Applications of Polymeric Smart Materials to Environmental Problems

H. Neil Gray¹ and David E. Bergbreiter²

¹Department of Chemistry, University of Texas at Tyler, Tyler, Texas; ²Department of Chemistry, Texas A&M University, College Station, Texas

New methods for the reduction and remediation of hazardous wastes like carcinogenic organic solvents, toxic materials, and nuclear contamination are vital to environmental health. Procedures for effective waste reduction, detection, and removal are important components of any such methods. Toward this end, polymeric smart materials are finding useful applications. Polymer-bound smart catalysts are useful in waste minimization, catalyst recovery, and catalyst reuse. Polymeric smart coatings have been developed that are capable of both detecting and removing hazardous nuclear contaminants. Such applications of smart materials involving catalysis chemistry, sensor chemistry, and chemistry relevant to decontamination methodology are especially applicable to environmental problems. — Environ Health Perspect 105(Suppl 1):55-63 (1997)

Key words: decontamination coatings, environmental sensors, responsive polymers, sensor coatings, smart catalyst, smart polymers, thermoresponsive

Introduction

Smart materials are materials that sense and respond to some change in their environment in a controlled and reproducible manner (1–3). Such changes in a material’s physical environment could manifest in the form of altered temperature (4–10), electrical field, pressure, sound (11), and illumination (12). Alternatively, chemical stimuli like changes in pH or the presence of some predetermined concentration of a hazardous material can represent an environmental change to which a polymer might respond (13–17; B Jorgenson, unpublished data). The current literature reveals a wide variety of inorganic materials that demonstrate intelligent behavior. These materials include alloys, ceramics, and composites used in actuator and shape memory applications or in the design of micromachines (18,19).

There are also a significant number of publications on the design of polymeric and biopolymeric smart materials for use in areas such as catalysis (6,10), sensors (14,15), decontamination (16,17), drug delivery (20), prosthetics (21), synthetic muscles (22), and other biomimetic processes.

Many if not most of the applications of polymeric smart materials can be considered environmentally important. Applications of smart materials involving catalysis chemistry, sensor chemistry, and chemistry relevant to decontamination methodology are especially relevant to environmental problems. Catalysis applications are important because of the environmental concerns associated with the production of chemical and hazardous wastes. Sensor chemistry and/or decontamination chemistry are important because of the past misuse of toxic materials. Neglect, carelessness, or ignorance have led to the contamination of entire facilities, soil, groundwater, and the atmosphere by carcinogenic solvents, toxic pesticides, and hazardous nuclear materials.

New approaches for detecting, preventing, and remediating environmental damage are important to environmental health. Procedures must be developed and implemented to reduce the amount of waste produced in chemical processes, to detect the presence and/or concentration of contaminants, and to decontaminate fouled environments. Here we present a peripatetic review of some of the contributions polymeric smart materials are making toward the realization of such procedures emphasizing work done in our laboratories.

Soluble Polymer-bound Catalysts and Substrates

Catalysis is a very important aspect of many industrial and laboratory processes. Two strategic approaches to catalysis are normally used. One sort of catalysis is heterogeneous catalysis. In this sort of catalysis, a solid catalyst (e.g., a zeolite or a metal) is used with a gaseous or liquid substrate. Such catalysts are often very practical industrially. They are readily used in high throughput processes and, as a consequence of their structure, facilitate catalyst/product separation. A second general strategy for using catalysts is homogeneous catalysis, which became increasingly popular in the 1950s and 1960s. In this case, the catalyst and substrate are both in solution. Such catalysts have become increasingly important in industrial processes because of their exquisite chemio-, regio- and stereoselectivity that complements that of enzymes. However, while homogeneous catalysts are now widely used, applications of these catalysts face the problem of catalyst (or catalyst–ligand) recovery and separation from products. Such recovery can require additional separation and purification procedures such as extraction and chromatography that can significantly increase the waste output of the process. In large industrial processes this can translate into tremendous amounts of chemical waste that could be avoided if better methods were developed and implemented for catalyst recovery. Furthermore, conventional methods do not always lead to the recovery of an active catalyst or catalyst–ligand complex. This leads to the need for additional procedures to regenerate and reuse these valuable materials.

