Smart Multifunctional Polymers

DE-FC26-03NT15407

Goal

The objectives of this research are to synthesize, characterize, and evaluate stimuli-responsive polymer systems that can be formulated into "smart" fluids with rheological and interfacial properties substantially superior to those currently available for enhanced oil recovery (EOR) with chemical (micellar) flooding. The ultimate goal of this program is to produce "smart" polymers that work in adverse conditions, for example, in offshore, high-salinity reservoirs in an efficient, environmentally safe manner.

Performer

University of Southern Mississippi
Hattiesburg, MS

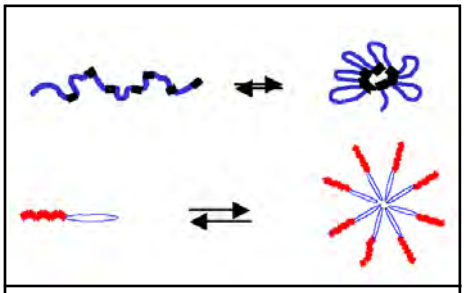
Results

This project has resulted in the synthesis of new monomers—some based on A-amino acids, and several novel chain-transfer agents (CTAs)—that have enabled the controlled polymerization of stimuli-responsive polymers with complex architectures. These copolymers have been characterized with regard to molecular weight and composition. The second phase of this project examines a) the solution properties of ion-containing polyelectrolytes and polyampholytes, which enhance viscosity; and b) the ability of polymeric micelles to form in reversible fashion and to sequester hydrocarbons.

Technical accomplishments include a) superior polyelectrolytes and polyampholytes based on monomer synthesized from ?-amino acids, b) new methods of polymer synthesis in aqueous solution, c) novel CTAs for block copolymer synthesis, and d) preparation of stimuli reversible micelles, or "polysoaps."

Benefits

Although a number of small-molecule surfactants have been utilized for micellar EOR, stimuli-responsive polymeric surfactants have not been tested in the field or the laboratory for advanced recovery. Polymeric surfactants responsive to pH and temperature can reversibly sequester model compounds, including tetradecane, naphthalene, and p-cresol. Unlike small-molecule surfactants, these unimeric polysoaps do not require concentrations above the CMC (critical micelle concentration) for sequestration of hydrocarbons, because each polymer contains intramolecular domains. Multimeric polysoaps also require very small concentrations for successful sequestration. The hydrophobically modified polymeric surfactants can undergo reversible polysoap-to-extended-coil transitions, depending upon conditions. Unimeric or multimeric micelles thus can be generated in response to pH, ionic strength, or temperature. Surface activity and thus oil mobilization and emulsification can, in theory, be reversibly manipulated. Synergism can also be attained by combining polymeric surfactant micelles and viscosifying polymeric fluids as displacement agents in EOR processes.



Conceptual behavior of responsive unimeric (top) and multimeric polymers (bottom).

Developing "smart" fluids with properties superior to those currently available for chemical flooding can greatly improve sweep efficiency and thereby bolster the cost-effectiveness of chemical EOR projects, increasing U.S. oil production and ultimate reserves.

