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Stimuli-Responsive Polymers and their Potential Applications in Oil-Gas Industry

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Polymers with properties well-controlled by minor environmental variations have been widely utilized in nanoscience, nanotechnology, and nanomedicine. Herein, the classification of stimuli-responsive polymers will be discussed and related to some possible applications in the oil-gas industry. Current studies of stimuli-responsive polymers in the oil-gas production are mainly focused on enhanced oil recovery (EOR) processes. Still, their potential applications in various aspects of the oil-gas industry from upstream, midstream, and downstream processes are found to be promising.

Keywords Stimuli-responsive polymers, controllable properties, oil-gas industry, enhanced oil recovery

1. Introduction

Through the years, scientists and engineers have designed a broad range of novel materials with interesting properties inspired from nature. Among those, polymeric systems capable of undergoing changes responding to internal or external stimuli are of great interest. The polymers are usually called stimuli-responsive polymers or “smart polymers.” The changes mainly include structure and property variations, whereas the stimuli may come from either chemical, physical, or biochemical source.1 Based on the structure-property relationship, chemists have fabricated synthetic polymers or modified natural polymers with well-controlled polymer composition, architecture, and predictable property upon exposure to different stimuli. Material engineers are inclined to emphasize the applications of these stimuli-responsive polymers or seek new polymeric materials to resolve current technological problems.

Due to the controlled properties brought about by minor environmental changes, stimuli-responsive polymers can be potentially utilized in many fields. Biocompatible polymers with stimuli-responsive behavior are very useful in drug delivery,2-4 bio-separation,5 and bio-catalysis.6 A surface grafted with stimuli-responsive polymers has been highlighted for its interfacial and wetting applications.7 For example, a smart surface
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with reversible switchable wettability could be potentially used in controlled transportation of fluids and water-proof coatings.\textsuperscript{8–9} The polymer material responsive to temperature or light could also be potentially utilized as sensors and actuators.\textsuperscript{10–11} Stimuli-responsive polymers based on catalytic systems have been widely employed as the recyclable catalyst for organic synthesis.\textsuperscript{12} Recently, there have been several excellent reviews in this area. Stimuli-responsive polymers have been mainly emphasized for their potential applications in nanoscience, nanotechnology, and nanomedicine.\textsuperscript{1,4,8,12–15} Currently, the most exciting innovations using smart polymers have been introduced in the biomedical field. However, the potential for oil-gas industrial applications of stimuli-responsive polymers are not as widely investigated.\textsuperscript{16}

Since the first successful oil well was drilled in 1859, especially after the industrial revolution in the late 1800s, petroleum has replaced coal as the primary fuel. Even today, it remains the primary source of energy in the world. Moreover, petrochemicals, chemicals derived from the petroleum or natural gas, play a very important role in today’s chemical industry. Plastics, fertilizer, solvent, pharmaceuticals, and other chemical products mainly come from petrochemical feedstocks. The oil-gas industry or petroleum industry, which includes the global processes of exploration, production, transportation, refining, and petrochemical synthesis represents the world’s largest industry. Over the years, due to modern refinery operations, what was once a 10–40% gasoline production can now be up to 70% from the same quality crude, and almost any available type of crude could be refined. The hydraulic fracturing and directional drilling revolution has unlocked unconventional resources from tight shale formation towards tertiary oil recovery. Despite the great successes, the difficulties in enhanced oil recovery (EOR) processes, long distances pipeline, property control of the injection fluid, and acid gas removal from raw natural gas still remain. These production challenges can all be classified as upstream, midstream, and downstream aspects of the industry. Aside from relying on new and sophisticated electronics, simulation tools, new metallic alloys, the utilization of new high performance, “smart” polymer and multifunctional materials is vital for improvement of these processes.

The rapid progress of design and synthesis of new stimuli-responsive polymers with controlled properties offers a wide range of possible applications. Recently, stimuli-responsive polymers have been reported for EOR processes.\textsuperscript{16–17} With precise property-control upon minor environmental changes, smart polymers can have great potential in other areas of oil-gas production such as drilling fluids, well-stimulation, flow-assurance, anti-corrosion, anti-scaling, asphaltene control, polymeric cements, coatings, demulsification, etc. The industry already widely uses polymers as pipes, coatings, thermosets, thermoplastics, elastomers, and calls them “non-metals.” Their performance and failure is widely studied due to their importance as components such as hoses, pipes, packers, liners, coatings, and parts in blow-out preventers (BOP), completion tools, and subsea engineering components. A main advantage is their lack of corrosive parts. For now, most of the polymer additive components can be considered the “other non-metals” which can be classified as part of the production chemicals menu.

Despite the numerous review papers published recently on stimuli-responsive polymer or polymers for oil-gas industry, to the best of our knowledge, the topic specifically on stimuli-responsive polymers for oil-gas industry has never been reviewed.\textsuperscript{1,4,14,18–20} This review will provide an overview of different types of the stimuli-responsive polymers, and at the same time, point their potential uses in the oil-gas industry. Barring aside for now the cost of producing these new polymers for commercial relevance and scale
(from gallons to tons), the current progress of stimuli-responsive polymers in this direction will be discussed.

2. Classification of Stimuli-Responsive Polymers

According to the reversibility of switchable properties, stimuli-responsive polymers could be either reversible or irreversible. Based on the material state, stimuli-responsive polymers can be in solution, in solid state, as film, or as gel. They can also be divided into the single-stimuli responsive polymers, dual-stimuli responsive polymers, and multiple-stimuli responsive polymers based on the number of stimuli they respond to. The most commonly used classification of stimuli-responsive polymer is based on stimuli. Herein, a discussion of stimuli-responsive polymers based on the number of stimuli they respond to will be presented. Further discussion on the classification based on the type of stimuli will also be discussed in the single-stimuli responsive polymer section.

2.1. Single Stimuli-Responsive Polymers

The stimuli could be grouped into three major categories: (1) physical, (2) chemical, and (3) biochemical stimuli. Every category has several types of stimuli as subgroups. For example, redox agent, ionic strength, or pH values are all included in the chemical stimuli.

2.1.1. Physical Stimuli-Responsive Polymers

Physical stimuli mainly include temperature, light, electrical potential, electromagnetic field, and pressure or mechanical stress. Among these, temperature-responsive and light-responsive polymers are more commonly studied.

2.1.1.1. Temperature-Responsive Polymers

As one of the largest classes in stimuli-responsive polymers, thermo-sensitive polymers (TSP) featuring a lower critical solution temperature (LCST) or an upper critical solution temperature (UCST) have been well-studied, while polymers with LCST are more commonly encountered recently. Figure 1 illustrates several examples of thermo-sensitive polymers, which are dominated by N-substituted polyacrylamides with LCST. Aside from the interactions between water molecules and polymer chains, the intermolecular interactions of the polymers also play an important role in the mechanism of the thermo-sensitivity of the TSPs. Hydrogen bonding of the amide group is always one of the major interactions, which can be adjusted by temperature. The temperature-responses of these thermo-sensitive polymers are highly reversible, which make them excellent candidates for smart devices and catalytic systems.

Poly(N-isopropylacrylamide) (PNIPAM), which has been synthesized by reversible addition-fragmentation chain-transfer polymerization (RAFT) or atom-transfer radical polymerization (ATRP) techniques, is one of the most well-known polymers with LCST behavior. It undergoes a reversible volume phase transition at 32°C due to the coil-to-globule transition. Poly(N,N-diethylacrylamide) (PDEAAM), poly(N-vinylcaprolactam) (PVCL), poly(2-isopropyl-2-oxazoline) (PIOZ), and poly(vinyl methyl ether) (PVME) are also thermo-sensitive polymers with the phase transition temperature at 33°C, 32°C, 48°C, and 35°C, and for most of these polymers, their LCSTs are also dependent on the molecular weight (MW) and solution concentration. Addition of salts will partially disrupt the polymer-water interaction and generally decrease the LCST, whereas the addition of a surfactant will result in an increase in phase transition temperature. To have a better LCST control, copolymerization of thermo-sensitive polymer segments with
hydrophilic or hydrophobic moieties is still one of the most used strategies. More specifically, randomly copolymerized PNIPAM with a small ratio of hydrophilic monomers will increase the LCST, whereas a small ratio of hydrophobic constituent could decrease the LCST of PNIPAM.\textsuperscript{13,26}

The study of thermo-sensitive polymers featuring a UCST is mainly focused on the zwitterionic polymers because of its biocompatibility and other special solution properties. With positively and negatively charged moieties at different monomer units or at the same monomer unit, zwitterionic polymers exhibit intra-electrostatic dipole-dipole association.\textsuperscript{27} Poly(sulfobetaine)s are one of the most well-studied zwitterionic polymers. They are insoluble or hardly soluble in water, while the problem could be resolved by the addition of salt. Lowe’s study on the synthetic poly(sulfopropyl-betaine)s indicated that it behaved increasingly as a polyanion with increased extension of chain conformation.\textsuperscript{28} Similarly, poly(3-[N-(3-methacrylamido-propyl)-N,N-dimethyl]-ammonio propionate sulfonate) (PSPP, as shown in Fig. 1f) exhibited a UCST behavior in water due to the strong intermolecular attraction, and the result showed that the UCST of the PSPP increased with the molecular weight of the polymer.\textsuperscript{29}

Aside from these temperature-responsive polymers derived from well-known thermo-sensitive monomers, other TSPs were also synthesized to cater different applications. Block copolymers based on the amphiphilic balance were also reported for their temperature responsive micellization. For example, due to the amphiphilic balance, a block copolymer poly(ethylene oxide)-b-poly(propylene oxide) (PEO-b-PPO) also exhibits temperature sensitivity in aqueous solution.\textsuperscript{30} As a substituent of PPO blocks, other

![Figure 1. Thermo-sensitive polymers: (a) Poly(N-isopropylacrylamide) (PNIPAM), (b) Poly(N,N-diethylacrylamide) (PDEAAM), (c) Poly(N-vinylcaprolactam) (PVCL), (d) poly(2-isopropyl-2-oxazoline) (PIOZ), (e) poly(vinyl methyl ether) (PVME), and (f) poly(3-[N-(3-methacrylamido-propyl)-N,N-dimethyl]-ammonio propionate sulfonate) (PSPP). (a)–(e) are thermo-sensitive polymers with LCST behavior, (f) is a thermo-sensitive polymer with UCST behavior.](image-url)
hydrophobic groups, like poly(1,2-butylene oxide) (PBO),\textsuperscript{31} poly(L-lactic acid) (PLLA),\textsuperscript{32} and (DL-lactic acid-co-glycolic acid) (PLGA)\textsuperscript{33} were also utilized to copolymerize with PEO to form thermo-sensitive block copolymers.

One application of thermo-sensitive polymer is their role in fabricating thermally controlled reversible surface wetting behavior. A PNIPAM polymer film was grafted on a controlled-roughness silicon surface via surface-initiated ATRP.\textsuperscript{34} The surface properties, the size of surface pores, the surface roughness, and the effective interfacial energy could be modified by the grafted stimuli-responsive polymers. The changes, reflected in large changes of contact angle, are reversible and controllable. Moreover, fabrication of a temperature sensor is another interesting application of thermo-sensitive polymers, which will be highlighted later.\textsuperscript{11}

2.1.1.2. Light-Responsive Polymers. During the last decade, research on light-responsive polymers (LRP) is particularly interesting due to its precise time and site control. Light responsive polymer exhibited great potential applications in controlled drug delivery system,\textsuperscript{35–36} self-healing material,\textsuperscript{37} reversible wettabiltiy,\textsuperscript{38} and recyclable catalyst.\textsuperscript{39} Considering the rapid progress of this area, several review papers have been published recently to summarize the progress of LRP, and they are mainly focused on the light-responsive block copolymers due to its special micellization and di-micellization property.\textsuperscript{4, 15} Based on the reversibility of photo-induced structural changes, light-responsive polymers could be divided into reversible LRPs and irreversible LRPs. Chemically speaking, reversible LRPs are the polymers containing photochromic moieties with reversible structural change, usually from structural isomerization; while irreversible LPRs are the polymers with photochromic moieties with irreversible structural changes, mostly chemical bond breakage.

2.1.1.2.1. Reversible Light-Responsive Polymers. There are mainly two types of reversible LRPs: the first type is the one with photo-induced structure-isomerization units (Figs. 2a–d). Some organic dyes, such as azobenzene,\textsuperscript{40–41} spiropyran,\textsuperscript{42–43} dithienylethene,\textsuperscript{44–46} and N-salicyliden-aniline,\textsuperscript{47–48} undergo a reversible structure isomerization upon the light irradiation with a specific wavelength range. The process is usually accompanied with a color change as well as polarity change. As a result, the polymer containing these kinds of photochromic units will undergo a solubility change in a specific solvent upon irradiation.

Azobenzene is one of the most well-studied photochromic molecules because of its reversible photo-isomerization depending on the wavelength of light source. It is worth noting that the isomerization process is accompanied by a strong polarity change as a result of the change in dipole moment (0 Debye for the trans-isomer and 3 Debye for cis-isomer).\textsuperscript{50} Our group synthesized a class of dendrons and dendrimers containing azobenzene units via a convergent method.\textsuperscript{51} The molecular shapes and sizes can be altered simply by UV or visible light irradiation. Another interesting study utilizing azobenzene group is the reversibility on surface wettabiltiy. With 7-[(trifluoromethoxyphenylazo)phenoxy]pentanoic acid as the photo-switcher, Lim and coworkers fabricated a nano-porous organic-inorganic hybrid multilayer film by layer-by-layer technique.\textsuperscript{38} With optimized bilayer number, the obtained film could be reversibly switched between superhydrophobic and superhydrophilic surface upon UV or visible light irradiation. Based on multi-azobenzene sugar alcohol derivatives, another group also developed a material with reversible adhesion.\textsuperscript{49} By simply irradiating the sample with either UV or visible light, the state of adhesion between two glass slides (as shown in Fig. 3) can be dramatically controlled due to the material’s induced phase transition. Recently, our group also demonstrated a photo-switchable nano-carrier based on the azobenzene functionalized polyethylenimine(PEI).\textsuperscript{52} The covalently bonded dendritic
polymers with trans-azobenzene groups will block the entrance of anionic guests to the PEI host due to the hydrophobic interactions between periphery trans-azobenzene groups on one PEI molecule, and the one with cis-azobenzene moieties will allow the entrance of anionic guests. The process is completely reversible even after five cycles of alternative UV and visible-light irradiation.

Photochromic spiropyran units also undergo a reversible isomerization upon irradiation of light with different wavelengths. Compared to azobenzene units, spiropyran features a larger polarity difference between hydrophobic spiropyran and hydrophilic merocyanine. Consequently, the block copolymer poly(ethylene oxide) (PEO)-block-poly(methacrylate) with poly(methacrylate) block bearing spiropyran side-chains exhibited an

Figure 2. Light-sensitive polymers with reversible photochromic moieties: (a) azobenzene, (b) N-salicyliden aniline, (c) spiropyran, (d) dithienylethene, and (e) coumarin. R is the backbone of the polymer (only one repeating unit is shown in the scheme).

Figure 3. A photo-chemically reversible liquefaction and solidification of multiazobenzene sugar-alcohol derivatives applied to reworkable adhesives. 49 © 2014, American Chemical Society. Reproduced by permission of American Chemical Society. Permission to reuse must be obtained from the rightsholder.
enhanced efficiency of reversible micellar dissociation-association process.\textsuperscript{43} Aside from azobenzene and spiropyran, salicylidene aniline is also known to exhibit keto-enol tautomerism both in its crystalline and solution phases,\textsuperscript{53} and dithienylethenes show reversible conversion between ring-open and ring-closed forms.\textsuperscript{44}

As another type of reversible LRPs, polymers with photo-induced cross-linking units are mainly focused on the polymers bearing coumarin groups as shown in Fig. 2e. The coumarin groups will undergo photo-dimerization through a cyclo-addition reaction upon UV irradiation at $>310$ nm, and the obtained cyclobutane bridges could be cleaved by UV light at $<260$ nm.\textsuperscript{54} It is a common knowledge that the micelles from the self-assembly of amphiphilic block copolymer may not be stable because physical interactions could be easily affected by concentration, temperature, pH, and salt concentration. In such cases, the photo-induced reversible cross-linking based on coumarin group is particularly advantageous. The coumarin moieties can be introduced into the hydrophobic block of the amphiphilic polymers. The self-assembled micelles from these polymers could be intermolecularly cross-linked by photodimerization of coumarin side groups. With this concept, Jiang et al. and Babin et al. fabricated both core-cross-linked polymer micelles and shell-cross-linked reverse polymer micelles, and they demonstrated that the cross-linking process is completely reversible by simply shining light of different wavelengths.\textsuperscript{55–56}

\textbf{2.1.1.2.2. Irreversible Light-Responsive Polymers.} Irreversible light-responsive polymers are generally the polymers with photo-cleavable groups at the backbone or side chains. Figure 4 shows several well-known photo-labile groups, such as o-nitrobenzyl groups, pyrene groups, and coumarin. The covalent bond will be broken into two parts, and the process is irreversible. As the most well-known photocleavable group, o-nitrobenzyl (ONB) based moiety has been widely investigated in polymeric systems. Insertion of the o-nitrobenzyl groups to the polymer backbone, especially as the linker of two blocks of the polymers, will result to a photocleavable polymer.\textsuperscript{57–58} One interesting study using o-nitrobenzyl group as the linker of the di-block copolymer is the formation of the nanoporous thin film by UV irradiation as shown in Fig. 5.\textsuperscript{59} A di-block copolymer polystyrene(PS)-$b$-PEO was synthesized by ATRP with o-nitrobenzyl moiety as the photocleavable linking unit. The photo-cleavage of ONB by UV light irradiation is

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure4.png}
\caption{Schematic illustration of photo-cleavable groups: (a) o-nitrobenzyl group, (b) pyrene group, and (c) coumarin.}
\end{figure}
successful within the thin film with aligned cylindrical morphology. Nanoporous PS thin film could be obtained by simply washing out the PEO by methanol and water. Theoretically, the pore size could be adjusted by modifying the molecular weight of the PEO and PS segments.

Moreover, the o-nitrobenzyl group could also be employed as the photochromic side groups of the amphiphilic di-block copolymers. The hydrophobic segment possessing an aryl methylester group, which is connected with the ONB, is linked to the polymer chain backbone. The UV irradiation will cleave the photochromic moieties as shown in Fig. 4 and convert the hydrophobic block (ester groups) to hydrophilic block (carboxylic acid). The obvious structure change of the block copolymer will break the self-assembled micelles and release the encapsulated hydrophobic cargo inside the hydrophobic core, such as Nile red. Similarly, other photochromic groups, like pyrene and coumarin, as shown in Fig. 4, are also explored as the photo-induced cleavable side groups in block copolymers.

2.1.1.3. Electronically Responsive Polymers. Electronic stimuli such as electrical potential or voltage could provide a simple, quick, and effective manner to control polymer property and morphology. Actually, all of the conducting polymers, including polyanilines, polypyrroles, polythiophenes, poly(carbazole) and their derivatives, are electronic-potential responsive or semiconductor polymers. They show electrochromic effects, especially in thin film form.