These problems were part of the impetus for the development of polymer-bound catalysts and reagents in the 1960s. Such polymeric supports were designed to provide improved methods for catalyst and/or reagent recovery without the additional waste production inherent in conventional processes. Initial developments in the area of polymer-bound catalysts and reagents involved the use of insoluble cross-linked polymers as supports for catalysts and reagents (23–27). The most famous of these polymeric support systems are...
insoluble divinylbenzene-cross-linked polystyrenes used as the solid phase in the Merrifield procedure for peptide synthesis (26,27). These solid-phase reagents were originally developed for peptide synthesis and are especially useful in such chemistry because their use eliminates the repetitive and costly purifications associated with these repetitive procedures.

From the late 1960s through the present, there has been a great deal of interest in the development of other insoluble polymer-bound reagents and catalysts. By the 1980s, the use of such insoluble polymer-bound materials had become commonplace (28). Indeed, polymer-bound reagents and catalysts are now commercially available. In most cases, these polymer-bound catalysts or reagents have been designed to mimic their conventional homogeneous analogs. While a polymeric reagent or catalyst may have unique chemistry in special cases, the common feature of all such reagents is their potential for simplified catalyst or reagent recovery and separation from the reaction product.

While insoluble polymer supports for reagents and catalysts have had some success, there are limitations associated with such materials. Insoluble polymer-bound reagents and catalysts generally have different selectivities and lower reactivities than similar homogeneous reagents and catalysts. Furthermore, the insolubility of such materials makes preparation and characterization of the supported reagents and catalysts more difficult, and diffusion-related restrictions often limit the range of usable substrates (29).

Conventional polymeric reagents are cross-linked and, hence, always insoluble. Linear polymers are soluble alternatives to these cross-linked polymers. These linear polymers also can be used as reagents and/or catalyst supports. In many of these cases, membrane filtration or the addition of a second solvent that is a poor solvent for the linear soluble polymer can usefully recover the polymer (30).

In the late 1980s a second alternative to insoluble polymer-bound reagents and catalysts was introduced by Bergbreiter et al. (5,6,10,29,31,32) and Doyle et al. (33). We recognized that many polymers have solubilities that change with temperature. More importantly, we recognized that the change in a polymer’s solubility could affect a bound catalyst’s or bound substrate’s reactivity. Macromolecular enthalpic effects due to crystallinity and entropic effects resulting from solvent–polymer interactions often lead to changes in solubility from complete insolubility to high solubility, as is seen for polyethylene oligomers (Figure 1). Thus, it is easy to see how such temperature-induced solubility changes could provide a simple method to recover catalysts and to control reaction rates.

Two types of soluble polymer-bound catalyst ligands were developed by our group. The earliest work in this area focused on the development of polyethylene-bound catalysts that have normal temperature-dependent solubility. Polyethylene oligomers like high molecular weight polyethylene are insoluble in all solvents at room temperature but soluble at higher temperatures (Figure 1). Thus, catalysts attached to such polymers can be prepared so that they behave as homogeneous catalysts at higher temperatures. Subsequent cooling can then be used to precipitate the polymer-bound catalyst. Simple filtration then effects catalyst recovery and separation from the reaction product without the need for additional chemical methods and the associated production of waste. Catalyst use, recovery, and reuse then requires a simple set of temperature changes, filtrations, and addition of fresh substrate solution as outlined in Figure 2 (29,31–33).

Much of the chemistry involved in the design and use of soluble polymer-bound catalysts possessing normal temperature-dependent solubility has already been reviewed (29). Here we will only briefly list two aspects of this chemistry that take advantage of the smart concept. First, this approach to catalyst use/reuse has an on/off character that is dependent on temperature.

Second, the complete insolubility of polyethylene at room temperature in all the solvents studied coupled with the multiple ligation of most transition metal catalysts makes these polyethylene-bound catalysts entropically advantageous for catalyst recovery. This is because catalyst recovery can be effected even if the catalyst contains only one polyethylene ligand in a group of ligands. This effect was used in some of our previous work with symmetric catalysts (33) and has been discussed in detail by Bergbreiter et al. (32). The principle involved is based on consideration of the likely amount of a complex like L3M that would be present in an equilibrium mixture of L3M, L2MP, LMP, and MP3 (L, low molecular weight ligand; M, a trivalent metal catalyst; P, soluble polymeric ligand). Assuming a ratio of L:M of 1:6 and equivalent ligand abilities for L and P, we have calculated that the concentration of L3M at equilibrium is negligible (<0.3%) because of entropic effects associated with equilibria between the species involved (e.g., the equilibrium L3M + P → L2MP + L would be 3 (favoring L2MP) even if L and P were present in equal concentrations and were equivalent as ligands). Thus, these polymeric ligands that are completely insoluble at room temperature can be used to completely recover catalysts even if some low molecular weight ligands (that could form soluble L3M species) are present.

