ROP of lactide + glycolide was a common answer, but this is a chain-growth polym., therefore Δ 5 pts was given for ROP

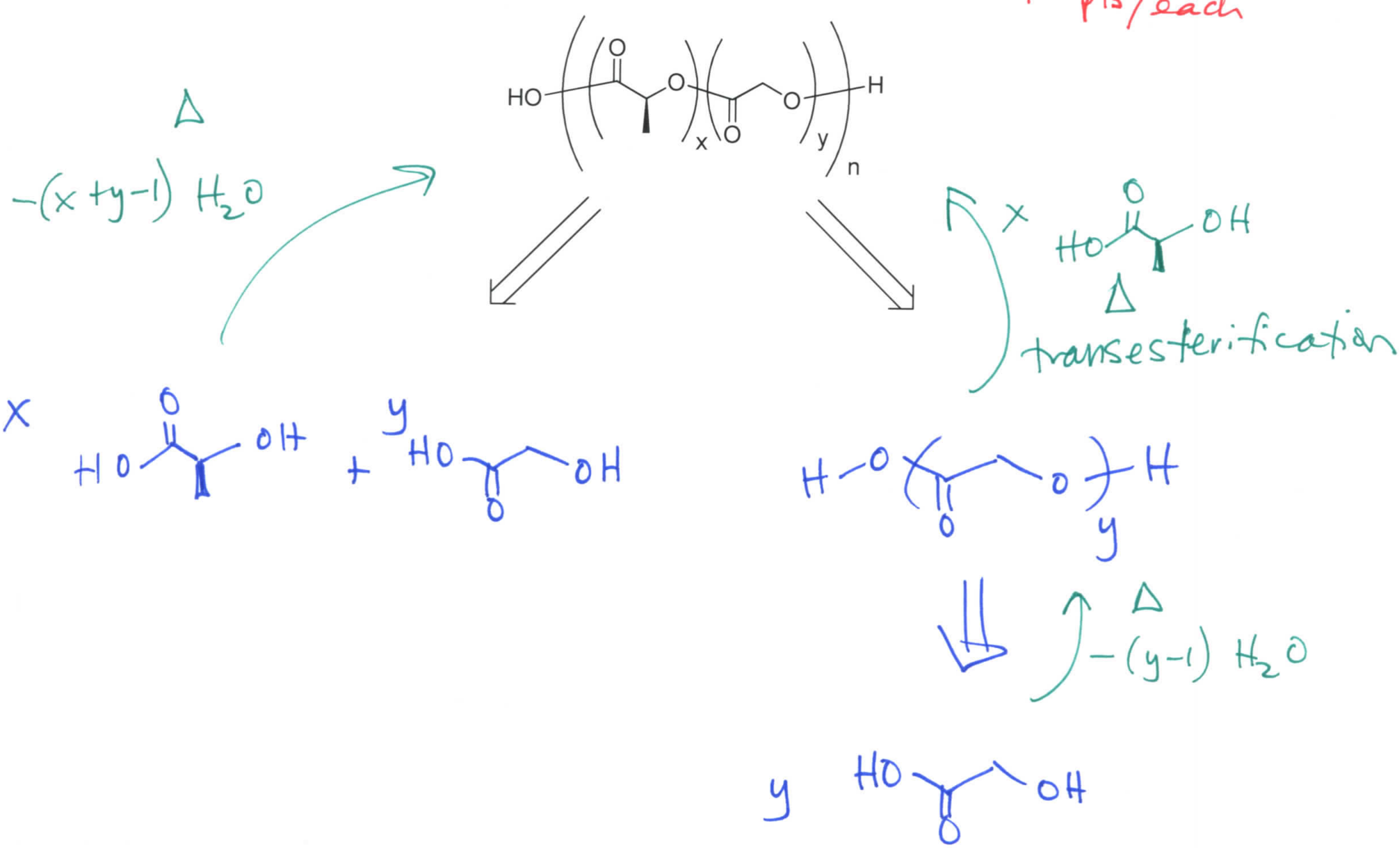
Name: ANSWER KEY [printed]

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

______________________ [signature]

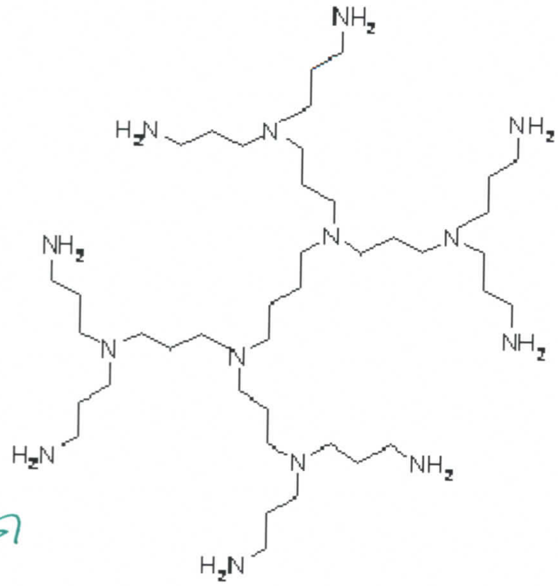
Final Exam, May 7, 2012, 100 pts
Polymer Chemistry, CHEM 466, Spring 2012
Texas A&M University, College Station, TX, USA

1. We discussed the use of poly(lactic acid) or polylactide in biomedical applications, such as in suture materials, and you've seen poly(glycolic acid) and polyglycolide on quiz #2. It is common for the properties of these two types of polyesters to be mixed, to obtain a polymer with intermediate crystallinity, hydrophobicity, mechanical properties and hydrolytic degradation rates, by the formation of copolymers that contain both types of repeat units along the polymer backbones. Consider only condensation, step-growth polymerization concepts, and reactions or side reactions that we have discussed for polyesters, to propose two quite different retrosynthetic routes that could be followed to give a mixed copolymer of lactic acid and glycolic acid repeat units. Work the retrosyntheses backward to the point that the forward syntheses begin from lactic acid and glycolic acid as the monomers, and provide the steps and reaction conditions that could be used to lead to the copolymer shown. Please note that your two approaches to this same copolymer structure may involve different numbers of steps. **[20 points]** 10 pts/each

