UV-Vis and DLS characterization of smart properties of PEG-PDMAEMA block copolymers synthesized by ARGET ATRP

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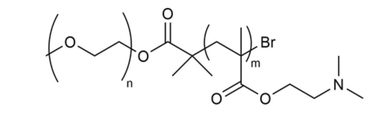
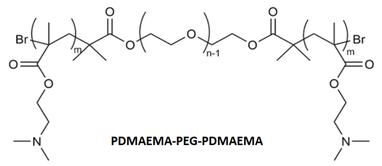
PEG-PDMAEMA Block Copolymers



PEG-PDMAEMA



PDMAEMA-PEG-PDMAEMA

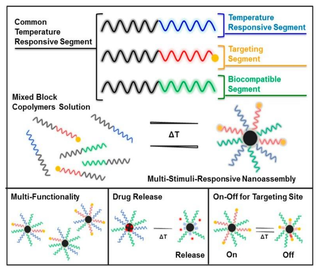
The Poly(ethylene glycol)–poly(2-(dimethylamino)ethyl methacrylate) (PEG-PDMAEMA) block copolymer is synthesized by Activator Regenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP).

In this process, PEG is a macroinitiator, which promotes the addition of PDMAEMA to form the linear block copolymer.

Triblocks have different architecture compared to diblocks when the PDMAEMA becomes hydrophobic due to changes in the environment. The triblock and diblock architectures lead to unique formations when insoluble.

Applications

Drug delivery



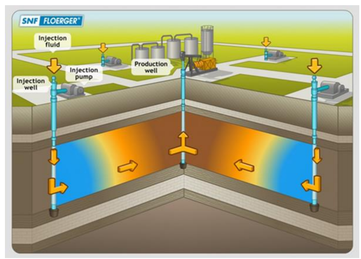
Kotsuchibashi, Y., Ebara, M., Idota, N., Narain, R., & Aoyagi, T. (2012, February 15). A 'smart' approach towards the formation of multifunctional nano-assemblies by simple mixing of block copolymers having a common temperature sensitive segment [Digital image].

PEG-PDMAEMA block copolymers can change solubility, which makes it a possible candidate for drug delivery.

Due to different temperature and pH, PEG-PDMAEMA is able to switch from hydrophobic to hydrophilic.

During the process, the structure of copolymer opens and allows to release drug.

Enhanced Oil Recovery



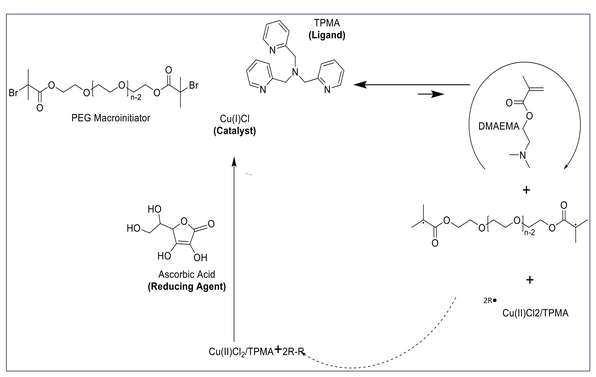
(2012, September 13). [Digital image]. Retrieved from https://2b1stconsulting.com/eor/

PEG-PDMAEMA block polymer have potential for use as a surfactant at oil.

Stimuli responsive molecular structures of the polymer have strong interaction between the interface of water and oil, reducing surface tension and creating enhanced oil recovery applications.

When changing temperature or pH, the viscosity of the solution will increase, which makes solution better mobilize any leftover oil and improves overall collection rate of the reservoir.

