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Non-fluorinated/non-PEGylated amphiphilic block copolymers and their crosslinked films as potential anti-biofouling coatings

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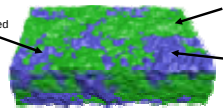
Polymer chemistry approach to anti-biofouling coatings

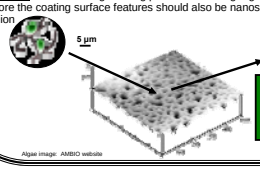
The role of a complex surface in fouling prevention

Several factors play a role in effective anti-biofouling surfaces:

- Film modulus
- Chemical composition
- Surface energy (contact angle)
- Longevity in marine environment
- Low/no environmental impact
- *Morphological and topographical complexities of the surface*



Hypothesis: The attaching/sensing proteins of fouling organisms function on the nanoscale, therefore the coating surface features should also be nanoscale in dimension to intercept/inhibit adhesion



Development of hyperbranched fluoropolymer-poly(ethylene glycol) polymer (HBFP-PEG) networks

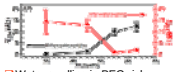
- Crosslinking step kinetically traps phase-separated amphiphilic domains on the nanoscale, forming complex surface features

Anti-fouling ability

- $HBFP^{(I)}$ has excellent anti-biofouling ability against *Ulva* sporelings

C. S. Gudipati, J. A. Finlay, J. A. Callow, M. E. Callow, K. L. Wooley *Langmuir* **2005**, *21*, 3044-3053.

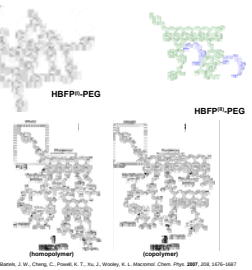
Unique mechanical properties



- Water swelling in PEG-rich domains rigidifies or softens these networks, depending upon the size of PEG-rich phases

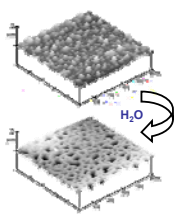
Xu, J.; Bohnsack, D. A.; Mackay, M. E.; Wooley, K. L., *J. Am. Chem. Soc.* **2007**, *129*, 506-507.
Xu, J., Bartels, J. W., Bohnsack, D. A., Mackay, M. E., and Wooley, K. L., *Adv. Funct. Mater.*, **2008**. (in press)

Different classes of HBFP-PEG



Bartels, J. W., Cheng, C., Powell, K. T., Xu, J., Wooley, K. L. *Macromol. Chem. Phys.* **2007**, *208*, 1676–1687

Water-responsive surface



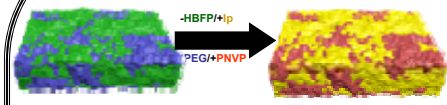
- The polymer network, when swollen with water, undergoes morphological rearrangement

Drawbacks to the HBFP-PEG system

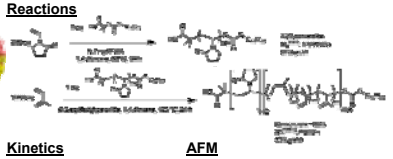
- Difficult/long synthesis for $HBFP^{(I)}$
- High cost of fluorinated monomers
- Oxidative degradation of PEG
- High VOC application

New generations of materials

A novel, non-PEGylated, non-fluorinated amphiphilic block copolymer: P(NVP-*b*-Ip)



Reactions



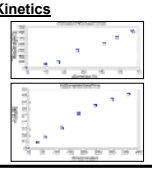
Parent polymer

- Poly(N-vinyl pyrrolidinone), or P(NVP), was prepared using *reversible addition fragmentation chain-transfer* (RAFT) controlled radical polymerization methods
- Polymerization proceeded in a living and controlled manner in both $\ln[M_0]/[M]$ *vs.* conversion and M_w *vs.* conversion

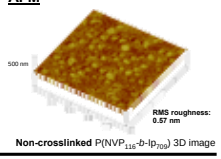
Chain extension

- Polymer was readily chain extended with isoprene (Ip), giving P(NVP-*b*-Ip)
- P(NVP-*b*-Ip) contains ~20% crosslinkable pendent alkene units
- Surface shows nanoscale phase segregated domains