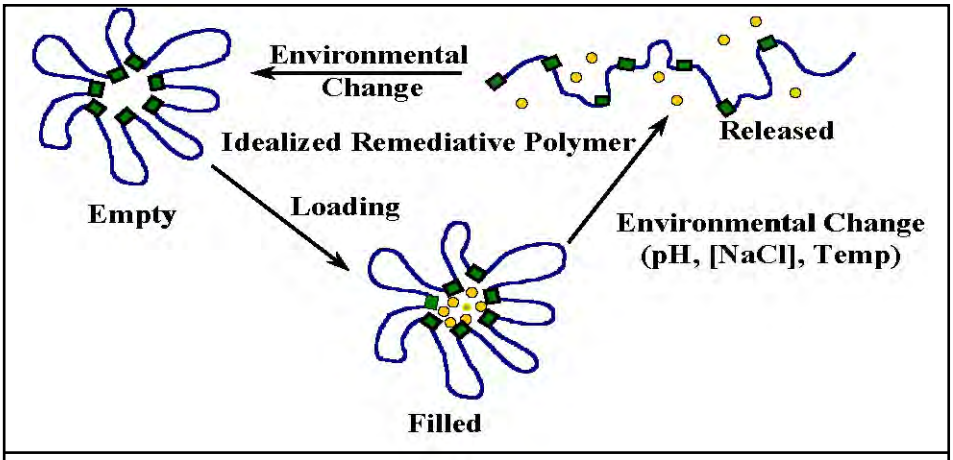
Background

The need for innovative petroleum recovery technologies has never been more critical for maintaining the economic, environmental, and technological security of the United States. Currently, the Nation's level of dependence on sources of oil from politically unstable countries is unprecedented. Global oil reserves continue to dwindle, yet the demand for petroleum-based feedstocks for materials and chemicals as well as oil-based fuels will continue to grow dramatically. More than two-thirds of all the oil discovered to date in America still lies in the ground, economically unrecoverable by current technology. Of that total, more than half resides at depths shallower than 5,000 feet. This volume represents more than 200 billion barrels of potential reserves not producible by current methodsm aking it an obvious target for advanced EOR technologies.

Summary

The advanced-polymer research team at USM has aggressively addressed construction of new structural fluids. Specifically, this is a two-phase project to synthesize, characterize, and evaluate the potential for stimuli-responsive, or "smart," multi-functional polymer (SMFP) systems for EOR use alone or in concert as mobility control agents in surfactant flooding. Such "smart" polymers utilize external stimuli—for example, pH, temperature, or salinity provided by the reservoir.

Two structural types of SMFPs are targeted that can work alone or in a concerted fashion in waterflood processes. Type 1 SMFPs can reversibly form micelles, termed "polysoaps," in water that serve to lower



Outline of how unimolecular micelles will entrap and release oil.

Publications

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"Water Soluble Polymers," A.B. Lowe and C.L. McCormick in the concise edition of the *Encyclopedia of Polymer Science and Technology*, third edition, for publication in 2007.

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"Polyampholyte Terpolymers of Amphoteric, Amino Acid-Based Monomers with Acrylamide and (3-Acrylamidopropyl)trimethylammonium Chloride," Ryan G. Ezell, Irene Gorman, Brad Lokitz, Neil Treat, Shawn D. McConaughy, and Charles L. McCormick, *Journal of Polymer Science Part A: Polymer Chemistry*, 44, pp. 4479-4493, 2006.

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"Synthesis, Aqueous Solution Properties, and Biomedical Application of Polymeric Betaines," Andrew B. Lowe and Charles L. McCormick, in *Polyelectrolytes and Polyzwitterions, Synthesis, Properties, and Applications,* Andrew B. Lowe and Charles L. McCormick, Eds., ACS Symposium Series 937, American Chemical Society, pp. 65-78, 2006.

"Reversible Addition Fragmentation Chain Transfer Polymerization of Water-Soluble, Ion-Containing Monomers," Brad S. Lokitz, Andrew B. Lowe, and Charles L. McCormick, in *Polyelectrolytes and Polyzwitterions, Synthesis, Properties, and Applications*, Andrew B. Lowe and Charles L. McCormick, Eds., ACS Symposium Series 937, American Chemical Society, pp. 95-116, 2006.

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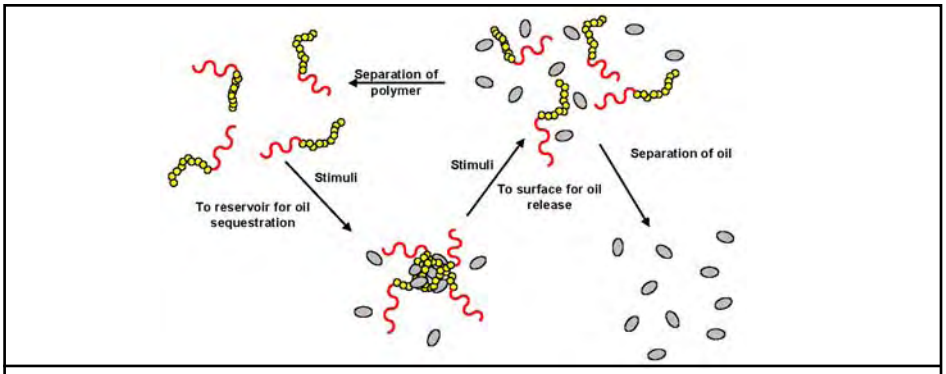
interfacial tension at the oil/water interface, resulting in emulsification of oil (Figure 1). Type 2 SMFPs are high-molecular-weight polymers designed to alter fluid viscosity during the recovery process (Figure 2).

