Solution Manuel

Exercises 1 : Dilute Solution

1.1. (a) $M_R = 10^3$ kg, $N_R = 1$; $M_B = 0.1$ kg, $N_B = 7$

$N_{total} = N_R + N_B = 8$

fraction $n_R = 1/8$ $n_B = 7/8$

(i) $\overline{M_n} = \sum_i n_i M_i = \frac{1}{8} 10^3 kg + \frac{7}{8}\, 0.1\, kg = 125\, kg\ (125.0875)$

(ii) $\overline{M_w} = \frac{\sum_i n_i {M_i}^2}{\sum_i n_i M_i} = \frac{\frac{1}{8}10^6 + \frac{7}{8}0.1^2}{125}\, kg = 1000 kg\ (999.3)$

(iii) $PDI = \frac{\overline{M_w}}{\overline{M_n}} = \frac{1000}{125} = 8$

(iv) The weight-average mass of the multi creature system is most critical to consider in this case. Mw biases for high mass creatures and it only takes one such creature to do serious damage to a vehicule.

(b) $N_1 = 100$ $n_1 = 100/210 = 0.4762$ $DP_1 = 100$

$N_2 = 100$ $n_2 = 100/210 = 0.4762$ $DP_2 = 1000$

$N_3 = 10$ $n_3 = 10/210 = 0.04762$ $DP_3 = 10000$

$N_{total} = 210$ $m_{mon} = 100 g/mol$ $M_i = DP_i \times m_{mon}$

(i) $\overline{M_n} = \sum_i n_i M_i = \frac{100 g}{mol}\left[\frac{100}{210} \cdot 100 + \frac{100}{210} \cdot 1000 + \frac{10}{210} \cdot 10000\right] = 1000\, kg/mol$

(ii) $\overline{M_w} = \frac{\sum_i n_i {M_i}^2}{\sum_i n_i M_i} = \frac{100^2}{10^5}\left[\frac{100}{210} \cdot 100^2 + \frac{100}{210} \cdot 1000^2 + \frac{10}{210} \cdot 10000^2\right] = 524 \frac{kg}{mol}$

(iii) $PDI = \frac{\overline{M_w}}{\overline{M_n}} = \frac{524}{1000} = 5.24$

1.2. Determining the volume fraction $\nu_1 = 0.9$ and $\nu_2 = 0.1$ the enthalpy of mixing is $\Delta H_m = 8.1$ cal

1.3. a) Entropy of mixing $\Delta S_m = - 1.38 \times 10^{-23}$ J/K (48 ln 0.75 + 16 ln 0.25) = 4.97×10^{-22} J/K

b) Entropy of mixing $\Delta S_m = - 1.38 \times 10^{-23}$ J/K (48 ln 0.75 + 1 ln 0.25) = 2.10×10^{-22} J/K

1.4. Determination of the number of water molecules per cm^3:

1g/1cm^3 x 0.95 x 1mol/18g X 6 $\cdot 10^{23}$ molecules/1mol = 3,18$\cdot$ 10^{22} molecules/cm^3

Determination of the number of polymer molecules per cm^3:

1,13g/1cm^3 x 0,05 x 1mol/250 000g x 6 $\cdot 10^{23}$ molecules/1mol = 1,36 $\cdot 10^{17}$ molecules/cm^3

ΔG_m = 1,38 10^{-23} J/K x 298K(0,4 x 3,18 $\cdot 10^{22}$ molecules/cm^3 x 0,05 + 3,18$\cdot 10^{22}$molecules/cm^3 ln 0,95 + 1,36$\cdot$ 10^{17}molec/cm^3 ln 0,05) = -4,1 J/cm^3

1.5. Determination of the interaction parameter χ for the system

- polyisoprene/dioxane: $\chi = \frac{{}^{88 g/mol}/_{1.03\ g/cm3}}{1.987\ cal7Kmol\ x\ 307K}(10-8.1)^2(\frac{cal}{cm3})$ = 0.51

- PMMA/CCl_4 : $\chi = \frac{{}^{154 g/mol}/_{1.59\ g/cm3}}{1.987\ cal7Kmol\ x\ 300K}(9.2-8.6)^2(\frac{cal}{cm3})$ = 0.06

- poly(vinyl acetate)/ ethanol: $\chi = \frac{{}^{46 g/mol}/_{0.79\ g/cm3}}{1.987\ cal7Kmol\ x\ 307K}(12.7-9.4)^2(\frac{cal}{cm3})$ = 1.1

  → here hydrogen bondings playing a role

General conclusion: predicted values of χ can be different to an experimental value (discussion of the assumptions for the model); from many polymer – solvent systems an empirical constant $\beta = 0.34$ could be determined.

Exercises 2: Polymer Structure in Solution and Molecular Weight Determination

2.1. the mean square end-to-end distance is given with $\langle h^2 \rangle = N b^2 C_\infty$

N is obtained by N = M/mmon

The root mean square end-to-end distance is

$$\langle h^2 \rangle^{1/2} = (\frac{M}{m_{mon}} b^2 C_\infty)^{\frac{1}{2}} = (\frac{10^7}{28}(2.5\text{Å})^2 6.0)^{\frac{1}{2}} = 3700\text{Å} = 370\ nm$$

R_{max} = bN = 8.9x 10^5 Å= 89 µm

2.2. insert the given values in the right units in $R_h = \frac{k_B\,T}{6\,\pi\,\eta_s D}$ = 2 nm

2.3. - Calculate Π for each height in the correct units (mol/g) with $\Pi = \rho\, g\, h$ (density ρ, gravity g)

- plot Π/cRT versus c → regression line
- intercept = $1/\overline{M_n}$
- slope = 2. Virial coefficient

c [kg/m^3]	h [m]	Π [Pa = kg/ms]	Π/cRT [mol/kg]
3.2	0.007	58.3695	7.362 x 10^{-3}
6.6	0.0182	151.7607	9.281 x 10^{-3}
10.0	0.0310	258.4935	0.01043
14.0	0.0544	453.6144	0.01307
19.0	0.0930	775.4805	0.01647

Regression line: y = 0.0006x + 0.0053 → $\overline{M_n}$ = 188 679 g/mol; A_2 = 0.0006 mol cm^3/g^2

Determination of θ-temperature: the system is measured at different temperature resulting for each temperature a 2. Virial coefficient. From a plot A_2 versus T can be for $A_2 = 0$ the θ-temperature obtained.

2.4. no mechanical pressure ($\Delta p = 0$) reducing the Poiseuille equation to

$\frac{\eta}{\varrho} = \frac{g\,\pi\,\Delta t\,R^4}{8\,\Delta V}$ = 9.86 x 10^{-7} m^2/s. η/ρ is the kinematic viscosity. In order to get the dynamic viscosity you need to know the density.

2.5. Using the proportionality $t_P/t_S \approx \eta_P/\eta_S = \eta_{rel}$ gives following values for the plot η_{sp}/c versus c based on the equation $\eta_{sp}/c = [\eta] + K[\eta]^2 c$

c (g/cm^3)	t (s)	η_{rel}	η_{sp}/c (cm^3/g)
0	65.8 = t_s	1.0	-
0.0054	101.2	1.54	99.629
0.0108	144.3	2.19	110.464
0.0162	194.6	2.46	120.83
0.0216	257	3.91	134.527

