



Synthesis of fluorinated silicon-containing amphiphilic copolymer and its demulsification performance

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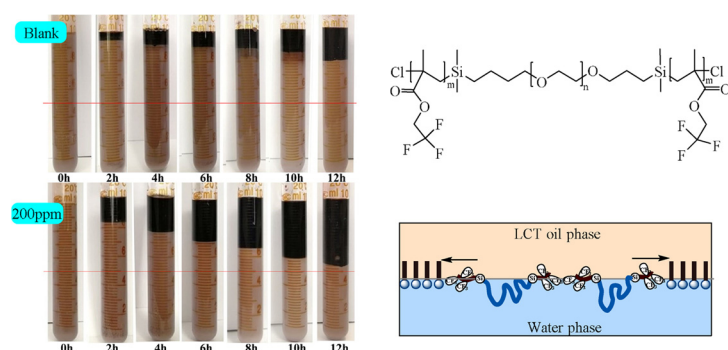
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GRAPHICAL ABSTRACT



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ABSTRACT

A series of novel fluorinated silicon-containing copolymers were prepared by atom transfer radical polymerization (ATRP). This was achieved by polymerization of 2,2,2-trifluoroethyl methacrylate (TFEMA) with the dimethylchlorosilane terminated allyl-substituted poly(ethylene glycol) (PEG). Their demulsification performance for low-temperature coal tar (LCT) /water emulsion were evaluated via bottle tests. The influences of demulsifier dosage, settling time and temperature on the demulsification efficiency were investigated in detail. The copolymers were able to remove more than 90% LCT from the LCT emulsion and provide good demulsification performance. The interfacial tension and interfacial rheology properties of LCT emulsions in the presence of the copolymers were systematically discussed. The results revealed that the copolymers did not affect the interfacial tension of the emulsion significantly, but decrease the elasticity of the interface film obviously. The solvophobicity of PTFEMA chains can not only effectively improve the diffusion rate of the polymer from the bulk to the interface, but also destroy the interfacial film structure and promote the coalescence of emulsion droplets.

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1. Introduction

Low temperature pyrolysis process (LTPP) is an economically efficient method for improving the utilization efficiency of low-rank coals (such as lignite). In China, LTPP technology has been promoted in recent years in Shanxi, Shaanxi, Inner Mongolia, and Ningxia province, and the low-temperature coal tar (LCT) production has reached 10 million tons each year. With the development of LCT deep processing technology, LCT has become an important raw material for both the energy and chemical industries [1,2].

In the LCT production process, the tar is condensed from the hot coke oven gas with ammonia liquor, and then the liquid mixture is delivered to decanter tank for settling [3]. Due to the presence of ammonia, phenols, and naphthalenes, the liquid mixture is used to form a stable emulsion, and the tar is particularly difficult to separate from the mixture. In the usual process, the mixture is settling in tar decanter at 60–80 °C for 40 h to achieve preliminary separation. To meet the requirements of subsequent distillation process, centrifugal separation, steam heating, flash dehydration, or a combination of these methods are applied in the tar dewatering process to further reduce the tar moisture to 0.5% or less. However, these processes require a quite long period of time and large storage quantities of materials, which cause environmental problems and safety hazards, and result in loss of economic return and environmental benefits. Therefore, the development of a rapid and high efficient demulsification technology for the emulsion of tar, is an important subject in the LCT production process.

Chemical demulsification is one of the effective ways to break emulsions, which involves the use of amphiphilic molecular as demulsifier to adsorb at the oil-water interface and accelerate the emulsion breaking process [4]. In contrast to the use of chemical demulsification in crude oil recovery, there are very few reports of demulsifier in coal tar separation, and especially for LCT. Due to the significant difference in coal tar and crude oil components, especially LCT have a high phenolic content about 10–50% and specific gravities of 0.95–1.06 [5,6], which resulting in a more stable emulsion, the demulsifiers for crude oil are usually not effective for breaking LCT emulsions. Therefore, it is necessary to develop special demulsifier for coal tar and study its demulsification mechanism.

It is well known that fluorinated amphiphilic polymers exhibit unique properties such as low surface tension, high thermal and chemical stability, and oleo-hydrophobicity [7]. Due to the high surface activity of the fluorinated polymers, it is often used as emulsifier for the preparation of supercritical CO₂ emulsions or microemulsions [8]. Moreover, fluorinated polymers are effective in stabilizing emulsions containing nanomaterials or immiscible polymers, and can be used to control emulsion phase inversion for coating applications [9–11]. However, fluorinated polymers have rarely been reported as demulsifiers.