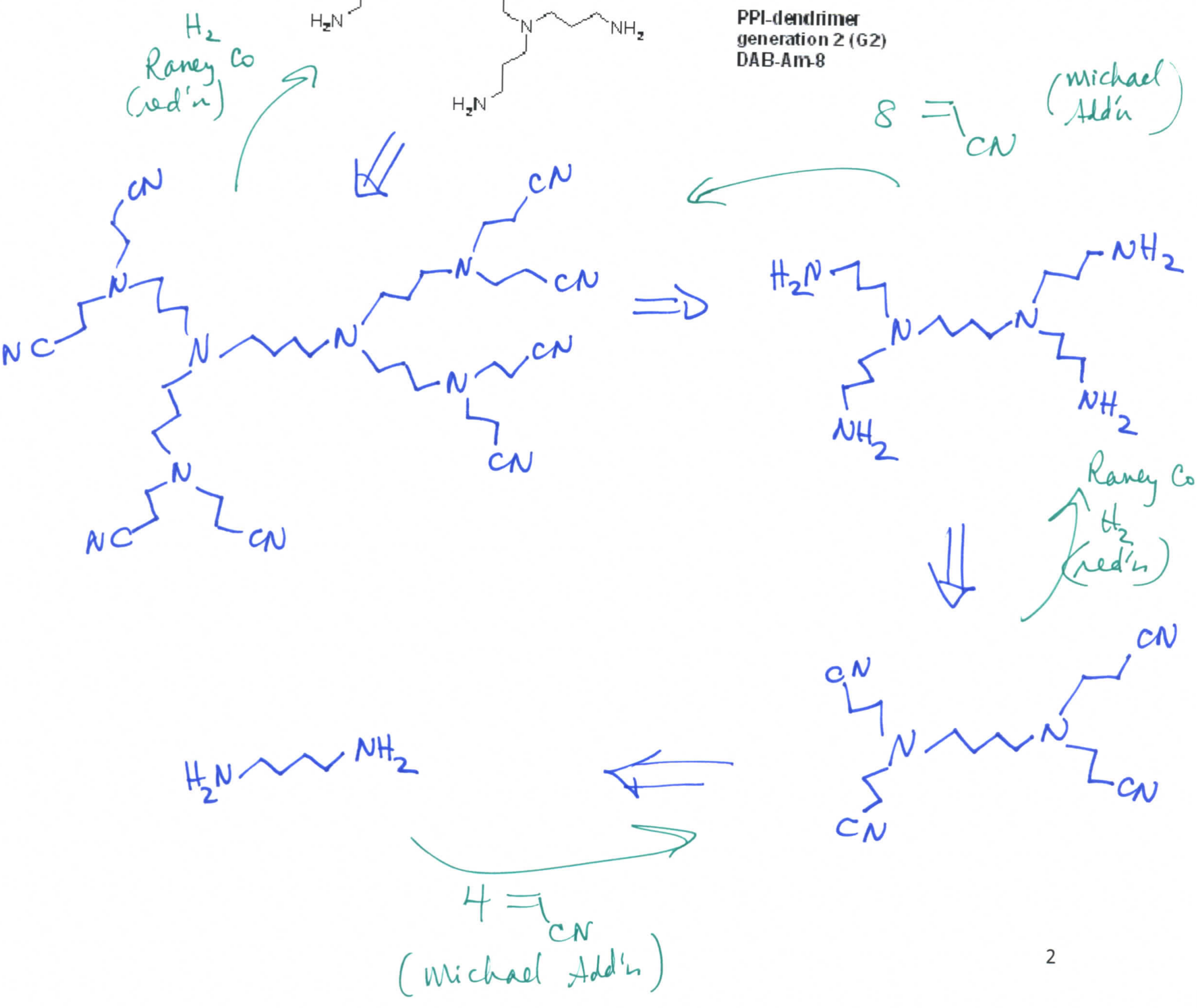


Name: ANSWER KEY [printed]

2. Provide a retrosynthetic route for the poly(propylene imine) dendrimer structure shown below (copied from http://www.symo-chem.nl/dendrimer.htm). **[10 points]**



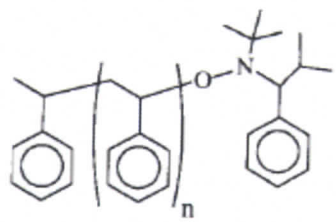
PPI-dendrimer
generation 2 (G2)
DAB-Am-8



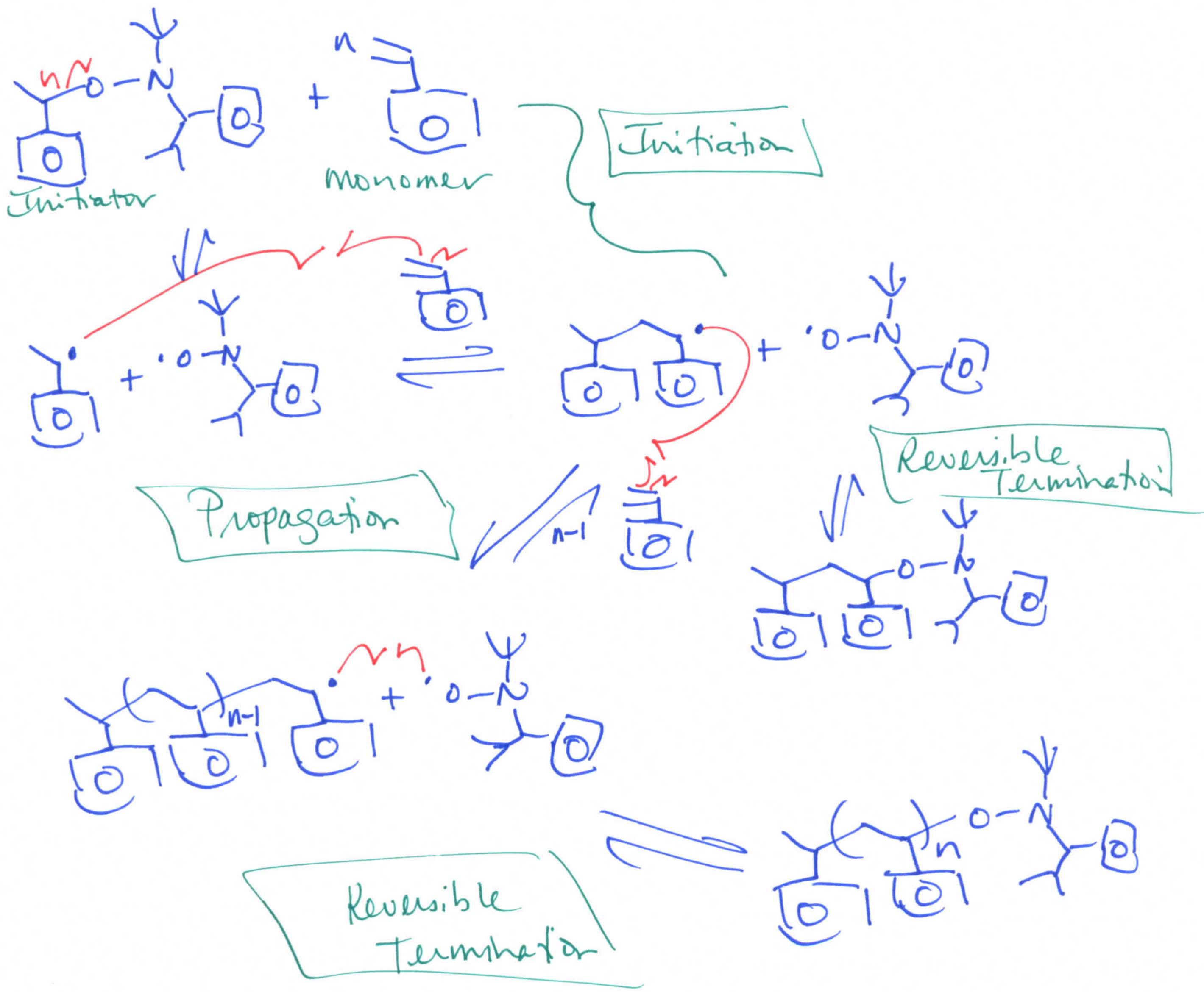
Name: ANSWER KEY [printed]

