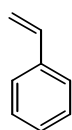


Lab 4

Anionic, Living Polymerization and Block Copolymers

Report Due: *In Lecture*, Wednesday, March 22**Report Revision Due:** *In Lecture*, Wednesday, April 5**Introduction**

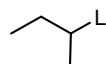
Anionic polymerization occurs by a chain growth mechanism similar to free radical polymerization, except that the active center for the initiation and propagation processes is anionic in nature. In this experiment, you will polymerize styrene using *sec*-butyllithium as the initiator in cyclohexane, and prepare block copolymers of styrene and isoprene.



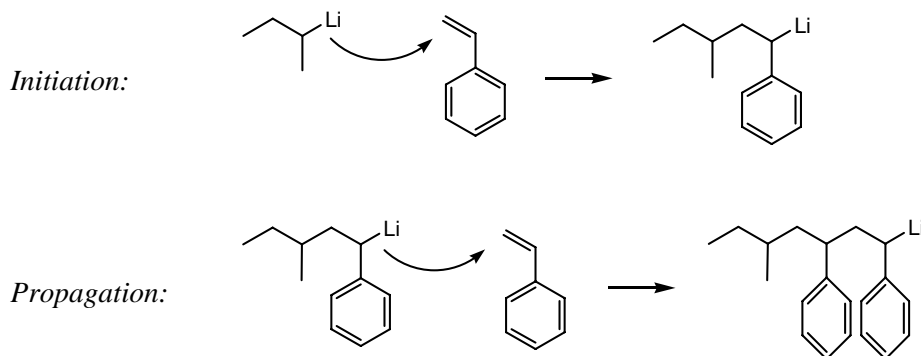
styrene



isoprene

*sec*-butyllithium

Anionic polymerization of styrene can be initiated by the addition of *sec*-butyllithium to the styrene double bond. This generates a styryllithium ion, which can then propagate by successive addition of styrene to the growing polystyryllithium species.



Anionic polymerization is one of a few polymerization techniques that can be termed “living”. Living polymerization requires that the active terminus does not experience chain transfer or termination, and that the rate of initiation (or crossover, in the case of block copolymerization) is faster than that of propagation. Under these conditions:

- 1) Initiated chains will continue to grow until all monomer supply is exhausted;
- 2) The anionic chain end is stable, and chain growth can be continued by adding more monomer;
- 3) Successive addition of different monomers will result in the formation of block copolymer architecture.

However, the requirements of living, anionic polymerization are strict. In order to prevent premature termination of the growing polymer chains, water and oxygen must be rigorously excluded from the reaction. All reagents, glassware and solvents must be dried prior to use. In addition, in order to make sure initiation is much faster than propagation, an extremely reactive alkyllithium initiator must be used. While the safety hazard that this will create is not great, it will make this the most hazardous lab you will perform in this course. (We will manage this hazard by having the TA's initiate your polymerizations for you.)

If there is no termination and no chain transfer, and the rate of initiation is greater than the rate of propagation, then the molecular weight distribution of polymers prepared by anionic polymerization can be extremely narrow. The distribution of chain lengths can be described by a Poisson distribution. As a good approximation, the polydispersity index (PDI) of this distribution is given by equation 4.1:

$$(4.1) \quad \frac{\overline{X_w}}{\overline{X_n}} = 1 + \frac{1}{\overline{X_n}}$$

At even at moderate degrees of polymerization, polymers prepared by anionic polymerization are essentially monodisperse (i.e., all of the chains are about the same length, and PDI = 1).

In this lab, you will synthesize polystyrene homopolymer, and PS-PI diblock and PS-PI-PS triblock copolymers, with target molecular weights given in Assignment 9. As a part of this Assignment, you will need to calculate the amount of monomer you will use for each block. **It is absolutely critical that you perform these calculations before coming to lab.**

You will also be characterizing your polymer products, both chemically and physically, using a number of analytical techniques. In this lab, you will be using multiple methods for verifying the molecular weights and weight distributions of your products. As in Lab 3, you will be using GPC to characterize the molecular weights of all of your polymers. You will also be using NMR to determine the molecular weight of PS, by calculating the ratio of initiator to monomer in that polymer.

