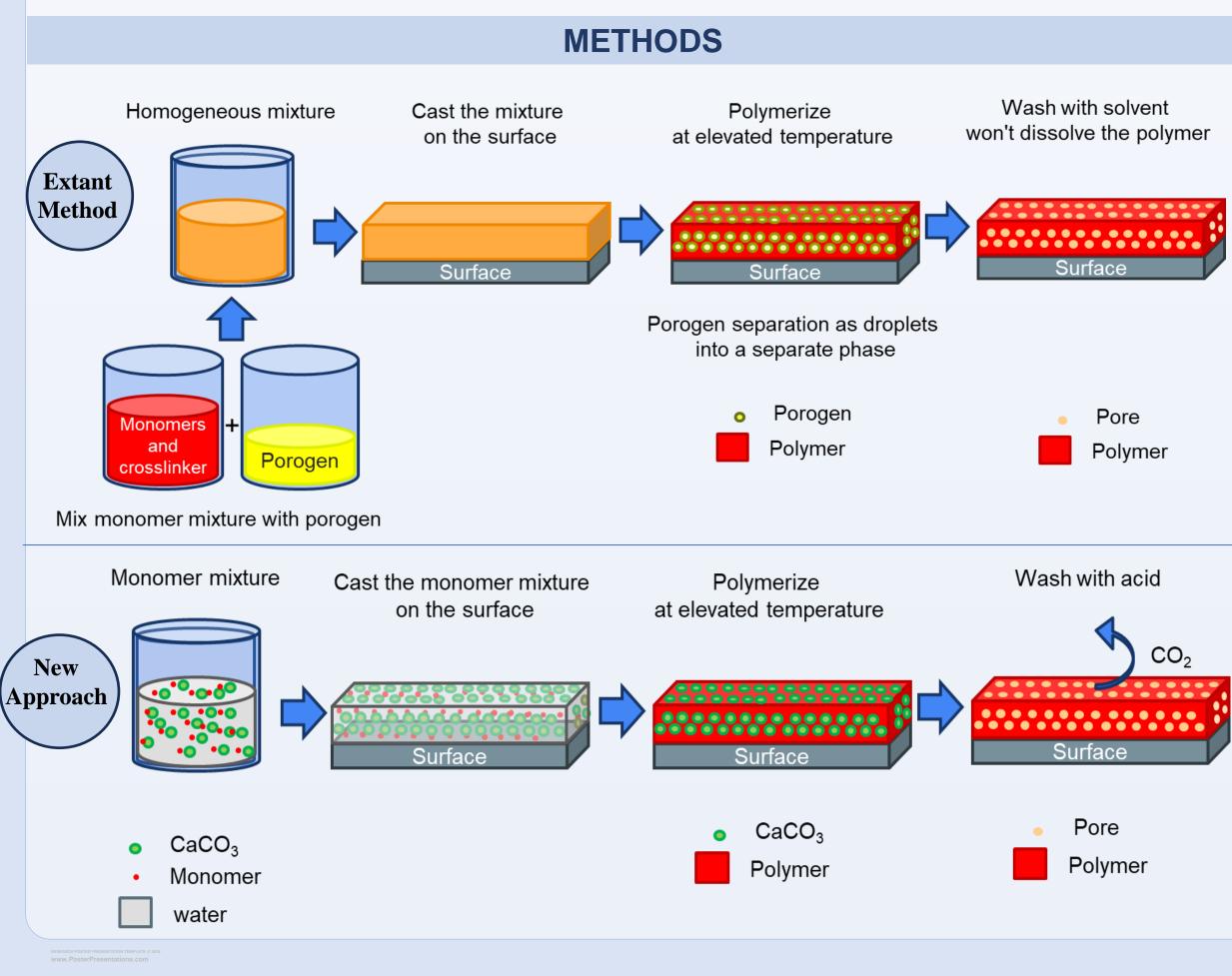


## **Creating Porous Polymers through Reactive Dissolution and Gas Evolution**

## Katy A. Arias, Enas N. Yousef and Purnendu K. Dasgupta\*

## **ABSTRACT**

Polymers are an integral part of our lives. While fully solid polymers serve many purposes, porous structures are useful to reduce material cost. Proper cross-linking obviates any loss of structural strength. Porosity also increases surface area; this improves sorption capacity. Microporous polymers with micron or sub-micron size pores, as well as macroporous polymers (that interconnect small pores with larger channels), are of interest as separation media. Such polymers are typically made by incorporating some substance, often called a porogen, that can initially be present with the monomers in a homogeneous solution. As the polymer forms, the porogen separates as droplets into a separate phase and can be washed out with an appropriate solvent that does not dissolve the polymer. We describe here a novel approach where the porogen is a solid particle of micron or submicron size. After polymerization it is removed by reactive dissolution, leaving a void. Further, the dissolution step involves gas evolution, producing fractures as the gas escapes beyond leaving a void where the particle was. We show initial results from experiments where a hyberbranching polymerization system incorporates CaCO<sub>3</sub> microparticles. After the polymerization, the polymer is treated with dilute acid, which dissolves and removes the particles with simultaneous evolution of Carbon dioxide.



