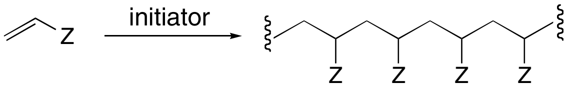
Chapter 30: Synthetic Polymers

♦ Chain-growth polymers—Addition polymers

[1] Chain-growth polymers with alkene starting materials (30.2)

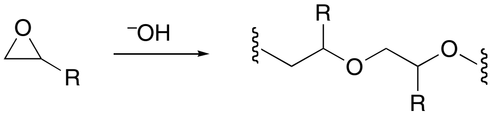
- General reaction:



- Mechanism—three possibilities, depending on the identity of Z:

Type	Identity of Z	Initiator	Comments
[1] radical polymerization	Z stabilizes a radical. Z = R, Ph, Cl, etc.	A source of radicals (ROOR)	Termination occurs by radical coupling or disproportionation. Chain branching occurs.
[2] cationic polymerization	Z stabilizes a carbocation. Z = R, Ph, OR, etc.	H–A or a Lewis acid (BF_3 + H_2O)	Termination occurs by loss of a proton.
[3] anionic polymerization	Z stabilizes a carbanion. Z = Ph, COOR, COR, CN, etc.	An organolithium reagent (R–Li)	Termination occurs only when an acid or other electrophile is added.

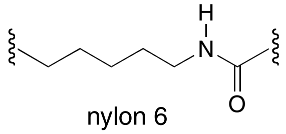
[2] Chain-growth polymers with epoxide starting materials (30.3)



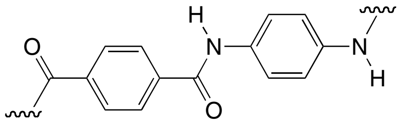
- The mechanism is S_N2.
- Ring opening occurs at the less substituted carbon of the epoxide.

◆ Examples of step-growth polymers—Condensation polymers (30.6)

Polyamides

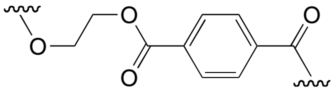


nylon 6

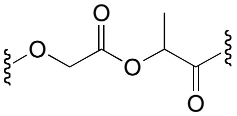


Kevlar

Polyesters

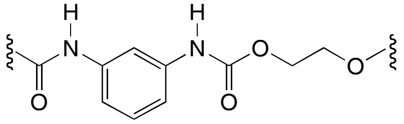


polyethylene terephthalate



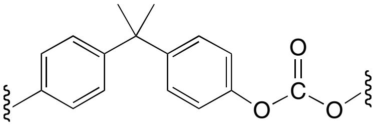
copolymer of
glycolic and lactic acids

Polyurethanes



a polyurethane

Polycarbonates



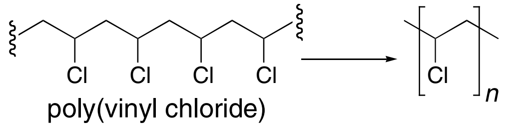
Lexan

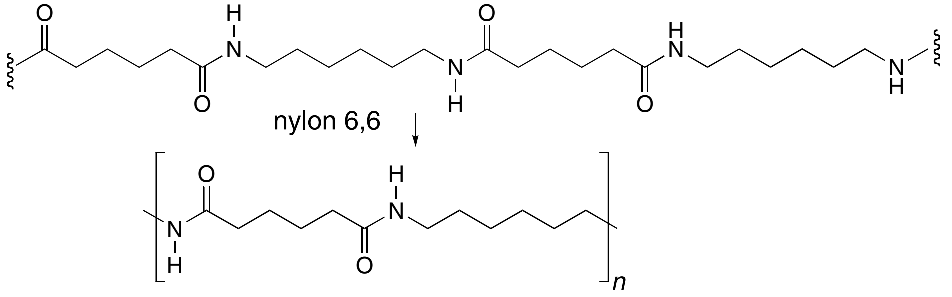
◆ Structure and properties

- Polymers prepared from monomers having the general structure CH_2=CHZ can be **isotactic**, **syndiotactic**, or **atactic** depending on the identity of Z and the method of preparation (30.4).
- **Ziegler–Natta catalysts** form polymers without significant branching. Polymers can be isotactic, syndiotactic, or atactic depending on the catalyst. Polymers prepared from 1,3-dienes have the *E* or *Z* configuration depending on the monomer (30.4, 30.5).
- Most polymers contain ordered crystalline regions and less ordered amorphous regions (30.7). The greater the crystallinity, the harder the polymer.
- **Elastomers** are polymers that stretch and can return to their original shape (30.5).
- **Thermoplastics** are polymers that can be molded, shaped, and cooled such that the new form is preserved (30.7).
- **Thermosetting polymers** are composed of complex networks of covalent bonds so they cannot be melted to form a liquid phase (30.7).

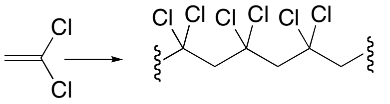
Chapter 30: Answers to Problems

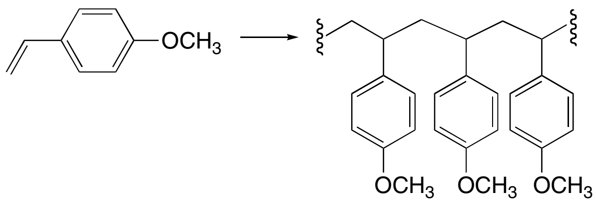
30.1 Place brackets around the repeating unit that creates the polymer.

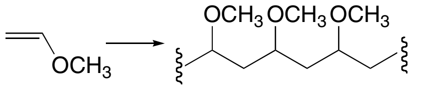


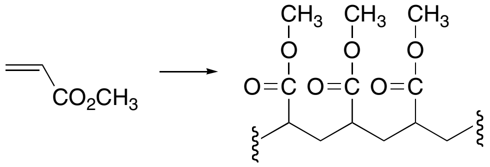


30.2 Draw each polymer formed by chain-growth polymerization.

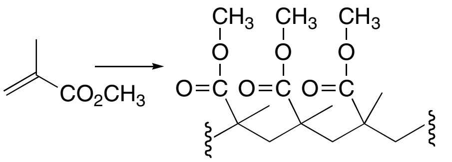
a.


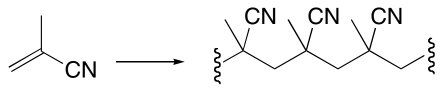
b.


c.


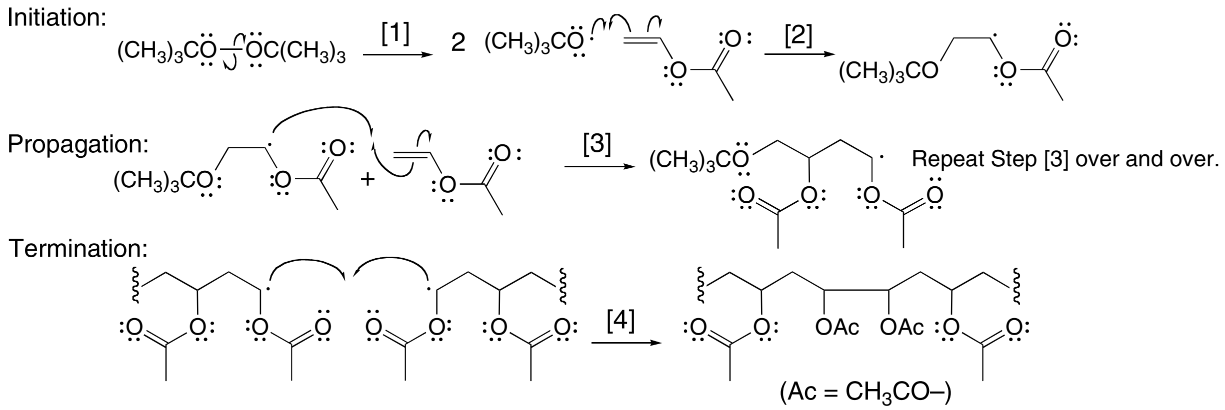
d.


30.3 Draw each polymer formed by radical polymerization.

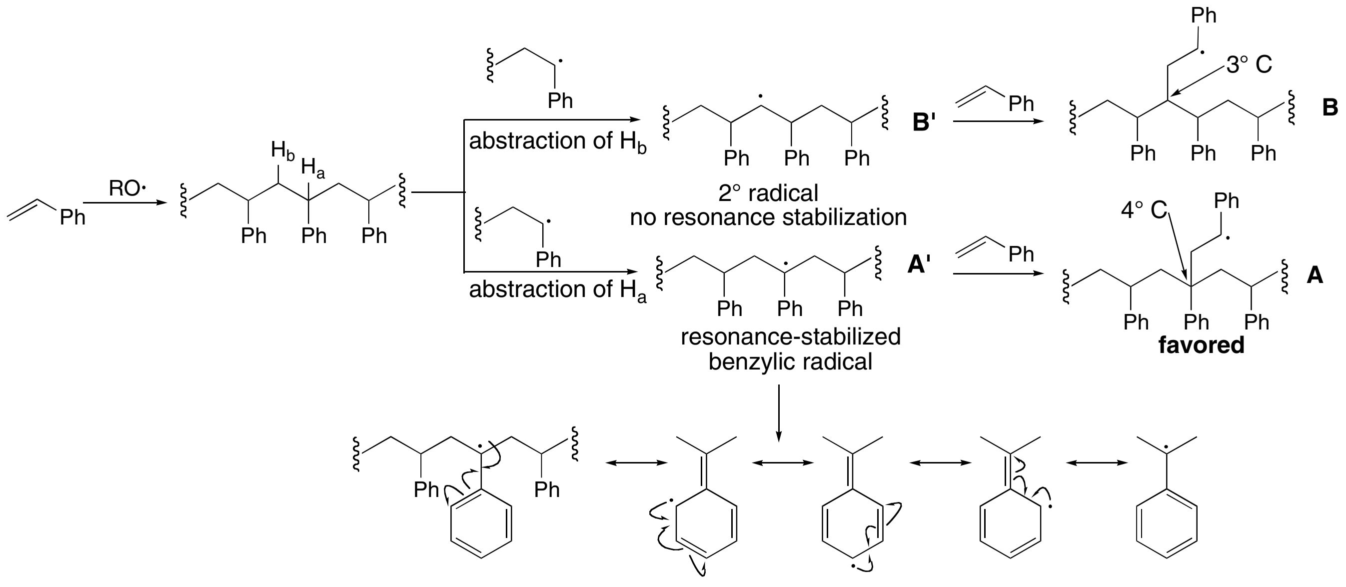
a.


b.


