

## IN FOCUS

**A rare superabsorbent hydrogel having excellent dimensional stability due to physically-interlocked nanogels**

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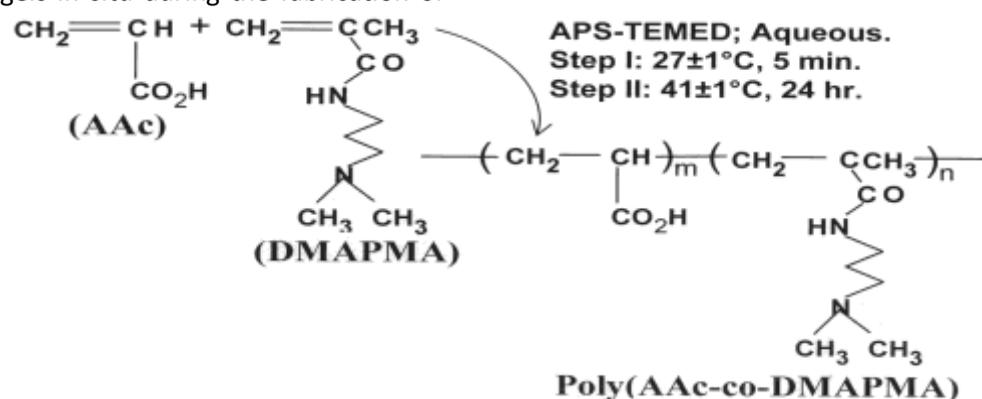
**H**ydrogels are three-dimensional networks of hydrophilic polymers.

The hydrophilicity and network structure allows imbibing and retaining large amount of water and biological fluids but prevents the dissolution of polymer chains/segments. Since the pioneering work of Wichterle and Lim in 1960 on crosslinked poly(2-hydroxyethyl methacrylate) [1], hydrogels have received significant attention in diversified fields due to their promising applications, such as drug delivery [2], bioseparations [3], immobilization of enzymes and cells [4], biosensors [5], and making artificial muscles [6].

The network structure in most of the stable hydrogels has been fabricated by using chemical crosslinkers. However, major concerns with chemically crosslinked gels include the difficulty in their processing and low biocompatibility [7].

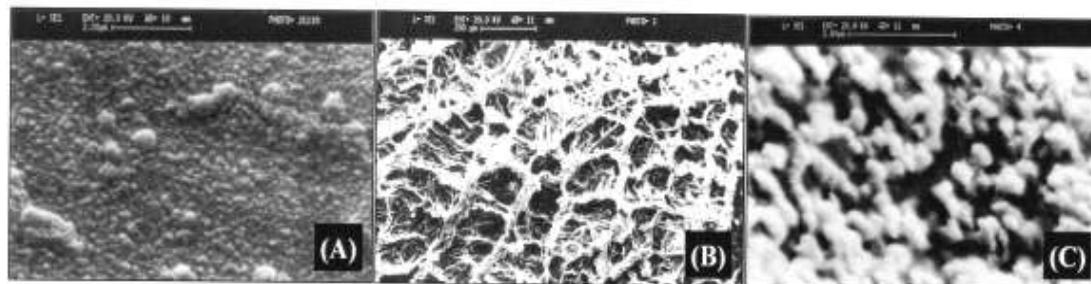
We have introduced a new concept in designing stable hydrogel without using any chemical crosslinker [8]. Anionic monomer acrylic acid (AAc) was copolymerized with cationic monomer N-[3-(Dimethylamino)propyl]-meth-

acrylamide (DMAPMA) in aqueous medium (Scheme 1). Proper adjustment of temperature and monomer-water ratio led to the formation of interlocked nanogels in situ during the fabrication of



**Scheme 1** Synthesis of poly(AAc-co-DMAPMA) hydrogel (PADMA)

monolithic poly(AAc-co-DMAPMA) gel (PADMA). A series of PADMA gels, having different monomer feed compositions, have been fabricated at 41±1°C in



**Figure 1** SEM micrographs of the surface of PADMA90: (A) before swelling; (B) after swelling in simulated body fluid (at low magnification); (C) after swelling in simulated body fluid (at high magnification).

thermostat, which rules out the involvement of thermal crosslinking behind the formation of stable crosslinked structure. Again, coulombic attraction and hydrogen bonding between AAc and DMAPMA units, as were identified through FTIR spectroscopy, could not explain the stability of PADMA gels in simulated body fluid (pH 7.4) and urea solution (H-bond breaker) respectively. The interlocked nanogels act as the stable building blocks, remain intact even when the gels imbibe simulated body fluid, as high as 30 times of its dry weight, and, thus, make the PADMA gels unique of its kind (Fig. 1).

