1. The copolyimide shown below was reported recently\(^1\) to exhibit tunable optical and electronic properties through charge transfer between the AMTPA and NTCDI units. Memory devices constructed from a series of these copolymers, with variation in the \(x\) value, gave a change from “volatile dynamic random access memory to nonvolatile write once read many memory characteristics as the NTCDI composition increased”.

(a) Provide a retrosynthetic pathway by which this copolymer structure could be prepared. To avoid confusion, please note that the 6-membered ring imides are part of the NTCDI monomer, which is shown below. [10 points]

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(b) State whether this copolyimide is a random/statistical copolymer or a block copolymer. [2 points]

(c) State whether the polymerization step of your retrosynthesis would proceed by a chain-growth or step-growth process. [2 points]

(d) State whether your polymerization would be controlled or un-controlled. [2 points]

(e) State whether the molecular weight distribution would be expected to be narrow or broad. [2 points]

(f) Draw the expected $D_P_n$ vs. % monomer conversion plot on the axes below. [4 points]

(g) Predict the thermal characteristics for this polymer, in terms of thermal transition temperature(s) and thermal decomposition temperature(s), and explain. [4 points]
2. As promised during lecture, this question requires that you provide a retrosynthetic analysis for the following molecular brush, which is prepared by a combination of RAFT polymerization and ROMP. Please note a few points: i) the termination step was not shown explicitly during the discussion of this molecular brush, but was illustrated during the final lecture of the course; ii) the chemical structure for N-phenylmaleimide is given and may be of use; iii) although the mechanism for RAFT polymerization was illustrated during lecture for a trithiocarbonate chain transfer agent, the mechanism is the same for the dithioester functionality.

(a) Provide a retrosynthetic pathway for the preparation of this molecular brush (your answer can continue onto the next page). [15 points]

\[
x = y = 0.5
\]

\[
\text{Ph} = \text{phenyl} = \begin{array}{c}
\text{O} \\
\text{N} \\
\text{Ph}
\end{array}
\]

\[
\text{N-phenylmaleimide}
\]
(b) Given that \( x = y = 0.5 \) and the styrene and N-phenylmaleimide units are alternating for the copolymer graft, predict the reactivity ratio values for the copolymerization of \( p \)-hydroxystyrene (1) and N-phenylmaleimide (2). [2 points]

\[
\begin{align*}
r_1 &= \\
r_2 &= 
\end{align*}
\]
(c) Choose one of your RAFT polymerization steps and draw the electron arrow-pushing mechanism for the RAFT polymerization, labeling all initiation, propagation and (reversible) termination steps. [6 points]
3. For the following cationic chain-growth, addition copolymerization:

\[
\begin{align*}
1) & \quad \text{Cl} \\
2) & \quad \text{Cl}
\end{align*}
\]

(a) Provide the products. [10 points]

(b) State which regioisomer for the isoprene repeat units is favored, and state and illustrate mechanistically the reason for your answer. [5 points]

(c) State at least one product in which this copolymer could be found, e.g. name the item that was shown during lecture. [2 points]

4. (a) For the following polypropylene segments, label their tacticities and predict whether they are likely to pack into crystalline or amorphous domains. [12 points]

(b) Describe the key features of the system that we discussed as being used by Dow to obtain olefin block copolymers with alternating semicrystalline and amorphous segments. [6 points]
5. For quiz #10, several students expressed interest in the broad range of applications for super glue, including those beyond typical daily applications, e.g., in the medical field, forensics, etc., and requested that a final examination question involve super glue. Therefore,

(a) provide the chemistry for any version of an α-cyanoacrylate “super glue”, including the monomer, initiator, mechanism of polymerization and the final polymer product structure; [12 points]

(b) state what kind of polymerization is involved; [2 points]

(c) state why this polymerization does not proceed while the monomer is stored in a closed tube. [2 points]
Equations, which may be of use:

Number-average molecular weight:
\[ M_n = \frac{\sum N_x M_x}{\sum N_x} \]

\( N_x = \) # moles of polymer chains having molecular weight, \( M_x \)

Weight-average molecular weight:
\[ M_w = \sum w_x M_x = \frac{\sum N_x M_x^2}{\sum N_x M_x} \]

\( w_x = \) wt fraction of polymer chains having molecular weight, \( M_x \)

Degree of polymerization:
\[ D_{P_n} = \frac{1}{1 - c} \]
\( c = \) extent of conversion of functional groups

\[ D_{P_n} = \frac{[\text{monomer}]_0 \cdot \% \text{ monomer conversion}}{[\text{initiator}]_0 \cdot f} \]

Polydispersity index:
\[ \text{PDI} = \frac{M_w}{M_n} \]

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: