UNIVERSITY OF TORONTO

FACULTY OF APPLIED SCIENCE AND ENGINEERING

FINAL EXAMINATION, APRIL 2001

Fourth Year - Program 6 (Elective)

CHE 463S - POLYMER SCIENCE AND ENGINEERING

Examiner - S.T. Balke

Note:

- Attempt all questions: marks total 100.
- This is a Type A Exam.
- The final three pages of this exam contain needed equations.
- **Unless otherwise specifically requested**, you of need not define the meaning symbols if you are using the same symbols as used in lectures.
- Be sure to label the axes of all graphs with symbols.
- Report all final answers to four significant figures.

Marks

1. A sample of polystyrene which is polydisperse in molecular weight is injected into a GPC operating with THF as the mobile phase. The chromatogram heights from the differential refractive index detector and corresponding retention volumes are as shown in Figure 1.0 and Table 1.0 below:

Figure 1

Retention Time
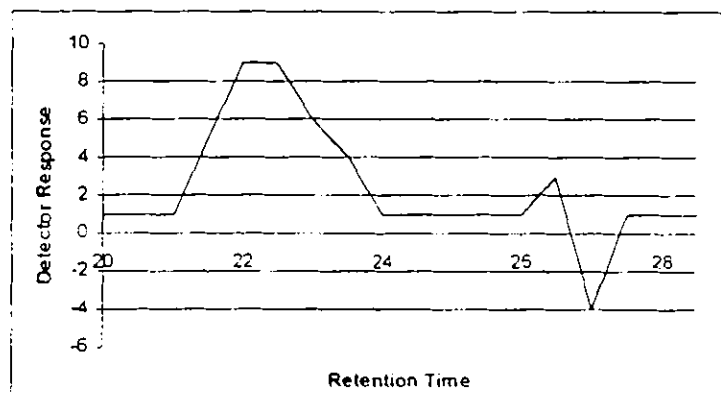
Question 1 Continued from Page 1

Table 1

Time [min]	Detector Response [mv]	Time [min]	Detector Response [mv]
20.0	1	24.5	1
20.5	1	25.0	1
21.0	1	25.5	1
21.5	5	26.0	1
22.0	9	26.5	3
22.5	9	27.0	-4
23.0	6	27.5	1
23.5	4	28.0	1
24.0	1	28.5	1

Mark Houwink Constants for Polystyrene in THF: $K_{PS} = 6.82 \times 10^{-3}$ cm^3/g and $a_{PS} = 0.766$

For this GPC analysis:

$\log J = 19.0 - 0.60\ v$ in THF
THF Flow Rate=0.95 cm^3/min

10   1a. Calculate the intrinsic viscosity of the whole polydisperse polymer from the chromatogram.

5   1b. Calculate the viscosity average molecular weight of the whole polydisperse polymer from the chromatogram.

1c. For star branched polystyrenes monodisperse in molecular weight, a factor, g' is used where g' is defined as the ratio of the intrinsic viscosity of the branched polymer of molecular weight M to a linear polymer of the same molecular weight M.

Marks

That is:

$$g' = \left(\frac{[\eta]_{branched}}{[\eta]_{linear}} \right)_M \qquad (1)$$

Also, for star branched polymers:

$$g' = \left(\frac{3f - 2}{f^2} \right)^{0.6} \qquad (2)$$

where f is the number of arms on the star.

10

Determine the molecular weight calibration curve in the above GPC chromatographic system for any five arm star branched polystyrene polymer taking branching into account.

2. Using a capillary rheometer to measure the viscosity of an unidentified polymer at 170°C to obtain data you plot the logarithm of the apparent wall shear rate (on the y axis) versus logarithm of the wall shear stress (on the x axis) and obtain a straight line with a slope of 0.780.

5

2a. Derive an equation for the straight line and state the quantities represented by the slope and intercept.

5

2b. Write the constitutive equation for the fluid allowing it to contain only one unknown constant.

5

2c. Name the type of fluid (be as specific as possible) and state how its viscosity varies with shear rate.

5

2d. Given that at a shear rate of $1000\ s^{-1}$ the viscosity was 800 Pa s, determine the unknown parameter in the constitutive equation.

Marks

<u>**Question 2 Continued from Page 3**</u>

5   2e.   This polymer is run through a "typical" single screw extruder at 40 rpm and
170°C. Estimate the average viscosity of the polymer in the extruder and provide
details supporting your estimate.

5   2f.   A polymer different that the one used in the previous parts of this question has a
melt flow index of 0.1 g/10 min. and an M_w of 200,000. Estimate the melt flow
index for the same type of polymer with an M_w of 150,000.

5   2g.   Given the following information on a "non-standard" melt flow indexer:

Temperature=170°C
polymer density = 1 g/cc (assume constant flow rate)
Diameter of capillary = 0.20955 cm
Length of capillary = 0.800 cm
Diameter of barrel = 2.00 cm
Note: 1 kg(f)=9.81 N

Assume: polymer density=1 g/cc; constant flow rate from the melt flow
indexer; same polymer as in parts 2a through 2e of this question.

You will use this device for shear refining samples. Degradation occurs at a
shear stress of 5.00 MPa. What mass should there be on the plunger to
maximize shear refining? Explain your reasoning and show calculations.

3.   You wish to scale-up a process involving the injection of free radical initiator into
polypropylene running in a single screw extruder for the purpose of manufacturing
"controlled rheology" polypropylene. The research work utilized a 1.905 cm
diameter extruder. The manufacturing extruder is 7.62 cm in diameter. The scale-
up method in the following table has been proposed.

Question 3 Continued from Page 4

|	Basic Relationships	Scale-Up Method
channel depth (H)	h	0.7
axial length (L)	l	1
screw speed (N)	v	-1.4
length of transition section	l_t	1
shear rate	$1+v-h$	-1.1
pumping rate	$h+2+v$	1.3
melting rate (low Br)	$1+0.5v+l_t$	1.3
melting rate (high Br)	$2+v+0.5nv+l_t$	1.6-0.7n
solids conveying rate	$h+2+v$	1.6
residence time	$l-1-v$	1.4
shear strain	$l-h$	0.3
power consumption	$1+n+2+nv+v-nh$	1.6-1.1n
SEC	$l-h+n+nv-nh$	0.3-1.1n
area/throughput	$l-h-1-v$	0.7

Answer the following regarding the scale-up of this reactive extrusion process:

6

i. Determine the two best values of the power law index for scale up considering (a) melting rate (high Br) and (b) SEC respectively.

4

ii. The average residence time in the small extruder is known to be 0.5 minutes. The half life of the peroxide initiator is 0.100 minutes at the operating conditions of the extruders. Assuming that your criterion is that less than 0.1 weight percent of the original concentration of initiator remains in the product, show quantitatively whether or not the scale-up is likely to be satisfactory. Explain.

5

iii. Sketch the cumulative molecular weight distributions that you would expect for the feed and for the product. Label your axes and use a logarithmic scale on the x axis.

5

iv. Sketch the normalized GPC chromatograms obtained from a differential refractive index detector that you would expect for the feed and for the product.

Marks

4. The figure below shows a plot of the instantaneous F_A versus f_A for $r_A = 0.50$, $r_B = 0.10$.

5   4a. Write the equation that was used to generate this figure and calculate the value of the instantaneous F_A for $f_A = 0.3$.

5   4b. Determine the ratio of the concentration of monomer A to the concentration of monomer B in the reaction mixture for there to be a number average sequence length of 5.0 in the sequences of A in the instantaneously produced polymer.

