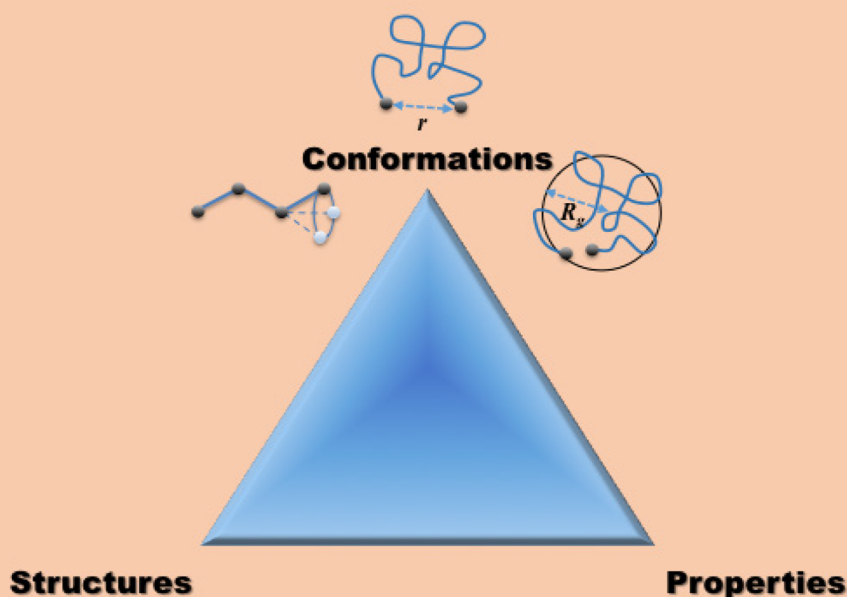




Conformations

Connecting the Chemical Structures
and Material Behaviors of Polymers

Alan Tonelli
Jialong Shen



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Contents

Preface.....	ix
Authors.....	xiii
Chapter 1 <i>Polymer Physics</i> or Why Polymers and Their Materials Can Behave in Unique Ways	1
Introduction	1
References	7
Discussion Questions.....	7
Chapter 2 <i>Polymer Chemistry</i> or the Detailed Microstructures of Polymers.....	9
Polymerization.....	9
Step-Growth Polymers.....	9
Chain-Growth Polymers	11
Chain-Growth Polymer Microstructures	12
Branching and Cross-Linking	14
Comonomer Sequences.....	17
References	18
Discussion Questions.....	18
Chapter 3 Determining the Microstructural Dependent Conformational Preferences of Polymer Chains	19
Introduction	19
References	41
Discussion Questions.....	42
Appendix 3.1: Fortran Program for Hexane “by-hand” Conformational Populations and Distances	43
Chapter 4 Experimental Determination of Polymer Microstructures with ^{13}C -NMR Spectroscopy	57
Introduction	57
Substituents Effects	58
References	67
Discussion Questions.....	67

Appendix 4.1: Polymer Macrostructures and the Kerr Effect.....	68
Appendix 4.2: Program (FORTRAN) Used to Calculate Molar Kerr Constants for Polymers	84
Chapter 5 Connecting the Behaviors/Properties of Polymer Solutions and Liquids to the Microstructural Dependent Conformational Preferences of Their Polymer Chains	109
Introduction	109
Intrinsic Viscosities of Dilute Polymer Solutions	112
Polymer Entanglement	115
Dynamic Behaviors of Polymer Solutions and Melts	120
References	120
Discussion Questions.....	121
Chapter 6 Connecting the Behaviors/Properties of Polymer Solids to the Microstructural Dependent Conformational Preferences of Their Individual Polymer Chains	123
Introduction	123
Solid Polymer Properties and Z_{conf}	124
Copolymer T_g s and Their Comonomer-Sequence Dependence	125
Melting Temperatures of Semi-crystalline Polymers	132
The Flexibilities of Polymers with 1,4-attached Phenyl Rings in Their Backbones	140
Poly(ethylene phthalates).....	140
Polymers with High Impact Strengths Well Below Their Glass-Transition Temperatures	144
Elastic Polymer Networks	149
Thermodynamics of Polymer Networks	151
Polymer Network Topology	152
Modulus of a Polymer Network	167
References	174
Discussion Questions.....	177
Appendix 6.1	178

