

## References and Notes

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$$\left| \frac{P'}{F_0} \right|^2 = \frac{1 + \omega^2 \tau^2}{(1 - \alpha \mu)^2 + \omega^2 \tau^2}$$

$$\tan(\phi) = \frac{\alpha \mu \omega \tau}{1 - \alpha \mu + \omega^2 \tau^2}$$
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  32. Supported by NSF grant ATM-9521389, NOAA grant NA86GP0314, and a grant to N.Z. from the NASA IPA program. We thank two anonymous reviewers for their constructive comments, K. Hales for help with the rainfall data, M. Cisse for processing the normalized difference vegetation index data, and V. Nelson for editorial assistance.

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## The Gelation of CO<sub>2</sub>: A Sustainable Route to the Creation of Microcellular Materials

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Compounds with strong thermodynamic affinity for carbon dioxide (CO<sub>2</sub>) have been designed and synthesized that dissolve in CO<sub>2</sub>, then associate to form gels. Upon removal of the CO<sub>2</sub>, these gels produced free-standing foams with cells with an average diameter smaller than 1 micrometer and a bulk density reduction of 97 percent relative to the parent material.

Carbon dioxide is nonflammable, relatively nontoxic, and naturally abundant, and is consequently promoted as a sustainable solvent in chemical processing. Carbon dioxide's "green" properties have provided the driving force for development of a number of new applications, such as replacement of organic solvents in polymerization (1), as a medium for conducting hydrogenations and oxidations in the absence of transport limitations (2), as a solvent in biocatalysis (3), and as a raw material in synthesis (4). Many of these applications have been made possible by the relatively recent discovery that certain functional groups, subsequently denoted "CO<sub>2</sub>-philic" (see below), enable miscibility of target compounds with CO<sub>2</sub> at moderate pressures (5). Development of CO<sub>2</sub>-soluble surfac-

ants, for example, permits CO<sub>2</sub>-based emulsion polymerization and dry cleaning. The design and synthesis of CO<sub>2</sub>-philic phosphine ligands has spawned a number of CO<sub>2</sub>-soluble metal catalysts. By combining concepts in CO<sub>2</sub>-philic design with an understanding of molecular assembly in solution, we have generated compounds that gel CO<sub>2</sub> at concentrations below 5 weight %. Creation of gels in CO<sub>2</sub> has allowed us to generate cellular polymers with a bulk density <5% of that of the parent polymer and cells <1  $\mu$ m. Generation of gels, and more recently foams, using CO<sub>2</sub> thus provides a technically and environmentally satisfying solution to a material fabrication problem.

A one-step, CO<sub>2</sub>-based route for generation of low bulk density, microcellular materials is of particular technical interest because these materials—organic analogs to silicate aerogels—have some intriguing applications (catalyst and separation supports, low-dielectric materials, insulation, tissue engineering scaffolds), and be-

cause current routes to organic and inorganic aerogels involve multiple process steps and large volumes of solvent. Commercial foaming processes using CO<sub>2</sub> are by contrast "greener," but they do not generate the combination of low bulk density and submicrometer pore size. These processes either add CO<sub>2</sub> to a polymer melt in an extruder or mix CO<sub>2</sub> with (polyurethane) precursor materials before polymerization. In either case, the pressure used is relatively low (30 to 100 atm), and thus the amount of CO<sub>2</sub> mixed with the polymer is usually <5 weight %. Foam with a very low bulk density (>95% density reduction relative to the parent polymer) is produced, but its cells can be as large as 1 mm (6). Research conducted during the 1980s and 1990s showed that high-pressure CO<sub>2</sub> (pressures up to 500 atm) can be used to swell thermoplastic polymers by as much as 30%, and that subsequent rapid depressurization produces a microcellular foam. Such methods readily produce foams with cells <2  $\mu$ m, but density reductions rarely exceed 65% (7). There would be considerable utility in a single-step process by which one could generate organic, low-density, microcellular materials with a benign foaming medium such as CO<sub>2</sub>.