Based on the conducting polymer, polyaniline (PANI), a two-dimensional patterned thin film was prepared via micro-transfer molding and electropolymerization techniques. As shown in Fig. 6, three different forms of polyaniline with different redox states and distinct colors could be easily modulated by electrochemical oxidation or reduction. The color changes of the patterned polymer layer could be quantitatively monitored by the electronic absorption spectrum of PANI.

The conformational orientation of polyelectrolytes can also be modified by electrical potential. The well-known study is the self-assembled monolayer (SAM) of (16-mercapto)-hexadecanoic acid (MHA) on a gold surface prepared by Chio, and by applying the alternating electrical potential, the MHA can undergo a straight to bent molecular conformation transition. The conformation transition will render a change on surface...
For a better wettability control on the solid surface, a superhydrophobic film based on polypyrrole was fabricated on a conducting surface by electrochemical polymerization. The reversible superhydrophobic-to-superhydrophilic transition of the film can be achieved by adjusting the electrical potential.\(^{69}\)

Another important application of electronically-responsive polymer is the fabrication of electronic field controlled actuators. For example, a polythiophene-based conductive polymer gel actuator was reported by Irvin et al.\(^{70}\) The actuator exhibited a reversible expansion/contraction behavior triggered by applying electrical potential, and the expansion against the wall will generate the axial pressure. The generated closure pressures could be used as a small-scale actuator valve.

Possible application of electrically conducting polymers is in controlled wetting behavior of conducting surfaces (electro-wetting), sensors, and actuators. In electro-wetting, it is possible to apply this film to oil-water separators for preparing produced oil for transport or for oil-spill clean-up. For sensors, these materials can often be electrochromic, potentiodynamic, semi-conducting (resistance), and even fluorescent. This means that they can be associated with certain analyte sensitivity (composition of produced oil, gas detection, and refined petroleum products). As actuators, they may be useful for the preparation of mechanical movements in micro-electromechanical systems (MEMS) or valves. An increasing electro-optical application is in the use of downhole sensors and optics in drilling tools and operations. Coil wire substitutes, energy generation, and maintaining conductivity pathways are some of the increasing environment in monitoring the “health” downhole. However, this is also associated sometimes with high temperature and high pressure (HTHP) conditions and brine or high salt concentrations which are already corrosive and destructive.

### 2.1.1.4. Magnetic Field Responsive Polymers

Magnetic field responsive polymers are generally obtained by incorporating colloidal magnetic particles\(^{71}\) or carbon nanotubes\(^{72}\) into the polymer materials. Combination of magnetic and elastic properties leads to a number of striking phenomena which are exhibited when applying magnetic fields.

![Diagram of redox states of polyaniline](https://example.com/diagram.png)

**Figure 6.** Three predominant intrinsic redox states of polyaniline (PANI): (a) Leucoemeraldine, fully reduced (−0.2 to +0.14 V vs. Ag/AgCl); (b) emeraldine, partially oxidized (+0.14 V to +0.45 V vs. Ag/AgCl); (c) pernigraniline, fully oxidized (+0.45 to 1.00 V vs. Ag/AgCl).\(^{67}\)
With high elasticity, giant deformational effect, anisotropic elastic, and swelling properties, along with the instant response to magnetic field, the nano-composite shows great potential in various applications.73

Magnetic field polymer composite gels were obtained by incorporating magnetic nanoparticles into the cross-linked PNIPAAm-co-poly(vinyl alcohol) gels.71 The polymer gels are randomly dispersed in solution when no magnetic field is applied. They rapidly aggregated in a non-uniform magnetic field, while they can form a straight chain-like structure when applying a uniform magnetic field.

Due to the enhanced physical and mechanical properties, magnetic field polymer composite shows great potential in pharmaceutics, cosmetics, paint production, and perhaps oil-gas industry. The elastic modulus of a magnetic poly(dimethylsiloxane) (mPDMS) was measured under a uniform magnetic field at 293 K.73 It is apparently seen that the field-free modulus of the material increases with the concentration of the filler particles. Two kinds of experimental arrangements, i.e., parallel and perpendicular, were used, depending on the direction of the field to the mechanical stress. It shows that there is a slight increase in the modulus as the increase of external magnetic field.

Possible applications are in the area of magnetic field controlled surfaces and phase behavior. The magnetic field can be used to provide mechanical stress or control the deposition of coagulated materials with magnetic particle content. Much like the light-responsive applications this can be limited to the field gradient of the electro-magnetic generating device and can be very local. Another use of the magnetic field effect is in heating. More recently, magnetic nanoparticle materials have been used in conjunction with magnetic imaging systems.

2.1.1.5. Pressure- or Mechanical-Stress Responsive Polymers. Pressure or mechanical force can also act as an external stimulus to trigger changes on density and/or structure of the polymer, which will then render the property modifications.8,74 For example, Zhang et al. reported a particularly interesting mechanically sensitive polymer film.75 The elastic polyamide film exhibited a triangular netlike structure, with average side length of 200 \( \mu \text{m} \) and fiber diameter of 20 \( \mu \text{m} \). The contact angle of water on this polyamide film was measured to be 151°. The average side length of the triangular structure of the polyamide film would be 450 \( \mu \text{m} \), when the film was biaxially extended to greater than 120%. At the same time, the water droplet will spread out into the space among the fibers, and polymer film will become superhydrophilic with the measured contact angle around 0°.

Considering industrial processes, especially for many processes in the petroleum industry, pressure or mechanical force is always one of the most important parameters to control. Therefore, the industrial applications of these polymers are particularly promising. For example, pressure-sensitive adhesives including acrylic polymer, styrene acrylic polymers, and carboxylated styrene-butadiene latex, are already commercially available. They are designed for either permanent or removable applications. Safety label for power equipment, automotive interior trim assembly, and sound/vibration damping films are examples of permanent applications. Removable adhesives are designed as a temporary bond, which can be removed after months or years. They are currently used as surface protection films, masking tapes, and price marking labels. Pressure changes can also be associated with flow behavior. It is possible to conceive of coatings that can be triggered to have a different wetting behavior in pressurized fittings or pipes that changes its wetting behavior at critical limits. Autonomic trigger of pressure response can also result in changes in dimensionality or trigger shape-memory function hence application in valves and membranes, e.g., valve regulation and produced water purification and filtration.
2.1.2. Chemical Stimuli-Responsive Polymers

2.1.2.1. pH-Responsive Polymers. The common feature of pH-responsive polymers is the presence of ionizable functional groups in their chemical structures, which are capable of donating or accepting protons upon environmental pH changes. The electrostatic repulsions between generated charges cause the alternations of the hydrodynamic volumes of polymer chains, which is capable of extending or collapsing. There are basically two types of pH-responsive polyelectrolytes: weak polyacids and weak polybases. As shown in Fig. 7, the representative acidic pendent group of weak acid is the carboxylic acid. Poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) with pH values around 5 will release protons and extend polymer chains under basic pH values. On the other hand, weak bases accept protons and swell under acidic conditions. The amine and amino groups in polyallylamine (PAM) and poly(N,N'-dimethyl aminoethyl methacrylate) (PDMAEMA), respectively, are responsible for these transitions.

