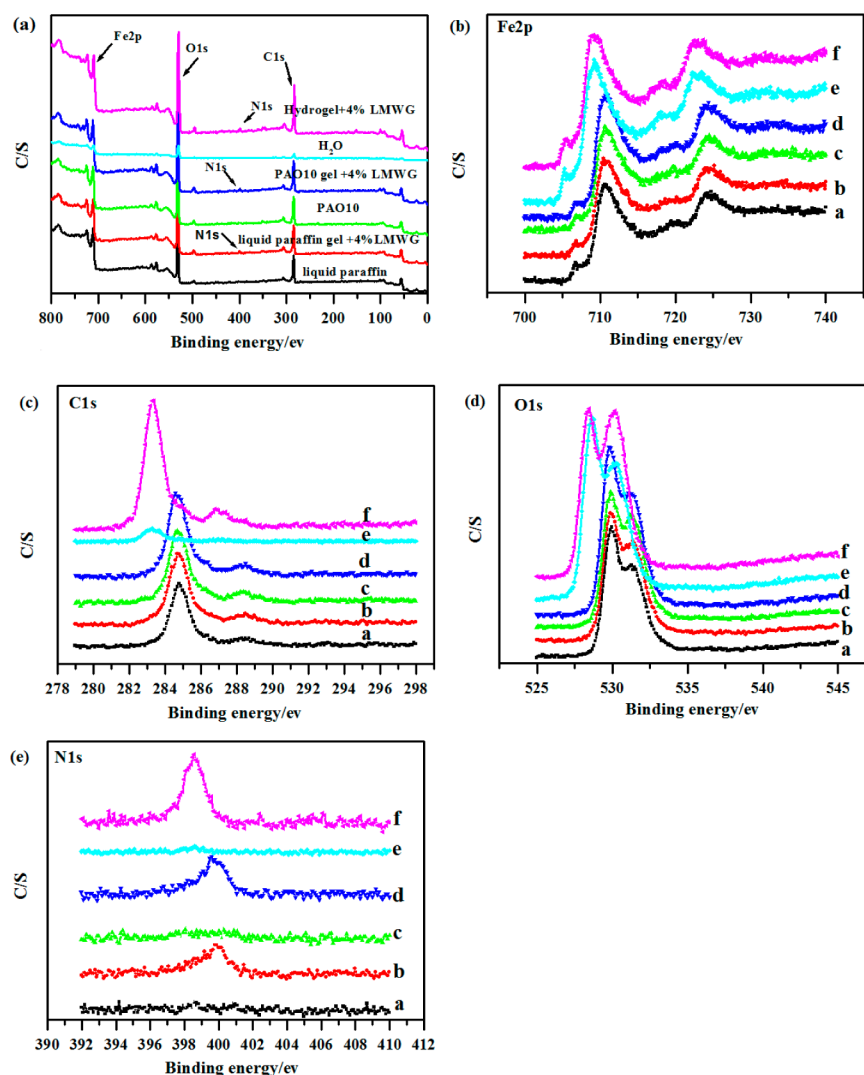

Figure 14. XPS spectra of (a) full spectra, (b) Fe 2p, (c) C 1s, (d) O 1s, and (e) N 1s of the worn surfaces lubricated by liquid paraffin (curve a) and gel with 4% LMWG (curve b), PAO10 (curve c), and PAO10 gel with 4% LMWG (curve d), H_2O (curve e), and hydrogel with 4% LMWG (curve f).

liquid paraffin and gels with different content of LMWG. We can see that the worn surfaces of the steel lubricated by pure liquid paraffin oil present severe scuffing with many deep and narrow grooves (Figure 11 a, a′). However, as to the steels lubricated by liquid paraffin gels, the wear scars are slight and relatively smooth. Scuffing is greatly alleviated (Figure 11 b, b′, 11c, c′), which indicates that these gels have excellent AW

properties. The corresponding 3D optical microscopic images are shown in Figure 11a″−c″, which further confirms the same behavior to that reported for friction and wear. Wear scars lubricated by liquid paraffin (Figure 11a″) are wider and deeper than that lubricated by paraffin gels (Figure 11 c″). The same phenomenon was also found on the worn surfaces of steel disks lubricated by other oil gels. These results are consistent with

the above measured wear volume results and indicate the excellent AW property by gels.

The SEM images of the steel surfaces that were worn while lubricated by PAO10, 2 wt % LMWG, 3 wt % LMWG and 4 wt % LMWG, and all the wear scars were obtained under the same conditions. Figure 12a, a′ shows that the worn steel surface under lubrication of PAO10 displays very rough and many wide wear scars with severe scuffing. The wear volume is very large. It can be seen that the worn surfaces under the lubrication of PAO10 gel with 2 wt % LMWG (Figure 12b, b′) are also very rough, but the diameter is considerably reduced. When concentration increased 3% (Figure 12c, c′), the wear scars are narrow and shallow, with small furrows and scratches on the friction surface. This result indicates that 3% gel lubricant has some certain AW property. However, when the concentration of LMWG reaches 4 wt % (Figure 12d, d′), the worn scars are quite smooth and show hardly any grooves. This indicates that the prepared PAO10 gel has the distinguishable AW properties, and the result is also consistent with the measured wear volumes in Figure 9.

The SEM morphologies of the worn steel surfaces lubricated by H_2O and hydrogel with different LMWG contents are shown in Figure 13. We can see that the wear surface lubricated by H_2O, (Figure 13a, a′) is very rough and show considerably wider and deeper wear scars. Thus, severe scuffing occurs in these cases. However, the wear scars lubricated by hydrogels with 1% and 2% LMWG, show relatively narrow and mild abrasive wear with no scuffing damage (Figure 13b, c′). When adding 3 and 4 wt % LMWG into water, the worn surfaces are slight and relatively smooth. From images Figure 13a–e, we can see that scuffing is greatly alleviated. The results demonstrate that the new prepared hydrogels have better antiwear properties than pure water.

XPS is a powerful tool to clarify the compositions and chemical state of the elements on the worn surfaces. The XPS spectra are shown in Figure 14a. It is clear that the major elements present on the surface are O, C, Fe, but considerable N is detected on the gel lubricated surface and attributed to LMWG physical absorption or chemical reaction with surface. High resolution XPS spectra of Fe 2p, C 1s, O 1s, and N 1s elements were collected before and after friction tests to further clarify the chemical states of elements, Figure 14b–e, and the binding energies of all samples are shown in Table S2 in the Supporting Information. It is seen that the binding energies of C, O, and N of the worn surfaces lubricated by the 4% LMWG liquid paraffin gel, 4% LMWG PAO gel and hydrogel all differ from the binding energies of neat LMWG (see Figure S1 in the Supporting Information). We assumed that specific tribochemical reactions occurred during the friction process and formed new compounds. The binding energies of Fe 2p, C 1s, O 1s, and N 1s of the worn surfaces lubricated by the 4% LMWG liquid paraffin gel and 4% LMWG PAO gel are similar to each other. This indicates oil gels have similar lubrication mechanisms. The binding energies of C 1s, O 1s, and N 1s of the worn surfaces lubricated by hydrogel all differ from the binding energies of liquid paraffin gel and PAO gel. The XPS spectral peaks of Fe 2p (Figure 14a–d) appear at 710.2–710.8 and 724.1–724.5 eV, and the O 1s (Figure 14a–d) peaks appear at 529.81–529.96 and 531.29–531.37 eV, which may be assigned to FeO, Fe_2O_3, Fe_3O_4, and FeOOH.[34,35] The C 1s (Figure 14a–d) spectra show two peaks. The largest peak can be ascribed to the C–C and C–H bonds in alkyl group with characteristic binding energy of the 284.5–284.8 eV. The

second peak may be assigned to the carbon atom of the C=O bond and C–O bond in organic compounds at 288.3–288.5 eV. These peaks indicate that the LMWG adsorb on the surface of steel.[36,37] There are no characteristic peaks of N 1s on the worn steel surface lubricated by pure liquid paraffin, PAO10 and H_2O. But for the corresponding gel, an obvious peak appears at 399.14–399.80 eV for worn steel surface lubricated by with 4% LMWG liquid paraffin gel and PAO10 gel, which possibly correspond to carbonitride and/or nitrogen oxides.[38,39] The bonding energy of C 1s at 283.26 and 286.96 eV for hydrogel, respectively, could indicate existing –CH_2– and C=O on the surface of wear scar from the LMWG hydrogel. In the XPS of O 1s, the binding energy at 528.65 eV, 530.26 eV for H_2O and 528.48 eV, 530.14 eV for hydrogel different with oil gel imply that O^{2-}, oxo- species, OH/O_{ads}, FeO, Fe_2O_3, and Fe=O exist on the surface lubricated by H_2O and hydrogel. N 1s peak appears at 398.5ev, which can be attributed to complex oxide species. This data of XPS of surface on the wear while lubricated by H_2O and hydrogel indicated complicated physics and chemistry reaction were likely to occur.[36,30] XPS analysis reveals that complicated tribochemical reactions occurred on the surfaces lubricated by all three types of gel lubricants under a collective impact of high pressure, exoelectron emission, and frictional heat on the specimen surface. On the basis of these data, it can be speculated apart from inorganic compounds (e.g., Fe_2O_3, Fe_3O_4, FeOOH, amine, or nitrogenoxide, formed on the worn surfaces), organic C–H, C–C bonding can be present at the worn surface. The excellent tribological properties can be ascribed to not only tribochemical protective film composed of Fe_2O_3, Fe_3O_4, and FeOOH but also physical absorption LMWG film.

