

POLYMERS

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Summary

This chapter addresses basic principles of chemical engineering of polymers and polymeric materials. At the beginning, the chapter introduces some general information concerning different classes of macromolecular systems, their molecular and supramolecular structure as well as the mechanisms of their synthesis with emphasis on some kinetic aspects of different types of polyreactions. Then, the chapter describes essentials of polymer physics. The main aim of this part is to give a comprehensive description of some phenomena characteristic to polymers, such as molecular weights and their distribution, chain architecture and basic properties of isolated macromolecules. The chapter treats also fundamental mechanical properties highlighting interrelationships between different rheological models and viscoelastic behavior of real polymeric materials. A considerable part of this chapter is devoted to issues concerning chemical and physical modification of polymeric materials indicating most important factors and methods to be considered at the designing properties of polymeric materials. A special attention has been paid to polymer blends as one of the most facile route of tailoring properties of polymers. Here the discussion is extended to cover some basic aspects of thermodynamics of mixing and its influence on the structure of blends. Also in this part, the methods of compatibilization of heterogeneous

polymer systems are briefly described. At the end of the chapter the reader can find a brief summary of the newest trends in polymer science. This subsection includes a concise description of polymer nanocomposites, methods and applications of controlled radical polymerization techniques as well as basic information on polymer-based DNA biosensors and the application of supercritical fluids in polymer technology.

1. Introduction

Polymers are long-chain molecules of very high molecular weights, measured in the hundreds thousands or millions. For this reason, the term “macromolecules” is often used when referring to polymeric materials. Polymers are ubiquitous and it is difficult to judge how important role they play. Biological polymers are of unparalleled importance as constituents of our bodies and of our food. Wood was certainly one of the first engineering materials, which was used by human beings. The use of silk, cotton, wool or flax is still widespread. The subject of this chapter is that of synthetic polymers that play important roles in diverse fields of chemical engineering both as a subject of technical syntheses as well as a construction materials used in chemical plants. The trade literature sometimes refers to polymers as plastics or resins. Many factors have contributed to the huge growth in polymer usage. Two of them are of primary importance: first the facility of being able to shape plastic under elevated temperature (thermoplastics). The second factor is the relatively high chemical resistance of these materials, which caused the replacement of a number of metal components – e.g. the use of plastic pipes instead of cast iron or steel etc.

2. Polymer Classification

In literal sense, the term polymer denotes a macromolecule made up by repetition of some simpler unit so called mers or monomeric units that are chemically linked into chainlike structures much as a chain is constructed of links. In formulas representing polymers, the end groups (usually coming from initiators) are often ignored because of their minor effect on the properties of polymer. The repeat unit is generally composed of one or two monomer units (rarely of three) and is well defined for simple polymers. A few examples of such polymer systems are given in Table 1.

Polymer	Monomer	Repeat unit (mer)
Polyethylene	$\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	$\left[\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right]_n$
Polypropylene	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{CH}_3 \end{array}$	$\left[\begin{array}{c} \text{CH}_2-\text{CH} \\ \\ \text{CH}_3 \end{array} \right]_n$

Polystyrene	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{C}_6\text{H}_5 \end{array}$	$\left[\text{CH}_2-\text{CH} \begin{array}{c} \\ \text{C}_6\text{H}_5 \end{array} \right]_n$
Poly(vinyl chloride)	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{Cl} \end{array}$	$\left[\text{CH}_2-\text{CH} \begin{array}{c} \\ \text{Cl} \end{array} \right]_n$
Polyisoprene	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C}-\text{CH}=\text{CH}_2 \end{array}$	$\left[\begin{array}{c} \text{H} \quad \text{CH}_3 \\ \quad \\ \text{C}=\text{C} \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \end{array} \right]_n$
Poly(vinyl acetate)	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{O} \\ \\ \text{H}_3\text{C}-\text{C}=\text{O} \end{array}$	$\left[\text{CH}_2-\text{CH} \begin{array}{c} \\ \text{O} \\ \\ \text{H}_3\text{C}-\text{C}=\text{O} \end{array} \right]_n$
Polytetrafluoroethylene	$\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ \text{C}=\text{C} \\ \quad \\ \text{F} \quad \text{F} \end{array}$	$\left[\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ \text{C}-\text{C} \\ \quad \\ \text{F} \quad \text{F} \end{array} \right]_n$

Table 1. Examples of simple polymers

Polymers composed of two or more kinds of monomeric units are called **copolymers**. A few examples of such systems are given in Table 2.

