



Technical Paper

Drawn Fiber Polymers: Chemical and Mechanical Features



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ABSTRACT

Drawn fiber monofilament represents a popular extrusion product used in many different types of industry applications. Generally superior to standard extrusion-only monofilament, the drawing process enhances many of the preferred properties of drawn fiber. Further examination of the chemical features of the materials used to make drawn fiber – including PVDF, PFA, ETFE, ECTFE, FEP, and PEEK – provides valuable insights into their properties. PVDF serves as a particularly instructive model to explain many of these features such as dipole-dipole chain interactions, London forces, and chain flexibility. A basic understanding of these elements can be applied to other polymers, particularly fluoropolymers, and can be used to approximate their properties. PVDF further highlights the sometimes misleading representation of chemical drawings with respect to the three dimensional topology of the polymer which underlies its material behavior. Building on a foundational knowledge of the chemical attributes, the mechanical properties can be examined with greater clarity. Features such as crystallinity affect properties including glass transition temperature (T_g), melt temperature (T_m), and strength. Stress-strain relationships, fundamentally the result of chemical aspects of the polymers, describe properties such as tensile strength, elongation, and deformation. Much like PVDF, a comparison of the various features of these polymers reveals patterns which can be used to interpret and even predict the behavior of these and similar polymers. The information within provides practical knowledge and understanding to help choose a best drawn fiber based on material, properties, and environment.

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INTRODUCTION: WHAT IS DRAWN FIBER?

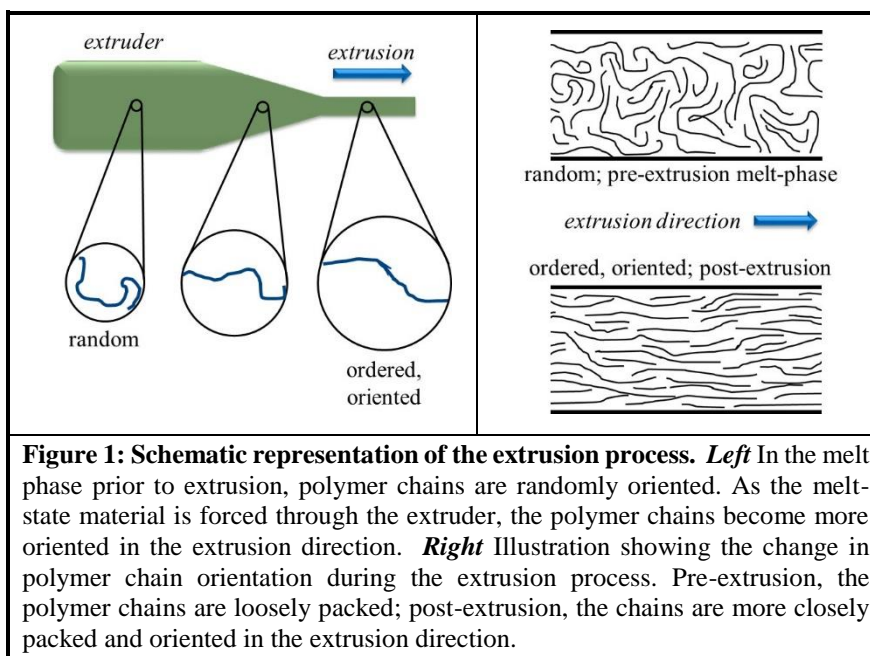
Drawn fiber is an improved monofilament fiber derived from polymer extrusion. The term drawn fiber comes from industry and is used to describe monofilament that has been pulled, stretched, or *drawn down* post-extrusion. Draw down itself denotes the characteristic that the fiber has been made thinner as a result of the drawing process; in this way, the fiber has been drawn down in size (diameter). With the additional step of draw-down, drawn fiber is distinct from ordinary monofilament. As a result of the drawing process, drawn fiber typically possesses superior mechanical properties to ordinary extruded monofilament vastly expanding the scope of drawn fiber applications.

PART I: THE DRAWING PROCESS AND APPLICATIONS

HOW IS DRAWN FIBER MADE?

EXTRUSION

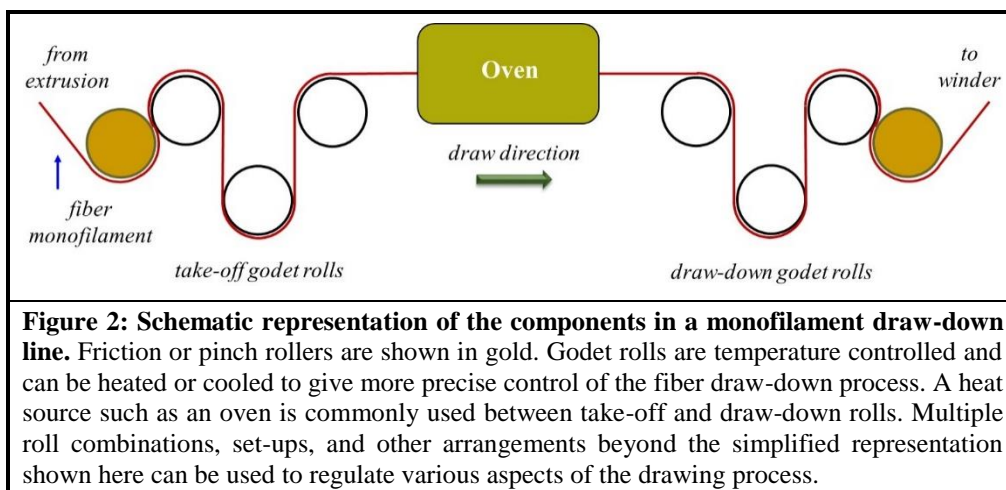
Monofilament, including drawn fiber, is extruded from molten polymer resin materials. These resins consist of very-long-chain polymer molecules. In the melt phase, these molecules are arranged in a random and disordered state (**Fig. 1 Left**). Extrusion initiates orientation of the polymer chains from a random to a more ordered arrangement (**Fig. 1 Right**). This orientation occurs in the extrusion direction [1-3]. The result of extrusion is a material with a much higher degree of polymer chain alignment. This more ordered positioning has significant impact upon the mechanical properties of the monofilament [3, 4].

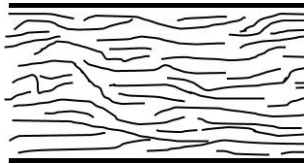
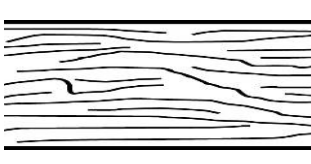


THE DRAWING PROCESS

Drawing down the monofilament takes the extrusion process one step further. This stretching and pulling of the fiber even stretches the polymer chains at the molecular level [2]. This carefully controlled draw-down process is carried out at elevated temperature to facilitate polymer chain mobility and increase chain molecule alignment. Draw-down is accomplished by passing the extruded monofilament through heat such as an oven or hot water bath. During stretching, the monofilament fibers are wound onto Godet rolls (also called *stands* or *draw stands*) (**Fig. 2**). This series of multiple off-aligned rolls is used to control stretching by turning at different speeds. Godet rolls themselves are also usually heated to promote

the drawing process. Godet rolls can be used in a vast array of combinations, set-ups, and other arrangements to precisely control phases of the drawing process. Godet rolls also provide a means to control slippage of the monofilaments. The draw-down process further orients the polymer chains in the machine direction allowing more close packing and increased density resulting in a smaller diameter of the drawn monofilament fiber [3-5]. Fiber that has been drawn down in this way also exhibits less elongation than the same fiber that has been extruded only. This expected consequence is because the drawing process stretches – or elongates – the fiber before it cools to normal or room temperature. Maximum fiber strength is achieved in the drawing process when the polymer chains have reached maximum alignment in the same (machine) direction (**Fig. 3**) [5].



Monofilament	Drawn Fiber
<p>Low tensile strength High elongation</p>  <ul style="list-style-type: none"> • extrusion only • moderate orientation • loose chain packing • less stretching 	<p>High tensile strength Low elongation</p>  <ul style="list-style-type: none"> • extrusion + draw-down • highly oriented • smaller diameter • close-packed chains
<p>Figure 3: Comparison of extrusion-only monofilament and drawn fiber monofilament. Ordinary monofilament (<i>left</i>) typically possesses lower tensile strength and higher elongation than drawn fiber (<i>right</i>).</p>	

APPLICATIONS

Drawn fiber, and in particular Zeus drawn fiber, is best be described as a performance fiber. This product is specifically aimed at more difficult or stringent application environments. Drawn fiber such as this is distinctive from inexpensive and more commoditized monofilaments as those commonly found in the textile industry, as an example. Indeed, Zeus drawn fiber can be found in applications ranging from aerospace, automotive, to medical industries but also in a surprising array of other fields. The polymers and processes used to make drawn fiber can be directed to give the monofilament many favorable chemical, mechanical, and physical attributes. These traits make drawn fiber especially versatile for high-stress or unfriendly environments. Coupling these advances with the ability to be woven or produced in extremely fine diameters, the possibilities for drawn fiber are extensive. Some specific examples are given here for an appreciation of the diverse capabilities and application prospects of Zeus drawn fiber.

Braiding – Perhaps the most common application of drawn fiber is as a woven over-braiding for hoses or sleeves to cover wire bundles (**Fig. 4A**). Used in the way, braiding offers protection from abrasion and rubbing as well as from physical trauma. Drawn fiber over-braiding also provides additional strength and increased burst pressure for fluid carrying hoses.

Weaves – Drawn fiber can be made into weaves that can be used for such applications as mist eliminators and for fine filtration. Scrims for backing of non-woven filter material are also a common application for drawn fiber wovens. Drawn fiber can also be woven to form support structures for composite materials that are in very popular use in aerospace and automotive industries. Chemical resistance of the particular drawn fiber polymer is often a key consideration here (**Fig. 4B**).

Medical braiding – Another very common use of drawn fiber monofilament is as medical braiding. This kind of application is most often as reinforcing braiding for catheters. A more recent variation on this application features drawn fiber braiding on gastroluminal bypass tubes also for strengthening reinforcement [6]. Medical tubes and catheters using drawn fiber braiding can be MRI-compatible if they contain no other substantial metal parts – a highly desirable feature in today’s medical sector (**Fig. 4C**).

Instrument strings – Drawn fiber is also highly amenable for use as instrument strings such as for a guitar or harp. While nylon strings for a classical style guitar may be familiar, drawn fiber can be made from a variety of polymer materials such as PVDF opening up the range of string applications (**Fig. 4D**).

Racquet strings – In a similar vein to instrument strings, drawn fiber can also be used for racquet strings. Here, the possibilities are quite broad considering the number of racquet sports including tennis, badminton, squash, and many others (**Fig. 4E**).

Belting – Drawn fiber can be used to create new or unusual components, too. A seam spiral is one such creation used to join the ends of industrial conveyor-type belts. An example of this type of belting can be seen at grocery store checkouts. Drawn fiber can also be woven into ribbons and used as a strengthen layer in belt manufacturing (**Fig. 4F**).

Brushes – Whether for push-brooms or scrub brushes, drawn fiber conveniently lends itself for this kind of application. Even tooth brushes are produced using drawn fiber bristles. Drawn fiber is especially suited for these kinds of application because of its durability, chemical resistance, and resistance to abrasion (**Fig. 4G**).

Chopped – Drawn fiber is very adaptable for use in structural composites when it is cut or chopped into small pieces and added to the composite. For example, the

chopped fiber can be sprayed onto a surface to give a random orientation and covered with a subsequent layer of resin, paint, or other top coating. In this way, the desired property resulting from the application of the chopped fiber would have more uniformity and less directionality. This type of application is superior to a thin film, for example, and is especially useful in composite forming for weight savings or improved structural integrity.

Formed parts – The thermoformability of drawn fiber allows it to be used to create formed parts (Fig. 4H). As

one example, drawn fiber can be heat-formed or wound to create a spring shape or formed to other shapes from its initial monofilament form.

Twisted cord or twine – This application of drawn fiber is frequently used when lacing or tying is required. The enhanced tensile strength of drawn fiber compared to ordinary monofilament is of particular benefit for drawn fiber cord and twine (Fig. 4I).

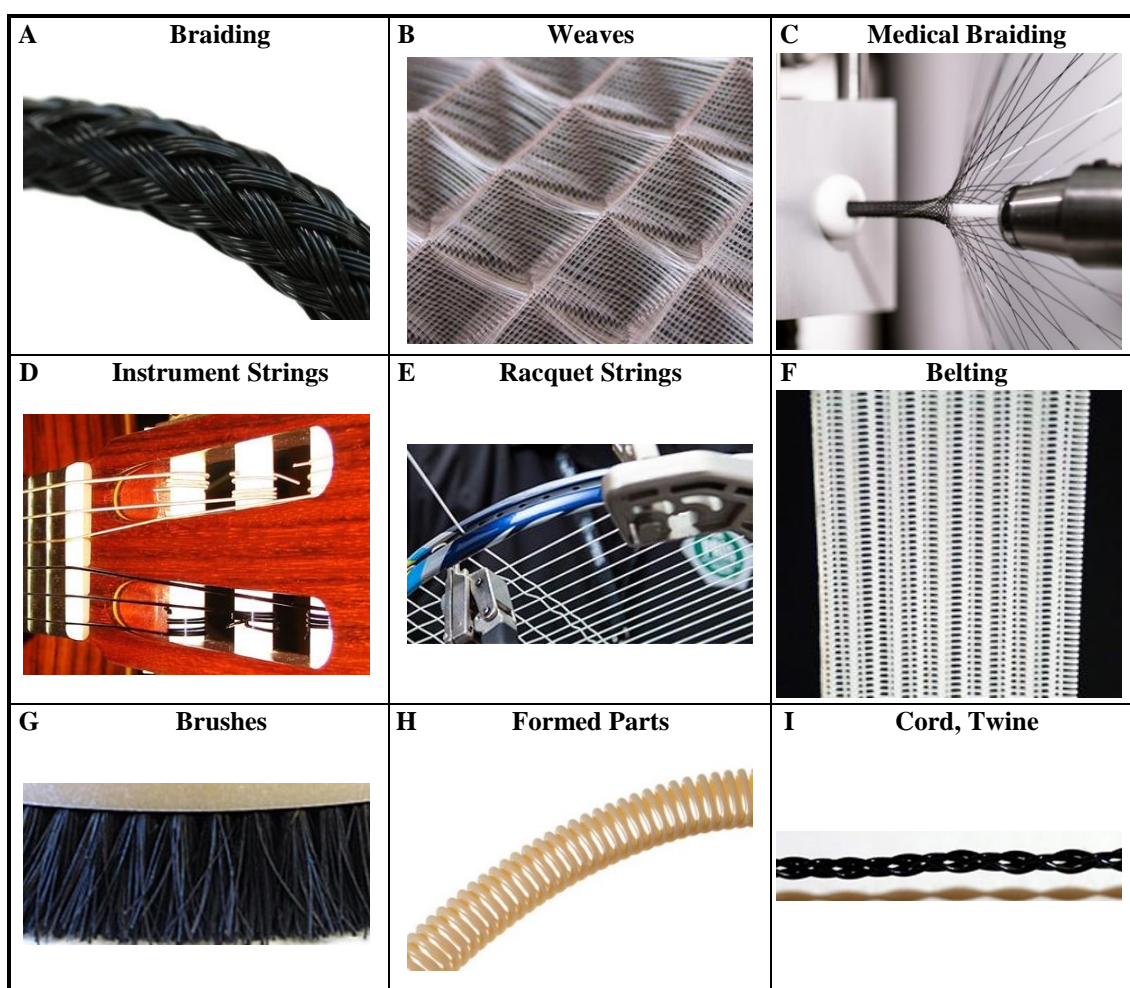


Figure 4: Overview of several drawn fiber applications and products. A) Black PEEK braided sleeve. B) Enlargement of ETFE weave used as a mist eliminator. C) PEEK drawn fiber being braided over a catheter. D) Instrument strings and E) racquet strings are also obvious applications of drawn fiber. F) PEEK drawn fiber used as a mesh in belting applications. G) Brushes can be made from multiple fiber polymers which have exceptional abrasion resistance. H) Formed parts such as a seam spiral can be made from Zeus drawn fiber. I) Drawn fiber makes high-tensile twine for applications requiring tying or lacing.

