

생유기화학
(*Bioorganic Chemistry*)

Synthetic Polymer-III
(합성고분자-3)

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임정균 교수



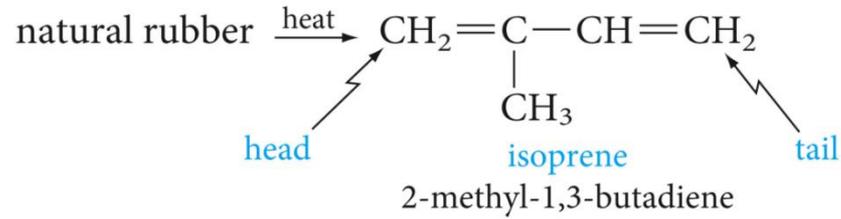
6. Diene Polymers: Natural and Synthetic Rubber

Natural rubber is an unsaturated hydrocarbon polymer.

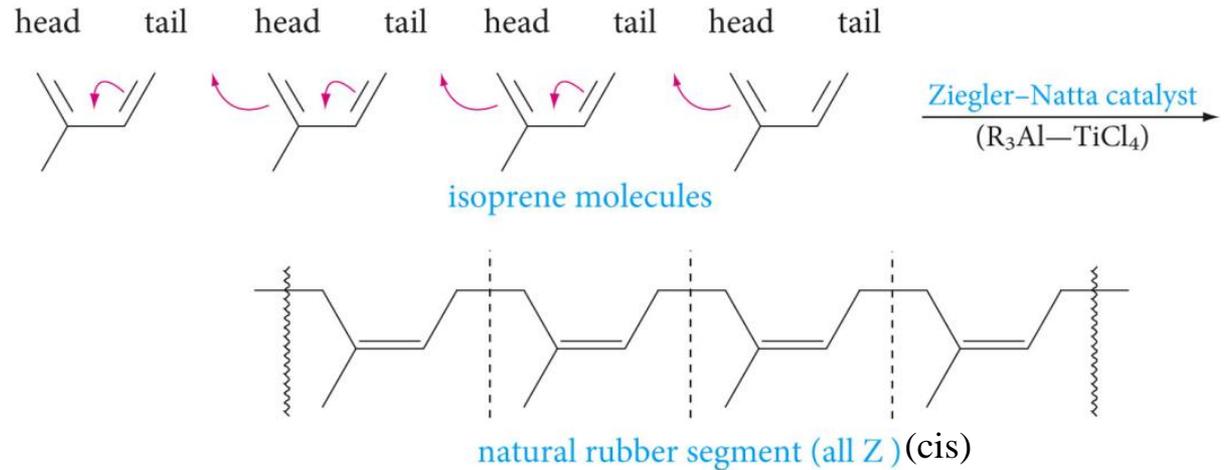


Latex (natural rubber) is obtained from the rubber tree.

(열대 수종의 수액으로부터 얻어짐)



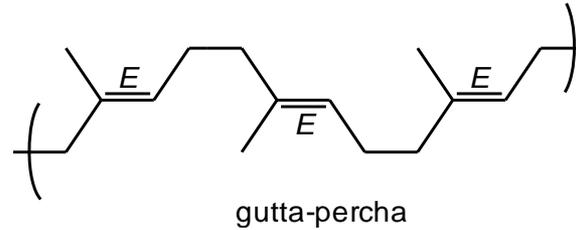
Ziegler-Natta촉매를 이용하여 인공적으로 합성도 가능하다.



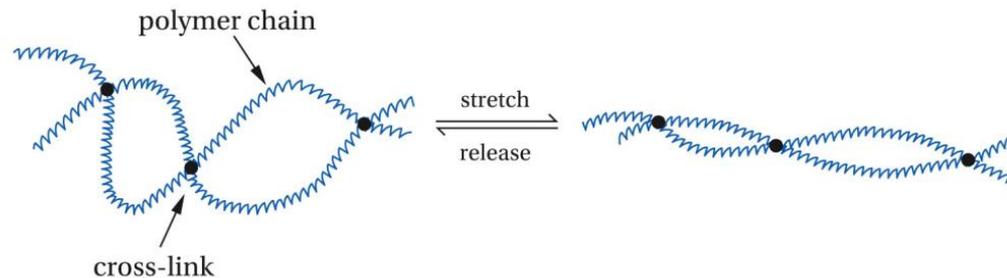
double bond가 계속 남아있고, Z geometry를 갖고 있다.
(cis polymer)

Problem 9. Gutta-percha is also a polymer of isoprene with E double bonds. Draw the structural formula for a three-monomer segment.

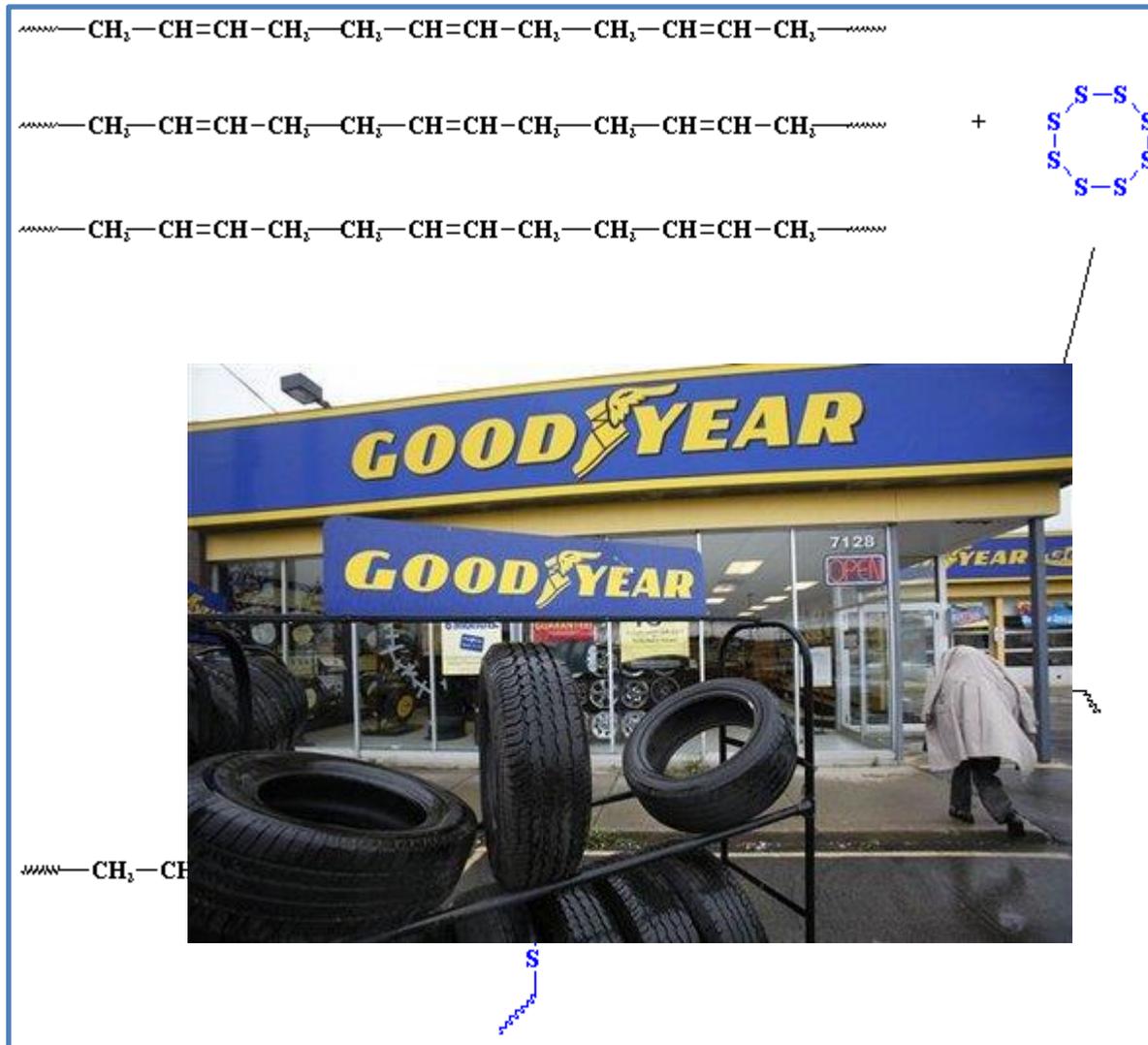
힌트: isopropene의 구조가 다름.



- 대부분의 고무는 원료와 제조 방법에 따라 다르지만 보통 분자량이 1백만을 넘고 이 경우 단량체가 15,000개 이상이다.
- 천연 (Crude) rubber는 폴리프로필렌 이외에도 2.5~3.5%의 단백질, 2.5~3.2%의 지방, 0.1~1.2%의 물, 그리고 소량의 무기물이 포함되어 있다.
- 천연고무는 가끔 끈적거리거나 불쾌한 냄새가 나거나 더운 날에는 물렁물렁해지고 추워지면 딱딱해지는 단점이 있다.
- **Vulcanization(가황)** 처리를 하면 폴리머 사슬들이 cross linking(가교)을 일으켜 고무를 더 강하게 만들 수 있다. 또한 고무가 늘어난 후에 다시 원래의 모양으로 복원되는 일종의 ‘기억’으로 작용한다.

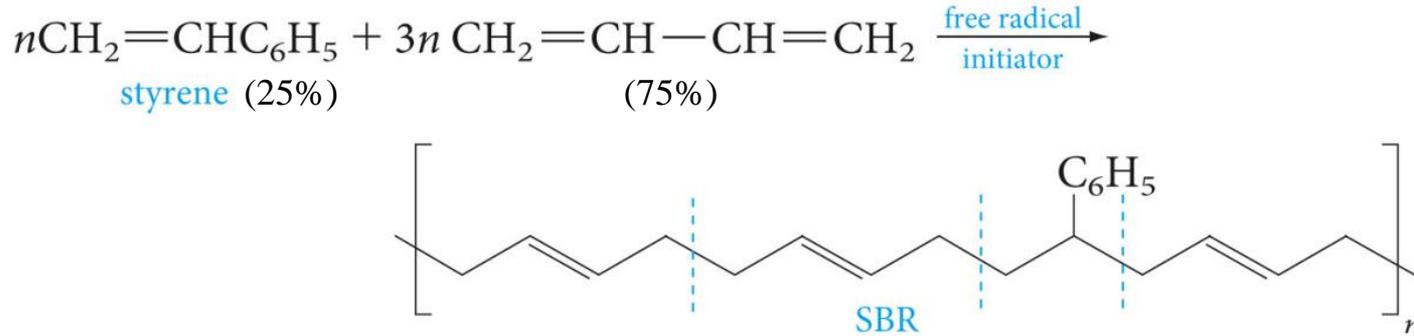


1839년에 어떤 호기심 많은 이가 천연고무를 좀 더 쓸모 있는 형태로 만들게 되었습니다. 이 사람이 세계적인 기업가인 찰스 굿이어(Charles Goodyear)입니다. 그는 천연고무가 든 항아리를 들고 부엌 주위를 배회하던 중 실수로 유황을 항아리에 쏟아붓고 말았습니다. 이 우연한 사고 이후 그는 이 황을 머금은 고무가 녹지 않고 열을 가하면 끈적거리게 되지 않는다는 것을 알게 되었죠. 또한 매우 추운 겨울 날씨에도 쉽게 깨지지 않는 것을 알아냈습니다. 그는 이것을 가황 고무(vulcanized rubber)라 불렀습니다.



- 그럼에도 불구하고, 천연고무로 타이어를 만들 경우 타이어의 공기압을 자주 체크해야했다. 고무가 다소 다공성(porous)이 있기 때문이었다.
- 천연 고무와 유사하면서도 화학적으로는 개선된 성질을 가지는 합성 고무(synthetic rubber)가 개발 되었다.

Elastomer: rubber-like polymer



대표적인 elastomer

Styrene-butadiene rubber (SBR)

- 20%의 butadiene은 1,4 addition이 아닌 1,2 addition 방식으로 중합되기도 한다.
- 천연고무와 달리 double bond는 E geometry를 갖고 있다.
- 점선은 각 단량체 단위를 보여준다.
- SBR의 연간 생산량은 천연 고무 생산량의 두 배 이상이다.

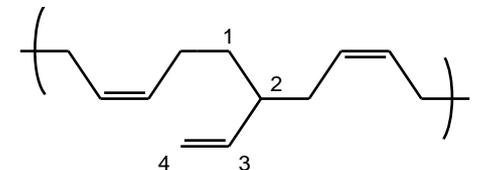
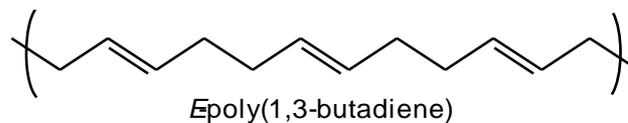
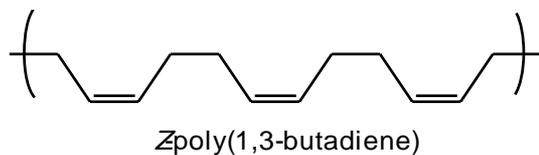


SBR에 carbon black이라는 충전제를 넣어서 타이어의 내구성을 10배 이상 증가시킬 수 있다.
(타이어가 검은 이유)

Carbon black은 탄성체에 가장 널리 사용되는 충전제이며, 강직도, 인장강도, 내마모성 등을 향상시키는 역할을 한다.

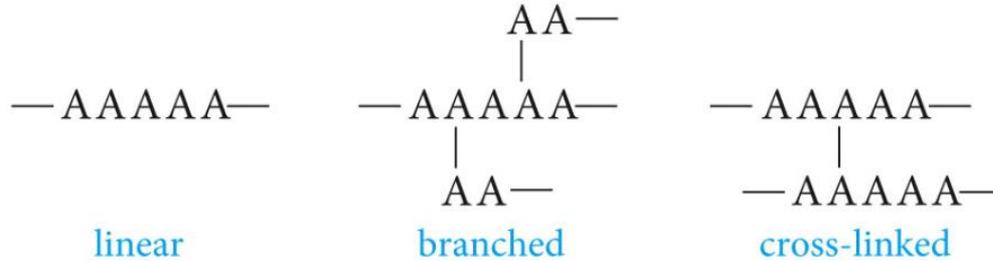
Problem 14.10 Draw the structural formula for a three-monomer segment of poly(1,3-butadiene) in which

- addition is 1,4 and double bonds are Z
- addition is 1,4 and double bonds are E
- addition is 1,2 for the middle unit and 1,4 for the outer units, with double bonds Z

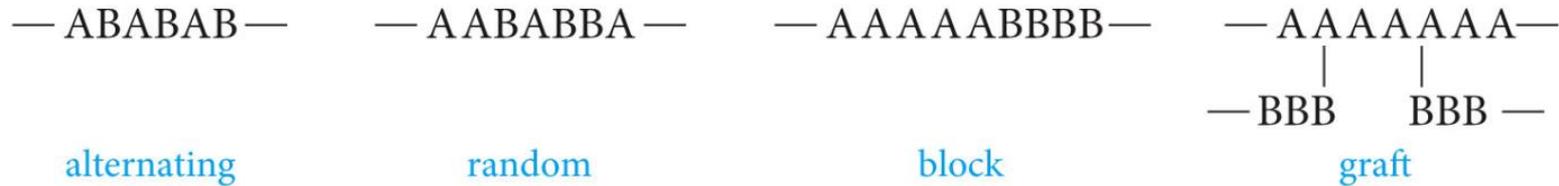


7. Copolymers (공중합체)

Homopolymers (단일 중합체) 한가지 monomer로부터 만든 폴리머

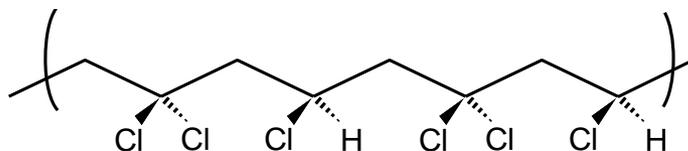


Copolymers (공중합체) monomer mixture로부터 만든 폴리머



- Radical A• reacts rapidly with B but slowly with A, and B• reacts rapidly with A but slowly with B. alternating —ABABAB— .
- Monomers A and B are equally reactive: random —AABABBA— .
- Monomer A is much more reactive than B toward all radicals. A will be consumed first, followed more slowly by B. A mixture of two homopolymer: $\text{—(A)}_n\text{—and—(B)}_m\text{—}$

Problem 11. 1,1-dichloroethene and vinyl chloride form a copolymer. The monomer units tend to alternate in the chain. Draw the structural formula for a 4-monomer segment.



