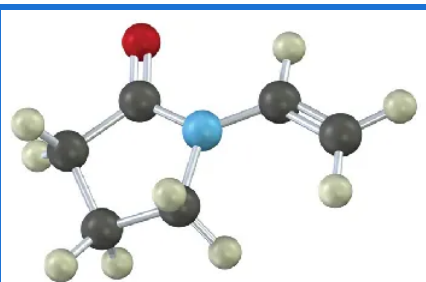
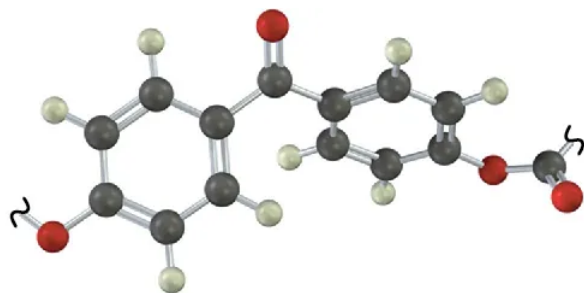


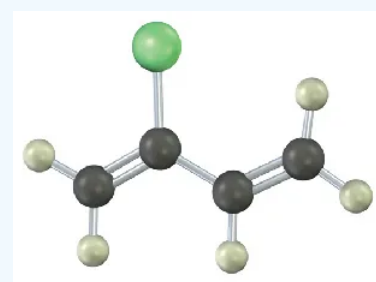
16.9: Additional Problems

Visualizing Chemistry

Identify the structural class to which the following polymer belongs, and show the structure of the monomer units used to make it:



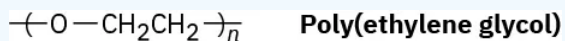
(b)



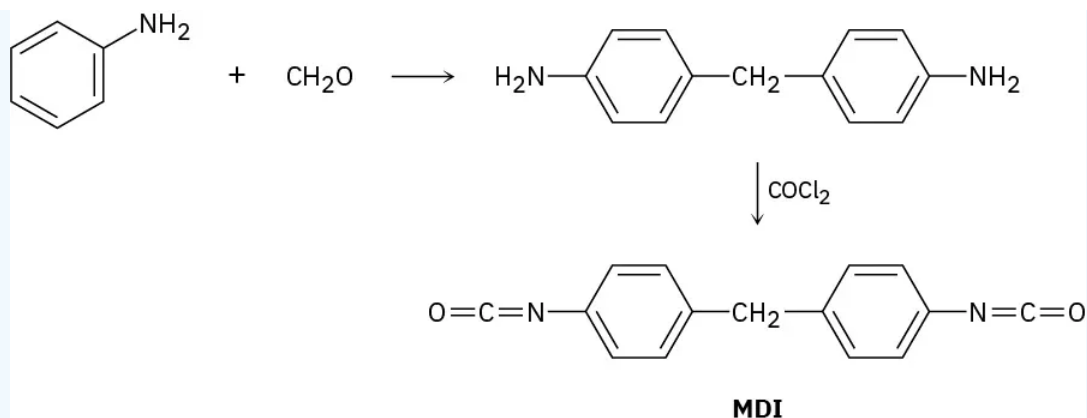
Mechanism Problems

Problem 31-15

Poly(ethylene glycol), or Carbowax, is made by anionic polymerization of ethylene oxide using NaOH as catalyst. Propose a mechanism.