In our previous work, we have synthesized a series of fluorinated amphiphilic polymers and evaluated their demulsification performance in lubricating oil emulsion [12–15]. It was found that the fluorinated groups could effectively improve the diffusion rate of the polymer from liquid phase to interface and result in an effective demulsification. However, the fluorinated segments will also significantly reduce the solubility of the polymers in water and organic solvents [16]. How to improve the interfacial activity of fluorinated polymers as much as possible while ensuring a certain solubility is one of the problems that need to be solved in designing fluorinated demulsifiers.

As the silane-based amphiphiles are long known for lower surface tension coupled with an exceptionally the surface activity in both aqueous and nonaqueous media [17], it is expected that the amphiphiles containing fluorinated and silane groups will show an interesting demulsification performance. Since silane groups do not have the oleo-hydrophobic nature of the fluorinated group, the introduction of silane groups has a relatively small effect on the solubility of the polymer in organic solvents. Therefore, we introduced two silane groups at both

ends of PEG, which can improve the interfacial activity of the polymer and not significantly affect its solubility in organic solvents. On this basis, we introduced TFEMA segments to further improve the demulsification performance. In this paper, we describe for the first time the synthesis of amphiphilic copolymers based on PEG as hydrophilic block and fluorinated carbosilane groups as hydrophobic block, and evaluated their demulsification performance in coal tar emulsion. In order to compare the effect of fluorinated groups on the demulsification performance, we also synthesized the non-fluorine-containing polymers with ethyl methacrylate as monomer, and compared their demulsifying properties and interfacial properties. The demulsification mechanism of the copolymer was proposed from the results of interfacial tension and interface viscoelasticity measurements.

2. Experimental section

2.1. Materials

Allyl bromide (99%), 2,2'-bipyridine (bpy, > 99.0%), ethyl methacrylate (EMA, 99%) were supplied by Acros Organics; Poly(ethylene glycol) (PEG, MW 1000), dimethylchlorosilane (98%), sodium hydride (60% dispersion in mineral oil), Tetrabutylammonium iodide ($\geq 99\%$), Copper(I) bromide (CuBr, 98%), Karstedt's catalyst (in xylene, Pt ~ 2%) were purchased from Sigma-Aldrich; 2,2,2-trifluoroethyl methacrylate (TFEMA, > 96.0%) was purchased from Xeogia Fluorine-Silicon Chemical Co., Ltd. (Harbin, China); the other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). LCT were obtained from the Boyuan Technology Co., Ltd. (Chifeng, Inner Mongolia, China) and were directly used without further treatment. The physical and chemical properties of the LCT were characterized in Table 1. The density and viscosity were measured at 20 °C.

Allyl bromide was vacuum distilled over calcium chloride. TFEMA was washed in 5% aqueous NaOH to remove the inhibitor and then with water, after that it was dried over anhydrous MgSO₄, and distilled over CaH₂ under reduced pressure before use. EMA was treated in the same process as TFEMA. Tetrahydrofuran (THF) was refluxed over sodium wire and distilled before use. Pyridine and chloroform were distilled over CaH₂ under reduced pressure. PEG was dried to constant weight under reduced pressure. CuBr was purified by the procedure described in the literature [18]. The other reagents were used without further purification.

2.2. Sample characterization

¹H NMR, ¹³C NMR and ¹⁹F NMR measurements were conducted using a Bruker AVANCE III NMR spectrometer, and samples were dissolved in CDCl₃. Fourier transform infrared (FT-IR) spectra were obtained in the range 4000–400 cm⁻¹ using a Bruker Tensor 27 spectrometer. The molecular weight and polydispersity of the polymers were measured using size exclusion chromatography (SEC) with polystyrene as standard, THF (1.0 mL min⁻¹) as the eluent. The dynamic light scattering (DLS) measurements were made using Nano-ZS (Malvern Instruments Ltd., UK), and six measurements were performed on each sample, with an average of 16 runs taken for each measurement.

2.3. Synthesis

allyl-PEG-allyl. All operations were carried out under nitrogen

Table 1
Properties of LCT.

Density (g/cm ³)	Viscosity (mm ² /s)	Carbon (wt %)	Hydrogen (wt %)	Oxygen (wt %)	Surfur (wt %)	Nitrogen (wt %)
0.9527	12.3	81.35	8.63	7.68	0.49	0.97

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