

## KE-100.3410 Polymer properties

## Exercise 5: Polymer solubility and gas permeation

**Exercise 5.1**

Polymer solubility in different solvents can be estimated using solubility parameters  $\delta$ . According to the Hansen model, the overall solubility parameter can be obtained as

$$\delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2}$$

where  $\delta_D$ ,  $\delta_P$  and  $\delta_H$  are the dispersive, polar, and hydrogen bonding parameters. In table 3-3 Hansen solubility parameters for some common solvents are listed.

Solvents	Solubility Parameter, $\delta^*$	
	(MPa) <sup>1/2</sup>	(cal cm <sup>-3</sup> ) <sup>1/2</sup>
n-Hexane	14.9	7.28
Carbon tetrachloride	17.8	8.70
Toluene	18.2	8.90
Benzene	18.6	9.09
Chloroform	19.0	9.29
Tetrahydrofuran	19.4	9.48
Chlorobenzene	19.6	9.58
Methylene chloride	20.3	9.92
1,4-Dioxane	20.5	10.0
N-Methyl-2-pyrrolidone	22.9	11.2
Dimethylformamide	24.8	12.1
Methanol	29.7	14.5
Water	47.9	23.4

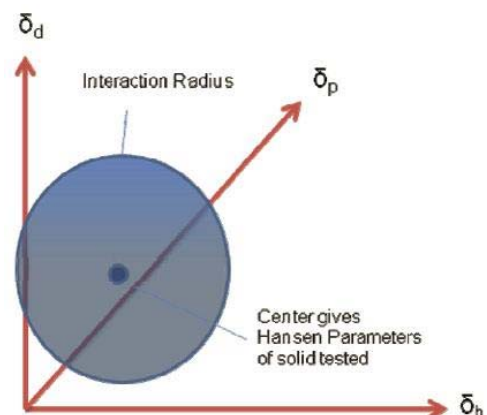
Fried, J.R., *Polymer Science and Technology*, 2<sup>nd</sup> ed., Prentice Hall 2003, pp. 115.

The best solubility is obtained when the solubility parameters of polymer and solvent are close to each other. For polymers the so called radius of solubility sphere ( $R_{AO}$ ) can be calculated. The liquids inside the sphere act as solvents and outside the sphere as non-solvents.

$$R_A = \sqrt{(2\delta_{D,P} - 2\delta_{D,S})^2 + (\delta_{P,P} - \delta_{P,S})^2 + (\delta_{H,P} - \delta_{H,S})^2}$$

where P refers to polymer and S to solvent.

$$\frac{R_A}{R_{AO}} < 1 \text{ for solvent and } \frac{R_A}{R_{AO}} > 1 \text{ for non-solvent.}$$



Estimate using the Hansen model whether PVC is soluble in the monomer vinyl chloride when the following parameters for PVC are known  $\delta_D=18.2 \text{ MPa}^{1/2}$ ,  $\delta_P = 7.5 \text{ MPa}^{1/2}$ ,  $\delta_H = 8.3 \text{ MPa}^{1/2}$  and  $R_{AO} = 3.5$  and for vinyl chloride:  $\delta_D = 15.4 \text{ MPa}^{1/2}$ ,  $\delta_P = 8.1 \text{ MPa}^{1/2}$ ,  $\delta_H = 2.4 \text{ MPa}^{1/2}$ . Choose the best solvent from the table for PVC.

### Solution 5.1

Calculate the radius of the solubility by substituting the solubility parameter values to the equation:

$$\begin{aligned} R_A &= \sqrt{(2\delta_{D,P} - 2\delta_{D,S})^2 + (\delta_{P,P} - \delta_{P,S})^2 + (\delta_{H,P} - \delta_{H,S})^2} \\ &= \sqrt{(2*18.2 - 2*15.4)^2 + (7.5 - 8.1)^2 + (8.3 - 2.4)^2} \approx 8.2 \end{aligned}$$

Compare  $R_A$  to  $R_{AO}$ .

$$\frac{R_A}{R_{AO}} = \frac{8,2}{3,5} \approx 2,3 > 1 \text{ thus PVC does not dissolve in its own monomer.}$$

Calculate the solubility parameter for PVC:

$$\delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2} = \sqrt{18.2^2 + 7.5^2 + 8.3^2} = 21.4$$

Choosing from solvent listed in the table the best choice would be 1,4-Dioxane since the solubility parameter  $\delta = 20.5$  is closest to PVC.