A second type of linear polymer-bound catalyst that has been developed more recently by Bergbreiter and colleagues involves the design of smart catalysts and substrates that use polymeric ligands and
supports that have inverse temperature-dependent solubility. It has been shown that such species are capable of controlling a catalyst's activity or a substrate's reactivity as a function of temperature (5,6,10,34). Whereas most molecules become more soluble when heated, many water-soluble polymers separate from solution upon heating. This unusual property, termed inverse temperature-dependent solubility, means that such polymers dissolve when cooled and phase-separate when heated above the lower critical solution temperature (LCST). While many chemists might find this effect unusual, the phase separation that occurs upon heating is very well known. In naturally occurring proteins, this process is called denaturation. A lapayer would recognize this effect when an egg is heated and the albumin protein precipitates as egg white. A detailed explanation of this process for proteins or synthetic polymers could be complicated, depending on the particular systems involved. However, a simple argument serves to identify some of the key factors. In this simple explanation, the dissolution enthalpy ($\Delta H$) due to hydrogen bonding of basic sites on the polymer with solvent favors dissolution. In contrast, the entropic organization ($\Delta S$) of the solvent required to achieve this hydrogen bonding is unfavorable. Since the free energy of dissolution is equal to $\Delta H - T\Delta S$, the free energy can change from being negative (favorable) to positive (unfavorable) as temperature increases. Thus, polymers are known to exhibit LCST behavior in strongly interacting solvents. What makes synthetic polymers somewhat more versatile in this respect than their biological counterparts is that synthetic polymers often redissolve when cooled (proteins usually do not "renature"). Moreover, the temperature at which phase-separation of a synthetic polymer from solution occurs can be changed by altering the structure of the polymer (6,35). Such materials have found applications in thermo-responsive membranes (36), the control of enzymatic reactions (37), the controlled delivery of biomolecules (38), and in glazings for solar energy devices (39). We expanded the utility of polymers demonstrating inverse temperature-dependent solubility to the development of ligands for use in the synthesis of smart catalysts—catalysts that demonstrate anti-Arrhenius reactivity or smart behavior (6,10).

Our initial studies of smart water-soluble catalysts and substrates focused on the modification of the end groups of commercially available water-soluble triblock copolymers of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO). We studied PEO-PPO-PEO-bound catalysts and substrates. Such polymers are commercially available from BASF (Wyandotte, MI) with varying ratios PEO/PPO (40). Depending on the molar ratio of the hydrophilic PEO and hydrophobic PPO blocks, the resulting materials have an LCST somewhere between 0 and 100°C.

Modification of these polymers to incorporate catalyst ligands or substrates employed one of two procedures. In the first case, we oxidized the primary hydroxyl groups of the triblock copolymer 1 using CrO$_3$/H$_2$SO$_4$. Subsequent treatment of the carboxylic acid so formed with thionyl chloride produced an acid chloride that was in turn treated with bis(diphenylphosphinoethyl)amine to produce a phosphine ligand 2 (Equation 1; $M_w$, weight average molecular weight). This ligand was soluble in water at low temperature (0°C) but phase-separated at high temperature (50°C). A subsequently formed cationic rhodium(I) complex 3 proved to be competent water-soluble polymer-bound hydrogenation catalysts with temperature-dependent solubility like that of the starting ligand.

A second approach to a thermally responsive smart ligand from the same PEO-PPO-PEO-type starting material used the chemistry shown in Equation 2. Here the terminal hydroxy groups were first mesylated with methanesulfonyl chloride. Nucleophilic substitution with LiP(C$_4$H$_7$)$_2$ followed by exchange with an Rh(I) complex formed a smart catalyst 5.