5   4c. Define what is meant by "azeotropic composition" and calculate the values of the instantaneous F_A and f_A for this co-polymerization. Hint: begin by simplifying the following equation:

$$\frac{d[A]}{d[B]} = \frac{[A]}{[B]} \frac{(r_A[A]+[B])}{(r_B[B]+[A])}$$

5   4d. Sketch the same type of plot as in 4a. for the case $r_A = .5$, $r_B = 1.0$ and state the values of the instantaneous F_A and f_A at its azeotropic composition.
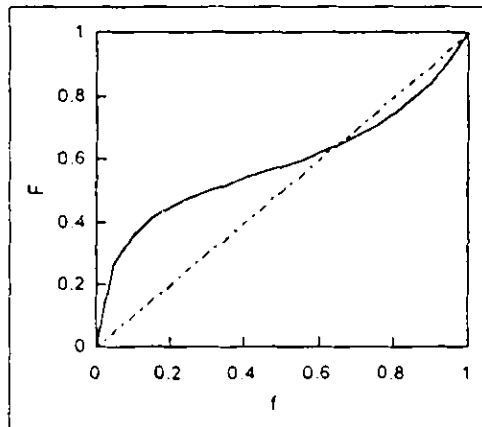
EQUATIONS

$$Q = \frac{\pi R^4}{8 \eta} \frac{d P}{d z}$$	$$X = \frac{[M]_0 V_0 - [M]V}{[M]_0 V_0}$$
$$v_z = \frac{1}{4\eta} \frac{d P}{d z} (R^2 - r^2)$$	$$R_p = k_p [M] \sqrt{\frac{2f \, k_d [I]}{(k_{t\,c} + k_{td})}}$$
$$\tau_R = \frac{R}{2} \left(\frac{d P}{d z} \right)$$	$$\ln (1 - x) = \int_{f_{A_0}}^{f_A} \frac{d f_A}{F_A - f_A}$$
$$F_A = \frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2}$$	$$\overline{F_A} \approx \frac{f_{A_0} - f_A (1 - x)}{x}$$
$$x = 1 - \left[\frac{f_A}{f_{A0}} \right]^\alpha \left[\frac{1 - f_A}{1 - f_{A0}} \right]^\beta \left[\frac{f_{A0} - \delta}{f_A - \delta} \right]^\gamma$$	$$\dot{\gamma}_w = \frac{4 Q}{\pi R^3} \left(\frac{3 n + 1}{4 n} \right)$$
$$\alpha = \frac{r_B}{1 - r_B}$$	$$\gamma = \frac{1 - r_A r_B}{(1 - r_A)(1 - r_B)}$$
$$\beta = \frac{r_A}{1 - r_A}$$	$$\delta = \frac{(1 - r_B)}{(2 - r_A - r_B)}$$

EQUATIONS (CONTINUED)

$P_{aa} = \dfrac{r_A f_A}{r_A f_A + f_B}$ $P_{bb} = \dfrac{r_B f_B}{f_A + r_B f_B}$	$W_N(M) = \dfrac{W(M)}{\displaystyle\int_0^\infty W(M)dM}$
$P_{ab} = \dfrac{f_B}{r_A f_A + f_B}$ $P_{ba} = \dfrac{f_A}{f_A + r_B f_B}$	$M_n = \dfrac{\displaystyle\int_0^\infty W(M)dM}{\displaystyle\int_0^\infty \dfrac{W(M)}{M}dM}$
$\overline{N_A} = \dfrac{1}{1 - P_{aa}} = \dfrac{1}{P_{ab}}$ $\overline{N_B} = \dfrac{1}{1 - P_{bb}} = \dfrac{1}{P_{ba}}$	$M_w = \dfrac{\displaystyle\int_0^\infty MW(M)dM}{\displaystyle\int_0^\infty W(M)dM}$
$W_N(\log M)d\log M = - W_N(v)dv$	$\displaystyle\lim_{c \to 0} \dfrac{\eta_{sp}}{c} = [\eta]$
$\dfrac{d(\log M)}{dM} = \dfrac{1}{2.303 M}$	

EQUATIONS (CONTINUED)

$M = (\dfrac{J}{K})\dfrac{1}{a+1}$	$[\eta] = \displaystyle\sum_{i=1}^{n} w_i [\eta]_i$
$\dot\gamma_w = \dfrac{4\,Q}{\pi\,R^3}\left(\dfrac{3+b}{4}\right)$	$\tau_{R\,0} = \dfrac{T_{R0}\,s^2}{2\,\pi\,R_i^2\,L}$
$Q = \dfrac{Wbh}{2} - \dfrac{bh^3}{12\eta}\dfrac{P}{Z}$	