Chapter 7	Biopolymer Structures and Behaviors with Comparisons to Synthetic Polymers.....	179
	Introduction	179
	Polysaccharides	179
	Proteins.....	184
	Polynucleotides.....	200
	References	212
	Discussion Questions.....	215
Index		217



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Preface

Among the materials found in Nature's many diverse living organisms or produced by human industry, those made from polymers are dominant. In Nature, they are not only dominant, but they are, as well, uniquely necessary to life. Without proteins to give form and function to a myriad of living animals and plants, without DNAs and RNAs to direct the syntheses of their unique sets of necessary proteins, and without the polysaccharides (cellulose, amylose, chitin, etc.) necessary to all living species, life as we experience on earth could not exist. Additionally, the ever increasing and unabated differential margin of production enjoyed by industrial polymers over metals and ceramics continues.

The world dominance of polymer materials is a result of their structural features. Their high molecular weight, long, 1-dimensional, and flexible chains, which lead to highly variable sizes and shapes, produce behaviors and properties that are unique to them and their resultant materials. Because in almost all instances, at least some of the bonds constituting polymer backbones can be rotated into several distinct conformations, the overall collections of potential polymer chain conformations, sizes, and shapes are nearly incomprehensibly large. More important is the ability of polymers to select among their conformations, and adopt those able to provide an appropriate internal response to their external environments and the forces they experience. In other words, polymer chains can be thought to have an *Inside* "mind of their own", their conformational preferences, which determine the *Outside* responses of materials made from them.

Clearly, materials made from small molecules, atoms, or ions, do not have this internal conformational degree of freedom. This is the reason why polymers, with their long flexible chains, and their materials show a number of behaviors and properties that are unique to them. We call the unique properties displayed by nearly all polymers *Polymer Physics* and describe several of them in [Chapter 1](#)—"Polymer Physics or Why Polymers and Their Materials Can Behave in Unique Ways". The only means for materials made from small molecules, atoms, or ions to respond to their environments and/or the forces placed upon them is through alterations in their collective arrangements or overall configurations. To establish which of these molecular configurations are most favorable and therefore likely, requires solving a many-body problem, which for macroscopic material samples is not presently possible.

On the other hand, 50 years ago, Flory (Flory, P. J. [1969], *Statistical Mechanics of Chain Molecules*, Wiley-Interscience, New York) showed how the distinct chemical structures of polymers can be rigorously accounted for when establishing the conformational preferences of their chains. Adopting the rotational isomeric state (RIS) model of polymer conformations (Volkenstein, M. V. [1963], *Configurational Statistics of Polymer Chains*, translated by Timasheff, S. N. and Timasheff, N. J. from the 1964 Russian Ed., Wiley-Interscience, New York; Birshstein, T. M. and Ptitsyn, O. B. [1964], *Conformations of Macromolecules*, translated by Timasheff, S. N. and Timasheff, N. J. from the 1964 Russian Ed., Wiley-Interscience, New York), Flory pointed out that the likelihood or populations of local polymer chain conformations are generally only pair-wise nearest neighbor dependent. In other words, the energy of a particular backbone bond conformation depends only upon the conformations of the bond in question and those of its immediate neighbors. Consequently, the energy of each overall conformation of a polymer chain of n backbone bonds, E_{conf} , is a summation of pair-wise-dependent local bond conformational energies, $E_{conf} = \sum_{i=2}^{n-1} E(\varphi_{i-1}, \varphi_i)$, where $E(\varphi_{i-1}, \varphi_i)$ is the local conformational energy when bonds $i-1$ and i adopt the conformations φ_{i-1} and φ_i .