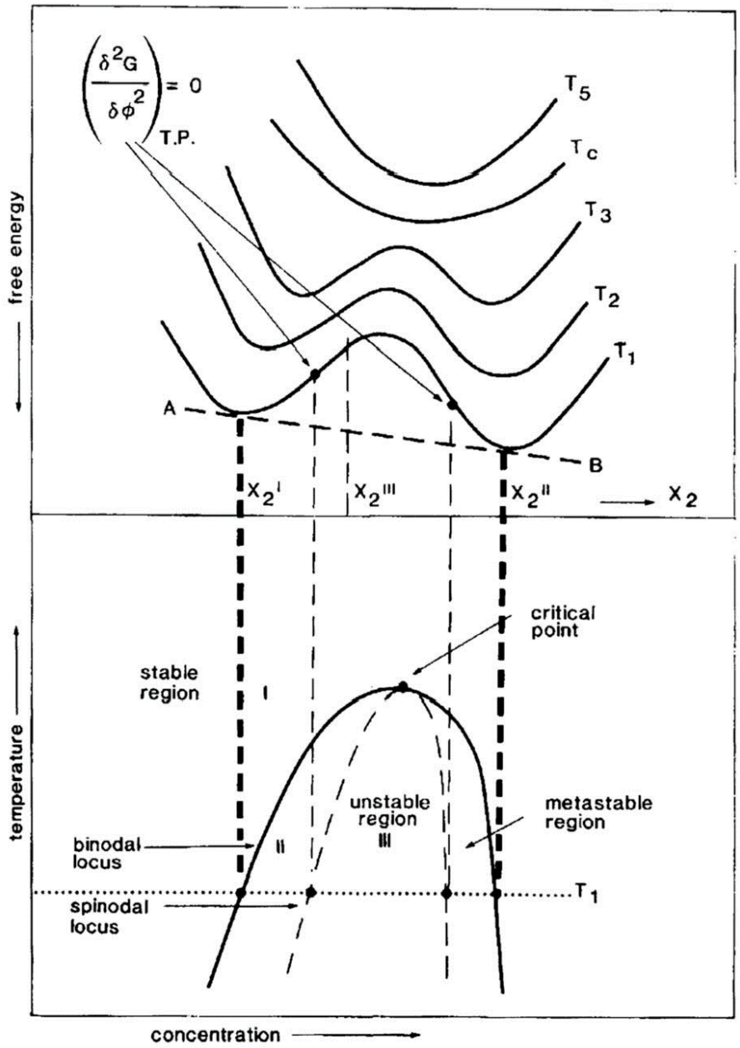
Regression line: y = 21.308 x + 87.597

The intercept of the graph η_{sp}/c versus c corresponds to the intrinsic viscosity $[\eta]$ = 87,597 cm^3/g.

Using the equation $[\eta]= KM^a$ and the given parameters the viscosity average molecular weight M_v is 600 238 g/mol

Exercises 3: Concentrated Solution and Phase Behavior

3.1. construction of the phase diagram showing an upper critical solution temperature.



3.2. Poly(isobutylene) -[$CH_2 - C(CH_3)_2$]- M = 56 g/mol

M (g/mol)	22 700	285 000	6 000 000
$1/T_c$ (1/K)	3.432×10^{-3}	3.134×10^{-3}	3.036×10^{-3}
N (=x)	291	319	329
$\frac{1}{\sqrt{N}} + \frac{1}{2N}$	0.0509	0.0141	0.0031

Regression line of a graph $1/T_c$ versus $\frac{1}{\sqrt{N}} + \frac{1}{2N}$ based on the Flory-Krigbaum equation:

$y = 8.23 \times 10^{-3}x + 3.01 \times 10^{-3}$

the intercept corresponds to $1/T_c$ → 1/intercept = T_θ = 332K

the slope value corresponds to $1/T_\theta\Psi$ → $\Psi = 0.3657$

By using the given equation for the interaction parameter: χ = 0.542

3.3.(a) at the critical point the second and the third derivation of the free energy should be zero

$$\frac{\delta^2}{\delta\phi^2}\left(\frac{\Delta G}{RT}\right) = \frac{1}{\phi_A N_A} + \frac{1}{(1-\phi_{A)}N_B} - 2\chi = 0$$

$$\frac{\delta^3}{\delta\phi^3}\left(\frac{\Delta G}{RT}\right) = -\frac{1}{\phi_A^2 N_A} + \frac{1}{(1-\phi_{A)}{}^2 N_B} = 0$$

The critical composition can be found by using the third derivation and solving following equation:

$$-(1-\phi_{A\,crit})^2 N_B + \phi_{A\,crit}^2 N_A = 0$$

Only the positive root is a valid composition, thus the critical composition is given by

$$\phi_{A\,crit} = \frac{\sqrt{N_B}}{\sqrt{N_A}+\sqrt{N_B}}$$

Substituting the critical composition into the equation of the second derivation gives a relation for the critical interaction parameter:

$$\chi_{crit} = \frac{\left(\sqrt{N_A}+\sqrt{N_B}\right)^2}{2N_A N_B}$$

In the case of a symmetric polymer blend ($N_A = N_B$) the critical composition is ½. For infinite molecular weight N → ∞ the interaction parameter $\chi_{crit} = 0$. In contrast to a polymer solution where $N_B = 1$ (solvent) the critical composition $\phi_{A\,crit} = 0$ and χ = ½.