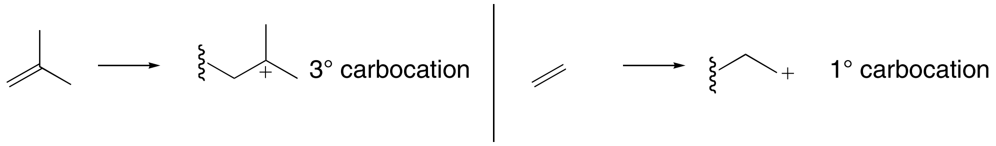
30.4 Use Mechanism 30.1 as a model of radical polymerization.



30.5 Radical polymerization forms a long chain of polystyrene with phenyl groups bonded to every other carbon. To form branches on this polystyrene chain, a radical on a second polymer chain abstracts a H atom. Abstraction of H_a forms a resonance-stabilized radical **A'**. The 2° radical **B'** (without added resonance stabilization) is formed by abstraction of H_b. Abstraction of H_a is favored, therefore, and this radical goes on to form products with 4° C's (**A**).



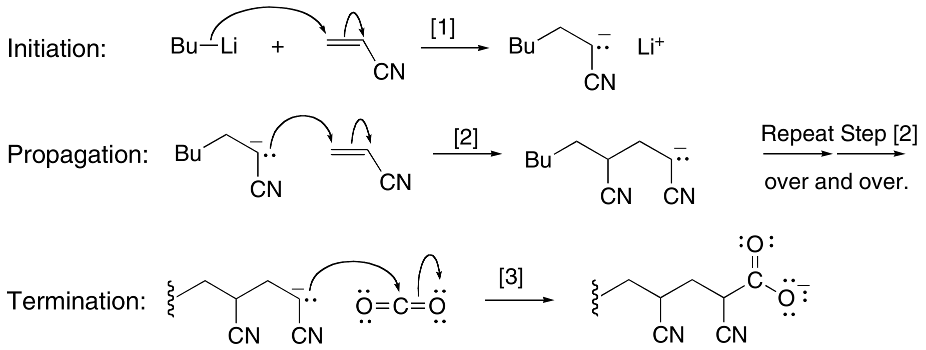
30.6 Cationic polymerization proceeds via a carbocation intermediate. Substrates that form more stable 3° carbocations react more readily in these polymerization reactions than substrates that form less stable 1° carbocations. $CH_2{=}C(CH_3)_2$ will form a more substituted carbocation than $CH_2{=}CH_2$.



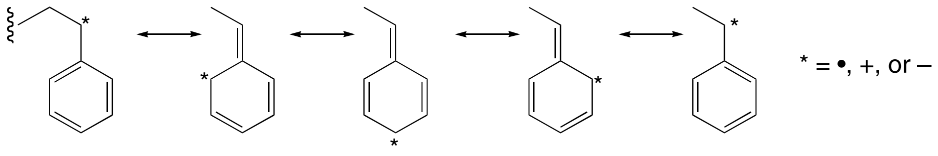
30.7 Cationic polymerization occurs with alkene monomers having substituents that can stabilize carbocations, such as alkyl groups and other electron-donor groups. Anionic polymerization occurs with alkene monomers having substituents that can stabilize a negative charge, such as COR, COOR, or CN.

a. $CH_2{=}C(CH_3)COOCH_3$	b. $CH_2{=}CHCH_3$	c. $CH_2{=}CHOC(CH_3)_3$	d. $CH_2{=}CHCOCH_3$
↑	↑	↑	↑
electron-withdrawing group **anion polymerization**	alkyl group **cationic polymerization**	an electron-donating resonance effect **cationic polymerization**	electron-withdrawing group **anion polymerization**

30.8 Use Mechanism 30.4 as a model of anion polymerization.

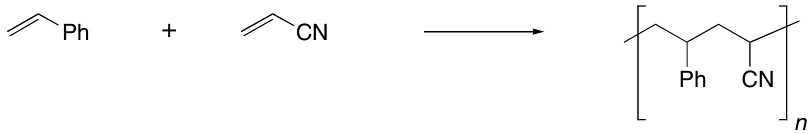


30.9 Styrene ($CH_2{=}CHPh$) can by polymerized by all three methods of chain-growth polymerization because a benzene ring can stabilize a radical, a carbocation, and also a carbanion by resonance delocalization.

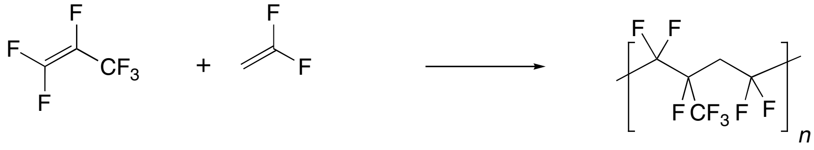


30.10 Draw the copolymers formed in each reaction.

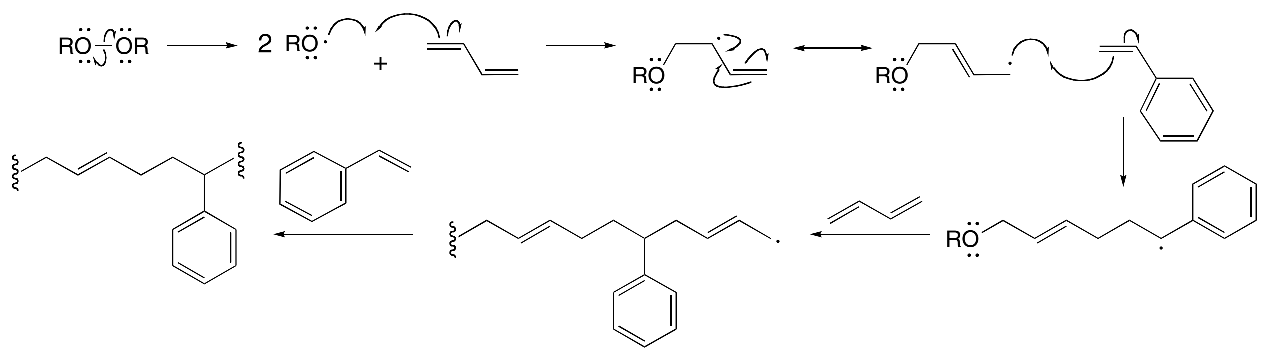
a.



b.

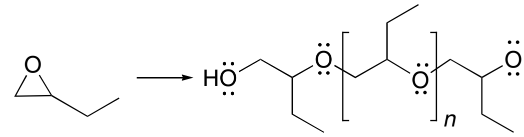


30.11

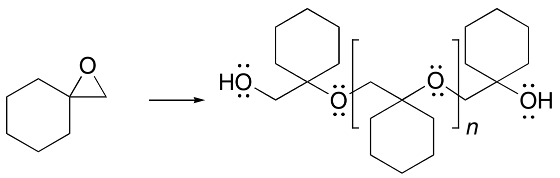


30.12

a.



c.



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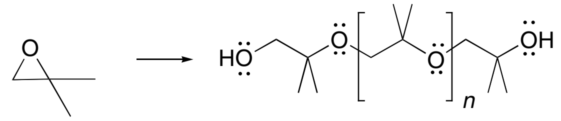
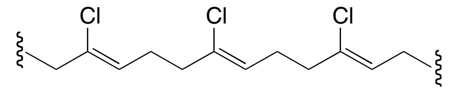
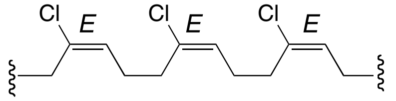


30.13

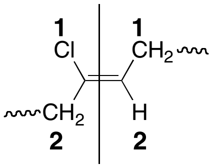


neoprene

All double bonds have the *Z* configuration.

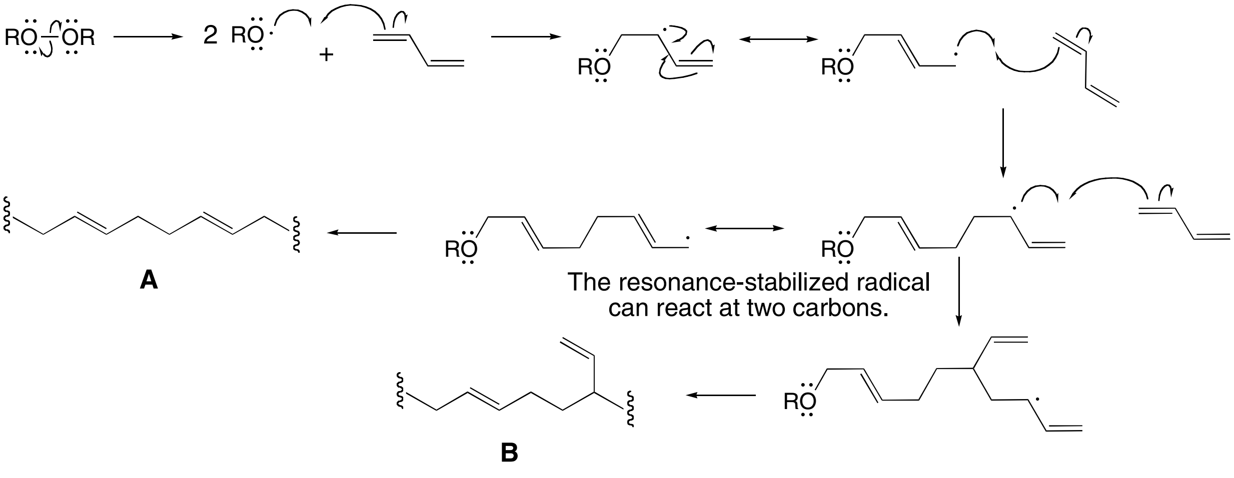


E configuration of each double bond



Two higher priority groups (1's) are on the same side of the double bond - - - > *Z* configuration.

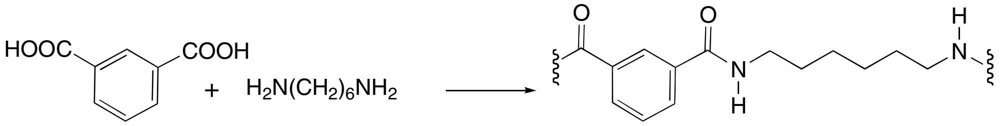
30.14



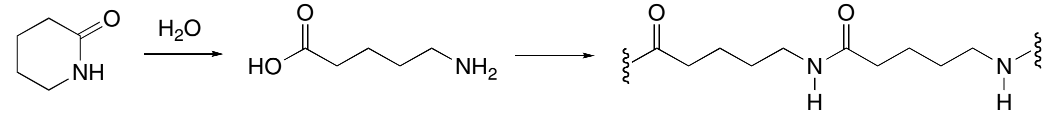
The resonance-stabilized radical can react at two carbons.

30.15

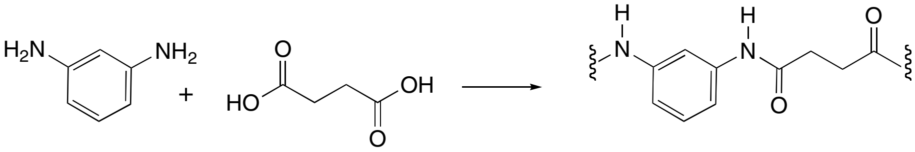
a.



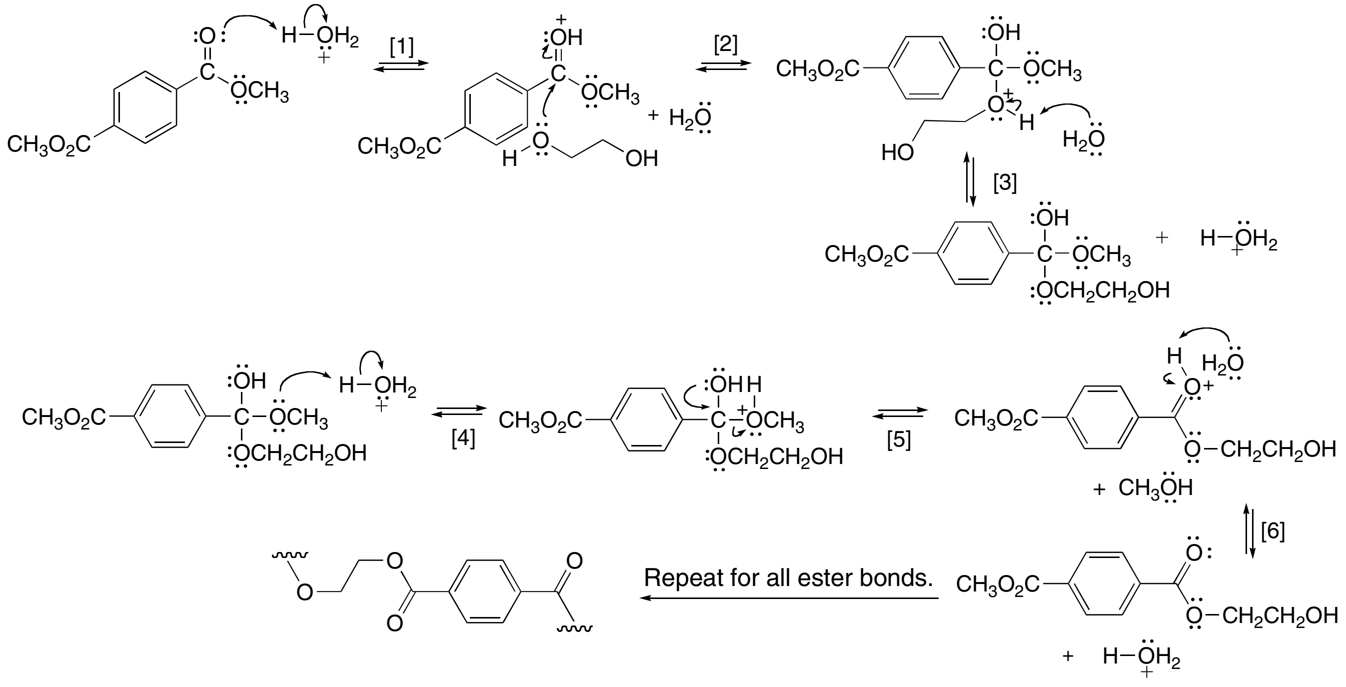
b.



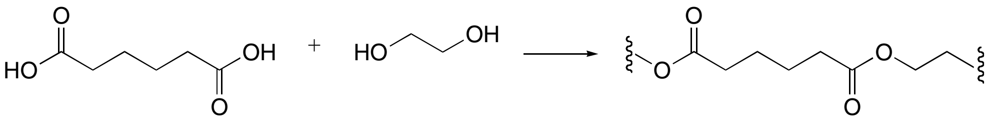
c.



30.16

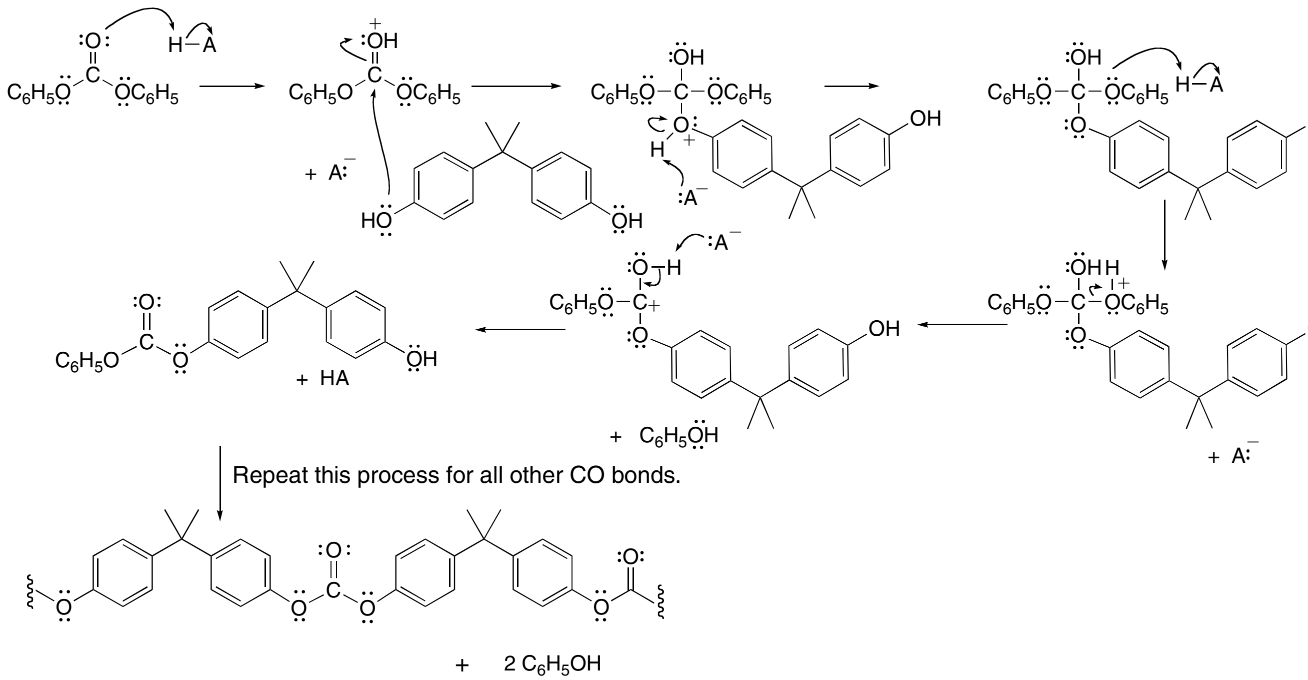


30.17

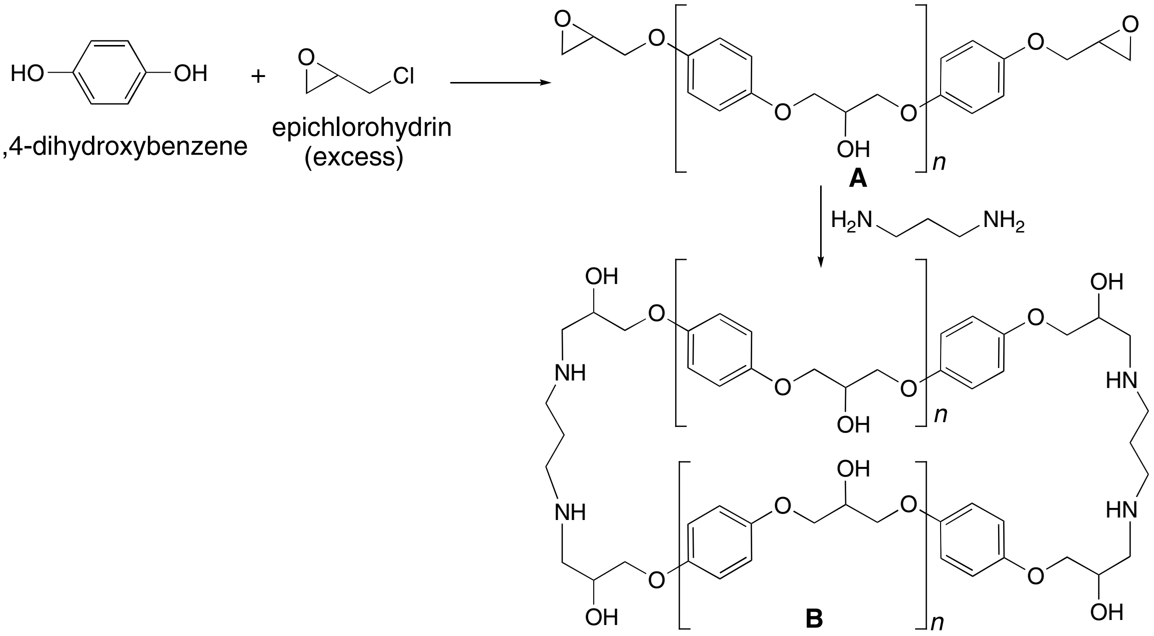


This compound is less suitable than either nylon 6,6 or PET for use in consumer products because esters are more easily hydrolyzed than amides, so this polyester is less stable than the polyamide nylon. This polyester has more flexible chains than PET, and this translates into a less strong fiber.