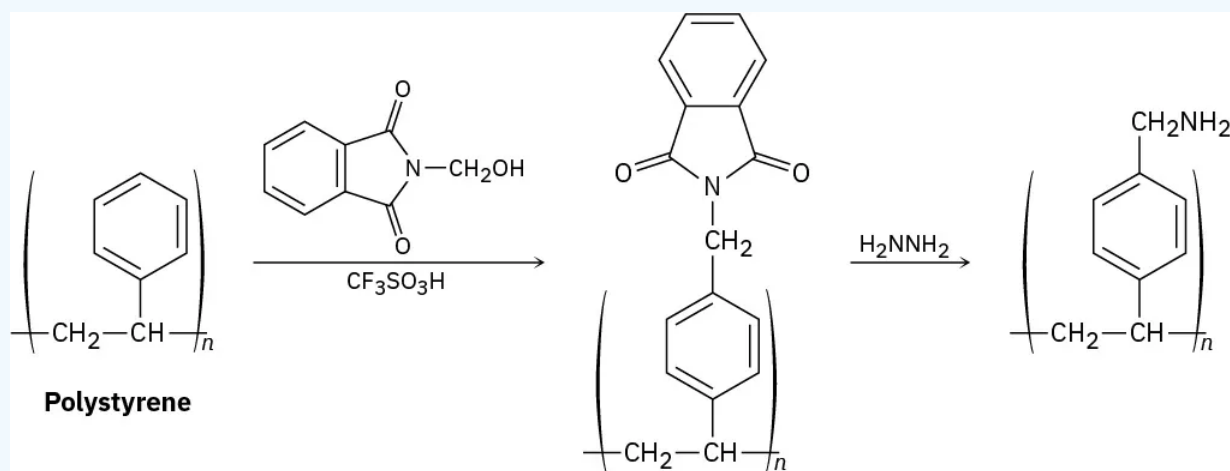


The polyurethane foam used for home insulation uses methanediiphenyldiisocyanate (MDI) as monomer. The MDI is prepared by acid-catalyzed reaction of aniline with formaldehyde, followed by treatment with phosgene, COCl_2 . Propose mechanisms for both steps.

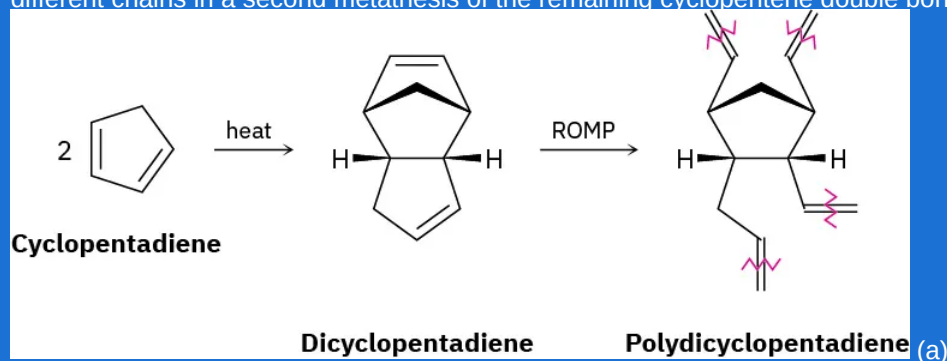


Write the structure of a representative segment of polyurethane prepared by reaction of ethylene glycol with MDI (Problem 31-16).

The polymeric resin used for Merrifield solid-phase peptide synthesis (Section 26.8) is prepared by treating polystyrene with *N*-(hydroxymethyl)phthalimide and trifluoromethanesulfonic acid, followed by reaction with hydrazine. Propose a mechanism for both steps.



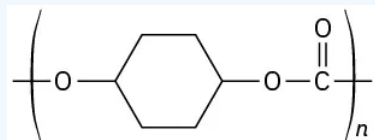
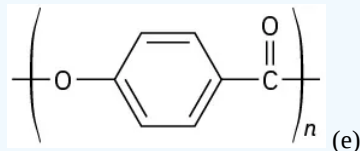
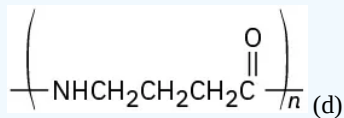
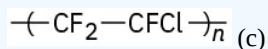
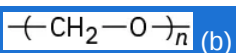
Polydicyclopentadiene (PDCPD), marketed as Telene or Metton, is a highly cross-linked thermosetting resin used for molding such impact-resistant parts as cabs for large trucks and earth-moving equipment. PDCPD is prepared by ring-opening metathesis polymerization of dicyclopentadiene, which is itself prepared from 1,3-cyclopentadiene. The polymerization occurs by initial metathesis of the more highly strained double bond in the bicyclo[2.2.1]heptane part of the molecule (Section 4.9) to give a linear polymer, followed by cross-linking of different chains in a second metathesis of the remaining cyclopentene double bond.



Show the mechanism of the formation of dicyclopentadiene from cyclopentadiene.

(b) Draw the structure of a representative sample of the initially formed linear polymer containing three monomer units. (c) Draw the structure of a representative sample of PDCPD that shows how cross-linking of the linear chains takes place.