### Exercise 5.2

The solubility parameter is related to cohesive energy-density  $E^{coh}$  or the molar energy of vaporization of a pure liquid  $\Delta E_v$ :

$$\delta_i = \sqrt{E_i^{coh}} = \sqrt{\frac{\Delta E_i^v}{V_i}}$$

where  $\Delta E_v$  is defined as the energy change upon isothermal vaporization of the saturated liquid to the ideal gas state at infinite dilution and  $V_i$  is the molar volume of the liquid. The solubility parameter of a polymer has to be determined indirectly or calculated by group-contribution methods. Calculation of  $\delta$  by a group-contribution method requires the value of

a molar attraction constant  $F_i$ , for each chemical group in the polymer repeating unit. Values of  $F_i$  have been obtained by regression analysis of physical property data for a large number of organic compounds. The solubility parameter of a polymer is then calculated from these molar attraction constants and the molar volume of the polymer.

$$\delta_i = \frac{\sum_{i=1} F_i}{V_i} = \frac{\sum_{i=1} F_i}{\frac{M_i}{\rho_i}}$$

Some values of the molar attraction constants are shown in the table. Calculate the solubility parameters using Van Krevelen constants for

- Polyisobutylene, density 0.924 g/cm<sup>3</sup>
- Polystyrene, density 1.04 g/cm<sup>3</sup>
- Polycarbonate, density 1.20 g/cm<sup>3</sup>

Table 3-2 Molar Attraction Constants at 25°C

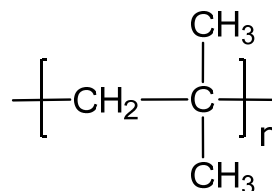
Group	Molar Attraction Constant, F (MPa) <sup>1/2</sup> cm <sup>3</sup> mol <sup>-1</sup>		
	Small <sup>18</sup>	Hoy <sup>19</sup>	Van Krevelen <sup>20</sup>
-CH <sub>3</sub>	438	303	420
-CH <sub>2</sub> -	272	269	280
>CH-	57	176	140
>C<	-190	65.5	0
-CH(CH <sub>3</sub> )-	495	(479)	560
-C(CH <sub>3</sub> ) <sub>2</sub> -	686	(672)	840
-CH=CH-	454	497	444
>C=CH-	266	422	304
Phenyl	1504	1398	1517
<i>p</i> -Phenylene	1346	1442	1377
-O- (ether)	143	235	256
-OH	—	462	754
-CO- (ketone)	563	538	685
-COO- (ester)	634	668	512
-OCOO- (carbonate)	—	(904)	767

Fried, J.R., *Polymer Science and Technology*, 2<sup>nd</sup> ed., Prentice Hall 2003, pp. 114.

### Solution 5.2

a) Based on the structure of polyisobutylene the molar attractions and molecular weight can be calculated:

Group	$F_i$	Amount	$\Sigma F_i$	$M_i$ (g/mol)
-CH <sub>2</sub> -	280	1	280	14.027
-C(CH <sub>3</sub> ) <sub>2</sub> -	840	1	840	42.081
		$\Sigma_i$	1120	56.108

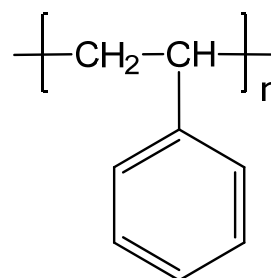


and then the solubility parameter can be calculated with the equation:

$$\delta_i = \frac{\sum_{i=1} F_i}{\frac{M_i}{\rho_i}} = \frac{1120 \text{MPa}^{1/2} \frac{\text{cm}^3}{\text{mol}}}{\frac{56.108 \frac{\text{g}}{\text{mol}}}{0.924 \frac{\text{g}}{\text{cm}^3}}} \approx 18.4 \text{MPa}^{1/2}$$