Based on such a simple concept, pH-sensitive polymers are designed for many potential applications. One interesting study is that the rate of water permeation could be controlled by the pH-sensitive polymer brushes as shown in Fig. 8. The porous poly(tetrafluoroethylene) membrane was first graft-polymerized with benzyl glutamate NCA, and then the grafted chains were hydrolyzed to yield poly(glutamic acid). The rate of water permeation through this poly(glutamic acid)-grafted polymer membrane was pH-dependent. It was found to be slower under high pH conditions and faster under low pH.

Figure 7. pH-sensitive polymers: (a) polyacids: poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA), and poly(4-styrenesulfonic acid) (PSSA); (b) polybases: poly(4 or 2-vinylpyridine) (PVP), polyallylamine (PAM); poly(vinyl imidazole) and poly(N,N'-dimethyl aminoethyl methacrylate).
conditions. pH-responsive polymers usually are polyelectrolytes and are commercially available to cater different applications. In the oil-gas industry field, one study showed that the sulfonated elastomeric polymers, which were copolymers of isoprene and sodium styrene sulfonate or terpolymers of isoprene, styrene, and sodium styrene sulfonate, could be used as viscosification agents when added to oil-based drilling fluids. They exhibited excellent performance to maintain pressure, cool drill bits, and lift cutting from the holes in the drilling operation, even at a high temperature. Another possible application is as fluid additives that can be triggered by changes in the pH condition of the whole fluid base resulting in a reversibility of function or phase, e.g., anti-scaling, emulsification, or amphiphilicity, and coagulation function. This means that such polymers are pH sensitive, and that pH control of the matrix is critical to keeping these additives stabilized or destabilized at a particular point in drilling (upstream) or transport (midstream).

2.1.2.2. Solvent-Responsive Polymers. Generally, macromolecular chains usually exhibit a coil-like conformation in solution, rather than adopting a stretching conformation. However, the polymer brush or polymer segment will present itself in a more stretched form in a better solvent, and shrink to some degree in a non-solvent. As a result, the block copolymers or mixed polymer brushes with different polarities or solubilities will display them with different conformations and hence different properties. For example, dendritic copolymers synthesized by Gitsov and Fréchet will exhibit different shapes when the polarity of the solvent changes.

The study of solvent-responsive polymers is mainly focused on the polymer brush due to its switchable surface properties. Based on the phase separation of different blocks, the surface properties of block copolymer brushes will be different when exposing to the solvents with different affinities to each block. A tri-block copolymer poly(styrene-block-2-vinylpyridine-block-ethylen oxide) (PS-b-P2VP-b-PEO) is a representative example of such a material to tune the balance among steric, electrostatic, and hydrophobic forces by exposing the polymers to different external solvents. A stimuli-responsive colloidal system based on the PS-b-P2VPS-b-PEO block copolymer brush was fabricated, and it showed a dramatic property transformation upon exposure to different solvents. In a mixed polymer brush system, two or more chemically different polymers are grafted on the same substrate. The materials’ surface properties are switchable depending on

![Figure 8. Explanation of pH-dependent water permeation through (a) porous membrane grafted with ionizable polypeptide, and (b) dense membrane composed of ionizable polypeptide.](image-url)
which polymer brush is in the exterior. The exposed polymer brush could be controlled by the environmental stimuli it was exposed to last. For example, a surfaced grafted with both polystyrene (PS) and poly(2-vinyl pyridine) (P2VP) can be described as a smart surface with the ability to respond in a controllable fashion. The surface wettability, quantified by contact angle measurement, will be different after toluene or ethanol rinsing, and the contact angle difference can be amplified on a rough surface.

Another interesting study regarding the solvent-sensitive polymer brush is the utilization of water and air as alternating external stimuli instead of two different solvents. An amphiphilic block copolymer containing poly(styrene), poly(4-octylstyrene), or polyisoprene as the hydrophobic segment, and poly(2,3-dihydroxypropyl methacrylate) as the hydrophilic segment was grafted onto the surface. The contact angle measurement indicated a hydrophobic surface due to the enrichment of the hydrophobic segment, but the hydrophilic groups dominated when soaked in water. Drying could be utilized to recover the hydrophobic surface. Similarly, polymer rearrangement and replacement of the hydrophobic groups at the top surface with hydrophilic groups when soaked in water were also demonstrated by several other groups.

2.1.2.3. Ionic Strength-Responsive Polymers. Generally, the mechanism of the ionic strength-responsive polymers is that the added salt will reduce the electrostatic interactions between copolymers or between polymers and other molecules. As a result, ionic strength always showed a strong effect on the solution behavior of the polyelectrolyte. Moreover, nonionic polymers, like poly(N-isopropylacrylamide) hydrogel also showed a sharp volume phase transition at a critical salt concentration. Liu et al. systematically studied the salt effect on the LCST behavior of the thermo-sensitive hyperbranched polymers in aqueous solution. In their report, the specific ranking of both anions and cations in reducing the LCST was provided.

Based on this concept, smart polymers could be used for bio-separation. For example, a poly(NIPAM-co-vinylimidazole) immobilized with Cu(II) metal ions could be used for protein separations. The Cu(II) charged polymer exhibited a specific interaction of the metal ion to the protein inhibitor, and the precipitation was induced by increased salt concentration. This is perhaps due to the reduction of the repulsive electrostatic strength of the polymers, and hence increased hydrophobic interactions. Moreover, by exchanging the counter-ions in the polyelectrolyte brushes, the surface properties, such as wettability, could be further modulated. However, the contact angle difference is still less than 75°, which needs to be further optimized.