Block copolymer와 graft copolymer는 특별한 방법으로 만들어진다.



block

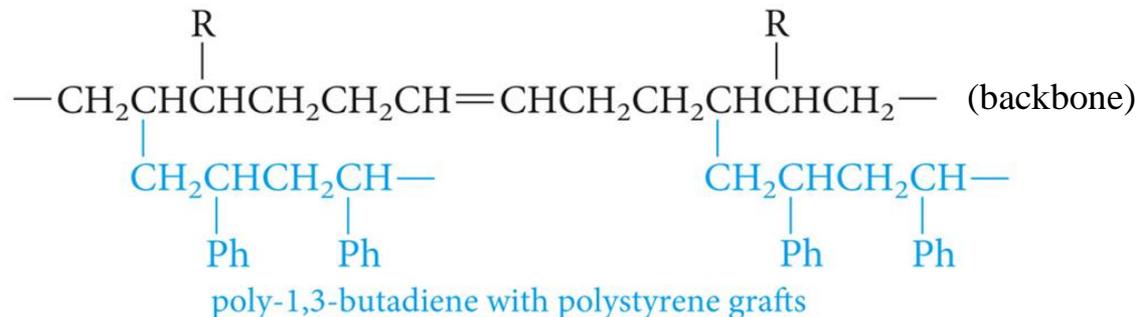


graft

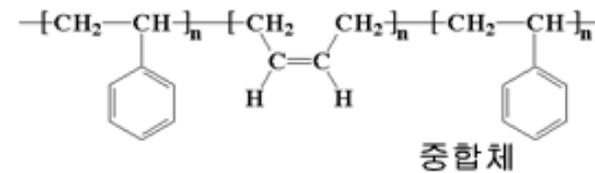
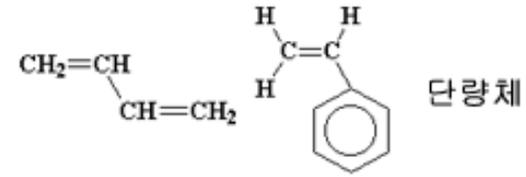
Block copolymer: Monomer A가 모두 중합시켜서 소진하여 block A를 만들고, monomer B를 첨가하여 중합을 시작하면 block B가 만들어진다.

Graft copolymer: Monomer A로 이루어진 homopolymer를 만든 후, monomer B를 첨가하여 homopolymer 사슬에 있는 작용기(double bond)로부터 새로운 중합반응을 시켜서 새로운 block을 접목시킨다.

Addition of free radical initiator $R\cdot$ and second monomer (styrene) will graft onto the polybutadiene backbone.



SBS고무 (Poly(styrene-butadiene-styrene))



- SBS고무(Poly(styrene-butadiene-styrene), SBSR)는 딱딱한 고무로서 신발 밑창, 타이어 등과 같이 내구성이 요구되는 곳에 사용된다.
- 블록 공중합체로서 단량체로서 스티렌과 부타디엔을 사용하고 있다.
- 아래 그림과 같이 폴리스티렌사슬사이에 폴리부타디엔사슬이 연결된 구조이다.



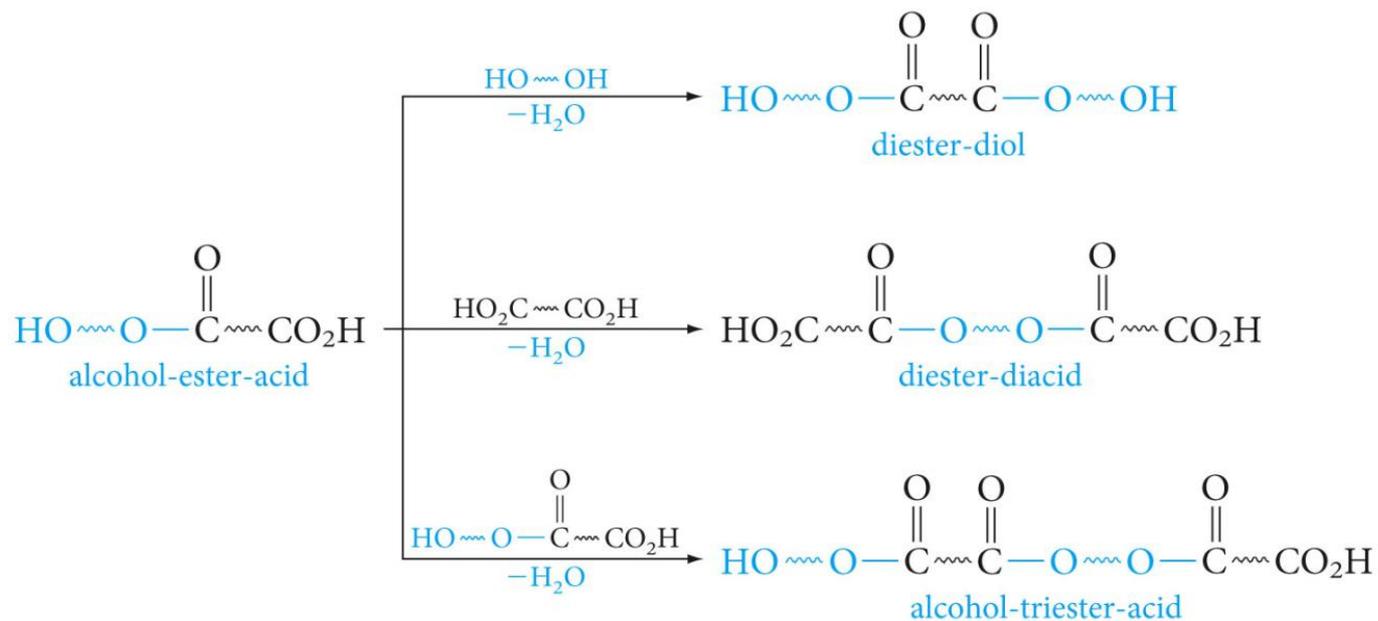
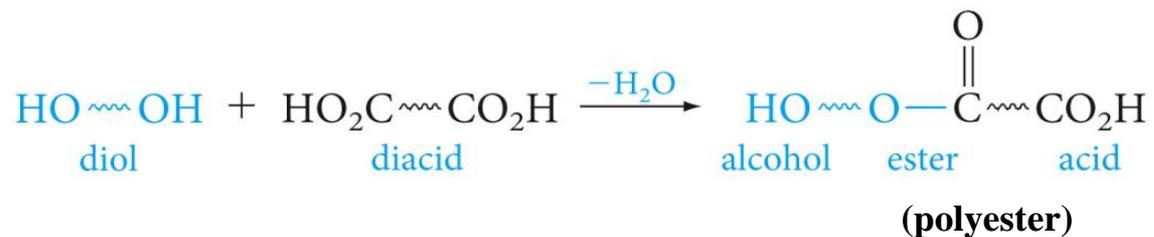
(Block copolymer)