b) Polystyrene

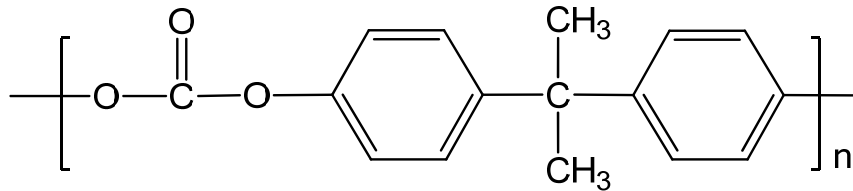
Group	$F_i$	Amount	$\Sigma F_i$	$M_i$ (g/mol)
>CH-	140	1	140	13.019
-CH <sub>2</sub> -	280	1	280	14.027
phenyl	1517	1	1517	77,106
		$\Sigma_i$	1937	104.152



And the solubility parameter can be calculated:

$$\delta_i = \frac{\sum_{i=1} F_i}{\frac{M_i}{\rho_i}} = \frac{1937 \text{MPa}^{1/2} \frac{\text{cm}^3}{\text{mol}}}{\frac{104.152 \frac{\text{g}}{\text{mol}}}{1.04 \frac{\text{g}}{\text{cm}^3}}} \approx 19.3 \text{MPa}^{1/2}$$

c) Polycarbonate



Group	F <sub>i</sub>	Amount	ΣF <sub>i</sub>	M <sub>i</sub> (g/mol)
-C(CH <sub>3</sub> ) <sub>2</sub> -	840	1	840	42.081
-OCOO-	767	1	767	60.008
p-phenylene	1377	2	2754	154.212
		Σ <sub>i</sub>	4361	256.301

And the solubility parameter can be calculated

$$\delta_i = \frac{\sum_{i=1} F_i}{\frac{M_i}{\rho_i}} = \frac{4361 \text{MPa}^{1/2} \text{cm}^3 \text{mol}^{-1}}{\frac{256.301 \text{g/mol}}{1.20 \text{g/cm}^3}} = 20.4 \text{MPa}^{1/2}$$

### Exercise 5.3

Polyvinylalcohol film (thickness 0.20mm) is laminated in between two LDPE films (thickness of each film 0.2 mm). Oxygen transfer coefficient for LDPE is  $2.2 \times 10^{-13}$  (cm<sup>3</sup>(STP)×cm)/(cm<sup>2</sup>×s×Pa) and for PVOH:  $6.65 \times 10^{-16}$  cm<sup>3</sup>(STP)×cm)/(cm<sup>2</sup>×s×Pa).

- What is the oxygen transfer coefficient for the laminate at 25°C?
- A product is packed in this laminate material. The gas volume of the package is 20 cm<sup>3</sup> and surface area is 250 cm<sup>2</sup>. How long is shelf life of the product when the oxygen concentration in the packet must not exceed 1.0 mol-%? Oxygen concentration is 0.0 mol-% just after the packaging.
- What would be the shelf life of a product packed in a similar LDPE packaging at room temperature?

### Solution 5.3

a)

Gas transfer coefficient in multilayer laminate depends on the properties of the individual layers in the laminate

$$\frac{l}{P} = \frac{l_1}{P_1} + \frac{l_2}{P_2} + \frac{l_3}{P_3}$$

Gas permeation can be calculated from equation

$$Q = \frac{P \times A \times t \times \Delta p}{l}$$

where

$Q$	gas flux permeated through	[cm <sup>3</sup> ]
$P$	Permeation coefficient	[cm <sup>3</sup> × cm/cm <sup>2</sup> × s × Pa]
$t$	time	[s]
$A$	surface area of the film	[cm <sup>2</sup> ]
$l$	thickness of the film	[cm]
$\Delta p$	pressure difference	[Pa]

Oxygen permeation coefficient  $P$ :

$$P = \frac{l}{\frac{l_1}{P_1} + \frac{l_2}{P_2} + \frac{l_3}{P_3}} = \frac{0.60mm}{\frac{0.20mm}{2.2 \times 10^{-13}} + \frac{0.20mm}{6.65 \times 10^{-16}} + \frac{0.20mm}{2.2 \times 10^{-13}}} = 2.0 \times 10^{-15} \frac{cm^3(NTP) \times cm}{cm^2 \times s \times Pa}$$

**b)**

For ideal gas the volume is equivalent to molar volume (1 mol-% = 1 vol-%). Laminate is ok for packaging until there is 20 cm<sup>3</sup> of oxygen transferred through the material:

$$Q = 20 \text{ cm}^3 \times 0.01 = 0.20 \text{ cm}^3$$

Partial pressure of oxygen outside the packet:  $p_1 = 0.21 \times 101 \text{ kPa} = 21000 \text{ Pa}$

Partial pressure of oxygen in the beginning  $p_{2,start} = 0 \text{ Pa}$  and when the oxygen concentration in the packet is 1.0 mol-%,  $p_{2,end} = 0.01 \times 101 \text{ kPa} = 1000 \text{ Pa}$ .

⇒ Approximation  $\Delta p \approx \text{constant}$

Time taken for oxygen transfer

$$t = \frac{Q \cdot l}{P \cdot A \cdot \Delta p} = \frac{0.20 \text{ cm}^3 \cdot 0.060 \text{ cm}}{2.0 \cdot 10^{-15} \frac{\text{cm}^3 \text{ cm}}{\text{cm}^2 \text{ s Pa}} \cdot 250 \text{ cm}^2 \cdot 21000 \text{ Pa}} = 1.1 \cdot 10^6 \text{ s} = \underline{13d}$$

c)

$$t = \frac{Q \cdot l}{P \cdot A \cdot \Delta p} = \frac{0.20 \text{ cm}^3 \cdot 0.060 \text{ cm}}{2.2 \cdot 10^{-13} \frac{\text{cm}^3 \text{ cm}}{\text{cm}^2 \text{ s Pa}} \cdot 250 \text{ cm}^2 \cdot 21000 \text{ Pa}} = 10400 \text{ s} = 2.9 \text{ h}$$

If the packaging material was LDPE-film, the time would be 10400 s which is less than 3 hours.

#### Exercise 5.4

Plastic soft drink bottles are made of poly(ethylene terephthalate) in Finland. Empty 1.5 dm<sup>3</sup> bottle is filled to 2.0 bar CO<sub>2</sub> pressure at 25°C and the cap is closed tightly. Carbon dioxide transfer coefficient for PET is  $P(\text{CO}_2, 25^\circ\text{C}) = 0.118 \times 10^{-13} \text{ cm}^3(\text{STP}) \times \text{cm} / (\text{cm}^2 \times \text{s} \times \text{Pa})$ . How long a time does it take for CO<sub>2</sub> pressure to drop one tenth?

#### Solution 5.4

Assume the bottle is cylinder with wall thickness of 1 mm, and diameter of the bottom is 8 cm. Assume also that gasses are ideal gasses and the CO<sub>2</sub> content in air is 0.03%.

$$\text{Volume of the cylinder: } V = \pi r^2 h \Rightarrow h = \frac{V}{\pi r^2}$$

Surface area of the cylinder:

$$A = 2\pi r h + 2\pi r^2 = 2 \left( \frac{V}{r} + \pi r^2 \right) = 2 \left( \frac{1.5 \cdot 10^3 \text{ cm}^3}{4 \text{ cm}} + \pi (4 \text{ cm})^2 \right) = 850,5 \text{ cm}^2$$

$$\text{Partial pressure of CO}_2 \text{ outside of the bottle is: } p_o = 0.0003 \cdot 101325 \text{ Pa} = 30.4 \text{ Pa}$$

Pressure difference between inside and outside of the bottle in the beginning (a):

$$\Delta p_a = p_a - p_o = 2 \cdot 10^5 \text{ Pa} - 30.4 \text{ Pa} = 199970 \text{ Pa}$$

Pressure difference at the end (e):  $\Delta p_e = p_e - p_o = 0.9 \times 2 \cdot 10^5 Pa - 30.4 Pa = 179970 Pa$