The smart behavior of these catalysts was demonstrated via the study of aqueous hydrogenations catalyzed by the cationic rhodium complex 3 (10). In these reactions, the initial mixture was homogeneous at low temperature and heterogeneous at high temperature. This inverse temperature-dependent solubility and the redissolution of the catalyst at low temperature is illustrated schematically in Figure 3. The consequences of these changes in solubility.
on hydrogenation rates are illustrated in Figure 4. Figure 4 shows the observed rate for hydrogenation of allyl alcohol by this catalyst at low and high temperatures. The thermostressive behavior of the catalyst is impressive. As shown, the catalyst, in effect, turns itself off when heated above the LCST for the polymer. While this example is illustrative, in an exothermic reaction such behavior could serve to moderate a reaction. Control of exothermic reactions minimizes by-products and would constitute an environmentally important aspect of catalysts heretofore only realizable with external thermal control. A crude calculation shows that the reaction should have increased in rate approximately 50-fold over this temperature range. In fact, the reaction rate decreased more than 10-fold. It is also important that this rate effect was reversible. When the reaction is cooled to 0°C, the catalyst redissolves and once again becomes active at its original rate. We have reported that such effects are also observed in hydrogenations of other substrates and could be observed through repeated heating/cooling cycles (40).

Since the starting triblock copolymer has an LCST that varies with the size of the hydrophilic and hydrophobic blocks, we reasoned that we should be able to tune the temperature at which these reactions turn on and off by varying the ligand structure. This tuning has proven to be possible and the result has been demonstrated in the case of a polymeric ligand with a less polar end group than the amidobiphosphine in 2. The specific example, 4, shown in Equation 2 is a monodendate phospine ligand with an LCST below 25°C that was prepared from a commercially available PEO-PPO-PEO copolymer (Pluronic 103 BASF, mw = 4950) with an LCST of 86°C.

Incorporation of the monodendate ligand 5 in a catalyst produced 6, a smart analog of Wilkinson's catalyst. This neutral rhodium (I) catalyst demonstrated intelligent behavior much like that of 3 but with a lower on/off temperature for catalyst activity (0–25°C at 1% concentration by weight in H2O). For this catalyst, the temperature cycle for the hydrogenation of allyl alcohol was 0°C, 25°C, and finally back to 0°C. As shown in Figure 4, the hydrogenation proceeded at 0°C with a turnover of 13 mol of H2/mol of Rh/hr. When the temperature was raised to 25°C, the catalyst phase separated and the reaction ceased to take up H2. Hydrogen uptake resumed after recooling the reaction to 0°C.

More recently, we have extended and expanded the concept of smart polymer supports to include thermostressive polymer-bound substrates (5). Substrates were attached to the polymer rather than the catalyst. In subsequent studies, we were able to show how a soluble polymer with an LCST can affect a bound substrate’s reactivity (40).

Two sorts of polymer-bound smart substrates have been studied to date. The first was 7. This nitroarene was attached to the ends of the aforementioned PEO-PPO-PEO triblock polymer via an ether bond. The resulting polymer phase separated from an aqueous solution when heated and had reactivity toward heterogeneous catalysts that generally decreased above the polymer’s LCST point. However, experiments shown in Figure 5 have on/off behavior for this allyl alcohol hydrogenation that is not as clean as was seen in the hydrogenation data described in Figure 4. We ascribed this to the character of the polymer support and we were thus moved to study reactions that would use other inverse temperature-dependent polymers as supports.

These subsequent studies focused on chemistry using poly(N-isopropylacrylamide) (PNIPAM)-bound substrates. These polymers can be used to prepare a variety of water-soluble substrates that separate from solution simply by heating above the LCST (~30°C). Such polymer-bound substrates not only undergo useful temperature-dependent changes in solubility and reactivity, they are also readily separable from other soluble catalysts and reagents via heating and subsequent decantation. The thermostressive phase separation of PNIPAM in aqueous solutions was first reported to occur at an LCST of 31 to 32°C by Hsksin and Guiett (41). Since then, a variety of applications have been devised to take advantage of this behavior (36–39). We have to date mainly used a copolymer of PNIPAM and acrylic acid or its derivatives as a smart substrate support.
Detailed studies of the effects of temperature on the hydrogenation of a PNIPAM-bound nitroarene have been reported. These results, illustrated in Figure 5, show that the hydrogenation of this polymeric substrate occurs in water at a rate like that of a similar propionamide derivative of m-nitroaniline when the reactions are carried out at 0°C (soluble polymer-bound substrate). As shown in Figure 6, the activity of this substrate suddenly changed with temperature between 33 and 39°C. This behavior was in contrast to the temperature-dependent reactivity of this same polymer in ethanol solution where normal Arrhenius behavior is seen.

