

090126 Introduction to Polymers

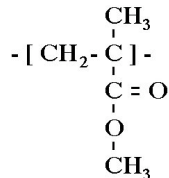
- 1) The following is from an article about research at Livermore-Berkley National Laboratories that came out last week:

In their latest research, Ritchie and the team expanded on advances made two years ago, when researchers developed a method to improve the strength of bone substitutes through a technique that involves freezing seawater. The freeze-casting technique has been refined and applied to an alumina/PMMA hybrid to create large porous ceramic scaffolds that closely mirror the complex hierarchical microstructure of nacre, or mother of pearl. The next step in creating tougher ceramics, say the researchers, is to improve the proportion of ceramic to polymer in their composites, and to replace the PMMA with a better polymer. Ultimately the aim is to eventually replace the polymer content with metal.
<http://www.industryweek.com/ReadArticle.aspx?ArticleID=18185>

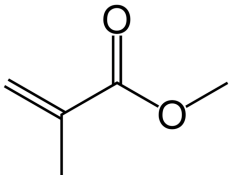
- a) Draw the structure of PMMA and give one common application.
 - b) Describe a synthesis of PMMA using free radicals.
 - c) What might be a better polymer than PMMA for this application? Explain why and give the structure of your replacement polymer.
 - d) The last sentence indicates that the polymer binder can be replaced with “metal”. Comment on the feasibility of such a simple replacement.
 - e) Give the structure of one polyester and give the name of this polymer, its common acronym, the monomers used to synthesize it and a common application.
- 2) There are two main mechanisms for polymerization.
- a) Name these two mechanisms and give an example of a polymer made by each.
 - b) Describe the difference between the two mechanisms.
 - c) Sketch a plot of the number average molecular weight as a function of time for the two mechanisms.
 - d) Give a function for the number average molecular weight as a function of the extent of reaction p .
 - e) Give a function for the polydispersity index as a function of the extent of reaction, p .
- 3) In class we made nylon 6,10 using an interfacial polymerization following a Schotten-Baumann Reaction (http://en.wikipedia.org/wiki/Schotten-Baumann_reaction).
- a) What are the monomers used to synthesize nylon 6, 10?
 - b) What solvents are used in the interfacial polymerization and in which solvent is each monomer dissolved?
 - c) How is the polymer separated from the reaction mixture in this reaction?
 - d) How is this reaction driven to a high extent of reaction, $p \Rightarrow 1$?
 - e) Typically a step growth polymerization, such as the reaction of epoxy glue, proceeds through a low viscosity stage (application of the glue), a viscous stage (early stages of setting/tacky glue) and finally a solid stage (cured glue). The interfacial nylon synthesis does not display these stages. Is this really a step growth polymerization? Explain your answer.

ANSWERS: 090126 Introduction to Polymers

1) a) Plexiglas, Lucite, Perspex (plastic windows and clear tabletops etc.)

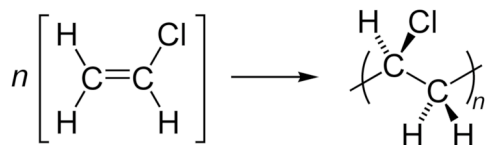


b) Methylmethacrylate



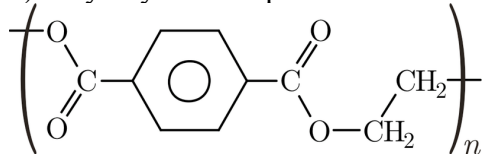
is the monomer it is initiated in a chain growth polymerization with a free radical initiator such as benzoyl peroxide in a solvent such as toluene at an elevated temperature ($\sim 90^\circ\text{C}$). The reaction can be terminated with water.

c) A more polar polymer might be better for interaction with the ceramic. One example is polyvinylchloride,

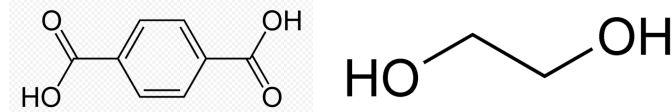


d) The process and product would be completely different for a metal binder. Basically it couldn't work in the same way so the comment about a metal is ridiculous. First a metal could only be used in the melt which is a low viscosity fluid at elevated temperature, probably hot enough to sinter the ceramic particles into a precipitated phase. The metal would crystallize when it cooled forcing further exclusion of the ceramic phase from the metal matrix. The ceramic and metal would not have good interfacial properties so it is most likely a powder would result if the suspension could be made uniform. The polymer melt is an ideal dispersant for the ceramic powder and a metal just couldn't perform this function.

e) Polyethylene terephthalate used for water and soda bottles (PET or PETE).



This is made from terephthalic acid and ethylene glycol in a step growth polymerization.



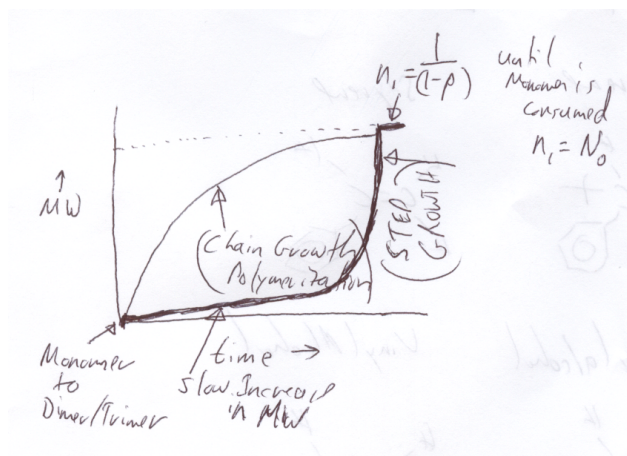
2) a) Step growth, polyurethane. Chain growth, polystyrene.

b) Step growth involves reaction of all monomers at once that combine to make dimers/tetramers etc. All monomers are consumed immediately when the reaction begins and

the molecular weight growth is slow. You need a extent of reaction of 1 for this reaction to yield high molecular weight polymers.

Chain growth involves initiation using an initiator and propagation of the polymer as a chain with a propagating chain end. High molecular weight is achieved early on and polymer is produced even at moderate extents of reaction. There is monomer present even at the end of the reaction that must be removed from the polymer generally.

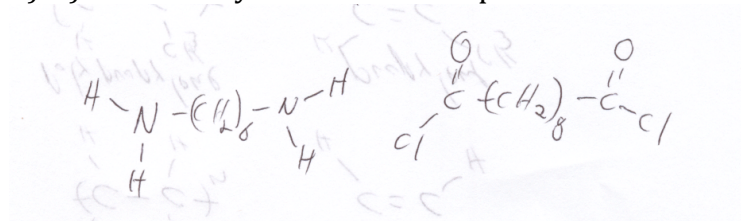
c)



d) $n_1 = n_n = 1/(1-p)$; $n_w = (1+p)/(1-p)$

e) $PDI = n_w/n_1 = (1+p)$

3) a) Hexamethyldiamine and adipic acid chloride



b) Hexane is used for the adipic acid chloride and water for the hexamethyldiamine.

c) The polymer precipitates at the interface of the two immiscible solvents.

d) The reaction is driven to $p \Rightarrow 1$ by removal of the polymer product and removal of the HCl byproduct by reaction with NaOH to form NaCl that dissolved in the water phase and H_2O .

e) It is really a step-growth polymerization because it proceeds through a step-growth mechanism. It does not seem to be the same kind of reaction as epoxy glue because the products are removed to drive the reaction rapidly and because the polymerization takes place in solvents which leads to a faster transport rate for reactants and an overall higher reaction rate.