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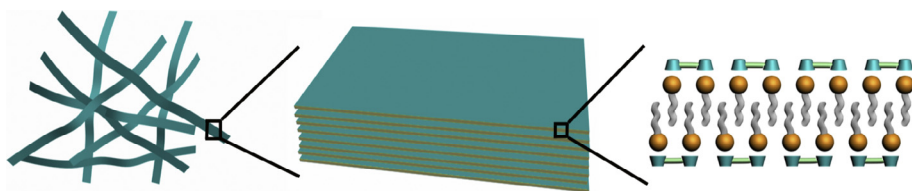
Ionogels of pseudogemini supra-amphiphiles in ethylammonium nitrate: Structures and properties



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GRAPHICAL ABSTRACT



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ABSTRACT

Thermoreversible ionogels formed by pseudogemini surfactants were prepared in protic ionic liquid, ethylammonium nitrate (EAN). Gemini-type supra-amphiphiles were formed by single-chain surfactants and bola-type molecules in a 2:1 M ratio. The structures of aggregates including polymorphous lamellar structures and fibrous networks constituted by multilayer lamellae were determined by optical microscopy observations, transmission electron microscopy (TEM) observations, small-angle X-ray scattering (SAXS) and X-ray diffraction (XRD) measurements. The mechanism of molecular arrangement in aggregates was proposed. Transformation temperatures of samples which are closely related to the stability of well-ordered molecules in aggregates, as well as the rheological properties of ionogels were investigated systematically. The work affords a new way to construct ionogel by using the supramolecular self-assembly of pseudogemini-type molecules, and brings new ideas for the future construction of ionogels.

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1. Introduction

Room-temperature ionic liquids (RTILs) constructed by asymmetric cations and anions are usually defined as molten salts with liquid state below 100 °C [1,2]. Numerous characteristics including high thermostability, chemical stability, good ionic conductivity, nonvolatility, wide electrochemical window and easy-design structure make IL-containing materials attractive in various fields [1–6]. The first discovered ionic liquid is ethanolanmonium nitrate with a melting point of about 55 °C, which was reported by Gabriel in 1888 [7]. Walden reported another famous protic RTIL, ethylam-

monium nitrate (EAN) in 1914, and its melting point is about 12 °C [8]. Due to the similar properties as water, such as the formation of three-dimensional hydrogen-bonded networks, EAN is a widely applicable medium for self-assembly [9–11]. It has been demonstrated that the specific solvent structure caused by the hydrogen bonding play an important role in the self-assembly of amphiphilic molecules [12]. So far, various self-assembled structures using EAN as the medium have been reported, including micelles [13,14], vesicles [15], liquid crystals [16], microemulsions [17–20], chiral ribbons and lamellar structures [21,22]. The driving forces for the self-assembly are usually noncovalent interactions, such as hydrogen bonding, solvophobic interaction, metal coordination-chelation interaction and π - π stacking interactions [23]. Different from hydrogels and organogels, ionogels refer to gels formed by

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different additives in RTILs. To prepare ionogels, we can add both organic and inorganic materials into RTILs. Common additives contain polymers, low-molecular-weight gelators, carbon materials and silica and so on [22,24–27]. The gelation of RTILs makes ionogels useful in solid devices [28]. Ionogels possess the good ionic conductivity as the original ILs [24,25], meanwhile, they display high mechanical properties [29,30], good thermal stability [30,31] and excellent lubricity [21,22].

Gemini surfactants contain two sets of hydrophilic headgroups and hydrophobic tails, which are covalently connected with a spacer. Compared to single-chain surfactants, gemini surfactants possess superior performances, such as the very low critical micelle concentration in water, which cutting down on surfactant consumption [32–35]. The synthesis of gemini surfactants is time-consuming and troublesome, so pseudogemini surfactants as the new generation of gemini surfactants have been constructed [34,36–39]. From the aspect of supramolecular self-assembly, pseudogemini surfactants which are traditionally constructed by two single-chain surfactants and one bola-type linker through the noncovalent interactions, belong to the gemini-type supra-amphiphiles [40,41]. Through various noncovalent interactions, diverse aggregates formed by pseudogemini surfactants have been reported, including micelles, vesicles, polymorphous lamellar structures and lyotropic liquid crystals [36,38,39,42,43]. Feng's group has investigated pH-switchable viscoelastic fluids constructed by pseudogemini surfactants systematically [42–44]. It is convenient and efficient to construct polymorphous aggregates by pseudogemini surfactants. Also, by introducing specific molecules with functional groups, we can obtain stimuli-responsive self-assemblies. So far, the reported self-assembly of pseudogemini surfactants is almost all in water. RTILs are another good media for pseudogemini surfactants to form self-assembled structures.