Kinetics



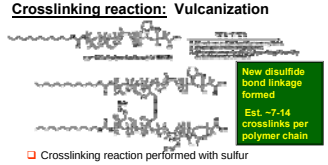
AFM



Non-crosslinked $P(NVP_{116}\text{-}b\text{-}Ip_{709})$ 3D image

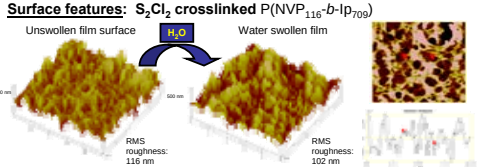
Crosslinked P(NVP-*b*-Ip): Surface properties

Crosslinking reaction: Vulcanization

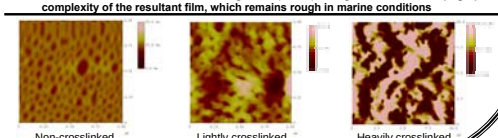


- Crosslinking reaction performed with sulfur monochloride (S_2Cl_2), a commonly used crosslinker in the rubber industry
- Mid-reaction, the films were cast onto microscope slides and allowed to dry, completing the reaction
- Resultant films have incredibly complex surface features
- Films swell in water, *and* retain rough character

Surface features: S_2Cl_2 crosslinked $P(NVP_{116}\text{-}b\text{-}Ip_{709})$



There is a *substantial increase* in roughness (~232x), along with increased topographical complexity of the resultant film, which remains rough in marine conditions

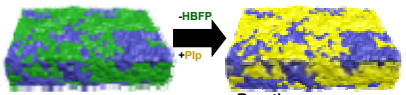


Effect of chain length: $PNVP_{116}\text{-}b\text{-}PIp_{xx}$

Bartels, J. W., Wooley, K. L. *Manuscript in prep.* **2008**

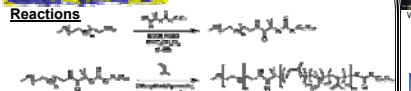
Non-fluorinated materials

Poly(ethylene oxide)-*b*-Poly(isoprene) networks



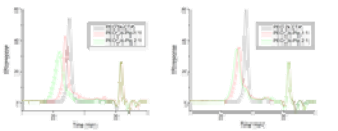
- Study composition changes in complex amphiphilic block copolymers and their effects on anti-fouling ability
- Major compositional change from HBFP-PEG materials:
  - Remove the HBFP component and replace with a non-fluorinated, high surface energy, crosslinkable, readily available monomer – isoprene
  - Use chemical crosslinking (S_2Cl_2) or photo crosslinking methods (UV initiated thiol-ene coupling) instead of substitution reactions or S_N2 reactions

Reactions

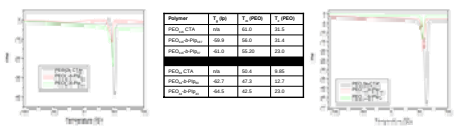


Surprising result: Resultant polymers are soluble in *every* solvent (except for water), including ether and hexanes!

PEO-*b*-PIp GPC



PEO-*b*-PIp Thermal Data

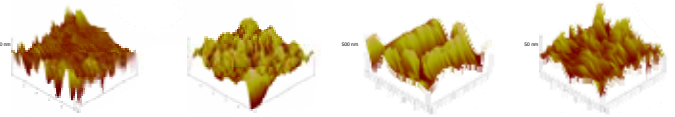


Polymer	T_g (lit)	T_g (PEO)	T_m (PEO)
PEO_{5k}-CTA	n/a	61.0	20.1
PEO_{5k}-*b*-PIp_{2k}	-58.9	58.0	19.4
PEO_{5k}-*b*-PIp_{5k}	-61.0	55.20	19.8
PEO_{2k}-CTA	n/a	60.4	8.85
PEO_{2k}-*b*-PIp_{2k}	-62.7	47.3	12.7
PEO_{2k}-*b*-PIp_{4k}	-64.5	42.5	23.0

- GPC shows successful chain extension (>90% efficiency) and reasonable PDI (~1.3)
- DSC data shows thermal transitions for respective blocks and influence on T_g/T_m

Complex surfaces: PEO-*b*-PIp

AFM



PEO_{5k}-*b*-PIp 2:1 | PEO_{5k}-*b*-PIp 1:1 | PEO_{2k}-*b*-PIp 2:1* | PEO_{2k}-*b*-PIp 1:1

