pH-Responsive Copolymer Films

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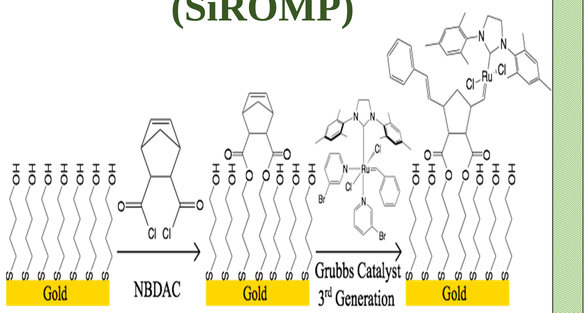
Abstract

pH-Responsive films are polymer films that react to changes in pH by accepting or donating protons, which changes the properties of the film. In this report, we have prepared pH-responsive ester and carboxylic acid copolymer films by SiROMP (Surface-initiated Ring Opening Metathesis Polymerization), coupled with a quick copolymer preparation step. We successfully prepared poly(norbornene diacyl chloride) (pNBDAC) films by vapor phase SiROMP. Due to the high reactivity of acyl chloride groups, we can easily modify the pNBDAC films with other functional groups. In the copolymer preparation step, pNBDAC films are immersed into an ethanol and water mixture to form the carboxylic acid and ester copolymer. The ratio of the ethanol-water mixture determines the composition of the copolymer film the reaction yields. Electrochemical Impedance Spectroscopy was used to characterize the film impedance at different pH values. The pH-responsive behavior of the copolymer film depends on its carboxylic acid and ester content.

Polymerization Method (SiROMP)

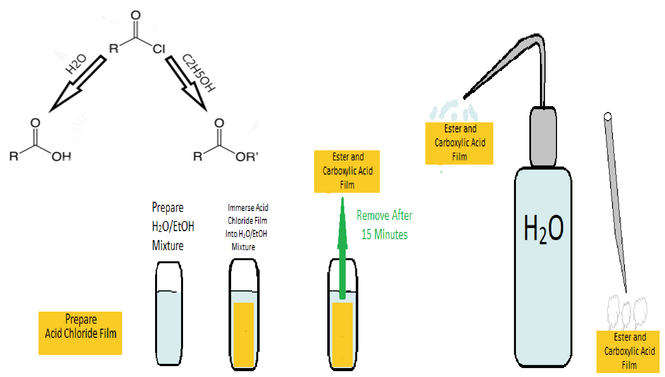


*From [1]Faulkner, Christopher J., et al.

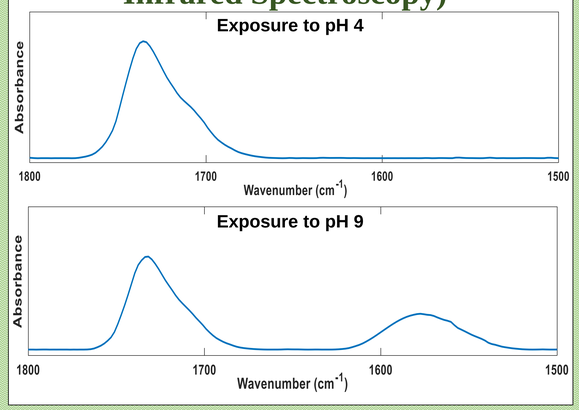
Benefits of SiROMP:

- Occurs quickly under mild conditions
- Offer control over film thickness.
- Allow the polymer to grow directly on many different substrates.
- SIP eliminates the need to deposit polymers "onto surfaces via spin-coating, dip-coating, solution-casting, or chemical adsorption"[2].

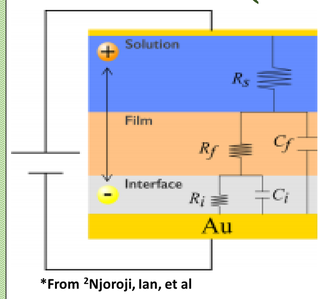
Copolymer Preparation Method



FTIR (Fourier-Transform Infrared Spectroscopy)