One of the unique features of this lab is that you will not only be synthesizing polymer, but you will also be forming it and mechanically testing it. All of the materials you will synthesize in this lab are thermoplastics; they can be melted, formed, and cooled without altering the fundamental physical properties of the bulk material. You will be using compression molding, probably the simplest method for forming thermoplastics, to create tensile specimens for testing. You will be molding your samples in the Polymer Processing Lab (Amundsen 324), which also houses equipment for other polymer processing techniques (including mixing, extrusion, injection molding and more).

Finally, you will test the stress-strain behavior of your solid, pressed samples using a tensile tester. Polymeric materials can exhibit plasticity, elasticity, or both, in response to deformation. The type of response naturally depends upon the structure and physical characteristics of the material, but also on the magnitude and timescale of the deformation. Nevertheless, nearly all materials are elastic over small deformations and short times. This elasticity is like that of a spring, and the elastic modulus E of a material is analogous to the Hookean spring constant k :

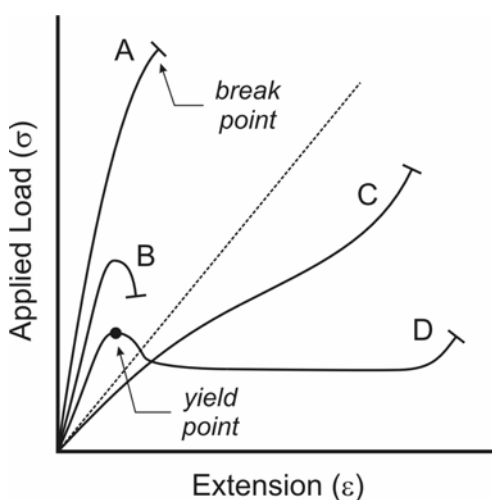
$$(4.2) \quad F = kx$$

$$(4.3) \quad d\sigma = E d\varepsilon$$

Both of the above equations are expressions of Hooke's Law; the first relates deformation (x , a distance) to applied force (F), and the second relates engineering stress (σ , a pressure, or force per area) to engineering strain (ε , a unitless fraction or percentage). One difference between the two expressions is that (4.2) presumes a single elastic spring constant over all deformations x , whereas (4.3) acknowledges that inelasticity makes σ and ε dependent variables, and that as a result E can vary with ε . (This is why Equation 4.3 is a differential equation.) Again, for small values of ε , many materials respond elastically and it is possible to simplify:

$$(4.4) \quad \sigma = E\varepsilon$$

You will be measuring the initial elastic modulus of your polymers with an instrument that grips a material sample at two ends, varies the force with which the sample is stretched, and simultaneously measures the resulting extension. By the end of this lab, you will be able to correlate the structures and block ratios of your polymers with their basic mechanical properties.



Characteristic stress-strain behavior and failure modes for different types of polymers. For each curve, the slope represents the elastic modulus, and the end represents failure of the material. (A) Brittle failure. Polymer A exhibits high resistance to extension, and then fails by cracking. (B) Ductile failure. Polymer B yields briefly under stress, but then breaks near the yield point. (C) Elastic extension. Polymer C, an elastomer, exhibits nearly linear elasticity over all extensions until it fails. (D) Ductile (plastic) extension. After yielding to stress, polymer D begins to flow and requires little additional force to extend it. Yield is sometimes accompanied by “necking”, where the material thins and stretches in one spot.

Experimental

Synthesis of styrene homopolymer and styrene-isoprene block copolymer by anionic polymerization (Feb 16/17)

The goal of this experiment is to synthesize defined polymers by anionic polymerization.

CAUTION: *sec*-Butyllithium is pyrophoric (burns in air) and poses a significant fire hazard. In this lab, your TA's will handle the *sec*-butyllithium for you. Keep reactions containing *sec*-butyllithium under an inert gas atmosphere at all times, and make sure to exclude air and water from the monomer, initiator, solvents, and polymerization solution. **We also recommend you wear protective gloves in addition to your goggles for this lab.**

CAUTION: You will use needles a number of times in this lab. Please be careful with them.

At the beginning of the lab period, the TA's will familiarize you with four lab "stations" that you will use in addition to your bench: (1) the argon balloon depot, (2) the solvent depot, (3) the monomer depot, and (4) the TA's initiator station.