As a means to generate low-density microcellular foam, we synthesized molecules that would dissolve in CO<sub>2</sub> under relatively moderate pressures, then associate in solution to form gels. Previous work has shown that gels can be created in traditional organic solvents through hydrogen bonding (8), association between ionic groups (9), or association between electron-donating and electron-accepting moieties (10). To form foams from such gels, it is necessary to preserve the supramolecular aggregates created in solution, both during and after solvent removal. Although it is possible to design molecules that aggregate in solution, for example through multipoint hydrogen-bond formation (11), only

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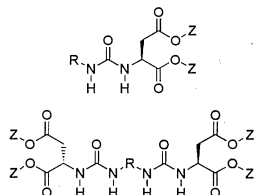
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rarely do the aggregates form structures that can be preserved after removal of the solvent (12). We surmised that by changing the temperature-pressure conditions of the initial solution of our model agents in CO<sub>2</sub>, we could induce a phase separation to produce an organic analog to the aerogel upon depressurization. Unlike traditional aerogel generation, we could then form these microcellular materials in a single step in CO<sub>2</sub> without the use of any additional solvent. Although molecular association in CO<sub>2</sub> has been previously observed, the molecules in question (surfactants) were designed to form spherical micelles, whereas we desire formation of supramolecular networks that will exist as stable entities in the absence of CO<sub>2</sub>.

All of the compounds synthesized and evaluated for this work incorporate CO<sub>2</sub>-philic functional groups (13) to allow dissolution in CO<sub>2</sub>. A number of compounds have been found experimentally to exhibit miscibility with CO<sub>2</sub> at relatively moderate pressures; these have since been labeled CO<sub>2</sub>-philic to distinguish them from traditional lipophilic and hydrophilic moieties. "CO<sub>2</sub>-philicity" may derive from the inclusion of functional groups that interact specifically with the carbon atom in CO<sub>2</sub>, from weak self-interaction of the solute, or both. Further, it is thought that the latter manifests itself as some combination of low solubility parameter, low interfacial tension, or low softening temperature. Effective CO<sub>2</sub>-philes include fluoroalkyl, fluoroether, and siloxane functional materials.

The use of multipoint hydrogen bonding to form macromolecular yet noncovalent architectures in solution has been explored extensively in recent years (8, 11, 12). Molecules have been synthesized that, when dissolved under appropriate conditions, form transparent gels via self-assembly into macromolecular rigid rods, disks, and three-dimensional networks. Although many different architectures can be formed depending on the shape and functionality of the precursors, many of these materials share common hydrogen-bonding functional groups such as amides, ureas, and ureidopyrimidone. We first prepared a number of "monomers" that contain one or two urea groups (to induce aggregate formation) and fluorinated groups to promote solubility in CO<sub>2</sub> at moderate pressures (class A and class B structures; Scheme 1). The use of aspartate residues in the construction of the compounds allows easy incorpora-



**Scheme 1.** Class A structures (**top**) and class B structures (**bottom**), with one and two urea groups, respectively.

tion of CO<sub>2</sub>-philic functional groups (through diester formation) as well as generation of the urea groups needed for hydrogen bonding (through reaction with isocyanates).

We evaluated the ability of several variations of the class A and class B structures to form cellular materials in CO<sub>2</sub> (Table 1). First, we measured the phase behavior to determine those conditions where a single-phase solution could be produced as a function of concentration. Foams were generated from single-phase solutions in CO<sub>2</sub> by (i) lowering the temperature, (ii) lowering the pressure, or (iii) lowering temperature and then pressure. When formed, aggregates were recovered after venting of the CO<sub>2</sub> and were then analyzed by scanning electron microscopy (SEM) (14). Behavior in CO<sub>2</sub> could be separated into three general types:

**Type I:** These compounds (typically powders) could dissolve in CO<sub>2</sub> at concentrations exceeding 5 weight % at room temperature (above a given threshold pressure that varied with molecular structure of the agent but was below 300 atm in all cases). Measurement of the resulting viscosity of the solution showed enhancement by a factor of 3 to 5 at <5 weight %. Removal of the CO<sub>2</sub> via pressure reduction yielded a foamed material (solid at room temperature and pressure) that was stable and could easily be handled and examined by SEM.

**Type II:** These compounds were soluble in CO<sub>2</sub> at concentrations less than 0.1 weight % at room temperature, at pressures up to the limit of the instrument (500 atm), but would dissolve at concentrations exceeding 5 weight % at elevated temperature (typically 70° to 90°C). Upon cooling at constant pressure (300 atm), the solution would exhibit a sharp phase separation

point (sudden complete opacity of the mixture). Removal of the CO<sub>2</sub> by gradual depressurization yielded a monolithic cellular or fibrillar material that was stable and could be handled and examined by SEM.

