CHEM-E2130 POLYMER PROPERTIES

EXAMINATION: 17.12.2021

14:00-18:00

6 questions, max 27 points

Q1)

Polystyrene was fractionated from a methyl ethyl ketone solution by additions of methanol. The osmotic pressure, π, was measured at 25 °C for one of the fractions dissolved in toluene at different concentrations, c. The results obtained are given in the following table. Calculate the number average of molar mass, and the second and third virial coefficient in the expansion of π/c against c. (5p)

c (kg/m^3)	π (N/m^2)
1.75	30.4
2.85	52.0
4.35	86.3
6.5	146.0
8.85	231.0

Q2)

A series of copolymers is prepared from caprolactone (CL) and trimethylene carbonate (TMC). The T_g of PCL is -60°C and the T_g of PTMC is -17°C.

A) Using *the simple rule of mixture* calculate the T_g's of 3 CL-TMC copolymers (choose 3 different monomer ratio's) and draw a graph of TMC weight fraction vs T_g using the 5 T_g's that you now have (the 3 you calculated + the 2 for the pure polymers). (2.5p)

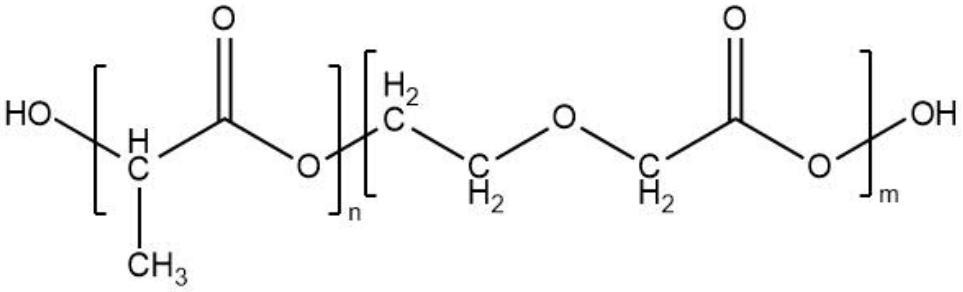
B) As question A shows, copolymerizing TMC with CL would result in an increased T_g (as compared to pure PCL). An alternative to increase the T_g of PCL would be to add a plasticizer. Using *the Fox equation*, calculate the weight fractions of plasticizer needed to achieve the same T_g's as those you calculated in A. The T_g of the plasticizer is 85°C. (2.5p)

Q3) Answer the following questions briefly (2p)

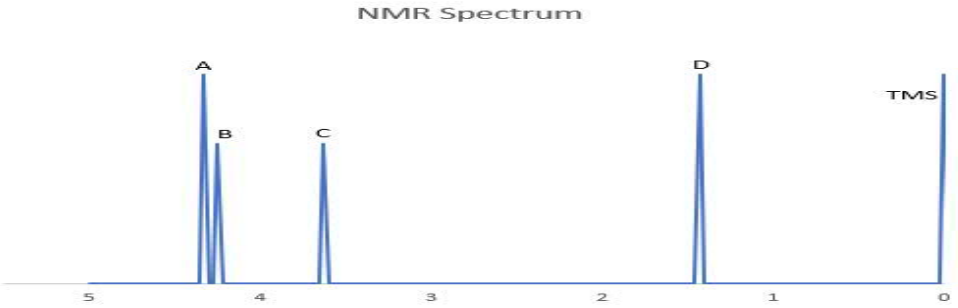
A) By which microscopy technique we can study the topography of a non-conductive sample?
B) Name three differences between SEM and TEM techniques.

Q4)

A co-polymer of monomers *n* and *m* is prepared.



A) Explain how many ^{1}H NMR peaks are generated by *m* and how these are split. (1.5 pts)
B) Explain how many ^{1}H NMR peaks are generated by *n* and how these are split. (1pt)
C) In the figure, a simplified ^{1}H NMR spectrum of this copolymer is shown (without splits). Explain, based on shielding and deshielding, which protons belong to peaks A, B, C & D (consider overlap). (2.5 pts) IGNORE the protons of the OH groups on the ends of the molecule.



Q5) (5p)

The viscoelastic properties of a surfactant solution were characterized by a frequency sweep measurement and the attached data was obtained. The rheological behavior of this surfactant solution can be described with the Maxwell model.

A) Determine the relaxation time of the surfactant solution.

B) How long does it take that the shear stress in this material reduces to 10 % of its initial value when a step strain is applied?

If needed, you can use Excel Solver, Origin, Matlab, etc. for data fitting.

ω [rad/s]	G' [Pa]	G'' [Pa]
0.428	1.329	7.621
0.628	2.772	10.82
0.924	5.563	14.81
1.351	10.46	18.99
1.985	17.69	21.93
2.915	26.03	22.17
4.279	33.72	19.85
6.283	38.9	15.71
9.224	41.91	11.65
13.53	45.11	8.198

Q6)

Poly(trimethylene carbonate) (PTMC) is a enzymatically degradable polymer that dissolves for example in chloroform. The solubility parameter δ of a polymer can be calculated through summation of the molar attraction constants F_i, for each chemical group in the polymer repeating unit, and dividing that with the molar volume of the polymer.

a. Calculate the solubility parameter δ for PTMC using Van Krevelen constants at room temperature. $\rho_{PTMC} = 1.31\ g/cm^3$ (2p)

b. By exposing PTMC to gamma irradiation, the polymer can be crosslinked. Describe the difference between how a PTMC polymer chain and a crosslinked PTMC network behave when immersed in chloroform. (2p)

c. You have an unknown sample of PTMC. What kind of information can you get about the sample by using gel permeation chromatography and why is the solubility in chloroform relevant for this method? (1p)

Table 3-2 Molar Attraction Constants at 25°C

	Molar Attraction Constant, F $(MPa)^{1/2}\ cm^3\ mol^{-1}$		
Group	Small[18]	Hoy[19]	Van Krevelen[20]
$-CH_3$	438	303	420
$-CH_2-$	272	269	280
>CH–	57	176	140
>C<	-190	65.5	0
$-CH(CH_3)-$	495	(479)	560
$-C(CH_3)_2-$	686	(672)	840
–CH=CH–	454	497	444
>C=CH–	266	422	304
Phenyl	1504	1398	1517
p-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