3. From the article Harth, E.; Hawker, C. J.; Fan, W.; Waymouth, R. M. *Macromolecules* **2001**, *34*, 3856-3862:

(a) Provide the starting materials and draw the forward sequence of electron arrow-pushing mechanistic steps for the preparation of the polystyrene structure, **12**, below. Be certain to label the initiation, propagation and (reversible) termination steps. **[10 points]**



12



Name: ANSWER KEY [printed]

(b) What general type of polymerization is involved for the preparation of **12**, **[2 points]**

chain-growth, addition polymerization

and what is the specific name for this particular sub-type of polymerization? **[2 points]**

controlled radical polymerization, nitroxide-mediated radical polym. (NMRP)

(c) List four characteristics of this specific type of polymerization: **[4 points]**

(i) an initiator is required

(ii) monomer reacts only w/initiator or propagating chain end

(iii) reversible termination mediates the polym

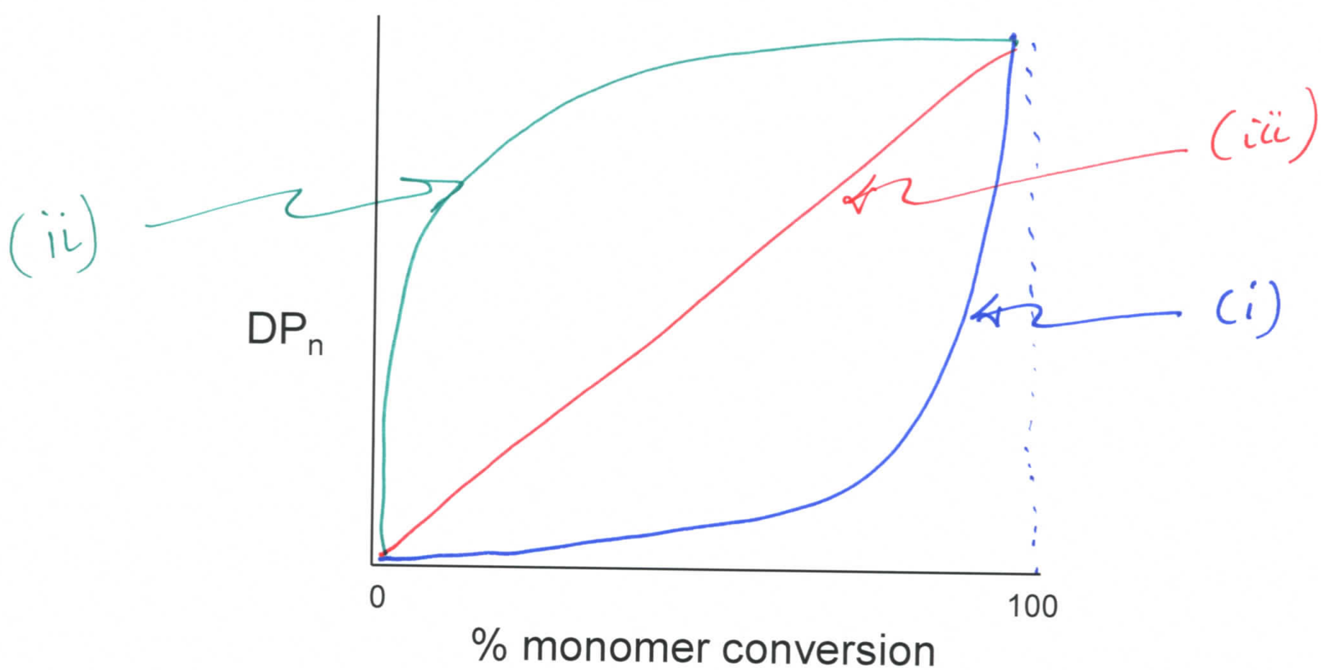
(iv) one radical species is reactive + initiates/propagates, whereas the nitroxide radical is stable + provides reversible termination