➔ χ_{crit} → 0 for polymer blend because the entropic contribution to the free energy of mixing is very small, in first approximation the entropic term can be thought of as zero. This corresponds to the fact that only very few miscible polymer blends exist.

(b) Polystyrene (M_{mon} = 104 g/mol) has a degree of polymerization of $N_{PS} = 10^5/104$ g/mol = 960

Polybutadiene (M_{mon} = 52 g/mol) has a degree of polymerization of $N_{PB} = 10^4/52$ g/mol = 192

As given

$$\chi = \frac{v_0}{k_B T}(\delta_1-\delta_2)^2 = \frac{100\cdot 10^{-30} m^3}{1.38\cdot 10^{-23}\frac{J}{K}\ x\ T}(1.87\cdot 10^4 - 1.62\cdot 10^4)^2\,\frac{J}{m^3} = \frac{45K}{T}$$

From (a) the critical interaction parameter is given as

$$\chi_{crit} = \frac{\left(\sqrt{N_{PS}}+\sqrt{N_{PB}}\right)^2}{2N_{PS}N_{PB}} = \frac{\left(960^{\frac{1}{2}} + 192^{\frac{1}{2}}\right)^2}{2\cdot 960\cdot 192} = 0.005$$

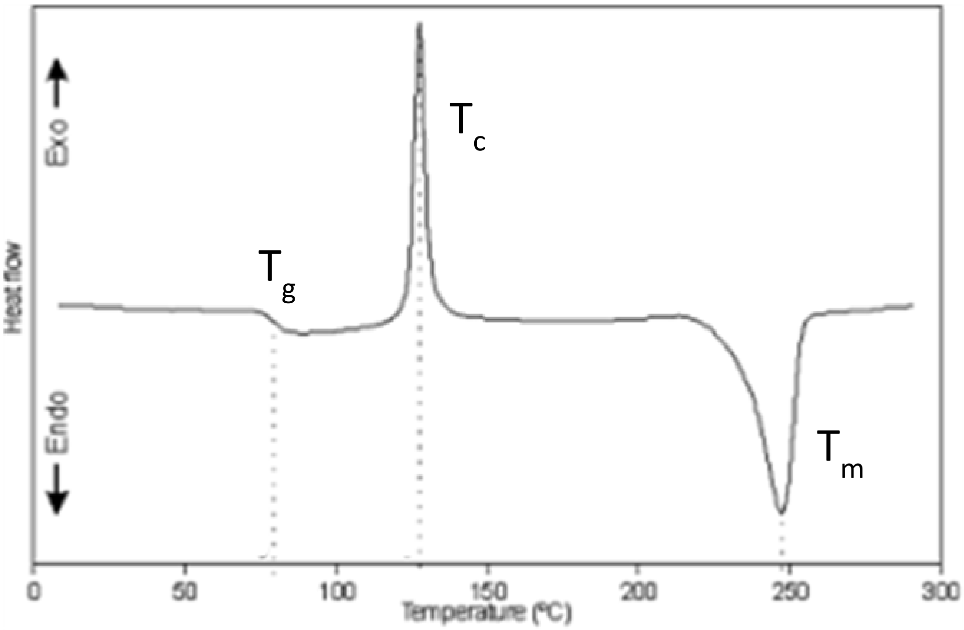
$\chi_c = \frac{45K}{T} = 0.005 \rightarrow T_c = 8250\,K$

Exercises 4: Amorphous State and Glass Transition

4.1. If 60°C is a glass transition, then heating the polymer slowly past 60°C would take it to the rubbery plateau region (elastic region), where the modulus E, and hence the hardness, would remain fairly constant with increase of temperature. For a melting transition, however, the modulus would drop rapidly and the polymer would become increasingly softer in a similar experiment. As a very simple test can be used the penetration of a weighted needle into the polymer as the temperature is increased.