(EIS) Electrochemical Impedance Spectroscopy



*From [2]Njoroji, Ian, et al

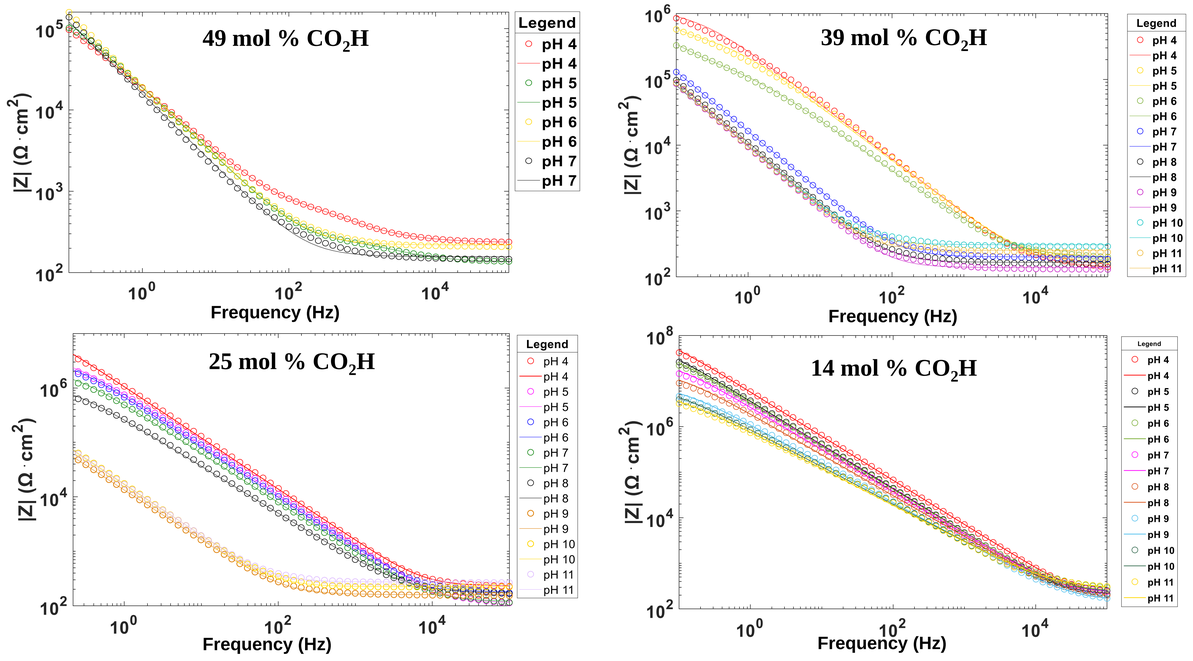
Electrochemical Cell

- Ag/AgCl *Reference Electrode*
- Au-coated Si *Counter Electrode*
- Au-Coated Si Substrate *Working Electrode*

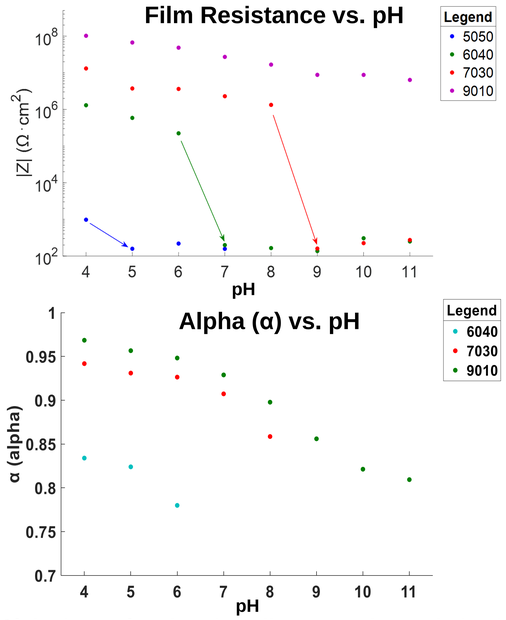
Model Fitting

- CPE (Constant Phase Element) used to fit Impedance Data
- $Z_{CPE} = [(j\omega)^{\alpha} Y_0]^{-1}$
- $C = Y_0(\omega'')^{\alpha-1}$
- ω'' = frequency (Hz) for which Z_{CPE} is a maximum

Results



pH Responsive Behavior



*Alpha is a value that describes capacitance behavior. A value of 1.0 represents a 'pure' capacitor.

Conclusion

We have successfully prepared pH-Responsive copolymer films by SiROMP with the ability to able to tune the carboxylic acid and ester concentration of the film by controlling the amount of water and ethanol we put into the copolymer preparation mixture.

The pH-responsive behavior of the copolymer film depends on its carboxylic acid and ester content

References

[1]Faulkner, Christopher J., et al. "Surface-Initiated Polymerization of 5-(Perfluoro-n-Alkyl)Norbornenes from Gold Substrates." *Macromolecules*, vol. 43, no. 3, 2010, pp. 1203–1209., doi:10.1021/ma902249m.
[2]Njoroge, Ian, et al. "Dynamic Anion-Adaptive Poly(Ionic Liquid) Films via Surface-Initiated Ring-Opening Metathesis Polymerization." *The Journal of Physical Chemistry C*, vol. 121, no. 37, 2017, pp. 20323–20334., doi:10.1021/acs.jpcc.7b05834.

Acknowledgment

VINSE NSF REU Grant Number: 1560414
DE-NE0008712