4. CONCLUSION

A new low-molecular-weight organic gelator was prepared and could gelate a variety of base lubricating oils (mineral oil, synthetic oil, and water). The gelator forms a fibrous network through collective intermolecular interactions (H-bonding, hydrophobic interaction) and lubricating oils are trapped in the cavities built up by supramolecular fibers. Rheological characterization indicated that the gel lubricant had good mechanical stability and viscoelasticity upon shearing. Under normal lubricating conditions, gels could liquefy and behave like oil lubricants. These characteristics make them potential high performance semisolid lubricants with significantly improved transportation, storage and anticreeping properties. Under optimized gelator concentration, gel lubricants have better lubricating performance than blank base oils because gelator itself can act as effective lubrication additive in base oils. SEM and XPS analysis revealed that not only complicated tribochemical reactions occurred on the surfaces lubricated by all three types of gel lubricants, but chemical and physical adsorption films also formed. The good tribological capacities of gel lubricant is ascribed to the polarity induced absorption of gelator molecules to form ordered films on sliding surfaces and further tribochemical reaction induced protective films on the sliding metallic surfaces. These phase changed supramolecular gel lube systems are expected to replace conventional lubricants, and used in peculiar machine components, such as gear, rolling bearing, and so on. In this way, it can effectively avoid base oil creeping and evaporating loss and so benefit to maintenance and operation.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: caimr@licp.cas.cn. Phone: +86 0931 4968079.
*E-mail: zhouf@licp.cas.cn. Phone: +86 0931 4968466.
*E-mail: wmliu@licp.cas.cn. Phone: +86 0931 4968166.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Cai, M.; Guo, R.; Zhou, F.; Liu, W. Lubricating a Bright Future: Lubrication Contribution to Energy Saving and Low Carbon Emission. *Sci. China: Technol. Sci.* **2013**, *56*, 2888–2913.

(2) Takahashi, K.; Shitara, Y.; Kaimai, T.; Kanno, A.; Mori, S. Lubricating Properties of TR Gel-lube—Influence of Chemical structure and Content of Gel Agent. *Tribol. Int.* **2010**, *43*, 1577–1583.

(3) Cai, M.; Liang, Y.; Zhou, F.; Liu, W. Functional Ionic Gels Formed by Supramolecular Assembly of a Novel Low Molecular Weight Anticorrosive/Antioxidative Gelator. *J. Mater. Chem.* **2011**, *21*, 13399–13405.

(4) de Loos, M.; Feringa, B. L.; van Esch, J. H. Design and Application of Self-Assembled Low Molecular Weight Hydrogels. *Eur. J. Org. Chem.* **2005**, *2005*, 3615–3631.

(5) Babu, S. S.; Praveen, V. K.; Ajayaghosh, A. Functional π-Gelators and Their Applications. *Chem. Rev.* **2014**, DOI: 10.1021/cr400195e.

(6) MakarevicÂ, J.; Jokić, M.; Perić, B.; Tomisić, V.; Kojić-Prodić, B.; Zinić, M. Bis(Amino Acid) Oxalyl Amides as Ambidextrous Gelators of Water and Organic Solvents Supramolecular Gels with Temperature Dependent Assembly Dissolution Equilibrium. *Chem.—Eur. J.* **2001**, *7*, 3328–3341.

(7) Edwards, W.; Smith, D. K. Enantioselective Component Selection in Multicomponent Supramolecular Gels. *J. Am. Chem. Soc.* **2014**, *136*, 1116–1124.

