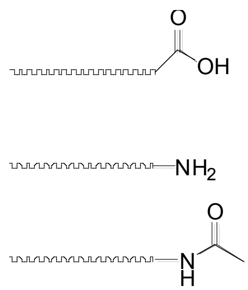
*Problem Set #2*

**15.**



28.9 mol

35.3 mol

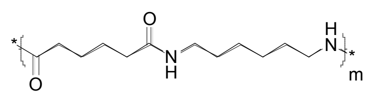
96.5 mol

$N_{end\ groups}$=160.7 mol

Each polymer chain has two ending groups, so n=80.35 mol

$m_{total}=10^6$ g

Neglecting ending groups, $M_n$=12445.6 g/mol



Degree of polymerization $N=2m=2*M_n/(M_1+M_2-36)=110$

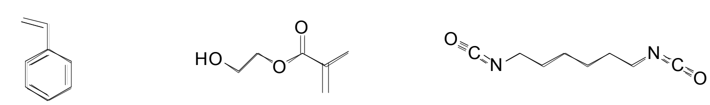
During the condensation step, assume amine and acid are equivalent

$$N=1/(1-p)=110$$

$$p=0.9909$$

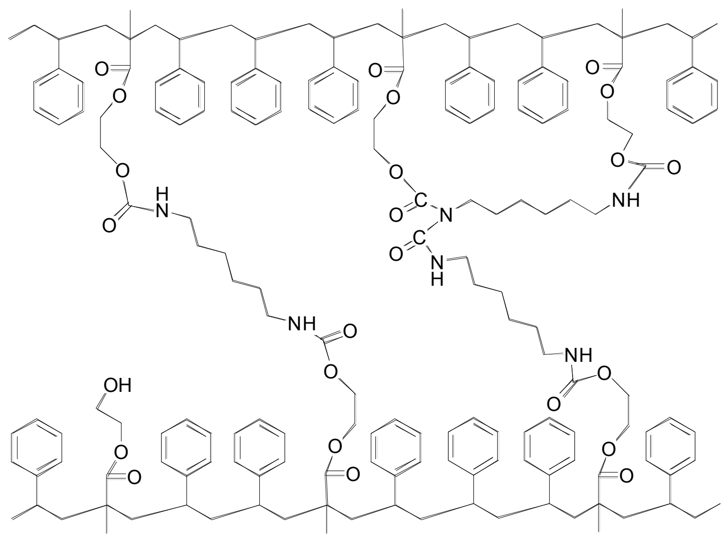
So, those numbers are consistent with each other

**16.**



styrene hydroxyethylmethacrylate hexamethylene diisocyanate

The crosslinked network is shown below, styrene and hydroxyethylmethacrylate are polymerized by addition reaction (chain polymerization), diisocyanates are crosslinking reagents which react with hydroxyl groups by condensation reaction, to form a complicated network.




Crosslinking reaction is carried out in dilute solution in order to get primarily intramolecular product, which means diisocyanates react with hydroxyl group within one polymer chain. While intermolecular reaction involves reaction between the polymer chains.

At high concentration, interaction between polymer coil will increase, resulting in some reaction between cyanate group on chain A and hydroxy groups on chain B. If concentration is low enough, the only chance for cyanate group in chain A is to react with some other hydroxyl group on the same chain to form a loop.

**17.**

So for step polymerization, the chance to get one x-mer chain is $N_x = p^{x-1}(1-p)$

For N polymer chains $N_x = Np^x(1-p)$ N=$N_0$(1-p)

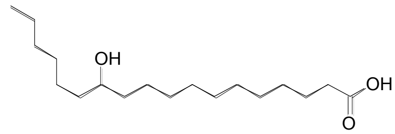
$$N_x = Np^x(1-p) = N_0(1-p)^2 p^{x-1}$$

$$\frac{\partial N_x}{\partial p} = -2(1-p)p^{x-1} + (x-1)p^{x-2}(1-p)^2 = 0$$

$$p_c = \frac{x-1}{x+1}$$

So when p< $p_c$, $N_x$ increases with x($\frac{\partial N_x}{\partial p} > 0$); when p=$p_c$, $N_x$ gets the maximum; when p>$p_c$, $N_x$ decreases.