Critical to the desired performance of these systems is the precise incorporation of selected functional monomers along the macromolecular backbone to serve as sensors or triggers activated by changes of the surrounding fluid environment. The placement of hydrophilic, hydrophobic, and triggerable monomers has been accomplished by controlled free radical polymerization utilizing aqueous Reversible Addition-Fragmentation Chain Transfer polymerization, a technique under intensive, continued development in USM laboratories. The stimuli-responsive functional groups can elicit conformational changes in the polymers, which in turn can alter surfactant behavior (Type 1), viscosity (Type 2), and permeability of the oil and aqueous phases. Thus, in principle, fluid-flow behavior through the porous reservoir rock can be altered by changes in electrolyte concentration, pH, temperature, and flow rate.



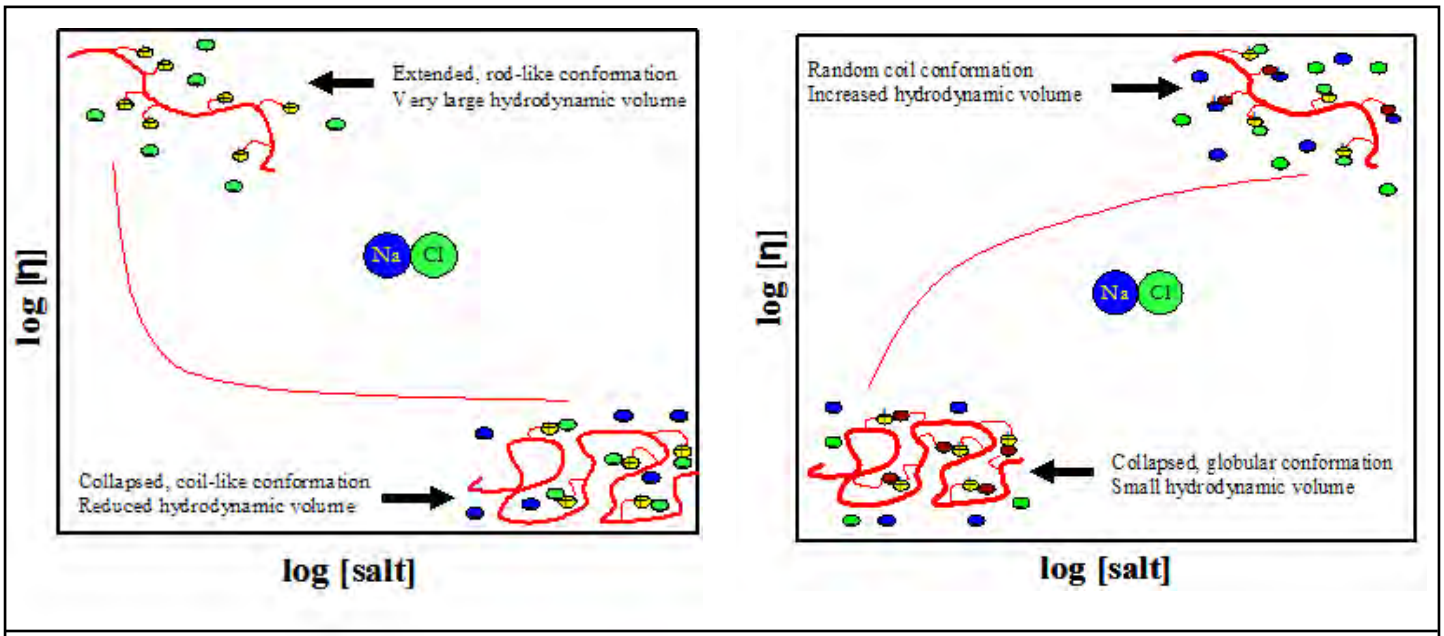
Outline of how multimeric micelles will entrap and release oil.

Current Status (February 2007)

This project is nearing the end of Phase II. A project extension has been requested.

Funding

This project was selected under the Public Resources Invested in Management and Extraction (PRIME) solicitation DE-PS26-03NT15375.



Left: the effect of electrolyte addition on the intrinsic viscosity ([η]) of a polyelectrolye in aqueous solution. Right: the effect of electrolyte addition on the intrinsic viscosity ([η]) of a polyzwitterion in aqueous solution.

Project Start: September 30, 2003
Project End: March 31, 2007

Anticipated DOE Contribution: $1,060,437
Performer Contribution: $297,411 (22 percent of total)

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