

# Polymers for Engineers

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## INTRODUCTION

It has become clear that sustainability and profits are important when dealing with polymeric materials. Polymer engineering covers aspects of the petrochemical industry, polymerization, structure and characterization of polymers, properties of polymers, compounding and processing of polymers and description of major polymers, structure property relations and applications. The basic division of polymers into thermoplastics, elastomers and thermosets helps define their areas of application. The latter group of materials includes phenolic resins, polyesters and epoxy resins, all of which are used widely in composite materials when reinforced with stiff fibres such as fibreglass and aramids.

The work of Henri Braconnot in 1777 and the work of Christian Schönbein in 1846 led to the discovery of nitrocellulose, which, when treated with camphor produced celluloid. Dissolved in ether or acetone, it is collodion, used as a wound dressing since the U.S. Civil War. Cellulose acetate was first prepared in 1865. In 1834, Friedrich Ludersdorf and Nathaniel Hayward independently discovered that adding sulfur to raw natural rubber (polyisoprene) helped prevent the material from becoming sticky. In 1844 Charles Goodyear received a U.S. patent for vulcanizing rubber with sulfur and heat. Thomas Hancock had received a patent for the same process in the UK the year before.

In 1884 Hilaire de Chardonnet started the first artificial fiber plant based on regenerated cellulose, or viscose rayon, as a substitute for silk, but it was very flammable. In 1907 Leo Baekeland invented the first synthetic polymer, a thermosetting phenol-formaldehyde resin called Bakelite. Around the same time, Hermann Leuchs reported the synthesis of amino acid N-carboxyanhydrides and their high molecular weight products upon reaction with nucleophiles, but stopped short of referring to these as polymers, possibly due to the strong views espoused by Emil Fischer, his direct supervisor, denying the possibility of any covalent molecule exceeding 6,000 daltons. Cellophane was invented in 1908 by Jacques Brandenberger who squirted sheets of viscose rayon into an acid bath.

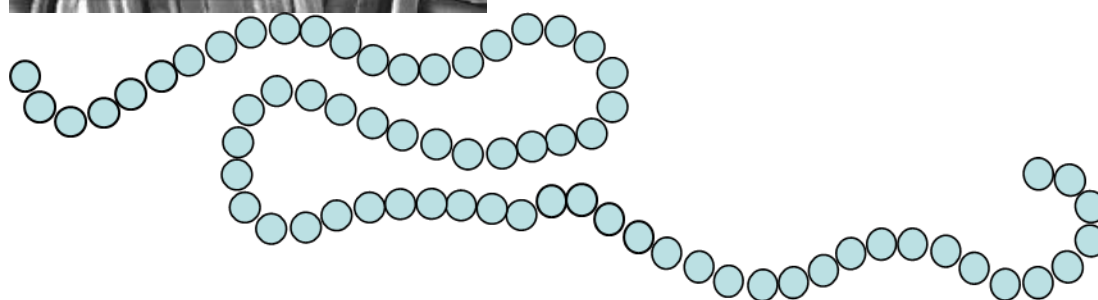
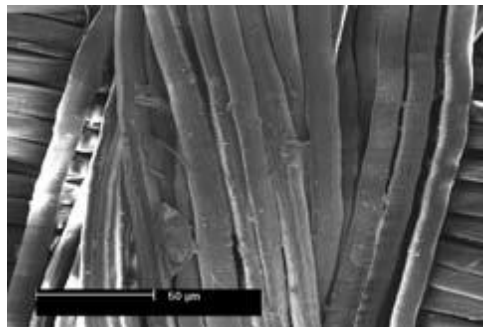
In 1922 Hermann Staudinger (of Worms, Germany 1881-1965) was the first to propose that polymers consisted of long chains of atoms held together by covalent bonds. He also proposed to name these compounds macromolecules. Before that, scientists believed that polymers were clusters of small molecules (called colloids), without definite molecular weights, held together by an unknown force. Staudinger received the Nobel Prize in Chemistry in 1953. Wallace Carothers invented the first synthetic rubber called neoprene in 1931, the first polyester, and went on to invent nylon, a true silk replacement, in 1935. Paul Flory was awarded the Nobel Prize in Chemistry in 1974 for his work on polymer random coil configurations in solution in the 1950s. Stephanie Kwolek developed an aramid, or aromatic nylon named Kevlar, patented in 1966.

