3a) first, we need to make the soft segment macrodiol → HO~~OH

(slight excess) $HO-CH_2CH_2OCH_2CH_2OH$ + $HOC(=O)(CH_2)_4C(=O)OH$ $\xrightarrow[\Delta]{-H_2O}$

see below $HOCH_2CH_2OCH_2CH_2O\left(C(=O)(CH_2)_4C(=O)OCH_2CH_2OCH_2CH_2O\right)_{20}H$

↳ to synthesize a soft segment with 20 repeat units (on average), we need a polymer with 40 structural units (2 structural units per repeat unit)

Taking into account the structural unit outside of the repeating units, we have

$$\overline{DP}_n = 41 = \frac{1+r}{1-r} \Rightarrow \boxed{r = 0.952}$$

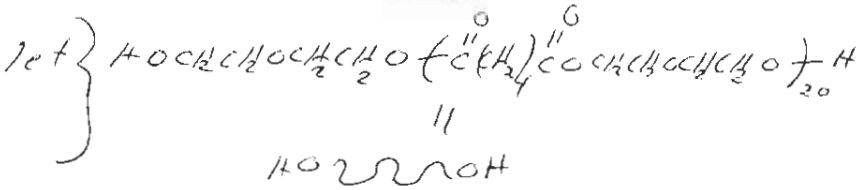
Thus, 1.05 moles of dialcohol should be reacted with 1.0 moles of diacid

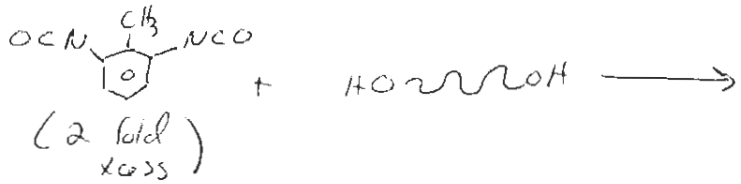
$$\left[ r = \frac{[COOH]_0}{[OH]_0} = 0.952 \right]$$

– we then use a 2-stp synthesis to create the segmented polyurethane-urea

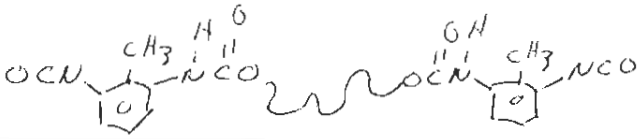
(3a cont)

**Step 1 (end capping step)**

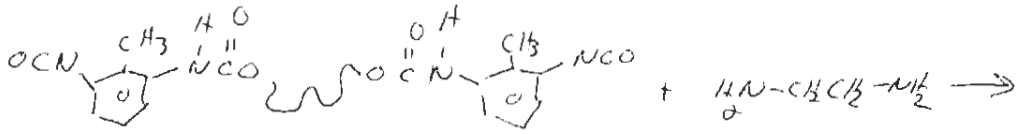


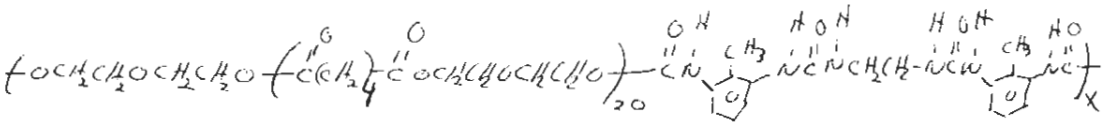


(2 fold excess)



**Step 2 (chain extension step)**





Soft Segment

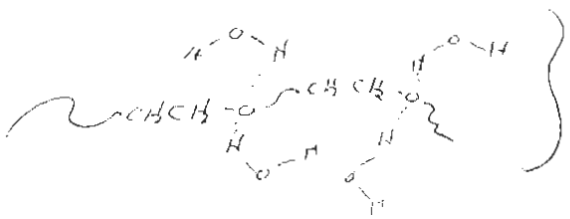
Hard Segment

(36)

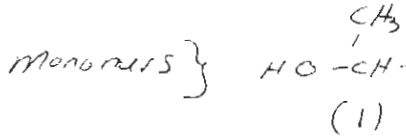
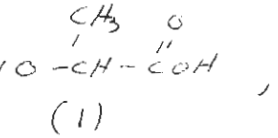

the isolated hard segments act as virtual crosslinks, thereby creating a material that is a tough elastomer (has "snap"). Any biomedical application that requires a tough flexible elastomer would be a good choice for a segmented polyurethane-urea. examples include: Synthetic implants like the Jarvic heart

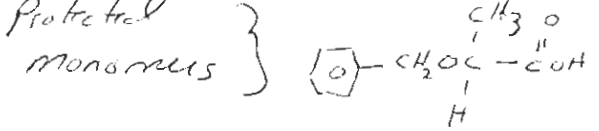
also note the the soft-segments in this case, look like poly(ethylene oxide) $-CH_2CH_2OCH_2CH_2O-$
(have segments that)
$\rightarrow$ $+CH_2CH_2O+_n$

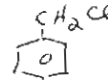
ethylene glycol segments of this type become highly hydrated and hence help resist the attachment of proteins, imparting some level of "bioinertness" to the implant



(4a)