If each polymer chain conformation $(\varphi_2, \varphi_3, \varphi_4, \dots, \varphi_{n-3}, \varphi_{n-2}, \varphi_{n-1})$ is considered a system, then the collection of all polymer chain conformations, N_{conf} , may be considered an ensemble of statistical mechanical systems, each with an energy E_{conf} . This leads to a soluble conformational partition function, Z_{conf} , for the individual polymer chain and all its attendant thermodynamic properties, because their pair-wise-dependent system energies, E_{conf} , are readily estimable (Hill, T. L. [1960], *An Introduction to Statistical Mechanics*, Addison-Wesley, Reading Massachusetts). In addition to their pair-wise-dependent conformational energies, because linear polymer chains are 1-dimensional systems, matrix multiplication methods were also developed by Flory (1969) for evaluating local and global chain properties, such as bond conformational populations and overall sizes [mean-square end-to-end distances ($\langle r^2 \rangle_0$) and radii of gyration ($\langle R_g^2 \rangle_0$)], with each appropriately averaged over all chain conformations N_{conf} .

Of course E_{conf} depends on the detailed microstructure of each chemically different polymer, and so too do their flexibilities (Z_{conf}), sizes, and shapes. As a consequence, the difference in behaviors and properties of materials made from chemically distinct polymers, which we call **Polymer Chemistry**, are directly connected to the differences in their conformational preferences. In [Chapter 2](#)—“Polymer Chemistry or the Detailed Microstructures of Polymers”, we establish the possible local polymer

microstructures and later describe and demonstrate how they can be experimentally established.

As indicated below, we take advantage of this feature of polymer chains to connect the behaviors and properties of their materials to their detailed chain microstructures:

Microstructures → Conformations → Overall Sizes, Shapes & Flexibility → Behaviors & Properties

The key step or feature of this approach is establishing the conformational preferences of individual polymer chains as a function of their detailed chemical microstructures, as described at length in [Chapter 3](#)—“Determining the Microstructural Dependent Conformational Preferences of Polymer Chains.” In [Chapter 4](#)—“Experimental Determination of Polymer Microstructures with ^{13}C -NMR Spectroscopy”—we show how the conformational characteristics of polymers are related to and used to assign their ^{13}C -Nuclear Magnetic Resonance (^{13}C -NMR) spectra, thereby permitting their microstructures to be determined by this experimental technique.

Finally in [Chapter 5](#)—“Connecting the Behaviors/Properties of Polymer Solutions and Liquids to the Microstructural Dependent Conformational Preferences of Their Polymer Chains”—and in [Chapter 6](#)—“Connecting the Behaviors/Properties of Polymer Solids to the Microstructural Dependent Conformational Preferences of Their Individual Polymer Chains”—we show which and how certain behaviors and properties of polymers and their materials can be connected to and explained in terms of their single chain microstructural-dependent conformations. In addition, we point out behaviors and properties dominated by interactions between polymer chains and between polymers and solvents, and, as a result, are not amenable to our ***Inside*** polymer chain microstructure $\leftrightarrow$ ***Outside*** polymer material property approach. These include polymer rheology, process-dependent structures and behaviors, two-phase crystalline and amorphous morphologies, softening or glass-transition temperatures, in addition to others.

We close our discussion in [Chapter 7](#)—“Biopolymer Structures and Behaviors, with Comparisons to Synthetic Polymers”—by comparing and contrasting the behaviors of synthetic polymers, with their comparatively simple microstructures, to those of biopolymers, whose microstructures and functions are infinitely more diverse.

We cannot fail to mention that no previously published polymer science, chemistry, physics, engineering, or materials text, aside from *Polymers from the inside Out: An Introduction to Macromolecules* (Tonelli and Srinivasarao, 2001), takes realistic account of the microstructure-dependent

conformational preferences of individual structurally distinct polymer chains when attempting to rationalize/understand the behaviors and properties of their materials. This despite the availability of conformational RIS models that have been or can readily be developed for most commercially important synthetic man-made polymers, and that are also relatively easy to implement.