PART II: DRAWN FIBER POLYMERS – CHEMICAL STRUCTURE AND PROPERTIES

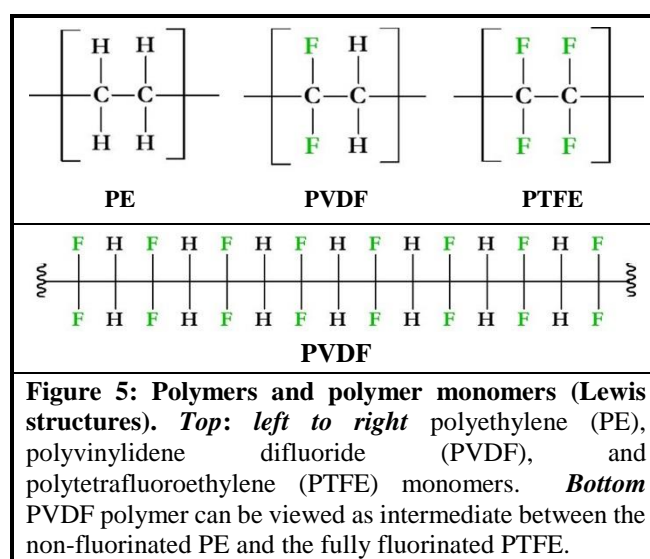
Drawn fiber is manufactured from a variety of polymer resins. Zeus produces drawn fiber monofilament in at least ten different resins. For a fundamental appreciation of several key features that most affect drawn fiber and polymer performance, this article focuses on drawn fiber produced from PVDF, PFA, FEP, ETFE, ECTFE, and PEEK polymer resins. Note that all of these polymers are fluoropolymers with the exception of PEEK. Collectively, these polymers provide an overview showing how minor changes to these molecules produce a material with significantly different properties. These six polymers are presented here illustrate several common themes.

PVDF – A BASIC FLUOROPOLYMER MODEL

Polyvinylidene difluoride, or PVDF, is a convenient and helpful model to illustrate how the incorporation of fluorine affects material attributes. Inclusion of fluorine often results in preferred chemical, physical, and mechanical properties which have made fluoropolymers highly popular in many industries today. PVDF is made by combining vinylidene difluoride monomers (**Table 1**)[7]. PVDF could be modeled or viewed as halfway between two other familiar polymers, the non-fluorinated polyethylene (PE), and the fully fluorinated polytetrafluoroethylene (PTFE) (**Fig. 5**). The structure of PVDF appears to be quite straightforward consisting of repeating $-\text{CF}_2-\text{CH}_2-$ units. However, not apparent in this simple two-dimensional depiction are several instructive features essential for a fluoropolymer discussion.

Firstly, solid state polymers exist in two distinct architectures: amorphous and crystalline. These phases are both composed of the same long-chain polymer

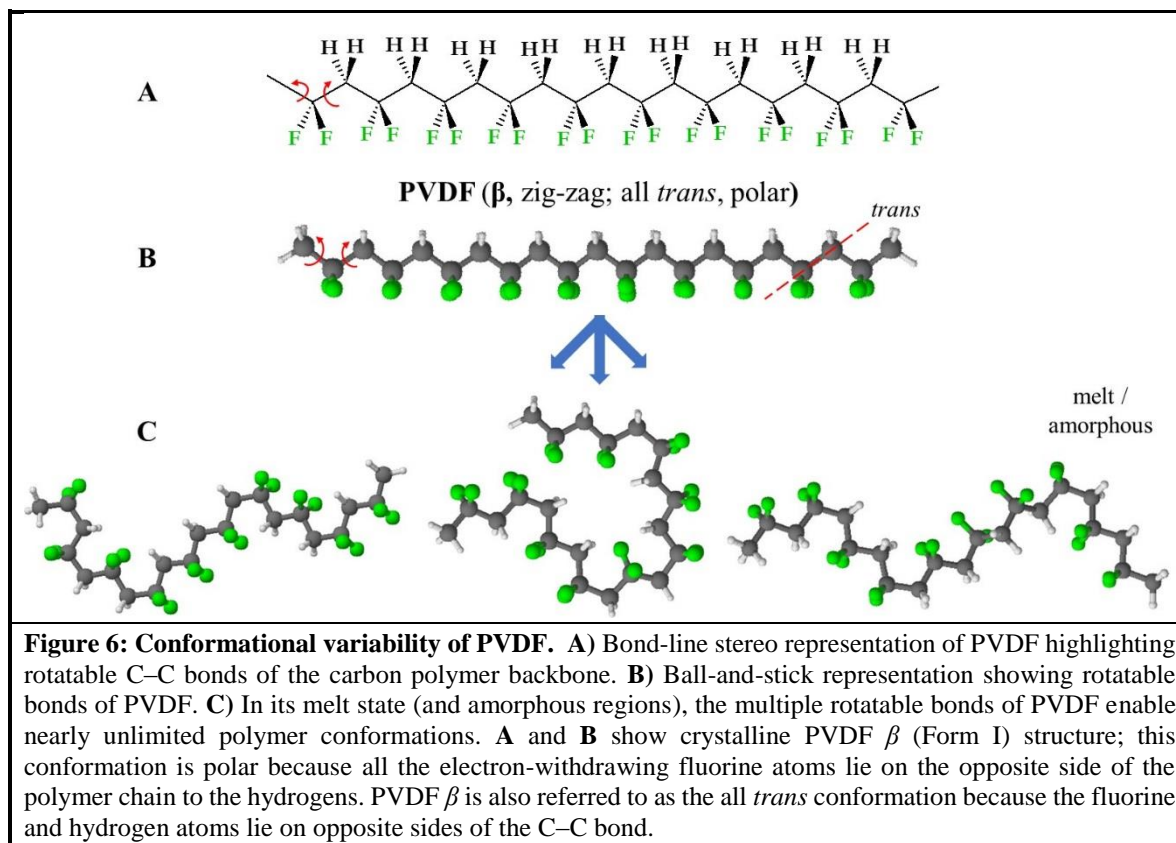
molecules making up the polymer mass but are arranged differently. The amorphous regions contain polymer chains that are generally arranged in a disordered or random manner. Crystalline regions contain molecules that have positioned a portion of themselves into part of a regular repeating pattern during cooling from the melt phase. These molecules or molecule segments are closely arranged due to their chain interactions and in their solid state form a crystal. Crystalline and amorphous regions are mixed throughout the solid state polymer. The proportion of crystalline versus amorphous regions affects the solid state polymer's final properties.



For PVDF, a simplified two-dimensional representation does not reveal its true molecular topology governing its crystalline and amorphous regions. PVDF is composed of only single bonds. Chemically, single bonds are generally rotatable, and this is true of all of the single bonds of PVDF (**Fig. 6A and B**). Most important are the rotatable C–C bonds of the carbon backbone of PVDF. These bonds are rotatable for the full length of the PVDF polymer chain. Thus, there are nearly limitless conformations of PVDF in its melt phase or amorphous regions as it returns to room temperature from its melt state (**Fig. 6C**).

<div><div><div><div>F</div><div>H</div></div><div>C=C</div><div><div>F</div><div>H</div></div></div><div>vinylidene difluoride</div></div> <div>+</div> <div><div><div>F</div><div>H</div></div><div>C=C</div><div><div>F</div><div>H</div></div></div> <div>vinylidene difluoride</div> <div>→</div> <div><div><div><div>F</div><div>H</div></div><div>C-C</div><div><div>F</div><div>H</div></div></div><div>PVDF</div></div> <tr><td><div><div><div><div>H</div><div>H</div></div><div>C=C</div><div><div>H</div><div>H</div></div></div><div>ethylene</div></div><div>+</div><div><div><div>Cl</div><div>F</div></div><div>C=C</div><div><div>F</div><div>F</div></div></div><div>chlorotrifluoro- ethylene 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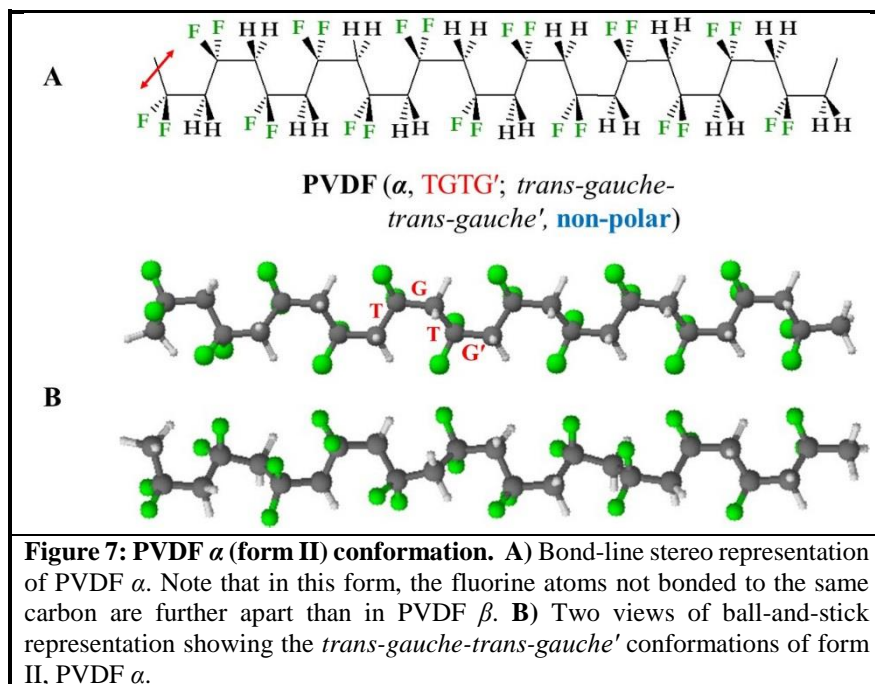
<p>Table 1: Six polymers and their immediate synthetic precursors used to produce Zeus drawn fiber. <i>Top to bottom:</i> Polyvinylidene difluoride (PVDF) is made by combining vinylidene difluoride monomers; ethylene chlorotrifluoroethylene (ECTFE) is made from ethylene and chlorotrifluoroethylene (CTFE); ethylene tetrafluoroethylene (ETFE) is produced from ethylene and tetrafluoroethylene (TFE); polyether ether ketone (PEEK) is produced from difluorobenzophenone and disodium hydroquinone; perfluorinated alkoxy alkane (PFA; shown as perfluorinated ethoxy) is made from TFE and perfluorinated vinyl ether; and fluorinated ethylene propylene (FEP) is produced from TFE and hexafluoropropylene (HFP).</p>
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For crystalline regions, PVDF is unusual in that it exhibits at least four well-defined crystalline conformations [8, 9]. Each of these forms has significant effects upon the behavior of PVDF. Form I, also known as PVDF β , is perhaps the simplest to visualize and understand. This form is similar to the common zig-zag pattern of an idealized aliphatic hydrocarbon (**Fig. 6A and B**) [10]. In PVDF β , the fluorine and hydrogen atoms along the C–C backbone lie approximately on opposite sides of one another; this conformation is referred to as all *trans* (**Fig. 6A and B**). PVDF β is also polar because of the electron-withdrawing ability of the fluorine atoms which are all on one side of the polymer chain opposite to the hydrogen atoms [11]. Due to its polar nature, PVDF β exhibits piezo- and ferroelectric properties which have made it the subject of much study [12].

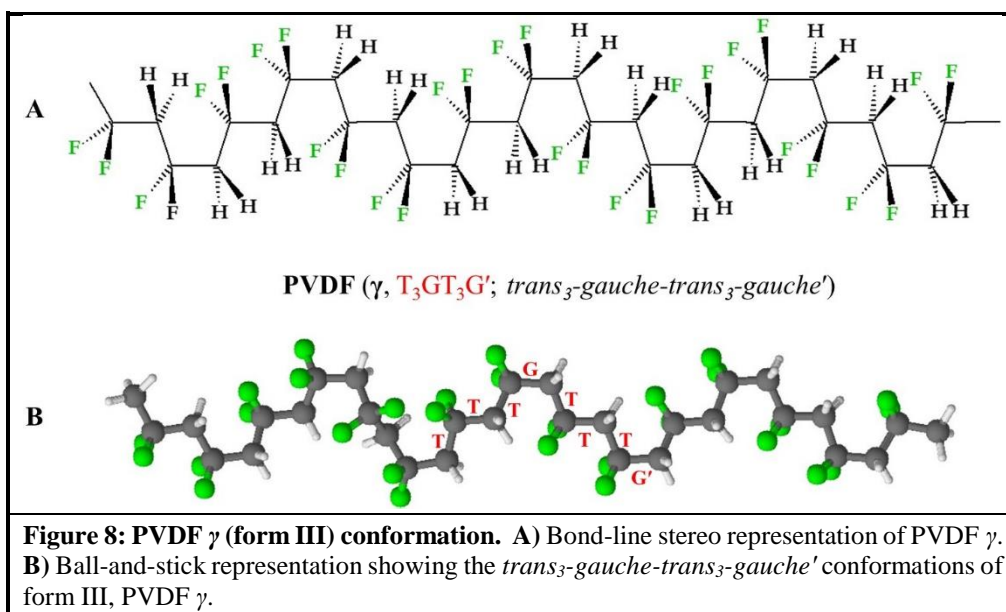
Form II, or PVDF α , exhibits an antiparallel conformation along its carbon backbone [11]. This

arrangement places the electron-dense fluorine atoms – which repulse one another – at a greater distance from each other than in the β phase (**Fig. 7A**). Consequently, the α phase of PVDF is the most stable and the one that forms during normal cooling and crystallization from the melt phase; it is the most common phase of PVDF [13]. The α phase of PVDF is also non-polar: While each C–F bond possesses a significant dipole moment, they are cancelled out by the antiparallel arrangement of the α phase conformer and its chain arrangement within the crystal [14]. PVDF α exhibits a *trans-gauche-trans-gauche'* (TGTG') conformation along its C–C backbone (**Fig. 7B**) [14–16]. In the α phase, each *gauche* conformation along the PVDF chain is twisted in a direction opposite the *gauche* conformation preceding it. In three dimensions, α PVDF thus exhibits a pattern twist-bend which affects how α PVDF crystallizes [17].

