Thickening of CO\textsubscript{2} Using Copolymer- Application in CO\textsubscript{2} Management

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ABSTRACT

The objective of this research was the design, synthesis and evaluation of fluorous CO\textsubscript{2} thickening agent for the better understanding and development of inexpensive non-fluorous CO\textsubscript{2} thickening agents. Firstly a highly CO\textsubscript{2}-philic, hydrocarbon-based monomer was identified for soluble in CO\textsubscript{2}. Secondly, synthesis of copolymer in which CO\textsubscript{2}-philic monomer was combined with a small proportion of CO\textsubscript{2}-phobic and philic (3-vinylaniline) associating groups for viscosity-enhancing intermolecular interactions to occur and a primary amine CO\textsubscript{2}-philic group for capturing CO\textsubscript{2}.

1. Introduction

Environmental issues are a major cause for concern in the world of today. Greenhouse gases are an environmental concern that is continuously increasing in importance, especially the emissions of carbon dioxide. Fossil fuel burning results in the emission of carbon dioxide. This additional carbon dioxide is upsetting the delicate balance that the earth manages naturally. In order to reduce the amount of carbon dioxide released into atmosphere, the carbon dioxide must be captured and stored, or sequestered. In order to store carbon dioxide, the gas must be captured prior to release into the atmosphere. One of the methods could be thickening/gelation of CO\textsubscript{2}.

The identification of highly CO\textsubscript{2}-soluble polymers composed of only Carbon, hydrogen, oxygen and nitrogen could facilitate the design of safe, inexpensive, environmentally benign “CO\textsubscript{2}-philes”. These compounds could enhance the performance and economics of CO\textsubscript{2}-based technologies that require the dissolution of amphiphiles, such as surfactants, chelating agents, thickeners, and dispersants and homopolymers or copolymers for CO\textsubscript{2} thickening. An extensive review of polymer solubility in dense carbon dioxide was previously conducted in an attempt to identify a thickener that would reduce the mobility of supercritical CO\textsubscript{2} flowing through porous media (Heller, et al. 1985). Although very little work on viscosity-enhancing associative thickener or polymer has been done. Therefore, the objective of the current work was to determine whether the fluoroacrylate-3-vinylaniline copolymer could be sufficiently soluble in CO\textsubscript{2} in the 298 to 373 K temperature range to increase the viscosity and decrease the mobility of carbon dioxide.

2. Experimental

\textbf{Copolymer Synthesis:} 3-vinylaniline [Aldrich, 97\%] was purified under vacuum distillation to remove KOH inhibitor. 1H,1H,2H,2H-perfluorodecyl acrylate [Aldrich, 97\%] was used after the inhibitor, 100 ppm tert-butylcatechol, was removed by adding the monomer Drop wise to an inhibitor removal column (Fig.1). Bulk, free radical polymerization, with AIBN as initiator, was used to obtain a random copolymer product.

\textbf{ROTARY EVAPORATOR}

\textbf{INHIBITOR REMOVAL COLUMN}

Fig. 1 Experimental setup

3. Results and Discussion

In a typical synthesis of the 71\% fluoroacrylate, 29\% 3-vinylaniline copolymer, 0.91 g (0.007873 mol) 3-vinylaniline, 10.00 g (0.01929 mol) fluoroacrylate, and 8.93*10\textsuperscript{-3} g (5.44*10\textsuperscript{-3} mol) of AIBN were added to a 50-ml glass ampule under an inert N\textsubscript{2} atmosphere. The ampule was sealed and placed in an oil bath at 338 K for 12 hours to promote polymerization. The reaction products were then dissolved in 100 g 1,1,2-trichlorotrifluoroethane. The copolymer was then precipitated by washing with 300 g methanol, while the unreacted monomer remained in solution. The copolymer produced, a white solid was recovered by filtration. The copolymer was washed two more times in a similar manner and dried under vacuum overnight (Fig.1). The structure of the copolymer will be confirmed using standard IR and NMR techniques. The resultant copolymer could be a random copolymer of these two monomers (Fig. 2).

\textbf{FLUOROACRYLATE (CO\textsubscript{2}-PHILIC COMPONENT)}\hspace{0.5cm}3-VINYLANILINE (INTERMOLECULAR ASSOCIATING GROUP)

\textbf{COPOLYMER}

Fig. 2 Free radical polymerization synthesis process
The fluoroacrylate functional groups in these copolymer imparted CO$_2$-philicity to the candidate thickening agent, thereby facilitating its dissolution in dense CO$_2$. The carbon dioxide insoluble 3-vinylaniline group in the thickener enhanced intermolecular associations with similar groups in neighboring molecules. These intermolecular associations led to the formation of macromolecular structures in solution that were capable of inducing viscosity increase or gelation when present in dilute concentration. At the same time the secondary amine group on 3-vinylaniline could act as chemical absorbent and can help in capture of CO$_2$ by binding with CO$_2$ through carbonate or bicarbonate chemical bonding. Further work has to be done for better understanding of such copolymers and their affinity towards CO$_2$ as a thickening agent.

4. Concluding Remarks
This study showed the feasibility to design a polymer that exhibit both high carbon dioxide solubility and the ability to enhance carbon dioxide through intermolecular associations and chemical absorption using a fluorinated copolymer. A 71 mol% fluoroacrylate-29 mol% 3-vinylaniline random copolymer was synthesized through bulk, free-radical polymerization. The thickening capability of the copolymer over the 298 to 373 K temperature range has to be performed, however, this thickening could be attributed to intermolecular stacking of the aromatic rings associated with the 3-vinylaniline monomer. Although this copolymer might be successfully thickened CO$_2$, fluorinated polymers are expensive, unavailable in bulk quantities, and environmentally persistent. Therefore, we are currently also investigating non-fluorous thickeners, which are composed solely of carbon, hydrogen, oxygen, and nitrogen.

Acknowledgements
This work was supported by ARAMCO Research Project of the office of KAIST-ARAMCO Initiative.

References