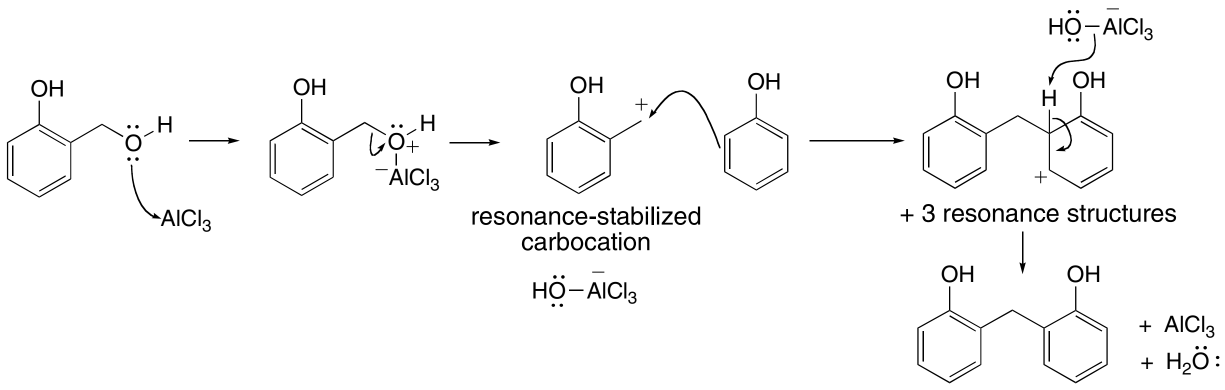
30.18


H–A
+ A:⁻
:A⁻
+ HA
+ C6H5OH
+ A:⁻
Repeat this process for all other CO bonds.
+ 2 C6H5OH

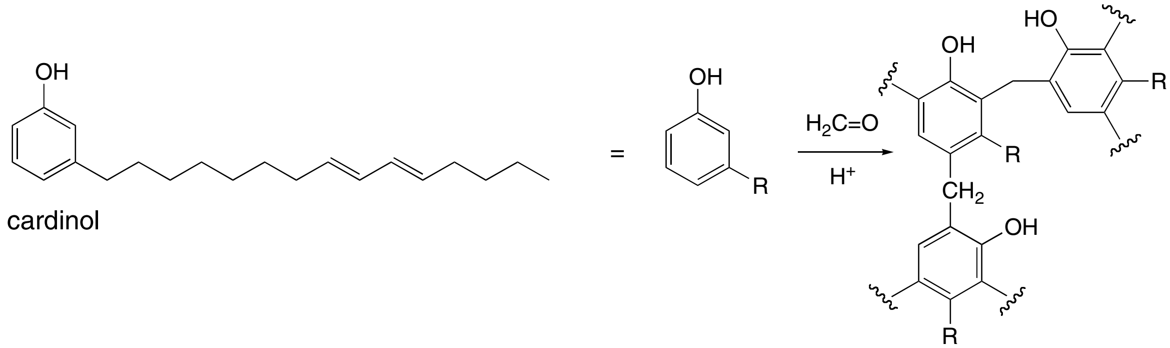
30.19


HO–OH
+
Cl
1,4-dihydroxybenzene
epichlorohydrin (excess)
A
n
H2N NH2
OH
NH
HN
B
n

30.20



30.21



30.22 Chemical recycling of HDPE and LDPE is not easily done because these polymers are both long chains of CH_2 groups joined together in a linear fashion. Since there are only C–C bonds and no functional groups in the polymer chain, there are no easy methods to convert the polymers to their monomers. This process is readily accomplished only when the polymer backbone contains hydrolyzable functional groups.

30.23 a. Combustion of polyethylene forms $CO_2 + H_2O$.

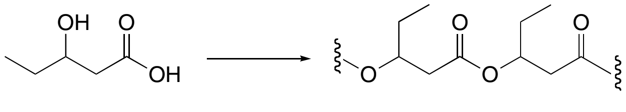
b. Combustion of polyethylene terephthalate forms $CO_2 + H_2O$.

c. These reactions are exothermic.

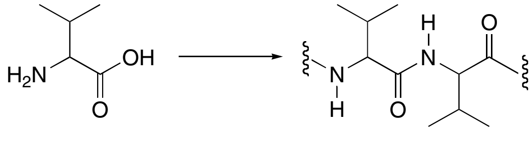
d. HDPE and PET must be separated from poly(vinyl chloride) prior to incineration because combustion of hydrocarbons (like HDPE) and oxygen-containing organics (like PET) releases only $CO_2 + H_2O$ into the atmosphere. Poly(vinyl chloride) also contains Cl atoms bonded to a hydrocarbon chain. On combustion this forms HCl, which cannot be released directly into the atmosphere, making incineration of halogen-containing polymers more laborious and more expensive.

30.24

a.

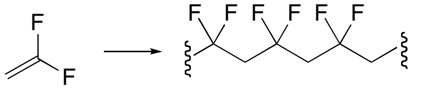


b.

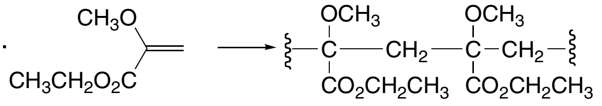


30.25 Draw the polymer formed by chain-growth polymerization as in Answer 30.2.

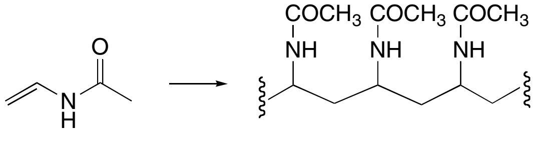
a.



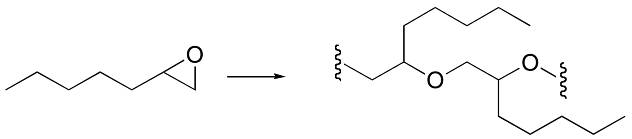
b.



c.

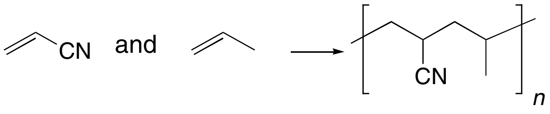


d.



30.26 Draw the copolymers.

a.



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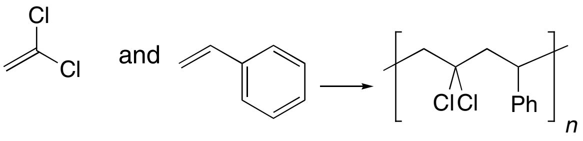

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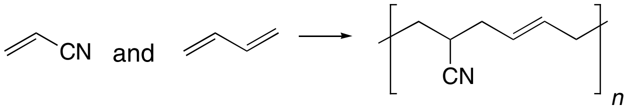
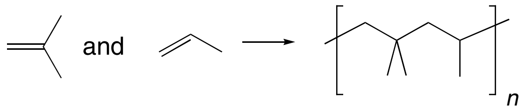
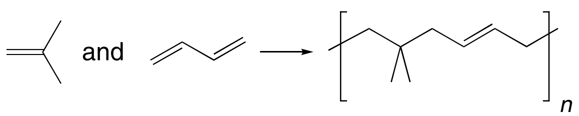


d.

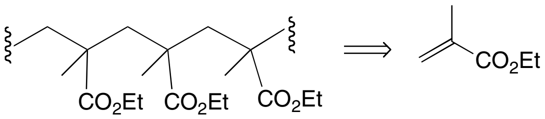


e.



30.27

a.



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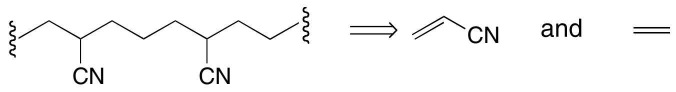
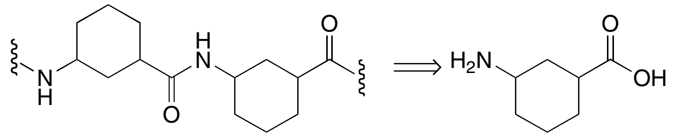
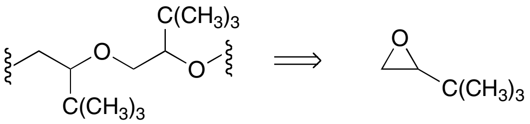


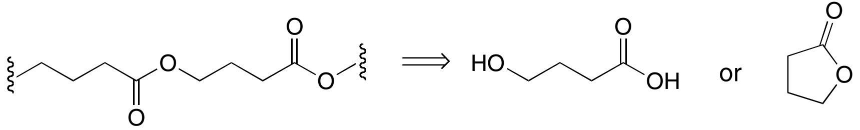
c.



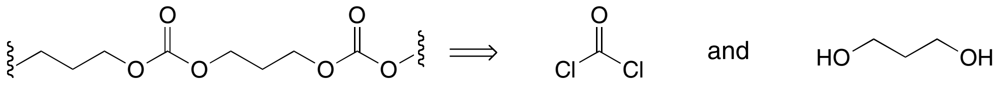
d.



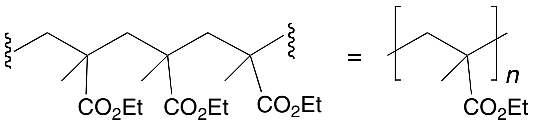
e.

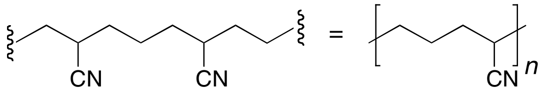


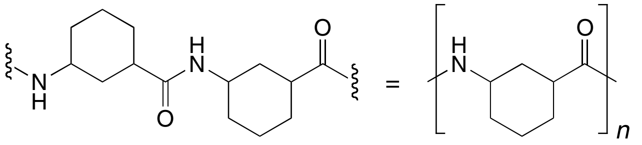
f.



30.28

a.


b.


c.