(8) Pal, A.; Ghosh, Y. K.; Bhattacharya, S. Molecular Mechanism of Physical Gelation of Hydrocarbons by Fatty Acid Amides of Natural Amino Acids. *Tetrahedron* **2007**, *63*, 7334–7348.

(9) Oda, R.; Candau, S. J.; Oda, R.; Huc, I. Gemini Surfactants, The Effect of Hydrophobic Chain Length and Dissymmetry. *Chem. Commun.* . **1997**, 2105–2106.

(10) Wang, D.; Hao, J. Multiple-Stimulus-Responsive Hydrogels of Cationic Surfactants and Azoic Salt Mixtures. *Colloid Polym. Sci.* **2013**, *291* (12), 2935–2946.

(11) Yamanaka, M. Urea Derivatives as Low-Molecular-Weight Gelators. *J. Inclusion Phenom. Macrocyclic Chem.* **2013**, *77*, 33–48.

(12) George, M.; Tan, G.; John, V. T.; Weiss, R. G. Urea and Thiourea Derivatives as Low Molecular-Mass Organogelators. *Chem.—Eur. J.* **2005**, *11*, 3243–3254.

(13) Skilling, K. J.; Citossi, F.; Bradshaw, T. D.; Ashford, M.; Kellam, B.; Marlow, M. Insights into Low Molecular Mass Organic Gelators: A Focus on Drug Delivery and Tissue Engineering Applications. *Soft Matter* **2014**, *10*, 237–256.

(14) Tu, T.; Bao, X.; Assenmacher, W.; Peterlik, H.; Daniels, J.; Dotz, K. H. Efficient Air-Stable Organometallic Low-Molecular-Mass Gelators for Ionic Liquids: Synthesis, Aggregation and Application of Pyridine-Bridged Bis(benzimidazolylidene)-Palladium Complexes. *Chem.—Eur. J.* **2009**, *15*, 1853–1861.

(15) Liu, J.; Yan, J.; Yuan, X.; Liu, K.; Peng, J.; Fang, Y. A Novel Low-Molecular-Mass Gelator with a Redox Active Ferrocenyl Group: Tuning Gel Formation by Oxidation. *J. Colloid Interface Sci.* **2008**, *318* (2), 397–404.

(16) Goh, C. Y.; Mocerino, M.; Ogden, M. I. Macrocyclic Gelators. *Supramol. Chemi.* **2013**, *25*, 555–566.

(17) D'Anna, F.; Vitale, P.; Marullo, S.; Noto, R. Geminal Imidazolium Salts: A New Class of Gelators. *Langmuir* **2012**, *28*, 10849–10859.

(18) Minakuchi, N. H.; Yamaki, K.; Tenno, D.; Nakashima, S.; Goto, K.; Mizuhata, M.; Maruyama, T. Versatile Supramolecular Gelators that Can Harden Water, Organic Solvents and Ionic Liquids. *Langmuir* **2012**, *28*, 9259–9266.

(19) Fan, M.; Song, Z.; Liang, Y.; Zhou, F.; Liu, W. Laxative Inspired Ionic Liquid Lubricants with Good Detergency and no Corrosion. *ACS Appl. Mater. Interfaces* **2014**, *6*, 3233–3241.

(20) Wei, J.; Cai, M.; Zhou, F.; Liu, W. Candle Soot as Particular Lubricant Additives. *Tribol. Lett.* **2014**, *53*, 521–531.

(21) Li, D.; Gao, P.; Sun, X.; Zhang, S.; Zhou, F.; Liu, W. The Study of TEMPOs as a Additives in different Lubrication oils for Steel/Steel Contacts. *Tribol. Int.* **2014**, *73*, 83–87.

(22) Escuder, B.; Juan, F.; Miravet, J. F. Insight on the NMR Study of Supramolecular Gels and Its Application to Monitor Molecular Recognition on Self-Assembled Fibers. *J. Org. Chem.* **2006**, *71*, 7747–7752.

(23) Tokuhiro, T.; Mamada, A.; Tanaka, T. NMR Study of Poly(N-isopropylacrylamide) Gels Near Phase Transition. *Macromolecules* **1991**, *24*, 2936–2943.

(24) Suzuki, M.; Nanbu, M.; Yumoto, M.; Shirai, H.; Hanabusa, K. Novel Dumbbell-Form Low-Molecular-Weight Gelators based on l-Lysine: Their Hydrogelation and Organogelation Properties. *New J. Chem.* **2005**, *29*, 1439–1444.