Calculate the average pressure difference:

$$\Delta p_{avg} = \frac{\Delta p_a + \Delta p_e}{2} = \frac{199970 Pa + 179970 Pa}{2} = 189970 Pa \approx 190000 Pa$$

At the end the bottle has 9/10 of the original pressure (10% drop in pressure), so flux of the CO<sub>2</sub> has (ideal gas  $p_1 V_1 = p_2 V_2$ ):

$$Q = V_2 - V_1 = \frac{p_1 V_1}{p_2} - V_1 = V_1 \left( \frac{p_1}{0.9 p_1} - 1 \right) = 1.5 dm^3 \left( \frac{1}{0.9} - 1 \right) = 0.17 dm^3$$

The time this has taken can be calculated:

$$Q = \frac{P \cdot A \cdot t \cdot \Delta p_{avg}}{l}$$

$$t = \frac{Q \cdot l}{P \cdot A \cdot \Delta p_{avg}} = \frac{0.17 \cdot 10^3 cm^3 \cdot 0.1 cm}{0.118 \cdot 10^{-13} \frac{cm^3 cm}{cm^2 s Pa} \cdot 850.5 cm^2 \cdot 190000 Pa} = 8.92 \cdot 10^6 s = 103 d$$

### Exercise 5.5

When solvent is added to polymer the change in free energy ( $\Delta G_M$ ) reveals whether the polymer will dissolve:

$$\Delta G_M = \Delta H_M - T \Delta S_M$$

Dissolution will happen when  $\Delta G_M$  is negative. Entropy of mixing  $\Delta S_M$  is always positive and can be expressed with Boltzmann relation:

$$\Delta S_M = k \ln \Omega$$

where  $k = 1.38 \times 10^{-23} J/K$  is Boltzmann constant and  $\Omega$  describes the different ways that solvent molecules  $N_1$  and polymer molecules  $N_2$  can be arranged. Applying Sterling approximation ( $\ln N! = N \ln N - N$ ) the entropy of mixing can be expressed:

$$\Delta S_M = -k(N_1 \ln v_1 + N_2 \ln v_2)$$

where  $v_1$  is the volume fraction of solvent and  $v_2$  volume fraction of polymer. Dimensionless Flory-Huggins parameter  $\chi_1$  can be applied to estimate the polymer-solvent interactions. The



parameter can be experimentally measured for each polymer-solvent combination. Using interaction parameter the enthalpy of mixing can be expressed:

$$\Delta H_M = kT \chi_1 N_1 v_2$$

Then the change in free energy follows:

$$\Delta G_M = \Delta H_M - T\Delta S_M = kT(N_1 \ln v_1 + N_2 \ln v_2 + \chi_1 N_1 v_2)$$

(Fried, J.R., *Polymer Science and Technology*, 2<sup>nd</sup> ed., Prentice Hall 2003, p. 96 – 102).

Calculate the change in free energy of mixing when 10% solution of polystyrene ( $M_n = 10000$  g/mol) in cyclohexane at 34 °C is prepared. Flory-Huggins parameter  $\chi_1$  is 0.50; density of cyclohexane is 0.7785 g/cm<sup>3</sup> and density of styrene 1.06 g/cm<sup>3</sup>.

### Solution 5.5

Volume fractions for cyclohexane  $v_1 = 0.9$  and for styrene  $v_2 = 0.1$ . Take volume of solution to be  $V = 1$  cm<sup>3</sup>. Calculate the number of solvent molecules (C<sub>6</sub>H<sub>12</sub>)  $N_1$ :

$$N_1 = n_1 N_A = \frac{V v_1 \rho_1}{M_1} N_A = \frac{1 \text{ cm}^3 \cdot 0,9 \cdot 0,7785 \frac{\text{g}}{\text{cm}^3}}{(6 \cdot 12,011 + 12 \cdot 1,008) \frac{\text{g}}{\text{mol}}} \times 6,025 \cdot 10^{23} \text{ mol}^{-1} = 5,02 \cdot 10^{21}$$