**Type III:** These compounds, like those of type II, were soluble in CO<sub>2</sub> at elevated temperature, although slow cooling of the solution led to precipitation of the material as a powder or as free-floating fibers rather than as a type II monolithic foam.

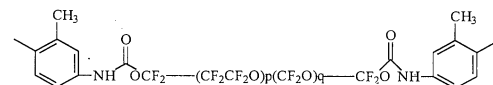
We found that small variations in the structure of the associating molecules led to large changes in their behavior in CO<sub>2</sub>. With the exception of 6, class B structures exhibited type II or III behavior and hence required elevated temperature to dissolve in CO<sub>2</sub>, apparently to break the strong self-interaction between the two urea groups. Alterations to the R group of class B structures produce substantial changes in behavior. For example, 1, when dissolved in CO<sub>2</sub> at slightly less than 5 weight %, produces a cellular material (via type II behavior) that exhibits a morphology (Fig. 1A) of "stacks" of small parallelograms. Despite the dense appearance of this material, its bulk density is reduced by 97% relative to the parent material (at 5 weight %, the resulting monolith fills the entire view cell). As can be seen in Fig. 1A, the pores (the spaces between the parallelograms) are sub-micrometer in size. Lengthening the R group from hexyl to dodecyl produces a foam with a more conventional porous structure, larger cells, and a slightly higher bulk density (Fig. 1B).

Changing the concentration of the agents in solution resulted in striking changes in the morphology of the foams. For example, lowering the concentration of 1 in CO<sub>2</sub> to <2.5 weight % (all other conditions the same) produces a ma-

**Table 1.** Solubility and foaming (type I, II, or III) of class A and class B compounds.

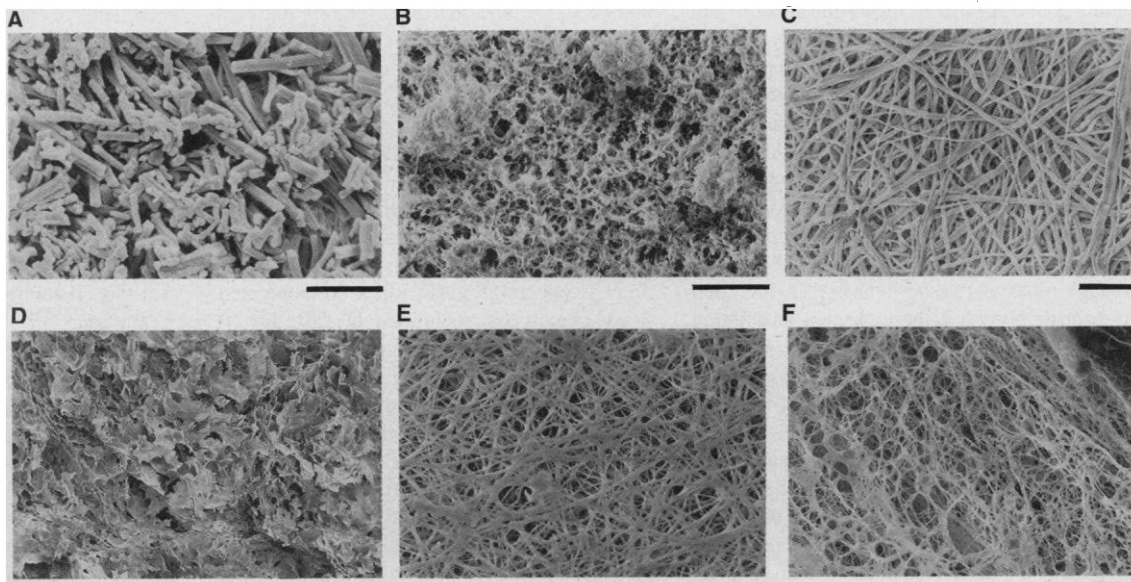
Compound	CO <sub>2</sub> -phile (Z group)	R group	Concentration (weight %)	Type
<b>Class B</b>				
1	(CH <sub>2</sub> ) <sub>2</sub> (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	(CH <sub>2</sub> ) <sub>6</sub>	2.2 to 4.9	II
2	(CH <sub>2</sub> ) <sub>2</sub> (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	(CH <sub>2</sub> ) <sub>12</sub>	4.0	II
3	(CH <sub>2</sub> ) <sub>2</sub> (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	1,4-Phenyl	1.9	III
4	(CH <sub>2</sub> ) <sub>2</sub> (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	1,4-Xylyl	3.35	III
5	(CH <sub>2</sub> ) <sub>2</sub> (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	Fluoroether*	2.5 to 4.8	III
6	Fluoroether†	(CH <sub>2</sub> ) <sub>6</sub>	1.5 to 5.0	I
<b>Class A</b>				
7	(CH <sub>2</sub> ) <sub>2</sub> (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	p-FC <sub>6</sub> H <sub>4</sub>	4.5	II
8	(CH <sub>2</sub> ) <sub>2</sub> (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	p-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2.5	III
9	(CH <sub>2</sub> ) <sub>2</sub> (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	3,5-bis(CF <sub>3</sub> )C <sub>6</sub> H <sub>3</sub>	6.0	I
10	(CH <sub>2</sub> ) <sub>2</sub> (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	1.0 to 5.0	I
11	(CH <sub>2</sub> ) <sub>2</sub> (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	Phenyl	2.0 to 5.1	II
12	(CH <sub>2</sub> ) <sub>2</sub> (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	Ethyl methacrylate	4.7	I