Copolymer	Comonomers	Repeat unit
Poly(butadiene- <i>co</i> -styrene) styrene-butadiene rubber	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{C}_6\text{H}_5 \end{array}$ $\begin{array}{c} \text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2 \end{array}$	$\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C}=\text{C} \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \end{array} \right]_n \left[\text{CH}_2-\text{CH} \begin{array}{c} \\ \text{C}_6\text{H}_5 \end{array} \right]_k$
Poly(vinyl chloride- <i>co</i> -vinyl acetate)	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{Cl} \end{array}$ $\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{O} \\ \\ \text{H}_3\text{C}-\text{C}=\text{O} \end{array}$	$\left[\text{CH}_2-\text{CH} \begin{array}{c} \\ \text{O} \\ \\ \text{H}_3\text{C}-\text{C}=\text{O} \end{array} \right]_n \left[\text{CH}_2-\text{CH} \begin{array}{c} \\ \text{Cl} \end{array} \right]_m$

1. Random (statistical) copolymers; the units A and B occur in random length sequences along the polymer chain.
2. Alternating copolymers; mers appear in the chain in alternating positions.
3. Block copolymers; copolymer contains a linear arrangement of blocks, a block being defined as a portion of macromolecule in which monomeric units differ in constitutional or configurational feature from adjacent part.
4. Graft copolymers; the one kind of units makes up the main chain, whereas the other units appear in short branches “grafted” to this main chain.

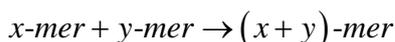
Polymers are named by rules laid out by the IUPAC Nomenclature Committee. Nevertheless other nomenclature systems have been used as well. The most simple and commonly used nomenclature system is probably that based on the source of the polymer. For example the polymers synthesized from ethylene or acrylonitrile, are named polyethylene and polyacrylonitrile, respectively. A number of the condensation polymers synthesized from two different monomers (as for example polyesters) have been named by structure based nomenclature systems. Thus the polymer from ethylene glycol and terephthalate acid is named poly(ethylene terephthalate). Table 3 provides selected polymer classes and their characteristic identifying groups.

Name	Identifying groups (main chain)
Polyamides	
Polyesters	
Polyethers	
Polyurethanes	
Polysiloxanes (silicones)	 where R ₁ and R ₂ denote alkyl group
Polyolefins	
Vinyl polymers	

Table 3. Main classes of synthetic polymers

3. Polymer Synthesis

The process by which a polymer is synthesized is the most important stage in producing a useful polymeric material. We can distinguish two extremes of simplified behavior during conversion of monomer to polymer: step-growth (condensation) polymerization and addition (chain-growth) polymerization. Chain and step polymerization differ in several features. The most important difference is in the character of the species that can react with each other. Another difference is the manner in which the size of polymer molecule depends on the extent of reaction (conversion). In step polymerization chains of any length x and y combine to form longer chains:



In chain polymerization, a chain of any length x can only add a monomer molecule and on such way continue its growth:



In chain polymerization the monomer concentration decreases steadily during the progress of the reactions, whereas in step polymerization the rapid monomer depletion occurs very soon after reaction begin (see Figure 2).

