Stimuli Responsive Nanolatexes and Latex Films

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Reactive Ionic Liquid Surfactants

Such reactive monomers found to produce interesting new copolymers:

Ultrastable nanolatexes
Reversibly porating membranes
Ionic liquid polyelectrolytes
Di-stimuli responsive diblocks
Surfactant Ionic Liquids (ILs)

\[
\begin{align*}
\text{Br}^- & \quad \text{BF}_4^- & \quad \text{PF}_6^- \\
\end{align*}
\]
Microporous Materials From Polymerized Microemulsion Gels

Photographs of polymer gels: (A) after microemulsion polymerization; (B) gel in (A) treated with 0.1M KPF$_6$ solution; (C) gel in (B) treated with 0.1M NaBr solution.
Microporous Materials From Polymerized Microemulsion Gels

SEM images of polymer gels (A) after microemulsion polymerization. (B) gel in (A) treated with aqueous 0.1M KPF$_6$. (C) gel in (B) treated with aqueous 0.1M NaBr solution.
Microporous Materials From Polymerized Microemulsion Gels
Nanolatex Primers

Latexes 20-28 nm diameter produced by microemulsion polymerization
SEM images of (4% IL-Br) latex film, peeled from a PTFE mold and treated with 0.1 M KPF$_6$. The top image shows the upper surface and the fresh fracture cross-sectional surface. The lower images show open cell pore structures in increasing magnifications, located on the upper surface of the film.
Stimuli Responsiveness to Anions

Photographs of (4% IL-Br) nanolatex coating on a glass slide, before (top left) and after (top right) treatment with 0.1 M KPF$_6$.

SEM images of film shavings in increasing magnification of top and fracture surfaces are shown at bottom left and right.
Stimuli Responsiveness to Anions

UV/Vis analysis ($\lambda \sim 800$ nm) of NaBr salt solution series after addition of (2 – 4% IL-Br content) nanolatexes. $<[\text{destabilization}]> = 0.24 \pm 0.06$ M NaBr
UV/Vis analysis ($\lambda \sim 800$ nm) of NaBF$_4$ salt solution series after addition of (2 – 4% IL-Br content) nanolatexes. $<[\text{destabilization}]> = 9.4 \pm 2.7$ mM NaBF$_4$
Stimuli Responsiveness to Anions

UV/Vis analysis ($\lambda \sim 800$ nm) of $\text{KPF}_6$ salt solution series after addition of (2 – 4% IL-Br content) nanolatexes. $<[$destabilization$]> = 0.40 \pm 0.09$ mM $\text{KPF}_6$
UV/Vis analysis ($\lambda \sim 800$ nm) of Na$_2$S salt solution series after addition of (4% IL-Br content) nano latexes. $<\text{[destabilization]}>$ = 1.8 M Na$_2$S
Stimuli Responsiveness to Anions

Poly IL-Br/PMMA Nanolatex Destabilization Concentrations of Various Salts in Aqueous Solution

<table>
<thead>
<tr>
<th>Salt</th>
<th>Nanolatex Destabilization Concentration (M, Visual)</th>
<th>Nanolatex Destabilization Concentration (M, UV/Vis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBr</td>
<td>0.21 ± 0.06</td>
<td>0.24 ± 0.06</td>
</tr>
<tr>
<td>NaBF₄</td>
<td>$7.4 \times 10^{-3} \pm 3.7 \times 10^{-3}$</td>
<td>$9.4 \times 10^{-3} \pm 2.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>KPF₆</td>
<td>$3.5 \times 10^{-4} \pm 1.8 \times 10^{-4}$</td>
<td>$4.0 \times 10^{-4} \pm 8.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>Na₂S</td>
<td>-</td>
<td>1.8</td>
</tr>
</tbody>
</table>

$1 \text{ M Na}_2\text{S} \Rightarrow I \sim 3 \text{ M}$
Nanolatex Primers
Comparison with commercially available latexes.
These nanolatexes form robust films.

<table>
<thead>
<tr>
<th>Latex type</th>
<th>Young's Modulus (MPa)</th>
<th>Particle Size (nm)</th>
<th>Monomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanolatex</td>
<td>50.5 ± 1.8</td>
<td>25</td>
<td>IL-Br/MMA</td>
</tr>
<tr>
<td>Commercial Latex 1</td>
<td>1.41 ± 0.03</td>
<td>297</td>
<td>Vinyl/Acrylic</td>
</tr>
<tr>
<td>Commercial Latex 2</td>
<td>4.0 ± 1.8</td>
<td>322</td>
<td>Vinyl/Acrylic</td>
</tr>
<tr>
<td>Commercial Latex 3</td>
<td>2.0 ± 0.6</td>
<td>256</td>
<td>Vinyl/Acrylic</td>
</tr>
<tr>
<td>Commercial Latex 4</td>
<td>1.4 ± 0.2</td>
<td>237</td>
<td>Styrene, Butyl Acrylate/Acrylonitrile Styrene, Butyl Acrylate/Styrenated Polymer/Polyalkylene Glycol</td>
</tr>
<tr>
<td>Commercial Latex 5</td>
<td>140 ± 16</td>
<td>990</td>
<td></td>
</tr>
</tbody>
</table>
Nanolatexes Are Good Film Formers

Transparent Latex Films Treated with Aqueous KPF$_6$
Nanolatex Primers

Pores can be generated in latex films by soaking in aqueous KPF$_6$. 