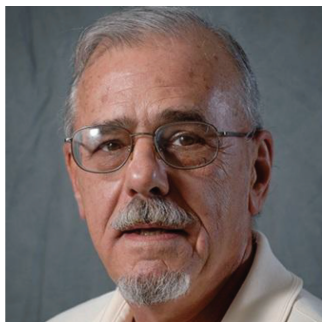
The reality is that *Polymer Chemistry* is seldom considered when trying to understand the behaviors of polymer materials. This is made abundantly clear in a recent perspective titled “Polymer Conformation-A Pedagogical Review” published in *Macromolecules* (2017), doi:10.1021/acs.macromol.7b01518 and written by Professor Zhen-Gang Wang in celebration of the 50th anniversary of the journal *Macromolecules*. Despite its title, this paper is really a perspective/review of *Polymer Physics*, because all polymers are considered to be randomly walking, freely rotating, or worm-like chains, without distinctive chemical microstructures that result in varying conformational preferences.

We fervently hope that, with the publication of our book, the neglect of polymer chemistry will no longer remain the case. Because without accounting for the conformational preferences of synthetic polymers, relevant relations between their distinct microstructures, behaviors, and material properties cannot be established, i.e., the relevance of the chemistry of individual polymer chains to the behaviors of their materials would remain largely a mystery.

To quote Flory, “Quantities such as molecular weight, radius of gyration, degree of branching, *etc.* that characterize the molecule as a whole do not suffice for an understanding of the virtually endless variations in the properties that distinguish one polymer from another. For this purpose it is necessary to examine the chemical structures of the constituent units, taking into account geometric parameters pertaining to chemical bonds, the conformations accessible to the chain skeleton and the resulting spatial configurations” (Flory, 1969).

It is more than obvious that our approach to the behavior of polymer materials, whose polymer chains can be thought to have an *Inside* “mind of their own”, their conformations, which determine the *Outside* responses of materials made from them, could not have been taken without the knowledge in Flory’s *Statistical Mechanics of Chain Molecules*. So on the golden anniversary of its publication, we gratefully express our gratitude for its many lessons.

Authors



Alan Tonelli, born in Chicago in 1942, received a BS in Chemical Engineering from the University of Kansas, in 1964 and a PhD in Polymer Chemistry from Stanford in 1968, where he was associated with the late “Father of Polymer Science” and Nobelist Professor Paul J. Flory. He was a member of the Polymer Chemistry Research Department at AT&T-BELL Laboratories, Murray Hill, NJ for 23 years. In 1991, he

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1 *Polymer Physics* or Why Polymers and Their Materials Can Behave in Unique Ways

INTRODUCTION

In this introductory chapter, we seek to describe polymers in only a minimal generic way that distinguishes them from small molecules, i.e., as long, high molecular weight, and flexible chains. Our purpose here is to demonstrate why these unique structural features alone result in behaviors and properties that are unique to polymers and the materials made from them. We call this *Polymer Physics*, because these unique polymer behaviors are manifested by virtually all polymers regardless of their detailed chemical microstructures. Of course the degree to which polymers with distinct microstructures evidence their unique *Polymer Physics* behaviors does depend on their detailed chemical microstructures, which we call *Polymer Chemistry* and is the main emphases of the following chapters.

If we compare the size of an ethane molecule $\text{CH}_3\text{--CH}_3$ with a molecular weight (MW) = 30 g/mol to a polyethylene chain $[\text{PE} = (-\text{CH}_2\text{--CH}_2\text{--})_n\text{--}]$, with $n = 25,000$ repeat units and a MW = 700,000 g/mol, which is not atypical, after magnifying each of them a billion times, ethane would be about a foot long and the fully extended all *trans* PE chain more than 4 miles in length. Clearly, polymers are in fact large molecules or **macromolecules**, and the following demonstration clearly shows how the difference in sizes between typical small molecules and long high molecular weight polymer chains can dramatically affect their behaviors.

We use the Cannon-Ubbelohde viscometer shown in [Figure 1.1](#) to measure the flow times of three liquids: water, a 0.5 wt% aqueous solution of ethanol $\text{E} = [\text{CH}_3\text{--CH}_2\text{--OH}]$, and a 0.5 wt% aqueous solution of poly(ethylene oxide) $[\text{PEO} = (-\text{CH}_2\text{--CH}_2\text{--O--})_n\text{--}]$, with a molecular weight of 4,000,000 g/mole and containing $n = 90,909$ repeat units, through the viscometer's capillary. You'll note that the repeat unit of PEO is closely similar to that of E. This choice was made to alleviate, as much as possible, differences in their chemistry, so that they are distinguished solely by their sizes.

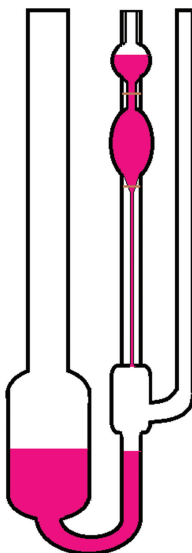


FIGURE 1.1 Cannon-Ubbelohde viscometer filled with a liquid. (Reprinted with permission from Shen, J. and Tonelli, A. E., *J. Chem. Educ.*, 94, 1738–1745, 2017. Copyright 2017 American Chemical Society.)

Flow times observed in the #1 Cannon-Ubbelohde viscometer, shown in [Figure 1.1](#), were, respectively, ~108, 107, and 343 seconds for water, 0.5% ethanol in water, and 0.5% PEO ($M = 4,000,000$) in water. (It is also possible to use a less expensive Fenske viscometer. See a video demonstration of us using a Cannon-Ubbelohde viscometer in the supporting information of Shen and Tonelli 2017.)

Division of the MW of PEO by the MW of E reveals the ratio of the number of small E molecules to the number of long PEO chains, i.e., $4,000,000/46 = 87,000$. There are 87,000 times more ethanol molecules than PEO chains in their 0.5 wt% aqueous solutions. Clearly, the much larger randomly coiling PEO chains dramatically slow the flow of the water molecules even though they constitute only 0.5 wt% of their aqueous solution, while the same weight and much greater number of small E molecules has virtually no effect on the flow of its 0.5 wt% aqueous solution. Later, in [Chapter 5](#), we learn that even at only 0.5 wt%, the repeat units of the large randomly coiling PEO chains are in close contact with all of the 99.5 wt% solvent water molecules, thereby retarding their flow through the viscometer's narrow capillary.

Our 2nd demonstration of *Polymer Physics* uses a simple rubber band to illustrate some unique behaviors of a network formed by cross-linking mobile liquid polymer chains. To form an elastic network that can easily be stretched and then reversibly returned to its unstretched state, i.e., to its

unstretched size and shape, when the stretching force is removed, three requirements must be met: (i) polymer chains, which can alter their sizes and shapes; (ii) the temperature must be higher than the softening temperatures (T_g and/or T_m) of the amorphous and/or crystalline regions of the polymer sample, because polymer chains must be mobile and able to change their conformations when the network is stretched; and (iii) to eliminate irreversible movements or flow of the polymer chains, they must be cross-linked into a network.

The volume of a stretched polymer network (see [Figure 1.2b](#)) differs little from the volume of the unstretched network (see [Figure 1.2a](#)). This can be confirmed visually by stretching a thick rubber band and noting that while its length obviously increases on stretching, both its width and thickness decrease. Consequently, the at-rest and stretched rubber bands have closely similar volumes. This implies that the average separation between chains remains constant, and therefore the interactions between polymer chains are not altered, suggesting that the change in interchain energy ΔU (interchain) ~ 0 upon network stretching.

In addition, as a comparison of [Figures 1.2a](#) and [b](#) makes plain, some of the chains between cross-links are extended, while some are compressed when the rubber network is uniaxially stretched. Stretching a polymer network clearly must cause the conformations of the chains between cross-links to change (See [Figure 1.3](#) for examples of PE chain conformations, both extended and compact). In [Chapter 3](#), we discuss the conformations of polymer chains in some detail.).

