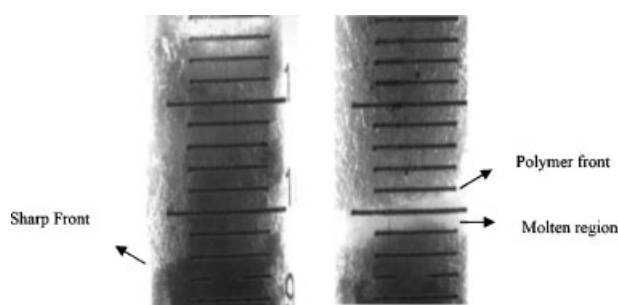


Water-Triggered Frontal Polymerization^a

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A totally new mode of frontal polymerization (FP) of acrylamide is established which is triggered by the simple addition of a minute, specific volume of water. Experimental conditions under which this mode of polymerization yields linear and water-soluble polyacrylamide were carefully established, paving the way to synthesize commercially pertinent homo- and copolymers. A new redox couple was identified to circumvent the imidization and the ensuing gelation, hitherto associated with FP of acrylamide. Effects of reaction variables such as type and concentration of redox couple and volume of water on measurable parameters of FP such as front velocity, front temperature, shape of front and yield have been studied. Two types of redox couples are reported. Nonplanar frontal regime was observed in few redox couples. We could visually observe helical patterns with naked eyes, while layered patterns were observable under SEM. Additionally, micro-phase separation and heterogeneity in the polymer matrix was observed due to unreacted pockets of monomer which evolve via bulk mode. This nonlinear phenomenon is described.



Introduction

Free radical frontal polymerization (FP) propagates through a sustained reaction at the interface.^[1] This highly

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exothermic reaction generates considerable heat for the reaction to continue within a narrow reaction zone. The heat transport via thermal diffusion to neighboring unreacted regions initiates further reaction and causes the interface to further propagate. These observations were first noted by Chechilo and Enikolopyan.^[2] Pojman et al.^[1,3,4] have since extensively examined the phenomenon. In recent years, three classes of FP such as: thermal FP,^[5] isothermal FP^[1,6] and UV initiated (photo) FP^[7,8] have emerged.

Redox reactions are well documented.^[9,10] Activation energies of redox polymerization reactions are typically $15 \text{ kcal} \cdot \text{mol}^{-1}$. These are usually highly selective to form specific primary radical species.^[10] Redox polymerization has not been explored in FP exhaustively. Pojman et al. demonstrated polymerization of methacrylic acid using dimethyl aniline as activator.^[3a] The same authors, for

^a Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mrc-journal.de>, or from the author.

acrylamide polymerization, reported oxidizers and/or redox couples such as ceric ammonium nitrate, ceric ammonium sulfate, bromate/malonic acid, lead dioxide, and lithium nitrate.^[3b]

In this note, we introduce redox FP of acrylamide triggered at ambient temperature and pressure by traces of water. The present work is the first report of FP using potassium peroxydisulfate in combination with a number of activators (reducing agents). Imidization is a problem in FP of acrylamide. Fortenberry and Pojman have tried to solve this problem by adding fillers (barium carbonate) to the reaction mixture.^[11] We have come up with a new method for the prevention of imidization, to yield commercially pertinent soluble, linear polyacrylamide.

Exotic patterns formed in FP can be investigated as nonlinear phenomena. Several workers have reported spin modes and pattern formation in FP.^[12–14] In our experimental systems, two types of patterns were observed: (i) clearly visible helical pattern along axial direction, and (ii) the layered pattern, observed predominantly along radial direction under scanning electron microscope (SEM). Helical patterns are formed due to nonplanar front propagation (spin modes). Experimental evidence and a number of rigorous mathematical analyses of causes and occurrences of helical patterns and factors affecting them have been well recorded in the literature.^[15] Volpert and Spade especially have explained the stability of steady state reaction front propagation. They also discuss the bifurcations of stable and unstable solutions, which can occur if interface dynamics is analyzed to determine the stability of steady state spatial propagation.^[15a,15e] On the other hand, layered pattern formation in FP has not been explored. In reaction diffusion systems, Winfree^[16] explained the spiral pattern formation as self-organization phenomena. Inamdar et al.^[17] extended this approach to FP and developed a theory of pattern formation. This was validated using FP of 2-hydroxyethyl methacrylate as the model reaction. The observations also revealed the formation of complex patterns, micro-phase separation and formation of porous networks under specific conditions. Clearly, variations in reaction chemistry, that is, rate and transport parameters give rise to differing modes of spatio-temporal spin motion.