In general, the stimuli provided by a change in solvent property or ionic strength can mediate the wetting and miscibility of polymeric films and additives. Of specific importance are in the different grades of produced oil and the mitigation of asphaltene, paraffins, or control of ions produced from the formation. Typically, produced oil is a water-in-oil emulsion and varies from location, geography, and formation to give light, medium, and heavy oil. The presence of sulfur, salts, asphaltene, and bitumen gives each type of oil its specific grade for refining. Solvent and ionic strength responsive polymers can be used to aid in the viscosity reduction and demulsification leading to efficient transport of produced oil without necessitating heating. In more upstream applications, such stimuli response or even lack of stimuli-response can be used to control the drilling fluid rheological behavior or deposition of additives to their intended role. Together with temperature, high ionic strength or brine condition can pose challenges in the rheological properties. Other important additive functions are fluid-loss agents, binders, weighting agents, and drag reducers. Of particular importance in hydraulic fracturing may be in hydrogel formation or a curing step in resin-coated proppants. Guar, which is a medium common for
gelation in drilling and hydraulic fracturing fluids, is particularly sensitive to ionic strength. Therefore, stimuli responsive polymers that can be made more superior to guar in terms of pH and ionic strength control are always of high interest.

2.1.3. Biochemical Stimuli Responsive Polymers. The biochemical stimuli responsive polymers are mainly the polymer materials responding to biochemicals, and hence exhibited great potential application in bio-related fields, especially in controlled drug delivery or gene delivery. For example, disulfide linkage-employing drug conjugates and disulfide cross-linked polymeric nanocarriers or liposomes could release the drugs or genes in the presence of reduced glutathione inside the cell.

The blood glucose level is one of the important criteria for a healthy body. A patient suffering diabetes mellitus needs an extra supply of insulin via periodic injection, while this treatment could not allow the blood glucose level to be maintained in a normal range. The glucose responsive polymer system could probably provide a self-regulating insulin release system depending on the glucose concentration in the blood. To achieve this target, several strategies including the ones based on pH-sensitive polymer hydrogel or glycopolymers were developed.

A possible application of biologically stimuli responsive polymers for the oil-gas production is in controlling bacterial colonies of biofilm formation as biocides or biostats that can mitigate problems with microbial corrosion (MIC) and in decreasing biogenic H₂S generation. Certain metabolites produced by these organisms can trigger specific action or function by these polymers resulting in their mitigation. They can also have possible uses in aiding bio-remediation by triggering environments or media conducive for enzymatic action of helpful microbes (bacteria eating oil).

2.2. Dual-Stimuli Responsive Polymers

There are several types of dual-stimuli responsive polymers. Theoretically, any combination of two single-stimulus responsive polymers is considered as a dual-stimuli responsive polymer. For example, temperature-responsive polymers are always combined with other stimuli, like light, pH, and magnetic field.

2.2.1. Combination of Thermo- and Light-Responsive Properties. Recently, Jochum and Theato published a good review on the temperature- and light-responsive polymers, one of the most important dual-stimuli responsive polymers. Most of the polymer materials are simply based on the copolymerization of thermo-sensitive monomers (Fig. 1) and light-sensitive monomers (Fig. 2 and Fig. 4). For example, a block copolymer with PNi-PAM as the thermo-sensitive block and spiropyran groups as the light-sensitive block was fabricated as shown in Fig. 9. The block copolymers could be used as temperature sensor due to the temperature-responsive linear and reversible bathochromic/hypochromic shift of the absorption spectra within a wide temperature range under UV irradiation.

Another interesting study with great potential use in oil-gas industry is the utilization of light- and temperature-responsive polymers to afford a stimuli-responsive emulsion with n-dodecane as the oil phase. Perrin et al. fabricated an amphiphilic photo-responsive polymer based on azobenzene-modified poly(acrylate), and it could play as the surfactant of the emulsion foams. The stability of the emulsion foams can be triggered by both temperature and light as shown in Fig. 10. Starting from a cold sample, the foam stability could be decreased with increasing temperature or upon UV irradiation, and no foam would be created during this process. Then the foamability could be recovered by
simply decreasing temperature, and this can be cycled for several times. Foams have also been used for drilling, fracturing, and enhanced oil recovery (EOR). Therefore, foam control can be utilized towards these applications.

2.2.2. Combination of Thermo- and pH- Responsive Properties. Utilization of temperature and pH as the solution variables have been of great scientific and technological interest because these factors are readily modified in a typical system. The pH-responsive properties are always associated with the polyelectrolytes. The presence of charges along the polymer chains will lead to complex intra- and inter-molecular interactions, and it will always have a strong impact on the structural, dynamic, and rheological properties of the system.

Recently, strategies such as modification of pH are employed to tailor the temperature of induced phase transition (PT) for different applications. It is well known that the incorporation of different amounts of charged monomers is an efficient way to modulate the PT temperature. The hydrogen-bonding interactions play an important role in the system of a pH-tunable PT temperature. For example, carboxylic groups could form hydrogen bonds with the amide groups of the PNIPAM structures, which are used to modify the LCST of the polymers.

One interesting study with great potential in oil-gas industry based on the combination of pH- and thermo-responsive polymers is their role as shear-thickening materials. The block copolymers have two characteristic features as shown in Fig. 11: (1) they featured a thermosensitive N-isopropylacrylamide backbone, and (2) the polymers bear a high fraction of hydrophobic side groups, and the solubility is ensured by the equal number of positive charges. Their phase behavior is governed by the competition between the hydrophobic alkyl groups and hydrophilic character of the charge. The hydrophilic character of a positive charge will prevail over the hydrophobic contribution of the alkyl chains when the alkyl groups are not long enough. The hydrophobic character of the dodecyl groups will be strong enough to prevail over the hydrophilic contribution of the alkyl chains when the alkyl groups are not long enough. The hydrophobic character of the dodecyl groups will be strong enough to prevail over the hydrophilic character of the charges. As shown in Fig. 11a, at low shear rate, the polymer chains adopt an intra-chain hydrophobic aggregation, with a possibility of some inter-chain junctions. When shear is applied, the aggregates are deformed. When above $\gamma_{\text{critical}}$, additional inter-chain hydrophobic junctions are formed (state C), which will render a higher viscosity fluid. The system behaves as a reversible network. At higher temperature, the polymer chains shrink,

Figure 9. A simple copolymer, poly(NIPAM-co-SP), could behave as a colorimetric thermometer exhibiting a temperature-responsive linear and reversible bathochrom/hysochromic shift in the absorption spectra under UV irradiation. SP: spiropyran. © 2009, American Chemical Society. Reproduced by permission of American Chemical Society. Permission to reuse must be obtained from the rightsholder.
Figure 10. Left pictures: the pictures show the foaming behavior of emulsions at temperature (a) below (T = 18°C) and (b) above (T = 26.6°C) phase inversion temperature (PIT). Right pictures: the pictures of the direct emulsion foams at T = 26°C before irradiation from the top (a) and from the side (b). The picture (c) was taken after UV-light exposure of 4 minutes, 7 minutes, and 9 minutes, indicating that light was a convenient stimulus to control emulsion foam stability.99 © 2010, Royal Society of Chemistry. Reproduced by permission of Royal Society of Chemistry. Permission to reuse must be obtained from the rightsholder.

