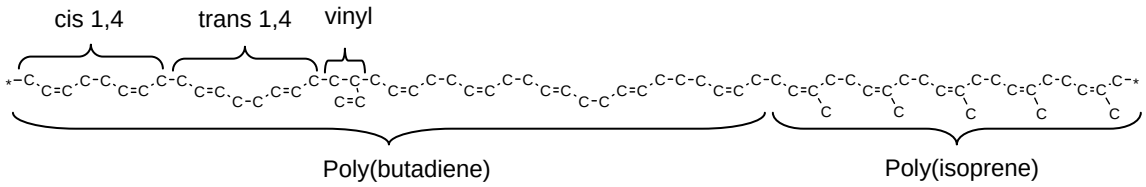
Problem 1.

BI diblock copolymer with 2:1 B:I molar ratio

15 repeat units → 10 B repeat units, 5 I repeat units

From given microstructure:

B	I
~ 5 cis 1,4 units	~ 5 cis 1,4 units
~ 4 trans 1,4 units	
1 vinyl (1,2) unit	



Note: There will be some trans 1,4, 1,2, and 3,4 isoprene repeat units present in the block copolymer, but in very small frequency as compared to cis 1,4 units.

Problem 2.

92.1 % 1,4 poly(butadiene)
7.9 % 1,2 poly(butadiene)

$M_0 = 54$; $M_n = 168000$ → $N = 3111$

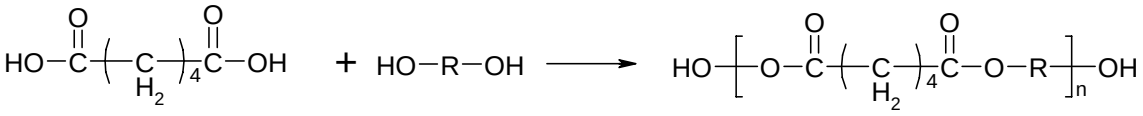
$N_{1,4} = (3111)(0.921) = 2865$
$N_{1,2} = 246$

$N_{1,4} : N_{1,2} = 11.6 : 1$
(on average 11.6 1,4 units per 1,2 unit)

Since there are 4 backbone carbon atoms in a 1,4 repeat unit and 2 in a 1,2 repeat unit:
Mean # of C atoms between ethyl branches in hydrogenated polymer: $(11.6)(4) + 1 =$ 47.4

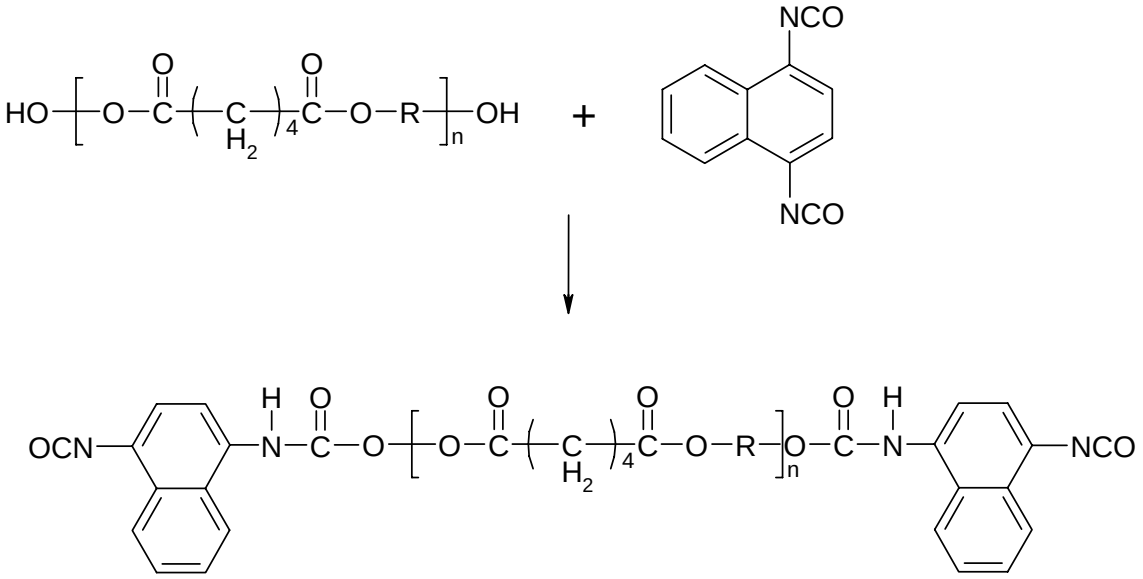
Problem 3.