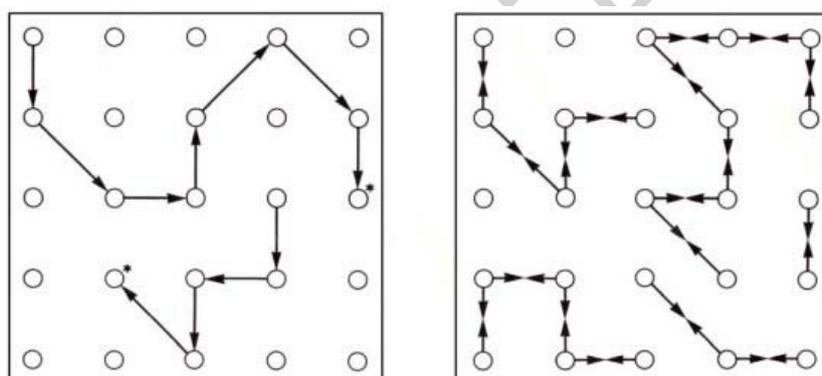
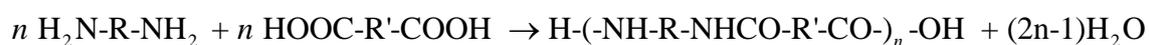


Figure 2. Scheme of chain polymerization (left) and step polymerization (right).

In chain polymerization in any time during the run of reaction only monomer, inactive high molecular polymer and small amount of growing (active) chains are present. Contrary, in step polymerization at any stage of reaction, all sizes of molecular species are present in a calculable amount.

All step polymerization fall into two groups depending on the type of monomer employed. The first involves two bifunctional monomers in which each monomer possesses only one type of functional group. The second involves a single monomer which contains two different functional groups. Synthesis of polyamides can serve as suitable example. Polyamides can be obtained from reaction of diamines with diacids



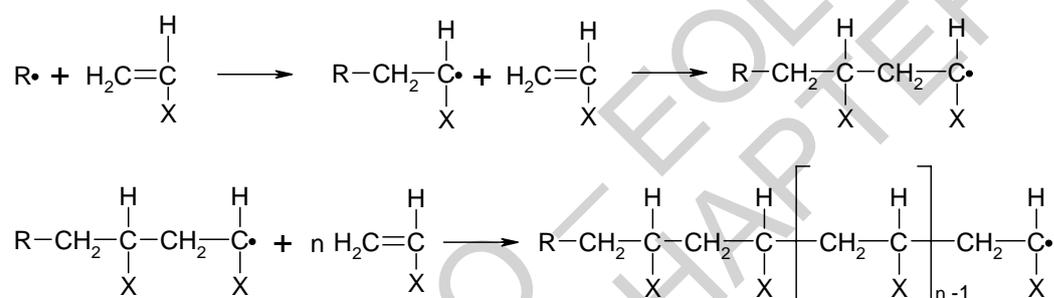
or from the reaction of amino acids with themselves



Polymerization of unsaturated monomers by chain polymerization is one of the most important methods that are used in polymer industry. Chain polymerization is initiated by reactive species R^\bullet produced from a compound I called an **initiator** (for example benzoyl peroxide or azobisisobutyronitrile that thermally decompose to free radicals):



The reactive species which may be a free radical, anion or cation adds to monomer by opening the double bond to form a new radical. The process is repeated as many times as many monomer molecules are successively joined to the continuously propagated reactive center:



Polymer growth is terminated by a destruction of macroradical by an appropriate mechanism depending on the type of reactive center and the particular reaction conditions.

4. Physics of Polymers

The physics of polymers describes the interrelationship between molecular structure of polymer chains, morphology and physical and mechanical behavior. Polymer chains have two basic properties. The first one is their high molecular weight and molecular weight distribution. The second is the conformation of the chains in space i.e. different arrangements of segments of the polymer chain caused by rotations around single bonds.

Taking into account different mechanism of polymerization reaction, various types of disappearance of an active center it becomes clear that the same polymer from different sources may have different molecular weight. In other words all polymers consist of macromolecules with a distribution of chain lengths. The two most important molecular weight averages are the **number-average molecular weight**, M_n ,

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} \quad (1)$$

where N_i is the number of molecules of molecular weight M_n , and the **weight-average molecular weight**, M_w ,

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \quad (2)$$

The ratio M_w/M_n serve as a measure of polydispersity; for perfectly monodisperse sample, i.e. a sample with uniform molecular weight $M_w/M_n = 1$. Some polymers can be produced at a commercial scale with values range smaller than 1.1 by using butyl lithium as the initiator in anionic polymerization.