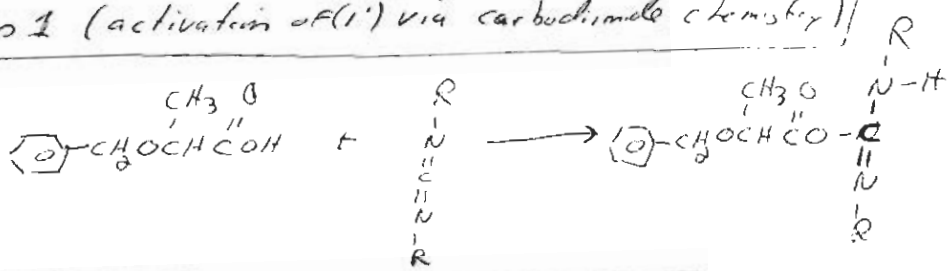
Monomers }  (1) ,  (2)

Protected Monomers }  (1') , (2') 

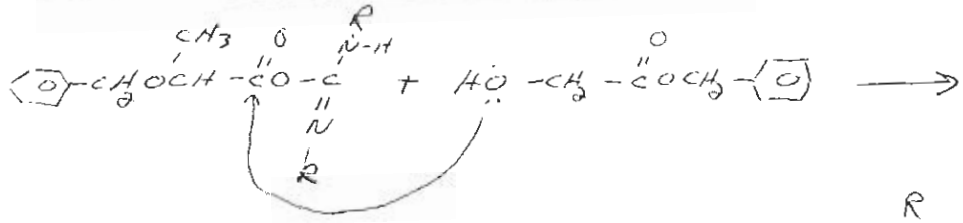
↳ (protected by reaction with  )

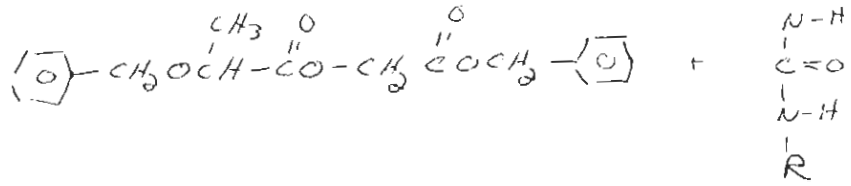
---

**Step 1 (activation of (1') via carbodiimide chemistry)**



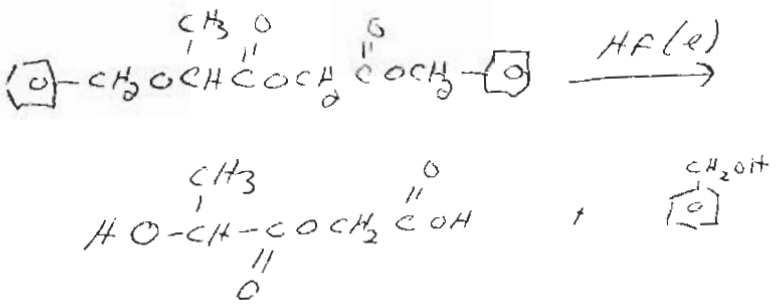
**Step 2 (reaction of activated (1') with (2'))**





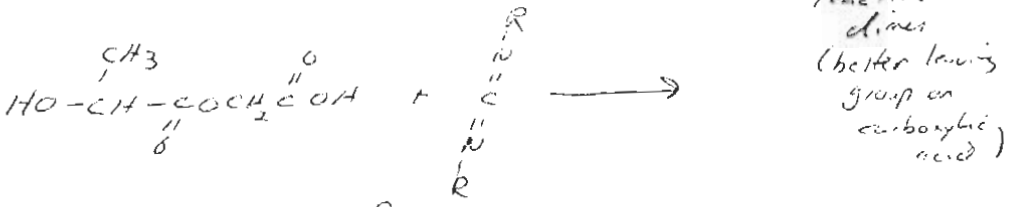
(4/4 cont)

**Step 3 (deprotection step)**

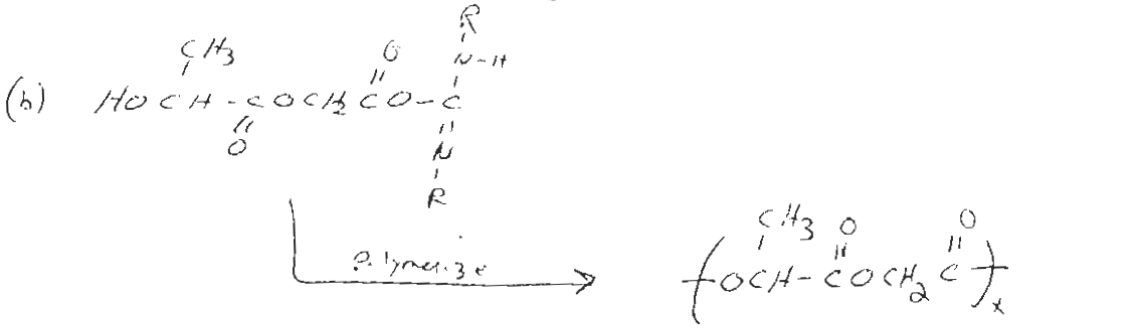


**Step 4 polymerization**

(a) 1st activate dimer with $R-N=C=N-R$ to make a more reactive dimer (better leaving group on carboxylic acid)



(b)



note: activation of the acid group with carbodiimide chemistry limits the amount of ester interchange that can take place during a direct esterification reaction. ester interchange would produce a random copolymer!

↳