Synthesis of the polyester:

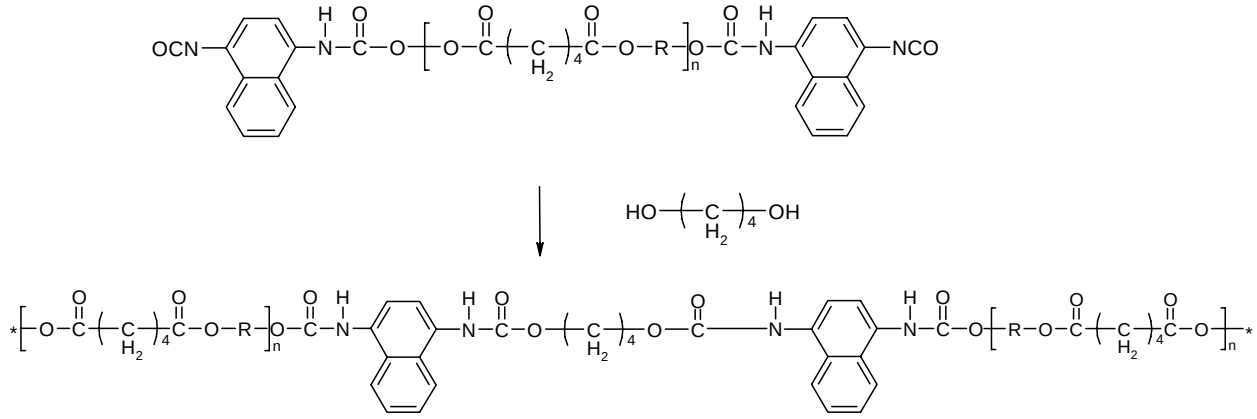


R = CH_2CH_2 or $CH_2CH_2CH_2$

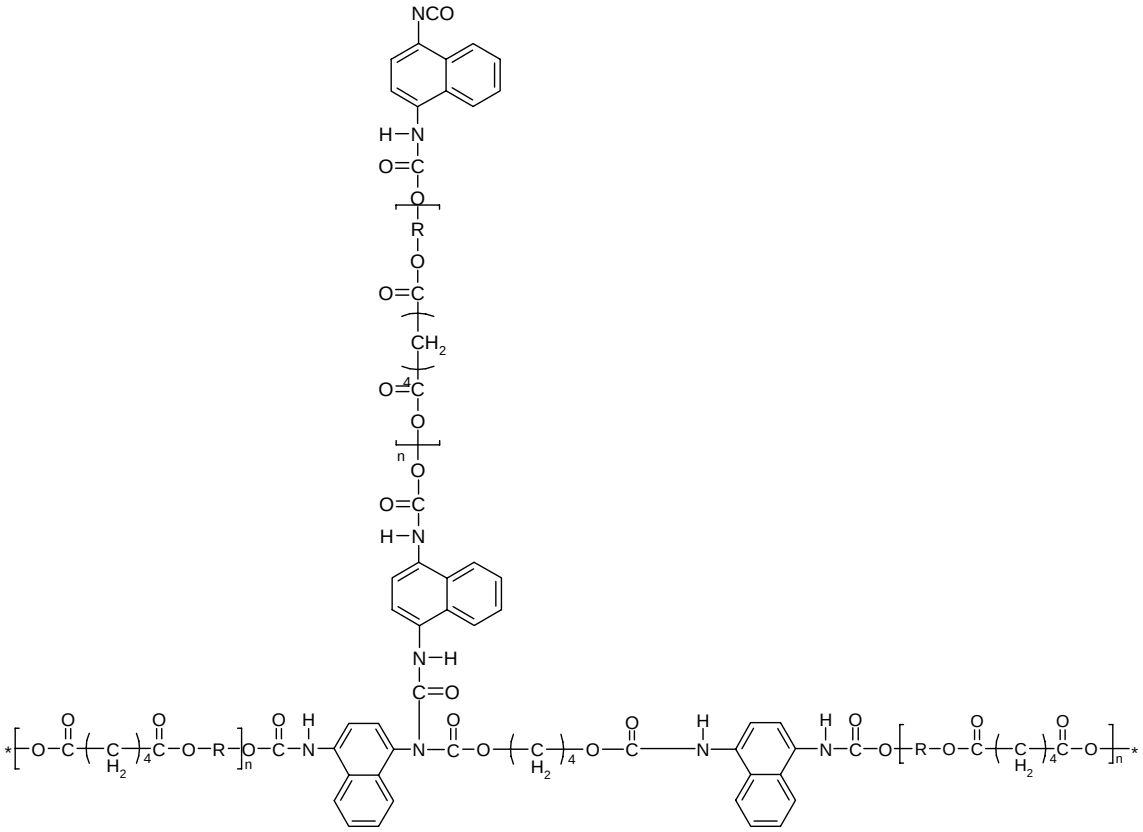
Addition of diisocyanate:



Crosslinking with 1,4-butanediol:



Crosslinking through isocyanate groups (NCO reacts with active N-H on extended polymer chain):



Problem 4.

$$n_i = \frac{m_i}{M_i} \qquad M_n = \frac{\sum_i n_i M_i}{\sum_i n_i} \qquad M_w = \frac{\sum_i n_i M_i^{\,2}}{\sum_i n_i M_i} = \frac{\sum_i m_i M_i}{\sum_i m_i} \qquad M_z = \frac{\sum_i n_i M_i^{\,3}}{\sum_i n_i M_i^{\,2}}$$

From the data we calculate: $M_n = 29100$; $M_w = 46100$; $M_z = 62500$

Problem 5.