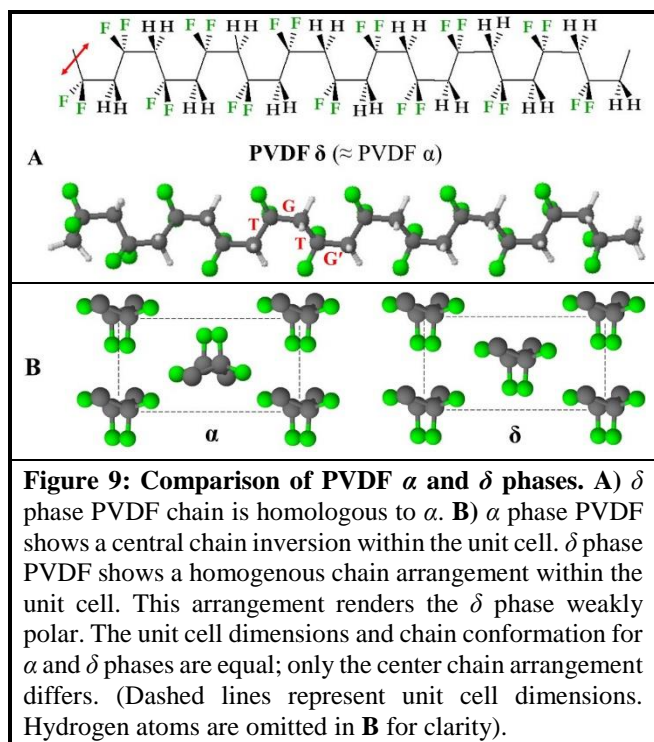


PVDF form III, or γ phase, exhibits a variation on the α conformational arrangement. PVDF γ has a rotation at every fifth carbon along the C–C backbone and shows three *trans* conformations followed by a *gauche* conformation, or T₃GT₃G' arrangement [13] (**Fig. 8A**). Similar to the α phase, the *gauche* conformations of γ

PVDF are turned opposite one another in three dimensional space. Compared in a side-by-side manner, γ phase PVDF could be viewed as somewhere intermediate between the α and β phases. Similar to β , γ PVDF also exhibits ferroelectric properties but are weaker than those in β [13].



Form IV is the δ phase of PVDF. This form is similar to α but exhibits different chain packing within the crystalline regions (**Fig. 9**) [14, 18-20]. δ PVDF polymer chains have the same conformation as α PVDF, and their unit cell dimensions within the crystal are the same. Within a five chain arrangement of δ PVDF, however, the innermost chain is inverted compared to α PVDF (**Fig. 9**). Recall that the α phase of PVDF is non-polar. The chain inversion of δ PVDF causes this crystalline phase to be weakly polar. Thus, δ PVDF is also known as α_p (polar) and it exhibits piezoelectric properties.



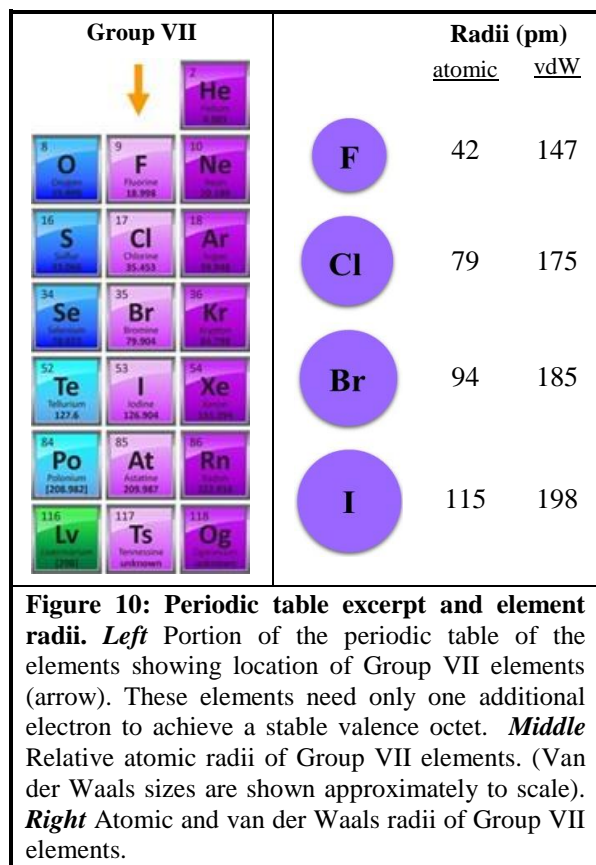
PVDF is an especially good example of how an apparent simple structure represented in two dimensions can mask critical attributes (**Fig. 5 Bottom**). The simple structure of PVDF, consisting of linearly arranged $-\text{CF}_2-\text{CH}_2-$ repeats, does not suggest its multiple solid state conformations. These varied phases of PVDF are the source of many highly significant features, and it is these features that produce such interesting and useful properties. Furthermore, of the multiple phases of PVDF,

the α phase is the most common and is the only non-polar phase. Such factors as these are not intuitive and illustrate the many considerations necessary when exploring polymer options whether for monofilament, drawn fiber, or other pivotal uses. [Note that further reference to PVDF will be with respect to the α phase (form II) only as it is the most relevant to a discussion of melt extrusion and drawn fiber uses].

FLUOROPOLYMERS AND AN OUTLINE OF FLUORINE CHEMISTRY

Many of the products that Zeus specializes in are produced from fluoropolymers. Zeus' drawn fiber is no exception. Since the first fluoropolymer was commercialized in the 1940's, these materials have become widely used in industries spanning aerospace to pharmaceutical. Manufacturers and consumers took notice of the unique properties conveyed to materials which included carbon-fluorine bonds [21]. Properties such as chemical and thermal resistance, low-friction and beneficial electrical attributes, and toughness all seemed to be improved compared to earlier generations of commercial polymer materials. But what is it about the inclusion of fluorine that leads to such material benefits? Why fluorine over every other element?

The nature of the carbon-fluorine bond lies at the heart of the marked properties of fluoropolymers. Fluorine is a Group VII element (**Fig. 10**). These elements need only one electron to attain an especially stable outer, or *valence*, shell electron configuration of eight. These eight electrons are known as an *octet*. Groups VII elements thus have an inherently strong tendency to gain an additional electron. This tendency to attract electrons is called *electronegativity*. Fluorine has the highest electronegativity of any element [22, 23]. Fluorine's high electronegativity is due in large part to its very small size, 42 pm (atomic radius) (**Fig. 10**) [24]. Thus, the electrons of fluorine are held much closer to its nucleus compared to other atoms, including other Group VII elements.



Group VII elements may gain an eighth electron in one of two ways. They may share an electron from another atom creating a bond with that atom or they may gain an electron without bonding and become a negatively charged ion. In fluoropolymers like PVDF, the small size fluorine together with its high electronegativity means that it forms very strong – and short – bonds, including those with carbon (**Fig. 11a**). Together with carbon's moderate electronegativity, the C–F bond distance of 135 pm is the second shortest in organic chemistry [25]. The result of such combined forces is that C–F bonds are highly stable and not prone to react with other atoms [26].

A second aspect of how fluorine contributes to the preferred qualities of fluoropolymers lies in fluorine's non-bonded electrons. When bonding to carbon (such as in fluoropolymers), fluorine is surrounded by six non-bonded – and very closely held and negatively charged – electrons, or three *lone pairs* (**Fig. 11b**). For Group VII halogens, these lone pair electrons are very stable paired but can form bonds with other atoms and are typically very good hydrogen bond (H-bond) acceptors [27]. However, unlike other halogens, the high electronegativity of fluorine

results in fluorine being a poor H-bond acceptor, and its lone pair electrons are highly unreactive [26, 27]. For fluoropolymers, these short, strong, and *unreactive* C–F bonds together with fluorine's unreactive valence shell electrons explain much of the chemical resistance observed in these materials.

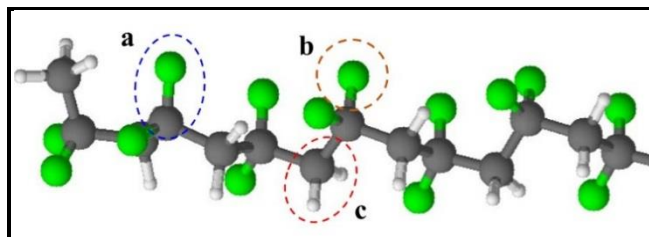


Figure 11: PVDF and fluoropolymers. *a*) C–F bonds are very strong and are the second shortest in organic chemistry. *b*) The three lone pairs of valence electrons of fluorine are very tightly held and are very unreactive even to hydrogen for H-bonding. *c*) The very small size of hydrogen allows it to approach much more closely to carbon than other atoms when bonding. Thus, C–H bonds are also very short, strong, and largely unreactive.

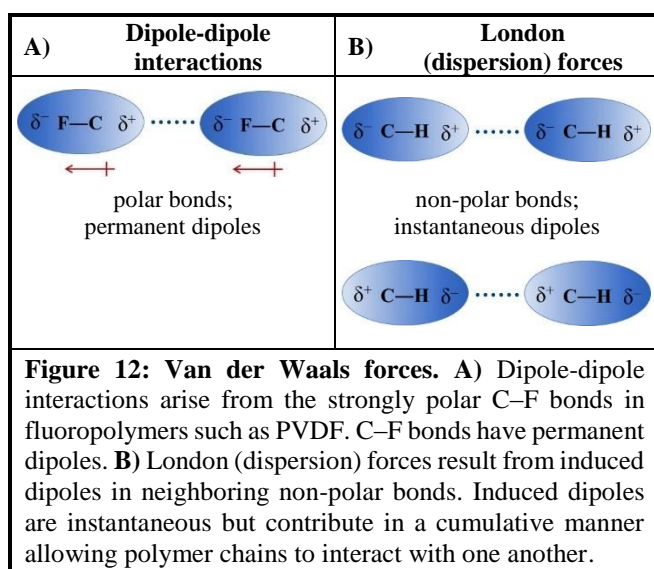
ZEUS DRAWN FIBER POLYMERS AND INTERACTIONS: FLUOROPOLYMERS

Another important theme common among the polymers to be described here (PVDF, PFA, FEP, ETFE, ECTFE, and PEEK) is not related to C–F bonds but to C–H bonds. Carbon possesses moderate electronegativity, 2.5 Paulings compared to 4.0 of fluorine, and hydrogen, too, possesses moderate electronegativity at 2.1 [22]. More importantly, however, is hydrogen's extremely small size, 53 pm (atomic radii) [24]. This very small size of hydrogen allows it to more closely approach carbon in a C–H bond. The result is an extremely short bond distance of 109 pm (**Fig. 11c**). Much like the C–F bonds, C–H bonds are also very strong (though not as strong as C–F) [28]. The C–H bond is essentially non-polar, non-acidic, and highly unreactive [28]. All of the polymers listed above contain C–H bonds, and all but PEEK contain C–F bonds. C–H and C–F bonds together account for much of the chemical reactivity for which many of these materials are known.

CHAIN INTERACTIONS

Having so many unreactive bonds, what holds polymers such as PVDF together? Why do the polymer

chains not simply fall away from each other? The answer once again can be found in their chemical bonds. Recall that electronegativity plays a fundamental role in attracting electrons towards an atom. Different atoms possess different degrees or strengths of attraction for electrons. When electrons are shared by atoms of different types to form a chemical bond, such as in C–F bonds, electrons are more strongly held by the atom with the higher electronegativity. This unequal sharing of electrons results in a permanent positive and negative pole – or *dipole* – of the bond though the electrons are still shared between the two bonding atoms. C–F bonds are strongly polarized towards the highly electronegative fluorine atoms. These polar bonds attract the opposite poles of adjacent or nearby dipoles of other molecules (**Fig. 12A**). Such dipole-dipole interactions are called van der Waals (vdW) forces [28]. For PVDF, vdW attractive forces are the primary forces that allow its polymer chains to interact with each other resulting from its many strongly polar C–F bonds (**Fig. 13**).



In the case of bonding atoms with similar or equal electronegativities, electrons are more evenly shared resulting in non-polar bonds. For these kinds of bonds, there are additional attractive forces stemming from momentary or instantaneous dipoles of the bonds. These attractive forces are a sub-category of vdW forces called *London* or *dispersion* forces [29]. In non-polar bonds such

as C–H bonds, the electrons oscillate between the two bonded atoms in a more or less equally shared manner. However, at any given instant, electrons may be more closely associated with one atom or the other which can be viewed as an instantaneous dipole. In this regard, this transient or fleeting dipole can induce a dipole, or push (repulse) electron density away, in a neighboring non-polar but polarizable bond. Such instantaneous dipoles, much like polar bonds, result in attractive forces between opposite poles of neighboring bonds albeit in a more transitory manner (**Fig. 12B**). London forces, thus, are the kinds of chain interactions present in simple hydrocarbons such as octane or polymers such as polyethylene which contain only non-polar C–H bonds. Van der Waals forces are distance dependent and are the weakest intermolecular forces. However, extended over long polymer chains, they have a cumulative effect which can be significant. These attractive forces (London and dipole-dipole) affect how easily or poorly the polymer chains can move or slip past one another (in the solid as well as melt phase) which determines mechanical and physical properties of the polymer material (**Fig. 13**) [1, 30, 31].

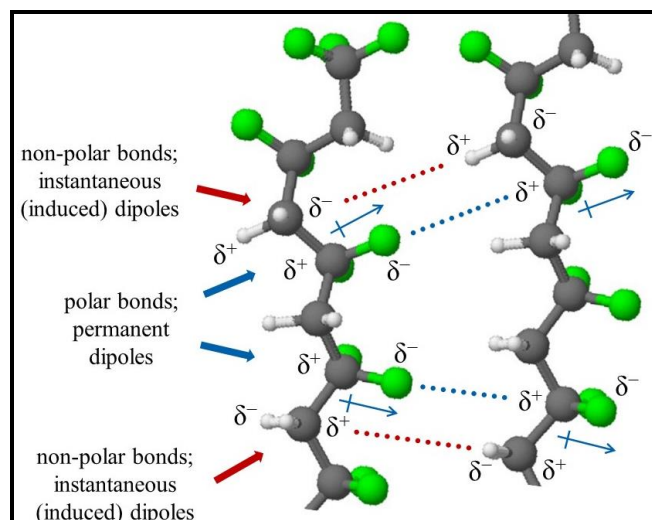


Figure 13: Van der Waals forces in polymer chains. Amorphous (random) conformation of PVDF showing chain interactions. C–F bonds possess permanent dipoles and attract opposite poles of nearby dipoles (blue). London forces result from induced dipoles created by oscillating and more equally shared electrons of C–H bonds (red).