There are now a large number of commercial polymers, including composite materials such as carbon fiber-epoxy, polystyrene-polybutadiene (HIPS), acrylonitrile-butadiene-styrene (ABS), and other such materials that combine the best properties of their various components, including polymers designed to work at high temperatures in automobile engines.

In spite of the great importance of the polymer industry, it took a long time before universities introduced teaching and research programs in polymer chemistry. An "Institut für Makromolekulare Chemie" was founded in 1940 in Freiburg, Germany under the direction of Hermann Staudinger. In America a "Polymer Research Institute" (PRI) was established in 1941 by Herman Mark at the Polytechnic Institute of Brooklyn (now Polytechnic Institute of NYU). Several hundred graduates of PRI played an important role in the US polymer industry and academia. Other PRI's were founded in 1961 by Richard S. Stein at the University of Massachusetts, Amherst, in 1967 by Eric Baer at Case Western Reserve University, in 1982 at The University of Southern Mississippi, and in 1988 at the University of Akron.

**Polymer** - a large molecule consisting of (at least five) repeated chemical units ('mers') joined together, like beads on a string. Polymers usually contain many more than five monomers, and some may contain

hundreds or thousands of monomers in each chain. Polymers may be **natural**, such as cellulose or DNA, or **synthetic**, such as nylon or polyethylene. A



molecule of high  $M_w$ , structure of which comprises of multiple repetition of units derived from molecules of low relative  $M_w$  (monomers).

## Theories on polymers

### Scheutjens–Fleer theory

Scheutjens–Fleer theory is a lattice-based self-consistent field theory that is the basis for many computational analyses of polymer adsorption.

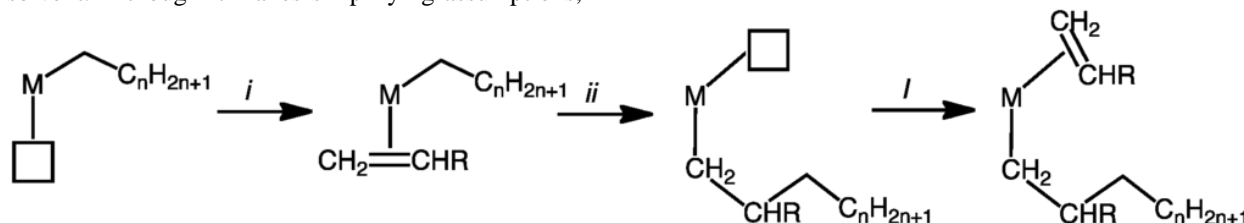
### Flory–Huggins solution theory

The Flory–Huggins solution theory is a mathematical model of the thermodynamics of polymer solutions which takes account of the great dissimilarity in molecular sizes in adapting the usual expression for the entropy of mixing. The result is an equation for the Gibbs free energy change  $\{\displaystyle \Delta G_{\{m\}}\} \Delta G_{\{m\}}$  for mixing a polymer with a solvent. Although it makes simplifying assumptions,

it generates useful results for interpreting experiments.

### Cossee–Arlman mechanism

The Cossee–Arlman mechanism in polymer chemistry is the main pathway for the formation of C–C bonds in the polymerization of alkenes. The mechanism features an intermediate coordination complex that contains both the growing polymer chain and the monomer (alkene). These ligands combine within the coordination sphere of the metal to form a polymer chain that is elongated by two carbons.