The use of temperature-responsive polymers in the development of smart polymer-bound catalysts and substrates provides two advantages over conventional synthetic methodologies. First, they provide a means for easy separation and recovery of polymer-bound catalysts, substrates, or reagents without the need for additional chemical procedures and the waste generated from such. Second, they are capable of controlling the temperature of a reaction. If the reaction temperature warms above the LCST of the polymer support, the catalyst or substrate phase separates and the reaction slows. As the reaction slows, the reaction temperature decreases until the polymer-bound catalyst or substrate redissolves and continues to react. Such materials could be useful in reactions that are strongly exothermic and difficult to control.

Future applications of polymers in catalysis are likely to increase for several reasons and these developments are likely to have an effect on environmental problems. First, there have been major advances in areas like combinatorial synthesis. This has led to the development of high-throughput catalyst screens that may prove useful if the small-scale reactions can be generalized to preparative scale chemistry. It is anticipated that many groups will develop approaches to combinatorial development and assay of catalysts once creative approaches to multiplexed screening assays are developed. Such chemistry could dramatically shorten the time required to develop and optimize a selective catalyst and the resulting catalysts would be environmentally significant in that the processes they catalyze could be designed to be more energy- and atom-efficient. We believe there is also considerable potential in the development of polymers with temperature-responsive solubility. We have already shown how such polymers can serve as reagent supports and ligands for smart catalysts. Our ongoing work is aimed at developing procedures to use these solubility changes to affect catalyst phase changes that would facilitate catalyst recovery. The polymers we have begun to study also have potential in environmentally compatible chemistry that could be carried out in water using water-soluble polymer-bound catalysts, substrates, or reagents.

**Smart Surfaces and Gels**

A second broad area of smart polymeric materials that is now developing is that of smart surfaces and gels. This area has attracted the interest of other groups. Our interest in this area is embryonic at present as we are still developing the necessary synthetic and analytical methodology to fully study chemical phenomena at functionalized surfaces. Other studies have shown, however, that smart polymeric materials have very intriguing properties that may make them especially useful. For example, the reversible adhesion of cells to PNIPAM-grafted polystyrene has been demonstrated by Takei et al. Future work has also been studied as a chromatographic support by Hosoya et al. In both cases, a thermally responsive polymer’s responsiveness has been translated into an interfacial application. We are confident that similar chemistry will be forthcoming that extends and expands on this sort of idea. Such chemistry could be important in areas as diverse as bioadhesion, marine fouling, and in coating chemistry—areas that have significant environmental implications.

**Polymeric Smart Coatings and Sensors**

A third broad area of interest in environmental chemistry is the remediation of nuclear waste- and chemical-contaminated structures, equipment, groundwater, and soil. Two important considerations when developing effective cleanup procedures are contaminant detection and removal. We have recently developed a new approach involving polymeric materials that act as responsive sensors. This approach was developed in a joint effort by Gray and Jorgensen at Los Alamos and is based on the design and use of water-based smart polymeric coatings for the decontamination of contaminated surfaces. These coatings consist of strippable polymeric compositions containing blends of polymers, copolymers, and additives that can be brushed or sprayed onto a surface as a solution or dispersed in aqueous media. Upon curing or drying, these coatings form strong films that can be easily peeled or stripped from the surface. When applied to a contaminated surface, these coatings display responsive behavior. Areas of contamination are indicated by a color change. As the coatings dry, the contaminant is drawn into and fixed in the polymer matrix. Subsequent removal of the coating with entrapped contaminants results in some degree of surface decontamination.

A typical example of the smart coatings developed is SensorCoat VI, developed for the detection and removal of...
both uranium and plutonium from contaminated surfaces. This coating (Figure 8) consisted of a blend of a low viscosity, partially hydrolyzed poly(vinyl alcohol) (12 wt%) and poly(vinyl pyrrolidone) (7 wt%) in water. The coating also contained a plasticizer (glycerin, 4 wt%), a chelating masking agent (0.5 wt%), and a colorimetric indicator [2-(5-bromo-2-pyridylazo)-5,5-diethyiaminophenol, 3 × 10^{-3} wt%]. The coating exhibited color changes for each contaminant (orange to purple for uranium and orange to red for plutonium) and was extremely effective at removing varying levels of both contaminants from surfaces.