In [Chapters 3](#) and [6](#), we will illustrate that large changes in the distances between cross-links can be achieved by bond rotations about a small number

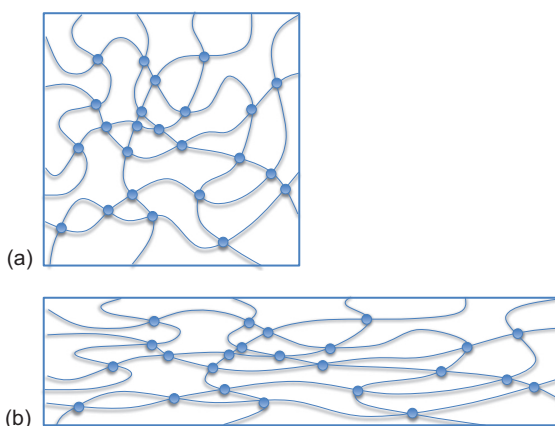


FIGURE 1.2 Cross-linked network (a) in unstrained at rest and (b) in strained states. (Reprinted with permission from Shen, J. and Tonelli, A. E., *J. Chem. Educ.*, 94, 1738–1745, 2017. Copyright 2017 American Chemical Society.)

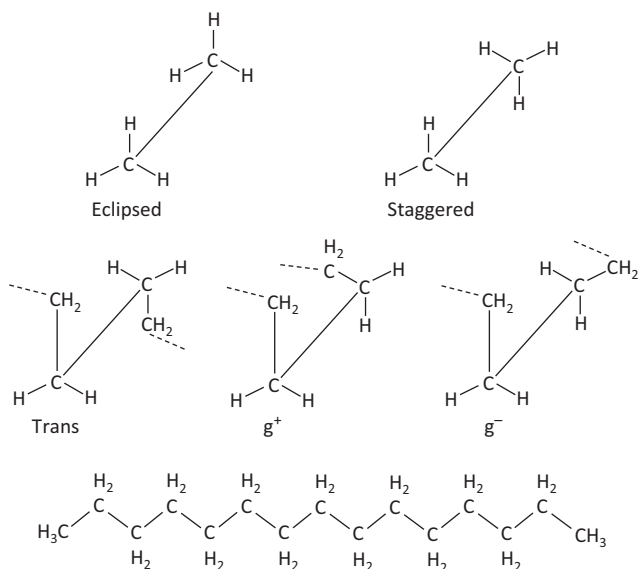
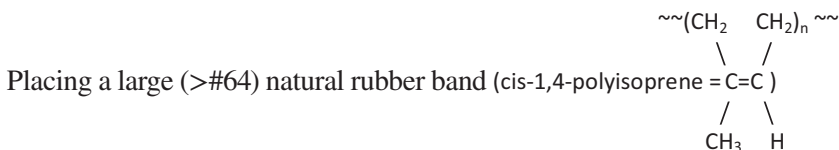


FIGURE 1.3 Sawhorse projections of ethane conformers (top), of trans and gauche conformers in PE (middle), and PE in the extended all trans conformation (bottom).

of the backbone bonds between cross-links. Because the number of bonds changing their conformations as the network is stretched is small in comparison to the total number of backbone bonds between cross-links, the change in polymer chain conformational energy is small or ΔU (intrachain) ~ 0 .

Since both inter- and intrachain contributions to the total change in internal energy that accompany network stretching are ~ 0 , we can assume network stretching is characterized by an overall $\Delta U \sim 0$. The first law of thermodynamics states that the energy of a system U can only be changed, raised or lowered, respectively, by the addition or removal of heat (Q) or by work (W) performed on or done by the system. Thus, $\Delta U = Q + W$, with heat into and work done on the system, raising the system's energy. Stretching of a polymer network is accompanied by a $\Delta U \sim 0$, so Q must equal $-W$ or $-Q = W$. This means that the work done on a polymer network upon stretching must be released in the form of heat to maintain an overall $\Delta U \sim 0$.



between your wet lips and quickly extending it will cause the heat escaping from the rubber band upon stretching to be detected by a warming

of your lips. (When doing this wear safety glasses and use sterile rubber bands, which are available.) The stretched rubber band may alternatively be placed between your wet lips and allowed to rapidly contract. In this instance, your wet lips should be able to sense the cooling produced by the heat absorbed from them by the contracting rubber band, counteracting the loss of energy produced by the work performed by the contracting rubber band. (See how we do it in the video included in the supporting information of Shen and Tonelli 2017.).

We have strongly suggested based on our rubber band demonstration that a stretched elastic polymer network does not contract and return to its at-rest unstretched state in order to lower its energy, because upon stretching or contraction $\Delta U \sim 0$. So what must be the origin of the restoring force? If it is not lowering the energy of the rubber, it must be increasing the entropy accompanying network contraction. Since stretching and contraction of the elastic polymer network does not result in a change in volume or in network density, this cannot be the source of the change in network entropy upon extension or contraction. The only remaining source for the entropy change which causes the stretched network to contract when the extensional force is removed must be associated with changes in conformations of the polymer chains between cross-links upon extension and retraction. Whether the distances between network crosslinks are increased or decreased upon extension of the network, the populations of the favorable conformations available to the stretched or compressed network chains are reduced. This reduction in conformational entropy upon extension is reversibly increased and recovered upon contraction as the chains resume sampling their complete equilibrium populations of conformations.

Our final demonstration of behaviors unique to polymers or *Polymer Physics* employs a 5% solution of poly(vinyl alcohol) [PVOH = $-(\text{CH}_2-\text{CH}-)_n-$]



in water, to which a small amount of a 5% aqueous solution of borax (sodium borate = $\text{Na}_2\text{B}_4\text{O}_7 \times 10\text{H}_2\text{O}$) has been added dropwise with stirring to form a gel often called “slime.” (Neither PVOH nor borax are toxic through handling, but wash hands thoroughly to avoid any chance of ingestion. See Casassa et al. 1986.)

Figure 1.4, shows the borate ions $[\text{B}(\text{OH})_4^-]$ generated upon dissolution of the borax are capable of interacting with the hydroxyl groups on the PVOH chains. As a result, non-covalent tetra-functional cross-links are formed, but are only weak physical attractions, which may be easily disrupted if the gel is strained.

The time-dependent behaviors/responses of materials made from long-chain flexible polymers are a unique and characteristic aspect of *Polymer Physics*. These properties can be easily demonstrated through the following

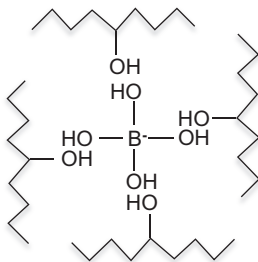


FIGURE 1.4 Schematic diagram showing the ability of borate ions produced in aqueous solutions of borax to form temporary, physical cross-links in PVOH solutions resulting in dilute “slime” gels.

three simple slime demonstrations. (See demonstration video included in the supporting information of Shen and Tonelli 2017 for explanations of the slime responses to forces applied for varying times.)

When the slime gel is removed from the beaker, rolled into a cylinder, and a portion is hung over the edge of a desktop, a single continuous strand forms and flows until it reaches the floor and puddles up. The relative weakness of the interactions between the borate ions and the PVOH hydroxyls are evidenced by this behavior. The single flowing continuous strand of slime also illustrates that, though dynamic, an overall cross-linked network is maintained due to the weak and temporary nature of the cross-links in slime. These cross-links, though not able to withstand the force of gravity, are continuously broken and reformed, allowing irreversible flow of the PVOH chains passed each other.

Next, we roll the slime gel into a ball and, from a height of several feet, drop it on a desktop. The slime ball bounces elastically several times before sticking to, spreading on, and forming a puddle on the desktop.

In our final slime observation, we once again roll the slime into a cylinder and pull it rapidly on both ends in an attempt to extend it very abruptly. The slime cylinder fails and breaks in a brittle manner if pulled quickly enough, with very little extension and sharp, flat fracture surfaces reminiscent of a broken icicle. A similar demonstration of brittle slime behavior induced by the application of large high frequency stresses can be accomplished by throwing a ball of slime very hard against a solid wall. This results in its fracture into a large number of small pieces, which are only recovered with tedious effort, so this demonstration should only be conducted on an outside wall.