The details of this mechanism can be used to explain the stereoregularity of the polymerisation of alkenes using Ziegler-Natta or metallocene catalysts. Stereoregularity is relevant for unsymmetrical alkenes such as propylene. The coordination sphere of the metal ligands sterically influences which end of the propylene attaches to the growing polymer chain and the relative stereochemistry of the methyl

groups on the polymer. The stereoregularity is influenced by the ligands. For the metallocene catalysts, the cyclopentadienyl ligands (or their surrogates) fulfill this role. For heterogeneous catalysts, the stereoregularity is determined by the surface structure around the active site on the catalyst particle, and can be influenced by additives such as succinates or phthalates, which tend to block specific

sites, while leaving others (with different stereoreactivity) to catalyze the polymerization.

### Polymer field theory

A polymer field theory is a statistical field theory describing the statistical behavior of a neutral or charged polymer system. It can be derived by transforming the partition function from its standard many-dimensional integral representation over the particle degrees of freedom in a functional integral representation over an auxiliary field function, using either the Hubbard-Stratonovich transformation or the delta-functional transformation. Computer simulations based on polymer field theories have been shown to deliver useful results, for example to calculate the structures and properties of polymer solutions (Baurle 2007, Schmid 1998), polymer melts (Schmid 1998, Matsen 2002, Fredrickson 2002) and thermoplastics (Baurle 2006).

### Mean field approximation:

A standard approximation strategy for polymer field theories is the mean field (MF) approximation, which consists in replacing the many-body interaction term in the action by a term where all bodies of the system interact with an average effective field. This approach reduces any multi-body problem into an effective one-body problem by assuming that the partition function integral of the model is dominated by a single field configuration. A major benefit of solving problems with the MF approximation, or its numerical implementation commonly referred to as the self-consistent field theory (SCFT), is that it often provides some useful insights into the properties and behavior of complex many-body systems at relatively low computational cost. Successful applications of this approximation strategy can be found for various systems of polymers and complex fluids, like e.g. strongly segregated block copolymers of high molecular weight, highly concentrated neutral polymer solutions or highly concentrated block polyelectrolyte (PE) solutions (Schmid 1998, Matsen 2002, Fredrickson 2002). There are, however, a multitude of cases for which SCFT provides inaccurate or even qualitatively incorrect results (Baurle 2006a). These comprise neutral polymer or polyelectrolyte solutions in dilute and semidilute concentration regimes, block copolymers near their order-disorder transition, polymer blends near their phase transitions, etc. In such situations the partition function integral defining the field-theoretic model is not entirely dominated by a single MF configuration

and field configurations far from it can make important contributions, which require the use of more sophisticated calculation techniques beyond the MF level of approximation.

### Higher-order corrections:

One possibility to face the problem is to calculate higher-order corrections to the MF approximation. Tsonchev et al. developed such a strategy including leading (one-loop) order fluctuation corrections, which allowed to gain new insights into the physics of confined PE solutions (Tsonchev 1999). However, in situations where the MF approximation is bad many computationally demanding higher-order corrections to the integral are necessary to get the desired accuracy.

### Renormalization techniques:

An alternative theoretical tool to cope with strong fluctuations problems occurring in field theories has been provided in the late 1940s by the concept of renormalization, which has originally been devised to calculate functional integrals arising in quantum field theories (QFT's). In QFT's a standard approximation strategy is to expand the functional integrals in a power series in the coupling constant using perturbation theory. Unfortunately, generally most of the expansion terms turn out to be infinite, rendering such calculations impracticable (Shirkov 2001). A way to remove the infinities from QFT's is to make use of the concept of renormalization (Baurle 2007). It mainly consists in replacing the bare values of the coupling parameters, like e.g. electric charges or masses, by renormalized coupling parameters and requiring that the physical quantities do not change under this transformation, thereby leading to finite terms in the perturbation expansion. A simple physical picture of the procedure of renormalization can be drawn from the example of a classical electrical charge,  $Q$ , inserted into a polarizable medium, such as in an electrolyte solution. At a distance  $r$  from the charge due to polarization of the medium, its Coulomb field will effectively depend on a function  $Q(r)$ , i.e. the effective (renormalized) charge, instead of the bare electrical charge,  $Q$ . At the beginning of the 1970s, K.G. Wilson further pioneered the power of renormalization concepts by developing the formalism of renormalization group (RG) theory, to investigate critical phenomena of statistical systems (Wilson 1971).

