

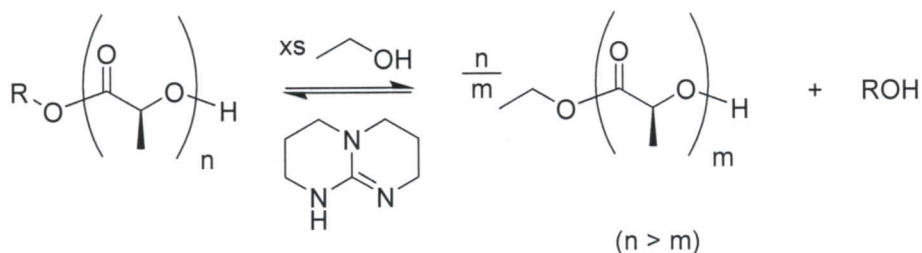
Name: ANSWER KEY [printed]

"On my honor, as an Aggie, I have neither given nor received unauthorized aid on this academic work."

_____ [signature]

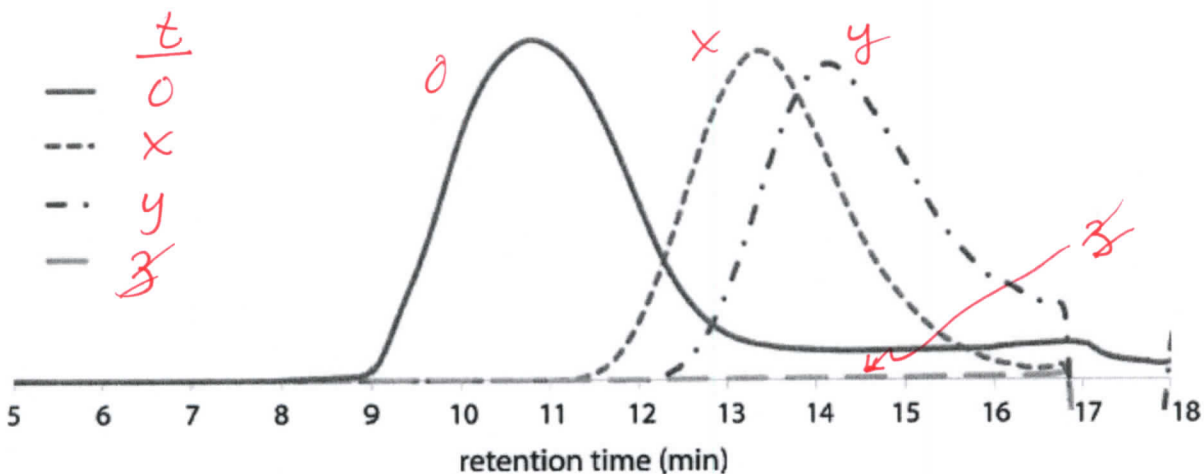
Exam II, March 7, 2013, 100 pts
Polymer Chemistry, CHEM 466, Spring 2013
Texas A&M University, College Station, TX, USA

1. The following questions are related to the reaction of polylactide with ethanol in the presence of TBD as an organocatalyst, as shown below and reported in F. A. Leibfarth *et al.* *J. Polym. Sci., Part A: Polym. Chem.* **2012**, 50, 4814-4822.



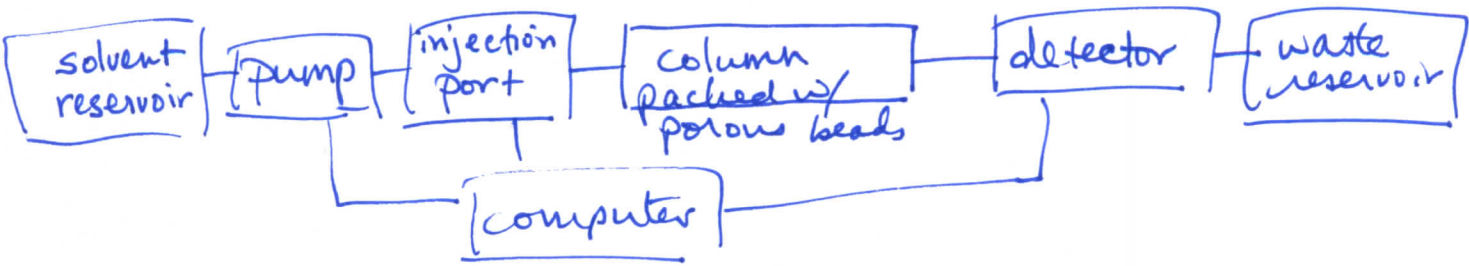
- (a) Explain what is being observed (in terms of what is occurring chemically) by the series of GPC traces shown below, from a reaction of polylactide with $3n$ molar equivalents of ethanol and $0.01n$ TBD. [4 points]

depolymerization by organocatalyzed transesterification reactions



- (b) Label each of the four GPC traces (either at the legend or on the traces directly) with the reaction time at which it would have been acquired, as $t = 0, x, y,$ and $z,$ where reaction time increases from $0 < x < y < z.$ [8 points]