4.2. (a) Stickiness of tape relies on London forces and chain mobility. If the latter is frozen below the glass temperature, the forces are also reduced because the electrons also move less.
(b) The balloon becomes smaller and smaller when it comes in contact with the liquid nitrogen and apparently loses almost its entire volume, because the air inside is liquefied by the action of nitrogen, and it undergoes a decrease in volume. Upon heating, the air boils again and the balloon resumes its initial volume, i. he regains his original form.
At low temperatures, rubber becomes brittle and loses its elasticity (glassy state, liquid like structure is frozen in). If external forces act on the balloon before heating up, the rubber shatters like glass.

4.3.



b) After the sample was cooled rapidly (quenched) the heating scan with the same heating rate as the shown scan following changes will be observed:

- The step of the glass transition will increase if the sample for the first scan wasn't quenched. Quenching avoids crystallization and the amorphous part is increased yielding in a higher step at Tg. The temperature of the Tg will be not changed no change of the rate)

- The recrystallization and the melting peak will occur at the same temperature as shown in the first scan, but the area of the peak can be changed depending how the sample was treated before.

c) If the heating rate is changed to 10°/min the Tg will shift to higher temperature whereas the temperatures of Tc and Tm will be the same. The area of the peaks will be decreased because of the higher rate the polymer chains have less time to rearrange them for crystallization.

4.4.

$$\log a_T = \log\frac{t_1}{t_2} = -\frac{17.4\,(T_1 - T_2)}{51.6 + \;(T_1 - T_2)}$$

$$(T_1 - T_2) = 3°\mathrm{C}$$

4.5.

a) calculate the viscosity at T_g:

$$\log\frac{\eta}{\eta_g} = -\frac{17.4\left(T - T_g\right)}{51.6 + \;\left(T - T_g\right)}$$

$$\log\eta_g = \log 2.5\,x\,10^5 + \frac{17.4\,(313 - 273)}{51.6 + \;(313 - 273)} \longrightarrow \eta_g = 1.03\,x\,10^{13}P$$

b) Calculate the viscosity at 50°C:

$$\log\eta_{50} = 13.013 - \frac{17.4\,(323 - 273)}{51.6 + \;(323 - 273)} \longrightarrow \eta_g = 2.69\,x\,10^4 P$$

4.6. T_{g1} (DEHP) = 187 K, T_{g2} (PVC) = 363 K.

Determination of the fraction of DEHP in order to change the T_g of the copolymer to 293 K

1/293 = w_1/187 + (1-w_1)/363 → $w_1 = \frac{\frac{1}{293}-\frac{1}{363}}{\frac{1}{187}-\frac{1}{363}} = 0.25$ (DEHP) → w_2 = 0.75 (PVC)

4.7. 1 = styrene, M_1 = 104 g/mol, T_{g1} = 368 K

2 = propylene M_2 = 42 g/mol T_{g2} = 263 K

With $n_1 = n_2 = n$ (equimolar) the fraction of propylene is given by $w_2 = \frac{n\,M_2}{n\,M_1 + n\,M_2} = 0.288$

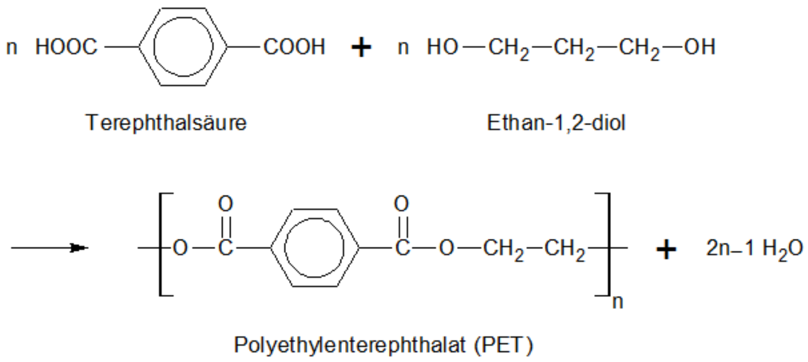
$W_1 = 1 - w_2$ = 1- 0.288 = 0.712

Insert in Fox equation: $1/T_g$ = 0.00303 → T_g = 330K

Exercises 5: Semicrystalline Polymers

5.1.

