The Journal of Supercritical Fluids 127 (2017) 129–136

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Enhancement of the CO_2-philicity of poly(vinyl ester)s by end-group modification with branched chains

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ARTICLE INFO

Keywords:
Poly(vinyl acetate-alt-maleate diester)
CO_2-philicity
Cloud point
Ab initio
Molecular dynamics

ABSTRACT

Four copolymers of vinyl acetate (VAc) and comonomers with different branched chains—dipropyl maleate (DPM), dibutyl maleate (DBM), diisobutyl fumarate (DiBF) and dineopentyl maleate (DNM)—were synthesised, and their CO_2-philicity was evaluated by cloud point measurements. It was shown that poly(VAc-alt-DNM), containing the highest branched structure degree, had a 10% lower cloud point pressure at 40 °C than poly(VAc-alt-DBM)'s, the best CO_2-philic hydrocarbon polymer available. Both ab initio calculations and molecular dynamics (MD) simulations showed that the highly branched structure weakened polymer–CO_2 interactions. However, the MD results for the cohesive energy density, solubility parameter, free volume fraction and radial distribution functions indicated that the more highly branched end groups contributed to an increase in the free volume fraction of the polymer, leading to low polymer–polymer interactions. Thus, the introduction of highly branched end groups into the polymer backbone was an efficient way to enhance the CO_2-philicity of hydrocarbon polymers.

1. Introduction

The sustainability and renewability of solvents used in industrial processes have received increasing attention, leading to a demand for 'green' solvents [1–3]. Supercritical carbon dioxide ($scCO_2$) is an ideal alternative for volatile organic solvents, which pollute the environment and have high disposal costs, because it is non-toxic, non-flammable, environmentally benign, and relatively cheap, and has a moderate critical temperature and pressure (T_c = 31.1 °C, P_c = 7.38 MPa) [4]. Thus, $scCO_2$ is widely used in extraction, reactions, polymer processing, and enhanced oil recovery (EOR) [5–9]. However, the poor polarity and low dielectric constant of $scCO_2$ limit its capability to dissolve polar and macromolecular substances. Water-in-CO_2 (W/C) microemulsions or CO_2-in-water (C/W) emulsions have been widely accepted as a promising alternative to overcome these disadvantages [10]. The thermodynamic stability, small micelle diameters (5–100 nm), and high mass transfer coefficient of W/C microemulsions allow them to act as reactors in which the reaction and separation processes occur simultaneously [11]. Thus, these microemulsions could be used to synthesise nanoparticles and extract active drugs and biomacromolecules [12–14]. C/W emulsions were applied as templating agents in the synthesis of cellular material, displacing agent in enhancement of oil recovery and extractants [15–17]. The ability of surfactants to stabilise these microemulsions or emulsions is of great importance. However, only a few fluorinated surfactants can form and stabilise W/C microemulsions or C/W emulsions, and these surfactants are expensive and toxic [14,18–21]. Hydrocarbon-based surfactants are economical and environmentally friendly. However, their low solubility in CO_2 prevents them from stabilising or forming these emulsions or microemulsions. The presence of CO_2-philic fragments determines the solubility of the surfactants in CO_2, which is key to the efficacy of the surfactant. A CO_2-philic tail has also been shown to be necessary for surfactants to form W/C microemulsions. A surfactant based on aerosol-OT (AOT) modified with twin vinyl acetate (VAc) oligomeric chains (AO-VAc) successfully stabilised W/C microemulsions, but AOT alone could not [22]. This finding indicates that CO_2-philic fragments play an important role in the formation of W/C microemulsions. These fragments reduce micelle–micelle interactions, thereby stabilising the microemulsions. The formation of C/W emulsions with high internal phase contents required surfactants with highly CO_2-philic chains, which enable surfactants to dissolve sufficiently in the CO_2 to stabilise high quantities of CO_2 in the emulsions [15].