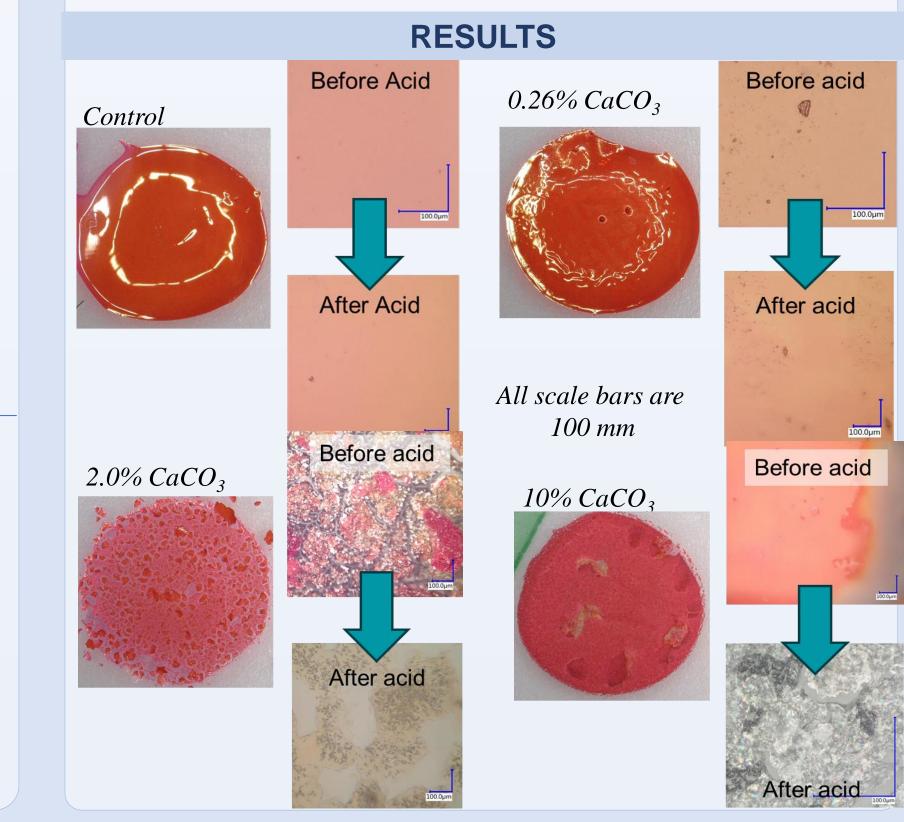
## **Department of Chemistry and Biochemistry. The University of Texas at Arlington, Arlington, TX 76019**

## **MATERIALS & INSTRUMENTS**

- VHX-5000 digital microscope was used to capture the polymer surface
- Calcium carbonate (CaCO<sub>3</sub>) with particle size ranges from  $12 68 \,\mu\text{m}$
- Methylamine (MA, 41% aq solution)
- 1,4-butanedioldiglycidyl ether (BDDE)
- Polystyrene petri dishes

### **EXPERIMENT**

- A mixture of 2.8 % MA and 7.2% BDDE in water was prepared
- CaCO<sub>3</sub> was added into the polymer mixture to prepare different w/v % suspensions (0.26%, 2%, 6%, and 10%)
- 50 µL of each mixture was placed on a sulfonated polystyrene dish and then placed in the oven at 80 °C overnight
- After the polymer set it was stained with eosin dye for 5 min, then washed with isopropanol
- Stained polymer washed with acetic acid for 1 min.



# $6\% CaCO_3$

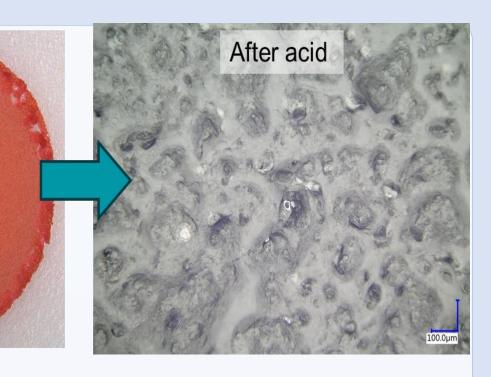
Before acid

The MA-BDDE polymer is a positively charged anion exchanger. It is stained pink by the anionic dye Eosin. In acid medium this takes on a yellowish hue. When the acid cannot easily access the polymer interior, just the intensity of the pink color may decrease. On prolonged exposure to acid and access to the polymer interior facilitated by pores, eosin bound to the polymer is washed off. Thus, both the morphology of the polymer and its apparent color after a short acid wash provides clues to the polymer structure. This method could be used to test ion concentrations in water samples, earth samples and even interplanetary soil exploration. Next, we will be using this method to make an anionic change in open tubular columns, which ion separation capacity depends on.

With increasing CaCO3 content of the in the prepolymer, both the porosity and the pore size of the polymer increases. The resolution of the present microscope is insufficient to reveal the pore structure at low CaCO<sub>3</sub> concentrations, but clearly shows the acid wash can remove the particles completely. We will be investigating in the future at Electron microscopic images of the polymer thus made with much smaller seed  $CaCO_3$  particles, which can be produced by grinding.

We gratefully acknowledge support from the National Science Foundation through CHE-2003324.

> Anal. Chem. 2007, 79, 14, 5462–5467: https://doi.org/10.1021/ac070690q



## DISCUSSION

## CONCLUSION

## **ACKNOWLEDGEMENTS**

## REFRENCES