Inspired by the construction of pseudogemini supra-amphiphiles, in present work, we prepared ionogels by using alkyl dimethylamine oxide (C_n DMAO)/sebacic acid (SA) and sodium alkyl sulfonate ($C_nH_mSO_3Na$)/N,N,N',N'-tetramethyl-1,3-propane diamine (TMPDA) in protic EAN, as shown in Scheme 1. Pseudogemini surfactants formed in a 2:1 M ratio due to the noncovalent interactions, including the electrostatic interaction, hydrogen bonding and solvophobic interactions. Microstructures of fibrous networks and lamellar structures were revealed by optical microscopy observations, transmission electron microscopy (TEM) observations, small-angle X-ray scattering (SAXS) and X-ray diffraction (XRD) measurements. Fourier transform infrared spectroscopy (FT-IR) results confirmed the existence of electrostatic attractions and hydrogen bonding between different molecules. Both differential scanning calorimetry (DSC) and rheological measurements were performed to investigate the properties of ionogels. The work presents a simple method, that is, pseudogemini-type supramolecular self-assembly, to prepare ionogels. It may provide helpful ideas for future development of ionogels.

2. Materials and methods

2.1. Materials

Dodecyl dimethylamine oxide (C_{12} DMAO) and tetradecyl dimethylamine oxide (C_{14} DMAO) aqueous solutions were purchased from Clariant Company in China. The products were freeze-dried and purified by recrystallization for at least three times in acetone. Sebacic acid was purchased from Shanghai Chemical reagents Co., Ltd. Reagent No. 3 Factory. Sodium dodecyl sulfonate and sodium tetradecyl sulfonate were purchased from Merck (Germany). N,N,N',N'-tetramethyl-1,3-propanediamine was purchased from J&K Scientific Co., Ltd. (China). The aqueous solu-

tion of ethylamine (65–70 wt%) and nitric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). They were used directly without further purification. EAN was prepared according to the reported method [45]. Briefly, in an ice bath, diluted HNO_3 was added into the aqueous solution of ethylamine slowly, then the mixture was stirred for two hours. The separation of water from the raw product has been detailedly described in a previous report [13].

2.2. Sample preparation

Calculated amounts of chemicals and EAN were added into glass tubes and heated until clear solutions were observed. Then they were cooled at the room temperature and different phases were obtained.

2.3. Methods and characterizations

Optical microscopy observations were carried out on an AXIOS-KOP $\alpha 40/40$ FL (ZEISS, Germany) microscope. We performed SAXS measurements by using a SAXSess mc^2 X-ray scattering system (Anton Paar) which was operated at 50 kV and 40 mA. The distance between the detector and the sample was 264.5 mm and the X-ray wavelength was 0.1542 nm ($Cu K\alpha$). The measured time for all samples was 900 s. pH values were measured on a METTLER TOLEDO FE20K pH meter at 25 °C. The phase-transformation temperatures were determined on a DSC8500 instrument (PerkinElmer, USA) from 0 to 100 °C at 5 °C min^{-1} . Rheological measurements were performed on a Haake RheoStress 6000 rheometer with a cone-plate sensor system (C35/1° Ti L07116, diameter: 35 mm, core angle: 1°), and the temperature was controlled by the circulator HAAKE DC10 cyclic water bath (Karlsruhe, Germany). The stress sweep measurements were carried out at a fixed oscillatory frequency of 1 Hz. With the frequency ranging from 0.1 to 100 Hz, oscillatory shear measurements were performed under an appropriate stress selected from the linear viscoelastic region. TEM results were observed on a JEOL JEM-1400 TEM operating at 120 kV. By using a Rigaku D/Max 2200PC diffractometer equipped with a graphite monochromator and $Cu K\alpha$ radiation ($\lambda = 0.15418$ nm), XRD patterns were measured in the range of $2^\circ < 2\theta < 12^\circ$. The FT-IR spectra were obtained from a VERTEX-70/70v FT-IR spectrometer (Bruker Optics, Germany). By taking 32 scans with a resolution of 4 cm^{-1} , spectra from 4000 to 400 cm^{-1} were measured. We performed the spectral manipulation by using the OPUS 6.5 software package (Bruker Optics, Germany). To prepare samples for measurements of TEM, XRD and FT-IR, EAN in ionogels was removed by using acetonitrile. The solvent exchange method has been reported in the reports [22,46].

3. Results and discussion

3.1. Aggregation behaviors

Two systems of C_n DMAO/SA and $C_nH_mSO_3Na$ /TMPDA were used to investigate structures and properties of pseudogemini in EAN at room temperature (RT), where n and m refer to the numbers of C and H atoms. Aggregation behaviors of two systems are shown in Fig. 1 and Fig. S1. Clear solutions of C_n DMAO/SA/EAN and $C_nH_mSO_3Na$ /TMPDA/EAN were obtained at high temperature, then they transformed to different states when cooling slowly to RT. With the variation of molar ratio (ρ , referring to molar ratios of SA to C_n DMAO and TMPDA to $C_nH_mSO_3Na$) and concentrations of C_n DMAO and $C_nH_mSO_3Na$, different phases including the clear solution, precipitate, sol and gel could be observed. Precipitates formed by C_n DMAO/SA at the top of the solution are needlelike

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