For a catalyzed AB condensation, $k_c$=2.47*$10^{-4}$ l $mol^{-1}s^{-1}$, the monomer is




12-hydroxystearic acid

For the unit of rate constant, it is a second order reaction (self catalyzed)

$$-\frac{dc}{dt} = kc^2$$

$$\frac{1}{c_0} - \frac{1}{c_0(1-p)} = -kt$$

Degree of polymerization x=1/(1-p)=15

$$p=14/15;\ c_0=3M;\ k=2.47*10^{-4}\ l\ mol^{-1}s^{-1}$$

So

$$t=18900s$$

**18.**

PMMA

$M_{monomer}$=100.12; M= 500,000; N=4994

For rigid rod: L=N*2.5*$10^{-10}$ m=1250 nm ≈ 1 micron

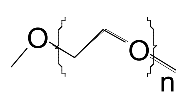
For condense ball: $V=\rho\frac{4\pi}{3}r^3 = \frac{500000}{6.02*10^{23}}$

R=5.8 nm ≈ 6 nm

For random coil: b=0.6 nm, so

$$Rg=\sqrt{\frac{N}{6}}b = 17.3nm \approx 20\ nm$$

**19.**




Two End groups have 6 Hs. For each monomer in the chain there are 4 Hs.

From NMR, we known Hs of ending groups: Hs from monomer =1:20

So, the number of ending groups to monomers is (1/6) :( 20/4) =1:30

So N=30

$M_n$=30*44+46(ending groups)=1366 (or without ending groups $M_n$=1320)

**20.**

10g PS $\qquad M_{w1}=\sum n_i m_i^{\ 2} / \sum n_i m_i = 100000$

$M_{n1}=\sum n_i m_i / \sum n_i = 70000$

$\sum n_i m_i = m_1 = 10g$

20g PS $\qquad M_{w2}=\sum n_i m_i^{\ 2} / \sum n_i m_i = 60000$

$M_{n2}=\sum n_i m_i / \sum n_i = 20000$

$\sum n_i m_i = m_2 = 20g$

$M_n=\sum n_i m_i / \sum n_i = (10+20)/(10/70000+20/20000) = 26250$

$M_w=\sum n_i m_i^{\ 2} / \sum n_i m_i = (100000*10+60000*20)/(10+20) = 73333$

**21.**

1 mol Decane $C_{10}H_{22}$ $M_1=142.28$

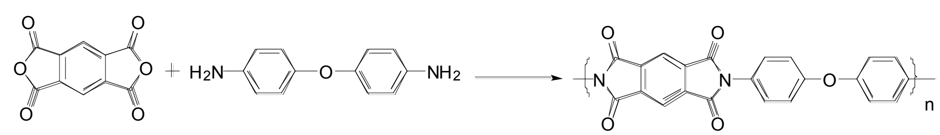
1 mol Tetradecane $C_{14}H_{30}$ $M_2=198.39$

$$M_n = (142.28 + 198.39)/2 = 170.34$$

$$M_w = (142.28^2 + 198.39^2)/(142.28 + 198.39) = 174.96$$

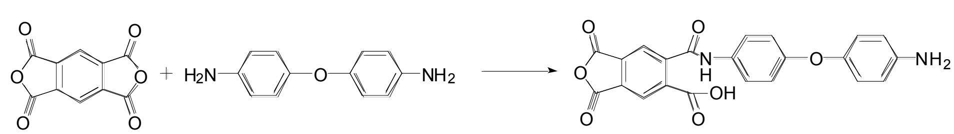
**22.**

(a)

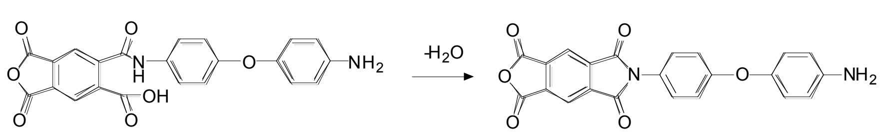


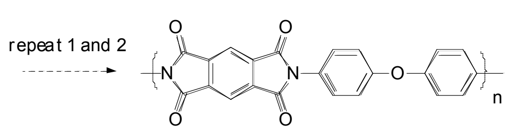
Procedure:

Step 1 Substitution

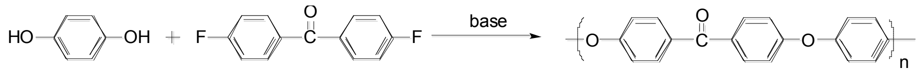


Step 2 Condensation





(b)



Procedure: