Principles of Polymerization Engineering

Molecular Weight and Molecular Weight Distribution Examples

Example 2-1

Calculate the osmotic pressure of a solution of 1 gram of sucrose (M= 342 g/gmol) in 100 cm^3 at 0 °C.

$$\lim_{c \to 0} \frac{\Pi}{c} = \frac{RT}{M} \quad \rightarrow \quad \Pi = c\frac{RT}{M} \qquad c = \frac{1}{100}\left(\frac{g}{cm^3}\right) = 10\left(\frac{g}{l}\right)$$

$$R = 0.082\left(\frac{l.atm}{mol.\,K}\right) \qquad T = 273.15\,K$$

$$\Pi = \frac{10}{342} \times 0.082 \times 273.15 = 0.655 \quad \text{atm}$$

Example 2-2

Calculate the number average molecular weight and second virial coefficient of the the solution of isobutylene in benzene with the following data at 25 °C:

$c\left(\frac{g}{100\,cm^3}\right)$	0.5	1.0	1.5	2.0
$\Pi\left(\frac{g}{cm^3}\right)$	0.505	1.03	1.58	2.15

$c\left(\frac{g}{cm^3}\right)$	0.005	0.01	0.015	0.02
$\frac{\Pi}{c}$	101	103	105.33	107.5

Example 2-2 (continued)

$$\frac{\Pi}{c}=\frac{RT}{\overline{M}_n}\left(1+A_2\overline{M}_n c+A_3\overline{M}_n^2 c^2+\ldots\right)$$

$$\overline{M}_n=\frac{RT}{\text{y-intercept}}$$ ⇨ $$\text{y-intercept}=\frac{RT}{\overline{M}_n}$$

$$\text{Slope}=RT\,A_2$$ ⇨ $$A_2=\frac{\text{Slope}}{RT}$$

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x= [0.005, 0.01, 0.015, 0.02]
y= [101, 103, 105.33, 107.5]
Coeffs = polyfit (x, y, 1)
Coeffs(1)=Slope;          Coeffs(2)= y-intercept
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R= 8.48e4 g.cm/mol.K; T= 298.15 K

M_n = 2.5603e+05 g/mol A_2= 1.7268e-05

Example 2-3

Calculate the number- and weight-average molecular weight of a polymer consisting of 9 moles of chains with a degree of polymerization of 3000 and 5 moles of chains with a degree of polymerization of 5000.

$$\bar{r}_n = \frac{\sum_{r=1}^{\infty} r N_r}{\sum_{r=1}^{\infty} N_r} = \frac{\int_0^{\infty} r N(r) dr}{\int_0^{\infty} N(r) dr} = \frac{(9\times 3000)+(5\times 5000)}{9+5} = 3714.3$$

$$\bar{r}_w = \frac{\sum_{r=1}^{\infty} r^2 N_r}{\sum_{r=1}^{\infty} r N_r} = \frac{\int_0^{\infty} r^2 N(r) dr}{\int_0^{\infty} r N(r) dr} = \frac{(9\times 3000^2)+(5\times 5000^2)}{(9\times 3000)+(5\times 5000)} = 3961.5$$

Example 2-4

Calculate the number- and weight-average molecular weight of a polymer consisting of 9 grams of chains with a degree of polymerization of 3000 and 5 grams of chains with a degree of polymerization of 5000.

$$\bar{r}_w = \frac{\sum_{r=1}^{\infty} r\,w_r}{\sum_{r=1}^{\infty} w_r} = \frac{\int_0^{\infty} r\,w(r)\,dr}{\int_0^{\infty} w(r)\,dr} = \frac{(9\times 3000)+(5\times 5000)}{(9+5)} = 3714.3$$

$$\bar{r}_n = \frac{\sum_{r=1}^{\infty} w_r}{\sum_{r=1}^{\infty} \frac{w_r}{r}} = \frac{\int_{r=1}^{\infty} w(r)}{\int_{r=1}^{\infty} \frac{w(r)}{r}} = \frac{(9+5)}{\frac{9}{3000}+\frac{5}{5000}} = 3500$$

Example 2-5

Calculate the PDI of a polymer with the below frequency function (molar or number molecular weight distribution); *α* is assumed constant.

$$F(r)=\frac{\exp\left(\frac{-r}{\alpha}\right)}{\alpha}$$

$$\bar{r}_n=\int_0^\infty r\,F(r)\,dr=\int_0^\infty r\,\frac{\exp\left(\frac{-r}{\alpha}\right)}{\alpha}\,dr=\alpha$$

⇒

$$F(r)=\frac{1}{\bar{r}_n}\exp\left(\frac{-r}{\bar{r}_n}\right)$$

$$\bar{r}_w=\frac{\int_0^\infty r^2F(r)\,dr}{\int_0^\infty r\,F(r)\,dr}=\frac{\int_0^\infty r^2\frac{1}{\bar{r}_n}\exp\left(\frac{-r}{\bar{r}_n}\right)dr}{\bar{r}_n}=2\bar{r}_n$$

⇒

$$PDI=\frac{\bar{r}_w}{\bar{r}_n}=\frac{2\bar{r}_n}{\bar{r}_n}$$

Example 2-6

Calculate the PDI of a polymer with the below weight fraction function (weight molecular weight distribution); α is assumed constant.

$$W(r) = r^5 \exp(-\alpha r)$$

$$\bar{r}_n = \frac{1}{\int\limits_{r=0}^{\infty} \frac{W(r)}{r}\, dr} = \frac{1}{\int\limits_{r=0}^{\infty} \frac{r^5 \exp(-\alpha r)}{r}\, dr} = \frac{\alpha^5}{4!}$$

$$\bar{r}_w = \int\limits_0^{\infty} r\, W(r)\, dr = \int\limits_{r=0}^{\infty} r^6 \exp(-\alpha r)\, dr = \frac{6!}{\alpha^7}$$

$$\int\limits_0^{\infty} W(r)\, dr = 1 \Rightarrow \int\limits_{r=0}^{\infty} r^5 \exp(-\alpha r)\, dr = 1 \Rightarrow \frac{5!}{\alpha^6} = 1 \Rightarrow \alpha = 2.221$$

$$PDI = \frac{\bar{r}_w}{\bar{r}_n} \approx \frac{3}{2} = 1.5$$

Example 2-7

Calculate the PDI of a polymer with the below integral distribution.

$$I(r) = \int W(r) = \begin{cases} \log r - 1 & 10 \leqslant r \leqslant 100 \\ 0 & r < 10 \\ 1 & r > 100 \end{cases} \Rightarrow W(r) = \frac{d\,I(r)}{dr} = \frac{1}{2.303\,r}$$

$$\bar{r}_n = \frac{1}{\int\limits_{r=10}^{r=100} \frac{W(r)}{r}\,dr} = \frac{1}{\int\limits_{r=10}^{r=100} \frac{1}{2.303\,r^2}\,dr} \approx 26$$

$$\Rightarrow PDI = \frac{\bar{r}_w}{\bar{r}_n} = \frac{39}{26} \approx 1.5$$

$$\bar{r}_w = \int\limits_{r=10}^{r=100} r\,W(r)\,dr = \int\limits_{r=10}^{r=100} \frac{1}{2.303\,r}\,r\,dr \approx 39$$

Example 2-8

Calculate the number- and weight average molecular weight of three different blends of two polymers with the same PDI as given below.

	Blend A	Blend B	Blend C	M_n	M_w
Polymer A	0.25	0.50	0.75	70000	210000
Polymer B	0.75	0.50	0.25	120000	360000

For Blend A, we have:

$$w_A = 0.25$$
$$w_B = 0.75$$

$$\overline{M}_n^{mix} = \frac{1}{\sum_{j=1}^{N}\left[\frac{w_j}{\overline{M}_{n,j}}\right]} = \frac{1}{\frac{0.25}{70000}+\frac{0.75}{120000}} \approx 101800 \frac{gr}{gr.mol}$$

$$\overline{M}_w^{mix} = \sum_{j=1}^{N} w_j \overline{M}_{w,j} = (0.25 \times 210000) + (0.75 \times 360000) = 322500 \frac{gr}{gr.mol}$$

Example 2-8 (continued)

With the calculations for Blend B, we will have:

$$\overline{M}_n^{mix}=\frac{1}{\sum_{j=1}^{N}\left[\frac{w_j}{\overline{M}_{n,j}}\right]}=\frac{1}{\frac{0.5}{70000}+\frac{0.5}{120000}}\approx 88400\,\frac{gr}{gr.mol}$$

$$\overline{M}_w^{mix}=\sum_{j=1}^{N}w_j\,\overline{M}_{w,j}=(0.5\times 210000)+(0.5\times 360000)=285000\,\frac{gr}{gr.mol}$$

With the calculations for Blend C, we will have:

$$\overline{M}_n^{mix}=\frac{1}{\sum_{j=1}^{N}\left[\frac{w_j}{\overline{M}_{n,j}}\right]}=\frac{1}{\frac{0.75}{70000}+\frac{0.25}{120000}}\approx 78200\,\frac{gr}{gr.mol}$$

$$\overline{M}_w^{mix}=\sum_{j=1}^{N}w_j\,\overline{M}_{w,j}=(0.75\times 210000)+(0.25\times 360000)=247500\,\frac{gr}{gr.mol}$$

Example 2-9

A mixture of three polymers, namely A, B, and C with the weight fractions of 25%, 50%, and 25% is prepared. Polymers A and B have the same monodisperse distribution with $M_{n,\mathrm{A}}=3M_{n,\mathrm{B}}$ and polymer C has a polydisperse distribution with $M_{w,\mathrm{C}}=2\times10^5$. If the molecular weight of this mixture determined by light scattering is about 112500 gr/grmol and its molecular weight by osmotic pressure is obtained to be 60000, calculate the PDI of polymer C.

$$PDI_A=PDI_B=1\Rightarrow \overline{M}_{n,A}=3\overline{M}_{n,B} \quad \overline{M}_{w,A}=3\overline{M}_{w,B}$$

$$\overline{M}_w^{mix}=\sum_{j=1}^{N} w_j\overline{M}_{w,j}=0.25\overline{M}_{w,A}+0.5\overline{M}_{w,B}+0.25\overline{M}_{w,C}=112500\frac{gr}{gr.mol}$$

$$0.25\left(3\overline{M}_{w,B}\right)+0.5\overline{M}_{w,B}+0.25\times200000=112500\frac{gr}{gr.mol} \quad \Rightarrow$$

$$\overline{M}_{w,B}=50000\frac{gr}{gr.mol} \quad \text{and} \quad \overline{M}_{w,A}=150000\frac{gr}{gr.mol}$$

Example 2-9 (continued)

We also have:

$$\overline{M}_n^{mix} = \frac{1}{\sum_{j=1}^{N}\left[\frac{w_j}{\overline{\overline{M}}_{n,j}}\right]} \Rightarrow \quad 60000\frac{gr}{gr.mol} = \frac{1}{\frac{0.25}{\overline{\overline{M}}_{n,A}} + \frac{0.5}{\overline{\overline{M}}_{n,B}} + \frac{0.25}{\overline{\overline{M}}_{n,C}}} \Rightarrow$$

$$60000\frac{gr}{gr.mol} = \frac{1}{1.666\times 10^{-6} + 1\times 10^{-5} + \frac{0.25}{\overline{\overline{M}}_{n,C}}} \Rightarrow$$

$$\overline{M}_{n,C} = 50000\frac{gr}{gr.mol} \Rightarrow \quad PDI_C = \frac{\overline{M}_{w,C}}{\overline{\overline{M}}_{n,C}} = \frac{200000}{50000} = 4$$

Example 2-10

If the molecular weight distribution of a polymer is given as below, obtain the PDI of this polymer in terms of *a*. Which of the discussed distributions resembles this distribution (discuss the cases of *a*=1 and *a*=2).

$$W(r)=r^{a}\exp(-br) \qquad 0<r<\infty$$

$$\bar{r}_n=\frac{1}{\int\limits_{r=0}^{\infty}\frac{W(r)}{r}dr}=\frac{1}{\int\limits_{r=0}^{\infty}r^{(a-1)}\exp(-br)\,dr}=\frac{b^{a}}{(a-1)!}$$

$$\bar{r}_w=\int\limits_{r=0}^{\infty}W(r)\,r\,dr=\int\limits_{r=0}^{\infty}r^{(a+1)}\exp(-br)\,dr=\frac{(a+1)!}{b^{(a+2)}}$$

$$\int\limits_{r=0}^{\infty}W(r)\,dr=1 \;\Rightarrow\; \int\limits_{r=0}^{\infty}r^{(a)}\exp(-br)\,dr=\frac{a!}{b^{(a+1)}}=1 \;\Rightarrow\; a!=b^{(a+1)}$$

Example 2-10 (continued)

$$PDI=\frac{(a+1)!(a-1)!}{b^{(a+2)}b^{a}}=\frac{(a+1)!(a-1)!}{(ba)!\left(\frac{a!}{b}\right)}=\frac{(a+1)!(a-1)!}{(a)!(a)!}=\frac{a+1}{a}$$

The distribution is similar to *Schulz* distribution.

$$\frac{k}{\bar{r}_n}=\frac{k+1}{\bar{r}_w}=\frac{k+2}{\bar{r}_z} \Rightarrow \frac{\bar{r}_w}{\bar{r}_n}=\frac{k+1}{k}=PDI$$

a=1 termination by disproportionation;

a=2 termination by combination.

Example 2-11

If a polymer has a *Wesslau* distribution with a PDI equal to 4, what will be the ratio of r_z to r_n?

The normalized ***Wesslau*** function is obtained when ***s*=-1**.

$$\bar{r}_n=\bar{r}_s\exp\left[\frac{(2s+1)\sigma^2}{2}\right]$$

$$\bar{r}_w=\bar{r}_s\exp\left[\frac{(2s+3)\sigma^2}{2}\right]$$

$$\bar{r}_z=\bar{r}_s\exp\left[\frac{(2s+5)\sigma^2}{2}\right]$$

$$\frac{\bar{r}_w}{\bar{r}_n}=\frac{\bar{r}_s\exp\left[\frac{(2s+3)\sigma^2}{2}\right]}{\bar{r}_s\exp\left[\frac{(2s+1)\sigma^2}{2}\right]}=\exp(\sigma^2)$$

$$\frac{\bar{r}_z}{\bar{r}_w}=\frac{\bar{r}_s\exp\left[\frac{(2s+5)\sigma^2}{2}\right]}{\bar{r}_s\exp\left[\frac{(2s+3)\sigma^2}{2}\right]}=\exp(\sigma^2)$$

$$\frac{\bar{r}_w}{\bar{r}_n}=\frac{\bar{r}_z}{\bar{r}_w}=4 \;\Rightarrow\; \frac{\bar{r}_z}{4\bar{r}_n}=4 \;\Rightarrow\; \frac{\bar{r}_z}{\bar{r}_n}=16$$

Example 2-12

Determine the symmetry of the below molecular weight distribution.

$$F(r)=\left(\frac{8r}{\bar{r}_n^2}\right)\exp\left(-\frac{2r}{\bar{r}_n}\right)$$

In order to calculate the symmetry of a distribution, one should calculate the ***coefficient of skewness*** or the third central moments of the distribution. Thus,

$$\gamma_1=\frac{\mu_3}{SD^3}=\frac{\mu_3}{\sigma^3} \qquad \mu_k=\sum_{j=0}^{k}\binom{k}{j}(-1)^{k-j}\alpha_j(\alpha_1)^{k-j} \Longrightarrow \mu_3=\alpha_3-3\alpha_2\alpha_1+2\alpha_1^3$$

$$\bar{r}_i=\frac{\sum_{r=1}^{\infty} r^i F(r)}{\sum_{r=1}^{\infty} r^{i-1} F(r)}=\frac{\int_{-\infty}^{\infty} r^i F(r)\,dr}{\int_{-\infty}^{\infty} r^{i-1} F(r)\,dr}=\frac{\alpha_i}{\alpha_{i-1}} \Longrightarrow \mu_3=\bar{r}_z\bar{r}_w\bar{r}_n-3\bar{r}_n^2\bar{r}_w+2\bar{r}_n^3$$

Example 2-12 (continued)

$$\bar{r}_w=\frac{\int\limits_{r=0}^{\infty} r^2F(r)\,dr}{\int\limits_{r=0}^{\infty} r\,F(r)\,dr}=\frac{\int\limits_{r=0}^{\infty} r^2\left(\frac{8r}{\bar{r}_n^2}\right)\exp\left(-\frac{2r}{\bar{r}_n}\right)dr}{\int\limits_{r=0}^{\infty} r\left(\frac{8r}{\bar{r}_n^2}\right)\exp\left(-\frac{2r}{\bar{r}_n}\right)dr}=1.5\bar{r}_n$$

$$\bar{r}_z=\frac{\int\limits_{r=0}^{\infty} r^3F(r)\,dr}{\int\limits_{r=0}^{\infty} r^2F(r)\,dr}=\frac{\int\limits_{r=0}^{\infty} r^3\left(\frac{8r}{\bar{r}_n^2}\right)\exp\left(-\frac{2r}{\bar{r}_n}\right)dr}{\int\limits_{r=0}^{\infty} r^2\left(\frac{8r}{\bar{r}_n^2}\right)\exp\left(-\frac{2r}{\bar{r}_n}\right)dr}=2\bar{r}_n$$

$$\mu_3=\bar{r}_z\bar{r}_w\bar{r}_n-3\bar{r}_n^2\bar{r}_w+2\bar{r}_n^3$$

$$\Rightarrow \quad \mu_3=3\bar{r}_n^3-4.5\bar{r}_n^3+2\bar{r}_n^3$$

$$\Downarrow$$

$$\mu_3=\frac{1}{2}\bar{r}_n^3>0$$

Step Polymerization Examples

Example 3-1

The polymerization rate equation of Nylon 6,6 (molecular weight of repeating unit equal to 226 gr/mol) in the stochiometric condistions is given by:

$$R_p = k[A]^{\frac{1}{2}}[B]^{\frac{1}{2}}$$

[A] and [B] stand for diamine and diacid groups respectively.

- Develop a relationship between conversion and time;
- If it takes 1 hour to increase the degree of polymerization from 10 to 40, calculate the polymerization rate constant.
- Calculate the molar and weight fractions of chains having a molecular weight of 2260 gr/mol after 2 hours of reaction.

$$R_p = -\frac{d[A]}{dt} = k[A]^{\frac{1}{2}}[B]^{\frac{1}{2}}$$

$$[A]_0 = [B]_0 \quad \rightarrow \quad [A] = [B] \quad \rightarrow \quad -\frac{d[A]}{dt} = k[A] \quad \rightarrow \quad [A] = [A]_0 \exp(-kt)$$

$$p = \frac{[A]_0 - [A]}{[A]_0} \quad \rightarrow \quad p = \frac{[A]_0(1-\exp(-kt))}{[A]_0} \quad \rightarrow \quad p = 1-\exp(-kt)$$

Example 3-1 (continued)

$$\overline{X}_n = \frac{1}{(1-p)} \quad \rightarrow \quad \overline{X}_n = \frac{1}{\exp(-kt)} = \exp(kt) \quad \rightarrow \quad t = \frac{\ln(\overline{X}_n)}{k}$$

$$t_2 - t_1 = \frac{1}{k}\ln\left(\frac{\overline{X}_{n1}}{\overline{X}_{n2}}\right) \quad \rightarrow \quad 1 = \frac{1}{k}\ln\left(\frac{40}{10}\right) \quad \rightarrow \quad k = \ln(4)\,hr^{-1} = 1.3863\,hr^{-1}$$

$$F(r) = p^{(r-1)}(1-p), \quad W(r) = r\,p^{(r-1)}(1-p)^2$$

$$r = \frac{\overline{M}_n}{\left(\frac{M_0}{2}\right)} \quad \rightarrow \quad r = \frac{2260}{\left(\frac{226}{2}\right)} = 20$$

$$p = 1 - \exp(-kt) = 1 - \exp(-2 \times 1.3863) = 0.9375$$

$$F(r) = 0.9375^{(20-1)}(1-0.9375) = 0.0183$$

$$W(r) = 20 \times 0.9375^{(20-1)}(1-0.9375)^2 = 0.0229$$

Example 3-2

The stochiometric polymerization of Nylon 6,6 from bifunctional monomers is carried out in the presence of an external catalyst with the initial concentration of 10 mole per liter.

A. Obtain the reaction rate constant of the polymerization if it takes 1 minute to reach a degree of polymerization of 10.

B. Obtain the reaction rate constant of the polymerization in the absence of an external catalyst under the same condistions.

A

$$\overline{X}_n = 1 + k'[M]_0 t$$

$$[M]_0 = 10 \times 2 = 20 \ \frac{mol}{l} \Longrightarrow 10 = 1 + k' 20 \times 60 \quad \Rightarrow \quad k' = 7.5 \times 10^{-3}$$

$$t = 1 \times 60 = 60 \ \sec$$

B

$$\overline{X}_n = \left(1 + 2k[M]_0^2 t\right)^{\frac{1}{2}} \Longrightarrow 10 = \left(1 + 2 \times k \times 20^2 \times 60\right)^{\frac{1}{2}} \quad \Rightarrow \quad k = 2.083 \times 10^{-3}$$

Example 3-3

The stochiometric polymerization of two bifunctional monomers is carried out in the absence of an external catalyst with the initial concentration of monomers of 10 mole per liter so that after a certain time the desired degree of polymerization is reached. To increase the polymerization rate, an external catalyst is used, which leads to a twofold increase in the reaction rate constant and decreases the reaction time by 50%. If the polymerization rate constant in the presence of the catalyst is 0.01 lit/(mol.min), obtain the time required to reach the desired degree of polymerization.

$$\overline{X}_n=\left(1+2k[M]_0^2t\right)^{\frac{1}{2}} \qquad \overline{X}_n=1+k'[M]_0t \qquad \overline{X}_n=\overline{X}'_n, \quad k'=2k, \quad t'=\frac{t}{2}$$

$$1+k'[M]_0t=\left(1+2k[M]_0^2t\right)^{\frac{1}{2}} \quad \Rightarrow \quad t'=\frac{2\left([M]_0-1\right)}{k'[M]_0}$$

$$[M]_0=10\times 2=20 \ \ \frac{mol}{l} \quad \Rightarrow \quad t'=190 \ \ min$$

Example 3-4

The polymerization of a bifunctional alcohol and a bifunctional acid is carried out in the presence of an external catalyst with the respective initial concentration of 4.0 and 4.2 mole per liter. If the time required to extend the degree of polymerization from 20 to 30 is 2.5 hours, obtain the reaction rate of the polymerization.

$$[A]=[OH]_0=4\times 2=8\ \frac{mol}{l}$$

$$[B]=[COOH]_0=4.2\times 2=8.4\ \frac{mol}{l}$$

$$\overline{X}_n=\overline{X}_{n,Max}\frac{1-r\exp\left(-(1-r)k'[B]_0t\right)}{1+r\exp\left(-(1-r)k'[B]_0t\right)} \Longrightarrow \ln\left[r\frac{\overline{X}_{n,Max}+\overline{X}_n}{\overline{X}_{n,Max}-\overline{X}_n}\right]=(1-r)k'[B]_0t$$

$$\ln\left[r\frac{\overline{X}_{n,Max}+\overline{X}_{n,1}}{\overline{X}_{n,Max}-\overline{X}_{n,1}}\right]=(1-r)k'[B]_0t_1=\beta t_1 \qquad \ln\left[r\frac{\overline{X}_{n,Max}+\overline{X}_{n,2}}{\overline{X}_{n,Max}-\overline{X}_{n,2}}\right]=(1-r)k'[B]_0t_2=\beta t_2$$

Example 3-4 (continued)

$$r=\frac{[A]_0}{[B]_0}=\frac{8.0}{8.4}=0.952 \qquad \overline{X}_{n,Max}=\frac{1+r}{1-r}\approx 41$$

$$\ln\left[r\,\frac{\overline{X}_{n,Max}+\overline{X}_{n,1}}{\overline{X}_{n,Max}-\overline{X}_{n,1}}\right]=(1-r)k'[B]_0t_1=\beta t_1 \quad \ln\left[r\,\frac{\overline{X}_{n,Max}+\overline{X}_{n,2}}{\overline{X}_{n,Max}-\overline{X}_{n,2}}\right]=(1-r)k'[B]_0t_2=\beta t_2$$

$$\beta t_1=1.017 \quad \Rightarrow t_1=\frac{1.017}{\beta}$$

$$\beta t_2=1.816 \quad \Rightarrow t_2=\frac{1.816}{\beta}$$

$$\Delta t=t_2-t_1=\frac{0.798}{\beta}=2.5\times 60=150\ min$$

$$\beta=5.323\times 10^{-3} \quad \Rightarrow \quad (1-r)k'[B]_0=5.323\times 10^{-3} \quad \Rightarrow \quad k'=1.320\times 10^{-2}\frac{l}{mol.min}$$

Example 3-5

The polymerization of a bifunctional alcohol and a bifunctional acid is carried out in the presence of an external catalyst with the respective initial concentration of 4.1 and 4.0 and an equilibrium constant of 500. If the reaction rate constant *k*'=0.0005 liter per mole per second, obtain:

A. maximum degree of polymerization in a closed system;

B. time required to reach the same degree of polymerization obtained above in an open driven system.

C. the molar and weight fraction of monomer in the closed system.

A

$$[A]=[OH]_0=4\times2=8\ \frac{mol}{l}$$

$$[B]=[COOH]_0=4.1\times2=8.2\ \frac{mol}{l}$$

$$r=\frac{[A]_0}{[B]_0}=\frac{8.0}{8.2}=0.976$$

$$K=\frac{r\,p_e^2}{(1-p_e)(1-rp_e)}=500\quad\Rightarrow\quad p_e=0.967\quad\Longrightarrow\quad \overline{X}_{n,e}=\frac{1+r}{1+r-2rp_e}\approx23$$

Example 3-5 (continued)

B

$$\overline{X}_n=\overline{X}_{n,Max}\frac{1-r\exp\left(-(1-r)k'[B]_0t\right)}{1+r\exp\left(-(1-r)k'[B]_0t\right)} \Longrightarrow \ln\left[r\frac{\overline{X}_{n,Max}+\overline{X}_n}{\overline{X}_{n,Max}-\overline{X}_n}\right]=(1-r)k'[B]_0t$$

$$\overline{X}_{n,Max}=\frac{1+r}{1-r}\approx 81 \quad r=\frac{[A]_0}{[B]_0}=\frac{8.0}{8.2}=0.976 \quad \overline{X}_n=\overline{X}_{n,e}\approx 23 \quad k'=0.0005\frac{l}{mol.s}$$

$$\Downarrow$$

$$t\approx 93.20 \quad min$$

C

$$F(r)=p^{(r-1)}(1-p) \;\Rightarrow\; F(1)=1-p=0.033$$

$$W(r)=p^{(r-1)}(1-p)^2r \;\Rightarrow\; W(1)=(1-p)^2=1.089\times 10^{-3}$$

Example 3-6

The polymerization of a bifunctional alcohol and a bifunctional acid is carried out in a closed system with an equilibrium constant equal to 50 and with the initial concentration of 5 mole per liter. Obtain the amount of water that should be removed to reach a degree of polymerization of 50.

$$[H_2O]=\frac{K[M]_0}{\overline{X}_n(\overline{X}_n-1)} \qquad [M]_0=5\times2=10\ \frac{mol}{l}$$

$$[H_2O]=\frac{50\times10}{50(50-1)}=0.2\ \frac{mol}{l}, \qquad V=1\ l \quad \Rightarrow \quad [H_2O]_{\text{at equilibrium}}=0.2\ mol$$

$$\overline{X}_n=\frac{1}{1-p}=50 \quad \Rightarrow \quad p=0.98$$

$$[H_2O]_{\text{total}}=(2\times5)\times0.98=9.8\ \frac{mol}{l}, \qquad V=1 \quad \Rightarrow [H_2O]=9.8\ \ mol$$

$$[H_2O]_{\text{to be removed}}=[H_2O]_{\text{total}}-[H_2O]_{\text{at equilibrium}}=9.8-0.2=9.6\ \ mol$$

Example 3-7

Calculate the maximum conversion of a polymerization of 2 moles glycerol and 3 moles phthalic acid to reach a degree of polymerization of 100.

$$f_{avg} = \frac{\sum N_i f_i}{\sum N_i} = \frac{(2\times 3)+(3\times 2)}{2+3} = \frac{12}{5} = 2.4$$

$$\overline{X}_n = \frac{2}{2-p f_{avg}} \quad \Rightarrow \quad p = \frac{2}{f_{avg}}\left(1-\frac{1}{\overline{X}_n}\right) = \frac{2}{2.4}\left(1-\frac{1}{100}\right) = 0.825$$

Example 3-8

Calculate the critical gel conversion of a polymerization of A and B monomers with the following combination scheme:

Monomer A: 4 moles monofunctional, 51 moles bifunctional, 2 moles trifunctional, and 3 moles tetrafunctional

Monomer B: 2 moles monofunctional, 50 moles bifunctional, 3 moles trifunctional, and 3 moles pentafunctional

Method A

$$r=\frac{\sum f_{A_i}N_{A_i}}{\sum f_{B_i}N_{B_i}}=\frac{(4\times1)+(51\times2)+(2\times3)+(3\times4)}{(2\times1)+(50\times2)+(3\times3)+(3\times5)}=0.984$$

$$\rho_A=\frac{\sum f_{A_i^*}N_{A_i^*}}{\sum f_{A_i}N_{A_i}}=\frac{(2\times3)+(3\times4)}{(4\times1)+(51\times2)+(2\times3)+(3\times4)}=0.145$$

Example 3-8 (continued)

$$\rho_B = \frac{\sum f_{B_i^*} N_{B_i^*}}{\sum f_{B_i} N_{B_i}} = \frac{(3\times 3)+(3\times 5)}{(2\times 1)+(50\times 2)+(3\times 3)+(3\times 5)} = 0.190$$

$$f_{avg}^{A^*} = \frac{\sum f_{A_i^*} N_{A_i^*}}{\sum N_{A_i^*}} = \frac{(2\times 3)+(3\times 4)}{2+3} = 3.6 \qquad f_{avg}^{B^*} = \frac{\sum f_{B_i^*} N_{B_i^*}}{\sum N_{B_i^*}} = \frac{(3\times 3)+(3\times 5)}{3+5} = 4.0$$

$$p_c = \frac{1}{\left\{r\left(1+\rho_A\left(f_{avg}^{A^*}-2\right)\right)\left(1+\rho_B\left(f_{avg}^{B^*}-2\right)\right)\right\}^{\frac{1}{2}}}$$

$$p_c = \frac{1}{\left\{0.984\left(1+0.145\left(3.6-2\right)\right)\left(1+0.190\left(4-2\right)\right)\right\}^{\frac{1}{2}}} = 0.773$$

Example 3-8 (continued)

Method B

$$r=\frac{\sum f_{A_i}N_{A_i}}{\sum f_{B_i}N_{B_i}}=\frac{(4\times1)+(51\times2)+(2\times3)+(3\times4)}{(2\times1)+(50\times2)+(3\times3)+(3\times5)}=0.984$$

$$f_{w,A}=\frac{\sum f_{A_i}^2N_{A_i}}{\sum f_{A_i}N_{A_i}}\frac{(4\times1^2)+(51\times2^2)+(2\times3^2)+(3\times4^2)}{(4\times1)+(51\times2)+(2\times3)+(3\times4)}=2.210$$

$$f_{w,B}=\frac{\sum f_{B_i}^2N_{B_i}}{\sum f_{B_i}N_{B_i}}=\frac{(2\times1^2)+(50\times2^2)+(3\times3^2)+(3\times5^2)}{(2\times1)+(50\times2)+(3\times3)+(3\times5)}=2.413$$

$$p_c=\frac{1}{\left\{r\left(f_{w,A}-1\right)\left(f_{w,B}-1\right)\right\}^{\frac{1}{2}}}=\frac{1}{\left\{0.984\left(2.210-1\right)\left(2.413-1\right)\right\}^{\frac{1}{2}}}=0.771$$

Example 3-9

The RIM of polyurethane mixture is carried out according to the below conditions. The final product should be a foam, although it is not. Why?

Raw Material	Amount (mole)	Functionality
Polyol (OH)	0.6	2.3
TDI (N=C=O)	0.5	2
Methylene Chloride	0.3	-

$$r = \frac{\sum f_{A_i} N_{A_i}}{\sum f_{B_i} N_{B_i}} = \frac{(0.5 \times 2)}{(0.6 \times 2.3)} = 0.725$$

$$\rho_A = \frac{\sum f_{A_i^*} N_{A_i^*}}{\sum f_{A_i} N_{A_i}} = 0 \qquad \rho_B = \frac{\sum f_{B_i^*} N_{B_i^*}}{\sum f_{B_i} N_{B_i}} = \frac{(0.6 \times 2.3)}{(0.6 \times 2.3)} = 1.0$$

Example 3-9 (continued)

$$f_{avg}^{A^*}=\frac{\sum f_{A_i^*} N_{A_i^*}}{\sum N_{A_i^*}}=0 \qquad f_{avg}^{B^*}=\frac{\sum f_{B_i^*} N_{B_i^*}}{\sum N_{B_i^*}}=\frac{(0.6\times 2.3)}{0.6}=2.3$$

$$p_c=\frac{1}{\left\{r\left(1+\rho_A\left(f_{avg}^{A^*}-2\right)\right)\left(1+\rho_B\left(f_{avg}^{B^*}-2\right)\right)\right\}^{\frac{1}{2}}}=\frac{1}{\left\{0.725\left(1+1\left(2.3-2\right)\right)\right\}^{\frac{1}{2}}}=1.03>1$$

Since the gel point conversion is greater than 1, the foaming agent escape the system before foaming happens. Thus the gel point conversion should be reduced to values lower than unity, which can be handled only by changing *r* value either by polyol o isocyanate.

Example 3-10

The polymerization rate equation of a polyurethane is given below. If the reaction rate constant is 0.02 liter per mole per min and A and B stand for isocyanate and hydroxyl groups respectively, calculate the time required to reach the gel conversion.

Raw Material	Amount (mole)	Functionality
$C_{17}H_{14}N_2O_2$	2	2
$C_8H_{18}O$	1.4	1
$C_6H_{14}O_3$	1.1	3
Benzene	1	-

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]$$

$$r = \frac{\sum f_{A_i} N_{A_i}}{\sum f_{B_i} N_{B_i}} = \frac{(2\times2)}{(1.4\times1)+(1.1\times3)} = 0.851$$

$$\rho_A = \frac{\sum f_{A_i^*} N_{A_i^*}}{\sum f_{A_i} N_{A_i}} = 0$$

$$\rho_B = \frac{\sum f_{B_i^*} N_{B_i^*}}{\sum f_{B_i} N_{B_i}} = \frac{(1.1\times3)}{(1.1\times3)+(1.4\times1)} = 0.702$$

Example 3-10 (continued)

$$f_{avg}^{A^*}=\frac{\sum f_{A_i^*}N_{A_i^*}}{\sum N_{A_i^*}}=0 \qquad f_{avg}^{B^*}=\frac{\sum f_{B_i^*}N_{B_i^*}}{\sum N_{B_i^*}}=\frac{(1.1\times 3)}{1.1}=3$$

$$p_c=\frac{1}{\left\{r\left(1+\rho_A\left(f_{avg}^{A^*}-2\right)\right)\left(1+\rho_B\left(f_{avg}^{B^*}-2\right)\right)\right\}^{\frac{1}{2}}}=\frac{1}{\left\{0.851\left(1+0.702\left(3-2\right)\right)\right\}^{\frac{1}{2}}}=0.831$$

$$-\frac{d[A]}{dt}=-\frac{d[B]}{dt}=k[A][B] \qquad \frac{[A]_0-[A]}{[A]_0}=p \;\Rightarrow\; [A]_0\frac{dp}{dt}=-\frac{d[A]}{dt}$$

$$r[B]_0=[A]_{0,} \quad [B]-[B]_0=[A]-[A]_0 \;\Rightarrow\; [B]=[A]+[B]_0(1-r)$$

$$-\frac{d[A]}{dt}=k[A]\left\{[A]+[B]_0(1-r)\right\} \qquad [A]_0\frac{dp}{dt}=k[A]_0(1-p)\left\{[A]_0(1-p)+[B]_0(1-r)\right\}$$

Example 3-10 (continued)

$$[A]_0 \frac{dp}{dt} = k[A]_0(1-p)\{[A]_0(1-p)+[B]_0(1-r)\}$$

$$\frac{dp}{dt} = k(1-p)\{r[B]_0(1-p)+[B]_0(1-r)\}$$

$$\frac{dp}{dt} = k(1-p)\{r[B]_0(1-p)+[B]_0(1-r)\} = k[B]_0(1-p)(1-rp)$$

$$\int_0^p \frac{dp}{(1-p)(1-rp)} = k[B]_0 t \;\Rightarrow\; \int_0^{0.831} \frac{dp}{(1-p)(1-0.851\,p)} = 0.02\times 4.7\,t$$

$$t = 39.244 \quad min$$

Radical Chain Polymerization

Example 4-1

Calculate the mechanism and kinetics of poly(methyl methacrylate) solution polymerization.