PS (polystyrene) : glassy

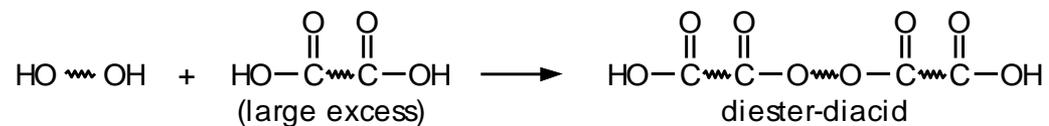
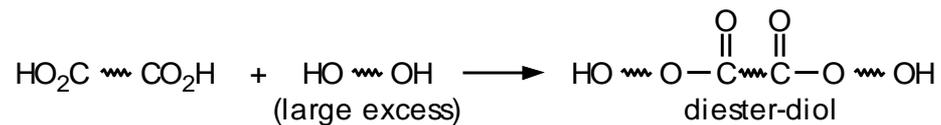
PB (polybutadiene) : rubbery

8. Step-Growth Polymerization: Dacron and Nylon

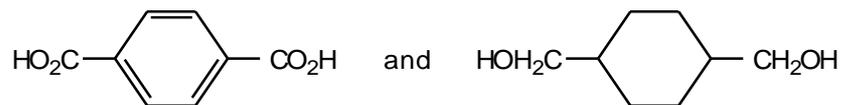
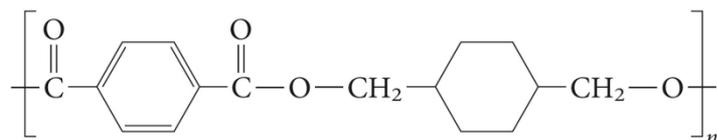
Reaction between two monomers which are difunctional.



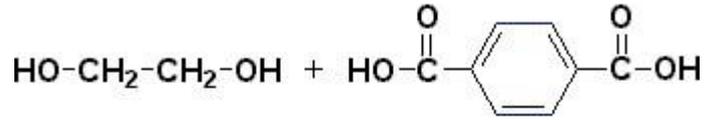
Problem 13. What product will be formed if a diacid is treated with a large excess of a diol?
 If a diol is treated with a large excess of a diacid?



Problem 14. Kodel is a polyester with the following structure, from what two monomers is it made?

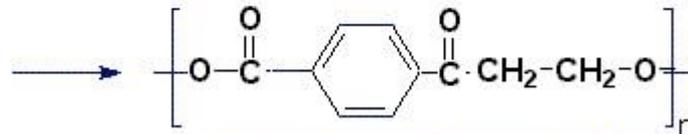


Biodegradable polymers



Ethylene Glycol

Terephthalic Acid



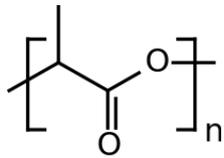
Polyethylene Terephthalate
(PET, PETE, Dacron(brand name))