\*Fluorolink B (Ausimont), molecular weight 3000:



†Oligomer of hexafluoropropylene oxide (DuPont), molecular weight 1200.

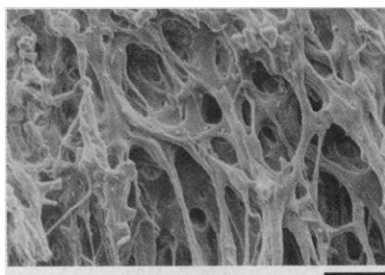
**Fig. 1.** (A) Foam produced using **1** at 4.86% initial composition in CO<sub>2</sub>. (B) Foam produced using **2** at 4.0% initial composition in CO<sub>2</sub>. (C) Foam produced using **1** at 2.2% initial composition in CO<sub>2</sub>. (D) Foam produced using **10** at 5% initial composition in CO<sub>2</sub>. (E) Foam produced using **12** at 4.7% initial composition in CO<sub>2</sub>. (F) Foam produced using **11** at 4.8% initial composition in CO<sub>2</sub>. All panels are SEM images; scale bars, 5  $\mu$ m (A, C, and F), 10  $\mu$ m (B and E), and 500  $\mu$ m (D).



terial (Fig. 1C) with submicrometer pores, a fibrillar morphology, and a bulk density comparable to that of the material in Fig. 1A (the monolith comprises less material but does not fill the entire volume available in the view cell). Some but not all of the materials in Table 1 exhibit a morphology-concentration correlation, but it is not yet clear how the chemical structure of the agents governs this correlation.

Changing the R group from alkyl to aromatic in class B compounds changes the behavior from type II (monoliths) to type III (precipitated as powders). Here, although the elevated temperature allows dissolution of these type III materials, the formation of large aggregates with type II morphology is apparently inhibited by the aromatic structures, even for **5**, where the R group contains aromatic groups with a highly CO<sub>2</sub>-philic fluoroether spacer. When fluoroether groups are used in the aspartate residue (the Z group), as in **6**, type I foams with a more traditional cellular appearance are formed.

As we expected, reducing the number of



**Fig. 2.** SEM image of foam produced from terpolymer of 1H,1H,2H,2H-perfluorodecyl acrylate (84 mol %), styrene (11 mol %), and sulfonated styrene (5 mol %) at 1.1 initial weight % in CO<sub>2</sub>. Scale bar, 5  $\mu$ m. For more details of the terpolymer synthesis, see *Science Online* ([www.sciencemag.org/feature/data/1044209.shl](http://www.sciencemag.org/feature/data/1044209.shl)).

urea groups from two to one (class A structures) produces type I materials more readily, yet still allows for types II and III to form, depending on the structure of the R group. Somewhat surprisingly, R groups that might be suspected to be relatively CO<sub>2</sub>-philic (*p*-fluorophenyl and *p*-trifluoromethyl phenyl in **7** and **8**), and hence to lead to solubility at room temperature, instead produced type II and III behaviors, requiring elevated temperature for dissolution. Addition of the second trifluoromethyl group (**8**) is needed for the molecule to dissolve at room temperature. The agents that produced type I behavior generally produced foams with a traditional porous morphology, with cells larger than 1  $\mu$ m (see Fig. 1D). However, the methacrylate-functional compound (**12**) exhibits type I behavior and also produces a foam with a fibrillar structure (Fig. 1E). The phenyl-functional material (**11**) exhibited type II behavior and produced very low density, microcellular foam monoliths that filled the view cell, like those produced from **1**, with a fibrillar microstructure (Fig. 1F).