Main reactions

$I \rightarrow 2R^{\bullet} + G\uparrow$	$R_d = 2 f k_d [I]$
$R^{\bullet} + M \rightarrow M^{\bullet}$	$R_i = k_i [R^{\bullet}][M]$
$2R^{\bullet} \rightarrow I'$	$R_{ti} = k_{ti} [R^{\bullet}]^2$
$M_n^{\bullet} + M \rightarrow M_{n+1}^{\bullet}$	$R_p = k_p [M_n^{\bullet}][M]$
$M_n^{\bullet} + M_m^{\bullet} \rightarrow P_{n+m}$	$R_{tc} = k_{tc} [M_n^{\bullet}][M_m^{\bullet}]$
$M_n^{\bullet} + M_m^{\bullet} \rightarrow P_n + P_m$	$R_{td} = k_{td} [M_n^{\bullet}][M_m^{\bullet}]$

$[I]$ initiator concentration (AIBN)
$[R^{\bullet}]$ primary radicals
$[I']$ produced initiator by primary radical recombination
G nitrogen gas released
$[M]$ monomer concentration
$[M_n^{\bullet}]$ concentration of living radicals with a chain length of n
P_n dead polymer with a chain length of n
k_d initiator decomposition rate constant
k_p propagation rate constant
k_{tc} termination by coupling (combination) rate constant
k_{td} ermination by disproportionationrate constant

Example 4-1 (continued)

Secondary reactions

$$M \rightarrow 2M^{\bullet} \qquad R_{di} = 2k_{di}[M]^2$$

$$M_n^{\bullet} + M \rightarrow M^{\bullet} + P_n \qquad R_{tr,M} = k_{tr,M}[M][M_n^{\bullet}]$$

$$M_n^{\bullet} + P_m \rightarrow M_m^{\bullet} + P_n \qquad R_{tr,P} = k_{tr,P}[M_n^{\bullet}][P_m]$$

$$M_n^{\bullet} + S \rightarrow P_n + S^{\bullet} \qquad R_{tr,S} = k_{tr,S}[M_n^{\bullet}][S]$$

$$S^{\bullet} + M \rightarrow S + M_1^{\bullet} \qquad R_a = k_a[S^{\bullet}][M]$$

$$M_n^{\bullet} + I \rightarrow P_n + I^{\bullet} \qquad R_{tr,I} = k_{tr,I}[M_n^{\bullet}][I]$$

$$I^{\bullet} + M \rightarrow I + M_1^{\bullet} \qquad R_a = k_a[I^{\bullet}][M]$$

$[S]$ solvent concentration

k_{di} monomer thermal initiation rate constant

$k_{tr,M}$ transfer to monomer rate constant

$k_{tr,P}$ transfer to polymer rate constant

$k_{tr,S}$ transfer to solvent rate constant

$k_{tr,I}$ transfer to initiator rate constant

k_a reinitation rate constant

Example 4-2

Calculate the kinetics equation (rate of reaction equation) of free radical polymerization for initiators with a long half life and when the half life of the initiator is not long.

$$R_p = k_p[M]\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}}$$

$$R_p = k_p[M]\left(\frac{f\,k_d[I]}{k_t}\right)^{\frac{1}{2}}$$

$$[I] = [I]_0 e^{-k_d t}$$

$$[M] = [M]_0(1-p)$$

$$p = 1 - \frac{[M]}{[M]_0}$$

Initiator with long half life

$$[I] = const. \longrightarrow R_i = const.$$

$$R_p = \frac{-d[M]}{dt} = k_p[M]\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}}$$

$$\downarrow$$

$$\frac{-d[M]}{[M]} = k_p\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}} dt$$

$$\downarrow$$

$$\ln\frac{[M]}{[M]_0} = -k_p\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}} t = -k_p\left(\frac{f\,k_d[I]}{k_t}\right)^{\frac{1}{2}} t$$

Example 4-2 (continued)

Initiator with long half life

$$\ln\frac{[M]}{[M]_0}=-k_p\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}}t=-k_p\left(\frac{f\,k_d[I]}{k_t}\right)^{\frac{1}{2}}t$$

$$\frac{[M]}{[M]_0}=\exp\left\{-k_p\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}}t\right\}=\exp\left\{-k_p\left(\frac{f\,k_d[I]}{k_t}\right)^{\frac{1}{2}}t\right\}$$

$$p=1-\exp\left\{-k_p\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}}t\right\}=1-\exp\left\{-k_p\left(\frac{f\,k_d[I]}{k_t}\right)^{\frac{1}{2}}t\right\}$$

Example 4-2 (continued)

Initiator with short half life

$$R_p=k_p[M]\left(\frac{f\,k_d[I]}{k_t}\right)^{\frac{1}{2}}$$

$$[I]=[I]_0\,e^{-k_d t}$$

$$R_p=\frac{-d[M]}{dt}=k_p[M]\left(\frac{f\,k_d[I]_0}{k_t}\right)^{\frac{1}{2}}\exp\left(-\frac{1}{2}k_d t\right)$$

$$\frac{-d[M]}{[M]}=k_p\left(\frac{f\,k_d[I]_0}{k_t}\right)^{\frac{1}{2}}\exp\left(-\frac{1}{2}k_d t\right)dt$$

$$\ln\frac{[M]}{[M]_0}=\frac{-2}{k_d}k_p\left(\frac{f\,k_d[I]_0}{k_t}\right)^{\frac{1}{2}}\left\{1-\exp\left(-\frac{1}{2}k_d t\right)\right\}$$

$$\frac{[M]}{[M]_0}=\exp\left[-2k_p\left(\frac{f[I]_0}{k_d k_t}\right)^{\frac{1}{2}}\left\{1-\exp\left(-\frac{1}{2}k_d t\right)\right\}\right]$$

Example 4-2 (continued)

Initiator with short half life

$$\frac{[M]}{[M]_0} = \exp\left[-2k_p\left(\frac{f[I]_0}{k_d k_t}\right)^{\frac{1}{2}}\left\{1-\exp\left(-\frac{1}{2}k_d t\right)\right\}\right]$$

$$\Downarrow$$

$$p = 1-\exp\left[-2k_p\left(\frac{f[I]_0}{k_d k_t}\right)^{\frac{1}{2}}\left\{1-\exp\left(-\frac{1}{2}k_d t\right)\right\}\right]$$

$$t \rightarrow \infty \quad \Longrightarrow \quad p_{Max} = 1-\exp\left[-2k_p\left(\frac{f[I]_0}{k_d k_t}\right)^{\frac{1}{2}}\right]$$

Example 4-3

The termination of styrene polymerization is mainly carried out by combination (coupling). If the rate constant of termination reaction varies before and after the extent of reaction of 20% as given below and initiation rate is assumed constant, calculate the reaction time required to reach an extent of reaction of 70%.

$$p<20\% \qquad k_{tc_1}=3.6\times10^{7}\ \frac{\text{l}}{\text{mol.s}} \qquad R_i=5\times10^{-6}\ \frac{\text{mol}}{\text{l.s}} \qquad [M]_0=9.6\ \frac{\text{mol}}{\text{l}}$$

$$p>20\% \qquad k_{tc}=k_{tc_1}\left[\exp(-p)(1-p)\right]^2\ \frac{\text{l}}{\text{mol.s}} \qquad k_p=176\ \frac{\text{l}}{\text{mol.s}}$$

$$p=1-\exp\left\{-k_p\left(\frac{R_i}{2k_t}\right)^{\frac{1}{2}}t_1\right\} \quad \rightarrow \quad 0.2=1-\exp\left\{-176\left(\frac{5\times10^{-6}}{2\times3.6\times10^{7}}\right)^{\frac{1}{2}}t_1\right\}$$

$$\downarrow$$

$$t_1=4811.19\,\text{s}=80.19\,\text{min}$$

Example 4-3 (continued)

$$\frac{-d[M]}{[M]}=k_p\left(\frac{R_i}{2k_{tc_2}}\right)^{\frac{1}{2}}dt$$

$$[M]=[M]_0(1-p)$$

$$\frac{[M]_0\,dp}{[M]_0(1-p)}=k_p\left(\frac{R_i}{2k_{tc_2}}\right)^{\frac{1}{2}}dt$$

$$\frac{dp}{(1-p)}=k_p\left(\frac{R_i}{2k_{tc_1}\left[\exp(-p)(1-p)\right]^2}\right)^{\frac{1}{2}}dt$$

$$\exp(-p)\,dp=k_p\left(\frac{R_i}{2k_{tc_1}}\right)^{\frac{1}{2}}dt$$

$$\int_{0.2}^{0.7}\exp(-p)\,dp=k_p\left(\frac{R_i}{2k_{tc_1}}\right)^{\frac{1}{2}}\int_0^{t_2}dt$$

$$\exp(-0.2)-\exp(-0.7)=176\left(\frac{5\times10^{-6}}{2\times3.6\times10^{7}}\right)^{\frac{1}{2}}t_2$$

$$t_2=6945.77\ \text{s}=115.76\ \text{min}$$

$$t=t_1+t_2=11756.97\ \text{s}=195.95\ \text{min}$$

Example 4-4

If the the concentration of free radicals in a free radical polymerization varies with the concentration of initiator and the rate of termination is related to initiator decomposition rate as given below, what percentage of the free radicals generated in the initiation process remains unreacted?

$$k_t = 10^8 k_d \qquad [M^\bullet] = 0.90 \times 10^{-4} [I]^{\frac{1}{2}}$$

Assuming QSSA: $R_i = R_t$

$$[M^\bullet] = \left(\frac{f\,k_d [I]}{k_t} \right)^{\frac{1}{2}}$$

$$0.90 \times 10^{-4} [I]^{\frac{1}{2}} = \left(\frac{f\,k_d [I]}{k_t} \right)^{\frac{1}{2}}$$

$$0.90 \times 10^{-4} [I]^{\frac{1}{2}} = 10^{-4} \times \sqrt{f}\,[I]^{\frac{1}{2}}$$

$$f = 0.90^2 = 0.81$$

$$\text{Percentage of Unreacted Radicals} = 100\,\% \times (1 - f) = 19\,\%$$

Example 4-5

A. Prove that if the ratio of k_p^2/k_t is high, the rate of reaction must be reduced to increase the degree of polymerization.

