

1 Polymer Mixtures: (15%)

1.1 Draw a sketch showing the spinodal and coexistence curves for the mixture of two different polymers having the same chain length. You will indicate the regions of the graph where the mixture is homogeneous (one phase) or phase separates (two phases). You will provide the axis legends and boundaries as well as the position of the minima of the spinodal and coexistence curves.

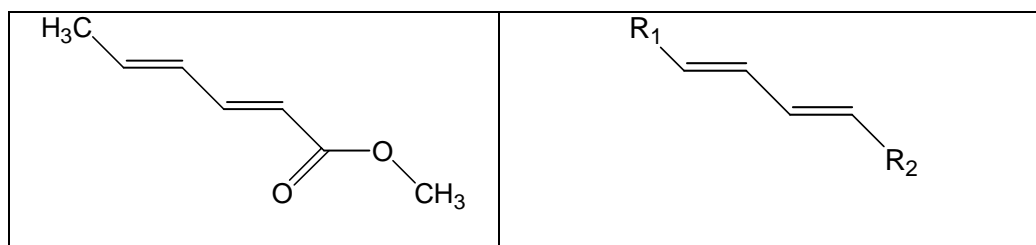
1.2 The difference of energy of mixing per site ($\Delta_M G / \text{site}$) takes the expression given hereafter:

$$\Delta_M G / \text{site} = kT \left(\frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \chi \phi_A \phi_B \right)$$

Give the three parameters besides ϕ_A and ϕ_B in this expression which affect $\Delta_M G / \text{site}$. Explain what they represent and how they favour or disfavour the mixing of the two polymers.

2 Stereochemistry: (25%)

2.1 In their recent work (*Macromolecules* **2003**, 36, 7055-7064), Takasu et al. describe the first threo-disyndiotactic polymerization of methyl 2,4-hexadienoate. The chemical structure of this monomer is given on the left, but you can use the simplified and equivalent structure of the monomer given on the right.



Give the structure of the threo-disyndiotactic polymer.

2.2 What type of catalyst would you use to carry out a syndiotactic polymerization? Sketch the mechanism of the polymerization. You will pay attention to whether it is the substituted or unsubstituted carbon of the incoming monomer which binds to the transition metal.

- 2.3 What are the two main differences between syndiotactic and isotactic polymerization?
- 2.4 Is the syndiotactic polymerization chain-end controlled or site-controlled? Make a sketch explaining how a defect in the incorporation of a monomer would affect the incorporation of the following monomers.

3 Mechanical Properties of Polymers (20%)

The glass transition (T_g) of polystyrene equals 100 °C whereas that of polybutadiene equals -102 °C.

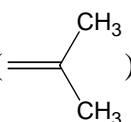
- 3.1 Sketch a plot of Log(modulus) as a function of temperature for temperatures ranging from 0 °C to +250 °C for polystyrene. Describe what happens at T_g and at the rubbery plateau, and how molecular weight affects the rubbery plateau.

- 3.2 On the same figure, sketch a plot of Log(modulus) as a function of temperature for temperatures ranging from -150 °C to +250 °C for polystyrene, polybutadiene, and poly(styrene-*b*-butadiene-*b*-styrene) rubber. The italicised *b* indicates that the polymer is blocky. Note that polystyrene and polybutadiene are immiscible and they phase separate. Also the styrene block is much smaller than the butadiene block.

You will describe with words what happens to poly(styrene-*b*-butadiene-*b*-styrene) as the temperature is increased from -150 °C to +250 °C.

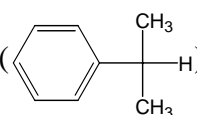
- 3.3 On the same graph, draw the stress-strain curves of a high-density polyethylene (HDPE) and a low-density polyethylene (LDPE) sample. You will explain how you would proceed to obtain the modulus of the material. Which material (HDPE or LDPE) will be tougher and how will it affect the stress-strain curve?

4 Ionic Polymerization (20%)

4.1 The polymerization of isobutylene () can be initiated with boron trifluoride (BF₃) and water.

Give the reaction scheme for:

- initiation
- chain transfer to monomer
- spontaneous termination
- termination by recombination with the initiator.

4.2 Describe the effect of isopropylbenzene () on the polymerization of isobutylene

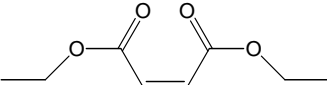
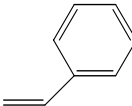
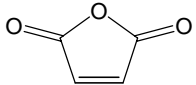
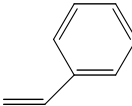
conducted in Section 4.1. What effect does the presence of isopropylbenzene have on the molecular weight of polyisobutylene?

4.3 Why does anionic polymerization proceed more quickly in dioxane (dielectric constant = 2.2) when the counterion changes as Li⁺(slow) < Na⁺ < K⁺ < Rb⁺ < Cs⁺ (fast)?

4.3 Why does anionic polymerization proceed more slowly in THF (dielectric constant = 7.6) when the counterion changes as Li⁺(fast) > Na⁺ > K⁺ > Rb⁺ > Cs⁺ (slow)?

5 Copolymerization (20%)

5.1 On the same graph, sketch F_1 (instantaneous copolymer composition) versus f_1 (instantaneous feed composition) for the monomer pairs listed hereafter:

Monomer 1	r_1	Monomer 2	r_2
Diethyl maleate (DEM) 	0.010	Styrene 	6.1
Maleic anhydride (MA) 	0.005	Styrene 	0.050

You will describe the nature of the polymers obtained and provide a reason for the observed differences.

5.2 Based only on the reactivity ratios, is the diethyl maleate or maleic anhydride monomer more reactive towards the styrene radical? You will explain your reasoning.

5.3 The Q and e values for styrene, maleic anhydride, and diethyl maleate are listed in the table below.

Monomer	Q	e
Styrene	1.00	-0.80
Diethyl maleate	0.053	1.08
Maleic anhydride	0.86	3.69

What do the Q and e parameters represent? According to the values listed in the table, describe the nature of the copolymers obtained from the copolymerization of styrene with diethyl maleate and styrene with maleic anhydride. Do your conclusions agree with those drawn from question 5.1?