Number of polystyrene molecules

$$N_2 = n_2 N_A = \frac{V v_2 \rho_2}{M_2} N_A = \frac{1 \text{ cm}^3 \cdot 0,1 \cdot 1,06 \frac{\text{g}}{\text{cm}^3}}{10000 \frac{\text{g}}{\text{mol}}} \times 6,025 \cdot 10^{23} \text{ mol}^{-1} = 6,39 \cdot 10^{18}$$

Calculate the change in free energy of mixing:

$$\begin{aligned} \Delta G_M &= \Delta H_M - T\Delta S_M = kT(N_1 \ln v_1 + N_2 \ln v_2 + \chi_1 N_1 v_2) \\ &= 1,38 \cdot 10^{-23} \frac{\text{J}}{\text{K}} \times 307,15 \text{ K} \times (5,02 \cdot 10^{21} \times \ln 0,9 + 6,39 \cdot 10^{18} \times \ln 0,1 + 0,5 \times 5,02 \cdot 10^{21} \times 0,1) \\ &\approx \underline{\underline{-1,24 \text{ J}}} \end{aligned}$$

## Polymer miscibility

Mixtures of polymers can be treated with the same thermodynamic approach as polymer solutions. The change in volume during mixing is ignored so they are not quite accurate. When mixing two polymers the change in free energy ( $\Delta G_M$ ) will tell whether polymers are miscible or there is phase separation:

$$\Delta G_M = \Delta H_M - T\Delta S_M$$

Mixture will be miscible when the  $\Delta G_M$  is negative. For polymer mixtures:

$$\Delta G_M = kT \left( \frac{V}{V_r} v_1 v_2 \chi_1 \left( 1 - \frac{2}{z} \right) + N_c (v_1 \ln v_1 + v_2 \ln v_2) \right)$$

where  $k = 1,38 \times 10^{-23}$  J/K is Boltzmann constant,  $T$  temperature,  $V$  volume of mixture,  $V_r$  volume of one polymer (the one with smaller monomer),  $v_i$  volume fractions of polymers,  $\chi_1$  Flory-Huggins parameter,  $z$  lattice coordination number (usually between 6 and 12),  $N_c$  number of molecule chains per volume unit (Sperling L.H., *Introduction to physical polymer science*, 4<sup>th</sup> ed., Wiley & Sons, 2006, p. 156-157). Flory-Huggins parameter can be calculated from:

$$\chi_1 = \frac{V_{m,1}}{RT} (\delta_1 - \delta_2)^2$$

where  $V_{m,1}$  is the molar volume of the polymer with higher amount or if equal composition the one with smaller monomer,  $T$  temperature,  $R = 8.3145$  J/(K mol) gas constant,  $\delta_i$  solubility parameters of the polymers.

### Exercise 5.6\*

Is 1000 g of polystyrene miscible with 1000 g polybutadiene at 150°C, when the molecular weights of both polymers are  $1 \times 10^5$  g/mol? What is the upper limiting molecular weight that the polymers are still miscible at that temperature? Would increasing the temperature enhance the miscibility when the molecular weights are  $1 \times 10^5$  g/mol? Solubility parameter for PS is  $\delta = 18.6$  (MPa)<sup>1/2</sup> and density  $\rho = 1.06$  g/cm<sup>3</sup>. Solubility parameter for polybutadiene is  $\delta = 17.2$  (MPa)<sup>1/2</sup> and density  $\rho = 1.01$  g/cm<sup>3</sup>. Can be assumed that lattice coordination number  $z = 6$ .

**Solution 5.6\***

$$\Delta G_M = kT \left( \frac{V}{V_r} v_1 v_2 \chi_1 \left( 1 - \frac{2}{z} \right) + N_c (v_1 \ln v_1 + v_2 \ln v_2) \right)$$

Polymer amounts are the same but the molecular weight of butadiene (C<sub>4</sub>H<sub>6</sub>) ( $M_{0,1} = 54.092$  g/mol) is smaller than the molecular weight of styrene (C<sub>8</sub>H<sub>8</sub>) ( $M_{0,2} = 104.152$  g/mol) and thus the molar fraction of polybutadiene is bigger. Thus polybutadiene is considered the “solvent”. Calculate the volume of the mixture and the volume fractions of the polymers:

$$V = V_1 + V_2 = \frac{m_1}{\rho_1} + \frac{m_2}{\rho_2} = \frac{1000 \text{ g}}{1.06 \frac{\text{g}}{\text{cm}^3}} + \frac{1000 \text{ g}}{1.01 \frac{\text{g}}{\text{cm}^3}} = 1933 \text{ cm}^3$$

$$v_1 = \frac{V_1}{V} = \frac{m_1}{\rho_1 V} = \frac{1000 \text{ g}}{1.01 \frac{\text{g}}{\text{cm}^3} \times 1933 \text{ cm}^3} = 0.512 \quad v_2 = 1 - v_1 = 1 - 0.512 = 0.488$$

$V/V_r$  is the number of molecules:

$$\begin{aligned} \frac{V}{V_r} &= \frac{V}{V_1} = \frac{V}{V_1} = \frac{V m_1 N_A}{V_1 M_{0,1}} = \frac{V \rho_1 N_A}{M_{0,1}} \\ &= \frac{1933 \text{ cm}^3 \times 1.01 \frac{\text{g}}{\text{cm}^3} \times 6.025 \cdot 10^{23} \text{ mol}^{-1}}{54.092 \frac{\text{g}}{\text{mol}}} = 2.18 \cdot 10^{25} \end{aligned}$$

Flory-Huggins parameter using the molar volume of butadiene

$$V_{m,1} = \frac{n_1}{V_1} = \frac{M_{0,1}}{\rho_1} :$$

$$\begin{aligned} \chi_1 &= \frac{V_{m,1}}{RT} (\delta_1 - \delta_2)^2 = \frac{M_{0,1}}{RT \rho_1} (\delta_1 - \delta_2)^2 = \frac{54.092 \frac{\text{g}}{\text{mol}} \times (17.2(\text{MPa})^{1/2} - 18.6(\text{MPa})^{1/2})^2}{8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}} \times 423.15 \text{ K} \times 1.01 \frac{\text{g}}{\text{cm}^3}} \\ &= \frac{0.054092 \frac{\text{kg}}{\text{mol}} \times (17.2 - 18.6)^2 \cdot 10^6 \text{ Pa}}{8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}} \times 423.15 \text{ K} \times 1010 \frac{\text{kg}}{\text{m}^3}} = 0.0298 \end{aligned}$$

$N_c$  number of molecule chains:

$$N_c = N_1 + N_2 = N_A(n_1 + n_2) = N_A \left( \frac{m_1}{M_1} + \frac{m_2}{M_2} \right)$$

$$= 6.025 \cdot 10^{23} \text{ mol}^{-1} \times \left( \frac{1000 \text{ g}}{1 \cdot 10^5 \frac{\text{g}}{\text{mol}}} + \frac{1000 \text{ g}}{1 \cdot 10^5 \frac{\text{g}}{\text{mol}}} \right) = 1.21 \cdot 10^{22}$$

Calculate the free energy of mixing:

$$\Delta G_M = kT \left( \frac{V}{V_r} v_1 v_2 \chi_1 \left( 1 - \frac{2}{z} \right) + N_c (v_1 \ln v_1 + v_2 \ln v_2) \right)$$

$$= 1,38 \cdot 10^{-23} \frac{\text{J}}{\text{K}} \times 423,15 \text{ K} \times \left( 2,18 \cdot 10^{25} \times 0,512 \times 0,488 \times 0,0298 \times \left( 1 - \frac{2}{6} \right) \right. \\ \left. + 1,21 \cdot 10^{22} \times (0,512 \times \ln 0,512 + 0,488 \ln 0,488) \right)$$

$$= \underline{582 \text{ J}}$$

$\Delta G$  is positive so the polymers are not miscible. Calculate the upper limiting molecular weight for miscible system. This is the case when free energy equals to zero i.e. the enthalpy and entropy of mixing are equal.

$$\Delta G_M = \Delta H_M - T \Delta S_M = 0 \Rightarrow \Delta H_M = T \Delta S_M$$