Experimental Part

Potassium peroxydisulfate (recrystallized in methanol) and reducing agent (Fluka) were powdered, and intimately mixed with acrylamide (recrystallized in methanol and dried) and loaded in thick-walled test tubes ($12 \times 145 \text{ mm}^2$) marked in 1 mm units. Polymerization was triggered by the addition of deionized water

(25–500 μL per 11.5 g reaction mixture) at room temperature ($31 \pm 1^\circ\text{C}$). After a specific induction period (IP), dictated by concentration of the redox pair and volume of water, a descending front of solid polymer formation was observable. The formation and propagation of fronts in these experiments were video-recorded (Red Lake Imaging; Motionpro model, 50–400 frames $\cdot \text{s}^{-1}$). The front velocity (rate of propagation, $\text{cm} \cdot \text{min}^{-1}$) and temperature profiles were measured. Effects of activator and oxidant concentration, diameter of the tube, and volume of water on parameters of FP such as shape of the front, front velocity, temperature profile, yield were investigated.

Polyacrylamide was formed either in imidized or in unimidized state depending upon the reaction condition (see latter). Imidized polyacrylamide gel was freed from unreacted acrylamide by repetitive extraction with acetone while unimidized polyacrylamide was purified by repetitive dissolution in water and precipitation in methanol. Percentage yield in different experiments was estimated after vacuum drying to constant mass at 45°C . Polymers were characterized by elemental analysis, GPC, SEM, and optical microscopy.

Results and Discussion

The well-established classical sequential initiation, propagation, and termination processes are all violated in FP due to fast reaction rates and high reaction temperature. Additionally, quite unlike in conventional free-radical FP, the present methodology is seen to have an IP prior to the onset of polymerization. When a trace, measured quantity of water was added (25–300 μL) from the top of the reactor, temperature dropped down marginally (by $\approx 0.5^\circ\text{C}$) and is followed by IP when the temperature was constant. Once radicals are formed (initiation), the temperature increases quite rapidly, and within 30–60 s reaches in excess of 150°C , triggering a front (propagation) by heat diffusion. The polymerization has thus two clearly discernible regions: first is IP and initiation and second is, propagation of front. The FP experiments were conducted using oxyacids of sulfur (thiosulfate/bisulfite/dithionite) in conjunction with peroxydisulfate. These experiments were grouped together as Set I. In the other set of experiments, salts of formic acid (ammonium formate, potassium formate, and sodium formate) with peroxydisulfate redox couple was used and experiments were termed as Set II. Amongst the several pairs studied by us, we illustrate using the data observed for potassium peroxydisulfate:sodium dithionite (Set I) and potassium peroxydisulfate:ammonium formate (Set II) systems as model water triggered FP.

IP and Initiation

Aqueous peroxydisulfate solutions are known to be photosensitive and decompose into sulfate free radicals, in the

presence of actinic light.^[10] In our experiments, we could not trigger front formation when experiments were conducted in the dark. This indicates the need for actinic light in the initiation step. Overall, the initiation step was complex and consisted of a series of reactions. The well-accepted mechanism is that after the primary step, sulfate free radicals react with water to produce hydroxyl free radicals. These in turn rapidly decompose the oxidizing ions.^[10] This reaction is zero order with respect to reductant concentration and first order with respect to the oxidant concentration. The activation energy of the reaction is $15.5 \text{ kcal} \cdot \text{mol}^{-1}$.^[10a] The general mechanism is^[10b]



All three $\text{SO}_4^- \bullet$, $\text{S}_x \bullet \text{O}_y^{(n-1)-}$, and $\text{OH} \bullet$ radicals can initiate polymerization. But as reducing sulfoxy compounds or radicals derived from them are very good scavengers of $\text{OH} \bullet$ radicals, polymerization is mainly initiated by sulfate radicals rather than $\text{OH} \bullet$ or $\text{S}_x \bullet \text{O}_y^{(n-1)-}$ radicals.^[10b] For acrylamide polymerization, Riggs and Rodriguez^[18] suggested that as the acrylamide is highly reactive towards the $\text{OH} \bullet$ radicals, initiation takes place with both sulfate and $\text{OH} \bullet$ radicals. In our reaction, traces of water are present at the top layer (μL). Therefore the $\text{OH} \bullet$ radical concentration is much lower than that of sulfate radicals.

Rate of solution polymerization of acrylamide (in tetrahydrofuran or carbon tetrachloride) has been shown to increase by the addition of water but no explanation has been offered.^[19] When top layer of the reaction mixture exposed to air is wetted by water, oxygen acts as cocatalyst and facilitates peroxydisulfate decomposition, which in turn triggers further redox initiation. After the IP, the exothermicity of redox initiated polymerization induces the front propagation. We confirmed the catalytic action of the reductant and water. In the absence of water, polymerization could not be initiated. Polymerization had a very long IP ($\approx 80 \text{ min}$) in the absence of reductant and could be triggered only at higher water volumes ($> 300 \mu\text{L}$). Similarly, along the expected lines, the induction time decreased with an increase in concentration of redox pair (see Supporting Information, Figure 1). IP was typically between 1 and 6 min, depending on the composition. IP was invariant beyond $500 \mu\text{L}$ of water but displayed an

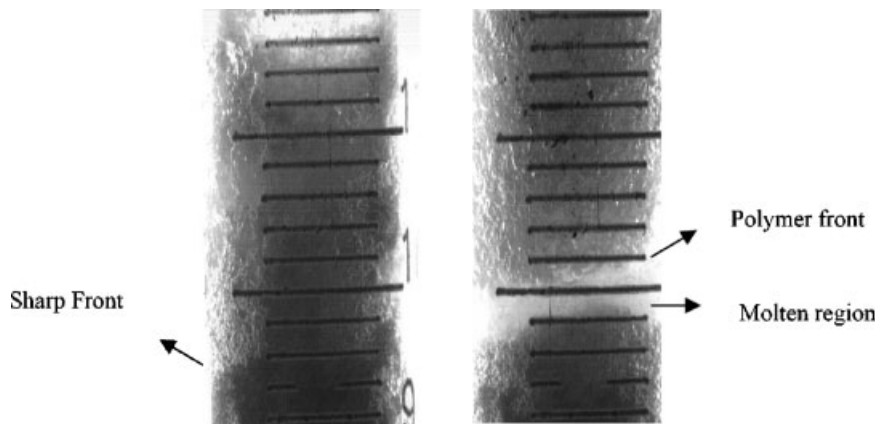


Figure 1. Snapshots showing the difference in nature of propagation of front between the two types of activators: left: potassium peroxydisulfate–sodium dithionite couple (200 μL water, 0.161 mol acrylamide; potassium peroxydisulfate and strong activator, sodium dithionite: 0.5 mol-% of acrylamide each) and right: potassium peroxydisulfate–ammonium formate couple (200 μL water, 0.161 mol acrylamide, 0.027 mol ammonium formate, 0.5 mol-% potassium peroxydisulfate).

oscillating behavior, in the volume range 25–300 μL . IP was least for 25 and 200 μL of water. This indicates that water acts only as an accelerator and that it evaporates/boils off during the reaction. If wetting generates the required critical radical concentration, a reaction is triggered. The mechanism of radical formation in FP is measurable only indirectly by investigating the effects due to added radical scavengers. Temperature did not rise beyond 45°C and propagation did not occur when reactions were carried in the presence of a radical scavenger (Tinuvin 770 from Ciba-Geigy).

With Set II redox system, the initiation step was a more complex one. Published literature is very scanty as well as contradictory. Ours is the first report of peroxydisulfate:ammonium formate as a redox pair. Shrivastava and Ghosh^[20] and Kapanna^[21] have investigated kinetics of the reaction between peroxydisulfate and formate ions. The activation energy was estimated to be $21.93 \text{ kcal} \cdot \text{mol}^{-1}$. The two papers express divergent views regarding the order of reaction with respect to formate ion. The peroxydisulfate decomposition is dependent on pH since:



Here, we may conjecture that, after actinic light triggers the production of $\text{SO}_4^- \bullet$ radicals, reaction is further catalyzed by the presence of H^+ ions derived from ammonium formate. Further, oxygen from the atmosphere and from the decomposition of peroxydisulfate under such conditions^[10a] accelerates the reaction by considerably increasing the generation of reactive radical species, thereby decreasing IP. Here also oxygen acts a cocatalyst, thereby reducing rather than increasing the IP.^[10c] IP varied in Set II

from 6 to 22 min, depending on ammonium formate concentration (see Supporting Information, Figure 2). IP showed a minimum with respect to ammonium formate concentration. At high and at very low concentrations, ammonium formate was seen to inhibit polymerization (see later). The reaction could not be triggered at lower concentration of ammonium formate. The threshold concentration for initiation of FP was established as 0.16:1 mol/mol with acrylamide. Other reducing agents (potassium and sodium formate) in this set had IP in the range of 30–40 min. These data also support the hydrogen transfer mechanism of ammonium formate, which is the basis for the higher catalytic efficiency of the same.



b)

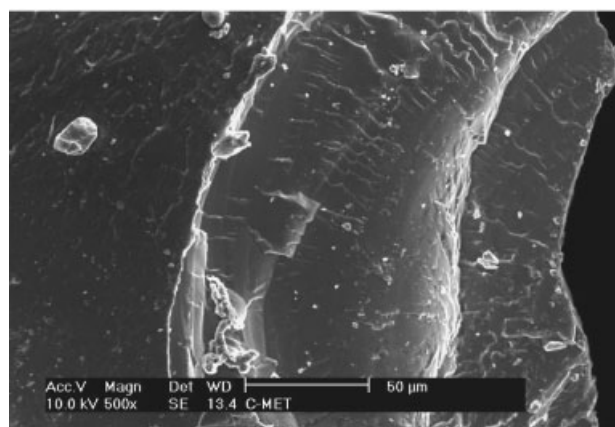


Figure 2. Surface morphology of typical polyacrylamide formed in Set I system (potassium peroxydisulfate:sodium dithionite, 8×10^{-4} mol each; reaction triggered by 100 μ L of water). (a) Snapshot showing helical pattern on the polyacrylamide surface (dimensions: 12×50 mm²). (b) SEM micrograph of the polymer showing layered pattern.

Front Propagation

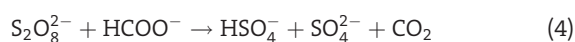
Thermal decomposition of peroxydisulfate is predominant at the front temperature. The rapid propagating reaction zone is followed by an ignition delay (due to heterogeneity of the reaction mixture) during the preheating of the neighboring layer. The heat is transported by conduction through gaseous and solid phases, convection through the gas phase and by radiation heat transfer. Varma et al.^[22] showed that wave propagation in heterogeneous media such as combustion depends upon *local* heat transfer and kinetics. In FP, the heat wave structure is described by constant propagation of wavepoints (in steady state). If the particles are big and packing density is lower, water penetrates unevenly and the structure of the heat wave may get disturbed. Here, the polymerization heat wave is dependent on the activator (reductant) type. While the Set I system produced a sharp front, with liberation of ammonia (litmus test), Set II redox systems produced a molten monomer region followed by a polymer solidification front (Figure 1).

In Set II, the front temperature recorded was around 180 °C. Ammonium formate decomposes at this temperature to give ammonia. Polymer front propagated in the form of small bubbles. These bubbles are gases released due to higher concentration of ammonium formate. The released gases are water vapor, ammonia, carbon dioxide and the vaporized monomer. As the concentration of ammonium formate is higher than that of the oxidant, the heat is partially utilized to decompose ammonium formate. As shown later, ammonium formate has a retarding effect and acrylamide melts at this temperature. The reaction rate therefore reduces and the front propagates in the form of a molten layer followed by a polymerization solidification front. The width of the propagating molten monomer region was ≈ 1 mm. This molten region penetrates into the crystalline monomer. The penetration occurs either by gravitation or surface tension energy of the crystallization monomer. It is determined by the heat transfer of the media and the penetration intensity of the melted monomer into free volume occupied by air vials.^[14e] Due to the very low activation energy required for initiation, concentration of free radicals is high in the Set I system. Polymerization is, therefore very rapid and polymerization advances as a sharp front even before acrylamide can melt.