General Problems



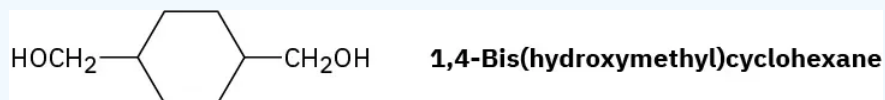
Problem 31-21

Draw a three-dimensional representation of segments of the following polymers:

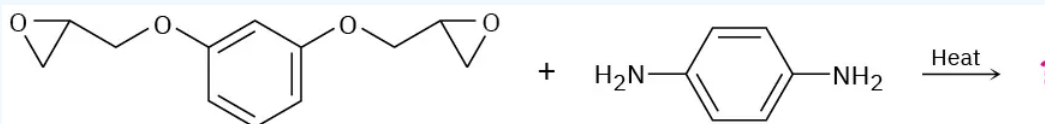
(a) Syndiotactic polyacrylonitrile

(b) Atactic poly(methyl methacrylate) (c) Isotactic poly(vinyl chloride)

Draw the structure of Kodel, a polyester prepared by heating dimethyl 1,4-benzenedicarboxylate with 1,4-bis(hydroxymethyl)cyclohexane.



Show the structure of the polymer that results from heating the following diepoxide and diamine:



Nomex, a polyamide used in such applications as fire-retardant clothing, is prepared by reaction of 1,3-benzenediamine with 1,3-benzenedicarbonyl chloride. Show the structure of Nomex.

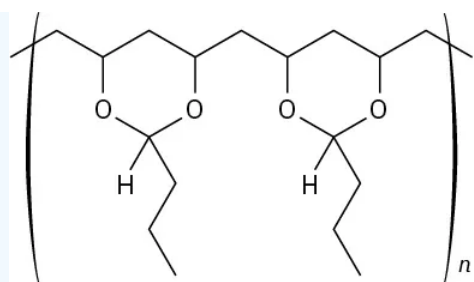
Nylon 10,10 is an extremely tough, strong polymer used to make reinforcing rods for concrete. Draw a segment of nylon 10,10, and show its monomer units.

1,3-Cyclopentadiene undergoes thermal polymerization to yield a polymer that has no double bonds in the chain. Upon strong heating, the polymer breaks down to regenerate cyclopentadiene. Propose a structure for the polymer.

When styrene, C₆H₅CH=CH₂, is copolymerized in the presence of a few percent *p*-divinylbenzene, a hard, insoluble, cross-linked polymer is obtained. Show how this cross-linking of polystyrene chains occurs.

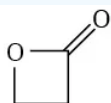
Nitroethylene, H₂C=CHNO₂, is a sensitive compound that must be prepared with great care. Attempted purification of nitroethylene by distillation often results in low recovery of product and a white coating on the inner walls of the distillation apparatus. Explain.

Poly(vinyl butyral) is used as the plastic laminate in the preparation of automobile windshield safety glass. How would you synthesize this polymer?



Poly(vinyl butyral)

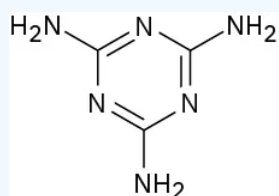
What is the structure of the polymer produced by anionic polymerization of β -propiolactone using NaOH as catalyst?



β -Propiolactone

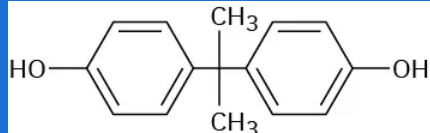
Glyptal is a highly cross-linked thermosetting resin produced by heating glycerol and phthalic anhydride (1,2-benzenedicarboxylic acid anhydride). Show the structure of a representative segment of glyptal.

Melmac, a thermosetting resin often used to make plastic dishes, is prepared by heating melamine with formaldehyde. Look at the structure of Bakelite shown in Section 31.7, and then propose a structure for Melmac.

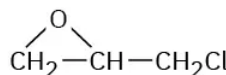


Melamine

Epoxy adhesives are cross-linked resins prepared in two steps. The first step involves S_N2 reaction of the disodium salt of bisphenol A with epichlorohydrin to form a low-molecular-weight prepolymer. This prepolymer is then "cured" into a cross-linked resin by treatment with a triamine such as $H_2NCH_2CH_2NHCH_2CH_2NH_2$.



Bisphenol A

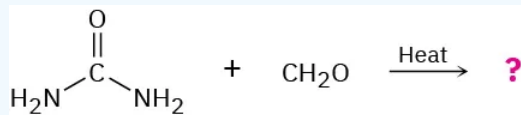


Epichlorohydrin (a)

What is the structure of the prepolymer?

(b) How does addition of the triamine to the prepolymer result in cross-linking?

The smoking salons of the Hindenburg and other hydrogen-filled dirigibles of the 1930s were insulated with urea-formaldehyde polymer foams. The structure of this polymer is highly cross-linked, like that of Bakelite (Section 31.7). Propose a structure.



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