Figure 11. (a) Chemical structural of the hydrophobically modified polymers based on NIPAM. (b) Schematic Representation of the possible mechanism behind the shear-thickening properties of the NIPAM-based hydrophobically modified polymers in aqueous solutions.101 © 2000, American Chemical Society. Reproduced by permission of American Chemical Society. Permission to reuse must be obtained from the rightsholder.
and the intra-chain hydrophobic aggregates are enhanced (state B). Consequently, higher shearing rate is needed to reach state C.

2.2.3. Dual-Responsive Polymers with Other Combinations. Dual-responsive polymers with other combinations are also possible to construct novel smart materials for real applications. For example, the nano-composite with the combination of thermo-responsive property and magnetic-field responsive property are potential tools for protein separation,\textsuperscript{102} and even as an artificial muscle.\textsuperscript{71}

2.3. Multi-Stimuli Responsive Polymer

The current study on multi-stimuli responsive polymers is mainly focused on responsive nanoparticles, and they are mainly used in drug delivery systems. Cheng et al. reviewed the recent progress of the dual and multi-stimuli responsive polymeric nanoparticles for programmed site-specific drug delivery.\textsuperscript{103} The multi-stimuli responsive nanoparticles or micelles are mainly self-assembled micelle from the linear block copolymers, and the stimuli are the combinations of temperature, pH, redox agent and magnetic field.\textsuperscript{104} Recently, covalently stable polymer nanoparticles are also reported based on a thermo-sensitive hyperbranched polymer.\textsuperscript{105} Until now, the potential industrial applications of the multi-stimuli responsive polymer nanoparticles are still rarely investigated.

While multi-responsive polymers can be quite complicated to quantify their response or even define structure-composition-property relationships, it should be noted that many factors for oil-gas production are complex and interdependent in the environment. From the upstream side, the demands for new materials will ever increase with deep see drilling, high temperature-high pressure (HTHP) conditions, high brine concentration, different formation erosion, and the demands of directional drilling. As such it is early to dismiss the potential of multi-stimuli responsive materials in some of the technical challenges that are yet to come.

3. Current Study of Stimuli-Responsive Polymers on Enhanced Oil Recovery

Nowadays, the dramatic decrease of easily explored oil and gas wells (conventional) has triggered focus on unconventional reservoirs. Moreover, only less than a half of the original oil in a subterranean petroleum reservoir could be produced by primary (depressurization) and secondary recovery (water flooding) techniques.\textsuperscript{106} Therefore, the oil-gas industry has been facing great technical challenges, such as drilling and completing complicated wellbore profile to increase recovery factors in ultra-deep wells or in harsh conditions.\textsuperscript{107} The greatest challenge concerning the possibility of increasing the efficiency of oil production is either by improving the current EOR technologies or by developing alternative methodologies. Chemical, miscible gas, and thermal recovery techniques are currently developed to increase oil recovery, and polymer flooding is one most promising flooding techniques.\textsuperscript{108} Recently, “smart” polymer systems have also been applied for the EOR process. Actually, the new-generation of smart materials should affect the properties of the injected fluid, including density, viscosity, wettability and mobility, along with the fluid-oil interaction and fluid-rock interactions.

Xanthan gum, a polysaccharide, is commercially extracted from the seeds of plant Cyamopsis tetragonoloba. It exhibits thickening capability when the gum is of high molecular weight (usually 2 to 50 \times 10^6 \text{ g/mol}).\textsuperscript{109} Xanthan gum displays good resistance
to high temperature. Previous studies showed that the solution viscosity of commercial xanthan gum remained constant for more than 2 years at 80°C, and loss of solution viscosity occurred at temperature above 100°C.\textsuperscript{110–111} The main disadvantage of xanthan gum is its susceptibility to bacterial degradation. Although biocides could be used to suppress the growth of xanthan gum degrading microorganisms, the use of biocide would render low environmental impact.\textsuperscript{16}

As the first polymer used as thickening agent, polyacrylamide exhibits thickening capability in its high molecular weight ($>10^6$ g/mol). Polyacrylamide is commonly designated as PAM and is classified as a water-soluble polymer. PAM is most often used to increase the viscosity of water or to encourage flocculation of particles present in water. One of its most common applications is in the wastewater treatment industry to form flocs or sediments based on insoluble hydroxides which can be filtered or removed more easily. PAM can also be used to treat water from mineral mining processes, including additives in the production of coal. In EOR, where high viscosity aqueous solutions can be injected to improve the economics of conventional water flooding, PAM-injected solutions assists in sweeping (or pushing) oil locked in a reservoir towards a production zone. This will result in improved volumetric sweep efficiency, that is, more oil is produced for a given volume of water injected into the well. However, polyacrylamide is mainly used as the reference for chemical modification. By far, the most used polymer in EOR application is the partially hydrolyzed polyacrylamide (HPAM) due to its several advantages such as high mechanical force tolerance, low cost, bacterial resistance, and shear thickening property in porous media at high shear rate.\textsuperscript{16} A relatively new class of water-soluble polymers for EOR application is the hydrophobically associative polymers. Results showed that higher thickening capability could be achieved compared to traditional polymers due to hydrophobic interactions.\textsuperscript{112–113}

For EOR application, the thermal dependence of solution viscosity is an important property of hydrophobically associative polymers. It is well known that increased temperature will lead to a viscosity decrease because an increase in temperature implies a decrease in association strength.\textsuperscript{115–116} However, several groups demonstrated different aqueous polymer solutions which displayed an increase in viscosity upon increasing the temperature.\textsuperscript{114,117–118} As shown in Fig. 12, the temperature increase will decrease the solubility of one of the components (LCST-groups) of the polymer. These less soluble polymers will self-aggregate with the hydrophobic groups of the polymers, which will lead to an increased solution viscosity.

McCormick et al. developed two types of water-soluble stimuli-responsive polymer for EOR process.\textsuperscript{18,119–124} The first type stimuli-responsive polymer was designed to lower interfacial tension at oil/water interface, and thus forming the oil/water emulsification. The other synthesized molecular polymers have the prospective applications in modifying fluid viscosity and mobility during the oil recovery process.