- Check the three-pronged clamps in your drawer to see if they hold small (14/20) joints. If not, take three of your larger clamps to the stockroom and exchange them for small ones. While you are there, check out two 100 mL, single-neck roundbottoms, two Magnastir stirplates, and two small crystallization dishes. Pick up two small rubber septa and a disposable, two shielded (purge) needles from the TA's, and two argon balloons from the balloon depot. Take everything to your bench.
- At your bench, place each of your two stirplates at the base of a clamp post, such that a three-pronged clamp can be mounted above it to eventually hold each roundbottom. Put one small stirbar in each flask.
- *Flame-dry your glassware.* Light your Bunsen burner. Clamp the neck of one of your flasks in one of your three-pronged clamps, such that you can hold the flask stably in your hand with the clamp. (Do not use a wooden pinch clamp instead.) With the clamp, hold and turn your flask over the Bunsen burner flame. You should see adsorbed water steam off of all of the surfaces of your flask, including the neck, as it dries. (Water vapor is lighter than air, so make sure you hold the flask neck-up to allow the steam to escape at least some of the time.) When you stop seeing the surface of your flask steam, remove your (*very hot!*) flask from the flame and carefully cap the neck with one of your septa. Mount the clamp above a stirplate. Repeat this for your other flask.
- When you are done flame-drying, turn off your Bunsen burner by blowing it out, then turning off the gas. When your flasks cool down a bit, pull the lips of the septa down over the flask necks to seal them tight.
- *Purge your flasks with argon gas.* Take one of your argon balloons, remove the needle shield, and insert the needle into the septum of one of your flasks before the balloon deflates. Then, also deshield one of your purge needles insert into the same septum. Your balloon should gradually deflate as the flask is purged. Once the balloon is empty, pull it out of the septum and replace it with your other, fresh balloon. Let this balloon deflate a little, but then remove your purge needle from the septum. *Your flask is now under a positive pressure of dry, argon gas.*
- Return your deflated balloon to the balloon depot and get four more balloons. Repeat the steps above to purge your other flask. Label your flasks "PS" and "PS-PI". Keep the balloons on your flasks throughout your polymer synthesis.
- *Charge your flasks with solvent.* Go to the solvent depot and find a flask containing anhydrous cyclohexane under an argon balloon atmosphere. Take this flask, along with the gastight syringe marked "CHX", to your bench. Insert the needle into the flask septum (but *above* the level of the liquid), and draw up 10 mL of *argon* from the cyclohexane flask headspace. Remove the syringe from the flask, and empty the syringe into the air. (This purges the interior of the syringe that had been previously sitting in air.) Then, draw cyclohexane liquid into the syringe, and transfer this to your roundbottom through the flask septum. Leave the balloon and septa on your flasks at all times, and do not let any air get into the flask. Use this technique to transfer 50 mL cyclohexane to each of your synthesis flasks. *Each time you puncture your septum, you leave behind a tiny hole. If you can, pass the*

syringe needle through the same septum hole each time to avoid shredding your septum. Return the cyclohexane flask and syringe to the solvent depot.

- At the monomer depot, get the styrene flask and syringe. Transfer the quantity of distilled styrene that you calculated before lab into each flask. Return the flask and syringe to the monomer station.
- Make an ice water bath for each of the flasks in the crystallization dishes. Keep these ready in case your polymerizations get hot to the touch.
- *Initiate polymerization.* Go to the initiator station, and get a TA to inject your calculated amounts of 1.4 M *sec*-butyllithium solution in cyclohexane into each reaction to initiate polymerization. Note any changes that you observe in the reactions when initiator is added.
- The reaction you are running is exothermic, and can race out of control. If you start to observe any of your polymerization reactions boiling, or the flask becomes hot to the touch, immerse it immediately in an ice bath. Take the reaction back off ice when things seem to have settled down. Let these reactions run for 30 minutes with constant stirring.
- 30 minutes after initiation, transfer the quantity of distilled isoprene that you calculated before lab into your PS-PI flask, followed by 1.0 mL distilled THF. Note any changes that you observe. Again, be prepared to cool your polymerization down if it gets out of hand. Let the PS-PI polymerization go for another 20 minutes.
- *Terminate polymerization.* At the end of each polymerization, immerse the reaction back in its ice bath, and inject 0.5 mL anhydrous methanol with the gastight syringe. Allow the reaction to quench a couple of minutes before recovering your polymer. *Feel free to recover the PS while the PS-PI is still polymerizing.*