Polymer chain shape is usually considered in terms of conformation and **configuration**. Polymer shape established by rotation about primary valence bonds is referred to as polymeric conformation. Configuration is the relative orientation in space of the atoms of polymeric stereoisomer, independently of spatial changes that occur by rotations around single bonds. Examples of different polymer conformations include random coil, helical, extended planar zigzag and folded-chain arrangements.

Solid polymers differ from ordinary, low molecular weight compounds in their physical state or morphology. Most polymers show simultaneously the characteristics of both **crystalline** and **amorphous solids**. Such polymers are called 'semicrystalline'. The terms crystalline and amorphous are used to indicate the ordered and disordered polymer regions, respectively. An ordered, regular chain structure is necessary to allow the chains to pack densely and form regular, three-dimensional crystal lattice. Thus, stereoregular polymers are more likely to be crystalline than those that have irregular chain structures. The completely random arrangement of polymer chain represents a physical extreme that may not be fulfilled in reality. Nevertheless, the polymers that do not show detectably ordered state are named amorphous polymers.

The randomly coiled chain presents a single isolated chain in an ideal non-interacting environment. Random coil (Figure 3) depicts unperturbed shape of the polymer chains in both dilute solutions and in the bulk amorphous state.

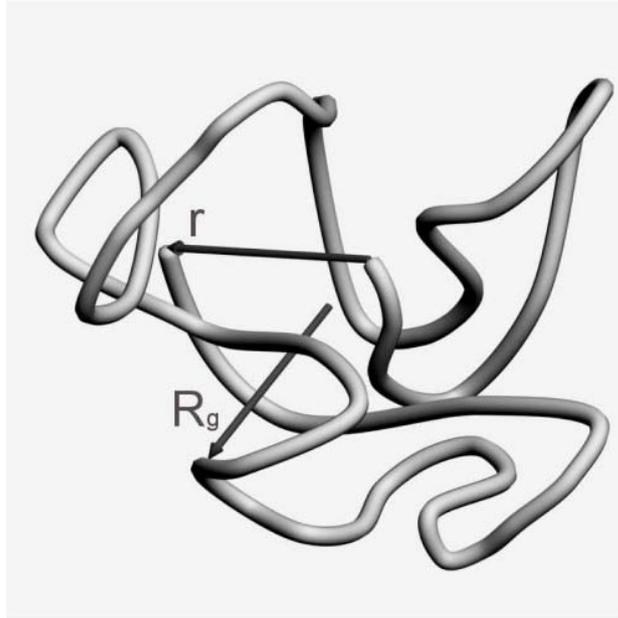


Figure 3. Schematic drawing of random coil.

The end-to-end distance and radius of gyration are two basic quantities describing the coil. The distance between the two ends of the chain given by a Gaussian probability distribution predicts that the average square end-to-end distance will be proportional to its molecular weight; that is,

$$\langle r^2 \rangle = \text{const} \times M \quad (3)$$

This prediction agrees very well with experimental observations in polymer concentrated solutions and in the melts.

The radius of gyration for a single polymer chain consisting of an assembly mass elements m_i , each located at a distance r_i from the center of gravity is given by

$$R_g^2 = \frac{\sum_i m_i r_i^2}{\sum_i m_i} \quad (4)$$

For sufficiently flexible molecules with high molecular weights the end-to-end distance divided by the square root of 6 yields the radius of gyration. Relation between $\langle r^2 \rangle$ and R_g^2 lead to the important conclusion that $R_g/M^{1/2}$ is constant.

Contrary to amorphous polymers having irregular chain structure, semicrystalline polymers show an order and regularity in large extent. The first attempt to explain the properties of semicrystalline polymers was the **fringed micelle model**. In this model the polymer molecules pass through several different crystalline regions with crystallites, whose dimensions are on the order of tens of nanometers (Figure 4). In such crystallites

segments from different polymer chain are precisely aligned together and undergo crystallization. Although this fringed micelle model may be adequate in some cases for sample rapidly crystallized from the melt, it fails for polymers crystallized slowly or from solution. Advanced characterization techniques such as X-ray diffraction, electron microscopy or NMR indicate that, in single crystals formed from dilute solution, polymer chains are oriented perpendicularly to the plane of the lamella (thin platelets having approximately 100 nm in planar dimensions). Since polymer molecules are much longer than the thickness of lamella (10 nm) the chain has to fold back on itself, as shown in Figure 4.

Not only are the polymer chains arranged to form crystallites, but these crystallites often aggregates into supermolecular structure. On the cooling from the melt, the first structure that forms is single crystal. Then these rapidly degenerate into hedrites that are intermediate in character to the single crystals and finally formed spherulites. The spherulites grow with a constant rate up to the moment when they touch each other. For spherulites which were nucleated at the same time, the area of contact is planar, if starting times differ, the boundary is bent.

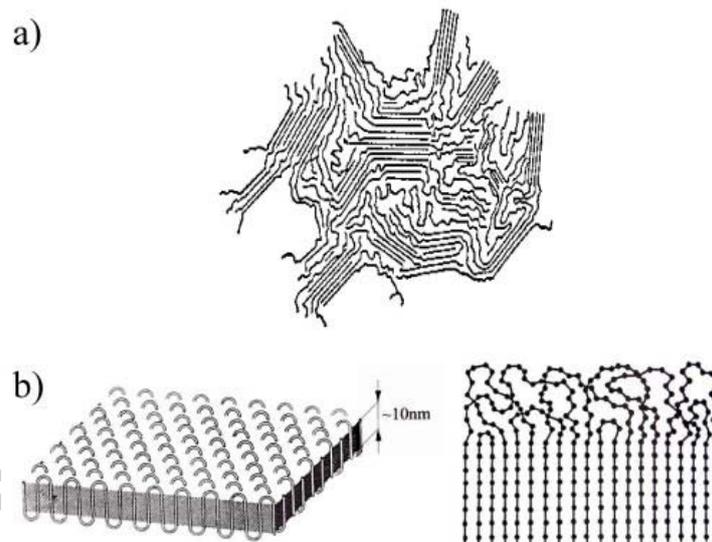


Figure 4. Fringed micelle model (a) and chain folded crystal (b) (schematic)

Time dependent properties are characteristic for long chain structures and represent the main difference between the stress-strain responses of classical materials such as metals, and the behavior of polymers. Time dependence is clearly manifested in thermoplastic polymers since crosslinked polymers show little, if any time dependent properties. The effect of time dependent mechanical properties is that high molecular weight polymers exhibit characteristics of both elastic solids and viscous liquids. To visualize **viscoelastic properties** of polymers usually one uses two linear mechanical models representing the extremes of the mechanical response spectrum. The spring represents a linear elastic solid (Hookean body) whose constitutive equation is very simply $\sigma = E\varepsilon$, where E is a elastic modulus, σ and ε represent stress and strain respectively. Similarly, a linear viscous fluid (Newtonian fluid) is represented by a dashpot, some art of piston moving in a cylinder filled with Newtonian fluid whose constitutive equation

is $\sigma = \eta(d\varepsilon/dt)$. Maxwell was the first who proposed a simple series combination of elastic body and viscous fluid to estimate the relaxation characteristics of linear viscoelastic polymers (Figure 5, left).

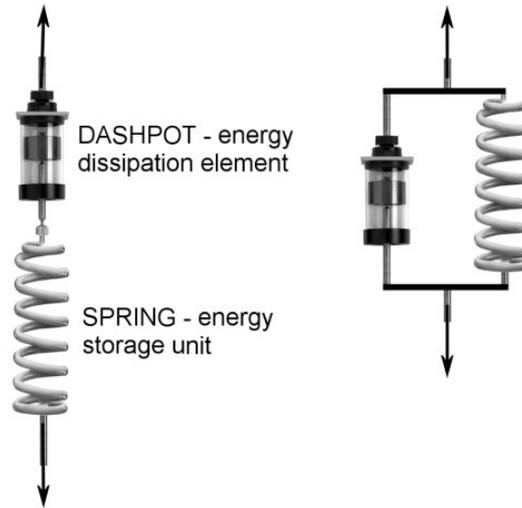


Figure 5. Maxwell's model (left) and Voigt-Kelvin's model (right)
 In the Maxwell's model the spring and dashpot support the same stress, so:

$$\sigma = \sigma_{\text{spring}} = \sigma_{\text{dashpot}} \quad (5)$$

Furthermore, the total strain of element is the sum of the extensions in the spring and dashpot:

$$\varepsilon = \varepsilon_{\text{spring}} + \varepsilon_{\text{dashpot}} \quad (6)$$