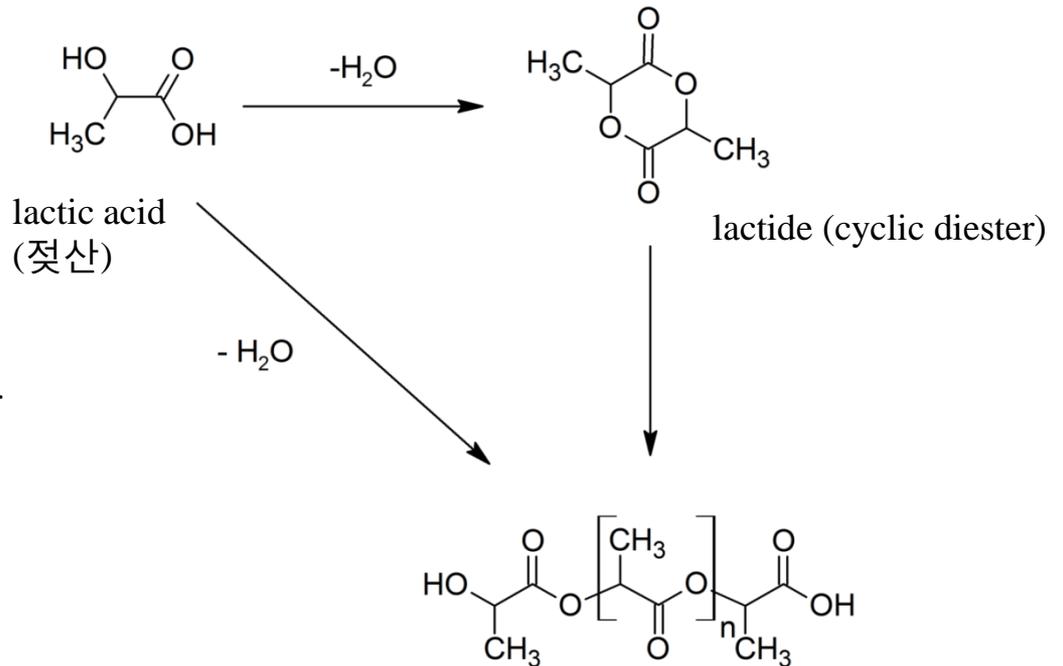
spun into fiber, textile



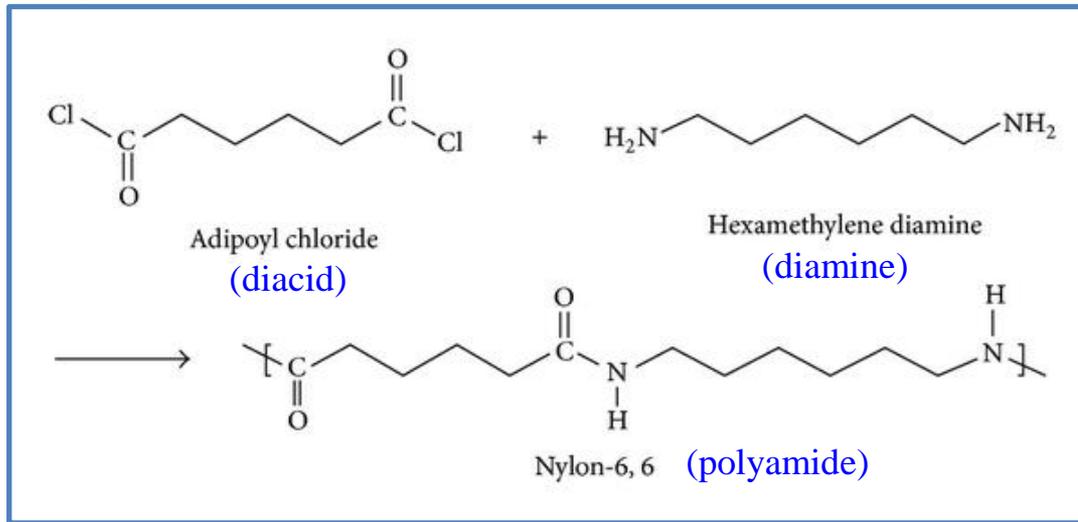
Poly(lactic acid), (PLA)



a biodegradable thermoplastic aliphatic polyester



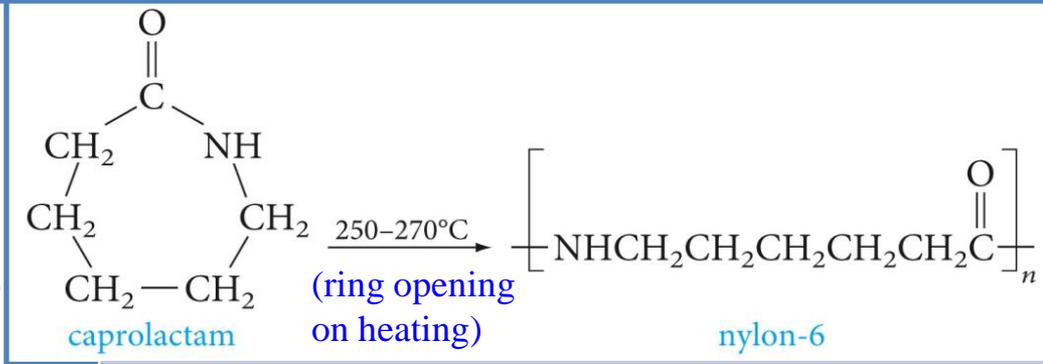
Nylon: polyamide step growth polymer



spun into fibers

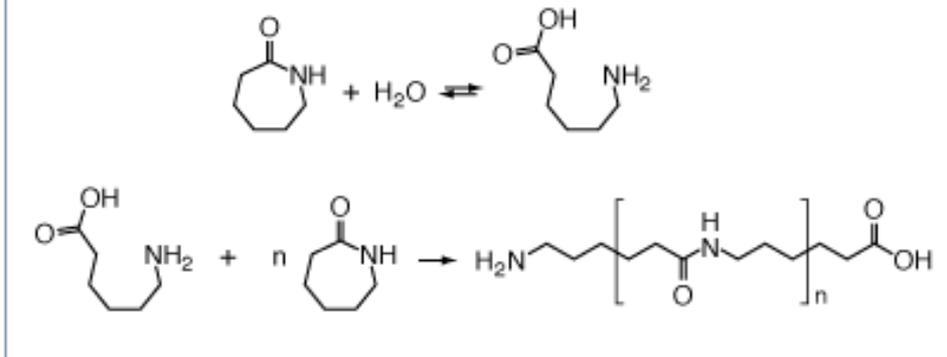
1938년 Dupont에서 스타킹으로 판매

(cyclic amide = lactam)

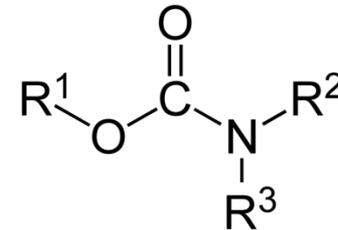
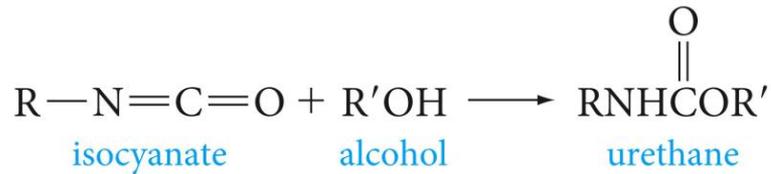


Nylon-6,10등도 있다.