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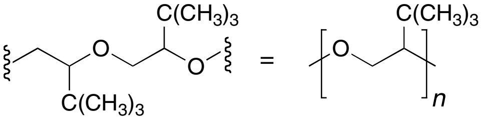

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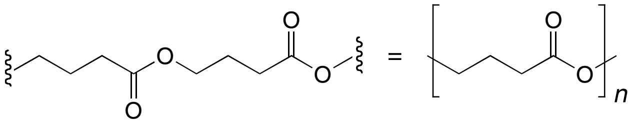

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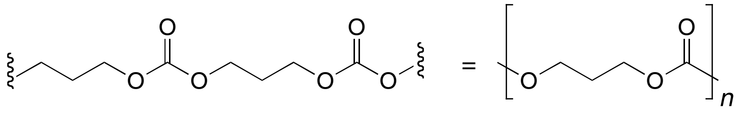
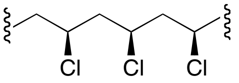


30.29 An **isotactic polymer** has all Z groups on the same side of the carbon backbone. A **syndiotactic polymer** has the Z groups alternating from one side of the carbon chain to the other. An **atactic polymer** has the Z groups oriented randomly along the polymer chain.

a.


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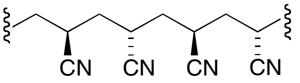

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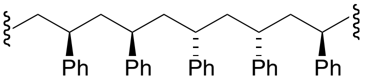
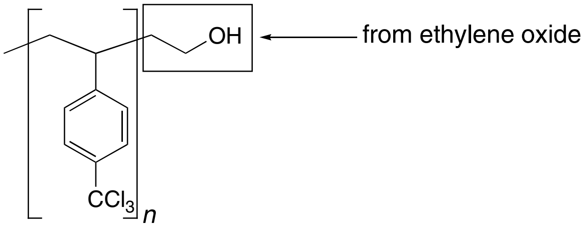
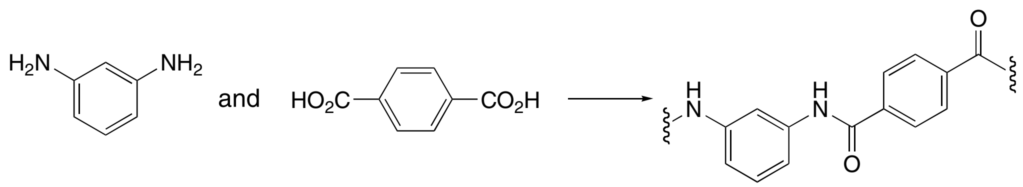


30.30



30.31

a.


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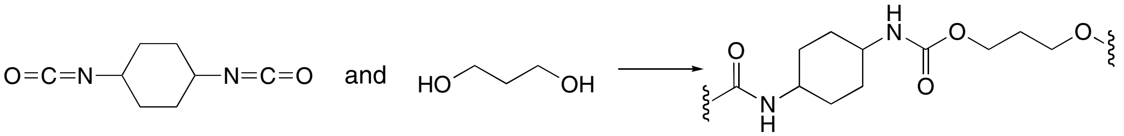

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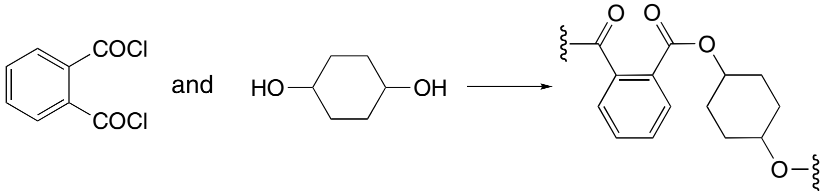

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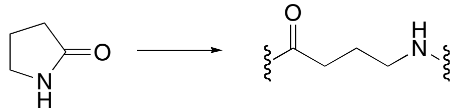

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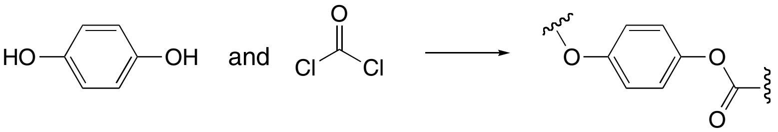

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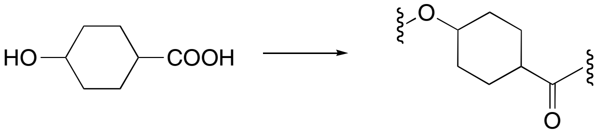
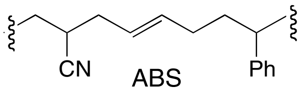
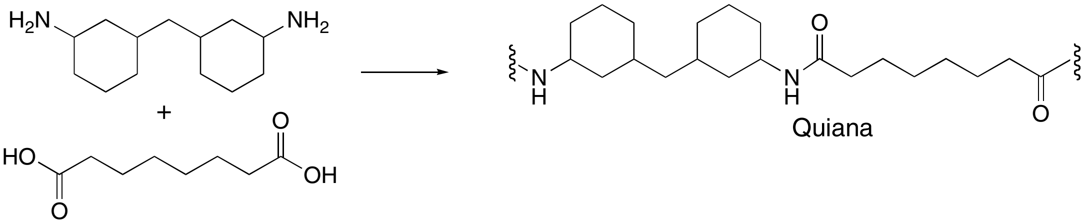


30.32

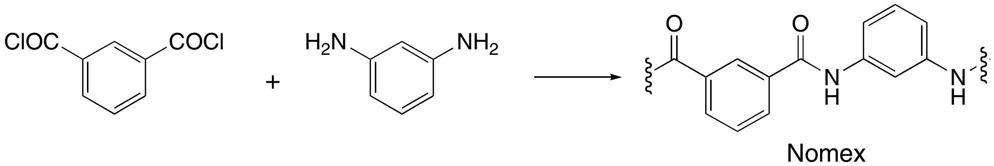


30.33

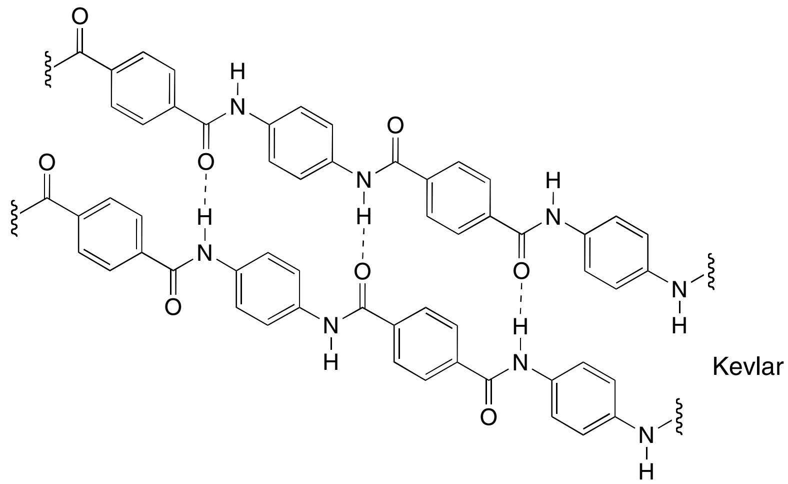
a.



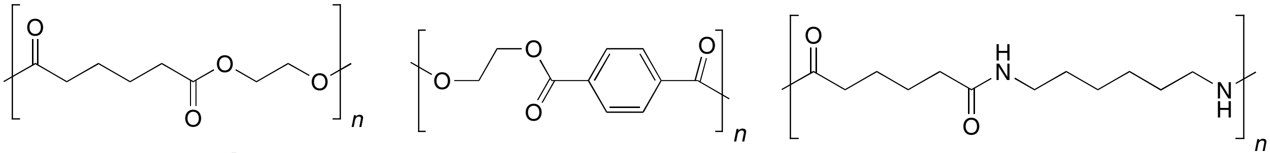
b.



30.34



30.35

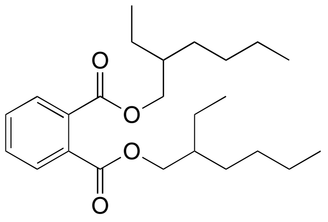


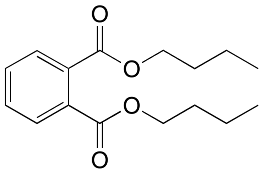
a. Polyester **A** has a lower T_g and T_m than PET because its polymer chain is more flexible. There are no rigid benzene rings so the polymer is less ordered.

b. Polyester **A** has a lower T_g and T_m than nylon 6,6 because the N–H bonds of nylon 6,6 allow chains to hydrogen bond to each other, which makes the polymer more ordered.

c. The T_m for Kevlar would be higher than that of nylon 6,6 because in addition to extensive hydrogen bonding between chains, each chain contains rigid benzene rings. This results in a more ordered polymer.