CHEMICAL PROPERTIES – A FOREWORD TO MECHANICAL ATTRIBUTES

PVDF – Taking PVDF once again as a representative fluoropolymer, much of its behavior can now be more easily explained. Aside from its carbon backbone, PVDF contains only very unreactive C–F and C–H bonds which are both short and strong. PVDF, therefore, is not prone to react chemically with most substances, including water. This characteristic translates into excellent chemical resistance for PVDF and very low water absorption (**Table 2**). The C–C bonds of the PVDF chain are fully bonded. They are less accessible, however, within the PVDF chain. Thus, they too are poorly reactive (**Fig. 14**). Secondly, PVDF has both dipole-dipole interactions and London forces regarding PVDF chain interactions with each other. These forces contribute to PVDF chains' ability to “stick together” resulting in increased tensile strength (**Table 2**). PVDF thus demonstrates how key features at the chemical level translate into observable polymer behavior.

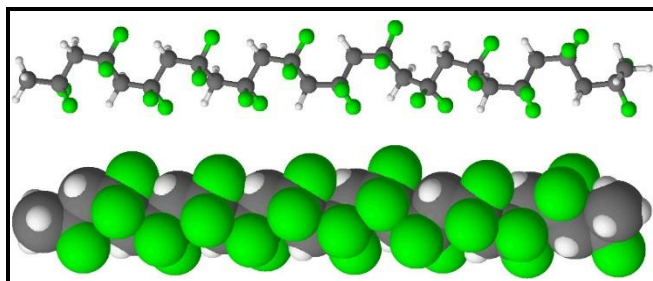


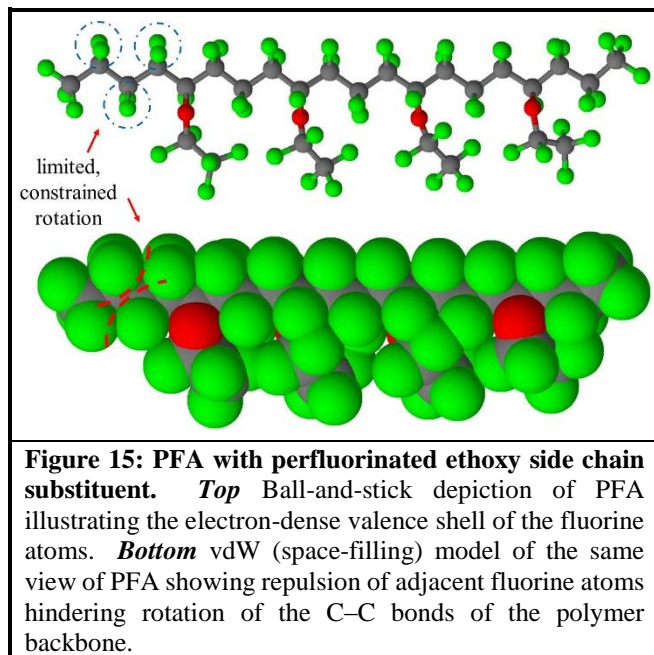
Figure 14: Two models of α phase PVDF. *Top* Ball-and-stick model of α phase (form II) PVDF showing bonding and arrangements of atoms in space. *Bottom* Van der Waals (space-filling) model of the same configuration. PVDF contains only unreactive C–F and C–H bonds, and its carbon atoms are less accessible for reactivity under most circumstances.

Electrical properties are also reflected by the kinds of bonds in PVDF. Although approximately half of PVDF is composed of strongly polar C–F bonds, fluorine's high electronegativity makes C–F bonds very difficult to move or change their electron distribution in an electric field. On the other hand, for the remainder of the PVDF chain, the C–H bonds are polarizable leading to a comparatively high dielectric constant of PVDF of 5.0 (**Table 2**). Compare this

to the dielectric constant for the perfluorinated PTFE, 2.1, with no C–H bonds [32]. From this aspect, the importance of bonding to more than merely mechanical attributes is also apparent.

Also stemming from PVDF's chemical features is its coefficient of friction. PVDF contains many fluorine atoms on its outer chain surface. Each of these fluorine atoms has three lone pairs of very tightly held and unreactive outer (valence) shell electrons. This aspect gives PVDF a certain degree of “non-stick” quality because of the poor potential for its valence electrons to react with other substances. PVDF's C–H bonds – though largely unreactive – do represent the potential for activity under certain conditions. As a vdW depiction illustrates, however, these hydrogen atoms are somewhat minimally exposed for reactivity when not terminal on the PVDF chain (**Fig. 14**). While also contributing to its excellent chemical resistance, these aspects of PVDF play a role in its moderately low coefficient of friction of 0.18 (**Table 2**). Comparing again to PTFE with its fully fluorinated structure, PTFE exhibits among the lowest coefficients of friction at 0.02.

PFA – Perfluoroalkoxy (perfluorinated alkoxy alkanes), or PFA, is a copolymer of tetrafluoroethylene (TFE) and a perfluorinated vinyl ether (**Table 1**). The monomers of PFA are not always in a 1:1 ratio, however. The perfluorinated alkoxy substituent is variable regarding the number of carbons on this side chain, thus it is most generically referred to as PFA. (When the perfluorinated alkoxy substituent is methoxy, this fluoropolymer is referred to as MFA). Notably, this popular polymer is most frequently produced with a perfluorinated ethoxy substituent (**Fig. 15**) [33]. PFA is similar to PTFE and PVDF (**Table 1**). The addition of a fluorinated alkoxy substituent to the main chain lowers the polymer's melting temperature from 335 °C (635 °F) for pure PTFE to 310 °C (590 °F) for PFA. This modification brings PFA into the melt-processable realm which translates into easier processing and lower production cost [34]. The alkoxy substituent can be on either side of the C–C backbone of the main polymer chain. This somewhat randomized placement of the perfluorinated alkoxy group reduces PFA's ability for close-packing of the chains. Thus, PFA exhibits less crystallinity (~60%) than the fully fluorinated PTFE which can exceed 90% (**Table 2**).

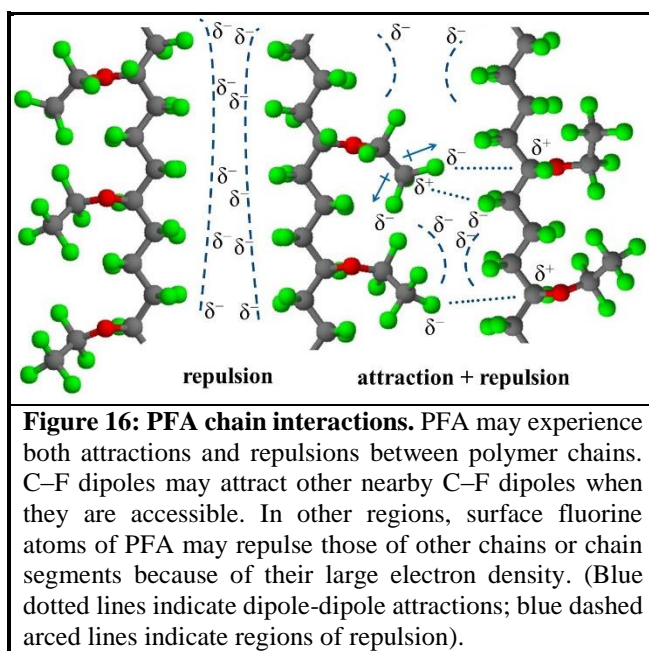


PFA also has what seems to be many rotatable single bonds along its C–C backbone (**Fig. 15 Top**). However, the large (negatively charged) electron density surrounding the fluorine atoms causes them to repulse one another [26]. Therefore, these C–C bonds (that are also bonded to fluorine atoms) cannot freely rotate. Forcing rotation of these single bonds would bring the fluorine atoms closer to one another – a highly unfavorable energy state. A vdW representation shows that the rotational limit imposed by the fluorine atoms of PFA extends throughout the polymer chain (**Fig. 15 Bottom**). Thus, PFA exhibits a relatively stable conformation as it cools from its melt state. Additionally, crystallinity is favored for chain segments that do not contain the bulky perfluorinated alkoxy substituent (**Table 2**) [35].

For chemical reactivity, PFA, too possesses many unreactive C–F and C–H bonds. Only oxygen remains as a potentially reactive site. In PFA, the oxygen is sp^3 hybridized and has two lone pair (non-bonded) electrons. Unlike those of fluorine, with its very high electronegativity, the lone pair electrons of oxygen are not as closely held. As a consequence, the lone pair electrons of oxygen are good H-bond acceptors and are somewhat basic on the Brønsted-Lowry spectrum. Thus, they may react – or interact – with some hydrogen-containing compounds. Mitigating this reactivity is the fact that the lone pair electrons of oxygen are not as freely accessible within the overall PFA polymer chain as a vdW

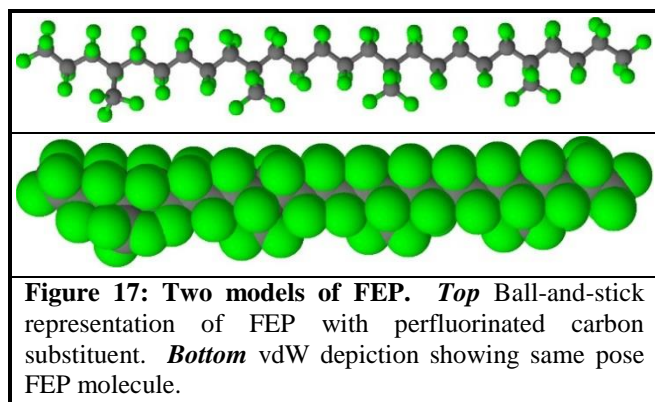
representation shows (**Fig. 15 Bottom**). Partly due to this inaccessibility, ether oxygens like those of PFA are typically not a very reactive species. Blocked by the sterics of the polymer chain, the oxygens of PFA are even less reactive than other small molecule ethers. Because of its unreactive C–F and C–H bonds and its poorly accessible oxygen lone pairs, PFA exhibits excellent chemical resistance – perhaps even superior to PVDF – and low water absorption.

PFA’s chain interactions can be explained by a closer examination of its polymer chain structure. PFA is mostly encapsulated by a “sheath” of unreactive fluorine atoms. PFA does possess vdW (dipole-dipole) attractions through its many polar C–F bonds. Alternatively, because of the large electron density surrounding the fluorine atoms, PFA chains also repel one another (**Fig. 16**). At any instant, some level of attractive dipole-dipole interactions occurs simultaneous while repulsion occurs at other places along and among the polymer chains. This is the nature of vdW forces in homologous polymers and bonds. (The C–O bonds are largely non-polar because of their opposing C–O–C structure and London forces are negligible for these bonds). PFA’s unreactive surface also contributes to its low coefficient of friction owing to lower interfacial forces (like PTFE) [35]. These aspects are also reflected in PFA’s significantly lower tensile strength because the polymer chains do not interact strongly with themselves compared to PVDF (**Table 2**).



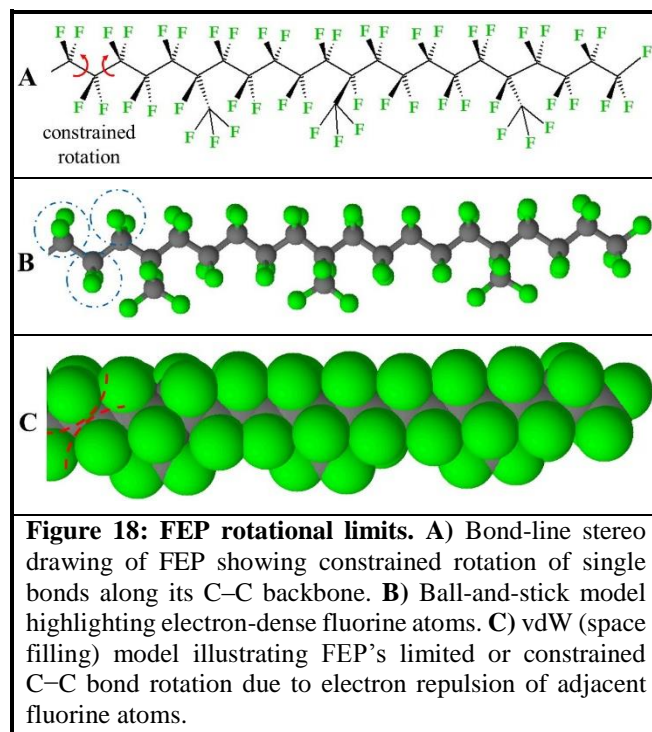
PFA's bonds also inform its dielectric behavior. PFA's dielectrics can best be attributed to its many C–F bonds and the strong electron-withdrawing power of fluorine. This phenomenon makes C–F bonds difficult to polarize further. Additionally, while individual C–O bonds may be slightly polar, the carbons on either side of the oxygen create a net dipole approaching zero. In this arrangement, these C–O bonds are difficult to polarize in an electric field. PFA thus exhibits comparatively low dielectric strength (**Table 2**).

FEP – Fluorinated ethylene propylene, or FEP, is synthesized from tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) via a radical reaction (**Table 1**). Incorporation of the HFP monomer reduces the melting point of PTFE from 335 °C (635 °F) to 260 °C (500 °F) for FEP with few negative effects [36]. As with PFA, with lower melting temperature usually comes easier processing and lower cost. The TFE and HFP monomers are also not in a 1:1 ratio. FEP chains typically contain about 5-20% HFP [37]. Similar to PFA, the perfluorinated (–CF₃) groups can be on either side of the polymer chain (**Fig. 17**). FEP is nearly totally fluorinated and is comprised almost entirely of unreactive C–F bonds. Thus, it is not surprising that FEP bears many similar properties to PTFE – and even PVDF and PFA (**Table 2**).



Like PFA (and PTFE), the single bonds of FEP cannot freely rotate because of the steric and electron repulsion of the vicinal fluorine atoms (**Fig. 18**). Consequently, FEP can adopt limited conformations in its solid state and may even include helical stretches similar to PTFE for regions that do not contain the –CF₃ substituent [38]. Compared to the perfluorinated alkoxy substituent of PFA (–OCF₂CF₃ in the example) or even of MFA (–OCF₃), the –CF₃ of FEP

is smaller allowing more close packing of the polymer chains supporting greater crystallinity (**Table 2**). FEP's conformational limits, especially apparent in a vdW representation, partly account for its crystallinity and therefore many of its final properties.



FEP's reactivity is largely the result of its protective “sheath” of unreactive fluorine atoms on its surface. This, too, gives FEP many attributes similar to PTFE. Furthermore, because the substituent on the main polymer chain is a perfluorinated carbon rather than an oxygen as in PFA, FEP is far less likely to react with hydrogen-containing compounds – including water (**Table 2**). FEP's water absorption is extremely low at ~0.004 %. FEP, perhaps as expected, shows excellent chemical resistance (**Table 2**).

FEP's chain interactions are also similar to PFA. However, without the oxygen and its lone pairs as in PFA, FEP exhibits almost exclusively dipole-dipole interactions from its C–F bonds. The chains of FEP may experience attractive forces in a manner similar to PFA from transiently accessible nearby dipoles. On the other hand and similar to PFA, repulsive forces dominate FEP chain interactions. With no C–H bonds and concomitant London forces to mitigate the repelling forces of the fluorine atoms,

FEP shows lower tensile strength compared to PFA and even more so than PVDF (**Table 2**).

ETFE – Ethylene tetrafluoroethylene, or ETFE, is a copolymer made from polyethylene and tetrafluoroethylene monomers (**Table 1**) [39, 40]. As may be expected, ETFE has attributes that combine those of PTFE and PE in their respective proportions. Unlike PTFE and FEP, ETFE does have rotatable bonds – an important contributing feature to its properties. The C–C bonds of the ethylene (–CH₂–CH₂–) groups which contain only vicinal hydrogen atoms and those C–C bonds adjacent to C–F bonds are the most easily rotatable (**Fig. 19**). As seen in other fluoropolymers, the C–C bonds of adjacent –CF₂ groups are not as easily rotated. ETFE thus can adopt multiple configurations in its amorphous and melt phases which affect attributes such as chain packing and crystallinity (**Fig. 20**).

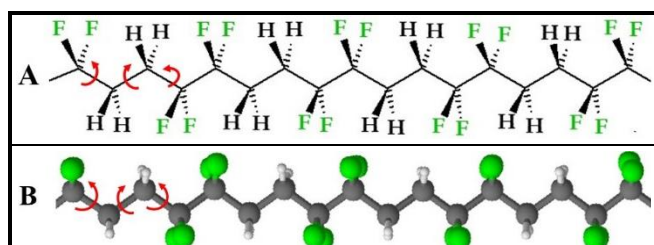


Figure 19: ETFE and rotatable bonds. A) Bond-line stereo and B) ball-and-stick representations showing rotatable bonds of ETFE. C–C bonds of adjacent –CH₂ groups and C–C bonds connecting –CH and –CF groups are the most easily rotatable in ETFE. C–C bonds with vicinal fluorine atoms are constrained from rotation.

The chemical reactivity of ETFE by now is probably becoming more clear. ETFE has many short and unreactive C–F and C–H bonds, and the valence electrons of fluorine are also very unreactive. However, the hydrogen atoms of ETFE are somewhat more accessible than in the polymers described thus far. Furthermore, the carbon atoms themselves may also be somewhat more chemically accessible by the bent nature of ETFE and its chain flexibility (**Figure 20**). These two areas represent potential sites of chemical reactivity. Therefore, ETFE does not show the same degree of chemical resistance as PVDF, PFA, or FEP (**Table 2**). Working in its favor regarding chemical resistance are the non-polar C–H bonds of ETFE; these bonds greatly reduce ETFE's water absorption. Therefore, ETFE exhibits slightly inferior chemical

resistance compared to the polymers discussed so far and water absorption that is comparable to PFA (**Table 2**). These phenomena also affect ETFE's ability to react with other materials to which it comes into contact. Thus, ETFE also shows a slightly higher coefficient of friction.

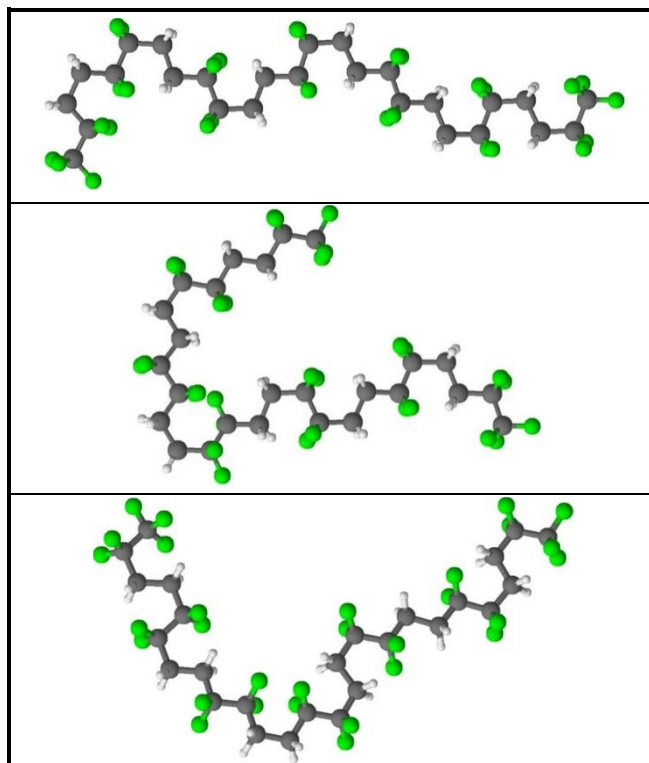


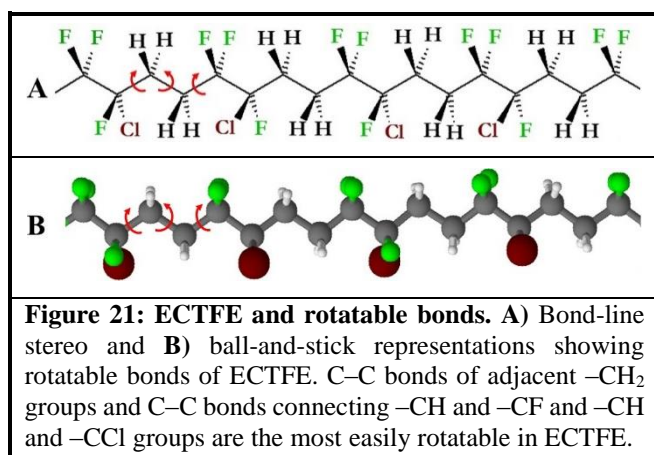
Figure 20: ETFE chain flexibility. ETFE's rotatable bonds result in considerable chain flexibility as illustrated by three representative conformational poses shown above. Although the bonds in ETFE themselves are poorly reactive, ETFE's chain flexibility exposes it to mildly increased potential for chemical reactivity.

ETFE chains exhibit significant vdW attractions. These chains have both dipole-dipole interactions from the permanent dipoles of the C–F bonds and London forces from induced dipoles in the non-polar C–H bonds (**Fig. 13**). With minimal repulsions and more extensive vdW attractions, the tensile strength of ETFE is noticeably greater compared to the almost completely fluorinated FEP (**Table 2**). In addition to affecting its chain interactions, the nature of ETFE's bonds affects its dielectrics. The C–H bonds of ETFE, while non-polar themselves, can be weakly polarized in an electric field. ETFE's dielectric constant is therefore slightly higher than the near fully fluorinated FEP (**Table 2**). From an overall view and of the

polymers described thus far, ETFE's bonding and resulting attributes places it between PFA and PVDF on the scale of fluoropolymer properties and performance.

ECTFE – Ethylene chlorotrifluoroethylene, or ECTFE, continues a variation on a theme: This polymer is made from polymerization of PE and chlorotrifluoroethylene (CTFE) via a radical reaction; it was among the first copolymers to incorporate ethylene units (**Table 1**) [41]. In ECTFE, one of the fluorine atoms of TFE has been substituted with a chlorine. Generally, in ECTFE the CTFE and PE monomers are not in a 1:1 ratio. However, newer synthesis methods have made this possible if required [34]. The chlorine in ECTFE may be on either side of the polymer chain similar to the perfluorinated alkoxy substituent of PFA. Also similar to several of the fluoropolymers described so far, the inclusion of chlorine allows ECTFE to be processed at a lower temperature [42]. The somewhat randomized incorporation of the CTFE monomer affects how ECTFE crystallizes and significantly affects its properties.

As a fluoropolymer, ECTFE has many features in common with PVDF, PFA, FEP, and others. ECTFE has multiple rotatable bonds and like the similar ETFE, these are the C–C bonds of the ethylene ($-\text{CH}_2-\text{CH}_2-$) groups and the C–C bonds joining $-\text{CH}-\text{CF}$ and $-\text{CH}-\text{CCl}$ groups (**Fig. 21**). Also similar to the polymers discussed so far, ECTFE is mostly composed of unreactive C–F and C–H bonds and unreactive valence electrons of the fluorine atoms – a common pattern of fluoropolymers. With the knowledge of these common features, many aspects of ECTFE's properties can now be inferred.

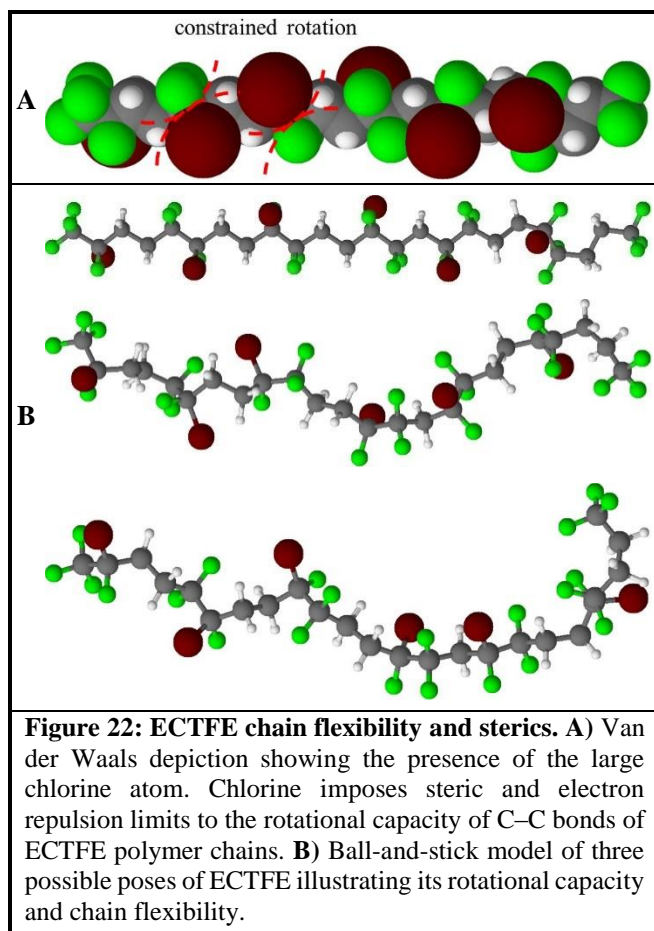


ECTFE's rotatable bonds make it capable of multiple configurations in a manner very similar to ETFE. This results in a moderately high degree of randomness which affects how the polymer will pack in its solid state. Most significant, perhaps, about ECTFE is its inclusion of chlorine. As with other previously described fluoropolymers, C–C bonds containing vicinal fluorine atoms are least capable of rotation because of the electron repulsion of the fluorine valence electrons. Exacerbating this limit further in ECTFE is the large size of chlorine, 79 pm – nearly double the atomic radii of fluorine (**Fig. 10**). This larger size of chlorine also results in its lower electronegativity compared to fluorine: 3.2 Paulings compared to 4, respectively [22, 23]. Chlorine adds a steric component in addition to the electron repulsion regarding the rotational limit of its C–C bonds (**Fig. 22A**). The overall result of replacing a fluorine atom with a chlorine in ECTFE is that it imposes more conformational limits upon the polymer chain. While still a moderately flexible polymer chain, ECTFE is not as flexible as PVDF or even ETFE (**Fig. 22B**).

Chemical reactivity is also different for ECTFE. Chlorine, like fluorine, is a Group VII element with three non-bonded lone pair electrons (**Fig. 10**). Chlorine, however, is larger and has lower electronegativity. Chlorine's valence electrons – those that are involved in bonding – therefore, are not held as strongly as those of fluorine and are susceptible to chemical reactivity. A vdW depiction of ECTFE helps to illustrate the comparatively exposed nature of chlorine due to its large vdW radius. As a result, the chlorine atoms of ECTFE are good H-bond acceptors unlike those of fluorine. This also means that ECTFE may interact with certain hydrogen-containing compounds including water. The consequence of these structural and chemical differences in ECTFE is a polymer with diminished chemical resistance and somewhat greater water absorption compared to ETFE, FEP, and PFA (**Table 2**).

Its chemical liabilities aside, the large chlorine atom of ECTFE also limits its chain packing and other physical features. Similar to ETFE, crystallinity in ECTFE is generally limited to approximately 50% (**Table 2**) [43]. This compares to the typically >90% crystallinity of PTFE, a very regular polymer with no bulky atoms such as chlorine or pendant side groups. Supporting the chain packing ability of ECTFE are its extensive attractive vdW

forces. Both the C–F and C–Cl bonds are polar and produce dipole-dipole interactions. London forces (induced dipoles) from the non-polar C–H bonds also contribute to ECTFE's chain interactions. For dielectric aspects, the predominating polar bonds of ECTFE are comparatively difficult to polarize in an electric field. This results in a dielectric constant similar to ETFE (**Table 2**).



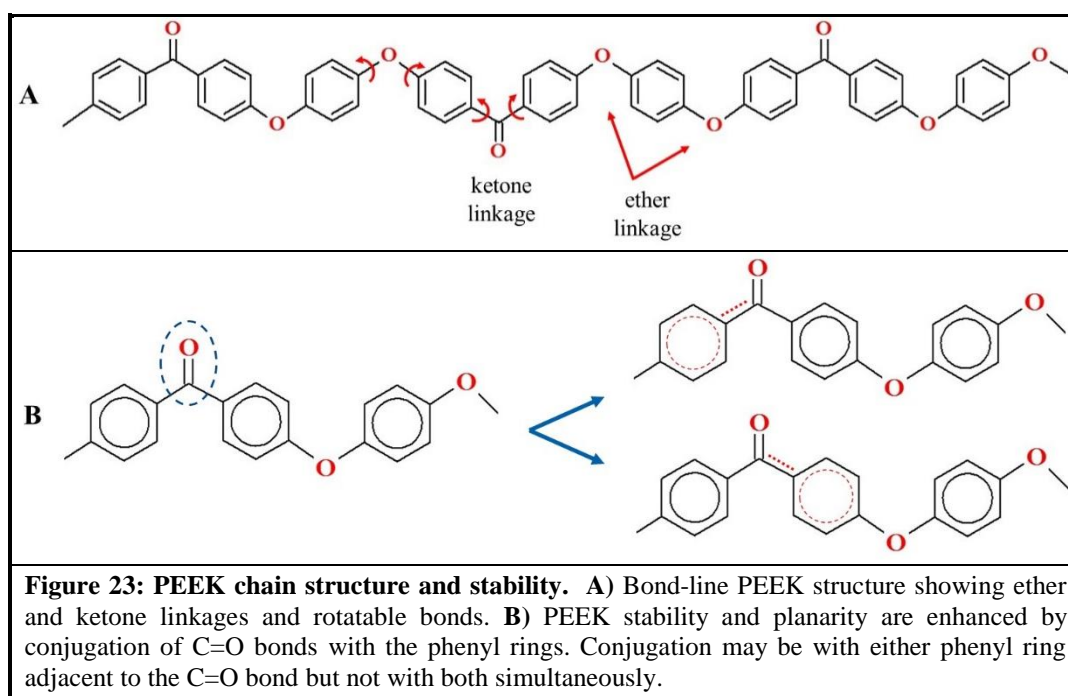
ZEUS DRAWN FIBER POLYMERS AND INTERACTIONS: PEEK

Thus far, the Zeus drawn fiber polymers discussed here have all been fluoropolymers. Collectively, they can be viewed as analogs of each other that fall between PE and PTFE. Through the addition or substitution of various atoms on the carbon backbone of these polymer chains,

properties can be directed to a certain extent to produce those that favor certain applications. With an understanding of some of the features of polymers such as PVDF, PFA, FEP, ETFE, and ECTFE, patterns emerge which can be used to estimate their properties. But what about polymers that do not share all of the features of fluoropolymers? Can a basic understanding of fluoropolymers be used to estimate properties of polymers that do not contain fluorine?

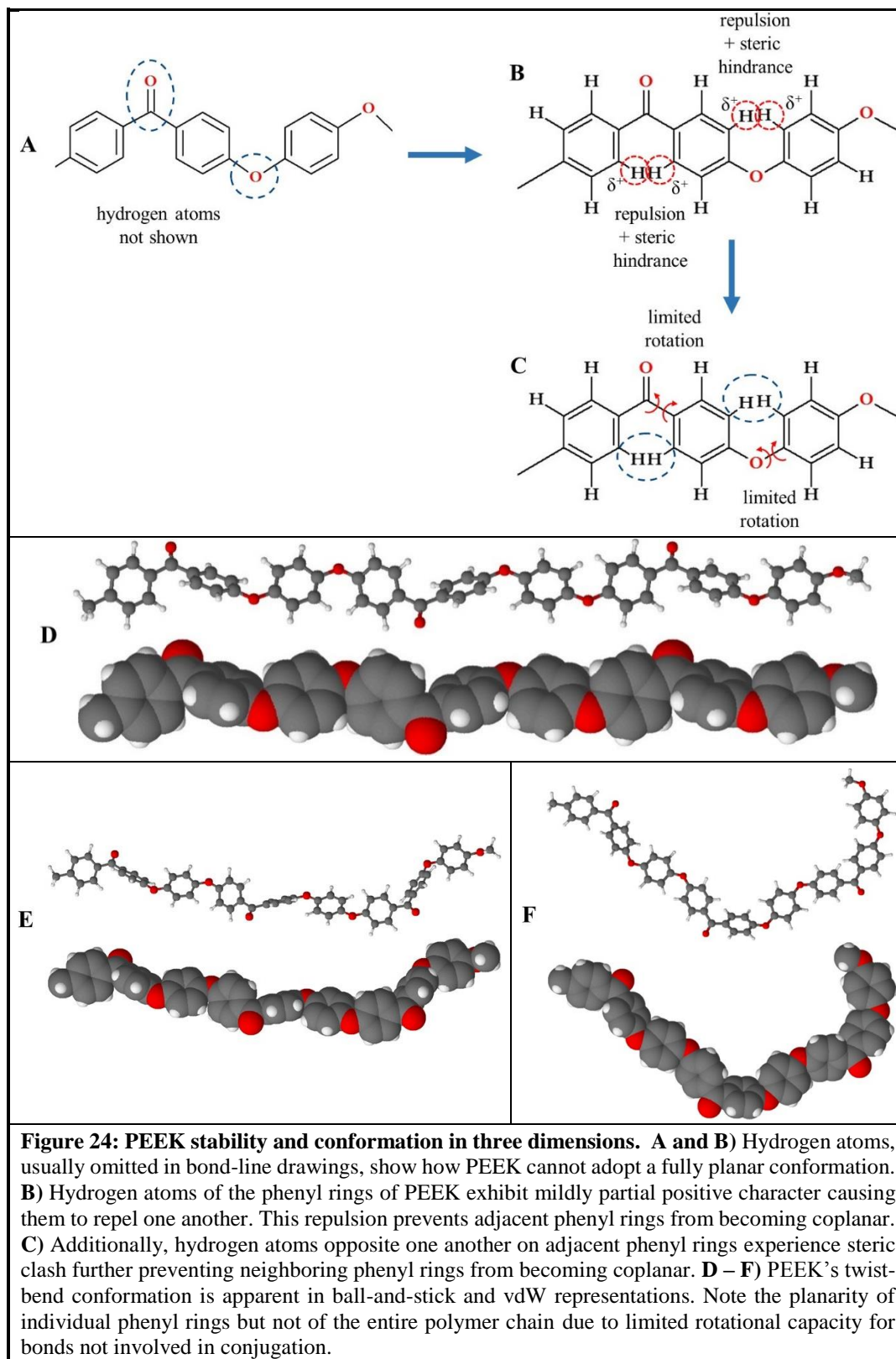
PEEK – Polyether ether ketone, or PEEK, will help answer this question. PEEK is perhaps one of the most popular non-fluorinated polymers. PEEK is synthesized from difluorobenzophenone and disodium hydroquinone (**Table 1**). However, PEEK itself does not contain fluorine. PEEK is composed of consecutive ether linkages separated by a ketone linkage joining phenyl rings. PEEK's incorporation of cyclic moieties (ring substituents) creates fundamentally different attributes compared to the fluoropolymers previously described.

First, the two-dimensional bond-line drawing might suggest that PEEK is planar. Despite the presence of planar ring moieties, PEEK is not planar but adopts twists based on the placement of the ether linkage oxygens (**Fig. 23A**). Like the single bonds of fluoropolymers, the single bonds of PEEK connecting the ether oxygens and ring moieties are rotatable. Secondly, the single bonds of the ketone linkages joining the phenyl rings may also be rotatable but with certain caveats. The C=O (carbonyl) double bonds of PEEK's ketone linkages can experience *conjugation* – an electron-sharing arrangement with nearby double bonds (**Fig. 23B**). In this case, those nearby double bonds are those of the ring substituents on either side of the C=O bond [44, 45]. In PEEK, conjugation allows the electrons of the C=O bonds and the phenyl ring to be shared across both of these features – a particularly stable arrangement. Conjugation may extend to either phenyl ring adjacent to the C=O ketone, but not to both. Conjugation increases the stability of the ketone and ring moieties and therefore of PEEK overall. Conjugation also results in increased planarity extending to encompass the C=O double bond that is involved in conjugation.



PEEK however, cannot adopt a fully planar conformation to include all of the phenyl rings. This limit is due to the hydrogen atoms on the phenyl rings (usually omitted in bond-line drawings) that lie opposite of the C=O bonds and ether oxygens (**Fig. 24A**). C–H bonds are usually taken as non-polar such as with the fluoropolymers described heretofore. On the other hand, in phenyl rings such as in PEEK and due to the unusual nature of its conjugated bonds, most of the electron density lies on the phenyl ring. These sp^2 hybridized carbon atoms of the phenyl rings bonded to hydrogen are very mildly polar towards carbon. The hydrogen atoms consequently take on a slight partial positive character causing them to repel one another (**Fig. 24B**). For the hydrogens opposite the C=O bond, those on the planar ring involved in conjugation with the C=O bond are coplanar with the ring. The hydrogen atom opposite the C=O on the ring not involved in

conjugation is repelled by the hydrogen opposite it. This condition causes the ring not conjugated with the C=O to dip either below or above the plane of the conjugated C=O and phenyl ring. This repulsion creates a twist in PEEK at these positions (**Fig. 24C**). The hydrogen atoms opposite the ether oxygen experience a similar phenomenon preventing those phenyl rings also from being coplanar (**Fig. 24C**). Compounding the repulsion aspects of these hydrogen atoms, these opposing atoms experience a steric clash merely from their too near positioning. These C–H bond distances plus the hydrogen vdW radii distance overlaps with the space occupied by the opposing hydrogen. Collectively, these features impede rotation of the single bonds connecting the phenyl rings of the ketone and ether linkages causing PEEK to adopt a twist-bend shape (**Fig. 24D**).



In light of PEEK's unique structure compared to the fluoropolymers discussed earlier, several facets are apparent that help explain PEEK's reactivity. Like fluoropolymers, PEEK has many short and stable C–H bonds (though they are mildly polar). Supporting PEEK's chemical resistance are its many phenyl rings comprised of conjugated C=C bonds. Conjugated bonds such as these are exceptionally stable and unreactive [46]. A vdW depiction of PEEK may suggest that its oxygen atoms are somewhat accessible for chemical reactivity. The C=O oxygens of PEEK are sp^2 hybridized and contain two sets of non-bonded lone pair electrons. Therefore, they are H-bond acceptors and may interact with other hydrogen-containing compounds including water. However, these C=O oxygen atoms are part of the very stable conjugated system with the phenyl rings making them much less prone to chemical reactivity [46]. On the other hand, the ether (C–O) oxygens, similar to PFA, are sp^3 hybridized and contain two sets of lone pair electrons (H-bond acceptors) also making them somewhat susceptible to reactivity with hydrogen. Not surprisingly, PEEK shows the highest water absorption of the polymers described here (**Table 2**). The vdW depiction of PEEK, however, suggests that further reactivity at these C–O oxygen atoms is mitigated by neighboring groups of atoms (bonded to the oxygen) which partially block access to these oxygens (**Fig. 24**). PEEK, hence, possesses very good chemical resistance but not as good as PFA or FEP (**Table 2**). PEEK's bonding also contributes to its low dielectric constant. PEEK's mildly polar C–H bonds mitigate a low dielectric constant while their opposing directionality creates a cancellation of a net dipole. This results in a dielectric constant of PEEK comparable to ETFE and ECTFE (**Table 2**). PEEK emphasizes the effects of phenyl rings and stability of conjugated systems upon polymer chain conformation and the resulting properties.

PART III: DRAWN FIBER MECHANICAL PROPERTIES

Zeus' drawn fiber can be produced from many different polymer resins, six of which have been discussed here in

some detail. These carbon chain backbone molecules, made from joining constituent monomers, form long-chain molecules sometimes extending hundreds of carbons long. In this polymeric form, properties are greatly altered from those of the monomers or even from shorter-chain homologs. This multiplicity of polymer formation along with their chemical structure forms the underpinning governing polymer properties. Attributes such as crystallinity, molecular weight, chain length, and simple-vs-complex structure become the basis for the final material properties observed at the macro level. Such fundamentals provide a framework, derived from the chemical aspects, to explain properties of the polymers described here and used to produce high performance drawn fiber monofilament.

CHAIN LENGTH

Polymer chain length is a principal feature of these molecules. Chain length is the result of consecutive addition of monomers until the synthesis process is halted. Polymer chain length generally can be controlled during synthesis by duration, concentration of monomers, and with the addition of reagents to terminate the synthetic process [47]. The synthetic reaction likewise can be allowed to terminate on its own upon exhaustion of the monomer reactants. Polymer chain length provides a way of relating the average number of repeating units in the polymer. For carbon backbone polymers such as those described here, C₆₀ for example, indicates that the average polymer molecule chain length for the material is 60 carbons. Chain length, therefore, can be inferred by molecular weight (and vice versa). Larger molecular weight polymers have more repeating units (and thus higher molecular weight) than their lower molecular weight homologs (**Fig. 25**). Many commercial polymers are generally described in this way instead of indicating the number of carbons. Referring to its polymer mass, PEG 5000, as one example, indicates polyethylene glycol with an average molecular weight of 5000. Polymers such as these are not a uniform collection of identical molecular weights. They are a mixture with certain chain lengths predominating.

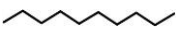
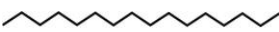
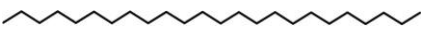
Polymer chain	Molecular formula and weight (MW)
	C ₁₀ H ₂₂ , 142
	C ₁₆ H ₃₄ , 226
	C ₂₄ H ₅₀ , 339

Figure 25: Relation of polymer chain length and molecular weight for the simple hydrocarbon polyethylene (PE). Molecular weight implicitly describes polymer chain length as molecular weight increases with addition of each $-C_2H_4$ monomer. For PE and similar carbon-backbone homologs, chain length is indicated by the number of carbon atoms shown in the molecular formula.

Polymer chain length is a crucial component of many of the polymer properties observed at the macro level. Chain length affects such fundamental properties as molecular weight, melt temperature, viscosity, and tensile strength [36]. These aspects distinguish polymers from small molecules. Longer chain polymers experience greater chain entanglement than their shorter chain homologs [48]. This greater entanglement contributes to greater chain-to-chain interaction facilitating increased vdW attractions. Together, these two factors support increased tensile strength [36] (**Fig. 26**). Long-chain polymers (with higher molecular weights) also require more energy to separate their polymer chains and shift the polymer mass from the solid to the melt phase. Long-chain polymers, therefore, exhibit higher melt temperatures, greater viscosity, and higher tensile strength than short-chain polymers with lower molecular weights.

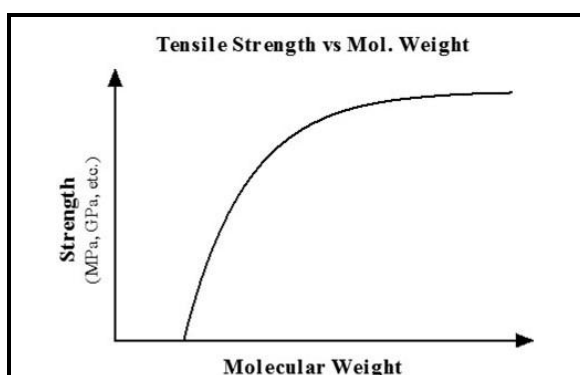


Figure 26: Relationship of molecular weight (MW) and tensile strength. Tensile strength increases with polymer MW until maximum chain interactions are attained relative to chain free ends.