To measure the effectiveness of the smart coatings, a variety of uranium- and plutonium-contaminated coupons (a small metal vise about 4" in diameter) were decontaminated. The coupons were weighed before and after contamination. Each contaminated coupon was analyzed via α-scintillation counting, then treated with the sensing strippable coating. All coatings were allowed to dry for at least 24 hr before removing. The coatings were stripped and the coupons were again analyzed via α-scintillation counting. Using the count rates before and after decontamination, decontamination factors (DF) were calculated using Equation 5, where \( \alpha_1 = \alpha \)-count before decontamination and \( \alpha_2 = \alpha \)-count after decontamination.

\[
DF = \frac{\alpha_1}{\alpha_2} \quad [5]
\]

Gray and Jorgensen studied the ability of the sensor coating to decontaminate several different types of surfaces contaminated with varying amounts of uranium and plutonium (16,17). The results are shown in Table 1 for uranium and Table 2 for plutonium.

The decontamination factors obtained for uranium were very high on all the surfaces and decreased as the amount of contaminant on the surface increased. This is probably due to a conflict between the time required for the larger amounts of contaminant to permeate into the polymer and the drying time of the coatings.

To determine the effectiveness of Gray and Jorgensen’s smart coating relative to that of commercially available strippable coatings in uranium decontamination, a popular commercial strippable coating was carried through the same decontamination procedure described in Equation 5. For a stainless steel coupon containing 28.7 mg of uranium contaminant, a DF of 276 was measured for the commercial coating. This value indicated that the commercial coating was only 25% as effective in uranium decontamination as the sensor coating developed by Gray and Jorgensen. Moreover, unlike the smart coating, the commercial coating did not have the ability to detect the presence of the contaminant.

The sensor coating was not as effective in plutonium removal as it was for uranium (Table 2); however, it was still much more efficient than commercially available strippable coatings. Two commercially available strippable coatings, ALARA DECON 114B (Carboline Co., Bartlett Nuclear, Inc., Plymouth, MA) and StripCoat TLC (Imperial, Division of Carboline Co., New Orleans, LA) were tested for their abilities to decontaminate plutonium-contaminated stainless steel coupons using the identical procedure as for our sensor coating (Figure 9). The results for these coatings are shown as the last two entries in Table 2. A comparison of the decontamination effectiveness for the sensor coating, ALARA DECON, and Stripcoat TLC is shown graphically in Figure 5. As seen from the DF values, the sensor coating is...
The contaminant-sensing ability of smart coatings has led to the initial development of in-line sensors for processes producing or destroying hazardous materials (B Jorgenson, unpublished data). Such sensors are thin polymer films or coated optical fibers that have reversible colorimetric responses to a specific material or materials. For example, initial studies have resulted in the development of a polymeric thin film sensor that can detect aqueous concentrations of uranium down to 20 ppb.

Sensors that incorporate polymeric smart materials have also been developed by Ayagari et al. for the detection of trace levels of organophosphorus pesticides, nerve agents, and Be(II) (14,15). Such sensors utilize molecular assembly as a method to interface conducting polymers with biochemical components and can detect organophosphorus pesticides and nerve agents down to 500 ppb and Be(II) down to 1 ppm.

**Conclusion**

Polymeric smart materials have considerable utility in environmental applications. In most cases and in the specific examples described above, we have emphasized using simple properties of polymers as matrices to bind metals in useful ways. In the case of catalysis chemistry, we have emphasized the value of minimizing waste and recovering and reusing catalysts. Our recent work has detailed how the seemingly anomalous inverse temperature-dependent solubility of polymers can be used to alternately start and stop reactions and to control or facilitate catalyst, product, or substrate isolation and recovery. These sorts of approaches can be applied to modified grafted surfaces and there are now intriguing precedents to suggest that it should be possible to prepare densely functionalized surfaces that can control interfacial chemistry. The material properties of reactive coatings that are designed to include sensing elements for detection and removal of hazardous materials, including radioactive contaminants, are an especially attractive application of smart polymeric systems that has topical relevance to thorny environmental problems that stem from the Cold War. It is clear that smart polymeric materials have found and will continue to find applications in areas significant to environmental health. Continued work on existing chemistry and future development of new chemistry can only lead to exciting new environmental applications.
REFERENCES