Note: Problem should read "M_i x 10^{-5} (g/mol)" or else we would not even have one repeat unit!

$$M_v = \left(\frac{\sum_i n_i M_i^{1+a}}{\sum_i n_i M_i} \right)^{1/a}$$

From data:

M_v in acetone: 662000; M_v in chloroform: 665000

Compare with M_n = 597000 and M_w = 671000

Generally the viscosity average molecular weight falls between the values of M_n and M_w for a flexible polymer.

Problem 6.

A distribution based on prominent members of the Golden Gopher football team:

Athlete	Mass (kg)	w_i	w_iM_i
Laurence Maroney (RB)	93	.15	13.95
Greg Eslinger (C)	129.5	.20	25.9
Brian Cupito (QB)	88	.14	12.32
Mark Setterstrom (OG)	134	.21	28.14
Jared Ellerson (WR)	91	.14	12.74
Mike Sherels (MLB)	105	.16	16.8

$$M_n = \frac{\sum_i M_i}{7} = 106.8\,\text{kg}$$

$$M_w = \sum_i w_i M_i = 109.9\,\text{kg}$$

$$PDI = \frac{M_w}{M_n} = 1.03$$

Despite the noticeable difference in size between the offensive linemen (Eslinger and Setterstrom) and the other players, the PDI indicates that this is a narrow distribution.

Go Gophers!

Problem 7.

$$w_i = \frac{z^{z+1}}{\Gamma(z+1)} \frac{{M_i}^z}{{M_n}^{z+1}} \exp\left(-\frac{zM_i}{M_n}\right)$$

$$\frac{\partial w_i}{\partial M_i} = \frac{z^{z+1}}{\Gamma(z+1)} \left[\frac{z{M_i}^{z-1}}{{M_n}^{z+1}} \exp\left(-\frac{zM_i}{M_n}\right) - \frac{{M_i}^z}{{M_n}^{z+1}} \frac{z}{M_n} \exp\left(-\frac{zM_i}{M_n}\right) \right]$$

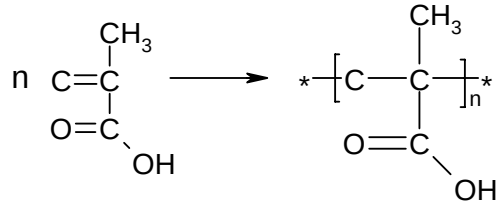
$$\frac{\partial w_i}{\partial M_i} = \frac{z^{z+2}}{\Gamma(z+1)} \exp\left(-\frac{zM_i}{M_n}\right) \left[\frac{{M_i}^{z-1}}{{M_n}^{z+1}} - \frac{{M_i}^z}{{M_n}^{z+2}} \right]$$

$$\frac{\partial w_i}{\partial M_i} = \frac{z^{z+2}}{\Gamma(z+1)} \frac{{M_i}^{z-1}}{{M_n}^{z+1}} \exp\left(-\frac{zM_i}{M_n}\right) \left[1 - \frac{M_i}{M_n} \right]$$

Thus if $M_i = M_n$, $\frac{\partial w_i}{\partial M_i} = 0$; corresponding to a maximum in w_i

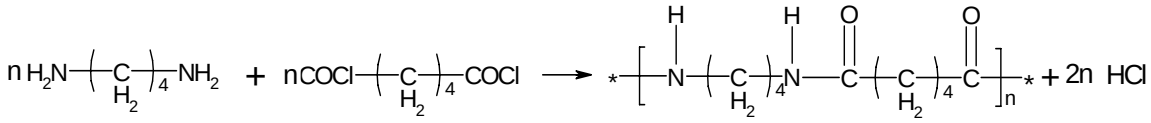
Problem 8.

(a)



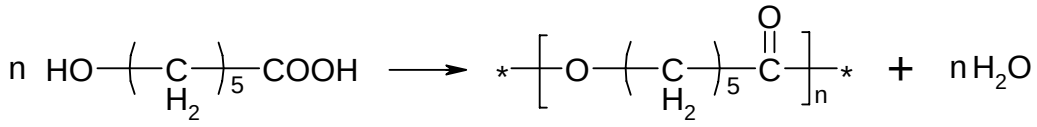
poly(methacrylic acid)

(b)



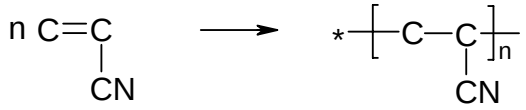
poly(tetramethylene adipamide) / Nylon 4,6

(c)



poly(caprolactone)

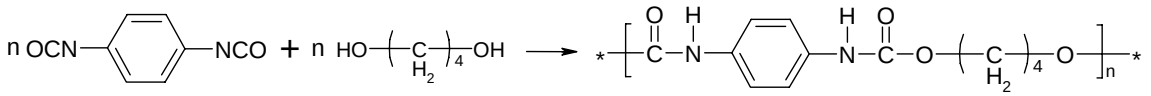
(d)



poly(acrylonitrile)

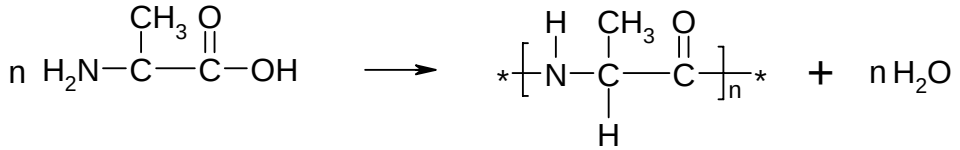
Note: This would usually be named poly(vinyl cyanide), but imagine the public relations backlash!

(e)



Poly(phenylene tetramethylene urethane)

(f)



poly(alanine)

Problem 9.

1206
- 108 (silver ion)
1098

Since the repeat unit of polystyrene is 104 g/mol, this peak corresponds to 10 repeat units, with 58 mass units as a remainder (likely sec-butyl lithium initiator fragment and terminal hydrogen end groups: 57 and 1, respectively)

Assuming only head-to-tail addition, there will be 2^n possible structures, with n=10; thus there are 1024 possible distinct chemical structures for the polystyrene represented by this peak.

Problem 10.

In general light scattering (gives M_w) and osmotic pressure (gives M_n) have errors of a few percent. Thus the answers by these two techniques agree well (although they have one more significant figure than justified!). However, it is unreliable to get M_w/M_n from two independent experiments, when the polydispersity is small.

Problem 11.

The carbon-carbon bonds in the backbone of the poly(styrene) chain can each take three forms: trans, gauche(+), and gauche(-). If we assume all three are equally likely (in reality, trans is slightly favored energetically), then there are 3^r possible conformations, where *r* represents the number of carbon-carbon bonds in the backbone. The poly(styrene) molecule from Problem 9 has 10 repeat units, and thus 19 carbon-carbon bonds (neglecting end groups). Therefore, the number of possible conformations is 3^{19}, or 116,226,147.

Problem 12.

$$R_g = b\sqrt{\frac{N}{6}} = b\sqrt{\frac{M}{6M_0}}$$

For poly(styrene): $R_g = (6.7)\sqrt{\frac{(100000)}{6(104)}} = 84.8\,\text{Å}$

For poly(ethylene oxide): $R_g = (6.0)\sqrt{\frac{(100000)}{6(44)}} = 116.8\,\text{Å}$

For poly(ethylene): $R_g = (5.9)\sqrt{\frac{(100000)}{6(28)}} = 143.9\,\text{Å}$

Despite similar statistical segment length values, the three polymers have very different R_g values. This is due to the fact that statistical segment length is defined on a per monomer basis (not per mass). The bulky side group of poly(styrene) accounts for much of the monomer mass, and results in poly(styrene) having many less backbone bonds than either poly(ethylene oxide) or poly(ethylene).

Problem 13.

The thermal history of the polymer is important when taking DSC measurements. Possible reasons for obtaining different T_g values for PMMA from two separate instruments include:

1. Different heating rates were used during scan.
2. Different cooling rates were used during quench.
3. The samples were held at different quench temperatures.
4. The samples were held at the same quench temperature, but for different lengths of time
5. At least one of the samples was not annealed to equilibrium (above T_g) before the quench.

Problem 14.

Since the unit cell dimensions of crystalline poly(ethylene) are known, a volume per unit cell can be calculated. The unit cell contains 2 repeat units, with M_0 equal to 28 g/mol, so a mass per unit cell can be also be calculated. Dividing this mass by the volume of the unit cell gives the density of the crystal. Using the crystal density, the amorphous density and the density of the polyethylene sample, the % crystallinity is given by:

$$\% \text{ crystallinity } = \frac{\rho_c}{\rho}\left(\frac{\rho - \rho_a}{\rho_c - \rho_a}\right)$$

Where ρ_c, ρ_a, and ρ are the densities of crystalline poly(ethylene), amorphous poly(ethylene), and the semi-crystalline poly(ethylene) sample respectively