Polymer Synthesis



- PDMAEMA block copolymers are synthesized by Activator Regenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP).
- ATRP is a catalytic process that can be mediated by several transition metal complexes with REDOX activity controlled by the balance between propagating free radicals and dormant species.
- Oxidatively stable Cu species act as reducing agent can also work on eliminating air and reducing radical traps.
- On the one hand, ARGET ATRP reduces cost, and it is more environmentally friendly than traditional ATRP because it uses less copper (I) than ATRP.
- Additionally, ARGET ATRP reduces side reactions induced by catalyst which enables the successful syntheses of higher molecular weights

Block Copolymers	Mn PEG (kDa)	Mn PDMAEMA (kDa)	Molar Ratio (PDMAEMA -) PEG – PDMAEMA Actual ratio : Appr. ratio		Dispersity
Diblocks:					
$mPEG_{44}$-b-$PDMAEMA_{19}$	2.0	3.0	1 - 0.44	1 - 0.5	1.31
$mPEG_{44}$-b-$PDMAEMA_{198}$	2.0	31.1	1 - 4.49	1 - 4.5	1.35
Triblocks:					
$PDMAEMA_{49}$-b-$mPEG_{45}$-b-$PDMAEMA_{49}$	2.0	7.69	1.08 - 1 - 1.08	1 - 1 - 1	1.42
$PDMAEMA_{94}$-b-$mPEG_{45}$-b-$PDMAEMA_{94}$	2.0	14.8	2.09 - 1 - 2.09	2 - 1 - 2	1.23
$PDMAEMA_{68}$-b-$mPEG_{136}$-b-$PDMAEMA_{68}$	6.0	21.7	0.58 - 1 - 0.58	0.5 - 1 - 0.5	1.38
$PDMAEMA_{117}$-b-$mPEG_{136}$-b-$PDMAEMA_{117}$	6.0	18.4	0.86 - 1 - 0.86	1 - 1 - 1	1.26

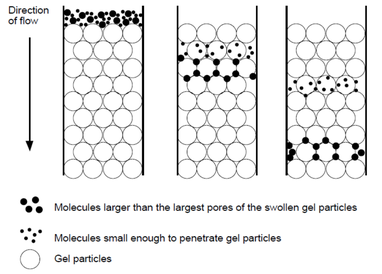
Polymer Characterization

Diblocks and triblocks were characterized using Nuclear Magnetic Resonance Spectroscopy (NMR) and Gel Permeation Chromatography (GPC)

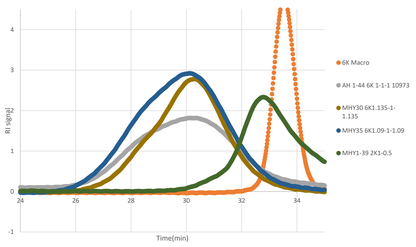
Gel permeation chromatography (GPC)

GPC can determine several important parameters:

- number average molecular weight (Mn)
- weight average molecular weight (Mw)
- weight average molecular weight (Mz)
- molecular weight distribution (PDI)



https://www.drgpinstitute.in/gel-permeation-chromatography/?utm_source=rss&utm_medium=rss&utm_campaign=gel-permeation-chromatography



GPC compare graph of diblock, triblocks and macroinitiator

These values are important because they affect many characteristic physical properties of the polymer.

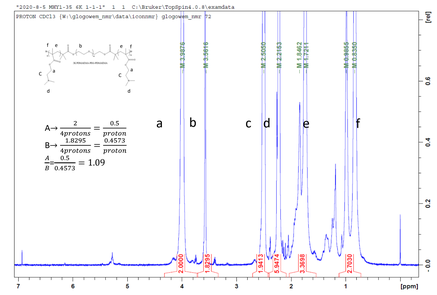
Small differences in these measured values from batch to batch can lead to significant differences in the end-use properties of the polymer.

Nuclear magnetic resonance(NMR)

NMR provides data on the molecular weight of the poly(ethylene glycol) (PEG) as well as the structure to determine a successful synthesis

The proton corresponding to each peak has a specific chemical shift on the x-axis, which is caused by the chemical and electronic environment of the proton. Letters are assigned to the integration of randomly matched peaks with polymers, as shown below

Integrate each peak, the ratio is determined by the peak values obtained from the PEG block and the PDMAEMA block, which gives the molar ratio.



NMR Spectroscopy of triblock polymer 6K1.09-1-1.09

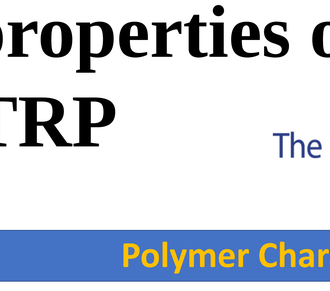
Characterization of Smart Properties

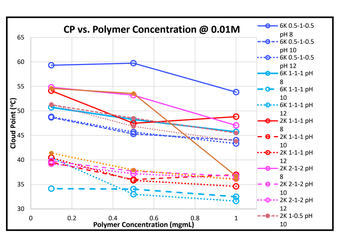
UltraViolet – Visible spectroscopy (UV-Vis)

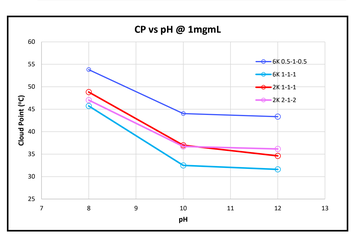
UltraViolet – Visible spectroscopy is used to determine the temperature at which the polymer solution turns from being clear to cloudy

The cloud point is the intersection between the drop in transmittance and the baseline (as shown in the graph on the right)

Using the UV-Vis, the effects of polymer concentration, pH and PDMAEMA degree of polymerization on cloud point can be determined

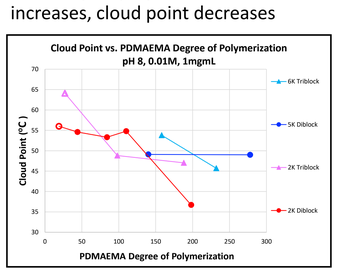


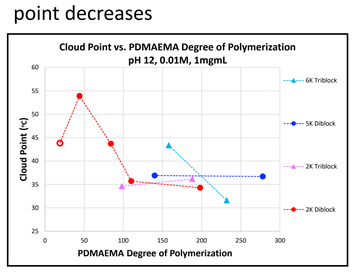




Generally, as polymer concentration increases, cloud point decreases

As pH increases above the pKa, cloud point decreases





pH 8 and pH 12: Generally, there is more variation in cloud point as PDMAEMA degree of polymerization decreases

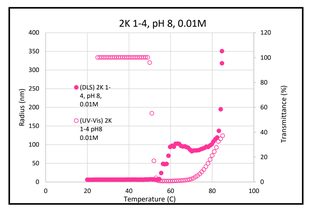
Dynamic Light Scattering (DLS)

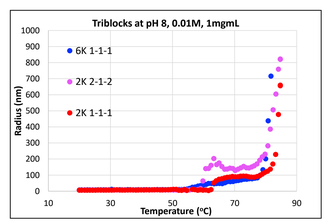
Dynamic Light Scattering is used to determines whether micelles or aggregates formed after the cloud point

Micelles are discrete clusters of ~100nm and aggregates are objects larger than 100nm

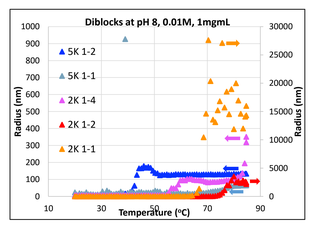
The DLS cloud point is the point at which the radius increases

The DLS cloud point is compared to the UV-Vis cloud point, as shown on the right, to ensure consistent data.

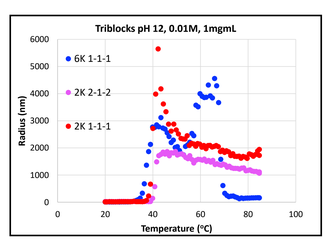




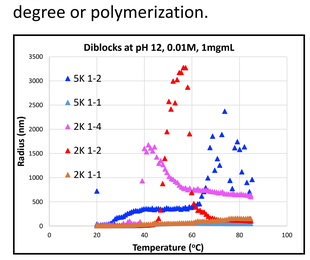
Triblocks at pH 8 form micelles after cloud point is reached, then aggregates as temperature increases



5K diblocks at pH 8 form micelles, whereas 2K diblocks form micelles or aggregates depending on PDMAEMA degree or polymerization.



Triblocks at pH 12 form large aggregates above the cloud point



Triblocks at pH 12 form large aggregates above the cloud point

Conclusion

- More characterization needs to be done on the UV-Vis and DLS to observe and confirm trends
- Using various instruments to characterize polymers and observe different properties

Acknowledgement

- Past research members
- Materials Science and Engineering Center at the University of Wisconsin – Eau Claire
- National Science Foundation for the RUI DMR Award, LSAMP award, and REU award