

Chapter I

熱可塑性エラストマーの調製と特性評価

—長鎖分子構造と物性の相関—

Preparation and Characterization of Thermoplastic Elastomers

Correlation between the Long-Chain Molecular Structure

and the Physical Properties

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1. Background and Purpose

Macromolecules are large molecules where atoms of elements such as carbon, nitrogen, and oxygen are connected via covalent bonding. In general, it often refers to a long-chain molecule (polymer) where a monomer is a repeating unit (Figure 1). Physical properties of polymers are greatly influenced by not only the chemical structure of the monomer but also the molecular characteristics of the macromolecular chain, such as molecular weight, molecular weight distribution, composition of polymer components. Thus, to improve the performance of materials composed of polymers, understanding polymers at the molecular level is essential.

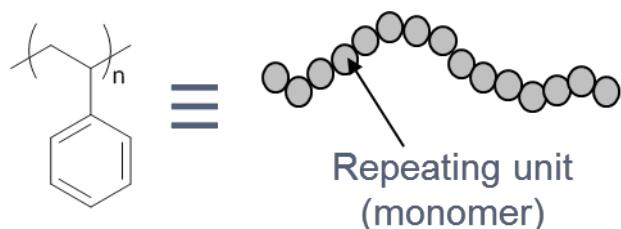


Figure 1. Chemical structure of polystyrene and schematic illustration of polymer composed of monomer units.

In this experiment, one of the objectives is for students to experience handling macromolecular compounds, which they have been learning through lectures on topics such as physical chemistry, functional macromolecular chemistry, and macromolecular physical chemistry. Specifically, polymer film preparation of commercially-available thermoplastic elastomers of block copolymers (global market $\sim \$5$ billion/year) that are used as bandaids, fomentations, and double-sided tapes, etc will be carried out by solution casting method. Properties of the polymer films will be evaluated by dynamic mechanical analysis and tensile tests. Through experiments, students will learn how the molecular properties of block copolymers (molecular weight, composition, etc.) affect the properties of thermoplastic elastomers (especially mechanical properties). Moreover, students will also learn what kind of polymer should be designed to attain highly functional and high performance materials.

2. Outline of Experiments and Experiment Schedule

In the experiments, students will belong to one of four groups (Group A1, Group A2, Group B1, and Group B2). Group A1 will co-work with Group A2 in pairs, whereas Group B1 will co-work with Group B2 in pairs. In order to prevent Covid-19 infection, the experimental contents and schedule conducted this year are somewhat different from the annually-conduced ones. Specifically, Groups A1 and A2 will complete their experiments on the 1st and 2nd days, and Groups B1 and B2 will complete their experiments on the 1st and 3rd days. The followings are the detailed experimental schedules.

Day 1 (Rm 123)	Experimental Schedule, Solubility Check, Film Preparation through Solution Casting, GPC Analysis
Day 2 (Rms 901 and 906)	Dynamic Mechanical Analysis, Tensile Tests, NMR Analysis
Day 3 (Rms 901 and 906)	Dynamic Mechanical Analysis, Tensile Tests, NMR Analysis

3.Experiments

3-1) Polymer Synthesis by Reversible Addition Fragmentation Chain Transfer Polymerization Technique. (In order to prevent Covid-19 infection, this experiment will not be performed this year.)

Polymer science is a relatively new academic discipline that started from discussions on the existence of macromolecular materials in the 1920s. Since WWII, many monomers were polymerized during 1930s, and many polymer compounds were synthesized. Polymerization reactions can be classified into chain polymerization, step polymerization, and ring-opening polymerization, etc. In this experiment, polymers are synthesized using living radical polymerization (especially reversible addition fragmentation chain transfer polymerization), which is a type of chain polymerization that has been aggressively developed in recent years. Living polymerization is a polymerization method where the chain transfer reaction and the termination reaction are suppressed. Especially, if the initiation reaction occurs sufficiently faster than the growth reaction, polymers with controlled molecular weight and molecular weight distribution can be obtained.