High-molecular-weight species including fluorinated polyacrylates [23,24], perfluoroalkyl ethers [25,26], and polysiloxanes [27,28] have been shown to dissolve in high quantities in CO_2 because of their low interface energy. However, both fluoropolymers and silicon-containing polymers are expensive, toxic, and environmentally hazardous, which limits their large-scale use. Hydrocarbon polymers are cheap and

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http://dx.doi.org/10.1016/j.supflu.2017.04.001
Received 14 February 2017; Received in revised form 23 March 2017; Accepted 1 April 2017

environmentally benign but have poor solubility in CO_2. Thus, efforts have been made to develop CO_2-philic hydrocarbon polymers and low-fluorine-content polymers [29–35]. In recent studies, polyvinyl acetate (PVAc) was found to be the most CO_2-philic hydrocarbon homopolymer. A 5 wt.% loading of PVAc with a number-average molecular weight (M_n) of 2060 g/mol could be dissolved in CO_2 under a pressure of 37.4 MPa at 25 °C [36]. Various approaches have been used to enhance the solubility of poly(vinyl ester) in CO_2, such as modification of its end group with a fluorine atom or copolymerisation of vinyl acetate (VAc) with a comonomer. Marty and Destarac reported the use of a partially fluorinated CO_2-philic polymer [30,35], finding that polymer–polymer interactions were reduced by the copolymerisation of VAc with a partially fluorinated vinyl ester. The cloud point pressure of a 0.2 wt.% loading (based on CO_2) of poly(vinyl acetate-co-vinyl trifluorobutyrate) with M_n = 4500 g/mol was reduced to 15.4 MPa at 40 °C, which was 45.5% lower than that of PVAc with M_n = 4600 g/mol under the same conditions [35]. Unfortunately, the polymers still contain a few fluorine atoms, although their CO_2-philicity was greatly improved. The copolymerisation of VAc with some hydrocarbon comonomers provided an effective method to obtain a CO_2-philic hydrocarbon fragment. Various monomers copolymerised with vinyl esters to enhance the CO_2-philicity of the PVAc based polymers. At 35 °C and 0.2 wt.% based on CO_2, the cloud point pressure of poly(vinyl acetate-alt-dibutyl maleate) with M_n = 4400 g/mol and PDI = 1.28 was decreased to 18.7 MPa, while that of PVAc with M_n = 4000 g/mol and PDI = 1.15 was 25.5 MPa [34]. Both ab initio calculations and molecular dynamics (MD) simulations proved that both polymer–polymer and the polymer–CO_2 interactions were reduced [31,32,35]. As previously reported, stronger polymer–CO_2 interactions and lower polymer–polymer interactions result in improved CO_2-philicity of a copolymer, and the latter is suggested to play a major role [10]. There remains great potential for improvements in the CO_2-philicity of copolymers to promote their application as surfactants to stabilise emulsions or microemulsions.

As the poly(vinyl acetate-alt-dibutyl maleate) exhibits a great CO_2-philicity of the hydrocarbon copolymers, some branched chains structure was introduced to modify the monomer dibutyl maleate to improve its CO_2-philicity. In this work, four comonomers with different branched chains—dipropyl maleate (DPM), dibutyl maleate (DBM), diisobutyl fumarate (DiBF), and dineopentyl maleate (DNM)—were designed to copolymerise with vinyl acetate. The effect of the branched chains on the CO_2-philicity of end-group-modified poly(vinyl esters) was investigated. The polymer–polymer interactions, polymer–CO_2 interactions, and free volume of the copolymers were determined using ab initio and MD simulations to understand the miscibility mechanism of the copolymers in CO_2. Study on the effect of the branched chains on the CO_2-philicity of polymers was promising to provide a further improvement on the hydrocarbon polymers' CO_2-philicity. Introduction of branch chain to enhance CO_2-philicity can help to design for hydrocarbon surfactants for more applications, instead of using the expensive and toxic fluorine-content surfactants.