B. What is the effect of monomer concentration on the degree of polymerization in this case?

C. If 25% of chains are terminated by combination and the degree of polymerization is equal to 400, calculate the kinetic chain length.

$$\bar{X}_n = \frac{R_p}{R_t} = \frac{k_p[M][M^\bullet]}{k_t[M^\bullet]^2} = \frac{k_p[M][M^\bullet]}{k_t[M^\bullet]^2}\,\frac{R_p}{R_p} = \frac{k_p^2[M]^2[M^\bullet]^2}{k_t[M^\bullet]^2 R_p} = \frac{k_p^2}{k_t}\,\frac{[M]^2}{R_p}$$

So, we can either increase $[M]$ or decrease R_p to increase degree of polymerization.

However, increasing $[M]$ is not always possible due to limitations such as reactor volume being constant.

$$\bar{X}_n = 2a\nu + (1-a)\nu = (1+a)\nu \quad \Longrightarrow \quad \nu = \frac{\bar{X}_n}{(1+a)} \qquad \nu = \frac{400}{(1+0.25)} = 320$$

Example 4-6

If the initiation of PMMA polymerization at 80 °C is carried out with 1% of AIBN initiator (with respect to monomer) and termination is by disproportionation,

A. Calculate the amount of chain transfer agent required to reach a number-average molecular weight of 2×10^4 gr.mol^{-1}?

B. What is number-average molecular weight of the polymer in the absence of chain transfer agent?

$$k_d = 9\times10^{-6}\,\mathrm{s}^{-1} \qquad f = 0.5 \qquad C_S = 0.66 \qquad d_M = 9400\,\mathrm{gr\,.\,cm}^{-3}$$

$$\frac{k_p^2}{k_{td}} = 0.0104\,\mathrm{mol.s}^{-1} \qquad M_M = 100\,\mathrm{gr.mol}^{-1} \qquad M_I = 164\,\mathrm{gr.mol}^{-1}$$

$$[M]_0 = 9.4\,\mathrm{mol.l}^{-1} \qquad [I]_0 = 0.0573\,\mathrm{mol.l}^{-1}$$

Example 4-6 (continued)

$$\frac{1}{\overline{X}_n}=\frac{(2-a)R_i}{2R_p}+C_M+C_S\frac{[S]}{[M]}+C_I\frac{[I]}{[M]}\xrightarrow[k_t=k_{td}]{a=C_M=C_I=0}$$

$$\frac{1}{\overline{X}_n}=\frac{R_i}{R_p}+C_S\frac{[S]}{[M]}\qquad R_i=2fk_d[I]\qquad R_p=k_p[M]\left(\frac{fk_d[I]}{k_t}\right)^{\frac{1}{2}}$$

$$\frac{1}{\overline{X}_n}=\frac{2fk_d[I]}{k_p[M]\left(\frac{fk_d[I]}{k_t}\right)^{\frac{1}{2}}}+C_S\frac{[S]}{[M]}\longrightarrow\frac{1}{\overline{X}_n}=\frac{2(fk_d[I])^{\frac{1}{2}}}{[M]\left(\frac{k_p^2}{k_t}\right)^{\frac{1}{2}}}+C_S\frac{[S]}{[M]}$$

$$\overline{X}_n=\frac{\overline{M}_n}{M_M}=\frac{2\times10^4}{100}=2\times10^2$$

If we consider all the calculation for the beginning of the reaction, we can use the initial values.

Example 4-6 (continued)

$$\frac{1}{\overline{X}_n}=\frac{2\left(f\,k_d[I]\right)^{\frac{1}{2}}}{[M]\left(\frac{k_p^2}{k_t}\right)^{\frac{1}{2}}}+C_S\frac{[S]}{[M]} \quad\longrightarrow\quad \frac{1}{\overline{X}_n}=\frac{2\left(f\,k_d[I]_0\right)^{\frac{1}{2}}}{[M]_0\left(\frac{k_p^2}{k_t}\right)^{\frac{1}{2}}}+C_S\frac{[S]_0}{[M]_0}$$

$$\frac{1}{2\times10^2}=1.0594\times10^{-3}+0.66\frac{[S]_0}{9.4} \quad\longrightarrow\quad \frac{1}{2\times10^2}=1.0594\times10^{-3}+0.66\frac{[S]_0}{9.4}$$

$$[S]_0=5.6123\times10^{-2}\ \ \text{mol.l}^{-1}$$

In the absence of a chain transfer agent we have $\frac{1}{\overline{X}_n}=\frac{2\left(f\,k_d[I]_0\right)^{\frac{1}{2}}}{[M]_0\left(\frac{k_p^2}{k_t}\right)^{\frac{1}{2}}}=1.0594\times10^{-3}$

$$\overline{X}_n=943.911 \quad\longrightarrow\quad \overline{M}_n=943.911\times100=94391.1\,\text{gr.mol}^{-1}$$

Example 4-7

What are the changes in the rate of polymerization and degree of polymerization of a free radical polymerization being run at 50 °C, if the temperature increases by 150%?

$$E_{\overline{X}_n} = -10\ \text{kcal.mol}^{-1} \qquad E_R = 25\ \text{kcal.mol}^{-1}$$

$$T_1 = 50 + 273.15 = 323.15\ \text{K} \quad T_2 = 1.5 \times 50 + 273.15 = 348.15\ \text{K}$$

$$\frac{R_{p,T_2}}{R_{p,T_1}} = \frac{A_R \exp\left(\frac{-E_R}{RT_2}\right)}{A_R \exp\left(\frac{-E_R}{RT_1}\right)} = \exp\left[\frac{-E_R}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

$$\frac{R_{p,T_2}}{R_{p,T_1}} = \exp\left[\frac{-25 \times 10^3}{1.987}\left(\frac{1}{348.15} - \frac{1}{323.15}\right)\right] = 16.376$$

Example 4-7 (continued)

$$\frac{\overline{X}_{n,T_2}}{\overline{X}_{n,T_1}}=\frac{A_{\overline{X}_n}\exp\left(\frac{-E_{\overline{X}_n}}{RT_2}\right)}{A_{\overline{X}_n}\exp\left(\frac{-E_{\overline{X}_n}}{RT_1}\right)}=\exp\left[\frac{-E_{\overline{X}_n}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right]$$

$$\Downarrow$$

$$\frac{\overline{X}_{n,T_2}}{\overline{X}_{n,T_1}}=\exp\left[\frac{10\times10^3}{1.987}\left(\frac{1}{348.15}-\frac{1}{323.15}\right)\right]=0.327$$

Example 4-8

PMMA polymerization in the presence of 100 gr.l^{-1} methylmethacrylate and 0.5 gr.l^{-1} BPO at 60 °C is carried with assuming termination by combination and no thermal initiation is considered. The initiator efficiency is 100% and the polymerization rate is much faster than the initiator consumption; regarding the data given below, calculate the number-average degree of polymerization at the onset of the polymerization and at 70 °C.

$$\frac{k_p^2}{k_t} = 0.01 \ \text{l.mol}^{-1}.\text{s}^{-1} \ \text{at} \ 60^\circ\text{C} \qquad E_{\overline{X}_n} = -60 \ \text{kJ.mol}^{-1} \qquad t_{1/2,60^\circ\text{C}} = 100 \ \text{hr}$$

$$M_{MMA} = 100 \ \text{gr.grmol}^{-1} \qquad M_{BPO} = 242 \ \text{gr.grmol}^{-1}$$

$$t_{1/2,60^\circ\text{C}} = 100 \ \text{hr} \quad \Longrightarrow \quad t_{1/2,60^\circ\text{C}} = 100 \times 3600 = 3.6 \times 10^5 \ \text{s}$$

$$k_{d,60^\circ\text{C}} = \frac{\ln 2}{t_{1/2,60^\circ\text{C}}} = \frac{\ln 2}{3.6 \times 10^5} = 1.925 \times 10^{-6} \ \text{s}^{-1}$$

Example 4-8 (continued)

$$[M]_0 = \frac{100\ \text{gr.l}^{-1}}{100\ \text{gr.grmol}^{-1}} = 1\ \text{grmol.l}^{-1}$$

$$f = 1$$

$$[I]_0 = \frac{0.5\ \text{gr.l}^{-1}}{242\ \text{gr.grmol}^{-1}} = 2.066 \times 10^{-3}\ \text{grmol.l}^{-1}$$