CRYSTALLINITY

Crystallinity is another important feature of solid phase polymers. Crystallinity affects properties such as hardness, density, impact resistance, and melt temperature [36]. While not directly correlated with molecular weight, crystallinity is related to molecular weight and chain length. Most importantly, crystallinity is a function of the chemical topology of the molecular chain and conformational limitations stemming from its chemical features [49]. Chain flexibility, including rotational capacity along atom-atom bonds and vdW forces, affect the way polymer chains can arrange themselves *in situ* leading to crystal formation from the melt phase [50, 51]. Simple chemical structure and that with less branching of the polymer chains favors crystal formation [50]. Conversely, complex chain structures and bulky side groups reduce the capacity for crystal formation [50]. PVDF's multiple rotatable bonds, for example, have significant impact on the manner in which it crystallizes from its melt state. This feature is shown in part by PVDF's at least four distinct crystalline phases. PTFE molecules, on the other hand, are rigid and can be viewed similarly to a group of pencils; PTFE thus can achieve a very high degree of crystallinity (**Table 2**) [43]. This phenomenon is also born out when comparing other fluoropolymers. FEP, with its fairly uniform topology, supports a higher degree of crystallinity than ECTFE with its large chlorine atom or PEEK with its twist-bend shape [52]. In PFA, the bulky $-OCF_2CF_3$ side group reduces its crystallinity (**Table 2**) [33]. On the other hand, crystallinity is favored within sufficiently long chain segments that do not contain bulky side-groups such as the perfluorinated alkoxy substituent of PFA [47]. This aspect, too, highlights a means of influencing crystallinity by changing the percent of monomers that produce polymer chain side groups.

Crystallinity is not uniform. Crystallinity can range from entirely amorphous (no crystallinity) to greater than 95% for solid phase polymers, depending on the polymer (**Fig. 27**). Crystallinity is also affected by environmental factors such as heat and the energetics of the polymer molecular environment [50]. Slow cooling of the melt phase polymer can increase crystallinity while rapid cooling reduces potential crystal formation [30]. Additionally, the more closely associated crystalline phase molecules compared to amorphous phase molecules

require more energy to separate [47, 50]. Solid phase polymers such as polystyrene with a high amorphous (less crystalline) character have lower melt temperatures and hardness. In an opposite manner, polymers such as FEP or PTFE with greater crystalline (lower amorphous) character have higher melt temperatures and hardness.

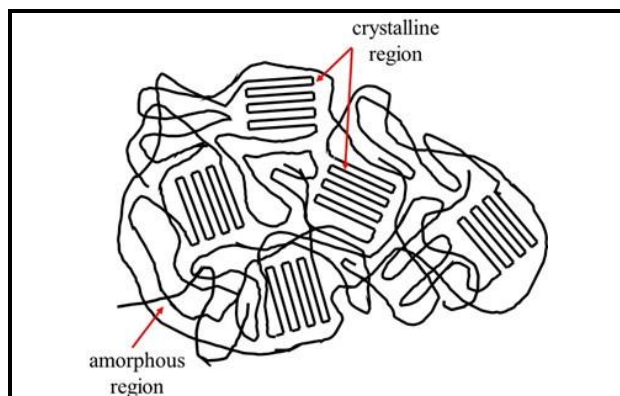


Figure 27: Depiction of crystalline and amorphous regions of a solid phase semi-crystalline polymer material. Amorphous regions are more disordered with randomly oriented polymer chains while crystalline areas are aligned in a regular and ordered arrangement.

GLASSY VS RUBBERY STATE

The extent of crystallinity of polymers is closely linked to the key polymer property of glass transition temperature, T_g . Solid phase polymers contain both crystalline and amorphous regions, and those molecules exist in different environments. Molecules in the amorphous region are highly constrained from movement but can vibrate to a small extent. This solid phase low temperature and restricted vibrational state of the polymer comprises the *glassy state* of the material and is only relevant to the amorphous region. Glassy state polymers show properties similar to crystals such as hardness, brittleness, and rigidity [50]. As the glassy state is heated, the polymer chains gain energy, become more mobile with increasing vibration, and gain in disorder. The polymer material then exhibits a *rubbery state* and takes on those properties that are most often associated with rubber. At this stage, the polymer still possesses amorphous and crystalline regions. The temperature range or zone at which the amorphous region becomes rubbery is known as the *glass transition temperature*, T_g , and this occurs *only for the amorphous region*.

For crystalline regions, their molecular chains are more closely packed. They are more ordered because of their regular (rather than random) arrangement within each crystal [47]. These polymer chains are even more restricted from movement than those in the solid state amorphous regions. Crystalline regions accordingly exhibit a melting point or temperature, T_m , where the solid phase turns to a liquid phase. Semi-crystalline polymers – polymer materials that possess amorphous and crystalline regions – exhibit both a T_g and a T_m . These two temperatures are fundamental characteristics of the polymer and help to establish its global properties and behavior [50].

(While there are other factors affecting polymer behavior, T_g , and T_m such as crosslinking of chains, pendant groups, and plasticizers, these shall not be discussed here, and this review will be concerned only with those characteristics with respect to the pure polymer).

Aside from mass, T_g can be viewed largely as the result of chain mobility. Factors which affect chain mobility must, therefore, affect T_g . Once again, chain length plays a vital role as more energy is required to energize – and mobilize – extended-chain molecules [36]. Chain length becomes less influential upon T_g , however, as chain length increases with proportionally fewer chain ends. T_g then becomes more a consequence of mere mass alone (**Fig. 28**) [53-55]. Other critical characteristics surrounding chain mobility, including chain flexibility (at the atom level) and chain interactions affect T_g [50]. Polymer chains with a high degree of chain flexibility can more easily be changed into a rubbery state from the glassy state [49]. This change or transition can occur with less input of energy – such as heat – for these more flexible molecules. Of the polymers described here, a general trend is apparent that as the fluorine content increases, chain flexibility decreases (PEEK notwithstanding) (**Table 1**) [21]. This point could be likewise be stated that as the hydrogen content increases, so does chain flexibility [21]. Chains that exhibit a high degree of attractive forces between them require more energy to be moved from the glassy to rubbery state [1, 49, 50]. Hence, chain flexibility, chain-chain interactions, and chain length play critical roles in determining T_g through their effects upon chain mobility.

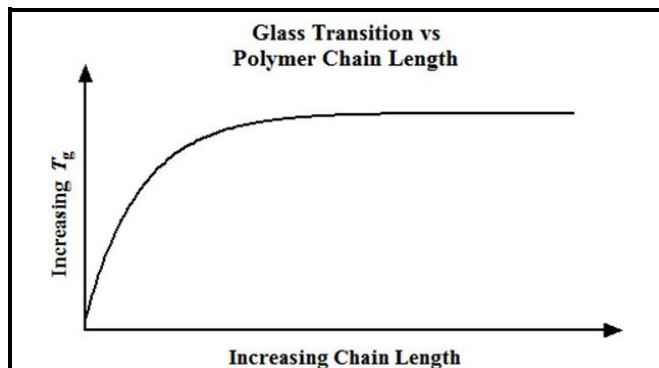


Figure 28: Relationship of glass transition temperature (T_g) and chain length. Effect of polymer chain mobility is seen in a graphical representation of T_g vs chain length. T_g increases with increasing polymer chain length but exerts less influence on T_g for very long or extended chains.

STRESS-STRAIN RELATIONSHIPS

The majority of polymer mechanical properties – and especially those of most popular interest – can be categorized under stress-strain relationships. These interconnections are unique for each material. Tensile strength, as a primary example, is of prime interest when discussing drawn fiber and other monofilament. In its simplest terms, tensile strength is the maximum force that a material can support without breaking. For a monofilament fiber, this force is applied in a linear (tension) direction and is accordingly distributed in cross section over the diameter of the fiber. Force applied through an area in this way is termed *stress*, σ (or mechanical stress), and expressed as force per unit of area: $\frac{F}{A}$. Stress applied to a material may cause the material to deform. Such deformation is defined as *strain*, ϵ . Mathematically, strain is the amount of deformation in the applied force direction divided by the initial length of the material (such as monofilament fiber). If the deformation of a material is measured in length: strain, $\epsilon = \frac{\text{change in length}}{\text{initial length}} = \frac{\Delta L}{L_0}$. Plotting stress vs strain graphically can be used to reveal several fundamental characteristics of the fiber. *Tensile strength* shows the applied stress upon fracture of the fiber (**Fig. 29**). *Yield strength*, on the other hand, shows the point where the linear elastic region of the stress-strain curve ends; this value illustrates where permanent deformation begins to occur (**Fig. 29**). Stress-strain relationships are a basic and convenient means to understand a material's behavior at the macro level.

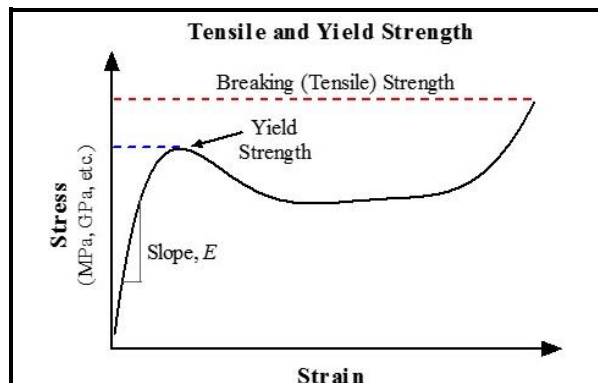
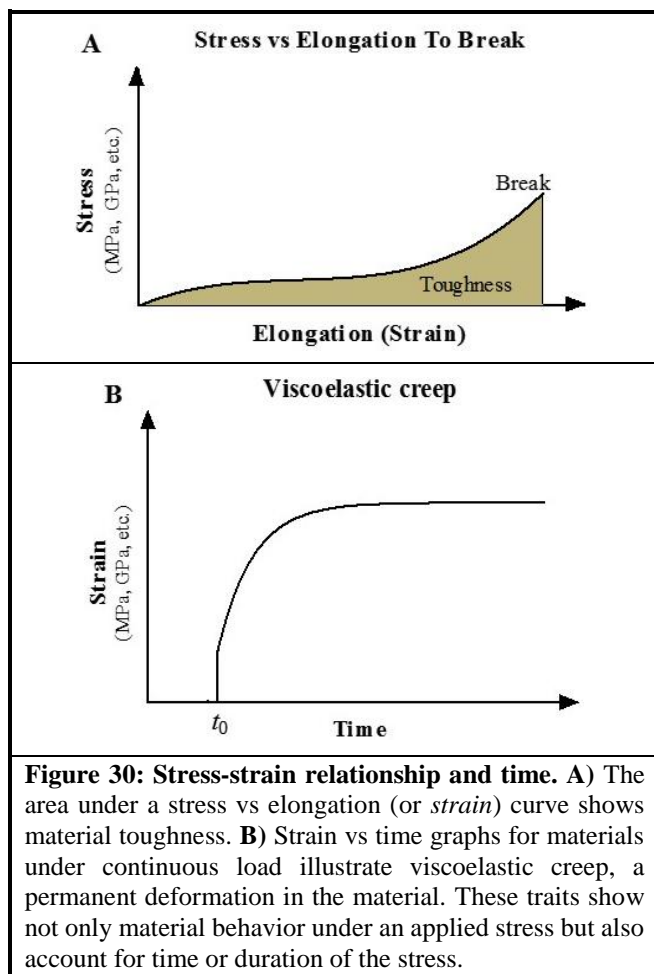


Figure 29: Stress vs strain graphical plot. Stress-strain graphs reveal fundamental attributes of materials such as those used to make drawn fiber. Yield stress shows where permanent material deformation begins while tensile strength measures the breaking force of the material. Tensile modulus, E , gives insight into the material's resistance to deformation; it characterizes the material's proportional deformation when subjected to stress.

Stress-strain curves can also be used to determine two other highly useful properties, *tensile modulus* and *toughness*. Tensile modulus, E (also known as Young's modulus), relates the stiffness of a material in the tensile direction. This characteristic could be viewed as the material's resistance to deformation. Tensile modulus is the ratio of stress (σ) to strain (ϵ): $E = \frac{\text{stress } (\sigma)}{\text{strain } (\epsilon)}$. E is determined from the slope of the near-linear region of elasticity of the material from the stress-strain plot (**Fig. 29**). This value gives an understanding into a material's proportional deformation under an applied stress. For a drawn fiber, this property helps to describe the fiber's stretching behavior.

In addition to direct measurements described above, the *area* under the stress-strain curve is also important. This region reveals the material's *toughness* (**Fig. 30A**). Toughness relates the material's ability to absorb energy before fracture or breaking. The greater the area under the stress-strain curve, the greater the material's toughness. For hard or brittle materials, toughness is low; for more stretchable or ductile materials, toughness is high. For drawn fiber, toughness translates to attributes such as abrasion resistance and wearing.



Time is also a consideration for materials which may experience stress. After the application of a load and elongation appears to cease, the material such as a fiber may continue to deform (stretch) though at a much slower rate. This time-dependent continued deformation under constant stress is called *creep*. This type of viscoelastic deformation is permanent and can be shown through a plot of strain vs time (Fig. 30B). The plot also shows how strain may become constant over time as the polymer material or fiber continues to deform. Here, too, molecular weight and chain flexibility play a role. Higher molecular weight polymers and those with less flexible chains result in increased resistance to creep because the chains are less easily able to move or slip past one another under load [56, 57]. Creep, hence, should be viewed as a long-term property when thinking about materials that will be used under load for extended periods.

MECHANICAL PROPERTIES: OVERVIEW

As detailed at the outset of this article, chemical structure lies at the root of properties of the polymers used to make Zeus drawn fiber. These properties include chemical, physical, and mechanical attributes. With closer examination of the chemical features of the polymers, several patterns emerge with respect to their behavior at the macro level. For fluoropolymers especially, trends in mechanical properties can be linked to patterns of their chemical features. While not all-encompassing, the information contained here can be used as a guide to help interpret and even predict some of the behavior observed in certain drawn fiber polymers.

For fluoropolymers, one such pattern helps to explain tensile strength. Processing methods aside, generally, as the amount or number of chain interactions increases, tensile strength for these polymers also increases (Fig. 31 and Table 2). FEP, as an example, with the least vdW attractive forces shows considerably lower tensile strength than PVDF which possesses both London and dipole-dipole attractions. Also linked to tensile strength is the polymer chain's ability to flex and bend as it cools to a solid state from the melt state. Polymers with less chain flexibility generally exhibit lower tensile strength. This, too, is expected because greater flexibility supports more chain entanglement leading to increased tensile strength. Rigid polymers, such as PTFE or FEP, are less capable of extensive entanglements and, with other aspects being equivalent, show comparatively lower tensile strength (Fig. 31 and Table 2). Polyethylene (PE), while the most flexible and most capable of chain entanglements, possesses only the weakest chain interactions – London forces. It too, thus, shows relatively low to moderate tensile strength with chain length being more important. Hence, while a particular polymer may possess fewer chain attractive forces, increasing polymer chain length during synthesis can compensate for otherwise comparatively lower tensile strength.