Polymer Recovery (Feb 16/17)

- Slowly pour the contents of each flask into separate beakers containing 200 mL methanol while actively stirring. (Please keep track of which sample was emptied into which beaker!) Your polymer material should precipitate from solution. If it doesn't, you may want to cool the solution in an ice bath, add more methanol, or (last resort) add some drops of water. Beat on the polymer glob in each test tube/beaker with a stir rod until the glob stiffens. It may look as though you've achieved liquid phase separation rather than precipitation. If this is so, it's likely that your top layer will be a mixture of methanol and cyclohexane, and that your bottom layer is a mixture of polymer and cyclohexane. To draw more cyclohexane out of the polymer, carefully decant off the methanol-cyclohexane mixture, and add fresh methanol. Keep doing this until you get solid material.
- Smell your material—likely, it still contains some cyclohexane. Cyclohexane has a high boiling point, so it's difficult to remove in the vacuum oven, and you should remove it by re-precipitation if possible. Re-dissolve your solid polymer in a *minimum* amount of methyl ethyl ketone (< 20 mL). Then re-precipitate this solution into methanol as you did above.
- Remove the coagulated polymer from each beaker, and discard the methanol solution into the waste containers.
- With your stir rod or spatula, try to squeeze as much residual solvent out of each polymer as possible. Dry the crystallization dishes you used for ice baths and tare each. Flatten out each polymer glob into its own dish, and dry your samples in the vacuum oven.

Yield (Feb 23/24)

- After the polymers are dry, weigh each polymer and calculate your yield. Scrape each of your polymer materials off of the Petri dish and into some container—folded up paper envelope, vial, anything.

NMR of PS and PS-PI: Endgroup determination and PI regiochemistry (Feb 23/24)

- Check out two NMR tubes from the stockroom.
- Follow the instructions from Lab 2 for preparing NMR samples of your two polymer products in CDCl_3 ; dissolve 25 mg of each material in 1 mL of CDCl_3 in separate vials, and transfer each to an NMR tube. Submit these samples to the TA.
- As before, your data will appear in the NMR “Data” directory, under the filename posted on the course Data website.

GPC of PS and PS-PI (scheduled by lab pair; Feb 23/24 or Mar 2/3)

- Follow the instructions from Lab 3 for performing GPC on your two polymer products. Use the spreadsheet/software you developed in that lab to analyze your data.

Compression molding PS, PS-PI and PS-PI-PS (scheduled by lab pair; Feb 23/24 or Mar 2/3)

The goal of this experiment is to form your samples in preparation for mechanical testing.

- This portion of the lab will be performed in Amundsen 324, in the Polymer Processing Lab. You will be molding and tensile testing in pairs-of-pairs (groups of four). Things the group will need to bring:
 - Two press plates and a dogbone mold. (TA should have these.)
 - Teflon film.
 - Micrometer calipers.
 - Scissors.
 - Materials to be tested: your polymers, plus pellets of Dexco 4111, 4211 and 4411 and commercial polystyrene.
- First, test whether your PS and PS-PI are durable enough to handle. Place one press plate flat on the benchtop, and then put a piece of teflon film on the plate. Scoop your material onto the Teflon. Pile your material high rather than spreading it too thin across the Teflon, so that it is all pressed effectively. Cover this with another piece of teflon, and then the other press plate.
- The TA will have set the press to 140 °C (more than 30 °C above T_g for the highest-melting block in your material). Load your sandwiched sample in the press using heat gloves. Let the sample sit in the press without applying any force for 5 minutes to allow the material to soften.
- Press your sandwich at a pressure of 500 lbs for about 5 minutes, followed by ~4000 lbs. pressure for 5 minutes. Then, release the pressure and, using heat gloves, remove your sandwich from the press. At the bench, take your Teflon sandwich out from between the plates and let it cool fully. Then, try to peel your material from between the films. If your