(v) $DP_n \propto$ % monomer conversion + can be controlled by [M]/[Initiator]

other answers also possible

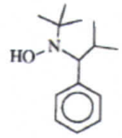
(d) Draw the typical DP_n *vs.* % monomer conversion plots on the axes below for: **[6 points]**

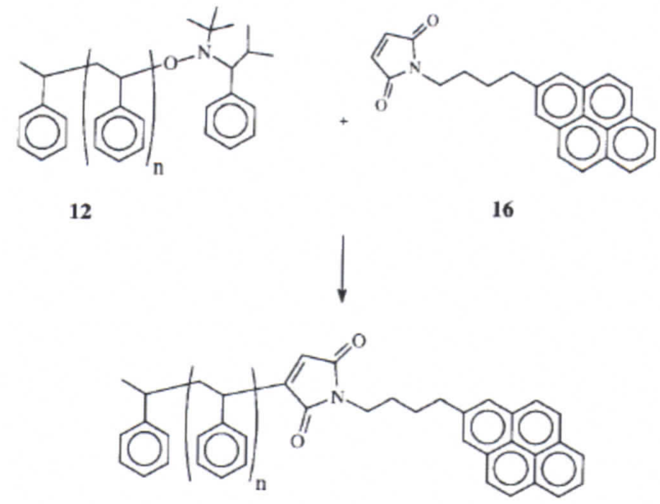
(i) condensation, step-growth polymerization
(ii) uncontrolled addition, chain-growth polymerization
(iii) controlled addition, chain-growth polymerization



Name: ANSWER KEY [printed]

(e) Reaction of the alkoxyamino ω-terminus of polystyrene, **12**, with a pyrene-substituted maleimide, **16**, afforded **17**

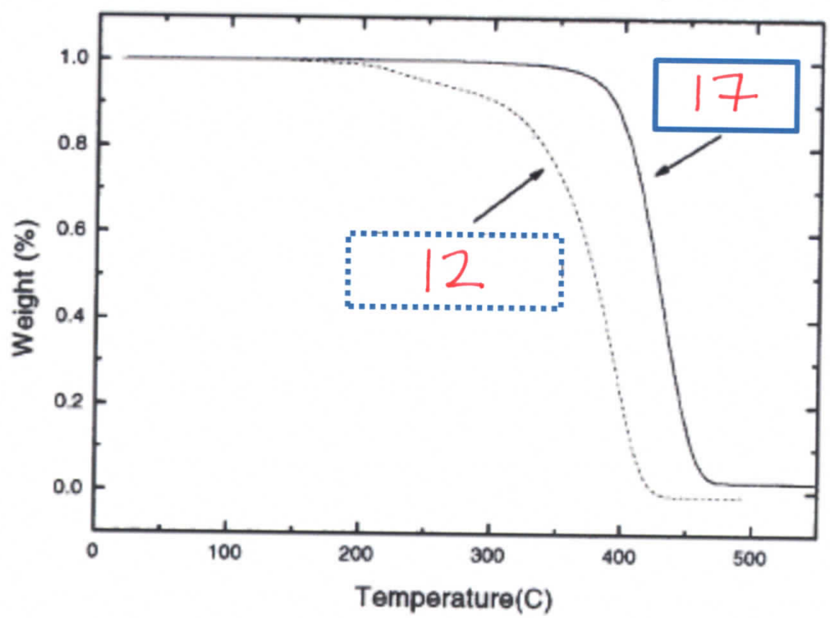
(+ ).