### **Renormalization group theory:**

The RG theory makes use of a series of RG transformations, each of which consists of a coarse-graining step followed by a change of scale (Wilson 1974). In case of statistical-mechanical problems the steps are implemented by successively eliminating and rescaling the degrees of freedom in the partition sum or integral that defines the model under consideration. De Gennes used this strategy to establish an analogy between the behavior of the zero-component classical vector model of ferromagnetism near the phase transition and a self-avoiding random walk of a polymer chain of infinite length on a lattice, to calculate the polymer excluded volume exponents (de Gennes 1972). Adapting this concept to field-theoretic functional integrals, implies to study in a systematic way how a field theory model changes while eliminating and rescaling a certain number of degrees of freedom from the partition function integral (Wilson 1974).

### **Hartree renormalization:**

An alternative approach is known as the Hartree approximation or self-consistent one-loop approximation (Amit 1984). It takes advantage of Gaussian fluctuation corrections to the  $O^{\text{th}}$ -order MF contribution, to renormalize the model parameters and extract in a self-consistent way the dominant length scale of the concentration fluctuations in critical concentration regimes.

### **Tadpole renormalization:**

In a more recent work Efimov and Nogovitsin showed that an alternative renormalization technique originating from QFT, based on the concept of tadpole renormalization, can be a very effective approach for computing functional integrals arising in statistical mechanics of classical many-particle systems (Efimov 1996). They demonstrated that the main contributions to classical partition function integrals are provided by low-order tadpole-type Feynman diagrams, which account for divergent contributions due to particle self-interaction. The renormalization procedure performed in this approach effects on the self-interaction contribution of a charge (like e.g. an electron or an ion), resulting from the static polarization induced in the vacuum due to the presence of that charge (Baeurle 2007). As evidenced by Efimov and Ganbold in an earlier work (Efimov 1991), the procedure of tadpole renormalization can be employed very effectively to remove the divergences from the action of the basic field-theoretic representation of the partition function and leads to an alternative functional integral

representation, called the Gaussian equivalent representation (GER). They showed that the procedure provides functional integrals with significantly ameliorated convergence properties for analytical perturbation calculations. In subsequent works Baeurle et al. developed effective low-cost approximation methods based on the tadpole renormalization procedure, which have shown to deliver useful results for prototypical polymer and PE solutions (Baeurle 2006a, Baeurle 2006b, Baeurle 2007a).

### **Numerical simulation:**

Another possibility is to use Monte Carlo (MC) algorithms and to sample the full partition function integral in field-theoretic formulation. The resulting procedure is then called a polymer field-theoretic simulation. In a recent work, however, Baeurle demonstrated that MC sampling in conjunction with the basic field-theoretic representation is impracticable due to the so-called numerical sign problem (Baeurle 2002). The difficulty is related to the complex and oscillatory nature of the resulting distribution function, which causes a bad statistical convergence of the ensemble averages of the desired thermodynamic and structural quantities. In such cases special analytical and numerical techniques are necessary to accelerate the statistical convergence (Baeurle 2003, Baeurle 2003a, Baeurle 2004).

### **Mean field representation:**

To make the methodology amenable for computation, Baeurle proposed to shift the contour of integration of the partition function integral through the homogeneous MF solution using Cauchy's integral theorem, providing its so-called mean-field representation. This strategy was previously successfully employed by Baer et al. in field-theoretic electronic structure calculations (Baer 1998). Baeurle could demonstrate that this technique provides a significant acceleration of the statistical convergence of the ensemble averages in the MC sampling procedure (Baeurle 2002, Baeurle 2002a).

