Polymers 1

A (4p)

What is a gel and a gelation process? What is the "gel fraction"? (Explain qualitatively, not with equations.) One usually divides gels into two classes. What is characteristic for them? Give one example of a gel TYPE from each class! (No need to draw chemical structures.)

Gel consists of similar subunits that are connected to form an "infinite" network. The gelation is the process in which the subunits become connected. The gel fraction is the fraction of bonds between subunits that are part of the infinite cluster that holds the gel together. Chemical gels: Covalent bonds link the subunits together, such as epoxy glues. Physical gels: Typically reversible interactions, not covalent bonds, for instance gelatin.

Comment: Some people just wrote down the equations. This gives no points. The physics must be explained!

B (4p)

What is "terminal time" and "plateau modulus" in the context of reptation theory? For each of these two parameters, describe whether or not it depends on the degree of polymerization! (You must motivate the answers.)

The terminal time is the characteristic time after which the polymers are no longer entangled and flow starts in the melt. It depends on the degree of polymerization since longer polymers have more entanglement points. The plateau value is the typical more of less constant stress one measures after a deformation before the terminal time. This depends on the distance between entanglement points and not N.

Comment: I should have used the term "plateau value" in the text instead of modulus, but it should be clear that the same physical phenomena is described.

C (2p)

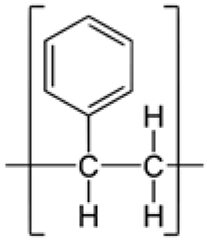
What is a lamellae in the context of polymers? Include a sketch of its structure!

Lamellae is the 2D sheet of crystalline polymers with aligned stretched coils. Parts of the coils are always sticking out on both sides of the lamellae since polymers are never fully crystalline.

Polymers 2

A (4p)

Polystyrene has the following structure:



It is dissolved in a good organic solvent with $\chi = -1$ and the molecular weight is 20800 g/mol. Calculate the Flory radius if the Kuhn length is 2 nm and the monomer length 4 Å.

m = 104 gmol^{-1}, $N = M/m$ = 200, rescaling gives R_F = 23 nm.

B (3p)

A brush of polystyrene has a thickness which is half the contour length. Assume the same solvent ($\chi = -1$). What is the grafting density?

$H = aN/2$ means that N can be removed from the equation for brush height, after rescaling only Kuhn length remains and for $\chi = -1$ one gets $\Gamma = b^{-2}/8$ = 0.0313 nm^{-2}.

C (3p)

The free energy of a coil, including conformational entropy, excluded volume and solvent interactions, can be written as:

$$E_{\text{tot}}(r) = \frac{3k_B T r^2}{2Na^2} + \frac{k_B T[1-2\chi]N^2 a^3}{r^3} + \text{constant}$$

In the derivation of the Flory radius, one makes the assumption that the volume of a segment is a^3. For a polymer like polystyrene, the aromatic side group is quite bulky compared with the main chain and one could imagine that the segment volume is better described by ca^2, where $c > a$ is a length corresponding to the extension of the side group. What will be the expression for the Flory radius based on this hypothesis? (Rescaling is not relevant in this purely theoretical treatment.)

Replace a^3 with a^2c, derive with respect to r, solve for: $R_F = [1 - 2\chi]^{1/5} c^{1/5} a^{4/5} N^{3/5}$.

Boltzmann's constant: $k_B = 1.38 \times 10^{-23}$ JK^{-1}

Avogadro's number: $N_A = 6.02 \times 10^{23}$ mol^{-1}

$T(°C) = T(K) - 273.15$

Polydispersity index (M_w/M_n):

$$M_{\mathrm{n}} = \frac{\sum_i n_i M_i}{\sum_i n_i} \qquad M_{\mathrm{w}} = \sum_i w_i M_i = \frac{\sum_i n_i M_i M_i}{\sum_i n_i M_i}$$

Random walk:

$$R = aN^{1/2}$$

Worm-like chain model ($b = 2l_p$):

$$R_{\mathrm{wlc}} = \left[2 l_{\mathrm{p}} r_{\max} \left[1 - \frac{l_{\mathrm{p}}}{r_{\max}} \left[1 - \exp\left(-\frac{r_{\max}}{l_{\mathrm{p}}} \right) \right] \right] \right]^{1/2}$$

Entropy:

$$S = k_{\mathrm{B}} \log(W)$$

Gibbs' free energy change:

$$\Delta G = \Delta H - T \Delta S$$

Flory radius (in solvent):

$$R_{\mathrm{F}} = [1 - 2\chi]^{\frac{1}{5}} a N^{\frac{3}{5}}$$

Alexander - de Gennes brush height:

$$H = \left[\frac{1 - 2\chi}{3} \Gamma \right]^{\frac{1}{3}} a^{\frac{5}{3}} N$$

Reptation theory terminal time:

$$t_{\mathrm{T}} = \frac{[aN]^2}{2 D_{\mathrm{CiT}}} = \frac{\zeta_{\mathrm{segment}} a N^3}{2 k_{\mathrm{B}} T}$$

Gelation threshold and gel fraction:

$$f_{\mathrm{c}} = \frac{1}{z - 1} \qquad p_{\mathrm{gel}} = 1 - p_0^{\,z} \qquad p_0 = 1 - f + f p_0^{\,z-1}$$

Rubber elasticity modulus:

$$Y = \frac{3 \rho k_{\mathrm{B}} T}{m N_{\mathrm{part}}} \qquad G_{\mathrm{e}} = \frac{\rho k_{\mathrm{B}} T}{M_{\mathrm{eff}}}$$

Oscillatory deformation $e(t) = e_0\sin(\omega t)$ stress response and dynamic modulus:

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \qquad \tan(\delta) = \frac{\mathrm{Im}(G_{\mathrm{DM}})}{\mathrm{Re}(G_{\mathrm{DM}})} \qquad G_{\mathrm{DM}}(\omega) = \mathrm{i}\omega \int_0^\infty \exp(-\mathrm{i}\omega t) G(t)\,\mathrm{d}t$$

Los Alamos National Laboratory Chemistry Division

Periodic Table of the Elements

1A	2A	3B	4B	5B	6B	7B		8B		11B	12B	3A	4A	5A	6A	7A	8A
1 H $1s^1$ hydrogen 1.008																	2 He $1s^2$ helium 4.003
3 Li $[He]2s^1$ lithium 6.941	4 Be $[He]2s^2$ beryllium 9.012											5 B $[He]2s^22p^1$ boron 10.81	6 C $[He]2s^22p^2$ carbon 12.01	7 N $[He]2s^22p^3$ nitrogen 14.01	8 O $[He]2s^22p^4$ oxygen 16.00	9 F $[He]2s^22p^5$ fluorine 19.00	10 Ne $[He]2s^22p^6$ neon 20.18
11 Na $[Ne]3s^1$ sodium 22.99	12 Mg $[Ne]3s^2$ magnesium 24.31											13 Al $[Ne]3s^23p^1$ aluminum 26.98	14 Si $[Ne]3s^23p^2$ silicon 28.09	15 P $[Ne]3s^23p^3$ phosphorus 30.97	16 S $[Ne]3s^23p^4$ sulfur 32.07	17 Cl $[Ne]3s^23p^5$ chlorine 35.45	18 Ar $[Ne]3s^23p^6$ argon 39.95
19 K $[Ar]4s^1$ potassium 39.10	20 Ca $[Ar]4s^2$ calcium 40.08	21 Sc $[Ar]4s^23d^1$ scandium 44.96	22 Ti $[Ar]4s^23d^2$ titanium 47.88	23 V $[Ar]4s^23d^3$ vanadium 50.94	24 Cr $[Ar]4s^13d^5$ chromium 52.00	25 Mn $[Ar]4s^23d^5$ manganese 54.94	26 Fe $[Ar]4s^23d^6$ iron 55.85	27 Co $[Ar]4s^23d^7$ cobalt 58.93	28 Ni $[Ar]4s^23d^8$ nickel 58.69	29 Cu $[Ar]4s^13d^{10}$ copper 63.55	30 Zn $[Ar]4s^23d^{10}$ zinc 65.39	31 Ga $[Ar]4s^23d^{10}4p^1$ gallium 69.72	32 Ge $[Ar]4s^23d^{10}4p^2$ germanium 72.58	33 As $[Ar]4s^23d^{10}4p^3$ arsenic 74.92	34 Se $[Ar]4s^23d^{10}4p^4$ selenium 78.96	35 Br $[Ar]4s^23d^{10}4p^5$ bromine 79.90	36 Kr $[Ar]4s^23d^{10}4p^6$ krypton 83.80
37 Rb $[Kr]5s^1$ rubidium 85.47	38 Sr $[Kr]5s^2$ strontium 87.62	39 Y $[Kr]5s^24d^1$ yttrium 88.91	40 Zr $[Kr]5s^24d^2$ zirconium 91.22	41 Nb $[Kr]5s^14d^4$ niobium 92.91	42 Mo $[Kr]5s^14d^5$ molybdenum 95.94	43 Tc $[Kr]5s^24d^5$ technetium (98)	44 Ru $[Kr]5s^14d^7$ ruthenium 101.1	45 Rh $[Kr]5s^14d^8$ rhodium 102.9	46 Pd $[Kr]4d^{10}$ palladium 106.4	47 Ag $[Kr]5s^14d^{10}$ silver 107.9	48 Cd $[Kr]5s^24d^{10}$ cadmium 112.4	49 In $[Kr]5s^24d^{10}5p^1$ indium 114.8	50 Sn $[Kr]5s^24d^{10}5p^2$ tin 118.7	51 Sb $[Kr]5s^24d^{10}5p^3$ antimony 121.8	52 Te $[Kr]5s^24d^{10}5p^4$ tellurium 127.6	53 I $[Kr]5s^24d^{10}5p^5$ iodine 126.9	54 Xe $[Kr]5s^24d^{10}5p^6$ xenon 131.3
55 Cs $[Xe]6s^1$ cesium 132.9	56 Ba $[Xe]6s^2$ barium 137.3	57 La* $[Xe]6s^25d^1$ lanthanum 138.9	72 Hf $[Xe]6s^24f^{14}5d^2$ hafnium 178.5	73 Ta $[Xe]6s^24f^{14}5d^3$ tantalum 180.9	74 W $[Xe]6s^24f^{14}5d^4$ tungsten 183.9	75 Re $[Xe]6s^24f^{14}5d^5$ rhenium 186.2	76 Os $[Xe]6s^24f^{14}5d^6$ osmium 190.2	77 Ir $[Xe]6s^24f^{14}5d^7$ iridium 190.2	78 Pt $[Xe]6s^14f^{14}5d^9$ platinum 195.1	79 Au $[Xe]6s^14f^{14}5d^{10}$ gold 197.0	80 Hg $[Xe]6s^24f^{14}5d^{10}$ mercury 200.5	81 Tl $[Xe]6s^24f^{14}5d^{10}6p^1$ thallium 204.4	82 Pb $[Xe]6s^24f^{14}5d^{10}6p^2$ lead 207.2	83 Bi $[Xe]6s^24f^{14}5d^{10}6p^3$ bismuth 208.9	84 Po $[Xe]6s^24f^{14}5d^{10}6p^4$ polonium (209)	85 At $[Xe]6s^24f^{14}5d^{10}6p^5$ astatine (210)	86 Rn $[Xe]6s^24f^{14}5d^{10}6p^6$ radon (222)
87 Fr $[Rn]7s^1$ francium (223)	88 Ra $[Rn]7s^2$ radium (226)	89 Ac~ $[Rn]7s^26d^1$ actinium (227)	104 Rf $[Rn]7s^25f^{14}6d^2$ rutherfordium (257)	105 Db $[Rn]7s^25f^{14}6d^3$ dubnium (260)	106 Sg $[Rn]7s^25f^{14}6d^4$ seaborgium (263)	107 Bh $[Rn]7s^25f^{14}6d^5$ bohrium (262)	108 Hs $[Rn]7s^25f^{14}6d^6$ hassium (265)	109 Mt $[Rn]7s^25f^{14}6d^7$ meitnerium (266)	110 Ds $[Rn]7s^15f^{14}6d^9$ darmstadtium (271)	111 Uuu (272)	112 Uub (277)		114 Uuq (296)		116 Uuh (298)		118 Uuo (?)