a)

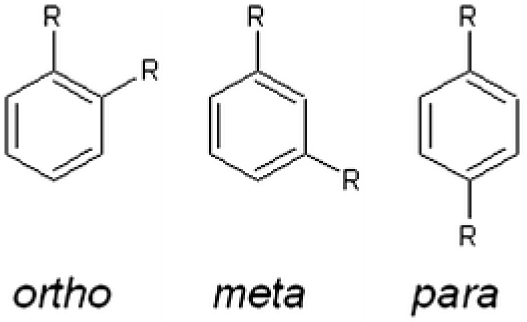


b) Both additive are disturbing the crystallinity, resulting in a decrease of the melting temperature. But the reason is different.

- CHDM replaces ethylene glycol: CHDM has 5 C-atoms instead of 2 C-atoms from ethylene glycol

→ it doesn't fit in the neighboring chains → regularity is disturbed

-Isophthalic acid instead of therephthalic acid



1,2- (ortho) or 1,3- (meta) linkages are asymmetric in contrast to the 1,4- (para) linkage. This produces an angle in the chain avoiding regularity

c) Transparent products can be obtained by quenching the molten polymer resulting in an amorphous polymer.

d) The crystallinity is given by weight. In order to calculate the density first the crystallinity by volume is needed:

$$X_c^V = \frac{\rho_a}{\rho_c} X_c^W = 0.47$$

The density of the polymer can be obtained by:

$$\rho_p = X_c^V (\rho_c - \rho_a) + \rho_a = 1410 \frac{Kg}{m^3}$$

e) by x-ray, DSC

5.2. Mass per unit cell:

2 repeat units/unit cell x 1 mol repeat units/6 x 10^{23} repeat units x 28g/ 1 mol repeat units =

9.30 x 10^{-23} g / unit cell

Volume per unit cell (all angle 90°):

(7.4Å x 4.9Å x 2.5Å)/unit cell x $[1\text{cm}/10^8\text{Å}]^3$ = 9.07 x 10^{-23} cm^3/unit cell

Density of the crystal: ρ_c = m/V = 1.025 g/cm^3

5.3. molecular weight of the two shortest chain:
Single pass: 1260
Double pass: 2530
Because of the end groups 60 must be subtracted from these molecular weights in order to obtain the polyethylene chain weight.
1260 – 60 = 1200
2530 – 60 = 2470
By dividing these values by the molecular weight of the monomer unit (28g/mol) the degree of polymerization is obtained:
1200 : 28 = 42,8 → DP 43
2470 : 28 = 88,2 → DP 88

DP of the double pass corresponds to twice the DP of the single pass and the number of monomers in the loop.
2 x 43 = 86, the difference to the value of the double pass is 2 monomers → loop contains 2 monomers.
Conclusion: the crystals exist of tightly folded chains showing an adjacent reentry. By using the length of the unit cell as the distance per repeat unit the thickness can be calculated to
43 x 2.53Å= 108, 79Å which match well with the experimentally measured value of 105Å.

5.4. The bulkiness of the substituent groups increases moving down the table. Also moving down the table, the melting points decrease, pass through a minimum, and then increase again.
There are two different effects working in opposition in these data:

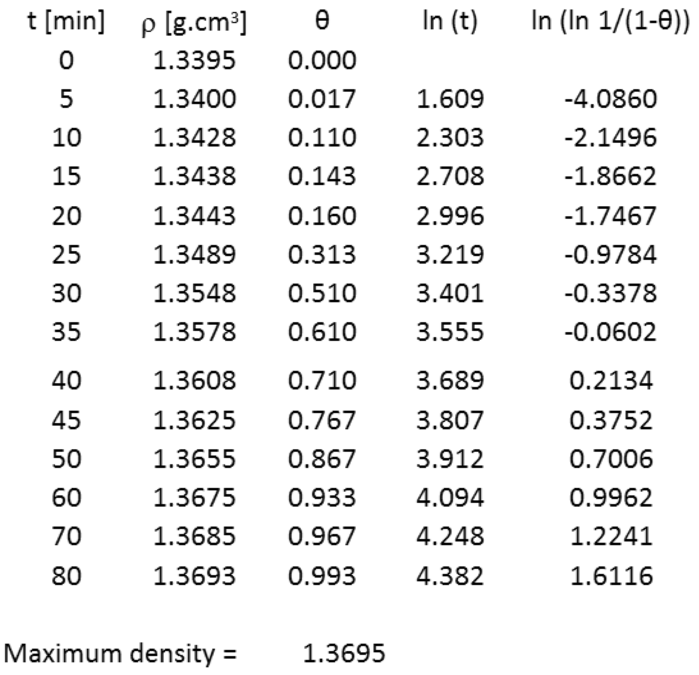
1. A the bulkiness of the substituents increases, the chains are prevented from coming into close contact in the crystal. The intermolecular forces that hold these crystals together are all London forces, and these become weaker as the crystals loosen up owing to substituent bulkiness. Accordingly, the value for the heat of fusion deceases moving down.
2. As the bulkiness of the chain substituents increases, the energy barriers to rotation along the chain backbone increases. This flexibility permits the molecules to experience a large number of conformations, especially in the liquid state, and therefore have high entropies. If the flexibility is

reduced, the entropy change on melting is less than it would otherwise be. Accordingly, the entropy of fusion decreases moving down the table.

The observed behavior of this series of polymers may be understood as a competition between these effects. For the smaller substituents, the effect on ΔH_f dominates and T_m decreases with bulk. For larger substituents, the effect of ΔS_f dominates and T_m increases with bulk.

5.5.

Density value for t = 0 corresponds to the density of the amorphous phase. By using the crystallinity by volume following data can be obtained:



t [min]	ρ [g.cm^3]	θ	ln (t)	ln (ln 1/(1-θ))
0	1.3395	0.000		
5	1.3400	0.017	1.609	-4.0860
10	1.3428	0.110	2.303	-2.1496
15	1.3438	0.143	2.708	-1.8662
20	1.3443	0.160	2.996	-1.7467
25	1.3489	0.313	3.219	-0.9784
30	1.3548	0.510	3.401	-0.3378
35	1.3578	0.610	3.555	-0.0602
40	1.3608	0.710	3.689	0.2134
45	1.3625	0.767	3.807	0.3752
50	1.3655	0.867	3.912	0.7006
60	1.3675	0.933	4.094	0.9962
70	1.3685	0.967	4.248	1.2241
80	1.3693	0.993	4.382	1.6116

Maximum density = 1.3695

Transforming the Avrami equation into a linear equation (here θ is crystallinity):

$$\ln(\ln\frac{1}{1-\theta}) = m\ln t + \ln K$$

Regression line: y = 2.0044 x – 7.2417

- ➔ m = 2
- ➔ ln K = -7.2417 → K = 7.16×10^{-4} min^{-2}

Exercises 6: Rubber Elasticity

6.1. The shear modulus is in the case of static measurements related to the Young modulus by G = E/3 = nRT resulting for G = 10^7 dynes/cm^2.

The retractive stress given by $= nRT\ (\alpha - \frac{1}{\alpha^2})$, using nRT = G and α = 2.5

for σ = 2.93 x 10^7 dynes/cm^2.

6.2. the molar ratio of styrene to butadiene in polymer = 23.5/(100-23.5) = 0.307
The average molar mass of chain lengths between cross-links $\overline{M_x}$ is

$$\overline{M_x} = \frac{(100-1.4)}{1.4}\left[\left(54\frac{g}{mol}\right)+(0.307)\left(104\frac{g}{mol}\right)\right] = 6052\frac{g}{mol}$$

For 20% elongation, α= 1.2, from equation $\sigma = \frac{\rho\ RT}{\overline{M_x}}\ (\alpha - \frac{1}{\alpha^2})$ = 2x10^6 dyne/cm^2
With 2% of the butadiene units crosslinked $\overline{M_x} = 4210\frac{g}{mol}$

The stress increases in proportion to the degree of crosslinking, Therefore,
$\sigma = \frac{6052\ g/mol}{4210\ g/mol}\ (2x10^6\,\frac{dyne}{cm^2})$ = 3x10^6 dyne/cm^2

6.3. by using the Flory-Rehner equation n is obtained by

$$n = \frac{-\left[\ln(1-\nu_2)+\ \nu_2\ +\ \chi\nu_2^2\right]}{V_1\left(\nu_2^{1/3} - \frac{\nu_2}{2}\right)}$$

With V$_1$ molar volume of toluene = M/ρ = 106 cm^3/mol and ν_2 = 1/4.88, n= 1.55 x 10^{-4} mol/cm^3.

The Young modulus is given as E = 3nRT = 1.15 x 107 dyne/cm^3.

Exercises 7: Viscoelasticity

7.1. Based on the incompressibility of the fiber material the volume at any moment is equal to the volume at t = 0: $\ell A = \ell_0 A_0$ resulting in

$$\frac{1}{A} = \frac{1+\ \varepsilon}{A_0}$$

The equation of state of the Kelvin-Voigt model

$$E\varepsilon +\ \eta\dot{\varepsilon} =\ \sigma = \frac{G}{A} = \frac{G(\,1+\ \varepsilon)}{A_0}$$

The strain rate $\dot{\varepsilon} = \frac{d\varepsilon}{dt}$ in dependence of the weight G is

$\frac{d\varepsilon}{dt} = \frac{G}{\eta A_0} + (\frac{G}{\eta A_0} - \frac{E}{\eta})\ \varepsilon$

In order to obtain a constant strain the expression must be 0: $(\frac{G}{\eta A_0} - \frac{E}{\eta})$= 0 → G = A$_0$E

The change of the length with the time results from the relation of the strain rate

$\dot{\varepsilon} = \frac{d\varepsilon}{dt} = \frac{d}{dt}\left(\frac{l-l_0}{l_0}\right) = \frac{E}{\eta}$ → $dL/dt = (E/\eta)\,\ell_0$

7.2. longest relaxation time (Maxwell model): $\tau_1 = \eta/G = 2 \times 10^5$ s = 2.3 days

7.3. there are two ways to proceed

a) using diffusion coefficient: with the Stoke – Einstein equation the R_h is obtained as

$$R_h = \frac{kT}{6\pi\eta_s D_t} = 3\ x\ 10^{-6}\ cm$$

The longest relaxation time corresponds to the rotational time of a sphere with radius R_h:

$$\tau_1 \sim \tau_{rot} = \frac{8\pi\eta_s R_h^3}{kT} \cong 10^{-4}s$$

b) using intrinsic viscosity $[\eta] = 0.088M^{1/2}$ (from graph)

$$\tau_1 \approx \frac{M[\eta]\eta_s}{RT} \approx 3\ x\ 10^{-5}s$$

Agreement is good because the difference is based on the different types of equation. For the diffusion coefficient is correct but from intrinsic viscosity is only a scaling relationship and does not include numerical prefactors.

7.4. based on the given equation the constant K_H can be obtained by:

$$K_H = \frac{1.5\ x\ 10^3 P}{(800)^{3.4}} = 2.02\ x\ 10^{-7}P$$

Viscosity of PS at 160°C with $Z_w = 950$ is $\eta = 2.69 \times 10^3$P

Using WFL equation to determine the viscosity at the reference temperature Tg:

$$lg\left(\frac{2.69\ x\ 10^3 P}{\eta_{Tg}}\right) = -\frac{17.44\ (T-Tg)}{51.6-(T-Tg)} = -9.376$$

$$\eta_{Tg} = 6.40 \times 10^{12}\ P$$

Using again WFL equation the temperature at which the viscosity will be 1.5×10^3 P can be determined

$$lg\left(\frac{1.5\ x\ 10^3 P}{6.40\ x\ 10^{12} P}\right) = -\frac{17.44\ (T-373)}{51.6-(T-373)}$$

➔ T = 436.6K = 163.6 °C

The temperature should be increased for 3.6°