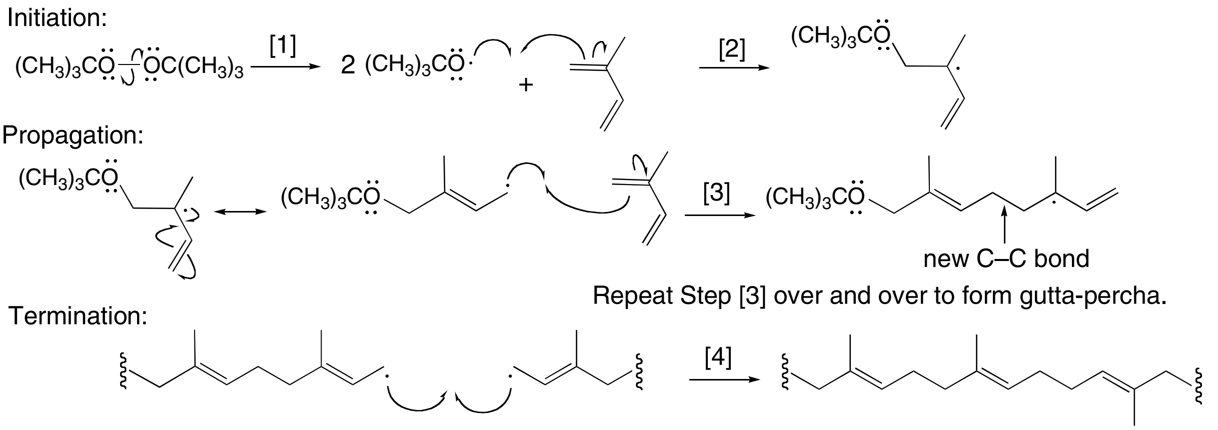
30.36


A


dibutyl phthalate

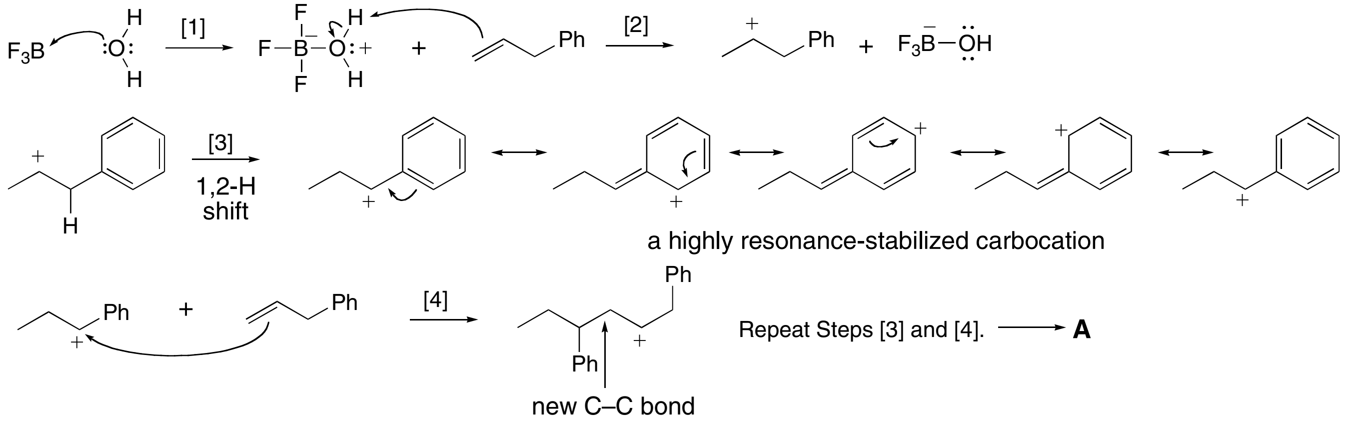
Diester **A** is often used as a plasticizer in place of dibutyl phthalate because it has a higher molecular weight, giving it a higher boiling point. **A** should therefore be less volatile than dibutyl phthalate, so it should evaporate from a polymer less readily.

30.37



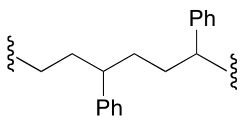
Repeat Step [3] over and over to form gutta-percha.

30.38

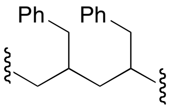


a highly resonance-stabilized carbocation

Repeat Steps [3] and [4]. ⟶ **A**



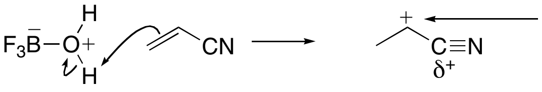
A
major product



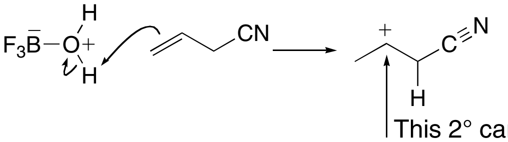
B

A is the major product formed due to the 1,2-H shift (Step [3]) that occurs to form a resonance-stabilized carbocation.
B is the product that would form without this shift.

30.39



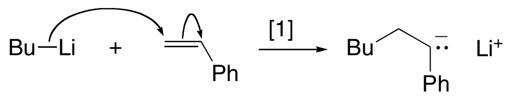
This carbocation is unstable because it is located next to an electron-withdrawing CN group that bears a δ^+ on its C atom. This carbocation is difficult to form, so CH_2=CHCN is only slowly polymerized under cationic conditions.



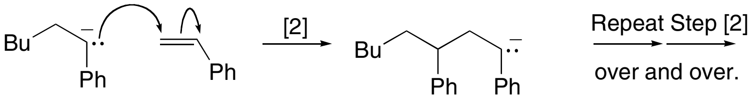
This 2° carbocation is more stable because it is not directly bonded to the electron-withdrawing CN group. As a result, it is more readily formed. Thus, cationic polymerization can occur more readily.

30.40

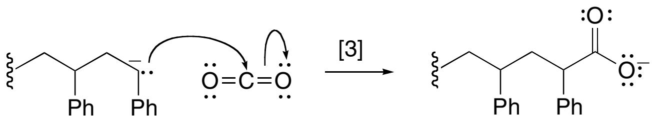
Initiation:



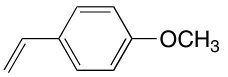
Propagation:



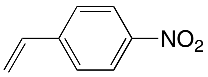
Termination:



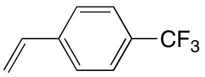
30.41 The substituent on styrene determines whether cationic or anionic polymerization is preferred. When the substituent stabilizes a carbocation, cationic polymerization will occur. When the substituent stabilizes a carbanion, anionic polymerization will occur.

a. 

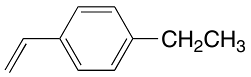
cationic polymerization

b. 

anionic polymerization

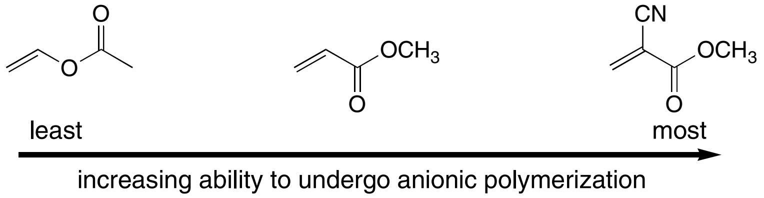
c. 

anionic polymerization

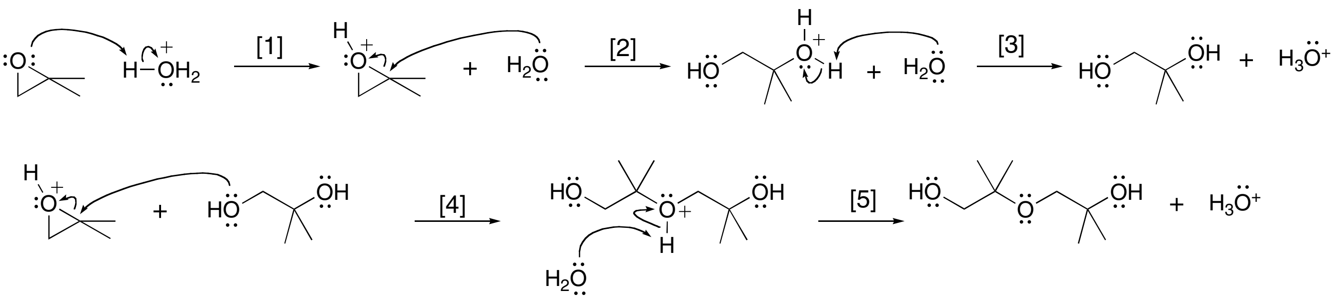
d. 

cationic polymerization

30.42 The rate of anionic polymerization depends on the ability of the substituents on the alkene to stabilize an intermediate carbanion: the better a substituent stabilizes a carbanion, the faster anionic polymerization occurs.

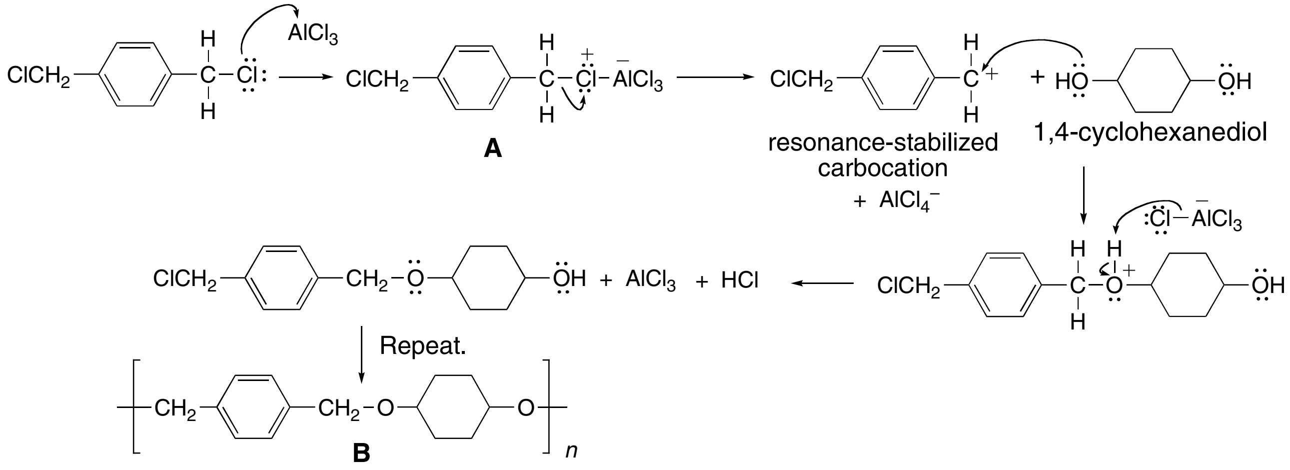


30.43 The reason for this selectivity is explained in Figure 9.9. In the ring opening of an unsymmetrical epoxide under acidic conditions, nucleophilic attack occurs at the carbon atom that is more able to accept a δ^+ in the transition state; that is, nucleophilic attack occurs at the more substituted carbon. The transition state having a δ^+ on a C with an electron-donating CH_3 group is more stabilized (lower in energy), permitting a faster reaction.

