Polymer Basics

Polymers are made of covalently bonded repeat units, called monomers, that make up long chains.

Polymer structure can be modified to achieve homopolymers, polymers made of a single repeat unit, or diblock copolymers, polymers containing two different repeat units on each end.

“Smart” Polymers

“Smart” polymers have the unique ability to dramatically change their properties under certain conditions. One property that can change is their solubility when the conditions such as pH, temperature, and/or concentration change.

Polymers are made of covalently bonded repeat units, called monomers, that make up long chains. Bonded repeat units, called monomers, that make up long chains. Poly(2-monomers, that make up long chains. Poly(ethylene glycol) or PEG (poly(2-ethyl methacrylate)) (PDMAEMA) is a smart polymer that changes its cloud point when conditions change, such as pH, polymer concentration, and ionic strength. When used in the diblock copolymer poly(ethylene glycol) or PEG-PDMAEMA, it maintains smart polymer properties and gains additional functionalities.

Applications

Smart polymers have potential future in the field of chemical enhanced oil recovery (EOR). Conventional methods are inefficient, leaving up to 65% of oil in the underground reservoirs. EOR increases the oil yields through the injection of water, polymer, and a surfactant. These additives help oil move towards the pump where it can then be recovered.

Cloud point is the temperature above which the polymer will change its solubility and form aggregates.

Poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) is a smart polymer that changes its cloud point when conditions change, such as pH, polymer concentration, and ionic strength. When used in the diblock copolymer poly(ethylene glycol) or PEG-PDMAEMA, it maintains smart polymer properties and gains additional functionalities.

Synthesis can be achieved using either chain or “living” polymerization methods. The living method has a more controlled growth and therefore increases uniformity. This results in a lower distribution of polymer chain length and molecular weight. This way, the properties are more similar and more defined for all chains. The more similar the properties of each polymer, the more consistent and predictable the behavior will be.

PDMAEMA is synthesized using a living polymerization called Atom Transfer Radical Polymerization (ATRP). By varying the ratio of monomer to initiator and the polymerization time, the molecular weight can be controlled.

Polymer Synthesis and Characterization

One way to test uniformity of the synthesized polymer is to measure the polydispersity index (PDI). It is a measure of the distribution of polymer chain lengths. A PDI of 1 indicates that all polymers are the exact same length. Living polymerization can achieve a PDI less than 1.2 for synthetic polymers.

PEG-Br 1:1 2k PEG
PEG-PDMAEMA 1:1 1.08 21300 8700
PEG-PDMAEMA 1:2 1.08 28000 15500

Gel Permeation Chromatography (GPC) is a method to measure PDI as well as relative molecular weight. It uses a series of columns with different sized pores to separate molecules based on size. The smaller the molecule, the more time it will take to go through the columns.

Proton Nuclear Magnetic Resonance Spectroscopy (1H-NMR) is a tool to calculate molecular weight. By comparing the integration of protons, (how many there are in the polymer chains) molecular weight can be calculated.

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Polymer Thermoresponsive Study

It is important to verify that PEG-PDMAEMA maintains the smart polymer property of changing solubility with temperature. UV-Vis spectroscopy is one tool used to measure the change in cloud point as variables such as molecular weight, polymer chain length ratios, polymer concentration, and buffer concentration change.

UV-Vis reads the absorbance of light by a sample. When polymer reaches its cloud point, aggregates form and blocks the light from transmission. The cloud point can be determined by the absorbance increasing above zero. Beer’s Law is used to show how Absorbance (A) varies as a function of the ratio of light in (I0) to light out (I). Zero absorbance means no aggregates are present and all light passes through the sample.

PEG-PDMAEMA thermoresponsive studies look at the change in the cloud point as the concentration changes. An increase in the concentration of polymer has a clear increase in the amount of absorbance/scattering. Increased concentration also lowers the cloud point.

Conclusions

• PEG-PDMAEMA is a smart polymer with properties that can be tuned.
• Samples are synthesized to achieve uniformity through living polymerization. They are characterized for PDI and molecular weight using GPC and 1H-NMR.
• UV-Vis spectroscopy shows the cloud point decreases as concentration increases.
• Rheology and tensiometry show that PEG-PDMAEMA increases the ability to mix water and oil by increasing the viscosity and lowering the interfacial tension. Smart properties are still under investigation.

Future Projects and Research Goals

• Change polymer architecture to determine impact on properties
• Test thermoresponsive as a function of pH and ionic strength
• Study aggregate size using dynamic light scattering

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