12 16

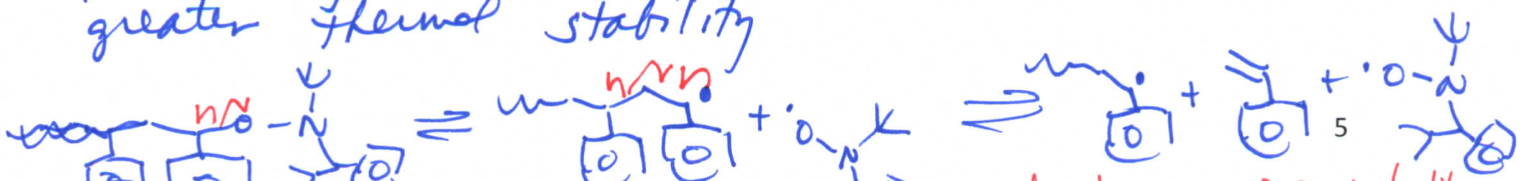
17

(i) Within the two boxes associated with the thermogravimetric analysis (TGA) traces of the following figure, assign which of the polymers was responsible for the TGA data by writing its compound number, **12** or **17**. **[2 points]**



(ii) Explain your answer to (i), in words and by showing the chemistry involved in the thermal degradation of the more thermally labile polymer. **[4 points]**

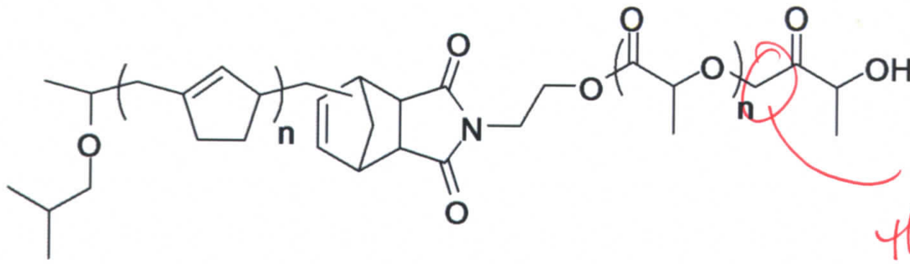
For 12, the alkoxyamino chain terminus undergoes homolytic bond cleavage at elevated temperatures, and allows for depolymerization-based degradation at temperatures above the ceiling temperature. In contrast, 17 lacks the alkoxyamino chain end, and therefore, exhibits greater thermal stability