$N_c$  is affected by molecular weights of the polymers. Since the molecular weights are equal,  $N_c$  can be written:

$$N_c = N_1 + N_2 = N_A(n_1 + n_2) = 2N_A \frac{m}{M_r}$$

Manipulate the equation and solve for  $M_r$ :

$$\Delta G_M = kT \left( \frac{V}{V_r} v_1 v_2 \chi_1 \left( 1 - \frac{2}{z} \right) + N_c (v_1 \ln v_1 + v_2 \ln v_2) \right) = 0$$

$$\Rightarrow \frac{V}{V_r} v_1 v_2 \chi_1 \left( 1 - \frac{2}{z} \right) + N_c (v_1 \ln v_1 + v_2 \ln v_2) = 0$$

$$\frac{V}{V_r} v_1 v_2 \chi_1 \frac{2}{3} + 2N_A \frac{m}{M_r} (v_1 \ln v_1 + v_2 \ln v_2) = 0$$

$$\begin{aligned}
&\Rightarrow 2N_A \frac{m}{M_r} (v_1 \ln v_1 + v_2 \ln v_2) = -\frac{2}{3} \frac{V}{V_r} v_1 v_2 \chi_1 \\
&\Rightarrow M_r = -\frac{N_A m (v_1 \ln v_1 + v_2 \ln v_2)}{\frac{1}{3} \frac{V}{V_r} v_1 v_2 \chi_1} \\
&= -\frac{6,025 \cdot 10^{23} \text{ mol}^{-1} \times 1000 \text{ g} \times (0,512 \times \ln 0,512 + 0,488 \ln 0,488)}{\frac{1}{3} \times 2,18 \cdot 10^{25} \times 0,512 \times 0,488 \times 0,0298} \approx \underline{\underline{7700 \frac{\text{g}}{\text{mol}}}
\end{aligned}$$

When the molecular weights of PS and polybutadiene are less than 7700g/mol, they form a miscible system at 150°C.

Solve the limiting T where the polymers with molecular weights of  $1 \times 10^5$ g/mol would be miscible. As previously the enthalpy and entropy would be equal to have zero free energy of mixing.

$$\frac{V}{V_r} v_1 v_2 \chi_1 \left(1 - \frac{2}{z}\right) + N_c (v_1 \ln v_1 + v_2 \ln v_2) = 0$$

Increasing temperature affect the Flory-Huggins parameter:

$$\chi_1 = \frac{V_{m,1}}{RT} (\delta_1 - \delta_2)^2 = \frac{M_{0,1}}{RT \rho_1} (\delta_1 - \delta_2)^2$$

Solving for the limiting temperature  $T_r$ :

$$\begin{aligned}
&\frac{V}{V_r} v_1 v_2 \chi_1 \left(1 - \frac{2}{z}\right) + N_c (v_1 \ln v_1 + v_2 \ln v_2) = 0 \\
&\Rightarrow \frac{2}{3} \frac{V}{V_r} v_1 v_2 \frac{M_{0,1}}{RT_r \rho_1} (\delta_1 - \delta_2)^2 = -N_c (v_1 \ln v_1 + v_2 \ln v_2) \\
&\Rightarrow T_r = -\frac{2 \frac{V}{V_r} v_1 v_2 M_{0,1} (\delta_1 - \delta_2)^2}{3 R \rho_1 N_c (v_1 \ln v_1 + v_2 \ln v_2)} \\
&= -\frac{2 \times 2,18 \cdot 10^{25} \times 0,512 \times 0,488 \times 54,092 \frac{\text{g}}{\text{mol}} \times (17,2(\text{MPa})^{1/2} - 18,6(\text{MPa})^{1/2})^2}{3 \times 8,3145 \frac{\text{J}}{\text{K} \cdot \text{mol}} \times 1,01 \frac{\text{g}}{\text{cm}^3} \times 1,21 \cdot 10^{22} \times (0,512 \times \ln 0,512 + 0,488 \ln 0,488)} \\
&= \underline{\underline{5478K}}
\end{aligned}$$

Temperature is so high that material would decompose before reaching that. Thus increasing temperature is not a valid method to enhance polymer/polymer miscibility.