Although the foams generated with these compounds are stable upon removal of the CO<sub>2</sub> (they easily support their own weight with no dimensional changes after days or weeks), they can be readily redissolved in CO<sub>2</sub>. Foams with a greater degree of permanence can be generated using compounds such as **12** (methacrylate-functional material) or an analog of **1** or **2** where a diyne functionality is included in the R group. Irradiation after foam formation would polymerize these materials.

CO<sub>2</sub>-soluble associating polymers were also generated (**15**) by copolymerization of the highly CO<sub>2</sub>-philic 1H,1H,2H,2H-perfluorodecyl acrylate with **12**, or with styrene followed by partial sulfonation of the phenyl groups. Copolymers of the fluorinated acrylate and **12** dissolved readily in CO<sub>2</sub> at room temperature and produced stable, transparent gels at concen-

trations of 5 weight % and below. Unlike the type I structures shown in Table 1, the viscosity enhancement created by these polymers was two to three orders of magnitude. Removal of the CO<sub>2</sub> produced free-standing foam monoliths with a very low bulk density (>97% density reduction) but larger cells (>10  $\mu$ m) than those described above. Gels and foams were produced even at levels of **12** in the copolymer as low as 6 mol %. Terpolymers of the fluorinated acrylate, styrene, and sulfonated styrene also produced transparent gels in CO<sub>2</sub> and foam monoliths with this type of microstructure (Fig. 2). Copolymers of the fluorinated acrylate with monomers that do not promote association in solution did not produce a large viscosity increase in CO<sub>2</sub>, nor did they produce foam monoliths upon depressurization. Rather, the cellular materials produced from these copolymers collapsed upon removal of the CO<sub>2</sub>.

A number of issues remain to be explored, including understanding the mechanism for morphology development in the foams, and hence why we have observed such striking changes in morphology upon changing either molecular structure or concentration. The CO<sub>2</sub> gels produced with the agents described above are not only precursors to microcellular materials, but could also have applications themselves. Gelation of CO<sub>2</sub> could be used to enhance the tertiary recovery of petroleum from aging fields and could also support CO<sub>2</sub>-based coating processes. Each of these applications requires less expensive, and hence nonfluorinated, analogs of the compounds described above, and some of these are now under development (**16**).

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13. The bisurea gelling agents were prepared by esterification of *N*-butoxycarbonyl (BOC)-aspartic acid in dichloromethane with 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDCI), 4-(dimethylamino)pyridine (DMAP), and 1*H*,1*H*,2*H*,2*H*-perfluorodecanol followed by deprotection with trifluoroacetic acid/CH<sub>2</sub>Cl<sub>2</sub> (50:50) and reaction with the appropriate mono- or bis-isocyanates in CH<sub>2</sub>Cl<sub>2</sub> with excess triethylamine. The resultant bisureas were filtered off and washed with CH<sub>2</sub>Cl<sub>2</sub>, 1% aqueous HCl, water, and more CH<sub>2</sub>Cl<sub>2</sub>. All compounds gave spectroscopic characteristics consistent with their structure and were shown to be >95% pure. For more details of the synthesis of fluorinated aspartate bisureas and ureas, see Science Online ([www.sciencemag.org/feature/data/1044209.shl](http://www.sciencemag.org/feature/data/1044209.shl)).
14. Foam samples were fractured, sputter-coated with gold, then analyzed by SEM as described [K. Parks and E. J. Beckman, *Polym. Eng. Sci.* **36**, 2417 (1996)]. Sizes given throughout this report are average diameters, as generated from these analyses of SEM images.
15. Monomers (styrene, *N,N*-dimethyl amino ethyl methacrylate, *n*-hexyl acrylate, 1*H*,1*H*,2*H*,2*H*-perfluorodecyl acrylate; Aldrich) were purified using conventional procedures (washing to remove inhibitors, drying, vacuum distillation as appropriate). Copolymers were prepared via bulk polymerization at 65°C using azobisisobutyronitrile (AIBN) (0.2 mol %, recrystallized from methanol). Copolymers were purified via dissolution in 1,1,2-trichloroethane or perfluoromethyl cyclohexane, followed by precipitation into methanol. Copolymer content was quantified using <sup>1</sup>H nuclear magnetic resonance. The aspartate methacrylate monomer was prepared using the scheme shown in (73) and 2-isocyanato ethyl methacrylate (Aldrich). Styrene-fluorinated acrylate copolymers were sulfonated using an SO<sub>3</sub>/acetic anhydride complex (acetyl sulfate).
16. We are developing CO<sub>2</sub>-philic hydrocarbons to form the building blocks for the next generation of such agents (E. J. Beckman, *Design of CO<sub>2</sub>-Philic Hydrocarbons*, paper presented at the Engineering Foundation Conference on Supercritical Fluids in Materials Processing and Synthesis, Davos, Switzerland, September–October 1999).
17. Supported by the U.S. Department of Energy (National Petroleum Technology Office, contract DE-AC26-98BC15108), NSF (grants CTS-9870925 and CHE-9817240), Air Products & Chemicals, and Cabot Oil & Gas.