In FP, front velocity and temperature are dictated by the initiator and subsequently by the concentration of free radicals.^[1] In the present case, it is dependent on concentrations of the oxidant and activator. A uniform velocity was observed after the IP (see Supporting Information; Figure 1 and 2). In both sets, front velocity was in the range $0.76\text{--}2$ cm \cdot min⁻¹, dependent only on concentration of the redox couple. Front propagation was faster in Set I. In Set II,

front velocity decreased exponentially with increase in ammonium formate concentration. Other formates in Set II showed a similar behavior, but the velocity was marginally higher.

Temperature profiles were sharp in both sets but differences were noted in maximum front temperatures (see Supporting Information, Figure 3). With Set I system, it was in the range 220–250 °C, while in Set II, it was in the range 150–180 °C. This temperature difference of 50–70 °C leads to interchain imidization in Set I polymers. In Set I, two radicals are produced per molecule of peroxydisulfate. The energy of activation is low and rate constants are high. For this reason, the reaction has higher front velocity and temperature. This lowers the selectivity and increases side reactions such as chain transfer and imidization. In Set II, ammonia has a catalytic effect while formate ion has an inhibitory effect.^[20]



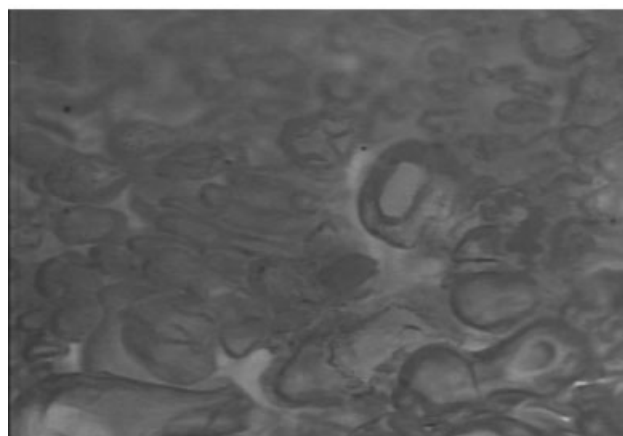
One of the products in reaction 4, either SO_4^{2-} or HSO_4^- , is also known to inhibit the reaction to the same extent as the parent formate ion.^[21] Thus, radical concentration in ammonium formate system is much lower than that in dithionite system. Moreover, ammonium formate was used in excess and thus acts as reacting diluent, adding further to the high retarding effect. All these factors suppress the concentration of reactive centers; depress the front temperature thereby effectively preventing imidization. We reconfirmed it by conducting the following experiment: We packed a mixture comprising of acrylamide, potassium peroxydisulfate and ammonium formate atop a (2 cm) column of acrylamide and potassium peroxydisulfate. We successfully triggered polymerization with water. Polymer formed in the top 2–3 cm of the reactor was water soluble while the polymer formed below was water insoluble (due to imidization).

Product

In all polymerizations of Set I, polymer rods were significantly yellowed in the center indicating imidization. It also had an outer white skin that was formed by the evolving monomer vapors escaping the walls of the reactor and getting polymerized there. In a few reactions, the central core was nearly charred due to very high temperature there. The extent of imidization was found to be 6–8%, confirming that reported by Pojman et al.^[11] Elemental analysis showed the presence of traces of sulfur indicating that termination is through disproportionation.^[18]

Polymer yields were $75 \pm 5\%$ and $85 \pm 5\%$ in Set I and Set II, respectively. Molar mass of polyacrylamide formed using ammonium formate:potassium peroxydisulfate sys-

a)



b)

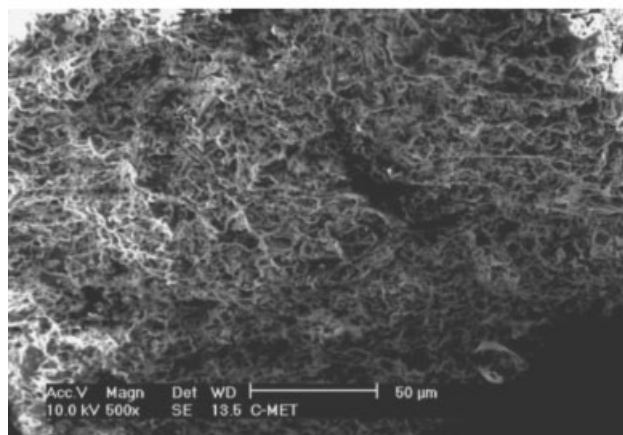


Figure 3. (a) Micro-phase separation observed under optical microscopy (Olympus BX 500 image analyzer, resolution $40\times$; dimension 1 mm) (potassium peroxydisulfate:sodium thiosulphate, 8×10^{-4} mol each, reaction triggered by 500 μL of water in a loosely packed reaction mixture); (b) representative SEM photograph of imidized polyacrylamide showing the formation of porous structure (potassium peroxydisulfate:sodium thiosulphate, 8×10^{-4} mol each, reaction triggered by 200 μL water).

tem was estimated by GPC (polyacrylamide standards) to be $\bar{M}_w 1.25 \pm 0.03 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$ with PDI 3 ± 0.5 . At all compositions, molar mass was relatively independent of the experimental parameters. A rise in the rate of active center formation and chain propagation increases the overall rate of conversion of the monomer to polymer. Contrary to this, an increase in the rate of termination retards this process, shortens the kinetic chain length and decreases the molecular weight of the polymer. Oxygen is known to play a dual role as catalyst and inhibitor.^[10b,10c] After initiation, oxygen acts as an inhibitor. Additionally, there is a “burning out” effect of radicals at high temperature.^[1,5] The lower conversions and molar masses observed are therefore along expected lines.

Dynamics

As seen previously, in Set II, the propagating homogeneous molten layer was followed by a polymerization front. Furthermore, the front propagated with small bubbles, which do not allow the generation of spin modes as it reduces heat conduction in the propagating layer. No visible instabilities were observed in set II polymers. In Set I polymers helical (seen by naked eyes) and layered (observed under SEM) patterns were noted and in a few reactions weak and complex patterns, micro-phase separation and porosity were also observed.

Uniform helical pattern formation indicates the presence of spin modes [Figure 2(a)]. The observed helical patterns along axial direction and layered pattern along radial direction (but slightly inclined to axis of motion) [Figure 2(b)] are due to nonplanar front propagation (spin modes). Patterns indicate loss of steadiness during polymerization by spatial and temporal periodic modes, due to competition between heat generated in the reaction zone and its diffusion to the cold reactants.^[15d] The formation of helical and layered patterns (spin mode) are explained as follows: the locus of points, from which spirals tilted at a small angle emanate around the core of spiral, follows a helical path. The pitch along radial direction, as seen from a SEM photograph between two helical turns, is about 40 microns and the vertical distance between two layers is about 5 microns. These spirals propagate until they reach the tube wall, while the decoupled motion of helical front, from which these spirals originate, descends towards the bottom of tube. The thermal balance, including exothermicity of reaction, is satisfied at tip of helix, the origin of spirals (or spin waves). The motion of the tip of helix, descending downwards, follows a helical path and together with the planar spiral propagation gives rise to a layered or winding staircase pattern. We are presently using this fundamental notion/model in mathematical analysis of pattern formation.

With increase in reactor diameter, the number of hot spots increases and front wave motion becomes more complex.^[14d] This was observed in our methodology. With an increase in reactor diameter and/or loose packing, additional features such as weak, complex patterns (not shown) and micro-phase separation [Figure 3(a)] were seen which resulted in a porous and heterogeneous polymer matrix. This effect was extensive with excess of water ($\geq 500 \mu\text{L}$). When the irregularity in packed solid increases water penetrates unevenly through the crevices at the beginning and heat is easily transferred to neighboring solid layers due to conduction. The simultaneous generation of radicals at adjacent layers leads to discontinuities in spatio-temporal motion, introducing irregularities in the pattern formation. This results in unreacted micro-cavities (monomer pockets), and the ensuing micro-phase separa-

tion may evolve via a partial bulk polymerization mode.^[23] Gases released tend to escape upward creating irregular pathways and further contribute to porosity in the polymer formed. The SEM photograph [Figure 3(b)] shows the formation of an interconnected porous structure in Set I polymer. Interestingly, this porosity is developed in the matrix without the use of a multi-vinyl crosslinker. The swelling ratio in water was estimated as $5.62 \text{ g} \cdot \text{g}^{-1}$ polymer. These polymers have potential in applications like hydrogels.

We could also trigger copolymerization of acrylamide and *N,N*-methylenebisacrylamide using ceric ammonium nitrate (reductant) and water. Water triggered FP is a unique simple way to synthesize polymers from solid monomers. This method gives an opportunity to study instabilities and to find ways to obviate them.

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