As specific experimental contents, polystyrene or poly(methyl methacrylate) will be synthesized from styrene or methyl methacrylate (Figure 2) of typical vinyl monomer by designing molecular weight for the target (Figure 3). Reaction will be performed under an inert gas at approximately 130 °C while stirring. The initiator used for the polymerization is 2,2'-2,2'-azobis(isobutyronitrile) (AIBN). For polymerization, reversible addition-fragmentation

chain-transfer (RAFT) agent is also added in the reaction flask. Details on the RAFT agent will be introduced on the day of the experiment. Please also pay attention to the changes in the viscosity of the solution in the flask prior to, during, and after the polymerization.

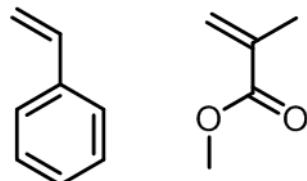


Figure 2. Chemical structures of styrene (left) and methyl methacrylate (right).

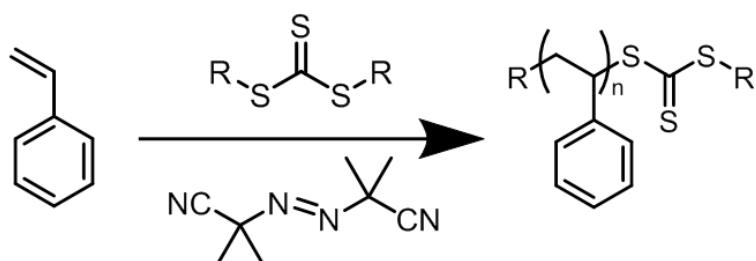


Figure 3. Synthetic scheme of polystyrene via RAFT polymerization.

3-2) Solubility Check to Various Solvents and Purification of Polymers Synthesized. (In order to prevent Covid-19 infection, polymer purification experiment will not be performed this year. Solubility check experiment will be performed as annually-conducted.)

Generally, monomers can not be fully consumed in a polymerization reaction. Therefore, solutions obtained after the polymerization reaction is a monomer solution of a polymer. To evaluate physical properties of a polymer obtained, the post-polymerization solution must be purified to extract only a polymer.

Purification method most commonly used in the purification of a polymer is a reprecipitation method. This method uses the differences in the solubility of a polymer and a low molecular weight compound such as a monomer or a dissolved impurity in order to precipitate only the polymer. First, a polymerization solution is dissolved in a solvent A (good solvent) that can dissolve both a polymer and a monomer. Then, prepare solvent B, which is a non-solvent only against the polymer. The amount of the solvent B should be 5 to 6 times the amount of solvent A (it does not matter if there is more than that). If you slowly pour the solution of solvent A to solvent B, the polymer precipitates, and a monomer (or impurity) diffuses into solvent B. An obtained polymer solid are separated through filtration or decantation (process for the separation of mixtures by removing a liquid layer).

At the time of film preparation, students handle polystyrene-b-polyisoprene-b-polystyrene (S-I-S) triblock copolymer (or poly(methyl methacrylate)-b-poly(*n*-butyl acrylate)-b-poly(methyl methacrylate) (M-A-M)) that is well-known as a commercially-available thermoplastic elastomer (Figure 5). Therefore, students have to know the solubility of constituent homopolymer that is one constituent block of triblock copolymer. Homopolymers of polystyrene and polyisoprene (or poly(methyl methacrylate and poly(*n*-butyl acrylate))) are available for solubility tests. Therefore, a 10-100 mg of homopolymer is placed in sample vials. Then, approximately 1 ml of solvent (such as tetrahydrofuran (THF), acetone, toluene, *n*-hexane, methanol, chloroform, water (Figure 4)) is added into these vials, and examine whether it dissolves or not, i.e., determine the good solvent or non-solvent for the homopolymer. A triblock copolymer is placed in sample vials in the same manner, and the good solvent and non-solvent will be determined. For your reference, solubility tests should also be performed on monomers (styrene, isoprene or methyl methacrylate, butyl acrylate).

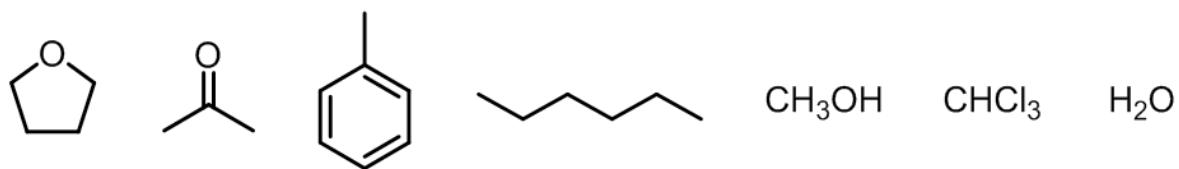


Figure 4. Solvents used in this experiment. Chemical structures of THF, acetone, toluene, *n*-hexane, methanol, chloroform, and water are displayed from left to right.

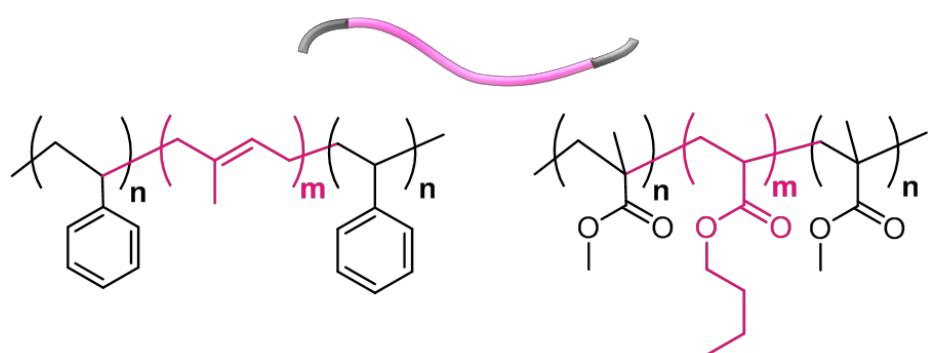


Figure 5. Schematic illustration and chemical structures of ABA triblock copolymer. Bottom left is chemical structure of S-I-S triblock copolymer and bottom right is chemical structure of M-A-M triblock copolymer.

3-3) Vacuum Drying of Polymers Synthesized. (In order to prevent Covid-19 infection, this experiment will not be performed this year.)

After reprecipitation of polymers synthesized, solvents are separated from polymers by filtration or decantation, a small amount of solvent still remains at the molecular level around the polymer solid. To further remove the remaining solvent, vacuum drying will be performed in a vacuum oven that is connected to a vacuum pump. Solvents will be removed almost completely by vacuum drying of polymers if long time-vacuum drying is performed. Operations will be explained at the laboratory.

3-4) Film Preparation of Thermoplastic Elastomers via Solution-Casting.

As one of the features of polymers, films can be prepared by such as a solution casting method. (Note that films can not be prepared from amorphous low-molecular weight compounds.) Here, the solution casting method is a film preparation method by dissolving polymer samples in a good solvent (for instance, dissolving a polymer of 0.2g in a solvent with concentration of several wt%) and evaporating the solvent gradually. In this experiment, thermoplastic elastomer films can be prepared via self-assembly by dissolving S-I-S triblock copolymer (or M-A-M triblock copolymer) that is a commercially-available thermoplastic elastomer in a good solvent followed by solution casting (Figure 6). In order to investigate the effects of differences in the molecular properties of block copolymers, , films of block copolymers with different molecular properties are also prepared, and the following measurements will be conducted as well for comparison.



Figure 6. Schematic illustration of ABA triblock copolymer (left), ABA triblock copolymer/AB diblock copolymer blend (center), ABA triblock copolymer with different composition (right).

3-5) Estimation of Molecular Weight and Molecular Weight Distribution with Gel Permeation Chromatography (GPC) Measurements.

The most notable characteristic of polymers is a large molecular weight (degree of polymerization). Physical properties of polymers are highly dependent on molecular weight, *i.e.*, molecular weight (or degree of polymerization and the length of a molecule) controls the

physical properties of the polymer materials. Also, with the exception of a few natural polymers, a polymer is typically a mixture of molecules with different molecular weights; thus in order to handle a polymer properly, it is important to know the molecular weight distribution. If the influence of the molecular weight and molecular weight distribution are found at the same time, it is difficult to determine the cause of the effect. Therefore, to study polymers, the samples with controlled molecular weight distribution are preferable.

Methods to measure molecular weight include: i) absolute molecular weight measurement methods (such as an osmotic pressure measurement method and a light scattering measurement method, etc.) and ii) relative methods, such as a gel permeation chromatography (GPC) method and a viscosity measurement method, etc., where samples with known molecular weights are used for calibration. A GPC method discussed in this experimental course allows measurements of molecular weight distribution and the average molecular weight in a reasonably short period of time. It is the most commonly used measurement method for molecular weight determination.

The separation is conducted in a column filled with highly cross-linked porous gel. Note that pore sizes in the gel are similar to the sizes of the polymer molecules. When a diluted solution of a polymer is injected into the solvent flowing through the column, a dissolved polymer molecule flows through the porous gel. It also diffuses into the pores in the gel depending on the size of a polymer molecule and pore-size distribution. Large molecules are unable to enter the gel; meanwhile, small molecules can invade the gel deeply. Therefore, the larger the molecule is, the shorter it remains in the gel, flowing out of the column quicker.

It is empirically known that by calibrating with standard polystyrenes with narrow molecular weight distribution (Figure 7a), a relationship of polymer concentration (c) and retention volume (V) (= GPC chromatogram, Figure 7b) can be converted to a relationship of

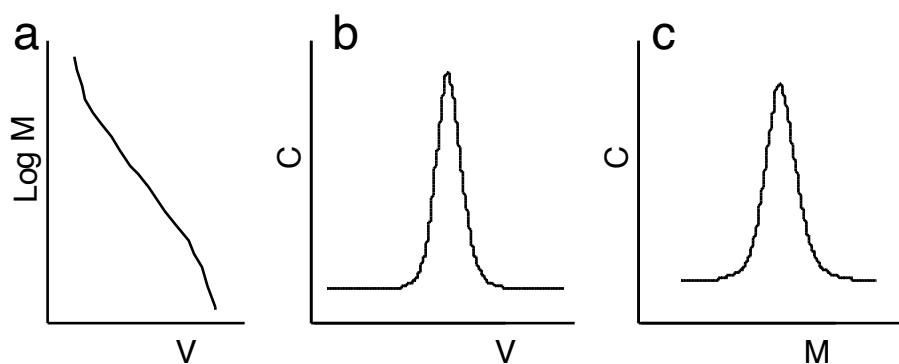


Figure 7 a) Calibration curve. b) Chromatogram. c) Molecular weight distribution curve.
polymer concentration (c) and molecular weight (M) (= molecular weight distribution curve, Figure 7c).

Since the time for experiments is limited, no GPC measurements are performed in this experimental classes, but the method of data analysis is as follows.

1) How to obtain a molecular weight distribution curve:

- (1) Draw a baseline across the whole chromatogram.
- (2) Divide the horizontal axis of the chromatogram in even sections, and measure the height of the chromatogram (h_i) in each section.
- (3) Standardize the height of all chromatograms.
- (4) Prepared calibration curve ($\log M$ vs. V count) is used to convert elution volume V_i to M_i in each section.
- (5) Plot M_i (Horizontal axis) against h_i (Vertical axis), and obtain the molecular weight distribution curve.

2) How to obtain number-average molecular weight and weight-average molecular weight from the GPC chromatogram:

Assume that the height of chromatogram (h_i) is a function of molecular species i. Then the weight (w_i) of molecular species (i) can be calculated from the elution volume ΔV_i of each section in the following equation:

$$w_i = C_i \Delta V_i \propto h_i \Delta V_i \quad (1)$$

As explained in eq 1, the chromatogram is divided in equal intervals, *i.e.*, divided into equal elution volume (ΔV_i), thus the weight of the whole sample (w) is calculated as follows:

$$w = \sum_{i=1}^n w_i \propto \Delta V_i \sum_{i=1}^n h_i \quad (2)$$

Number of moles (n_i) of molecular species (i) is given in the following equation:

$$n_i = \frac{w_i}{M_i} \propto \frac{h_i \Delta V_i}{M_i} \quad (3)$$

Also, M_n and M_w are each given in the equations 4 and 5, respectively.

$$M_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{\sum w_i}{\sum n_i} \quad (4)$$

$$M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{\sum w_i M_i}{\sum w_i} \quad (5)$$

Substitute equations 1, 2, and 3 into equations 4 and 5, the following equations are devived.

$$M_n = \frac{\sum h_i}{\sum h_i/M_i} \quad (6)$$

$$M_w = \frac{\sum h_i M_i}{\sum h_i} \quad (7)$$

3-6) Molecular Weight Determination by Nuclear Magnetic Resonance (NMR) Method.

End group analysis by utilizing NMR is one method to measure molecular weight, where the degree of polymerization is determined by paying attention to protons of the end group. NMR can determine composition of block copolymers. Although students will not measure NMR in this experimental classes, NMR data will be acquired by preparing a solution with a deuterated solvent, filling the solution into an NMR tube, and placing the tube into the machine.

3-7) Dynamic Mechanical Analysis.

As the temperature of a polymer is increased from the glassy state, it would reach its glass-transition temperature. It is known that at the temperature above this point, it will reach a liquid-like state specific to polymers, known as a melt state, which is neither a solid nor a typical liquid of low molecular weight compounds. In a melt state, segmental motions of the frozen polymer chain becomes possible, exhibiting a flow behavior. Although a polymer melt flows, it forms entanglements, which is dependent on the length of the molecular chain of the material; thus, it is a viscoelastic material that possesses both elasticity and viscosity, if one focused on its mechanical properties. It exhibits rubber elasticity depending on the situation. Here, elasticity refers to a property where the material can return to its original shape even after a force is applied, and ideally, the amount of deformation is proportional to the applied force (Hooke's law). On the other hand, viscosity is a property where the material flows when force is applied and it does not return to its original state even after the force is removed. Ideally, the rate of change of flow is proportional to the applied force (Newton's Law).

Rubber elasticity is the elasticity that is specific to polymer chain networks formed by cross-links, entanglements, etc. The elastic modulus from rubber elasticity is not as high as the modulus of metals or ceramics. Ideally, the modulus from rubber elasticity (typically, same as the rubbery plateau modulus (G_N), sometimes simply called elastic modulus) depends on the cross-link density of polymer networks, which is dependent on the chain length of polymer network strands. Rubber elasticity is also associated with high stretchability of materials. The rubbery plateau modulus G_N of an ideal rubber is determined by $G_N = (\rho RT) / M_x$, where M_x , is

the (average) molecular weight of the polymer chain between cross-links, ρ is the density of rubber, T is the absolute temperature, and R is the gas constant.

Block copolymers with a melt polymer component and a glassy polymer component at room temperature, which are attached to each other, form domains consisting of glassy polymers in a self-assembled state at an equilibrium (Figure 8). On the other hand, the block copolymers do not flow since melt polymer components are connected to glassy domains regarded as physical cross-links; therefore, they behave as a material that exhibit rubber elasticity. As the term of rubber elasticity is, the material behave as a rubber or an elastomer. When the temperature of the material is increased, it flows since glassy polymer components become a melt state and the whole material also becomes a melt state. If the temperature is decreased, the material exhibits rubber elasticity again; therefore, such a material is called a thermoplastic elastomer (TPE). TPE films can be prepared by solvent casting of a solution of a block copolymer in which a melt polymer and a glassy polymer at room temperature are connected each other via covalent bond.

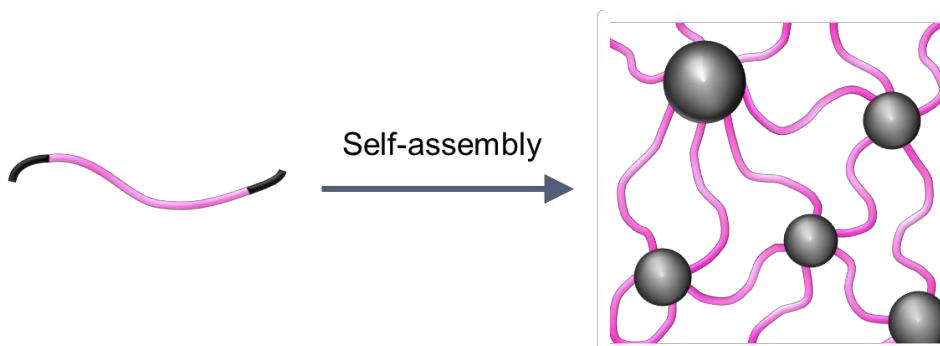


Figure 8. Schematic illustration of self-assembly of ABA triblock copolymer.

Dynamic mechanical analysis can be used to evaluate the rubbery plateau modulus G_N of TPE. In the dynamic mechanical analysis, a stress σ (force applied per unit area) generated is measured when a oscillatory (shear) strain γ (the degree of deformation) is applied. A stress varies at intervals as a strain varies, and it can be divided into one component derived from elasticity and the other component derived from viscosity. The coefficient of elasticity-derived component is the storage modulus G' , and the coefficient of viscosity-derived component is the loss modulus G'' . $G = (G'^2 + G''^2)^{1/2}$ is the magnitude of the sample's dynamic modulus (or called complex modulus), and when G is a constant value in the measurement region, that G is G_N . In general, $G' \gg G''$ in the solid state, and thus G' may be regarded as G_N .

Operations to be conducted in the experiments are as follows:

- (1) Prepare a circular shape sample from a TPE film with a uniform thickness by using a die cutter.
- (2) After the zero point adjustment is performed with the parallel plates (jigs) attached on the upper side and the lower-side, the circular shape sample is placed on the lower-side parallel plate and then it is sandwiched between the upper-side and lower-side parallel plates.
- (3) Start the measurement by entering the sample thickness (automatically read by the device), sample size, jig conditions, angular frequency, applied strain, number of measurement points, measurement temperature range etc. into the PC.

3-8) Tensile Tests of TPEs.

Tensile tests (mainly at room temperature) are used to evaluate the rubber elasticity of TPE. In tensile tests, a stress (a force per unit area) generated by deformation is measured. Operations to be conducted in the experiments are as follows:

- (1) Prepare a dumbbell-shaped sample from a TPE film with uniform thickness by using a die cutting.
- (2) Measure the thickness of a dumbbell-shaped sample by using a micrometer.
- (3) Adjust the zero point of the machine, then put the dumbbell-shaped sample into sample folders.
- (4) Enter the values of a sample thickness, a sample length (when the machine reads automatically), a elongation rate into the PC program, and start measurements.

3-9) Observation of Polymer Samples with Optical Microscopy. (In order to prevent Covid-19 infection, this experiment will not be performed this year.)

A homogeneous film with single phase can be prepared from a sample with a single polymer component; however, a film of a sample with multiple components can not be completely uniform, especially a film of a blend might show non-uniformness (phase-separation with more than two phases) at a scale of micrometers or millimeters. Such non-uniformness of samples directly affects the physical properties. Therefore, optical microscopy will be performed to observe uniformness of samples. Operations will be explained at the laboratory.

4. Questions

Question 1:

Estimate the compositions of triblock copolymers, using NMR measurement results.

Question 2:

Based on the experimental results, concisely answer the solubility of the triblock copolymer, constituent homopolymers of the triblock copolymer, and the monomers. Use the following signs. + : soluble, \pm : slightly soluble, - : insoluble.

Question 3:

Estimate the number-average molecular weights (M_n) of triblock copolymers, which is calibrated with polystyrene standards by using GPC measurements.

Question 4:

- Draw G' and G'' curves of films of commercially available triblock copolymers by using the results of dynamic mechanical analysis, where the vertical axis is an angular frequency ω [s^{-1}] and the horizontal axis is G' [Pa] and G'' [Pa].
- Read the rubbery plateau modulus (G_N) from the data. Also, if the values differ among samples, briefly consider the reason(s) by indicating the keyword(s) that should be underlined.

Question 5:

- Draw stress-strain curves from the results of tensile tests for film samples. (Vertical axis: stress σ (Pa); Horizontal axis: strain ε .)
- Read Young's modulus E (stress per unit strain when strain is sufficiently small, Pa), breaking elongation ϵ_b (elongation at break, %), tensile strength σ_{max} (maximum stress, Pa) from the data. If the values differ among samples, briefly consider the reason by indicating the keyword(s) that should be underlined. What is the relationship between the Young's modulus E and the rubbery plateau modulus G_N ?

Question 6:

Propose a molecular design for preparing high performance thermoplastic elastomers (TPEs). Provide chemical structures, degree of polymerization, molecular weight, additives, physical and chemical properties of constituent blocks . State what physical property values are expected to be improved.

5. References

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4. Polymer Handbook, Brandrup et al. (Wiley Interscience)