## References:

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## Ionic liquids as property modifiers of surfactant solutions

CHEMCOS News Bureau

Room temperature ionic liquids are being studied extensively due to their interesting properties like existence of ion pairs and assumption of liquid state under ambient conditions. Ionic liquids are also known to alter the properties of aqueous surfactant solutions. Studies of aqueous solutions are particularly desirable because of the ease of handling solutions and their wide applicability in ambient systems. In a recent communication, a concentration dependant effect of ionic liquids on the surface properties of

Sodium dodecylsulphate, a common anionic surfactant, has been established.

The ionic liquid used is 1-Butyl-3-methylimidazolium tetrafluoroborate - bmim[BF<sub>4</sub>]. The critical micelle concentration (CMC) of SDS solution decreases when bmim[BF<sub>4</sub>] is dissolved upto a concentration of 2 wt. %. An increase in aggregation number and micellar size is also observed. The extent of decrease in CMC is comparable to that in the case of a solution of Magnesium ions. However, further increase in the concentration of bmim[BF<sub>4</sub>] to 30 wt. % results in a reversal of the above trends. The trend at lower concentration is attributed to shielding of repulsions between the anionic head groups of SDS by the bmim<sup>+</sup> groups. At higher concentrations, however, restricted dissociation of bmim[BF<sub>4</sub>] confers a co-solvent like behaviour, reducing hydrophobicity and favouring micelle formation.

The fluorescence behaviour of pyrene, a nonpolar fluorescence probe, depends on the polarity of its immediate environment. This property is utilized to study the interactions between SDS micelles and bmim[BF<sub>4</sub>] by determining the critical micelle concentration, aggregation number, etc. Another interesting probe, Pyrene-1-carboxaldehyde, utilizes the modification in its energy level diagram with solvent polarity. Changes in quantum efficiency and shifts in  $\lambda_{max}$  values are interpreted so as to understand the phase transformations occurring in the system.

## Reference:

Concentration-Dependent Dual Behavior of Hydrophilic Ionic Liquid in Changing Properties of Aqueous Sodium Dodecyl Sulfate *J. Phys. Chem. B* **2007**, *111*, 13307-13315.

Ushati Das outlines the properties of room temperature ionic liquids and recent studies on the same in her article.

## Self-healing rubber

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A unique form of rubber with self-healing properties has been reported [1] by a team of researchers in Paris. The design is based on small molecules that can form supramolecular networks. The synthesis of the new rubber species involves functionalizing carboxylic acid groups of fatty acid dimers with groups that can form multiple hydrogen bonds, for e.g. di (amidoethyl) urea and diamido tetraethyl urea. The fascinating aspect of this rubber is its self-healing property. When a rubber piece is cut or broken into smaller ones and the pieces are brought together for some time at room temperature, they can self-heal without any external heating or even kneading. The healed scars are not visible and the cycle of stretching, breaking and healing can be repeated several times.

This self-healing property is attributed to strong supramolecular associations between N-H and C=O groups on the surfaces of the broken pieces. The intensity of characteristic bands corresponding to free N—H bending motion decreases and that of bound N—H bending motion increases with time during healing process. This suggests that the mechanism of healing involves H-bond re-association. On the other hand, when the rubber piece is not mended immediately after it is broken, the number of non-associated groups decreases as some of the free groups find partners within the same broken piece

thereby reducing the extent of healing. The broken pieces have been found to heal after as long as one week, when maintained at 23°C. However, as the temperature at which the broken pieces are maintained is increased, there is a decrease in the waiting time. At 120°C the pieces have to be brought together within five minutes of breaking otherwise a freshly cut piece does not adhere to a non-broken sample indicating the strong affinity of surface groups to link within themselves.

Although detailed investigations are required to improve the extent of deformation under continued stress, it seems that soon it would be possible to link broken rubber articles by simply bringing them together!

**Reference:**

1. Nature, Vol 451, 21 February 2008, 977 – 980