### **Gaussian equivalent representation:**

In subsequent works Baeurle et al. (Baeurle 2002, Baeurle 2002a, Baeurle 2003, Baeurle 2003a, Baeurle 2004) applied the concept of tadpole renormalization, leading to the Gaussian equivalent representation of the partition function integral, in conjunction with advanced MC techniques in the grand canonical ensemble. They could convincingly demonstrate that this strategy provides a further boost in the statistical convergence of the desired ensemble averages.

### **Hoffman nucleation theory:**

Hoffman nucleation theory is a theory developed by John D. Hoffman and coworkers in the 1970s and 80s

that attempts to describe the crystallization of a polymer in terms of the kinetics and thermodynamics of polymer surface nucleation.[1] The theory introduces a model where a surface of completely crystalline polymer is created and introduces surface energy parameters to describe the process. Hoffman nucleation theory is more of a starting point for polymer crystallization theory and is better known for its fundamental roles in the Hoffman-Weeks Lamellar Thickening and Lauritzen-Hoffman Growth Theory.

### **Polymer morphology:**

Amorphous regions lack the energy needed to order into folded regions such as those seen in the Crystalline state. Polymers contain different morphologies on the molecular level which give rise to their macro properties. Long range disorder in the polymer chain is representative of amorphous solids, and the chain segments are considered amorphous. Long range polymer order is similar to crystalline material, and chain segments are considered crystalline.

The thermal characteristics of polymers are fundamentally different from those of most solid materials. Solid materials typically have one melting point, the  $T_m$ , above which the material loses internal molecular ordering and becomes a liquid. Polymers have both a melting temperature  $T_m$  and a glass transition temperature  $T_g$ . Above the  $T_m$ , the polymer chains lose their molecular ordering and exhibit reptation, or mobility. Below the  $T_m$ , but still above the  $T_g$ , the polymer chains lose some of their long-range mobility and can form either crystalline or amorphous regions. In this temperature range, as the temperature decreases, amorphous regions can transition into crystalline regions, causing the bulk material to become more crystalline over all. Below the  $T_g$ , molecular motion is stopped and the polymer chains are essentially frozen in place. In this temperature range, amorphous regions can no longer transition into crystalline regions, and the polymer as a whole has reached its maximum crystallinity.

### **Nucleation:**

Nucleation is the formation and growth of a new phase with or without the presence of external surface. The presence of this surface results in heterogeneous nucleation whereas in its absence homogeneous nucleation occurs. Heterogeneous nucleation occurs in cases where there are pre-existing nuclei present, such as tiny dust particles suspended in a liquid or gas or reacting with a glass

surface containing  $SiO_2$ . For the process of Hoffman nucleation and its progression to Lauritzen-Hoffman Growth Theory, homogeneous nucleation is the main focus. Homogeneous nucleation occurs where no such contaminants are present and is less commonly seen. Homogeneous nucleation begins with small clusters of molecules forming from one phase to the next. As the clusters grow, they aggregate through the condensation of other molecules. The size continues to increase and ultimately form macroscopic droplets (or bubbles depending on the system).

Nucleation is often described mathematically through the change in Gibbs free energy of  $n$  moles of vapor at vapor pressure  $P$  that condenses into a drop. Also the nucleation barrier, in polymer crystallization, consists of both enthalpic and entropic components that must be overcome. This barrier consists of selection processes taking place in different length and time scales which relates to the multiple regimes later on.[2] This barrier is the free energy required to overcome in order to form nuclei. It is the formation of the nuclei from the bulk to a surface that is the interfacial free energy. The interfacial free energy is always a positive term and acts to destabilize the nucleus allowing the continuation of the growing polymer chain. The nucleation continues as a favorable reaction.