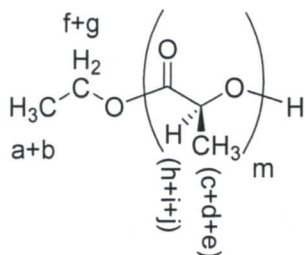
(c) Draw a schematic illustration of the components that comprise a GPC system. [14 points]



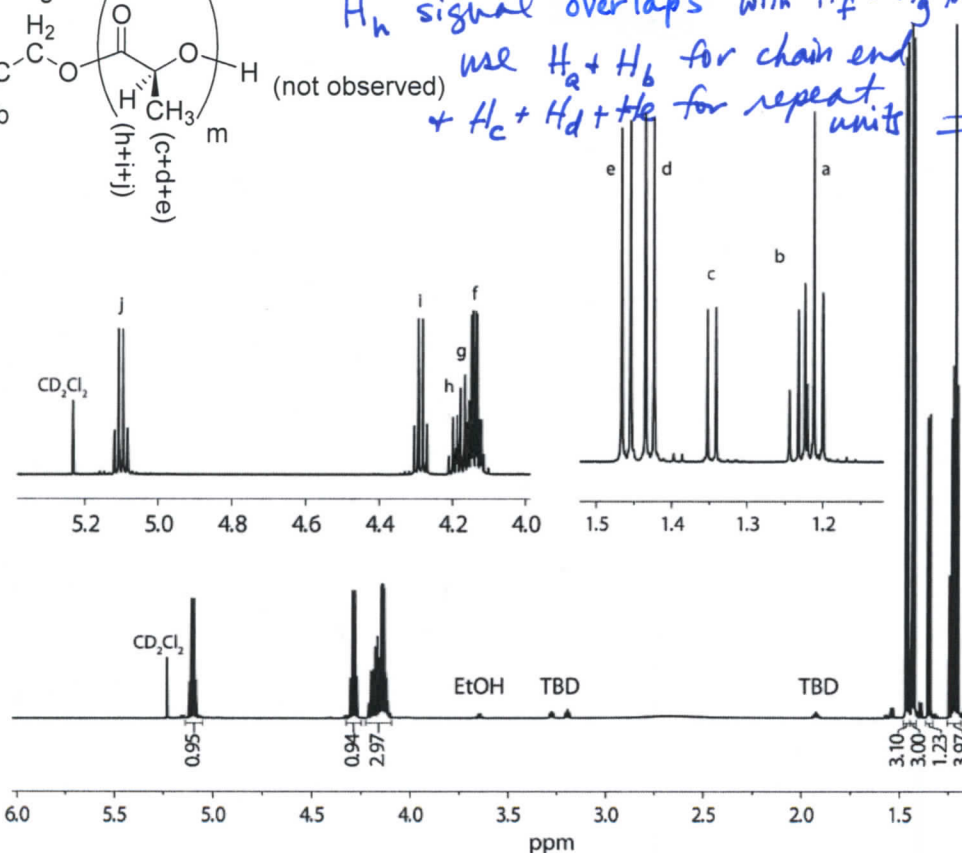
(d) Indicate the parameter that determines the retention time that a molecule experiences during analysis by GPC, how the magnitude of the value for that parameter affects the retention time, and why. [6 points]

hydrodynamic volume, V_h ; as V_h increases, retention time decreases; larger molecules are excluded from higher #'s of pores, so diffuse into + out of fewer pores + reside in the column for a shorter time

(e) Given the ^1H NMR spectrum below, calculate the average degree of polymerization, m . A few notes: there are 2 inset spectra that are simply expanded views of regions of the entire spectrum (note the scale to identify the regions); integrals are not drawn on the spectrum, rather the integration values are given below each set of peaks; there are multiple signals (sets of peaks) for each type of proton of the structure; so please review carefully the assignments that are made on the structure; recall the reaction that generated this sample—it makes the problem a bit tricky. [8 points]



Since H of OH end not observed + H_n signal overlaps with $H_f + H_g$ signals, use $H_a + H_b$ for chain ends + $H_c + H_d + H_e$ for repeat units



$$\Rightarrow 3(H_a + H_b) = 3.97$$

$$\Rightarrow \text{CH}_2 \text{ end groups} = 1.32$$

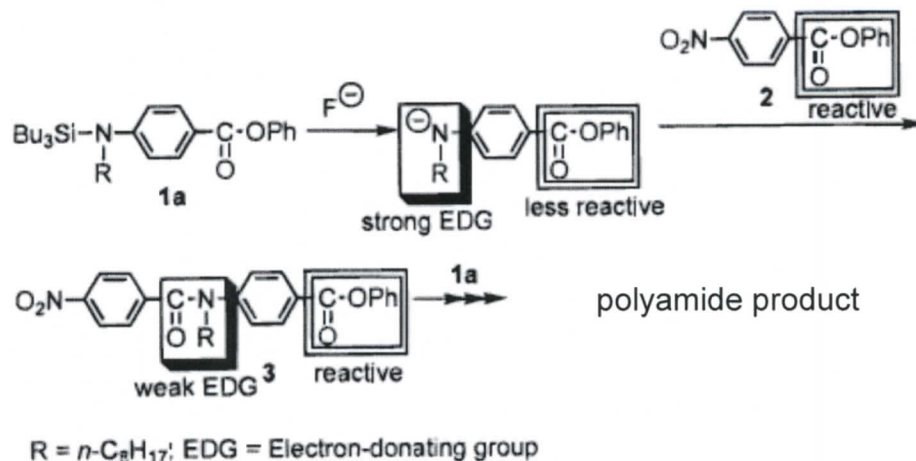
$$3(H_c + H_d + H_e) = 1.23 + 3.00 + 3.10 = 7.33$$

$$\Rightarrow \text{CH}_3 \text{ repeat units} = 2.44$$

$$\frac{\text{repeats}}{\text{ends}} = \frac{2.44}{1.32} = 1.85$$

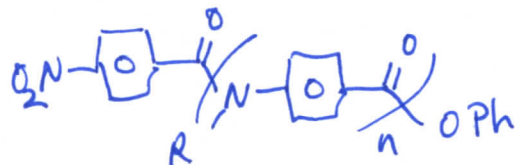
\therefore primarily monomers + dimers

2. For the chain-growth polycondensation polymerization reported in T. Yokozawa *et al.* *J. Am. Chem. Soc.* **2000**, 122, 8313-8314, employing an activated form of **1a** as the monomer and **2** as the initiator, as illustrated below, controlled polymerization was confirmed to afford well-defined polyamide products.

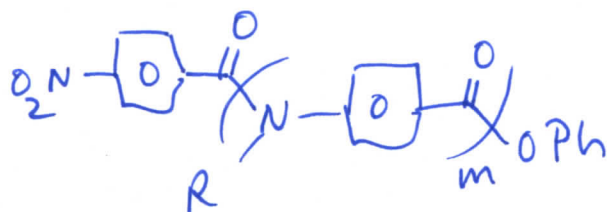


As one of the techniques applied to confirm controlled "livingness" of the polymerization, an initial prepolymer was prepared and then an additional aliquot of monomer was added.

- (a) Draw the chemical structure for the initial prepolymer (the "polyamide product" in the scheme above). [4 points]