The equation for strain may be differentiated and equated to zero (since $d\varepsilon/dt = 0$ in the stress relaxation mode), and then, since the derivatives of viscous and elastic strain components are equal and opposite, one can simply calculate time dependent spring strain and finally stress relaxation which is expressed as follows:

$$\sigma(t) = E \cdot \varepsilon_E = \sigma_0 \cdot \exp\left(\frac{-Et}{\eta}\right) \quad (7)$$

An additional time constant parameter, called **relaxation time** τ_R , ($\tau_R = \eta/E$), is often used to characterize viscoelastic polymers. With real polymers there exists not only one, but a whole spectrum of relaxation times. This spectrum can be exemplified through the use of a model with a number of Maxwell bodies in parallel arrangements. Application of the Maxwell's model allows at least qualitative prediction of polymer behavior in an engineering stress-strain test. For example at any given strain the stress increases with the strain rate that is, material appears stiffer showing a higher modulus value. Many constant-strain situations exist also in engineering practice where plastic parts are deformed between more rigid parts.

Deformation under constant load (**creep**) is one of the most important and relevant fact of viscoelastic behavior in commercial polymeric system. Many polymers creep at ambient or elevated temperatures and in consequence product designers should not only pay attention to the magnitude of mechanical loads but also have to take in consideration the time history of such loading. Creep deformation occurs in a variety of practical situations: internal pressurization of pipes, bottles and tanks, compressive loading of sheets, loaded ropes etc. Voigt-Kelvin's model consisting of parallel elastic and viscous elements (Figure 5, right) is suitable for describing deformation in such situations. According this model, the time dependent strain, $\varepsilon(t)$, is given by following equation:

$$\varepsilon(t) = \frac{\sigma}{E} \left(1 - \exp\left(-\frac{Et}{\eta}\right) \right) \quad (8)$$

Unlike Maxwell's model, the deformation of Voigt-Kelvin's element stops before the applied stress is terminated. If the stress is removed after equilibrium has been reached, the strain decays exponentially. Furthermore the Voigt-Kelvin model is not suitable for representing the stress relaxation phenomena.

Macromolecular materials usually possess entropic elasticity together with viscous and energy-elastic components. Such behavior can be described very satisfactorily by a four-element model, so called Burger's body, in which a Hookean body, a Kelvin's body, and a Newtonian body are combined.

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Biographical Sketch

Jacek Piękowski was born in Radom (Wielkopolska Region), Poland; he obtained his Master of Science in Institute of Organic Technology and Polymers at Wrocław University of Technology (1971). He received his PhD from Wrocław University of Technology (1976) and D.Sc. from Dresden University of Technology (Germany, 1988). He is currently professor at Faculty of Chemistry at Wrocław University of Technology and leader of Polymer Engineering and Technology Division. His research projects are related to modification of polymers as well as synthesis of modifiers for toughened plastics. The main fields of interest are polymer blends. Currently the research program is focused on two subjects: functionalization of polymers and applying them as compatibilizer in immiscible blends and characterization of the structure and properties of reactive polymer mixtures. The other field of research considers the development of polymeric nanocomposites based upon organophilic layered silicates. In professor Piękowski's group several synthetic routes are examined to produce polymer/organoclay nanocomposites, aiming at improving exfoliation of organoclay. Prof. Piękowski has written over hundred research publications and reports. He is member of the Polish Chemical Society and Association of Engineers and Technicians of Chemical Industry, he was visiting scientist at Dresden University of Technology, Institute of Advanced Medical Materials in Essex, Albert-Ludwigs-University in Freiburg, Martin-Luther-University in Halle, Institute of Macromolecular Chemistry in Prague.