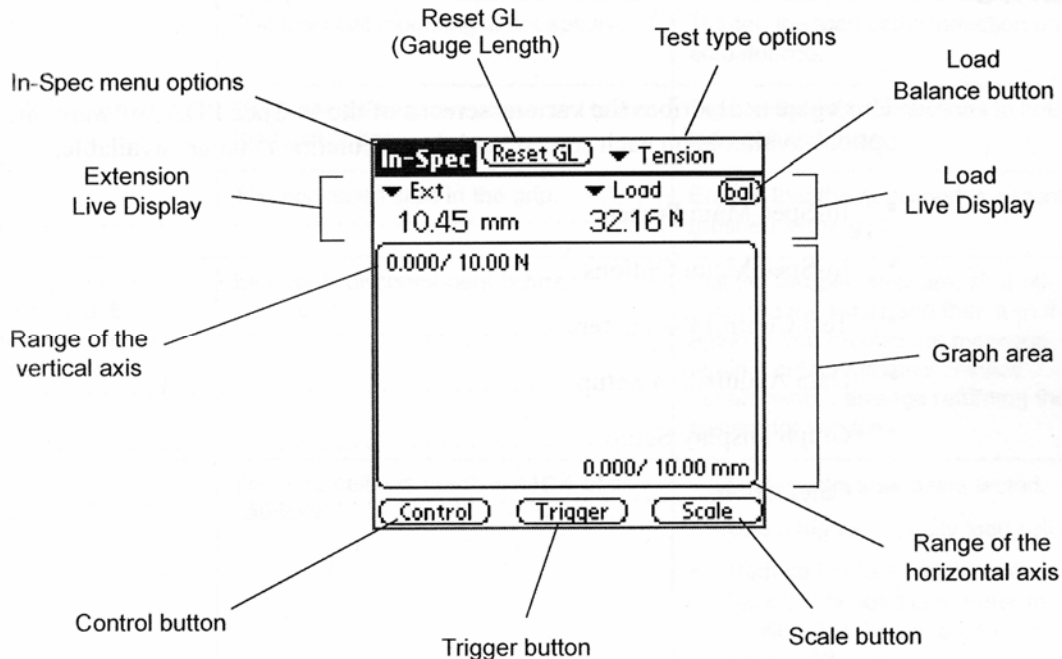
material cracks or shatters while you are removing from the Teflon, you probably won't be able to press tensile specimens from it. If your pressed material looks sturdy, on the other hand, break it into small pieces and get ready to press it in the dogbone mold.

- *To press dogbone tensile samples*, cover a press plate with Teflon as you did above, but then put the dogbone mold on top of this. Scoop some of your material into the mold. Again, pile your material high to avoid holes and gaps in the specimens. Cover this with another piece of teflon, and the other press plate.
- Load your sandwiched sample in the press. Let the sample sit without applying force for 5 minutes; then press your polymer into the mold at a pressure of 500 lbs for about 5 minutes. Release the pressure, remove your sandwich from the press, and allow it to cool. Lift the press plate and look through the Teflon film (but don't remove it) to check to see that your dogbone molds are filled with material; if you see any gaps, cool the material and load in some more polymer. Close the sandwich again, and return it to the hot press. Once again, give your material 5 minutes to soften.
- Next, press your sample at 8000 lbs. pressure for 5 minutes. Stop the pressure, and remove the sample with heat gloves. Allow your sample to cool. If the dogbones look good, remove them from the mold and cut any excess material ("sprue") away from the samples. Measure both the width and thickness of each dogbone using a set of micrometer calipers. Also measure the length of the narrow section of the dogbone; even though the tensile instrument may pull on more than this part, we will assume that the tensile load is borne entirely by the narrow portion of the sample.¹

Mechanical testing of PS homopolymer and PS-PI and PS-PI-PS block copolymers (scheduled by lab pair; Feb 23/24 or Mar 2/3)

- Load one of your samples between the grips of the Instron In-Spec 2200. First, make sure that the grips are separated by enough space that they grip only the wide sections of your tensile specimen. The position of the grips can be controlled with the up and down arrow buttons on the instrument. Then, tighten the screw knobs onto your sample.
- You will be controlling the instrument mostly from the attached Clié PDA. You can use the stylus or any pointed object to input data into the PDA. The Clié is stuck to the instrument by Velcro pads; feel free to pull the PDA off, but don't yank on the connecting cable. If you need to, turn the PDA on and open the In-Spec software. The PDA display should look something like the diagram on the next page. This screen provides real-time data on the force (Load) being applied by the instrument, and the resulting extension (Ext) of the material. These should be displayed in Newtons and mm, respectively. If not, change the units in the **In-Spec -> Options -> Preferences** menu.
- If the material you are testing feels soft, in the **Control** menu, set the extension **Speed** to 0.500 mm/sec, set the final extension (**Chan:Ext**) to 50 mm; if it is hard, set the extension **Speed** to 0.020 mm/sec and the final extension to 2 mm. Also set the instrument (**Action**) to **Stop** when it a run is finished. Check the box to make files **AutoSaved** to the filename of

¹ Tensile specimens for this lab are designed according to the guidelines published in "Standard Test Method for Tensile Properties of Plastics", American Society for Testing and Materials (ASTM) standard D638. ASTM (<http://www.astm.org>) publishes standard testing methods for an amazing number of materials properties; the *Annual Book of ASTM Standards*, which contains all current ASTM standards, is available in Walter Reference.



your choice. The instrument will add a sequential number to this name for each of your runs. Press **OK** to go back to the main screen.

- Press the **Reset GL** and **bal** buttons to zero the extension and load indicators.
- Make sure there are no cables or obstacles that might get caught by extension of your sample. When you are ready to run, press the **Play/Stop** button on the instrument to begin. Watch as the instrument stretches your sample; if your sample appears to slip out from the grips, or tears gradually, you should discard the data from that run and try another sample. The PDA will show your stress-strain curve as it is measured. Record what your sample looks like as it deforms.
- When the run is complete, press the down arrow on the instrument until most of the load has been relieved, and remove your sample from the grips.
- Your stress-strain curve may have gone beyond the range of the display. If so, press **Scale** to go to the Scale menu, and press both **Auto Set** buttons. Press **OK** to return.
- For any sample that hasn't broken, repeat your tensile measurement a couple of times to get a sense of how your material fatigues. (Fatigue testing usually involves thousands of cycled tensile tests, but this experiment will at least tell you how reversibly elastic your materials are.)
- Run all of your tensile tests according to these preceding instructions, and make sure you record the sequence of samples you run in your notebook. When you have finished them all, go to the **In-Spec -> File -> Load** menu to make sure the PDA has AutoSaved your files. Load each file, and check out and scale each curve on the display. (For reasons that I don't understand, it is necessary to do this for your files to transfer successfully to the computer.) Press **Cancel** to go back to the main screen.
- Exit the In-Spec software by tapping on the "Home" icon on the PDA. Carefully unplug the PDA from the tensile tester cable, and connect it to the laptop cable. Press "HotSync" on the PDA, and then the big HotSync logo button, to transfer your data files to the laptop. The PDA

should beep as it connects to the computer; if this doesn't happen, you may need to turn the PDA off and on again and try HotSyncing again. Your files should appear in the Desktop folder labeled "Data Folder".²

- These files are in a PDA format that Mac and Windows spreadsheets won't recognize. To convert the files to text (.txt) format, use the "File Converter" program on the Desktop.
- Transfer your files to some portable device. Unfortunately, the Instron laptop doesn't have a floppy drive, but it does have USB ports; if you have a USB thumbdrive, this might be the easiest way to get your files. Otherwise, get a TA to help out.
- When your HotSync and file conversion and transfer are done, exit the HotSync software, unplug the PDA from the laptop, and reconnect it to the tensile tester cable. Re-start the In-Spec program on the PDA, and delete your files from the PDA in the **In-Spec** -> **File** -> **Load** menu. Mount the PDA back on the Velcro pads.

Lab Writeup (due Wednesday, March 22, 3:35 pm)

Your report for Lab 4 will look very much like a *Macromolecules* paper—plenty of data, and plenty of discussion.

Most importantly, try to make your paper argue a point about the materials that you and the rest of the class made. Is there anything general you can say about the relationship between the structures of these polymers and their properties? The notes below list a few things that you should include in your paper, but you should organize your report around its message rather than these small items.

Abstract. In this report, you will summarize your conclusions in an abstract. Though it appears first in your manuscript, you should probably write it last, after you have finished the bulk of the paper.

Introduction. You will probably want to introduce block copolymers here, and cite both what you already know about them in general, and also what you know about styrene-isoprene copolymers in particular. You should introduce your polymer system, and state any hypothesis you might be testing about the polymers' properties.

Experimental.

- Make sure you describe your polymer synthesis in detail. *Include color!* Anionic polymerization is colorful, and this color actually gives some indication of how well your reaction went. (I.e., it would be helpful for someone trying to reproduce your experiment to know.)
- You used a number of instruments to obtain data. Make sure you describe them and the way you used them.
- Polymer processing can have important effects on materials properties. Describe the way your materials were processed and how they looked before and afterwards.

² You may find, after some searching, that some of your files that were on the PDA don't sync with the laptop. This can happen if a strange character was inserted into your filename when you were writing with the stylus. To solve this problem, on the PDA, open the program FileX—a file utility on the PDA—and rename your file to get rid of the offending character.

Results and Discussion.

- Create a table that shows your predicted molecular weights, along with the M_n and M_w values you determined by GPC and by NMR, for all of the polymers you discuss in your paper (including those from other pairs). If there is data for any commercial polymers you used, you may also want to include that here. You may also want to tabulate regiochemistry and block fraction data for your polymers. How does your experimental data compare with your calculations? With the literature on polyisoprene regiochemistry? If something looks off, what are possible sources of error?
- The data in a GPC trace gives numerical data on M_n and M_w , but its shape can also hint at whether there are multiple components present or not. For example, homopolymer that failed to add additional monomer would appear in a different location than copolymer within the same sample. How do your GPC traces look?
- One characteristic, predicted feature of living polymerization is that polydispersity should remain low even at high molecular weights. (In fact, Equation 4.1 shows that PDI actually decreases with increasing molecular weight. However, this trend is only observable at extremely low degrees of polymerization, and you should probably not be able to observe this trend in your data.) Did the class' polymerizations exhibit this feature?
- You have considerable latitude in designing the part of your report that illustrates the physical properties of your (and others') materials, and how those properties vary with polymer characteristics. You may want to consult chapters 6 ("Mechanical Properties of Metals") and 16 ("Characteristics, Applications and Processing of Polymers") of Callister's *Materials Science and Engineering: An Introduction* to give you an idea of how to interpret your stress-strain curves. Questions you may want to ask yourself:
 - Which materials were plastic, and which were elastic? What features of these general types of materials were observed in your samples?
 - How plastic or elastic were they? How do their initial elastic moduli (e.g., from 0%-10% extension) compare? Do the moduli make sense in terms of reported values for component homopolymers?
 - Are there any trends in yield stresses, elongation at yield, stress at break, or elongation at break?
 - How did your materials respond to repeated stress? Did your materials just get progressively weaker, or did the elastic behavior change more dramatically for the second extension run compared to the first? Can you explain these changes? (If your materials broke on the first test, check out the data others have posted to the Discussion Board—if their data looks better than yours, then use it.)
 - How might these properties relate to the chemical and physical characteristics of the polymer chains in your material? In their structural organization? Prof. E. L. Thomas (Dept. of Materials Science, MIT) and others have studied the relationship between deformation and morphology in styrene-isoprene copolymers; does their work inform yours?
- Balance your use of text, schemes and graphs to make any points you make, and make your paper flow. You should feel free to contact the Writing Intensive TA to discuss your

writing, or the course TAs or instructor to discuss the physical meaning of your experimental results.

Also use a *Conclusion* to wrap things up.

Revised Lab Report (due Wednesday, April 5, 3:35 pm)

You will have the opportunity to revise your report after we grade it the first time. You will be able to recover up to 20 points from the initial grading, not including any points you lost for turning in the report late. We will hand back your report in lab on March 24/25, with corrections to be made. You are particularly encouraged to meet with Andy Taton in his office (Kolthoff 455) immediately after lab to talk specifically about what you might improve in this report.