Lanthanide Series*	58 Ce $[Xe]6s^24f^15d^1$ cerium 140.1	59 Pr $[Xe]6s^24f^3$ praseodymium 140.9	60 Nd $[Xe]6s^24f^4$ neodymium 144.2	61 Pm $[Xe]6s^24f^5$ promethium (147)	62 Sm $[Xe]6s^24f^6$ samarium (150.4)	63 Eu $[Xe]6s^24f^7$ europium 152.0	64 Gd $[Xe]6s^24f^75d^1$ gadolinium 157.3	65 Tb $[Xe]6s^24f^9$ terbium 158.9	66 Dy $[Xe]6s^24f^{10}$ dysprosium 162.5	67 Ho $[Xe]6s^24f^{11}$ holmium 164.9	68 Er $[Xe]6s^24f^{12}$ erbium 167.3	69 Tm $[Xe]6s^24f^{13}$ thulium 168.9	70 Yb $[Xe]6s^24f^{14}$ ytterbium 173.0	71 Lu $[Xe]6s^24f^{14}5d^1$ lutetium 175.0
Actinide Series~	90 Th $[Rn]7s^26d^2$ thorium 232.0	91 Pa $[Rn]7s^25f^26d^1$ protactinium (231)	92 U $[Rn]7s^25f^36d^1$ uranium (238)	93 Np $[Rn]7s^25f^46d^1$ neptunium (237)	94 Pu $[Rn]7s^25f^6$ plutonium (242)	95 Am $[Rn]7s^25f^7$ americium (243)	96 Cm $[Rn]7s^25f^76d^1$ curium (247)	97 Bk $[Rn]7s^25f^9$ berkelium (247)	98 Cf $[Rn]7s^25f^{10}$ californium (249)	99 Es $[Rn]7s^25f^{11}$ einsteinium (254)	100 Fm $[Rn]7s^25f^{12}$ fermium (253)	101 Md $[Rn]7s^25f^{13}$ mendelevium (256)	102 No $[Rn]7s^25f^{14}$ nobelium (254)	103 Lr $[Rn]7s^25f^{14}6d^1$ lawrencium (257)

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CHEMISTRY

element names in blue are liquids at room temperature
element names in red are gases at room temperature
element names in black are solids at room temperature