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# Reversible Molecular Adsorption Based on Multiple-Point Interaction by Shrinkable Gels

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A general approach is presented for creating polymer gels that can recognize and capture a target molecule by multiple-point interaction and that can reversibly change their affinity to the target by more than one order of magnitude. The polymers consist of majority monomers that make the gel reversibly swell and shrink and minority monomers that constitute multiple-point adsorption centers for the target molecule. Multiple-point interaction is experimentally proven by power laws found between the affinity and the concentration of the adsorbing monomers within the gels.

Many proteins can specifically recognize and reversibly bind small target molecules. The binding site contains contacts from several amino acids from different locations along the protein chain. Even a slight change in the backbone conformation at distant sites can alter the spatial arrangement of these contact points and change the binding constant. Most synthetic polymers contain only one or two different types of monomer units, which might suggest that a similar type of specific reversible adsorption would be difficult to achieve with these materials.

We present a general approach for creating polymer gels that can recognize and capture a target molecule by multiple-point interaction and that can reversibly change their affinity to the target by more than one order of magnitude. The polymers consist of two species of monomers, each having a different role. The majority monomer species control network density and make the gel reversibly swell and shrink in response to an environmental change such as temperature. The minority monomers come into sufficient proximity to each other when the supporting gel shrinks so that they can function as multiple-point adsorption centers for the target molecules. This adsorption can be switched on and off by the reversible gel phase transition.

To demonstrate the general principle, we carefully selected the monomers for the gels and their targets. As target molecules, we chose

pyranine-3 and pyranine-4 for two reasons. First, they have three or four charges, respectively, allowing multiple-point interactions through the Coulomb force, a simple physical interaction. It was convenient that there are two types of pyranine with a different number of charges that allowed us to test the dependence of adsorption on the number of contact points. Second, their strong fluorescence and clearly separated ultraviolet (UV) adsorption peaks allow an accurate determination of the degree of adsorption by the gels, even at very low concentrations.

As adsorbing molecules, we chose methacrylamidopropyltrimethylammonium chloride (MAPTAC), which carries one positive charge. We envisioned that three or four MAPTAC groups would capture one pyranine molecule. A small amount of MAPTAC was embedded by copolymerization within a thermosensitive polymer network of *N*-isopropylacrylamide (NIPA) in the monomer ratio of less than 1/30 (1, 2). In pure water, the gels underwent a thermal phase transition from the low-temperature swollen phase to the high-temperature shrunken phase at ~33°C. In the synthesis, the monomers were dissolved in methylsulfoxide along with cross-linker, *N,N'*-methylenebisacrylamide (BIS). Free-radical polymerization was initiated with azobisisobutyronitrile. The chemical structures of the monomers are shown in Fig. 1.

The release of a captured pyranine molecule requires replacement with another negative ion. We chose chloride ions for this role. Sodium chloride at a concentration of 100 mM was used so that pyranine and chloride ions could rapidly replace each other upon swelling and shrinking; that is, their affinities for the gels were comparable at this concentration. The gels showed a discontinuous volume change in water, but the transition became continuous when the salt was

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<sup>1</sup> **Synthesis of Fluoropolymers in Supercritical Carbon Dioxide**

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