depolym to give volatile products ⇒ ↓ mass %

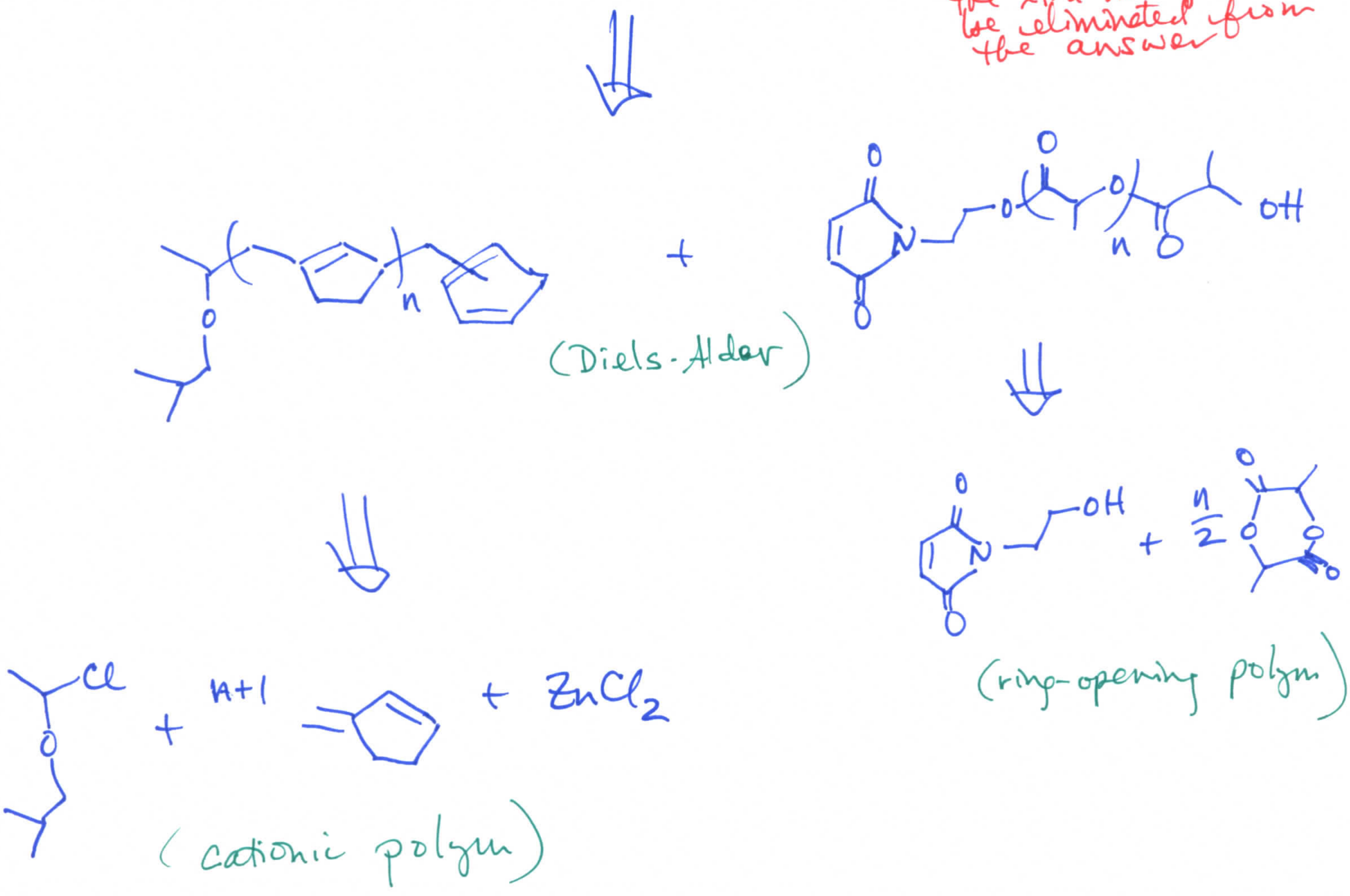
Name: ANSWER KEY [printed]

4. Provide a retrosynthetic analysis for the block copolymer of the cyclic diene 3-methylenecyclopentene, 2, and lactide, as reported in Kobayashi, S.; Lu, C.; Hoye, T. R. and Hillmyer, M. A. *J. Am. Chem. Soc.* **2009**, *131*, 7960-7961. **[10 points]**



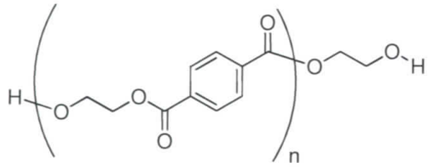
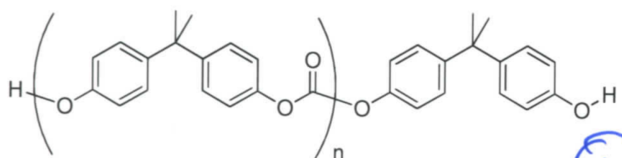
poly-**2**-*b*-polylactide

please note: this mistake was part of the published structure — the xtra methylene should be eliminated from the answer



Name: ANSWER KEY [printed]

5. (a) Evaluate and compare the following polymer structures to predict a ranking of their T_g values, with 1 being the highest and 3 being the lowest. **[3 points]**
   (b) Provide brief explanations for your predictions. **[6 points]**
   (c) State one product or application, in which each polymer is commonly employed. **[6 points]**

Polymer Structure	T_g ranking	Explanation	Typical product/application
	2	combination of aromatic + aliphatic groups + polar esters	beverage containers, etc. (PET)
	1	highest aromatic content + polar carbonates	eye glasses, CDs/DVDs, etc. (BPA polycarbonate)
 (for the application, state whether it is for low or high degree of branching)	3	only aliphatic chains w/ or w/out branching (LDPE or HDPE, respectively)	LDPE - bubble packing HDPE - milk jugs + other containers, etc.

Name: ANSWER KEY [printed]

6. Describe briefly the part of Professor Aida's lecture on April 17, 2012 that you found most interesting, in terms of the application, the characteristics or properties of the materials that provided performance in that application, and the composition and structure of the materials. **[15 points]**

Many possible answers, related to:

Bucky gels, e.g. as elastic conductors

Bucky plastics

mobile Braille devices + other actuators

supramolecular block copolymer nanotubes

etc.