Termination by combination $\Rightarrow \bar{X}_n = 2\,\nu$

$$\nu = \frac{k_p[M]}{2\left(f\,k_d k_t [I]\right)^{\frac{1}{2}}}$$

$$\Downarrow$$

$$\bar{X}_n = \frac{k_p[M]}{\left(f\,k_d k_t [I]\right)^{\frac{1}{2}}}$$

$$\Leftarrow$$

$$\bar{X}_n = \frac{0.1 \times 1}{\left(1 \times 1.925 \times 10^{-6} \times 2.066 \times 10^{-3}\right)^{\frac{1}{2}}} = 1585.69 \approx 1586$$

Example 4-8 (continued)

$$\frac{\overline{X}_{n,T_2}}{\overline{X}_{n,T_1}}=\frac{A_{\overline{X}_n}\exp\left(\frac{-E_{\overline{X}_n}}{RT_2}\right)}{A_{\overline{X}_n}\exp\left(\frac{-E_{\overline{X}_n}}{RT_1}\right)}=\exp\left[\frac{-E_{\overline{X}_n}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right]$$

$$E_{\overline{X}_n}=-60\ \text{kJ.mol}^{-1}$$

$$\Downarrow$$

$$\overline{X}_{n,T_2}=1586\times\exp\left[\frac{60\times10^3}{8.314}\left(\frac{1}{343.15}-\frac{1}{333.15}\right)\right]=843.45$$

Example 4-9

Develop the kinetic equations for an equilibrium addition polymerization.

$$M_n\bullet + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{n+1}\bullet$$

$[M]_e$ monomer concentration at equilibrium

$K = \dfrac{k_p}{k_{dp}}$ Equilibrium constant

at equilibrium $R_p = R_{dp} \Longrightarrow k_p[M_n^\bullet][M] = k_{dp}[M_{n+1}^\bullet]$

at equilibrium where $[M] = [M]_e$ one may assume $[M_n^\bullet] = [M_{n+1}^\bullet]$

$$\Big\Downarrow$$

$$[M]_e = \frac{k_{dp}}{k_p} = \frac{1}{K}$$

Example 4-9 (continued)

$$R_{pt} = -\frac{d[M]}{dt} = R_p - R_{dp} = k_p[M_n^\bullet][M] - k_{dp}[M_{n+1}^\bullet] \qquad [M_n^\bullet] = [M_{n+1}^\bullet] = [M^\bullet]$$

$$\Downarrow$$

$$R_{pt} = -\frac{d[M]}{dt} = k_p[M^\bullet][M] - k_{dp}[M^\bullet] = k_p[M^\bullet]\left([M] - \frac{k_{dp}}{k_p}\right)$$

$$R_{pt} = -\frac{d[M]}{dt} = k_p[M^\bullet]\left([M] - [M]_e\right) \qquad [M^\bullet] = \left(\frac{f\,k_d[I]}{k_t}\right)^{\frac{1}{2}} \qquad [I] = [I]_0 \exp(-k_d t)$$

$$\Downarrow$$

$$R_{pt} = -\frac{d[M]}{dt} = k_p\left(\frac{f\,k_d[I]_0}{k_t}\right)^{\frac{1}{2}} \exp\left(-\frac{k_d t}{2}\right)\left([M] - [M]_e\right)$$

Example 4-9 (continued)

$$R_{pt}=-\frac{d[M]}{dt}=k_p\left(\frac{f\,k_d[I]_0}{k_t}\right)^{\frac{1}{2}}\exp\left(-\frac{k_d t}{2}\right)\left([M]-[M]_e\right)$$

$$\Downarrow$$

$$-\frac{d[M]}{[M]-[M]_e}=k_p\left(\frac{f\,k_d[I]_0}{k_t}\right)^{\frac{1}{2}}\exp\left(-\frac{k_d t}{2}\right)dt$$

$$\Downarrow$$

$$\int_{[M]_0}^{[M]}-\frac{d[M]}{[M]-[M]_e}=\int_0^t k_p\left(\frac{f\,k_d[I]_0}{k_t}\right)^{\frac{1}{2}}\exp\left(-\frac{k_d t}{2}\right)dt$$

$$\Downarrow$$

$$\ln\left(\frac{[M]-[M]_e}{[M]_0-[M]_e}\right)=-\frac{2}{k_d}k_p\left(\frac{f\,k_d[I]_0}{k_t}\right)^{\frac{1}{2}}\left\{1-\exp\left(-\frac{k_d t}{2}\right)\right\}$$

Example 4-9 (continued)

$$\ln\left(\frac{[M]-[M]_e}{[M]_0-[M]_e}\right)=-\frac{2}{k_d}k_p\left(\frac{f\,k_d[I]_0}{k_t}\right)^{\frac{1}{2}}\left\{1-\exp\left(-\frac{k_d t}{2}\right)\right\}$$

$$[M]_0\gg[M]_e$$

$$[M]_0-[M]_e\approx[M]_0$$

$$\ln\left(\frac{[M]-[M]_e}{[M]_0}\right)=-2k_p\left(\frac{f[I]_0}{k_d k_t}\right)^{\frac{1}{2}}\left\{1-\exp\left(-\frac{k_d t}{2}\right)\right\}$$

Equilibrium
polymerization

$$[M]-[M]_e=[M]_0\exp\left[-2k_p\left(\frac{f[I]_0}{k_d k_t}\right)^{\frac{1}{2}}\left\{1-\exp\left(-\frac{k_d t}{2}\right)\right\}\right]$$

$$[M]=[M]_0\exp\left[-2k_p\left(\frac{f[I]_0}{k_d k_t}\right)^{\frac{1}{2}}\left\{1-\exp\left(-\frac{1}{2}k_d t\right)\right\}\right]$$

Non-equilibrium
polymerization

Chain Copolymerization

Example 6-1

The copolymerization of two vinyl monomers with the initial ratio of monomer 1 to monomer 2 equal to 7:3, which can be assumed constant during the whole reaction, is carried out at 60 °C. If the rate of initiation is equal to 10^{-6} mol/(l.s) and the the cross termination reaction rate constant is equal to the geometric mean of homotermination rate constants (φ=1), regarding the QSSA:

A. Obtain the termination rate constant.

B. Develop the copolymerization rate equation in terms of total monomer concentration.

C. Calculate the time required to reach a conversion of 40%.

$$r_1=0.7, \quad r_2=1.2, \quad k_{11}=300\ \frac{l}{mol.s}, \quad k_{22}=100\ \frac{l}{mol.s}$$

$$k_{td,11}=1\times10^8\ \frac{l}{mol.s}, \quad k_{td,22}=1\times10^4\ \frac{l}{mol.s}$$

Example 6-1 (continued)

A $$k_{12} = \frac{k_{11}}{r_1} = \frac{300}{0.7} = 428.57 \quad \frac{l}{mol.s}$$

$$k_{21} = \frac{k_{22}}{r_2} = \frac{100}{1.2} = 83.33 \quad \frac{l}{mol.s}$$

$$k_{td,12} = k_{td,21} = \left(k_{td,11} \times k_{td,22}\right)^{\frac{1}{2}} = \left(10^8 \times 10^4\right)^{\frac{1}{2}} = 10^6 \quad \frac{l}{mol.s}$$

$$\bar{k}_t = \left(\frac{f_1}{k_{21} f_1 + k_{12} f_2}\right)^2 \left(k_{t11} k_{21}^2 + k_{t12} k_{12} k_{21}\left(\frac{f_2}{f_1}\right) + k_{t22} k_{12}^2 \left(\frac{f_2}{f_1}\right)^2\right)$$

$$\bar{k}_t = \left(\frac{0.7}{83.33 \times 0.7 + 428.57 \times 0.3}\right)^2$$

$$\left(10^8 \times 83.33^2 + 10^6 \times 428.57 \times 83.33\left(\frac{0.3}{0.7}\right) + 10^4 \times 428.57^2 \left(\frac{0.3}{0.7}\right)^2\right) = 9.96 \times 10^6 \frac{l}{mol.s}$$

Example 6-1 (continued)

Since the feed fraction is assumed constant during the copolymerization, the overall termination rate constant is considered intact.

B

$$R_p=\frac{r_1[M_1]^2+2[M_1][M_2]+r_2[M_2]^2}{\left(\frac{r_1[M_1]}{k_{11}}\right)+\left(\frac{r_2[M_2]}{k_{22}}\right)}\left(\frac{R_i}{2\overline{k}_t}\right)^{\frac{1}{2}} \Rightarrow R_p=\frac{r_1f_1^2+2f_1f_2+r_2f_2^2}{\left(\frac{r_1f_1}{k_{11}}\right)+\left(\frac{r_2f_2}{k_{22}}\right)}[M]\left(\frac{R_i}{2\overline{k}_t}\right)^{\frac{1}{2}}$$

$$R_p=\frac{0.7\times0.7^2+2\times0.7\times0.3+1.2\times0.3^2}{\left(\frac{0.7\times0.7}{300}\right)+\left(\frac{1.2\times0.3}{100}\right)}\left(\frac{10^{-6}}{2\times9.96\times10^6}\right)^{\frac{1}{2}}[M]$$

$$R_p=3.729\times10^{-5}[M]$$

Example 6-1 (continued)