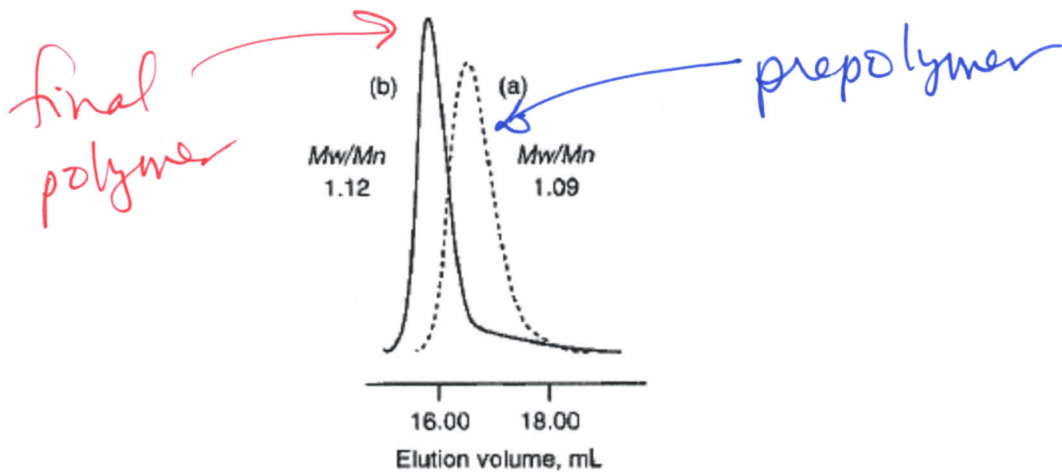


- (b) Draw the chemical structure for the final polymer that would result after the introduction of additional monomer. [4 points]



where $m > n$
and depends on
amount of
additional
monomer
added

- (c) Indicate on the figure below, containing overlaid GPC traces, which trace would be generated by the prepolymer and which would be generated by the final polymer (the y-axis is not shown, but it is simply the detector response). [4 points]

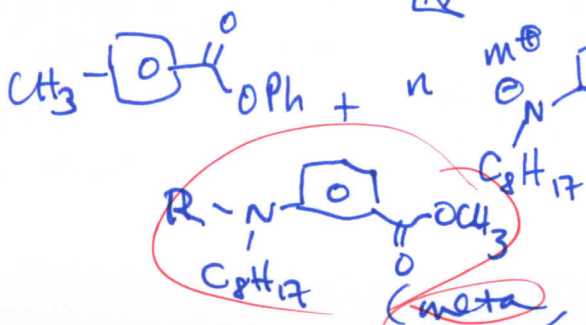
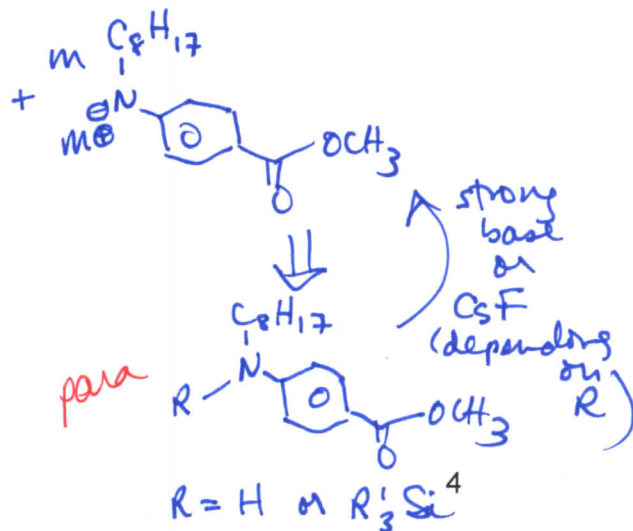
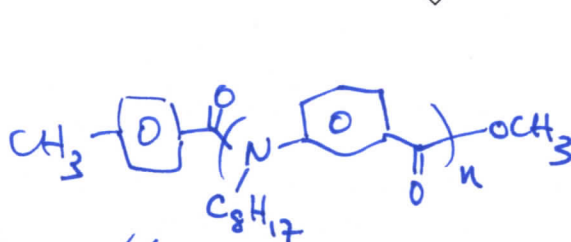
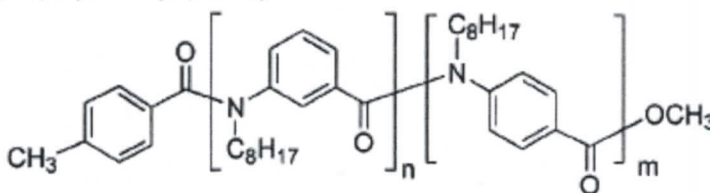


- (d) Describe two characteristics of this final polymer, revealed in the overlaid GPC traces above, that allowed for confirmation of the controlled "livingness" of the polymerization. [4 points]

narrow mol. wt. distribution

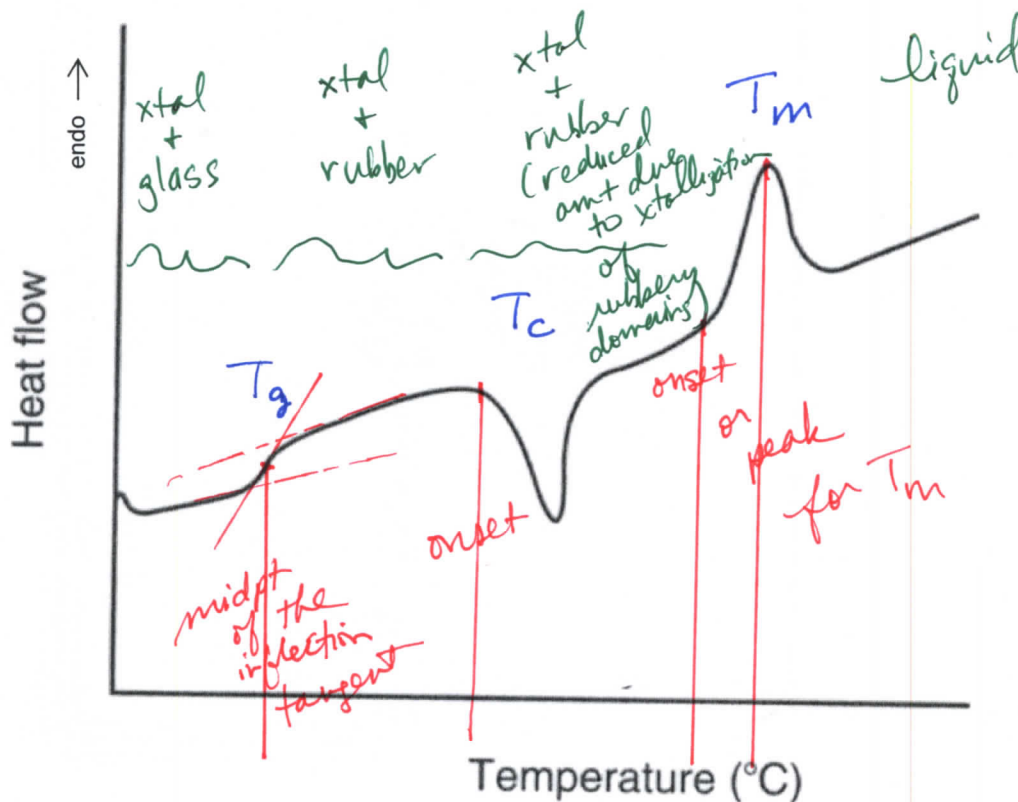
chain extension of prepolymer (shift of peak to shorter retention time) vs. growth of new polys (if not "living")

- (e) Using similar concepts to those above, provide a retrosynthetic pathway for the preparation of the following block copolymer. [8 points]

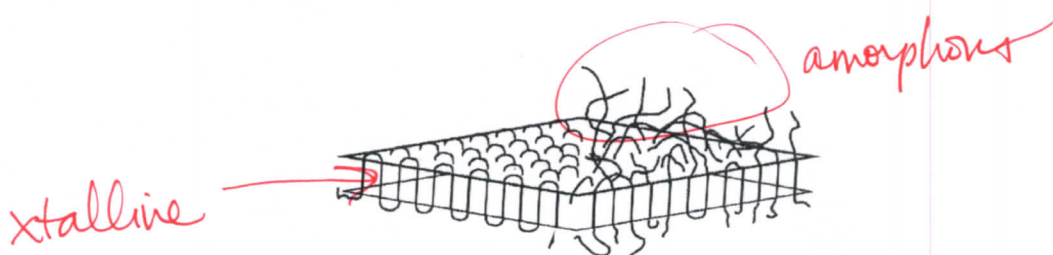


(meta, same as for para conditions)