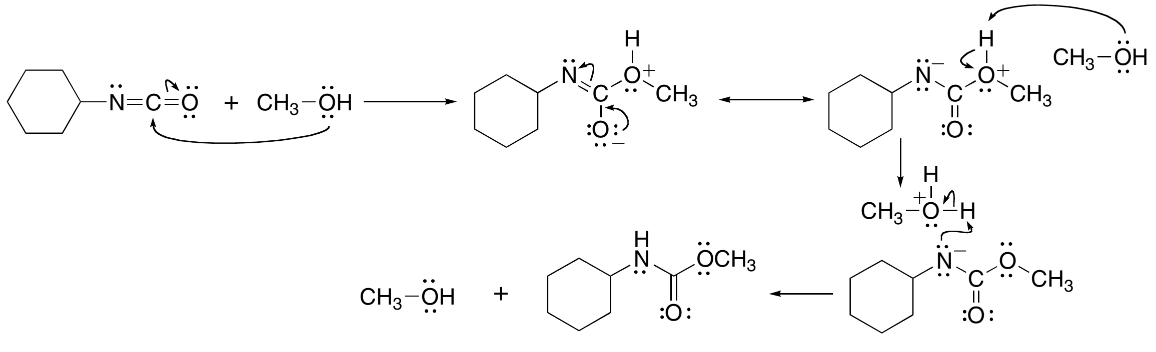


Repeat Steps [4] and [5] over and over.

30.44

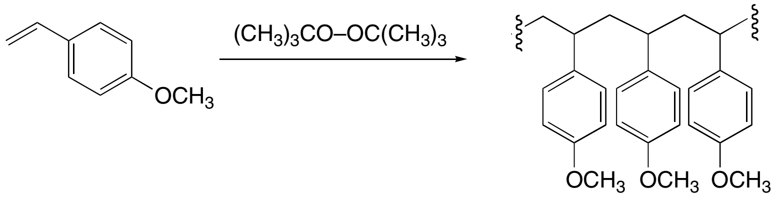


30.45

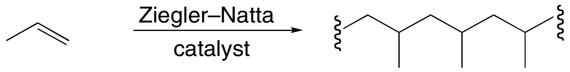


30.46

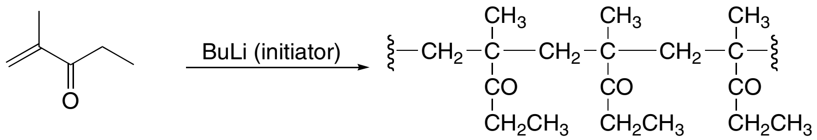
a.



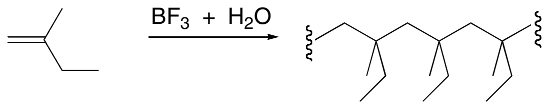
b.



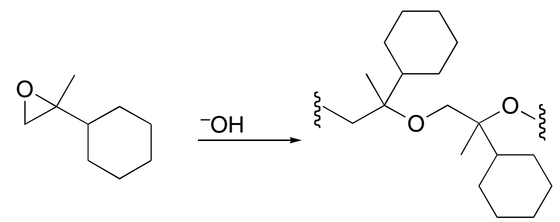
c.



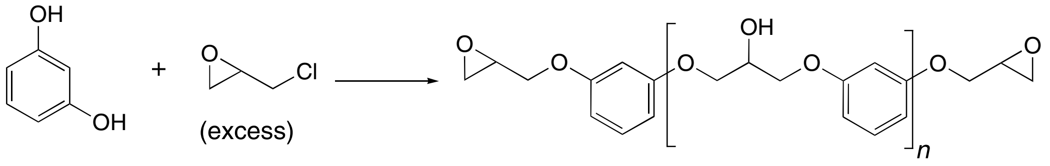
d.



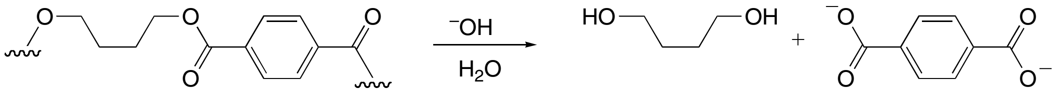
e.



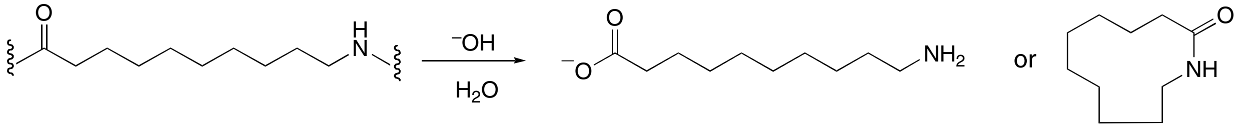
f.



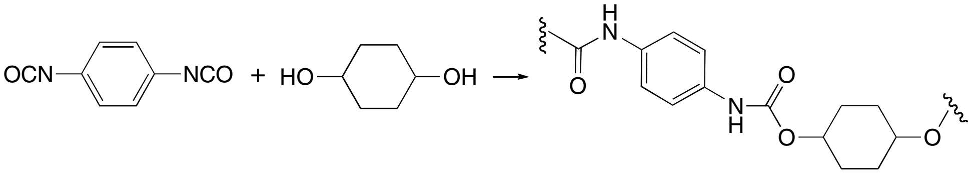
g.



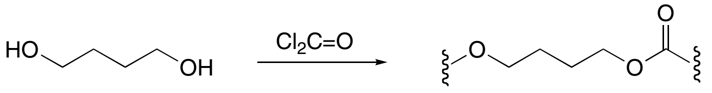
h.



i.

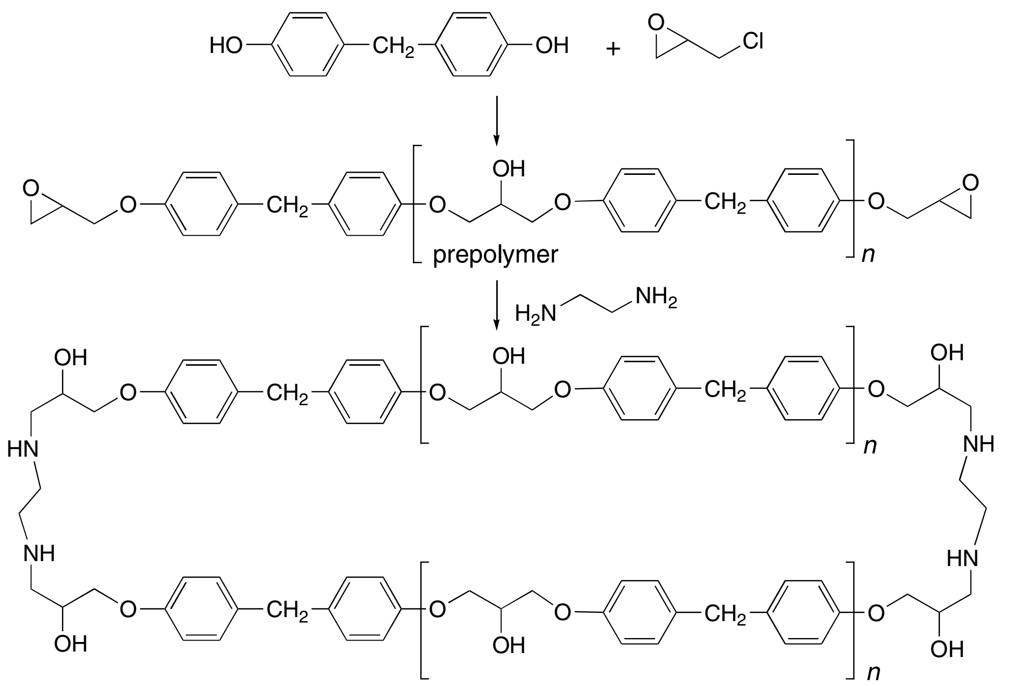


j.



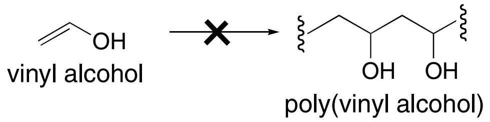
30.47 Polyethylene bottles are resistant to NaOH because they are hydrocarbons with no reactive sites. Polyester shirts and nylon stockings both contain functional groups. Nylon contains amides and polyester contains esters, two functional groups that are susceptible to hydrolysis with aqueous NaOH. Thus, the polymers are converted to their monomer starting materials, creating a hole in the garment.

30.48



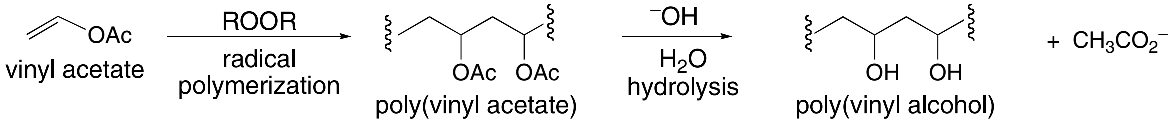
30.49

a.

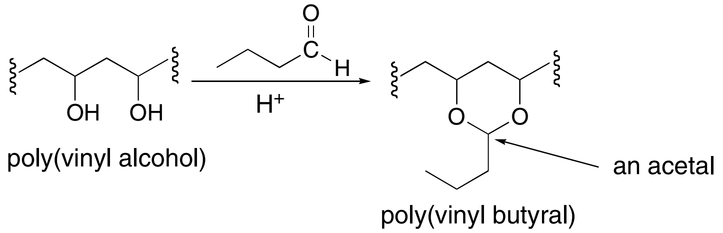


Poly(vinyl alcohol) cannot be prepared from vinyl alcohol because vinyl alcohol is not a stable monomer. It is the enol of acetaldehyde (CH_3CHO), and thus it can't be converted to poly(vinyl alcohol).

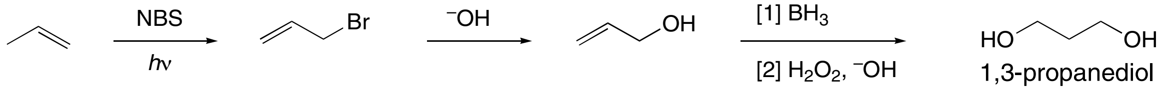
b.



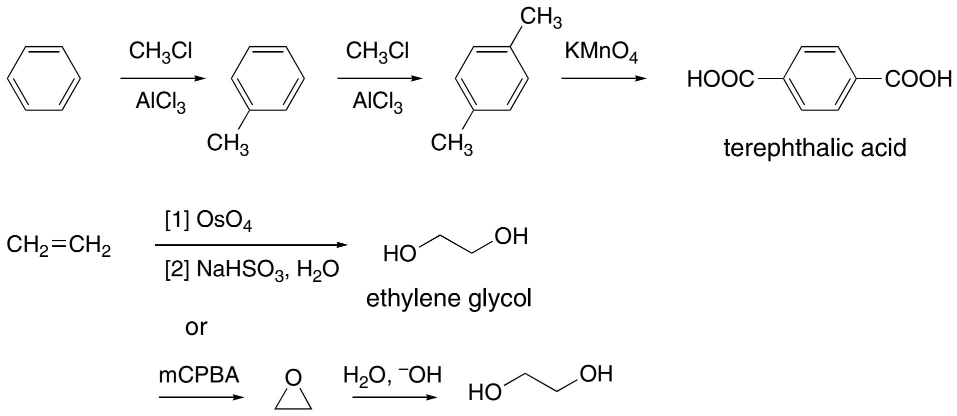
c.



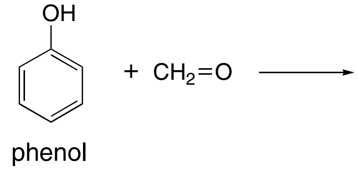
30.50

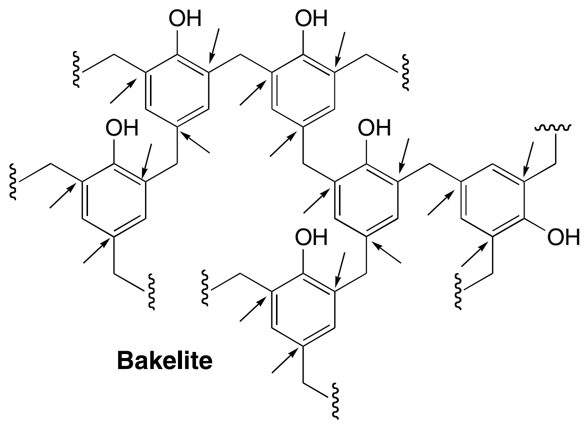


30.51



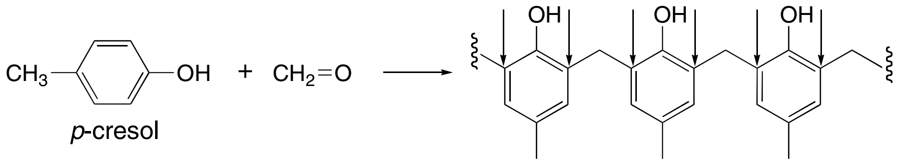
30.52





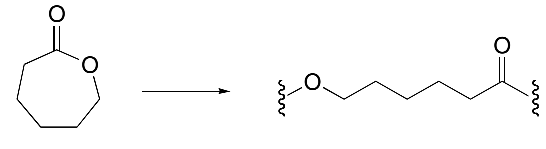
Since phenol has no substituents at any ortho or para position, an extensive network of covalent bonds can join the benzene rings together at all ortho and para positions to the OH groups.

Bakelite

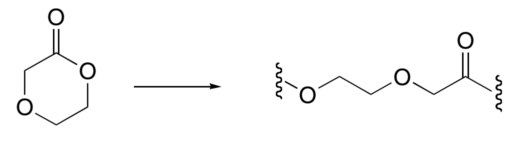


Since *p*-cresol has a CH_3 group at the para position to the OH group, new bonds can be formed only at two ortho positions so that a less extensive three-dimensional network can form.

30.53

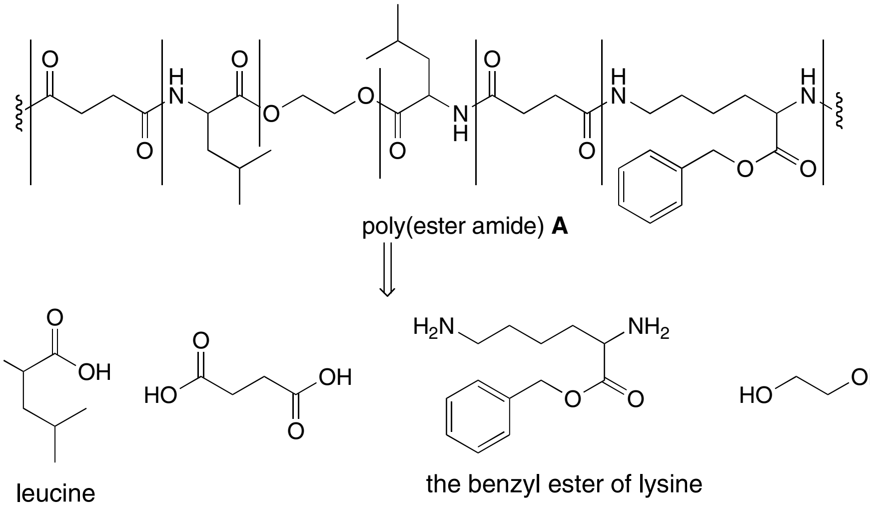
a. 

ε-caprolactone polycaprolactone

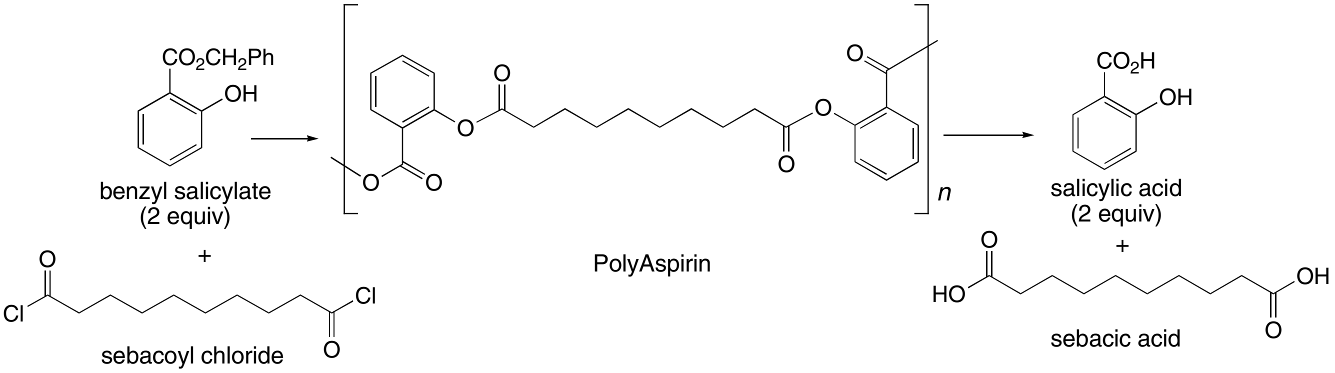
b. 

p-dioxanone polydioxanone

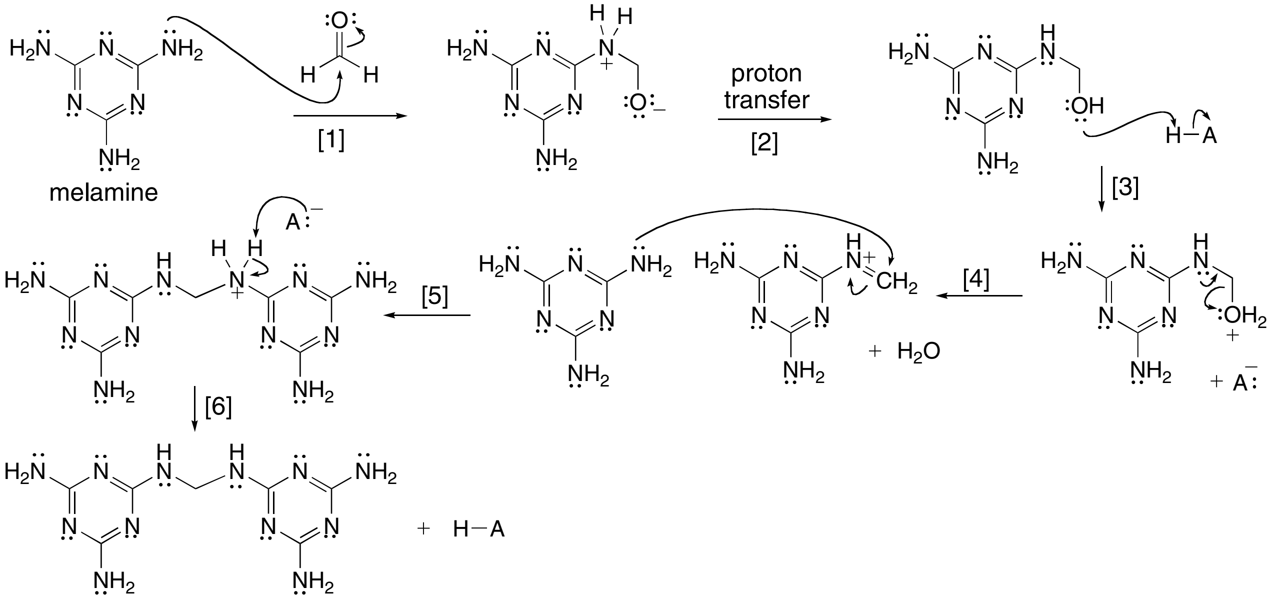
30.54



30.55

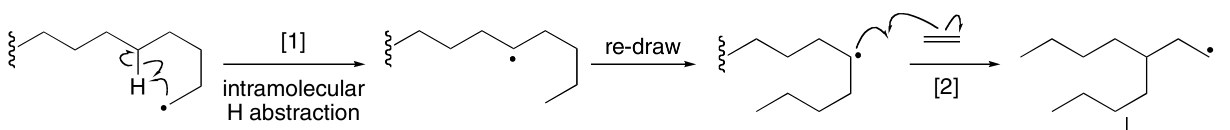


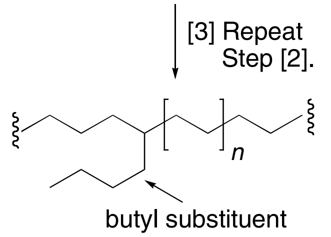
30.56



30.57

a.





b. Abstraction of the H is more facile than abstraction of the other H's because the H atom that is removed is six atoms from the radical. The transition state for this intramolecular reaction is cyclic, and resembles a six-membered ring, the most stable ring size. Other H's are too far away or the transition state would resemble a smaller, less stable ring.

30.58