*Note scale

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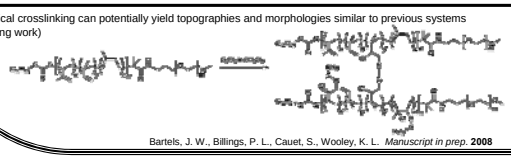
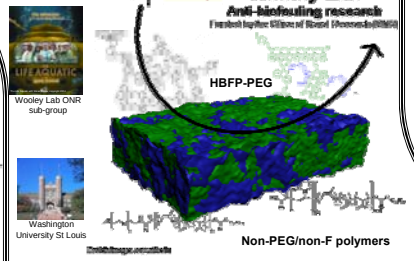
icular note is PEO_{2k}-*b*-PIp oss section below)

- Chemical crosslinking can potentially yield topographies and morphologies similar to previous systems (ongoing work)



Bartels, J. W., Billings, P. L., Cauet, S., Wooley, K. L. *Manuscript in prep.* **2008**



Wooley Lab ONR sub-group

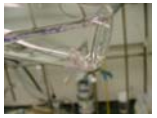
Washington University St Louis

Ongoing work

Future directions for non-Fluoro/non-PEG systems

Different solubility characteristics in H_2O:

A platform for low VOC application and crosslinking



- Longer polyisoprene block lengths are not soluble/dispersible in H_2O ($P(NVP_{116}\text{-}b\text{-}Ip_{68})$)

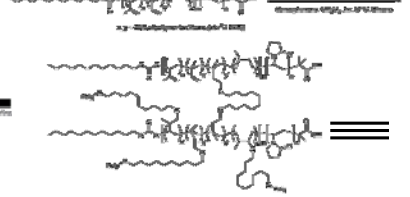
- Lower polyisoprene block lengths are readily dispersed in water ($P(NVP_{116}\text{-}b\text{-}Ip_{25})$)

Low VOC application

- Block copolymers with smaller isoprene chains can be water-dispersed and crosslinked

- Further development of crosslinking chemistry and methods are ongoing

Alternative crosslinking strategies: Thiol-ene reaction



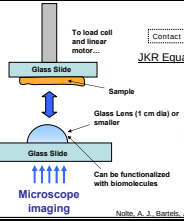
- Polyisoprene backbone can be crosslinked using thiol-ene chemistry (benzophenone family photoinitiator) in both systems

Control experiment (no thiol or benzophenone) after 6 hr UV exposure yields no reaction

Crosslinked thiol-ene organogel product (swollen with CH_2Cl_2)

Johnson, Kendall, and Roberts (JKR) adhesion tests (collaboration w/ NIST)

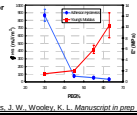
- Adhesion test can determine materials properties such as Young's modulus, as well as adhesion hysteresis
- Glass tester can be silane-functionalized with biomolecules, which could potentially mimic living organism attachment



JKR Equation:

$$a^3 = \frac{3R}{4E}\left(P + 3\pi G R + \sqrt{6\pi G R P + (3\pi G R)^2}\right)$$

Contact radius, Lens radius, Reduced modulus, force, Energy release rate



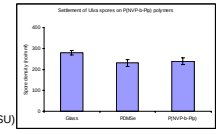
Sample	E^* (MPa)	GHYS (mJ/m²)
HBFP(I)-PEG30	1.5 ± 0.2	870 ± 80
HBFP(I)-PEG45	2.1 ± 0.2	74 ± 3
HBFP(I)-PEG55	5.9 ± 0.7	53 ± 10
HBFP(I)-PEG63	10 ± 2	34 ± 8

Tests are also being conducted on non-PEG/non-Fluoro materials, as well as nanocomposited HBFP-PEG materials

Nolte, A. J., Bartels, J. W., Wooley, K. L., *Manuscript in prep*

Anti-fouling assays

- Submit samples for anti-biofouling assays, including:
  - Algae (Callows lab in Birmingham)
  - Barnacles (Wendt lab at Cal Poly)
  - Tube worms (Hadfield lab at Hawaii)
  - High throughput in-lab testing (Webster lab at NDSU)
- Issues with macroscale surface roughness need to be overcome to provide accurate anti-fouling data



The settlement of *Ulva* spores on P(NVP-*b*-PIp) crosslinked polymers

Each point is the mean from 90 counts on 3 replicate slides. Bars show 95% confidence limits.

The authors wish to acknowledge Ke Zhang for the computer generated images

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