Chemical resistance also reveals itself when examining fluoropolymers collectively. As a reference, PE shows exceptional resistance to a broad spectrum of chemicals because it is comprised entirely of very poorly reactive C–H bonds. For fluoropolymers, as fluorine atoms are added to the hydrocarbon chain and replace hydrogen

atoms, chemical resistance improves further still (**Fig. 31 and Table 2**). Chemical resistance is also tied to the polymer's ability to bend and flex which can expose chemical moieties for reactivity. This observation fits well with the pattern of chain flexibility. Accordingly, with one supporting the other, as the fluorine content increases, the polymer chains become more rigid and likewise resistant to chemical reactivity – not only because of the increasing abundance of unreactive fluorine atoms on the polymer chain surface but because of less exposure to potential reactivity.

T_m and T_g also display an understandable trend. PE shows the lowest T_g and T_m ; it has only weak London forces attracting other PE chains. However, as the number of interactive (attractive) forces increases, so does T_g in particular. This increase is partly the result of chain flexibility allowing more chain interactions (**Fig. 31 and Table 2**). T_m , however, is not as obvious because it involves the transition of the crystalline portion of the polymer from a solid to a liquid phase. Therefore, crystallinity in addition to chain interactions affects T_m . Typically, the more crystalline proportionality of the solid phase polymer, the greater its T_m . PFA, however, may appear to be somewhat of an exception because of its comparably lower crystallinity. PFA's T_m can be explained by its perfluorinated alkoxy side chain. This side group can vary in length and inhibits PFA close chain packing and crystal formation (**Fig. 31 and Table 2**). Increasing the length of this side chain, on the other hand, increases the polymer's molecular weight which increases PFA's T_m (**Fig. 31 and Table 2**). So, while T_g and T_m are the result of the collective forces within the polymer, they nonetheless can be explained through a mindful examination of polymer's features.

PEEK's unique structure presents an opportunity to further use the information provided earlier. PEEK's high tensile strength can be partly explained by reviewing its chemical features. PEEK is a moderately flexible polymer chain falling perhaps between ECTFE and PFA in the spectrum of the other fluoropolymers described here (**Table 2**). This flexibility increases the potential for chain entanglement. Moreover, PEEK's twist-bend conformation means that PEEK chains do not easily slip past one another in a mobile phase and when under tension (**Fig. 31**). These two factors enhance PEEK's tensile strength considerably. Also, despite PEEK's

comparatively lower crystallinity, the presence of the phenyl rings substantially increases PEEK's molecular weight compared to a straight-chain linear polymer such as PVDF. As with PFA, this higher molecular weight results in higher T_g and T_m for PEEK. Conversely, the presence of oxygen with its two lone pair electrons increases PEEK's potential for reactivity with hydrogen-containing species and water resulting in somewhat diminished chemical resistance (**Fig. 31 and Table 2**). On the whole, it is PEEK's unique phenyl ring-based structure and its twist-bend conformation that produces many of its highly desirable features.

SUMMARY

Zeus drawn fiber monofilament is a popular product with diverse application potentials. Several factors, including key processes, polymers, and extrusion designs, enable Zeus to produce high performing monofilament fiber. The drawing process, as a follow-up to extrusion, creates a monofilament that is more dense with more polymer chains per area. A consequence of the drawing process is a monofilament with greater tensile strength and less elongation than standard monofilament that has only been through the extrusion process. Zeus also has the ability to control the drawing process to achieve many application-specific fiber attributes. This capability is one of the reasons Zeus drawn fiber has found widespread uses ranging from medical braiding, hose over-braiding, weaves, to belting applications.

Zeus manufactures drawn fiber from at least ten different polymer resins. Fluoropolymers such as PVDF, ETFE, ECTFE, PFA, FEP, and the non-fluoropolymer PEEK, have become especially widely used. These polymers exhibit many preferred traits resulting from their unique chemical make-up. PVDF in particular serves as an instructive model to illustrate fluoropolymer behavior because it possesses many of the chemical features present in other fluoropolymers such as ETFE, ECTFE, PFA, and FEP. Key features of these fluoropolymers include dipole-dipole interactions and London forces – both attractive vdW forces – which enable the polymer chains to interact with one another. Also illustrative in PVDF are its rotatable bonds. Because many of PVDF's features are present in the other fluoropolymers, they can be modeled

into those fluoropolymers as an aid to estimate the properties in similar fluoropolymers.

PVDF is also unique in that it exhibits at least four well-defined crystalline phase conformations. These multiple phases have significantly different properties and highlight the importance of gaining a basic level of understanding to choose a best polymer for a given application. From a structural perspective, this characteristic of PVDF illustrates the importance of appreciating what appears to be a simple structure (such as the Lewis or bond-line structure) can in reality be much more complex and have significant consequences on the resulting polymer's performance.

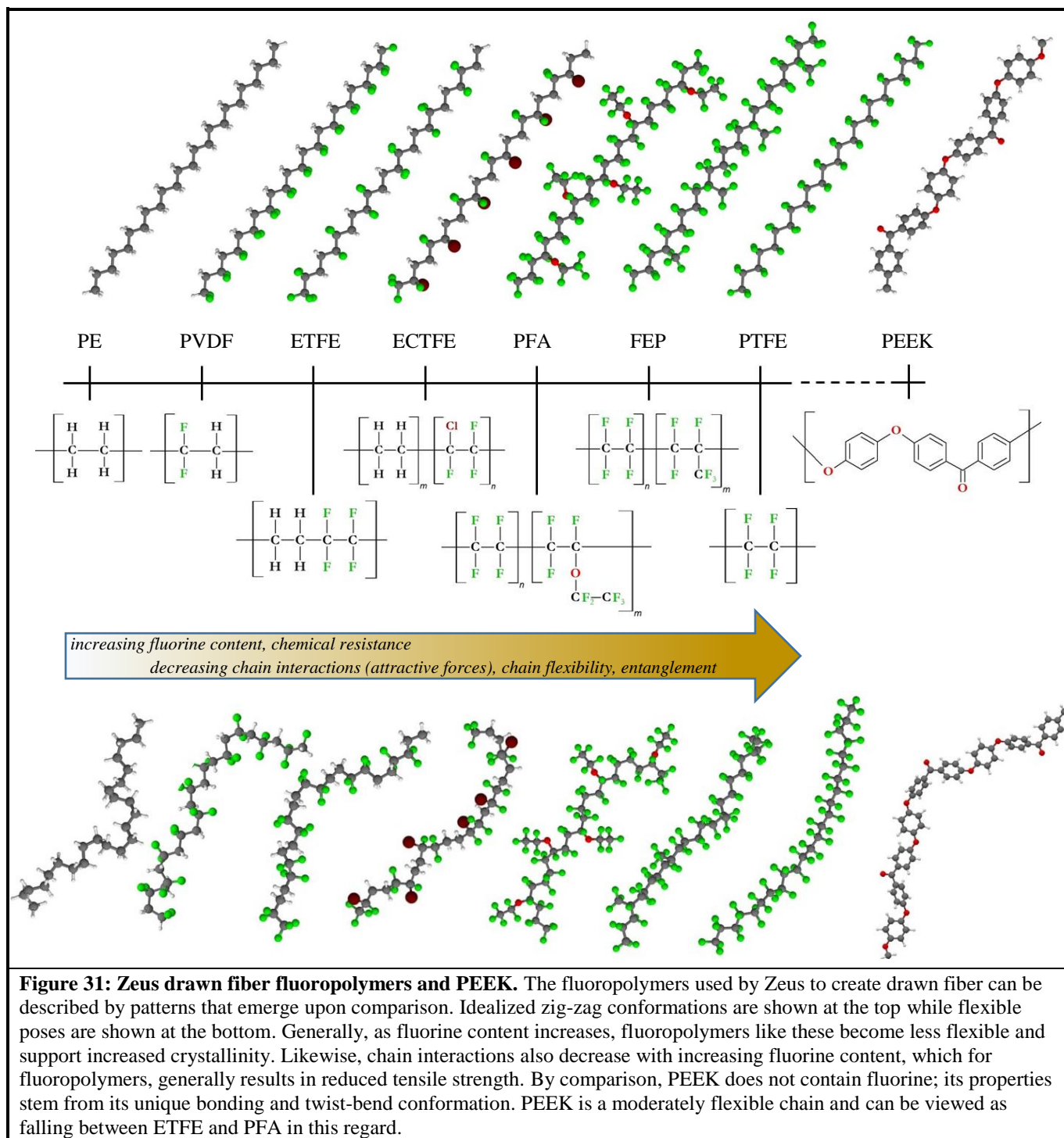
PEEK is another popular polymer used by Zeus for drawn fiber though it does not contain fluorine. PEEK's properties are largely the result of its unique bonding compared to simpler linear straight-chain polymers. PEEK's multiple ring structures cause it to adopt a twisted and bent conformation. This shape makes the polymer chains of PEEK more difficult to move or slip past one another enhancing PEEK's strength. PEEK's stable ring structures, conjugated bonding, and minimally exposed oxygen atoms reduce PEEK's reactivity. As a non-linear carbon chain, PEEK highlights the effects of ring structures in lieu of fluorine to produce a polymer with beneficial features rivalling some fluoropolymers.

Several basic mechanical properties complement an understanding of the chemical aspects of Zeus drawn fiber polymers. Chain length, chain flexibility, and complexity of the polymer chain are key factors in determining mechanical properties. Longer polymer chain length results in increased tensile strength and T_g . Chain

flexibility, a direct consequence of the chemical features of the chain, governs elements such as crystallinity and chain entanglement. Those factors in turn affect tensile strength, T_g , and T_m . Crystallinity is also affected by whether the polymer chain contains bulky side groups such as in PFA compared to simple linear chains like those of PTFE or ETFE.

Much of the mechanical properties of interest regarding drawn fiber fall under the category of stress-strain relationships. Key descriptors such as the point of deformation, breaking strength, resistance to deformation, and elongation help to characterize the polymer drawn fibers. Time is also a consideration. A fiber (or other material) under a continuous load may experience a time-dependent deformation known as creep. Stress-strain response over time should be a consideration when a material or fiber will be used in this way.

From this overview of drawn fiber polymers, several helpful patterns emerge through an informed comparison. Generally, as fluorine content of the polymer increases, chain flexibility decreases. With increased chain rigidity comes increased potential for crystallinity and reduced potential for chain entanglement. Also apparent is that as polymer's fluorine content increases, so does the polymer's chemical resistance. These patterns can be applied to other polymers, especially fluoropolymers, and used to estimate their properties when considering other material options. Each of the details described here has profound affects upon the mechanical properties of drawn fiber and merit careful consideration when choosing a most appropriate drawn fiber product.



Property	PE	PVDF	ETFE	ECTFE	PFA	FEP	PTFE	PEEK
Tensile Strength, 0.011" fiber (MPa)	345	783	367	256	261	97	–	638
Elongation at Break, 0.011" fiber (%)	37	31	23	30	25	44	–	30
Density (g/cm ³)	≥0.91	1.8	1.8	1.7	2.1	2.1	2.2	1.3
Crystallinity (%)	45 – 75	35 – 70	50	50	48 – 70	70	> 90	25 – 35
Chemical Resistance	Very Good	Excellent	Very Good	Moderate	Excellent	Excellent	Excellent	Very Good
Coefficient of Friction	0.18	0.14 – 0.23	0.05 – 0.40	0.25	0.04 – 0.20	0.04 – 0.20	0.02 – 0.20	0.34
Flexural Modulus (GPa)	0.3 – 1.3	1.3 – 7.0	0.7 – 1.2	1.7	0.5 – 0.7	0.5 – 0.6	0.5 – 0.6	3.6 – 4.1
Water Absorption (%)	<0.01	<0.06	<0.03	<0.1	<0.03	0.004	<0.001	0.10 – 0.45
Working Temperature (°C / °F)	65 / 149	150 / 302	150 / 302	148 / 298	260 / 500	205 / 401	260 / 500	250 / 482
Melt Temperature (°C / °F)	125 to 180 / 257 to 356	210 / 410	250 / 482	242 / 468	310 / 590	260 / 500	335 / 635	343 / 649
Glass Transition Temperature, T_g (°C / °F)	- 125 / -257	-30 to -40 / -22 to -40	40 – 130 / 104 – 266	85 / 185	90 / 194	80 / 176	127 / 261	150 / 302
Dielectric Constant (1 MHz)	2.3	4.5 – 5.5	2.5	2.6	1.9 – 2.1	2.0	2.1	2.6

Table 2: Overview of properties for drawn fiber polymers and representative samples. Values for six of the polymers Zeus uses to produce drawn fiber monofilament. Tensile and elongation values are from 0.011" (0.279 mm) diameter fiber samples. Note that the properties shown are representative and may vary based on proprietary and non-proprietary processing methods, some of which are described here. Other factors such as resin synthesis and fiber manufacturer can also affect fiber properties. (–) = fiber not available for manufacture by Zeus. PE and PTFE information are included for comparison only. (Comparative chemical resistance: moderate = poorest; resistant to selective but moderately broad range of chemical compounds; excellent = best; resistant to the broadest range of chemical compounds).

ABOUT THE AUTHOR



Dr. Kevin J. Bigham is the Technical Writer for Zeus. Kevin earned undergraduate degrees in Chemistry and Biochemistry from the College of Charleston before going on to graduate training at the Medical University of South Carolina. There, he earned his PhD with concentrations in Biomedical and Pharmaceutical Sciences. Dr. Bigham brings his broad experience and scientific knowledge spanning the manufacturing sector to biomedical research to produce varied content for the company's technical and lay audiences.

ABOUT ZEUS

Zeus is the world's leader in polymer extrusion technologies. For over 50 years, Zeus has been serving the medical, aerospace, energy exploration, automotive, and fiber optics industries. Headquartered in Orangeburg, South Carolina, Zeus employs approximately 1,500 people worldwide and operates multiple facilities in North America and internationally. You can find us at www.zeusinc.com.

CONTACT US

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OTHER INFORMATION

A portion of the information provided here is presented in our free webinar series, "Zeus Drawn Fiber Essentials – Deciding Which Is Right For You." These video presentations provide more step-by-step discussion and further insight on this topic. Part I of this two-part series, "PVDF and Introduction To Fluorine Chemistry" can be found [here](#); Part II, "Chemical Overview and Properties Comparison," can be viewed [here](#).

Should you be more interested in mechanical properties, you may want to refer to our quarterly newsletter *RESINATE* which can be found on our website <https://www.zeusinc.com/>. Issue No. 5, "Drawn Fiber: Polymers, Processes, and Properties Primer" provides an abridged discussion of some of the material described here. Regardless of which option you choose, we remain committed to providing solutions that change businesses, markets, and lives. Through free educational components and relevant information, our goal is to help you make the best decisions in designing and manufacturing your next product.

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