Chemical processes, mainly surfactant injection and polymer flooding, have attracted much attention in the field of polymer science related to EOR processes. Polymer flooding, based on the principle of decreasing the mobility difference between injected and in-place reservoir fluids, is designed to reduce channeling effects. The displacing phase should have mobility equal to or slightly lower than the mobility of the reservoir fluid. Water soluble polymers can be used to increase the viscosity of the flooding phase and reduce the permeability of flooding phase to the porous rock, hence creating a more efficient and uniform front to displace oil from the reservoir.\textsuperscript{108}
McCormick’s study has mainly focused on the zwitterionic water-soluble polymers due to their unique responsiveness to saline media. Their initial study showed that compared to conventional anionic poly(acrylamide) containing acrylate functionalities, the copolymers of acrylamide (AM), and low mole fractions of sodium 3-acrylamido-3-methylbutanoate (AMBA) are exceptional viscosifiers. The block copolymers are able to maintain the viscosity in media with even high salt concentration and high temperatures. A series of pH-responsive poly(zwitterions) (PZs) with both polyampholyte and polybetaine architectures are synthesized and analyzed comprehensively. The model PZs are AMBATAC and AMDAP with chemical structures as shown in Fig. 13 and both of the PZs are synthesized via free radical polymerization in aqueous solution. The size exclusion chromatography (SEC) and viscometric data indicated that the AMDAP copolymer exhibited a more open, random coil conformation and greater polymer-solvent interactions. On the other hand, the AMBATAC copolymer exhibited a more pronounced stimuli-responsive solution viscosity, and it could maintain a high solution viscosity over a wide range of NaCl concentrations and pH values. With the technologically stimuli-responsive nature, it should be possible to produce more original oil in place and that of by-passed unrecoverable oil by conventional chemical flooding. However, their role in real application in the EOR field still needs to be further demonstrated.

Another interesting example of utilizing smart polymers for EOR process was demonstrated by Philippova and Khokhlov recently. Two stimuli-responsive polymer systems based on hydrophobically decorated polyelectrolyte have been developed to resolve the two most important problems in oil production process. One is designed for water control in a producing well, which can find the site of the water influx by itself and then block it. The other is designed to use in hydraulic fracturing, and it acts as a thickener in aqueous medium while it transforms into a low-viscosity liquid when in contact with the oil phase.

The chemical structure of the hydrophobically modified polyacrylamide (HM-PPA1) was shown in Fig. 14a, and a 2 wt% HM-PPA1 solution in a water-ethanol mixture (60/40) was used as the initial solution. To model the contact of the polymer with reservoir water or oil phase, the polymer solution was added to 20 mL of a saline solution.
containing 30 g/L of sodium chloride and 3 g/L of calcium chloride or 20 mL of n-heptane, respectively. As shown in Fig. 14b, the storage modulus of the sample in contact with water is higher than the loss modulus over a wide frequency range. At the same time, the storage modulus of the sample in contact with n-heptane is well below the loss modulus, which means the sample has not experienced gelation process. Moreover, the combination of stimuli-responsive polymer system (HM-PAA2) and a 1.125 wt% surfactant (erucylbis(hydroxyethyl)methyl-ammonium chloride) aqueous solution showed a high solution viscosity, and the gel system will be formed. However, after contacting with n-heptane, the system viscosity drops, and the gel system will transform into a liquid.

The first successfully field-tested stimuli-responsive polymer is called “BrightWater,” which was utilized to increase the sweep efficiency in an oil reservoir. It is a kind of polymeric nanoparticle which can expand to multiple times of its original volume upon activation, mostly by temperature. After expansion, the polymeric nanoparticle with huge volume will block the pore throat and direct the injection flow into low-permeability zones, which may never be touched.

4. Perspectives

Although the stimuli-responsive behaviors of synthetic polymers, such as polyelectrolytes, have been well known for many decades, recently synthesized functional stimuli-responsive polymers display an excellent structure- and property-control upon receiving a selectively external stimulus. The great progress of polymerization technologies, especially controlled polymerization methods, such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT), play an important role on the formation of well-defined polymer structures. Moreover, the design of stimuli-responsive polymers is also attributed to progress in other several areas, such as optimized monomer synthesis, precisely controlled nanostructure fabrication, and physical theories regarding polymer-polymer interactions and polymer-environment interactions.
However, the design and synthesis of smart polymers with a rapid and precise response upon exposure to a specific stimulus for a particularly special application is still a great challenge for polymer scientists.

Currently, a major application of stimuli-responsive polymers is in the biomedical field, especially in the controlled-drug delivery system. Several stimuli, such as pH, magnetic field, light, and temperature could be utilized to trigger the release of the encapsulated cargos, such as drugs. Light is a particularly interesting stimulus due to the precise time and site control, while the utilization of the near IR light is preferred over UV or visible light considering real-time application.

Polymer materials, obtained either from natural polymers or from bio-based or petroleum-based feedstocks, have been used in oil-gas industry. Polymer flooding has been
shown to have great advantages in the EOR process. Recently, polymer scientists and engineers tried to bridge the gap between the oil-gas industry and stimuli-responsive polymers. Zwitterionic water-soluble polymers with pH-response behaviors have been demonstrated to serve as efficient oil/water surfactants and fluid viscosifiers. The hydrophobically decorated polyelectrolytes with both solvent- and pH-response were demonstrated as smart materials for water control and hydraulic fracturing in the EOR process. In fracking industry, the reversible gels are also utilized to deliver the propants into a tight formation, which will help the oil release process.

Considering the rapid progress of stimuli-responsive polymers with numerous emerging and exciting studies, they should be explored for many potential applications in the oil-gas industry aside from the EOR process. From upstream, midstream, and downstream, the needs are enormous and challenging. The nano-sensors based on stimuli-responsive polymer could probably be used to monitor the temperature, pH, or pressure of the pipeline and oil reservoir. The smart surface, typically with reversible superhydrophobic-superhydrophilic transformation, may be applied in the controlled fluid transportation. The oil-water foamability controlled by light and temperature may show great promise in the oil recovery process. The shear-thickening materials based on hydrophobically modified water-soluble stimuli-responsive polymers might be useful in terminating unwanted flow or sealing unwanted channels. It is true that the cost of the stimuli-responsive polymer would be a big challenge for their real applications in oil gas industry. There are always possibilities, such as using a minute amount of expensive polymers as additives in cheaper materials, small amount of stimuli-responsive polymer as highly effective material, or producing low-cost stimuli-responsive polymers. Currently, more efforts are still needed from polymer scientists and petroleum engineers working together to apply these possible techniques to improve operations and cost-effectiveness in the oil-gas industry.

**References**