![Image of pore generation in latex films](image-url)
# Nanolatex Primers

Topcoat cross-cut adhesion/thickness (µm) results for nanolatex-based pigmented primer

<table>
<thead>
<tr>
<th>Topcoat</th>
<th>Aluminum</th>
<th>Plastic</th>
<th>Wood</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bare</td>
<td>Primer</td>
<td>Primer + KPF₆</td>
</tr>
<tr>
<td>Enamel</td>
<td>5B/45</td>
<td>5B/58</td>
<td>5B/60</td>
</tr>
<tr>
<td>Flat-L</td>
<td>Fail/50</td>
<td>5B/78</td>
<td>5B/65</td>
</tr>
<tr>
<td>A-Epoxy</td>
<td>5B/27</td>
<td>5B/47</td>
<td>5B/63</td>
</tr>
<tr>
<td>U-Alkyd</td>
<td>5B/63</td>
<td>5B/60</td>
<td>5B/62</td>
</tr>
<tr>
<td>HS-Epoxy</td>
<td>5B/162</td>
<td>5B/156</td>
<td>5B/152</td>
</tr>
</tbody>
</table>

![Image: Adhesion Test Results]

11 July 2011, Particles 2011
Summary

Nanolatexes ultrastable

Nanolatex films 10x-35x tougher than commercial latex films

Excellent adhesion on various substrates (aluminum, plastic and wood)

Can be used to design and fabricate new classes of filters

11 July 2011, Particles 2011
Nanolatexes as Waterborne Dispersing Aids?
Nanolatex Dispersions of WC Nanopowder
(C. Giordana, et al.)
Nanolatex Dispersion of WC
Nanolatex Dispersion of WC
Nanolatexes as Stabilizers for Waterborne Dispersions
(Thank you Markus Antonietti!)
Carbon single wall nanotube (SWCNT) latex film casting
Nanolatex Dispersions of SWCNT

Equivalent optical density (average absorbance over 600-400 nm)

16,000 OD/wt fraction

$\varepsilon_{500} \sim 28.6 \text{ cm}^2/\text{mg}$
Latex Super Primers

Equivalent optical density (average absorbance over 600-400 nm)
Proposed Exfoliation Mechanism For SWCNT
MWCNT Unwinding by Nanolatex Stabilization
MWCNT Dispersions
How Concentrated? (All using 20% nanolatex)

<table>
<thead>
<tr>
<th>wt%</th>
<th>$\varepsilon_{500\text{nm}}/(\text{cm}^2/\text{mg})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.48</td>
<td>55.2</td>
</tr>
<tr>
<td>1</td>
<td>56.5</td>
</tr>
<tr>
<td>2</td>
<td>57.1</td>
</tr>
<tr>
<td>3</td>
<td>60.3</td>
</tr>
<tr>
<td>4</td>
<td>59.2</td>
</tr>
</tbody>
</table>

$<\text{avg}> \sim 57.7$

$2 \times 28.6}^{\text{SWCNT}} = 57.2 \sim 57.7}^{\text{MWCNT}}$
MWCNT Dispersions
How much needed for complete exfoliation?

0.5-4% MWCNT – Critical amount of nanolatex varies from 0.23 to 0.31 weight fraction of MWCNT

Concentrated to 10-17% by ultrafiltration
Saturation Adsorption of Nanolatex on MWCNT
Nanolatex Stabilization of HydroThermal Carbon (2% HTC in Water) (M. Titirici et al.)

$\varepsilon_{500\text{nm}} > 15.5 \text{ cm}^2/\text{mg}$

![Graph showing optical density vs. sonication time for different samples.](chart.png)
Apparent Porosity of HTC K60G2N
Importance of Porosity in Dispersing HTC

Suggests significant potential for improvement
HRTEM of Highly Porous HTC
3D HRTEM of High Porosity HTC
OD_{500nm} vs Sonication Time

E_{500nm} > 55 \text{ cm}^2/\text{mg}
TEM of HTC Dispersion

- NL stabilized
- TB stabilized
What about Graphene?

$\varepsilon_{500\text{nm}}/(\text{cm}^2/\text{mg})$

<table>
<thead>
<tr>
<th>Material</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNT</td>
<td>28.6</td>
</tr>
<tr>
<td>HTC</td>
<td>&gt; 55</td>
</tr>
<tr>
<td>MWCNT</td>
<td>&gt; 57.7</td>
</tr>
<tr>
<td>Graphene</td>
<td>15.3 (? ? ? ? ?)</td>
</tr>
</tbody>
</table>
Graphene Waterborne Dispersions
Nanolatex Stabilization

New lower bound to optical extinction!

$\varepsilon_{500\text{nm}} > 54 \text{ cm}^2/\text{mg}$

$\varepsilon_{500\text{nm}} = 15.3 \text{ cm}^2/\text{mg}$

$\varepsilon_{660\text{nm}} = 13.9 \text{ cm}^2/\text{mg}$

Lotya et al., JACS 2009, 131, 3611

1,100x more concentrated than in Lotya et al.

11 July 2011, Particles 2011
What about Graphene?

\[ \varepsilon_{500\text{nm}} / (\text{cm}^2/\text{mg}) \]

- SWCNT: 28.6
- HTC: > 55
- MWCNT: > 57.7
- Graphene: > 54
Graphene Waterborne Dispersions
Opto-Rheological Fluids

OD ~ 1 (transparent) ➔ Turbid @ 1,000 rpm
Graphene Waterborne Dispersions
Opto-Rheological Fluids
Summary

Our waterborne graphene dispersions are opto-rheological, being reversibly transformed from transparent to turbid by couette flow fields.

These collective nanocarbon waterborne dispersions are useful for delivering micron to nanosize carbon particles for various applications, including printing, photothermal heating, inkjet writing of wiring (circuits and RFID), conventional composites, and as fuels for indirect carbon fuel cells.
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