1. Whitesides GM. What will chemistry do in the next twenty years? Angew Chem Int Ed Engl 29:1209–1218 (1990).
2. Garnier F. Functionalized conducting polymers—towards intelligent materials. Angew Chem Int Ed Engl 28:513–517 (1989).
3. Yanagida H. Intelligent materials—a new frontier. Angew Chem Int Ed Engl 27:1389–1392 (1988).
4. Aguilar, GA. Studies of Estery and Ether Reactivity at Functionalized Polyethylene-Silica Interfaces. Ph.D. dissertation, Texas A&M University, College Station, TX, 1996.
5. Bergbreiter DE, Caraway JW. Thermoresponsive polymer-bound substrates. J Am Chem Soc 118:6092–6093 (1996).
6. Bergbreiter DE, Mariagnanam VM, Zhang L. Polymer ligands that can regulate reaction temperature in "smart" catalysts. Advanced Materials 7:69–71 (1995).
7. Nagayama H, Maeda Y, Shimasaki C, Kitano H. Functionalized polymer chains with temperature-responsive polymer-chemical hybrids. Macromol Chem Phys 196:611–620 (1995).
8. Takei YG, Aoki T, Saniu K, Ogata N, Sakurai Y, Okano T. Dynamic contact angle measurement of temperature-responsive superhydrophobic poly(N-isopropylacrylamide) grafted surfaces. Macromolecules 27:6163–6166 (1994).
9. Galaev IY. Thermoreactive hydrogels in biotechnology and medicine. Biochem-Moscow 59:1093–1096 (1994).
10. Bergbreiter DE, Zhang L, Mariagnanam VM. Smart ligands that regulate homogeneously catalyzed reactions. J Am Chem Soc 115:9285–9286 (1993).
11. Chen CS. Passive suppression of vibration and noise in smart structures made of layered media. In: Smart Structures and Materials: Smart Materials. Vol 2189 (Varadan VK, ed). Bellingham WA: The International Society for Optical Engineering, 1994;208–210.
12. Giewerczky LM, Landi LM, Liebman M, Brittain WJ, Foster MD. Synthesis and characterization of a photoactivable monolayer. In: Smart Structures and Materials: Smart Materials. Vol 2441 (Jardine AP, ed). Bellingham, WA: The International Society for Optical Engineering, 1995;2–11.
13. Chen GH, Hoffman AS. A new pH-responsive and temperature-responsive copolymer for possible use in protein conjugation. Macromol Chem Phys 196:1251–1259 (1995).
14. Ayyagari M, Pande R, Lim JO, Kamath M, Beladakere N, Gao H, Marx K, Tripathy S, Kumar J, Samuelson L, Akkara J, Kaplan D. Biotinylated polyalkylthiophene thin films and monolayers that specifically incorporate phycobiliproteins: toward smart materials. In: Proceedings of the International Society for Optical Engineering, 14–16 February 1994, Orlando, FL. Bellingham, WA: The International Society for Optical Engineering, 1994;116–125.
15. Ayyagari MS, Pande R, Kamtekar S, Gao H, Marx KA, Kumar J, Tripathy SK, Akkara JA, Kaplan DL. Molecular assembly of proteins and conjugated polymers—toward development of biosensors. Biotechnol Bioeng 45:116–121 (1995).
16. Gray HN, Jorgensen B. The Development of Sensing, Strippable Polymeric Coatings for Nuclear Decontamination, LA-UR 95-3854. Los Alamos, NM: Los Alamos National Laboratory, 1995.
17. Gray HN, Jorgensen B. Sensing Strippable Coatings, U.S. Patent Application S-80, 449. Los Alamos, NM: Los Alamos National Laboratory, 1995.
18. Walker JA, Gabriel KJ, Mehregany M. Thin film processing of Ti-Ni shape memory alloy. Sensors Actuators A—Physical 21:243–246 (1990).
19. Kuriyama K. Millimeter-sized joint actuator using a shape memory alloy. Sensors Actuators A—Physical 20:57–64 (1989).
20. Kost J, Langer R. Responsive polymer systems for controlled delivery of therapeutics. Trends Biotechnol 10(4):127–131 (1992).
21. Lenroe EM, Radicic WN, Knapp MS. Implications of smart materials in advanced prosthetics. In: Proceedings of the International Society for Optical Engineering, 14–16 February 1994, Orlando, FL. Bellingham, WA: The International Society for Optical Engineering, 1994;84–101.
22. Pei Q, Inganas O, Lundstrom I. Bending bilayer strips built from polyaniline for artificial electrochemical muscles. J Smart Struct Mat 3:367–372 (1993).