2. Experimental

2.1. Materials

Vinyl acetate (VAc, 99%, Aladdin) was sequentially washed three times with both saturated sodium bisulfite solution, sodium carbonate (Na_2CO_3, 10 wt.%) solution, and deionised water then dried over anhydrous magnesium sulphate and distilled under vacuum. Azobisisobutyronitrile (AIBN, Aladdin) was recrystallised from ethanol three times. *p*-Toluene sulfonic acid (99%, TsOH, Aladdin), maleic anhydride (99%, Aladdin), DBM (99.5%, Aladdin), DiBF (98%, TCI), n-propanol (99.5%, Aladdin), neopentyl alcohol (99%, Energy Chemical), potassium ethyl xanthate (98%, Adamas) and methyl 2-bromopropionate (97%, Adamas) were used as received.

2.2. Synthesis of DPM, DNM, and poly(vinyl acetate-alt-maleate diester)

Maleic anhydride, n-propanol, and TsOH were added to a round-bottom flask equipped with a Soxhlet extractor filled with active 4 Å molecular sieves in a molar ratio of 10:40:1, and heated at reflux with stirring for 60 min. The solution was dried by rotary evaporation and then distilled under vacuum to furnish DPM in a 92% yield.

Maleic anhydride, neopentyl alcohol, and TsOH were added to a round-bottom flask with a manifold in a molar ratio of 10:22:1, along with methylbenzene. The mixture was heated to reflux was stopped when no further water was generated. The crude product was purified by silica gel column chromatography. The resulting product was dried at 50 °C under vacuum for more than 24 h to furnish DNM in an 80% yield. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra of DPM and DNM are shown in Figs. A.1–A.4 in the Supplementary Information.

Poly(vinyl acetate-alt-maleic diester) was synthesised by free radical polymerisation in isopropanol. For the free radical polymerisation, equimolar quantities of vinyl acetate and maleic diester were added to a flask with AIBN (0.5 wt.% based on the total weight of both monomers). The monomers were dissolved in isopropanol (20% based on the volume of monomers). The reaction was carried out at 70 °C for 16 h under nitrogen protection. The copolymers of VAc and DPM, DBM, DiBF, and DNM were named PVDPM, PVDBM, PVDiBF, and PVDNM, respectively.

After the polymerisation, the solution of PVAc and PVDBM was separated from unreacted monomers by precipitation, e.g., into cold n-hexane. For the further purification, the precipitates were diluted with chloroform and reprecipitated in cold n-hexane three times. The final precipitates were dried in a vacuum oven at 60 °C for 48 h. Solutions of PVDiBF and PVDNM in ethanol were purified using a regenerated cellulose dialysis bag (with a molecular weight cut-off of 1000 g/mol) and then dried in a vacuum oven at 60 °C for 48 h.

2.3. Characterisation of poly(vinyl acetate-alt-maleate diester)

All the copolymers were analysed by 400 MHz ^1H NMR in $CDCl_3$ using a Bruker DMX 500 spectrometer. The molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC, Agilent, PL-GPC50) using THF as the eluent.

2.4. Cloud point pressure measurements in CO_2

A high-pressure variable volume view cell equipped with a pressure sensor (YMC-1N, with a precision of ± 0.035 MPa) and a thermocouple-controlled (T type, with an accuracy of ± 0.1 °C) thermostat was used to measure the cloud point pressure of the polymers [31,32]. The initial volume of the cell was set at 25.6 mL, and the initial pressure and temperature at 20 MPa and 25 °C, respectively. The density of CO_2 at 20 MPa and 25 °C is 914.2 kg/m^3 [37]. CO_2 (22.86 g) and polymer (0.0457 g, i.e., 0.2 wt.% based on CO_2) were loaded into the cell with a magnetic stirrer, and the cell was sealed. Thereafter, the cell was heated to a chosen temperature (35 °C, 40 °C and 45 °C). The mixture was stirred magnetically for 30 min, during which a single transparent phase formed. The cloud point was observed by expanding the volume slowly. The polymer–CO_2 solution, as viewed from the sapphire glass window, became cloudy at a certain lower CO_2 pressure because of phase separation, and this pressure was defined as the cloud point pressure and denoted P_c. The P_c of each copolymer was measured at least 3 times to ensure experimental reliability. The experimental error was less than ± 1%. The optical images of cloud point measurement are shown in Fig. 1.