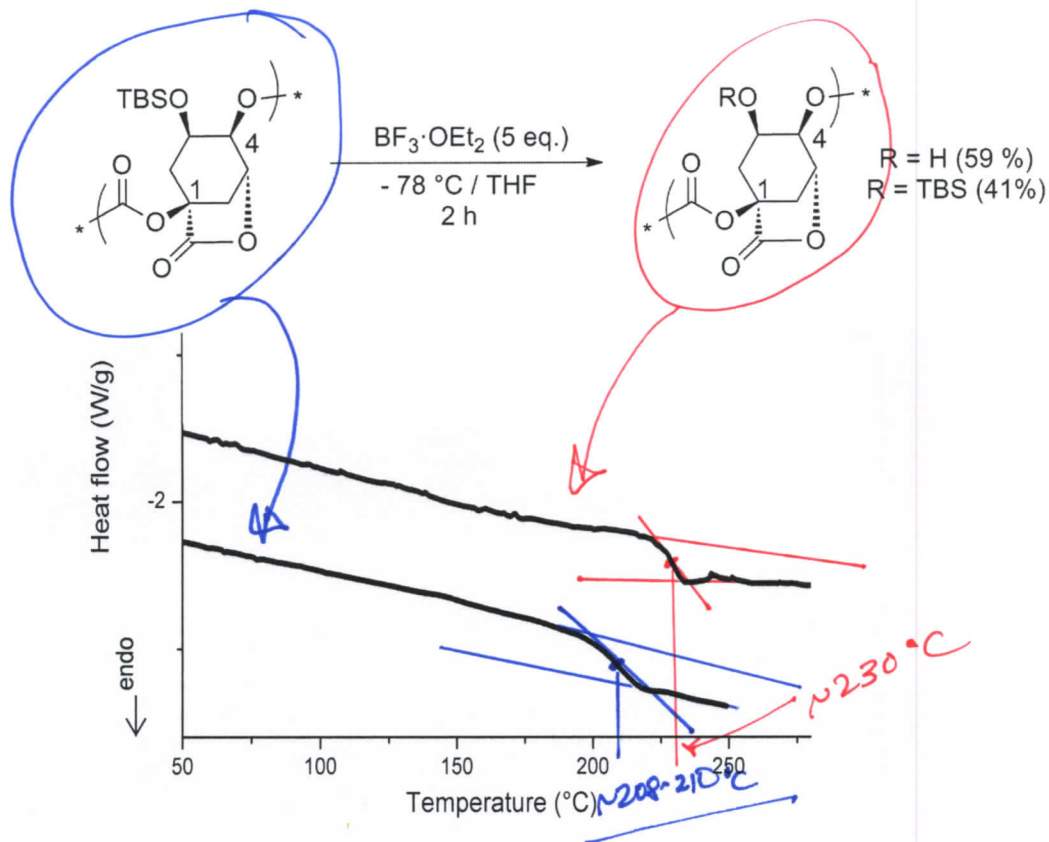
3. Directly on the schematic illustrations of a DSC trace (Figure 12.6 of your textbook—please note that the heat flow axis is opposite to that discussed during lecture) and polymer chain packing (Figure 13.15 of your textbook) shown below:



- (a) Label the thermal transitions along the DSC trace, including their types (e.g. T_m , T_g , T_c). [6 points]
- (b) Identify (with a line extending from the trace to the temperature axis) the positions along the DSC trace at which the temperature value for each transition would be measured. [6 points]
- (c) Indicate the physical states of matter that are expected to be present in the sample at the various temperature ranges along the DSC trace. [8 points]
- (d) Label the physical states of matter within the regions of the polymer chain packing structure below, as being either crystalline or amorphous. [4 points]



For the chemical reaction, showing partial deprotection of a poly(quinic acid carbonate) by removal of a portion of the *tert*-butyldimethylsilyl (TBS) ether protecting groups to give hydroxyl functionalities, and accompanying DSC traces:



(e) Use arrows to point each chemical structure to its corresponding DSC trace. [4 points]

(f) State how the assignments of structures to traces was made, *i.e.* state which characteristics of the structures/compositions would lead to a higher or lower T_g value and why. [4 points]

- TBS groups have high free volume and give lower T_g than OH groups
- OH groups are capable of H-bonding increasing intra- + inter-molecular interactions and give higher T_g

(g) Interpret the DSC traces (show your work for the analysis), to provide an estimation of the T_g values for both traces. [4 points]

$\sim 210^\circ\text{C}$ and $\sim 230^\circ\text{C}$

Equations, which may be of use:

Number-average molecular weight:

$$M_n = \frac{\sum N_x M_x}{\sum N_x}$$

 $N_x = \# \text{ moles of polymer chains having molecular weight, } M_x$

Weight-average molecular weight:

$$M_w = \frac{\sum w_x M_x}{\sum N_x M_x} = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

 $w_x = \text{wt fraction of polymer chains having molecular weight, } M_x = \frac{N_x M_x}{\sum N_x M_x}$

Degree of polymerization:

$$DP_n = \frac{1}{1 - c}$$

 $c = \text{extent of conversion of functional groups}$

Polydispersity index:

$$PDI = \frac{M_w}{M_n}$$

Critical extent of reaction:

$$p_c = \frac{2}{f_{av}}$$

Average degree of monomer functionality:

$$f_{av} = \frac{\sum N_i f_i}{\sum N_i}$$

Textbook:

Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry*, 2nd Edition; CRC Press, Taylor & Francis Group: Boca Raton, FL, USA, 2007