Polymerisation of ε-caprolactam to polyamide 6

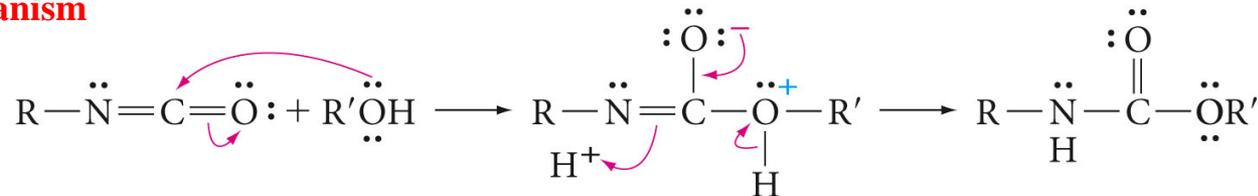


9. Polyurethanes and Other-Step Growth Polymers



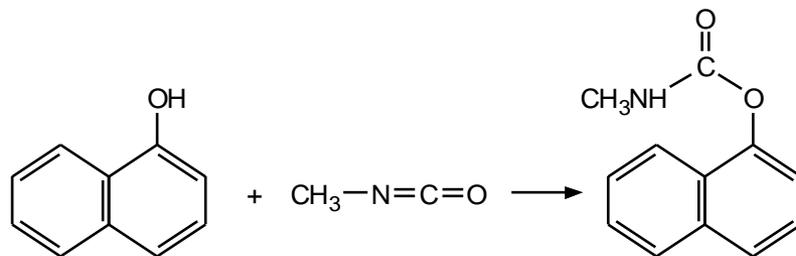
urethane (carbamate)의 구조: a single carbonyl group에 ester와 amide group이 있다.

mechanism

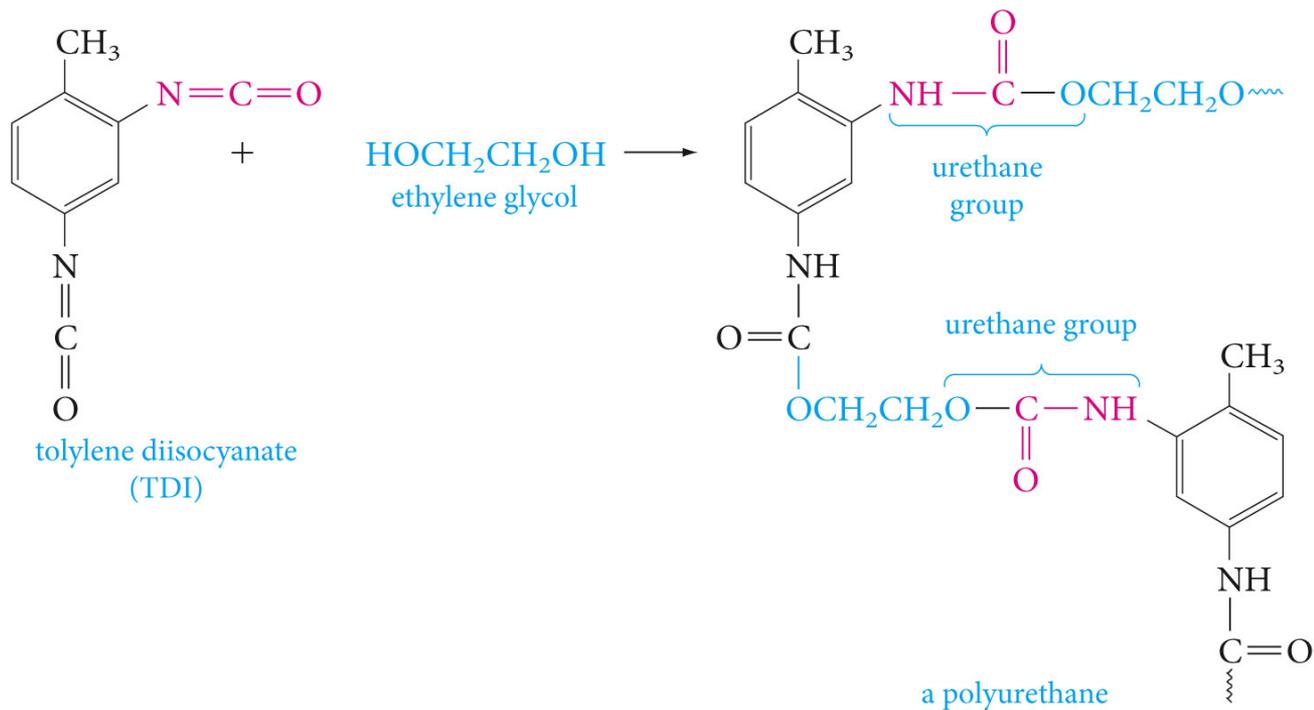


Polyurethane은 diisocyanate와 diol의 step growth polymerization으로 얻어진다.

Problem 15. 1-Naphthyl-*N*-methylcarbamate is made from methyl isocyanate and 1-naphthol. Write the equation.



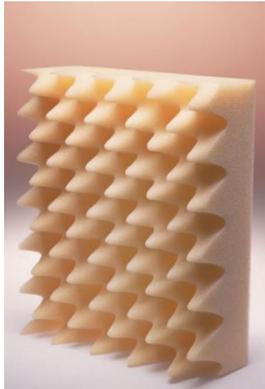
No small molecule is eliminated.



Polyurethane을 foam(포말) 형태로 제조하고 싶을 때....