In the three “experiments,” the slime gel responded in very distinct ways when stressed differently. A cylinder of slime hung over the edge of a desktop flowed irreversibly as it was subjected to the constant application

of gravity. The slime ball dropped onto the desktop bounced elastically several times before puddling up. The slime cylinder that was rapidly extended was observed to fail in a brittle manner. To summarize and conclude, the manner in which the slime gel responded was, in addition to its magnitude, sensitively dependent on the frequency of the applied force, i.e., the amount of time the force was applied.

Each of the behaviors briefly demonstrated in these *Polymer Physics* demonstrations are unique to polymers and their materials. Detailed reasons for each are subsequently provided in [Chapters 5](#) and [6](#), where the magnitudes of their responses are seen to be dependent on their chemical microstructures and the conformational preferences resulting from them. There, we begin to rationally understand the *Inside* “minds of their own,” i.e., their microstructural dependent conformational preferences, and how these are connected to and determine the *Outside* responses of polymer materials.

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Shen, J., Tonelli, A. E. (2017), *J. Chem. Educ.*, 94 (11), 1738–1745.

DISCUSSION QUESTIONS

1. What is the principal reason that polymers and their materials show behaviors distinct from materials made from small molecules and atoms?
2. How can the addition of such small amounts of polymer solutes (<1 wt%) to small molecule solvents so dramatically slow down the flow of their solutions?
3. Given no further information, how would you expect polypropylene with a MW = 42,000 and poly(vinyl chloride) with a MW = 62,000 to affect the viscosities/flow times of their solutions?
4. Why did we conclude that the resistance to stretching a rubber band is entropic in origin?
5. As we stretch a cross-linked polymer network, such as a rubber band, some chains between cross-links are stretched, while others are shortened or compressed. How does this effect the number of conformations they can adopt, i.e., their conformational entropy?
6. What do the rubber-band and slime DEMOS have in common, and how do they differ?
7. We observed that even though the slime solution and gel that was formed upon addition of a small amount of borax contained only ~5% PVOH, its responses to deformation were very dependent on the frequency or time of the applied force. Discuss the reason(s) why?



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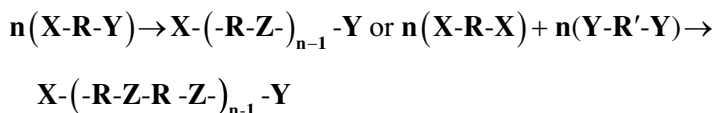
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2 *Polymer Chemistry or the Detailed Microstructures of Polymers*

POLYMERIZATION

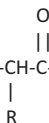
STEP-GROWTH POLYMERS

Polymers are made by linking together small molecules called monomers. All monomers must possess the ability to undergo at least two linking reactions to be inserted into and eventually produce a polymer chain. Linear polymers result from the exclusive linking together of bi-functional monomers. As examples, single molecules containing two functional groups -X and Y- that react with each other to form a covalent link -Z-, or two different molecules each with a pair of reactive function groups (X-R-X) and (Y-R'-Y) that also form covalent links -Z- can be used to make polymers produced in a Step-Growth fashion:



For instance, the common classes of synthetic polymers, polyesters, and polyamides, are made from monomers where X and Y are a carboxylic acid group and a hydroxyl or an amine group, respectively. Proteins are

synthesized from bifunctional α,ω -amino acids $(\text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH})$, with 20



different R groups (see [Chapter 7](#)).

The polyesters and polyamides are generally termed Step-Growth polymers because of the mechanism or way they grow from a large collection of monomers into a sample with many fewer, but much longer polymer chains. A collection of polymers with a reasonably high average molecular weight (MW) is not achieved until nearly all of the functional groups (-X, Y-) have been converted to -Z- links (Carothers 1936; Flory 1953). The fact that the reactivity of, or reaction rate between, -X and Y- functional groups is generally independent of the sizes of the molecules they are attached