23. Pritman, Jr. Polymer-supported catalysts. In: Comprehensive Organometallic Chemistry. Vol 8 (Wilkinson G, ed). Oxford: Pergamon, 1992;553–574.
24. Hartley FR. Supported Metal Complexes. A New Generation of Catalysts. Dordrecht: Kluwer Academic Publishers Group, 1980.
25. Mathur N, Narang CK, Williams RE. Polymers as Aids in Organic Chemistry. New York: Academic Press, 1980.
26. Merrifield RB. Solid phase synthesis. Angew Chem Int Ed Engl 24:799–810 (1985).
27. Birr C. Aspects of the Merrifield Peptide Synthesis. Berlin: Springer Verlag, 1978.
28. Bergbreiter DE. Attachment of ligands and reagents to polymers that dissolve...sometimes. CHEMTECH 17:686–690 (1987).
29. Bergbreiter DE. Soluble polymer-bound catalysts. In: Functional Polymers (Bergbreiter DE, Martin CR, eds). New York: Plenum Press, 1989;143–158.
30. Geckeler KE. Soluble polymer supports for liquid phase synthesis. Adv Polym Sci 121:31–79 (1995).
31. Bergbreiter DE, Treadwell DB. Polyethylene carboxylate-bound triruthenium clusters as oxidation catalysts. Reactive Polymers 12:291–295 (1990).
32. Bergbreiter DE, Poteat JL, Zhang L. Complexation of europium using polyethylene carboxylic acid. Reactive Polymers 20:99–109 (1993).
33. Doyle MP, Eismont MY, Bergbreiter DE, Gray HN. Enantioselective metal carbene transformations with polyethylene-bound soluble recoverable dirhodium(II)-2-pyrrolidinone-5(S)-carboxylates. J Org Chem 57:6103–6105 (1992).
34. Karakhanov EA, Maksimov AI, Predeva ZV, Utukin AM, Filippova YA. Molecular design of catalysts on the basis of functionalized poly(ethylene oxide) and block copolymers of ethylene oxide and propylene oxide. Macromol Symp 105:67–74 (1996).
35. Schild HG. Poly(N-isopropylacrylamide): experiment, theory and application. Prog Polym Sci 17:163–249 (1992).
36. Taylor LD, Cerankowski LD. Preparation of films exhibiting a balanced temperature dependence to permeation by aqueous solutions: a study of lower consolute behavior. J Polym Sci Polym Chem Ed 13:2551–2570 (1975).
37. Dong LC, Hoffman AS. Thermally reversible hydrogels—swelling characteristics and activities of copoly(N-isopropylacrylamide-acrylamide) gels containing immobilized asparaginase. ACS Symp Ser 350:236–247 (1987).
38. Afrassiabi A, Cadwell LA, Hoffman AS. Effect of temperature on release rate of biomolecules from thermally reversible hydrogels. J Membr Sci 33:191–200 (1987).
39. Gundlach DP, Burdett KA. Lower critical solution temperature (LCST) polymer-solution for clear/cloud glazing applications. J Appl Polym Sci 51:731–737 (1994).
40. Caraway JW, Bergbreiter DE. Soluble polymers as catalysts and substrate supports in catalysts. In: Catalysis of Organic Reactions (Malz RE Jr, ed). New York: Marcel Dekker, 1996.
41. Heskins M, Guillett JE. Solution properties of poly(N-isopropylacrylamide). J Macromol Sci Chem A2:1441–1449 (1968).
42. Terrett NK, Gardner M, Gordon DW, Kobylicz RJ, Steele J. Combinatorial synthesis—the design of compound libraries and their application to drug discovery. Tetrahedron 51:8135–8173 (1995).
43. Murphy MM, Schullek JR, Gordon EM, Gallop MA. Combinatorial organic synthesis of highly functionalized pyrrolidines: identification of a potent angiotensin-converting enzyme-inhibitor from a mercaptoacyl proline library. J Am Chem Soc 117:7029–7030 (1995).

44. Burgess, K, Lim, HJ, Porte, AM, Sulikowski, GA. New catalysts and conditions for a C-H insertion reaction identified by high throughput catalyst screening. Angew Chem Int Ed Engl 35:220–222 (1996).

45. Takei YG, Aoki T, Sanui K, Ogata N, Sakurai Y, Okano T. Temperature-modulated platelet and lymphocyte interactions with poly(N-isopropylacrylamide)-grafted surfaces. Biomaterials 16:667–673 (1995).

46. Hosoya K, Sawada E, Kimata K, Araki T, Tanaka N, Frechet JMJ. In-situ surface-selective modification of uniform size macroporous polymer particles with temperature-responsive poly-N-isopropylacrylamide. Macromolecules 27:3973–3979 (1994).