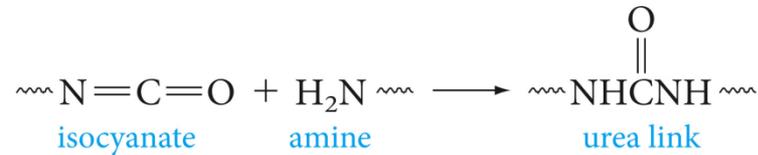
polyurethane varnish(니스)



polyurethane foam

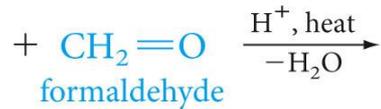
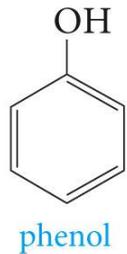


- 물을 소량 첨가, 물은 isocyanate와 반응이 가능하다.
- 중간체인 carbamic acid는 불안정하여 쉽게 분해되어 amine과 CO₂를 배출한다.
- 기포가 생겨서 foam 형태가 된다. 즉 첨가된 물의 양으로 foam의 밀도가 결정된다.

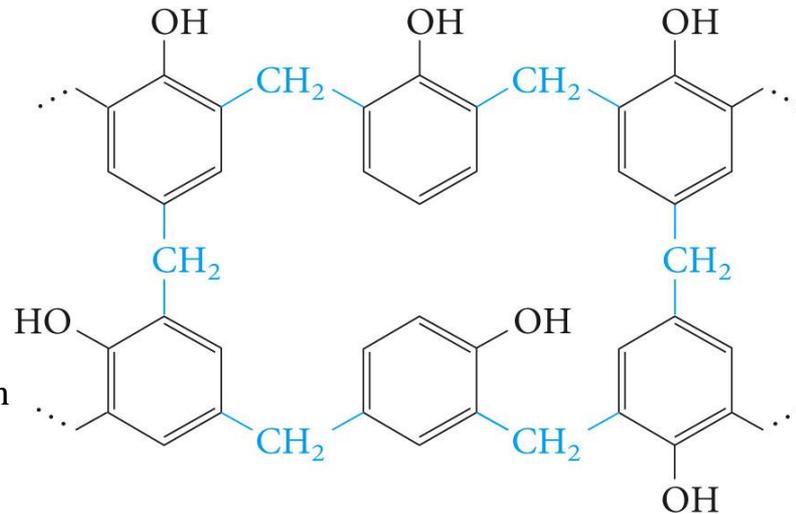


- 생성된 amine은 다시 isocyanate와 반응을 해서 urea를 만들 수가 있다.
- 이것은 cross linking (가교) 역할을 한다.
- Cross linking이 적을 경우: 신축성이 우수한 섬유 (Spandex, Lycra)가 된다.

Other step-growth polymers



(electrophilic substitution reaction)

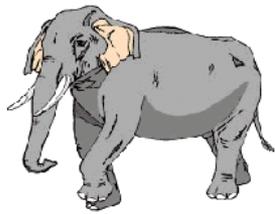


segment of Bakelite

(highly cross-linked, ortho- and para position에 methylene group)

Thermosetting polymer(열경화성 고분자): 가열하면 가교가 더 진행되어 딱딱하고 불용성인 물질로 변함, 원래의 상태로 돌아가지 않음.

Bakelite는 기구 손잡이, 고온에서 견딜 수 있는 missile nose cone의 제조에 쓰인다.

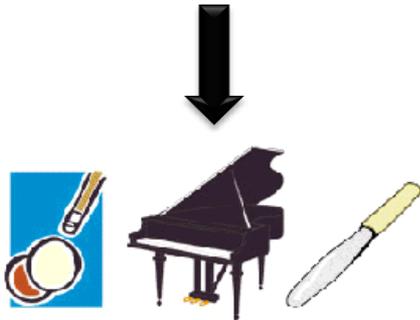


Ivory was highly prized for its beauty, durability, and suitability for carving.

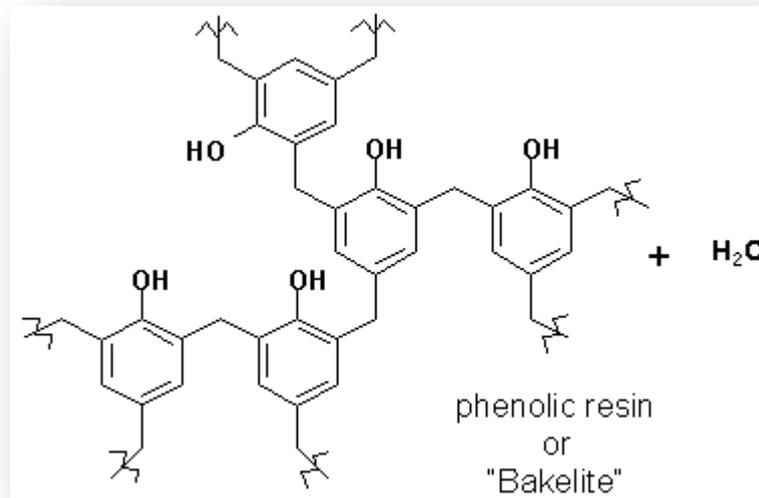
The teeth of the hippopotamus, walrus, narwhal, sperm whale, and some types of wild boar are also composed of ivory, however never found much commercial value because of their small size.

Since ancient times, ivory was used widely.

Unless a replacement had been found, elephants would now be extinct. There was a great need for a synthetic material to replace elephant-tusk ivory. In 1907, the Belgian chemist Leo Baekeland developed a synthetic replacement, called Bakelite. This is made by another polymerization process, between phenol and formaldehyde heated together. The reactions are complex, but the final result is a hard "plastic" made of crosslinked polymer chains.



(당구공, 피아노키, 칼 손잡이)



This was the first true synthetic material (there are no natural analogues). It was used for billiard balls, piano keys and knife handles from 1907, and rapidly replaced ivory.

Mechanism of formation of Bakelite