(25) Iqbal, S.; Rodríguez-Llansola, F.; Escuder, B.; Miravet, J. F.; Verbruggen, I.; Willem, R. HRMAS ^{1}H NMR as a Tool for The Study of Supramolecular Gels. *Soft Matter* **2010**, *6*, 1875–1878.

(26) Basit, H.; Pal, A.; Sen, S.; Bhattacharya, S. Two-component Hydrogels Comprising Fatty Acids and Amines: Structure, Properties, and Application as a Template for the Synthesis of Metal Nanoparticles. *Chem.—Eur. J.* **2008**, *14*, 6534–6545.

(27) Peng, J.; Xia, H.; Liu, K.; Gao, D.; Yang, M.; Yan, N.; Fang, Y. Water-in-oil Gel Emulsions from a Cholesterol Derivative: Structure and Unusual Properties. *J. Colloid Interface Sci.* **2009**, *336*, 780–785.

(28) Takahashi, K.; Shitara, Y.; Kaimai, T.; Kanno, A.; Mori, S. Direct Observation of Thermo-Reversible Gel-Lubricants in EHL by FT-IR Micro-Spectroscopy. *Tribol. Online* **2008**, *3*, 131–136.

(29) Nobuyoshi, O.; Sobahan, M.; Kenji, T.; Shigeki, M.; Yuji, S. Construction of Phase Diagram up to 2 GPa and 200°C for Thermo-Reversible Gel Lubricants by Diamond Anvil Cell. *Lubr. Sci.* **2009**, *21*, 183–192.

(30) Cai, M.; Liang, Y.; Zhou, F.; Liu, W. Tribological Properties of Novel Imidazolium Ionic Liquids Bearing Benzotriazole group as the Antiwear/Anticorrosion Additive in Poly(ethylene glycol) and Polyurea Grease for Steel/Steel Contacts. *ACS Appl. Mater. Interfaces* **2011**, *3*, 4580–4592.

(31) Nobuyoshi, O.; Sobahan, M.; Kazuo, M.; Kentaro, S.; Yuji, Y.; Yoshitaka, T.; Shigeki, M.; Yuji, S. Tribological Properties and Film Formation Behavior of Thermoreversible Gel Lubricants. *Tribol. Trans.* **2010**, *53*, 722–730.

(32) Fan, M.; Song, Z.; Liang, Y.; Zhou, F.; Liu, W. In Situ Formed Ionic Liquids in Synthetic Esters for Significantly Improved Lubrication. *ACS Appl. Mater. Interfaces* **2012**, *4*, 6683–6689.

(33) Liu, G.; Wang, X.; Zhou, F.; Liu, W. Tuning the Tribological property with Thermal Sensitive Microgels for Aqueous Lubrication. *ACS Appl. Mater. Interfaces* **2013**, *5*, 10842–10852.

(34) Cai, M.; Liang, Y.; Zhou, F.; Liu, W. A Novel Imidazolium Salt with Antioxidation and Anticorrosion Dual Functionalities as the

Additive in Poly(ethylene glycol) for Steel/Steel Contacts. *Wear* **2013**, *306*, 197−208.

(35) Song, Z.; Fan, M.; Liang, Y.; Zhou, F.; Liu, W. Lithium-Based Ionic Liquids: In Situ-Formed Lubricant Additive Only by Blending. *Tribol. Lett.* **2013**, *49*, 127−133.

(36) http://www.srdata.nist.gov/xps/.

(37) Liu, B.; Xi, H.; Li, Z.; Xia, Q. Adsorption and Corrosion-Inhibiting Effect of 2-(2-{[2-(4-Pyridylcarbonyl)hydrazono]methyl}-phenoxy)acetic Acid on Mild Steel Surface in Seawater. *Appl. Surf. Sci.* **2012**, *258*, 6679−6687.

(38) Cai, M.; Zhao, Z.; Liang, Y.; Zhou, F.; Liu, W. Alkyl Imidazolium Ionic Liquids as Friction Reduction and Anti-Wear Additive in Polyurea Grease for Steel/Steel Contacts. *Tribol. Lett.* **2010**, *40*, 215−224.

(39) Song, Z.; Liang, Y.; Fan, M.; Zhou, F.; Liu, W. Lithium-Based Ionic Liquids Functionalized by Sym-Triazine and Cyclotriphospha-zene As High Temperature Lubricants. *Tribol. Int.* **2014**, *70*, 136−141.