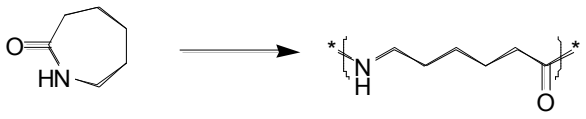
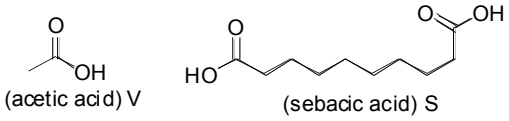
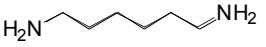
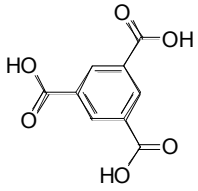
PS #4

31.









1 mol monomer	c_0(mmol)	-COOH(mmol)	-NH_2(mmol)	N_{chain}(mmol)	M_n*10^{-3}
1.	-	5.4	4.99	(5.4+4.99)/2	21.7
2.	V 20.5	19.8	2.3	(19.8+c_0+2.3)/2	5.30
3.	S 10.2	21.1	2.3	(21.1+2.3)/2	9.66
4.	H 10.2	1.4	19.7	(1.4+19.7)/2	10.6
5.	T 6.7	22.0	2.5	c_0+2.5	12.28

* $M_{caprolactam}=M_0=113$; $M_n= (1/N_{chain})*M_0$
* Reaction 1, 3, 4: The number of chains equals to half of the end groups.
* Reaction 2: Each polymer chain has either an end-capped carbonyl group (here we assume the conversion of acetic acid is 100%) or an amine (NH_2) end group. N_{chain}=(20.5+2.3) (mmol) and M_n=5 k. We can also calculate the average number according to two end groups: N_{chain}= (19.8+(20.5+2.3))/2, and the answer is 5.3 k.
*Reaction 5: Assume all the T is converted into polymer, so there are two kinds of polymer chains: one with a NH_2 end group and one with a T unit.

The trend of MW with the additives is consistent with the polymerization mechanism. Water, acid and base play the role as the initiators of ring-opening polymerization. When adding acetic acid, which is a more efficient initiator than water (concentration of initiators increases), so M_n of the final polymer decreases a lot. When adding diacids or diamines, M_n doubles as two chains are connected by the difunctional molecule. When adding triacids, it could initiate three chains to form a star polymer with a bigger M_n.

32.

Moles water($*10^3$)/mole caprolactam	M_n*10^{-3}	M_w*10^{-3}	$*M_w/M_n=(1+p)$	p
49.3	13.4	20.0	1.493	0.493
34.0	16.4	25.6	1.561	0.561
25.6	17.9	29.8	1.665	0.665
20.5	19.4	36.6	1.887	0.887

* We can't use M_n to calculate p by using $N_n=1/(1-p)$, because of the following reason:

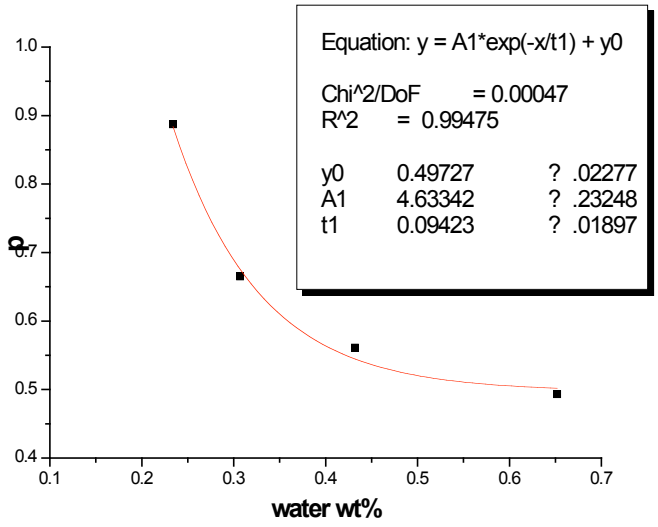
The water-initiated polymerization of caprolactam is characterized by three main equilibrium reactions, which are: ring opening (K1), condensation (K2), and addition (K3). Both ring opening (hydrolysis of caprolactam) and addition (the direct attachment of a molecule of caprolactam to an endgroup of a polymer molecule) are the principal reactions, whereas the condensation equilibrium determines the final degree of polymerization. Before condensation, all the narrow dispersed polymers with $M_{n,0}$ of about several thousand are formed in the solution by chain addition mechanism.

Based on above description, if more water is added, condensation conversion will be less favored, so we will get polymers with a lower molecular weight. Above experimental results proved our expectation.

Calculation of residual water:

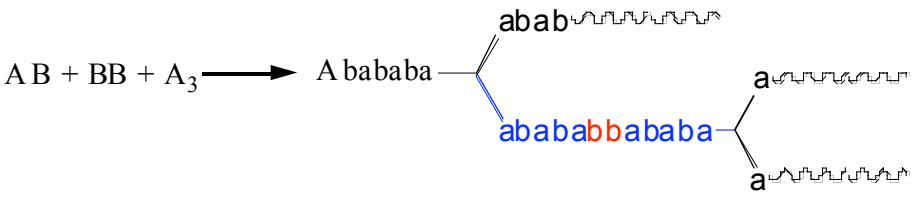
Moles water($*10^3$)/mole caprolactam	M_n*10^{-3}	N_n	N_{chain}(mmol)	*Left water(mmol)	H_2O wt%
49.3	13.4	118.6	8.4	40.9	0.652
34.0	16.4	145.1	6.9	27.1	0.432
25.6	17.9	158.4	6.3	19.3	0.307
20.5	19.4	171.7	5.8	14.7	0.234

*Because each polymer consumes one water molecule, $n_{water,f}=n_{water,i}-n_{chain}$



When conversion is close to 1, the final water content is about 0.2% at 225 ºC, which is consistent with the value in the book (0.15% @ 290 ºC).

33.



Above structure illustrate the network formed from AB+BB+A_3 system

The blue chain is between two branching points.Assume B groups are in excess, the extent of reaction for A groups is p. $r = \frac{\nu_A^0}{\nu_B^0} < 1$; $\nu_A{}^0$ is the total A groups

$$\rho_A = \frac{\nu_{A,f}}{\nu_A^0} \qquad \rho_B = \frac{\nu_{B(AB)}}{\nu_B^0}$$

There is only one BB unit in the blue chain, so we can calculate the probability of forming such a chain

$$A_3 + BA \longrightarrow A_2abA \qquad p \cdot \rho_B$$

$$A_2abA+BA \longrightarrow A_2ababA \qquad (p\cdot\rho_B)^2$$

Assume m BA unit before BB, the probability is $(p\cdot\rho_B)^m$

$$A_2a(ba)_{m-1}bA+BB \longrightarrow A_2a(ba)_{m-1}babB \qquad (p\cdot\rho_B)^m\cdot p(1-\rho_B)$$

$$A_2a(ba)_{m-1}babB+AB \longrightarrow A_2a(ba)_{m-1}babbaB \quad (p\cdot\rho_B)^m\cdot p(1-\rho_B)rp\cdot(1-\rho_A)$$

Assume n AB units after BB, the total probability is $(p\cdot\rho_B)^m\cdot p(1-\rho_B)[rp\cdot(1-\rho_A)]^n$

The final unit is A_3, so the probability of forming a blue chain is

$$(p\cdot\rho_B)^m\cdot p(1-\rho_B)[rp\cdot(1-\rho_A)]^n\cdot rp\cdot\rho_A$$

Considering different possibilities of m and n, the branch coefficient is expressed as

$$\alpha=\sum_{m=0}(p\cdot\rho_B)^m\cdot p(1-\rho_B)\sum_{n=0}[rp\cdot(1-\rho_A)]^n\cdot rp\cdot\rho_A$$

$$\alpha=\frac{rp^2\rho_A(1-\rho_B)}{(1-p\rho_B)[1-rp(1-\rho_A)]}$$

We also know α=1/(f-1)=0.5, solving p,

$$p^2(3r\rho_A-2r\rho_A\rho_B-r)+p(\rho_B+r-r\rho_A)-1=0$$

$$p_c=\frac{r\rho_A-r-\rho_B+\sqrt{(\rho_B+r-r\rho_A)^2+4(3r\rho_A-2r\rho_A\rho_B-r)}}{2r(3\rho_A-2\rho_A\rho_B-1)} \qquad \text{A}$$

When ρ_B=1, we expect that p_c>1, because no network can form between A_3 and AB
From above expression, we have

$$p_c=\frac{r\rho_A-r-1+\sqrt{(r-1-r\rho_A)^2}}{2r(\rho_A-1)}=\frac{1-r\rho_A}{r-r\rho_A}>1 \qquad \text{B}$$

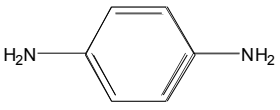
Expression B derived from A is reasonable, indicating A is right, even though the final expression is not very clear.

34.

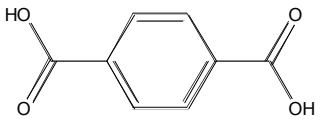
(a) Linear: no branch point
(b) Network: two AB_2 branch points can be connected by some A_2 molecules
(c) Network: two AB_2 branch points can be connected by some AB molecules
(d) Network: two A_3 points can be connected by both B_2 and A_2 molecules
(e) Branch: two B_3 can't be connected together
(f) Network: A_2B_2 can be connected by A_2 or B_2 molecules

35.

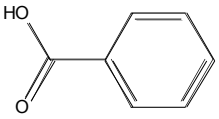
A B B'



aminoaniline



terephthalic acid



benzoic acid

M_a=108 M_t=166 M_b=122

Wt%=39.31% wt%=59.81 wt%=0.88%

N_a=50.461 : N_t=49.951 : N_b=1

Neglecting the endgroups, M_n=24116; dop=M_n/((M_a+M_t-36)/2)=202.42

$$r = \frac{v_A}{v_B + 2v_{B'}} = \frac{50.461*2}{49.951*2+2} = 0.9904$$

$$N_n = \frac{1+r}{1+r-2rp}$$

$$202.42 = \frac{1+0.9904}{1+0.9904-2*0.9904*p}$$

P=0.99989

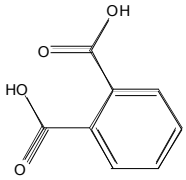
If the benzoic acids were doubled

$$r = \frac{v_A}{v_B + 2v_{B'}} = \frac{50.461*2}{49.951*2+4} = 0.9713$$

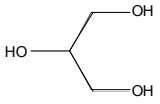
And p was 0.99988,

N_n=68.2

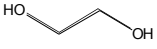
36.



phthalic acid
B_2



glycerol
A_3



ethylene glycol
A_2

Molar ratio: 1.5 0.5 0.7

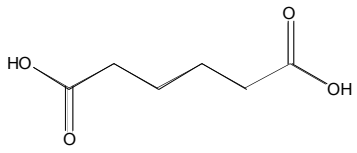
$$p_c = \frac{1}{\sqrt{r + r\rho(f-2)}}$$

$$r = \frac{0.5*3+0.7*2}{1.5*2} = 0.9667$$

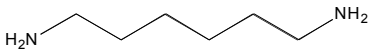
ρ=1.5/2.9=0.5172

p_c=0.8257

37.



adipic acid



hexamethylene diamine

M_{acid}=146 M_{amine}=116

For stoichiometry balanced situation,

$$N_n = \frac{1+r}{1+r-2rp}$$

p=0.995 N_n=10000/((146+116-36)/2)=88.5

r=0.9874

If p_A=0.995, p_B=rp=0.9824 (the choice of "A" and "B" is arbitrary)

The end groups are acids or amines, and the ratio is 1.013(0.995:0.9824).

38.

For example: polyurethanes made from 1,4-diisocyanato-benzene and Butane-1,4-diol