C

$$R_p = -\frac{d[M]}{dt} = [M]_0 \frac{dp}{dt}$$

$$R_p = 1.274\times10^{-5}[M] \quad ⇨ \quad \frac{dp}{dt} = 3.729\times10^{-5}(1-p) \;\Rightarrow\; \frac{dp}{(1-p)} = 3.729\times10^{-5}\,dt$$

$$[M] = [M]_0(1-p)$$

$$\int_0^{0.4} \frac{dp}{(1-p)} = \int_0^{t} 3.729\times10^{-5}\,dt \quad \Rightarrow \quad \ln(1-p)\big|_0^{0.4} = 3.729\times10^{-5}\,t$$

$$t = \frac{-\ln(0.6)}{1.274\times10^{-5}} = 13698.43 \;\; sec = 228.307 \;\; min$$

Example 6-2

The copolymerization of two vinyl monomers at azeotropic point is carried out at 70 °C. If the rate of initiation is equal to 10^{-8} mol/(l.s) and the the cross termination reaction rate constant is equal to the geometric mean of homo-termination rate constants. Assuming termination by combination, regarding the QSSA, and a constant reaction volume:

A. Obtain the reaction conversion after 90 min.

B. Calculate the sequence length average of each monomer.

C. Calculate the instantaneous number-average molecular weight.

$$r_1 = 0.6, \quad r_2 = 0.4, \quad k_{11} = 400 \ \frac{l}{mol.s}, \quad k_{22} = 800 \ \frac{l}{mol.s}$$

$$k_{td,11} = 1 \times 10^8 \ \frac{l}{mol.s}, \quad k_{td,22} = 3 \times 10^7 \ \frac{l}{mol.s}$$

$$M_{w,M1} = 104 \frac{gr}{grmol}, \quad M_{w,M2} = 100 \frac{gr}{grmol}, \quad \rho_1 = \rho_2 = 1000 \frac{gr}{l}$$

Example 6-2 (continued)

A

$$f_1 = F_1 = \frac{(1-r_2)}{(2-r_1-r_2)} = \frac{(1-0.4)}{(2-0.6-0.4)} \Rightarrow f_1 = F_1 = 0.6$$

Since the copolymerization is carried out , $F_1 = \langle F_1 \rangle = 0.6$

$$k_{12} = \frac{k_{11}}{r_1} = \frac{400}{0.6} = 666.67 \quad \frac{l}{mol.s}$$

$$k_{21} = \frac{k_{22}}{r_2} = \frac{800}{0.4} = 2000.0 \quad \frac{l}{mol.s}$$

$$k_{tc,12} = k_{td,21} = (k_{tc,11} \times k_{tc,22})^{\frac{1}{2}} = (10^8 \times 3 \times 10^7)^{\frac{1}{2}} = 5.477 \times 10^7 \quad \frac{l}{mol.s}$$

Example 6-2 (continued)

$$\bar{k}_p = \frac{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}{\left(\frac{r_1 f_1}{k_{11}}\right) + \left(\frac{r_2 f_2}{k_{22}}\right)} \Rightarrow \bar{k}_p = \frac{0.6 \times 0.6^2 + 2 \times 0.6 \times 0.4 + 0.4 \times 0.4^2}{\left(\frac{0.6 \times 0.6}{400}\right) + \left(\frac{0.4 \times 0.4}{800}\right)} = 690.91 \frac{l}{mol.s}$$

$$\bar{k}_t = \left(\frac{f_1}{k_{21} f_1 + k_{12} f_2}\right)^2 \left(k_{t11} k_{21}^2 + k_{t12} k_{12} k_{21} \left(\frac{f_2}{f_1}\right) + k_{t22} k_{12}^2 \left(\frac{f_2}{f_1}\right)^2\right) \Rightarrow$$

$$\bar{k}_t = \left(\frac{0.6}{2000 \times 0.6 + 666.67 \times 0.4}\right)^2$$

$$\left(10^8 \times 2000^2 + 5.477 \times 10^7 \times 2000 \times 666.67 \left(\frac{0.4}{0.6}\right) + 3 \times 10^7 \times 667.67^2 \left(\frac{0.4}{0.6}\right)^2\right)$$

$$= 7.61 \times 10^7 \frac{l}{mol.s}$$

Example 6-2 (continued)

$$p=1-\exp\left\{-\bar{k}_p\left(\frac{R_i}{2\bar{k}_t}\right)^{\frac{1}{2}}t\right\}=1-\exp\left\{-690.91\left(\frac{10^{-8}}{2\times7.61\times10^{7}}\right)^{\frac{1}{2}}\times90\times60\right\}=0.0298$$

B

$$\bar{n}_1=\frac{p_{12}}{\left(1-p_{11}\right)^2}=\frac{1}{p_{12}}=\frac{r_1[M_1]+[M_2]}{[M_2]}=\frac{r_1f_1+f_2}{f_2}=\frac{0.6\times0.6+0.4}{0.4}=1.9$$

$$\bar{n}_2=\frac{p_{21}}{\left(1-p_{22}\right)^2}=\frac{1}{p_{21}}=\frac{r_2[M_2]+[M_1]}{[M_1]}=\frac{r_2f_2+f_1}{f_1}=\frac{0.4\times0.4+0.6}{0.6}=1.267$$

Example 6-2 (continued)

C

$$\bar{X}_n = \frac{R_p}{(2-a)(\frac{R_t}{2}) + k_{tr,M}[M^\bullet][M] + k_{tr,S}[M^\bullet][S] + k_{tr,I}[M^\bullet][I]} = \frac{R_p}{(2-a)(\frac{R_t}{2})}$$

terminationa only by combination $\Rightarrow$ $a=1$

$$\bar{X}_n = \frac{R_p}{\left(\frac{R_{tc}}{2}\right)} = \frac{\bar{k}_p[M]}{\bar{k}_{tc}[M^*]} \quad \text{QSSA} \quad \Rightarrow \quad \bar{X}_n = \frac{\bar{k}_p[M]_0(1-p)}{\left(\frac{\bar{k}_{tc}R_i}{2}\right)^{\frac{1}{2}}}$$

$$[M]_0 = [M_1]_0 + [M_2]_0 = \sum_{i=1}^{2}[M_i]_0 \qquad [M_i]_0 = \frac{n_{i,0}}{V_i} = \frac{\frac{m_{i,0}}{M_{w,m_i}}}{V_i} = \frac{\frac{\rho_i V_{i,0}}{M_{w,m_i}}}{V_i} = \frac{\rho_i \varphi_{i,0}}{M_{w,m_i}}$$

Example 6-2 (continued)

$$[M_i]_0 = \frac{n_{i,0}}{V_i} = \frac{\dfrac{m_{i,0}}{M_{w,m_i}}}{V_i} = \frac{\dfrac{\rho_i V_{i,0}}{M_{w,m_i}}}{V_i} = \frac{\rho_i \varphi_{i,0}}{M_{w,m_i}}$$

$[M_i]_0$: *Initial molar concentration of monomer i*
$n_{i,0}$: *Initial moles of monomer i*
$m_{i,0}$: *Initial mass of monomer i*
M_{w,m_i}: *Molecular weight of monomer i*
ρ_i: *Density of monomer i*
$\varphi_{i,0}$: *Initial volume fraction of monomer i*
V_i: *Total reaction volume*

$$[M]_0 = \sum_{i=1}^{2} [M_i]_0 = \sum_{i=1}^{2} \frac{\rho_i \varphi_{i,0}}{M_{w,m_i}} = 10^3\left(\frac{\varphi_{1,0}}{104} + \frac{\varphi_{2,0}}{100}\right)$$

$$\frac{f_{1_0}}{f_{2_0}} = \frac{0.6}{0.4} = \frac{[M_1]_0}{[M_2]_0} = \frac{\dfrac{\rho_1 \varphi_{1,0}}{M_{w,m_1}}}{\dfrac{\rho_2 \varphi_{2,0}}{M_{w,m_2}}} = \frac{\dfrac{\varphi_{1,0}}{M_{w,m_1}}}{\dfrac{\varphi_{2,0}}{M_{w,m_2}}} = \frac{\varphi_{1,0}}{\varphi_{2,0}} \times \frac{M_{w,m_2}}{M_{w,m_1}} = \frac{\varphi_{1,0}}{\varphi_{2,0}} \times \frac{100}{104} \quad \Rightarrow \quad \frac{\varphi_{1,0}}{\varphi_{2,0}} = \frac{1.56}{1}$$

Example 6-2 (continued)

$$\frac{\varphi_{1,0}}{\varphi_{2,0}}=\frac{1.56}{1}$$

$$\varphi_{1,0}+\varphi_{2,0}=1$$

$\Rightarrow$

$$\varphi_{1,0}=0.609$$

$$\varphi_{2,0}=0.391$$

$\Rightarrow$

$$[M]_0=10^3\left(\frac{\varphi_{1,0}}{104}+\frac{\varphi_{2,0}}{100}\right)=10^3\left(\frac{0.609}{104}+\frac{0.391}{100}\right)=9.766\,\frac{mol}{l}$$

$$\overline{X}_n=\frac{\overline{k}_p[M]_0(1-p)}{\left(\frac{\overline{k}_{tc}R_i}{2}\right)^{\frac{1}{2}}}=\frac{690.91\times9.766\times(1-0.0298)}{\left(\frac{7.61\times10^7\times10^{-8}}{2}\right)^{\frac{1}{2}}}=10613.963$$

$$\overline{M}_{w,m}=\langle F_1\rangle M_{w,m_1}+\langle F_2\rangle M_{w,m_2}=0.6\times104+0.4\times100=102.4$$

$$\overline{M}_n=\overline{X}_n\times\overline{M}_{w,m}=10613.963\times102.4=1086869.79=1.09\times10^6\ \frac{gr}{grmol}$$