



CHEMICAL ENGINEERING OF POLYMERS: PRODUCTION OF FLEXIBLE, FUNCTIONAL MATERIALS

MATTHEW TIRRELL

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, U.S.A.

(Received: 1 July 1995)

Abstract—Polymers, with their large spatial extent and chemical variety, afford materials scientists the opportunity to be architects at the molecular level. Once the architecture is decided, however, the task of construction moves to the chemical engineer to build the material in a faithful, stable and efficient manner. This involves assembling not only the molecular structure but also the larger scale internal micro- and meso-structure of the material. New processes are continually becoming available to the chemical engineer to accomplish these ends. New catalysts, new macromolecular building blocks, reactive processing, self-assembly, manipulation of phase behavior, applications of strong orienting fields and genetic engineering of materials are among the processing of polymers is the ability to measure product characteristics. Scattering and imaging methods have been the most powerful and the fastest growing techniques giving insight into polymer structure. Chemical engineering is as central as it always has been to leadership in the development and processing of polymers and other soft materials.

INTRODUCTION

Polymeric materials are architecturally designed at the molecular level. Since macromolecules have large spatial extent, and have a multiplicity of subunits of subunits and components built into them, molecular design is an important part of the conception and use of polymers. Chemical engineers are the building construction analogy breaks down rather quickly in the production of polymers. End-use properties, which are the ultimate measure of the efficacy of a polymer manufacturing operation are generally affected as much by the chemical and physical processing as by the molecular design. Polymer production is not simply a matter of executing the molecular blueprint. There is a level of interaction between the process and the product with polymers that is much richer, more complex and more intricate than for most chemical products. Polymer properties are not intrinsic, as are the properties of simple chemicals, but rather they can be manipulated widely by polymerization and processing conditions (see Fig. 1).

For this reason, chemical engineers producing polymers must be conversant in molecular design and molecular designers must be aware of processing considerations. (Wimberger-Friedl, 1995). Even the most basic polymer, polyethylene, exhibits new aspects in this regard. A recent workshop on industrial perspectives in polymer manufacturing (Layman, 1994) generated a remarkable statement to the effect that the highest priority need of the industry is the ability to *tailor* the polyethylene molecule more accurately. This chemically simple polymer of methylene units with occasional branches, which accounted for more than 20 of the 70 billion pounds of plastics produced in the U.S. in 1993, and which one might have thought

provided little opportunity to tailor, is still a very lively arena for innovations in chemistry and processing.

With these thoughts in mind, this article will review recent accomplishments and future prospects for progress relevant to chemical engineering research. As we embark on this, we should be conscious of the fact that a similar review was prepared several years ago (Tirrell, 1991). As we proceed, there are opportunities to compare the perspective advanced five years ago to this one. They are not identical and some of the reasons for that are interesting and will be discussed. We begin this review with a discussion of reaction chemistry applied to polymers. Physical phenomena, such as rheology, dynamics and interfacial phenomena are dealt with next. Developments in experimental techniques and instrumentation, which are greatly advancing our understanding of relationships between structure and properties of polymers, are discussed in this connection. We conclude with a section on processing of polymers. Throughout, the aim is several-fold: to inform the reader about the role of chemical engineering in this area; to make clear the special engineering challenges (common to much of chemical processing of materials) when the product is a material the quality of which is judged by end-use properties; and most importantly, to illuminate significant new fields of research for chemical engineers.

POLYMER REACTIONS

Catalysis of polymerization

It is commonplace assertion (Wirth, 1994; National Research Council, 1994) that new developments in synthesis and construction of new polymeric materials

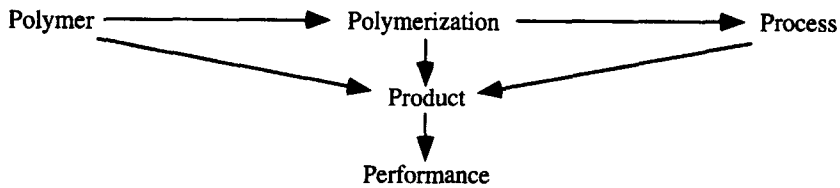


Fig. 1. Schematic interplay among the "five p's" representing: molecular design, polymerization, processing, product applications and end-use properties. Adapted from Wimberger-Friedl (1995).

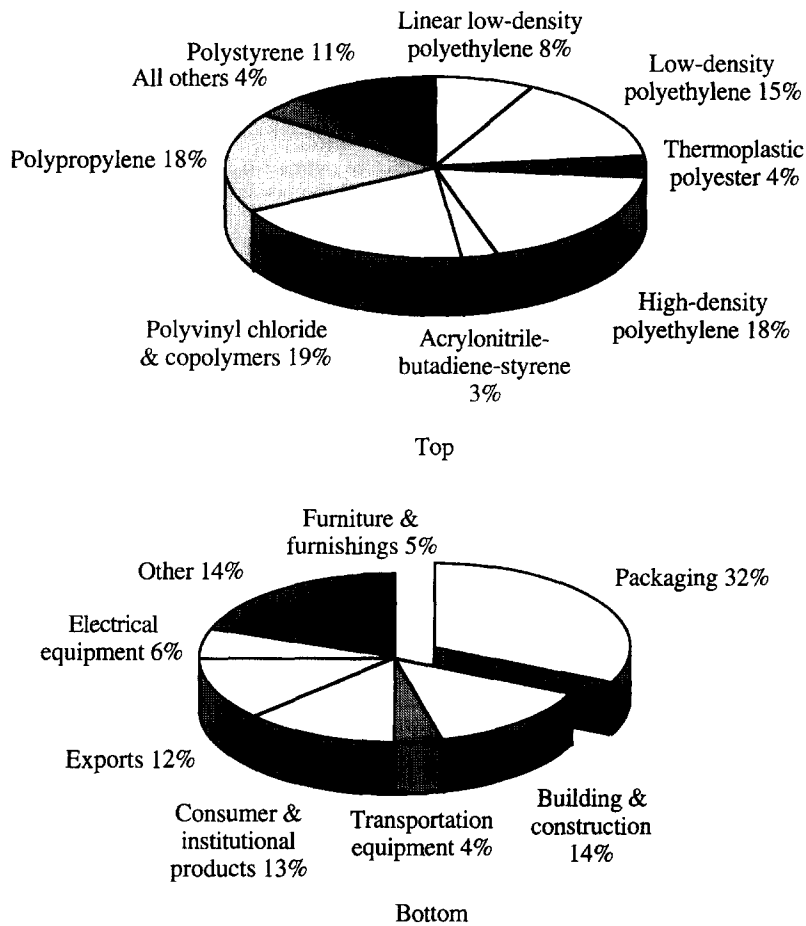


Fig. 2. (Top) U.S. production of thermoplastics by type, 1990. Adapted from National Research Council (1994). (Bottom) Categories of uses for thermoplastics in the U.S., 1990. Adapted from National Research Council (1994).

will come more in the specialty polymer areas, such as high-performance engineering plastics and polymeric additives for other products, than in the main commodity polymer areas. However, as the remarks in the Introduction let on, the scope for innovative advances in polymerization of these commodity polymers is far from exhausted and some recent activity in catalyst development has run counter to this conventional view. Five standard commodity thermoplastics: polyethylene (typically classified into high- and low-density categories), polypropylene, polyvinyl chloride, polystyrene and thermoplastic polyester, constitute more than half of the 250 billion pounds of world-

wide production of plastics; see Fig. 2. This production volume naturally provides considerable motivation for attention and, combined with elasticity in price and a widening array of applications with more finely tailored properties, gives rise to conditions favoring significant developments.

Polyolefin production is dominated by products of organo-metallic, Ziegler-Natta catalysis, including high-density polyethylene (HDPE), linear, low-density polyethylene (LLDPE) and polypropylene (PP). Several factors drive catalysis research in this field. These include: increases in catalytic activity (of order 10^8 g polymer/metal h, at constant monomer

concentration, in the most active examples) (Kaminsky *et al.*, 1992; Alt *et al.*, 1994); control of molecular architecture, molecular architecture, molecular weight distribution and resulting improvements in properties (Coates and Waymouth, 1995; Reisch, 1995; Spaleck *et al.*, 1992; Kaminsky and Steiger, 1988); and mechanistic insight into the polymerization (Huang and Rempel, 1995). For polyethylene, the principal goal is the control over the number, placement and length of branches in the repeating methylene unit structure; for polypropylene, the main goal is control of the level of crystallizable, isotactic placement of the propylene monomers in the chain.

Chemical engineering has been particularly important to the development of commercial Ziegler–Natta polymerization, and to enhancement of mechanistic insight, over the last decade. An issue of prime significance for heterogeneously catalyzed Ziegler–Natta polymerization has been the especially broad molecular weight distributions that evolve, even when polymers with excellent stereochemical control are being produced (Schmeal and Street, 1971, 1972). Various origins of these broad distributions have been proposed: diffusion-limited access to catalytic sites, exacerbated by the heterogeneous nature of the catalyst and the high production of insoluble polymer that quickly envelops the catalyst particles; multiplicity of types of active sites within one catalyst system; and temporal deactivation of catalysts during polymerization. Ray and coworkers (Nagel *et al.*, 1980; Floyd *et al.*, 1986a, b, 1987; Hutchinson *et al.*, 1992) led the way in the analysis of diffusion limitations in heterogeneous catalysis, developing a realistic and versatile, multigrain model, which showed how the structure of growing polymer particles could produce molecular weight distributions approaching the large observed breadths. Deactivation as the main source of molecular weight polydispersity has been ruled out. Experimental support for the role of multiple sites is found, for example, in the early results (Dotson *et al.*, 1995) which showed great variations in polydispersity between different kinds of catalysts, as well as more recent results with metallocene catalysts (Kaminsky and Steiger, 1988) which have only one site and give quite narrow distributions. While the weight of evidence suggests that diffusion limitations are important, over time it has become more likely that multiple catalytic sites do exist and that they must be invoked in modeling the performance of traditional Ziegler–Natta catalysts to represent properly the broad experimental molecular weight distributions seen in practice (Galván and Tirrell, 1986a, b; McAuley *et al.*, 1990; de Carvalho *et al.*, 1989, 1990). Fundamental analysis of diffusion-controlled catalytic reactions has been the key to these insights.

Until recently, homogeneous Ziegler–Natta catalysts have been less important commercially than heterogeneous versions, but this is rapidly changing (Horton, 1994; Van Santen, 1995). The main component of homogeneous Ziegler–Natta catalyst systems is

the group 4b transition metallocenes, typically titanium, zirconium or hafnium, with bulky, substituted cyclopentadienyl ligands. In 1980, Kaminsky and coworkers (Sinn and Kaminsky, 1980) discovered that the presence of methyl alumoxane (MAO) with these metallocenes produced an extremely active catalyst for ethylene polymerization. Chien *et al.* (1991) went on to develop one of the most promising systems for high activity, stereoregular propylene polymerization, a *bis*-indenyl zirconocene or titanocene with a bridging unit between the two ligands (Wild *et al.*, 1985) to lock the ligands into a symmetric or asymmetric configuration to produce the desired stereochemistry, as sketched in Fig. 3. In general, products of these catalysts are different from heterogeneous Ziegler–Natta polymerization in that they have higher degree of stereoregularity, narrow molecular weight distribution and more uniform sequence distribution in copolymers of ethylene and higher α -olefins.

Huang and Rempel (1995) describe some of the applications that the capabilities of these new catalysts open up. Among them are: 100% atactic polypropylene for blending with elastomers, homogeneous copolymers for LLDEPE, polycycloalkenes for stable high strength, high-temperature applications, and elastomeric polypropylene, consisting of blocky sequences of isotactic and atactic polypropylene. This last application has been advanced nicely recently by Coates and Waymouth (1995), who have developed an “oscillating” catalyst, depicted in Fig. 3, where the bulkiness of the substituted indene ligand generates a rotation frequency for switching between isotactic-producing and atactic-producing positions that is comparable to the growing chain lifetime. The configurational switches are made during the growth of each chain and stereoblockiness, leading to elastomeric behavior, is built into the macromolecules.

Metallocene catalysts offer many possibilities to synthesize novel polyolefins (Horton, 1994; Reisch, 1995). Variants of this class could conceivably begin to displace other commodity plastics as well as create new engineering plastics. There are research challenges to meet before this potential is fully realized. Molecular weights of these polymers are often lower than desirable for the application. MAO, at the levels currently employed, is expensive and should be reduced in amount or replaced. There may be a need to develop heterogeneous versions of these catalysts, for various reasons, including the control of polymer particle morphology (see next section), without sacrificing their marvellous advantages. Heterogeneous catalyst development would bring analysis of diffusion controlled reaction back to the fore.

Macromolecular building blocks

Increasingly, polymeric materials are being, and will continue to be, synthesized, not directly from monomers, but from preformed, functionalized, macromolecular subunits. This is particularly true for multicomponent macromolecules. These building blocks are, in the simplest case, end-functionalized

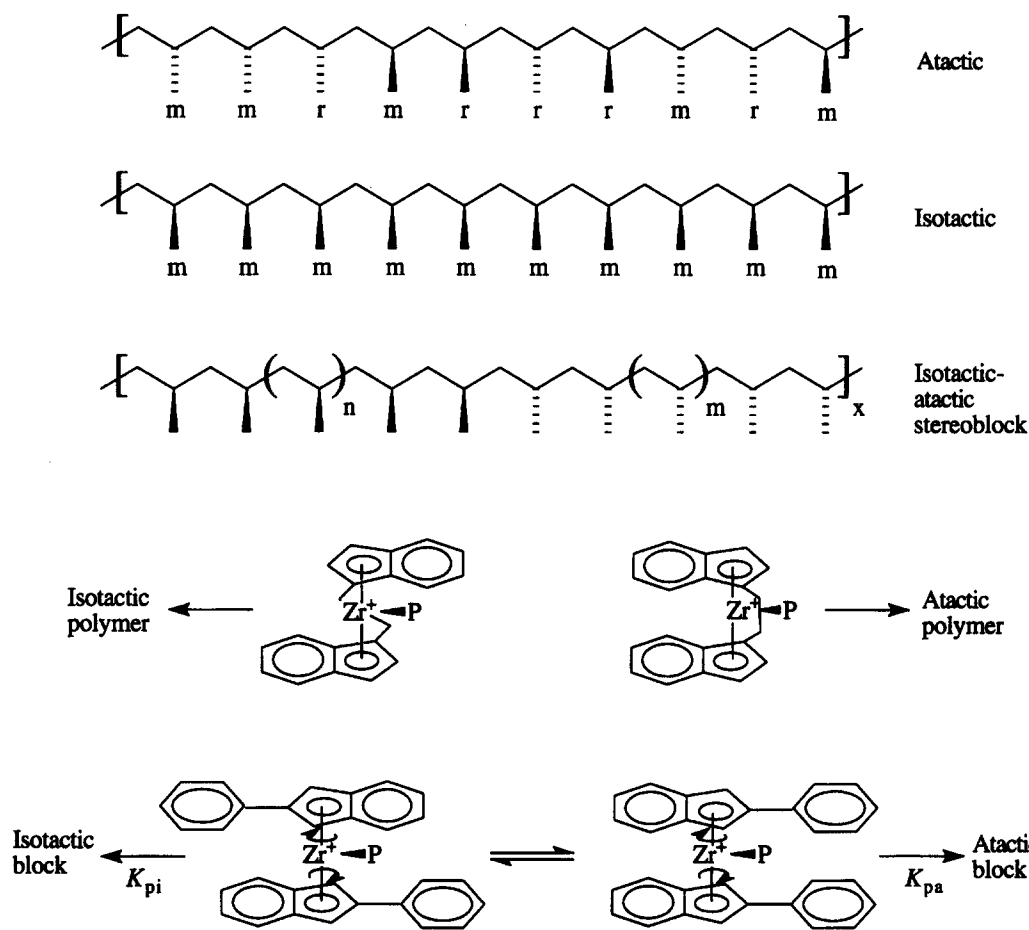


Fig. 3. Various stereochemistries for polypropylenes can be produced by metallocene catalysts. Adapted from Coates and Waymouth (1995).

oligomers or polymers (sometimes called telechelics) that are linked into larger structures by coupling reactions. More complex examples of subunits are highly structured molecular objects and particles that fuse into the desired materials.

This modular construction of polymeric materials raises some particular challenges for chemical engineers. One generic challenge is in the production of the subunits. In order to achieve many of the desired properties of materials put together in this manner, the subunits have to be made with a level of precision unprecedented at the production scale. Near perfect uniformity in molecular architecture and in degree of functionalization is often desirable. A second generic challenge is the creation of the reaction environments for assembly of the modules into materials. Ways of meeting these challenges are advanced in subsequent sections. This section deals with the motivation for the examples of new developments in macromolecular building blocks.

An intriguing development in the last few years, unanticipated in a review five years ago (Tirrell, 1991), is the burst of activity in the synthesis and applications of dendrimer polymers (Voit, 1995). In several ways, activity in this area typifies this subset of re-

search on macromolecular building blocks (Fréchet, 1994). The term "functional polymer" is often used to describe polymers that carry reactive functional groups that can participate in chemical processes without degradation of the original polymeric unit. Functional polymers are abundant in nature. Molecular architecture has significant effects on the characteristics of functional polymers. Most polymers consist of largely linear chains that are randomly coiled and entangled with their neighbors. Introduction of substantial amounts of branching is always accompanied by substantial changes in flow properties. Highly branched and star-like polymers have significantly lower melt viscosities than linear polymers of the same molecular weight (Graessley, 1974). From the point of view of functionalization, a major effect of branching is the multiplication of reactive chain ends.

Dendrimers are highly branched, three-dimensional macromolecules with branch points at every monomer, as illustrated in Fig. 4 from Fréchet (1994), leading to a structure that has essentially as many end-groups as it has monomer units. When synthesized by controlled, convergent growth, these dense regular structures adopt compact, well-defined

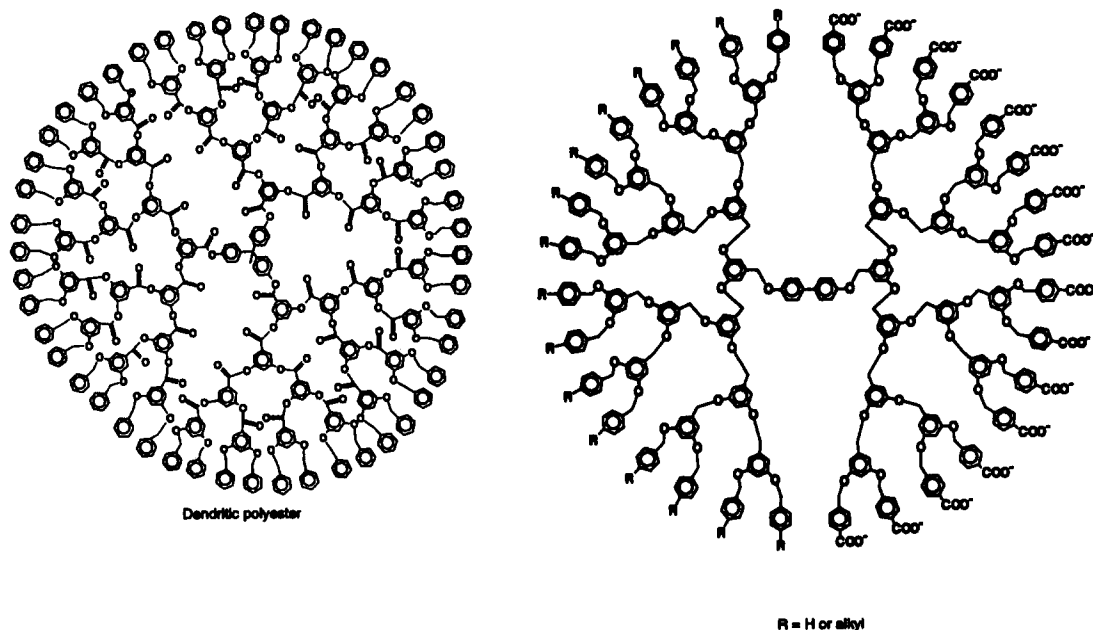


Fig. 4. (Left) Dendritic polyester. (Right) Amphiphilic dendrimer. Adapted from Fréchet (1994).

spherical shapes and, in initial explorations, have begun to exhibit physical properties not seen even in other more traditional forms of highly branched polymers. For example, the intrinsic viscosity of dendrimeric polymers (Mourley *et al.*, 1992) goes through a maximum with increasing molecular weight, in striking contrast to the monotonic increase with molecular weight in linear polymers. This is due to the fact that intrinsic viscosity measures the molecular volume pervaded per unit molecular mass; for higher generation dendrimers, the mass increases faster than the pervaded volume. Some other highly ramified products, known as hyperbranched polymers, also exhibit some of these physical phenomena, but lack the structural precision and its potential advantages (Kim and Webster, 1990).

Tomalia and Dvornic (1994) have succinctly summarized some of the exciting new applications for dendrimers being explored in industry and universities for these molecules. These include uses as polymeric catalyst particles and nanoscale reactors (Turro *et al.*, 1991), molecular mimics of micelles (Jansen *et al.*, 1994), delivery vehicles for magnetic resonance imaging agents, immuno-diagnostics and gene therapy (Haensler and Zoka, 1993), and building blocks for more elaborate supermolecular structures (Tomalia, 1994). The molecular features enabling these applications are persistent and controllable nanoscale dimensions in the range from 1 to 100 nm, some control over shape via molecular design of the dendrimer core (Fréchet, 1994), precise masses that can approach 100,000 (with polydispersities of $M_w/M_n \approx 1.0005$), chemically reactive surface functionality, interiors that can be specifically tailored to hydrolytically or thermally demanding environments,

and designable solvophilicity at the surfaces (even with controlled, local variation over the surface of the same molecule, see Fig. 4).

Dendrimers are species on the low side of the borderline of size and mass between molecules and particles, occupying a position somewhat analogous to fullerenes, though their synthesis is much more versatile and controllable. There is exciting activity in several quarters aimed at extending the desirable features exhibited by these structures up to larger sizes (molecular masses of 10^8 – 10^9) and different controllable shapes. Stupp has termed these target species "molecular objects" (Stupp *et al.*, 1993). Large, two-dimensional, flat sheet polymers are examples of such objects. Like dendrimers, they possess persistent shapes under changing thermal and phase state conditions and have well-defined, functionalizable surfaces. In general, though, molecular objects are being constructed with forms of monomer interconnection different from the highly branched route to dendrimers, two-dimensional cross-linking, molecular recognition, noncovalent bonding and nematogenic or self-assembly tendencies are among the routes being used to form large molecular objects. One can readily imagine applications for stratified two-dimensional polymers, where functionalized top and bottom strata would link an active middle stratum into a larger structure. Several alternative concepts are illustrated in Fig. 5 (from Stupp, see Acknowledgements). Treating surfaces with two-dimensional molecular objects, where desired surface functionality has been built into the molecule, bears a relationship to alternative surface treatments by adsorption of self-assembly something like the difference between wallpaper and painting. In the former, the desired pattern is preformed,

Concepts in Advanced Materials with 2D Polymers

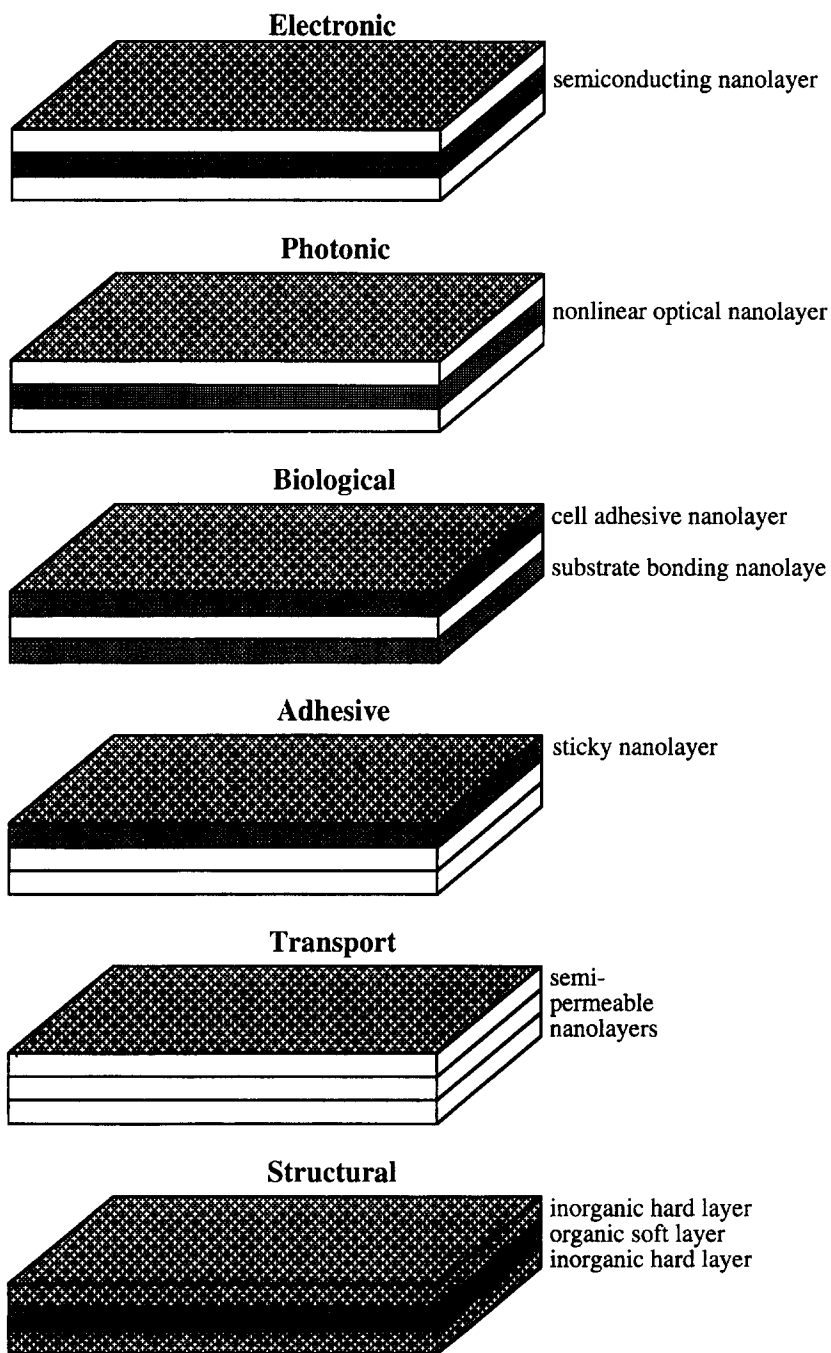


Fig. 5. Possibilities envisioned by Stupp (see Acknowledgments) for different structures and applications of two-dimensional polymers.

then applied; in the latter, pattern is created during the application process. Both have their uses. Other sorts of molecular objects under study are cylindrical (Imrie, 1995) and virus shapes (Kwon *et al.*, 1994) and molecular ribbons and tapes (Whitesides *et al.*, 1991; Lehn *et al.*, 1992). Additional polymer systems of

special molecular geometry are discussed by Eisenbach *et al.* (1995).

In the same spirit, the next step up the size scale from the nano- to the micro-level, and equally important to the chemical processing of advanced polymeric materials, is the production of polymer particles of

well-defined size. Emulsion and dispersion polymerization are the common routes for the production of these materials. Surface functionalization, in the form of core-shell morphologies and other routes, gives particles similar roles to those of smaller molecular objects in materials development. Galli (1994) describes the key role of particle size and morphology control in polyolefin manufacturing and, how it is possible, directly from the reactor, a broad range of polyolefin products in spherical form, with a soft, porous morphology. Spherical-form polymer particles are utilizable without any pelletization operation, which is expensive and risks degrading product properties. The importance of particle size and shape control in the solids flow and handling properties, vital in polymer processing, is being increasingly understood and is a point of contact between important issues in polymer materials and particle technology (Zukoski, 1995).

To the extent that well-defined functionalized polymers, molecular objects and particles are important for the future of polymeric materials, chemical engineers will have to learn to produce them in large scales, with unprecedented levels of precision and control. This has implications, in turn, for necessary developments in instrumentation and process control.

Noncovalent synthesis

Intermolecular coupling by routes other than covalent bonds can be very important in producing or interlinking the building blocks of the previous section. Noncovalent bonding is also of great importance in linking polymeric materials with their surroundings, as in adhesive or composite materials and applications. In a larger sense, noncovalent bonding is the foundation of supramolecular materials synthesis. Within the last few years, "supramolecular science" has become the cumulative title to describe the rapidly emerging achievements at the contact lines among chemistry, physics and biology (Ringsdorf, 1994). It applies the principles of self-organization, regulation, replication, communication and cooperativity, generally life-science-derived principles, to the development of new materials. Further attributes of biological systems, such as morphogenesis, pain (i.e. intrinsic capacity for defect detection) and healing (defect repair), may eventually also be instilled in materials.

Most current systems based on noncovalent synthesis are considerably less sophisticated than biology, though they may be based on the same types of intermolecular interactions, such as hydrogen bonding, electrostatic interactions, hydrophobic interactions or π - π stacking. Many biological materials are composed of hierarchical scales of structures. For example, in connective tissue, long molecules (≈ 100 Å) form helices (≈ 100 nm) which organize into fibers on the micron scale, which, in turn, organize into a fibrous network structure at the largest scale. Noncovalent forces are often the binding mechanism between different structural scales. These ma-

terials are naturally very important in themselves and provide stimulating impetus for the development of new, soft composite materials.

Several areas of current activity illustrate the research problems and potential for interesting developments in this area. Work on multilayer, thin films typifies some of the possibilities. Many of the applications are related to those illustrated in Fig. 5. The modification of the surface of solids with polymers has become a major challenge in both basic research and applied materials science. Tailoring of surface properties enables control of properties such as chemical binding for sensor applications, biocompatibility, conductivity for anti-static coatings, adhesion and friction. Controlled surface treatments permit the construction of a materials surface property while retaining desirable bulk materials properties.

Decher and coworkers (Decher and Schmitt, 1992; Decher *et al.*, 1994; Schmitt *et al.*, 1993) have pioneered a new technique of constructing multilayer polymer assemblies by consecutively alternating adsorption of anionic and cationic polyelectrolytes and/or bipolar amphiphiles. This synthesis process is driven by the electrostatic attraction between opposite charges as illustrated schematically in Fig. 6. In contrast to chemisorption methods (Gun and Sagiv, 1986; Whitesides *et al.*, 1991) that require a reaction yield of 100%, or lateral cross-linking, in order to stabilize a certain surface functional density after each reaction step, no covalent bonds need to be formed. Additionally, an advantage over the classic Langmuir-Blodgett method (LB) (Roberts, 1990) is that adsorption processes are relatively independent of substrate size and geometry, whereas LB deposition works only on large, smooth substrates.

The principle of self-assembly of multilayers in this fashion is sketched in Fig. 6. A solid substrate with a positively charged surface is immersed in a solution of the anionic polyelectrolyte and a layer of polyanion is adsorbed (step A). The surface can adsorb polyanion until all of the surface charges are compensated by adsorbed anions. If the adsorbate concentration in solution is high, however, the adsorbed polymers will retain many unbound anions exposed to the interface with the solution. In this way, the charge of the surface is effectively reversed. After rinsing in pure water, the substrate is immersed in a solution of cationic polyelectrolyte. Polycations adsorb on the anionic surface (step B) and, again with sufficient reservoir in solution, the surface charge can be overcompensated and reversed back to positive. Repetition of steps A and B in a cyclic fashion leads to an alternating multilayer assembly. The minimum charge functionality per molecule necessary to accomplish this is two and the first examples of this method of assembly were accomplished with bipolar (i.e. double-ionic-headed, sometimes called bolaform) amphiphiles. Mao and coworkers (Mao *et al.*, 1993, 1994, 1995) have produced such assemblies with cationic bolaform amphiphiles and anionic polyelectrolytes and have measured their mechanical properties in compression. The

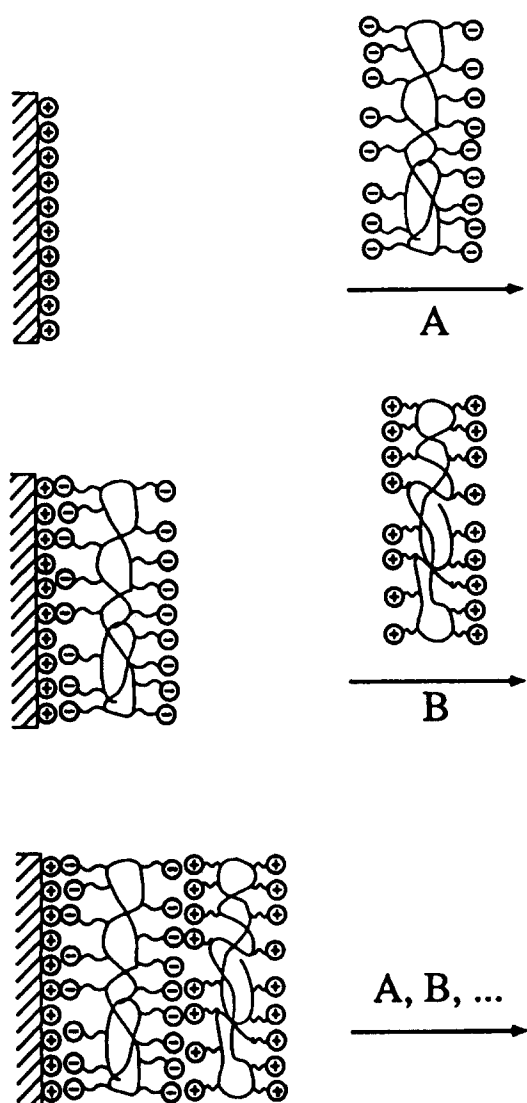


Fig. 6. Schematic diagram depicting build-up of multilayer assemblies by sequential adsorption of anionic and cationic polyelectrolytes. Counterions omitted for simplicity. Adapted from Decher *et al.* (1994).

synthetic options are widely varied. The ability to continue the sequential adsorption reproducibly through a large number of adsorption cycles has been demonstrated often and for many different molecular combinations (Mao *et al.*, 1993, 1994, 1995; Decher and Schmitt, 1992; Decher *et al.*, 1994; Schmitt *et al.*, 1993).

This inversion and reconstruction of surface properties can be viewed as a simple form of template-controlled growth regulated by molecular recognition. The solid-liquid interface acts as a template for the deposition of the subsequent layers. The next layer, if adsorbed properly, will refunctionalize the surface, providing a template for the following layer. Sequential adsorption of two compounds produces an alternating sequence $(AB)_n$, but there is no requirement that this be a two-cycle process. The only re-

quirement for the construction of more complex film architectures, such as $(ABCB)_n$ or $(ABCDEF)_n$, is that a single molecular layer be deposited in each cycle that effectively overcompensates the previous surface functionality. Such structures will have useful properties in their own right and can also serve as scaffolds and templates for insertion of other structural and functional elements (Maoz *et al.*, 1995).

This line of materials production by noncovalent synthesis is by no means confined to surface reconstruction. In bulk media, polyelectrolyte complexes made of two oppositely charged polyelectrolytes also spontaneously form complexes, sometimes termed simplexes, which exhibit interesting material properties (Kabanov and Zezin, 1984). Stable porous and selective membrane structures have been made by this route. Similarly, complexes of polyelectrolytes and surfactants of opposite charge have been shown (Antonietti and Conrad, 1994; Antonietti *et al.*, 1994) to assemble spontaneously into materials possessing internal, layered or cylindrical microstructures and interesting, elastomeric properties. In these ways, these noncovalently bonded materials resemble the structures formed by amphiphilic molecules and polymers (Bates and Fredrickson, 1990).

Conceptually closely related to these polymer-surfactant complexes are synthetic, nanophase, organic-inorganic hybrid materials (Dangani, 1992). In these materials, polymers are bound by adsorption within an inorganic host, for example, a layered silicate, which generally imposes some ordered microstructure on the assembly. Polymers are inserted into these microstructures by several routes: intercalation of a monomer followed by polymerization (Cao and Mallouk, 1991), polymer intercalation from solution (Messersmith and Stupp, 1992), or from the melt (Vaia *et al.*, 1993). These nanocomposites combine the high strength and thermal stability of ceramics with the processibility and crack-deflecting properties of polymers. The dielectric properties of these materials are essentially the same as the bulk polymer making them very attractive materials for insulating layers in microelectronics applications. The converse of these organic-inorganic hybrids, where the inorganic phase largely determines the morphology of the composite, is the interesting work going on in several chemical engineering groups, using the self-organizing properties of organic molecules, such as amphiphilic polymers and surfactants, to make templates for inorganics, such as zeolites or microstructured ceramics, where the organic may eventually be removed by high-temperature processing (Archibald and Mann, 1993); Fig. 7 illustrates some possibilities. Stucky, Chmelka and coworkers (Monnier *et al.*, 1993; Firouzi *et al.*, 1995) have demonstrated a strong surface templating effect in the synthesis of these materials.

Research efforts by chemical engineers in this general field of noncovalent synthesis is needed in many directions. Relative to covalent bonds with energies ranging from 100 to 300 kcal/mol, bonding in noncovalent assemblies is very weak with bond energies

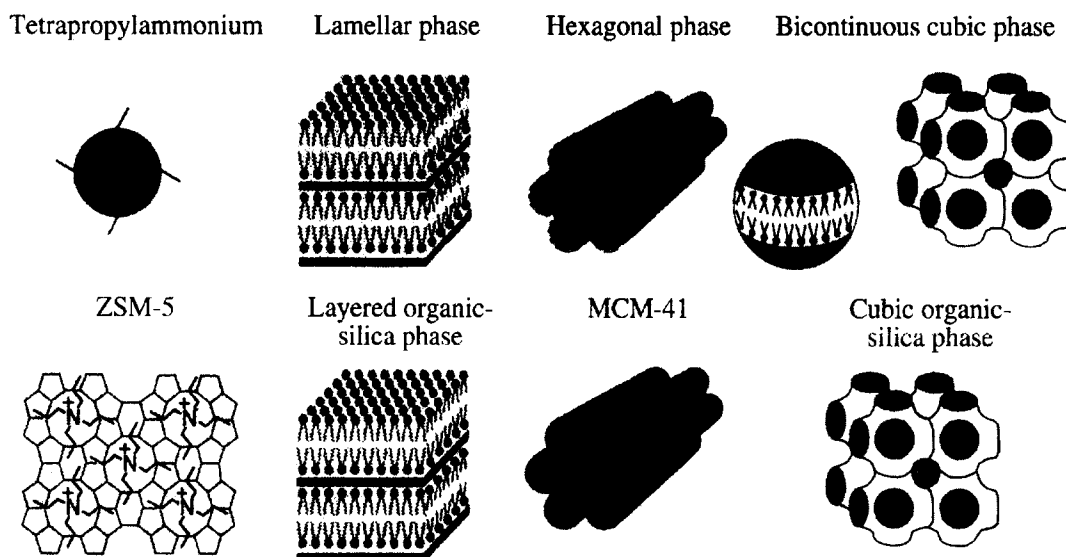


Fig. 7. Some architectures that can be obtained by organic templating of inorganic materials: (top) organic molecules and aggregates; (bottom) the zeolite or microporous oxide. Adapted from Davis (1992).

(hydrogen, electrostatic, dipolar, van der Waals) in the neighborhood of 0.1–5 kcal/mol. Effective processing of these materials will require development of understanding of the kinetics of these physicochemical processes, analogous to chemical reaction kinetics. Such syntheses require the development of multiple sets of interactions coordinated in time and space. This remark, in fact, applies to *all self-assembly processes* where overwhelming attention has been given to the structures formed and insufficient investment has been made in kinetics, mechanisms and ultimate properties of the resultant materials. Most of the examples cited here consist of materials built up from electrostatic interactions with other molecules and surfaces. Weak bond energies implies either weak structures or that multiple bonds have to be formed to stabilize noncovalent structures. In general, noncovalent structures are soft (meaning exhibiting significant responses to weak stimuli, such as ambient thermal energy), but can be strengthened as much as desired by additional bonding. Polymeric nematicogens, such as thermotropic, main-chain liquid crystalline polymers, owing mainly to their high cost have not made much commercial success as hard, stiff materials. However, for applications where higher cost can be borne, such optoelectronic properties, polymers capable of organizing themselves through noncovalent nematic interactions are increasingly important (Imrie, 1995).

Biological synthesis of polymeric materials

A theme underlying several phases of the foregoing discussion is the growing need for the precise synthesis of modular building blocks for polymeric materials. Whether for surface modification or for noncovalent synthesis by molecular recognition or for precise control of material properties, the needs for

exquisite tailoring and uniformity of macromolar structure have never been greater. This, coupled with the potential to eliminate reliance on petroleum feedstocks, is driving strong efforts in the synthesis of macromolecular materials by microorganisms. Macromolecular synthesis of polymers by biological routes is a large subset of the emerging field of biomolecular materials (Tirrell *et al.*, 1994). With increasing frequency, new materials or processing strategies are emerging, inspired by biological examples or developed directly from biological systems. Researchers are engineering bacteria or other organisms to synthesize monomers for polymer production. They are synthesizing and expressing artificial genes to produce protein-like materials with mechanical properties of silk, or other materials containing elastic fibers (Bailey, 1995). The aim is to harness the efficiency of biosynthesis. Organisms carry out astonishingly elaborate sequences of organic reactions that convert simple building blocks into complex natural products. The comparable degree of efficiency in an industrial chemical process would be the equivalent of converting a single chemical feedstock into end products without having to isolate or purify any intermediate. Examples of commercially successful monomer or polymer precursor (Mobley, 1994) production via biosynthesis include: the ICI invention of a selective bacterial oxidation of benzene to produce 5,6-*cis*-dihydroxycyclohexa-1,3-diene (DHCD) which is conventionally chemically acylated and free radically polymerized to polyphenylene (which becomes an organic semiconductor on doping) and; the General Electric fungal, regiospecific, hydroxylation of biphenyl to the 4,4'-dihydroxy derivative, which is used to prepare GEs engineering plastic Ultem II.

A number of bacteria produce biodegradable polyhydroxyalkanoate (PHA) polyesters. The most

common PHA, poly(3-hydroxybutyrate (PHB), an energy and carbon reserve material in many bacteria (Anderson and Dawes, 1990), is accumulated as intracellular granules under nutrient-limiting conditions other than carbon limitation. A wide variety of other PHA are also synthesized in response to nutrient deficiencies. PHB is quite brittle and melts at 180 K. PHA copolymers are considerably more flexible and are stable at temperatures high enough to withstand conventional plastics processing methods. A PHA copolymer developed by ICI is in commercial use in biodegradable films, coatings, molded materials such as bottles, and controlled drug release applications. Engineering PHA-producing organisms are to assimilate and utilize effectively for synthesis of a variety of unnatural, but inexpensive and mechanically beneficial, PHA copolyesters (Jackson and Srienc, 1994).

Engineering protein and polypeptide-based material is attracting increasing attention and has enormous possibilities for new materials from structural proteins, like silk, collagen, and elastin that have long intrigued materials scientists (Urry *et al.*, 1992), to materials optimized for other properties such as cell adhesion or chemical and biological sensors. Genetically engineered bacterial systems offer superior control over the architecture of polymer chains. New routes to materials synthesis will increasingly require precise molecular units. The basic strategy involves, as a first step, the solid-state synthesis of double-stranded DNA segments that code for the desired amino acid repeat units. More than one of these segments may be stitched together with ligation enzymes to produce multiple coding units arranged in tandem. This synthetic DNA sequence (an artificial gene) is then inserted into a plasmid and the recombinant molecule introduced into a strain of *Escherichia coli* that can express the protein. However, use of these genetic engineering techniques to produce unnatural proteins and polypeptides presents several problems, outlined by Tirrell *et al.* (1994). First, repetitive DNA sequences are highly susceptible to rearrangement and deletion. Second, the messenger RNA needed to synthesize a "foreign" protein may be subject to rapid degradation. Third, because most amino acids are specified by more than one codon, it is possible to select a sequence in the artificial gene that is inefficiently processed during protein synthesis. Finally, foreign proteins may be toxic to the host cell and kill it before useful amounts of the protein is synthesized.

Despite all these adversities, progress is being made (Creel *et al.*, 1991; McGrath *et al.*, 1992; Dougherty *et al.*, 1993; Parkhe *et al.*, 1993). *De novo* design of protein-based materials opens great possibilities for imaginative molecular architecture. A materials design target that has received considerable attention is the synthesis of polypeptides that could fold over and back at regular intervals to produce a lamellar protein crystal, as illustrated in Fig. 8. Construction details that have to be attended to include the secondary structure of the lamellar-spanning chains (α -helical or

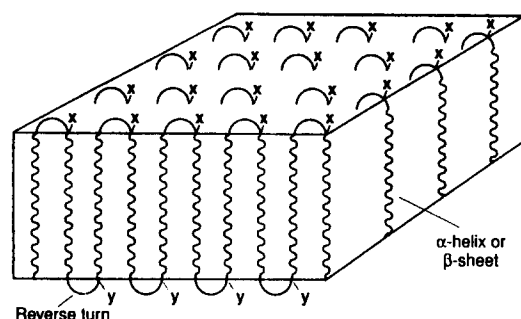


Fig. 8. Polypeptide chains that could fold back and forth at regular intervals would produce synthetic lamellar protein crystals of well-defined size and with predetermined functional groups positioned on fold surfaces. Compare with Fig. 5. Adapted from Tirrell *et al.* (1994).

β -sheet), the size and thickness of the crystals and the chemical functionality of the two surfaces. A major challenge that is being approached in several ways is how to incorporate entities beyond the naturally occurring amino acids. Successes have been achieved in incorporating elements such as selenium (via selenomethionine) and fluorine (via *p*-fluorophenylalanine) (Tirrell *et al.*, 1994).

Environmentally benign synthesis of polymers

The foregoing sections deal with chemical engineering developments in polymer production that are driven by the creation of new polymer structures and properties. There are other drivers of new polymerization methods. Among the most challenging technically is the pursuit of more environmentally friendly commercial reactions for monomer and polymer production. An example of an alternate process with an environmental rationale is a route to polycarbonate, an impact-resistant engineering thermoplastic developed by General Electric, which does not involve the use of phosgene. Condensation polymerization of phosgene with bisphenol-A is the traditional route. The newer technology (Wirth, 1994) replaces phosgene with diphenylcarbonate (which is transesterified with bisphenol-A to make polycarbonate) which, in turn, is produced from methanol and carbon monoxide. The key to this process is a detailed understanding of the process variables and careful process control.

A second example in the synthesis area driven by environmental rationale pertains to the production of fluorocarbon polymers, such as Teflon and related materials, which are used extensively for their low energy surface properties, as lubricants in computer disk drives, protective coatings and sealants (Scheirs *et al.*, 1995). Fluoropolymers are generally insoluble in most organic solvents, but are readily soluble in the chemically similar chlorofluorocarbon solvents (CFCs). However, scientific evidence and governmental regulation now dictate diminishing use of CFCs owing to environmental concerns, posing technical problems for the polymerization and processing of fluoropolymers (Haggan, 1995). DeSimone and

coworkers (DeSimone *et al.*, 1992, 1994; Shaffer and DeSimone, 1995) have demonstrated that supercritical CO₂ is an excellent alternative to CFCs for conducting homogeneous solution homo- and copolymerizations of fluorinated monomers. They have shown that it is possible to synthesize high molecular weight fluoropolymers at reasonable rates in supercritical CO₂. The more widespread use of supercritical CO₂ as a polymerization and processing solvent is being explored, giving further impetus to the field of supercritical solvents in general (McHugh and Krukoni, 1986; Savage *et al.*, 1995).

POLYMER PHYSICAL PHENOMENA

Recognition of additional fundamental parameters governing phase behavior and entanglement

Organization of information about the physical phenomenology of polymers in a form that displays some universal character is particularly useful for engineering purposes. Key to this is the identification of all the fundamental governing parameters for the behavior of interest. Our long experience with scaling and dimensional analysis teaches us this. For the purposes of the first part of this discussion, we are going to confine our attention to rheological, diffusion and phase behavior of polymers. Chemical engineering insight into thermodynamics, phase equilibria and transport phenomena has long been a mainstay of progress in polymer physical science (Bird *et al.*, 1987). Much of the spectrum of bulk behavior in these areas for long-chain polymers has been organized in terms of just five fundamental parameters: χ , the interaction energy (in units of kT) that must be paid to move a segment into an environment where it interacts with a segment of different chemical nature; N , the number of segments per chain; b , the effective (often called the "statistical") segment size (Flory, 1969); ζ , the friction coefficient per segment; and M_e , the molecular weight between entanglements. These are the parameters in which the theories of polymer physics are written; the data are plotted in terms of these or their combinations.

Phase behavior of polymers is influenced by the first three parameters and, in fact, the first two act in combination, with χN being the important parameter. This combination signifies that chain length, N , becomes an effective thermodynamic parameter in the sense that a small intersegmental effect, χ , can be multiplied into an arbitrarily large intermolecular effect by increasing the molecular weight. Mixtures of chemically different polymers of equal N have a critical point for demixing at $\chi N = 2$ and Φ (volume fraction) = 0.5. Multicomponent polymers in addition to blends, such as block copolymers, also exhibit phase behavior governed largely by χN .

Phase transitions involving ordered states on a mesoscopic scale occur in a wide variety of materials of interest from solid-state physics to structural biology to applied materials science. These transitions present a rich field of current interest for chemical engineers

both from a fundamental point of view and for their significance in controlling material structure and properties. Classes of materials exhibiting this behavior include thermotropic and lyotropic liquid crystals and block copolymers. Block copolymers can be viewed as displaying both lyotropic and thermotropic behavior since phase transitions can be induced by changing the composition, f , and temperature, T , respectively (Förster *et al.*, 1994). Symmetrical ($f = 0.5$, that is, both blocks of equal chain length) diblock copolymers are conventionally represented, and experimentally found, to have a transition between a disordered phase and an ordered lamellar phase at $\chi N \approx 10$ (Leiber, 1980). Typically, two limiting regimes in the "phase diagram" are distinguishable for the ordered regime. (We note that since χN and f are not intensive variables, this is not a proper phase diagram in strict thermodynamic terms.) In the strong segregation limit (SSL), $\chi N \gg 10$, enthalpic effects dominate, leading to a sharp interfacial composition profile that approaches a step function. In the weak segregation limit, $\chi N \approx 10$, entropic contributions become more important, leading to a broad interface with a composition profile that tends toward a sinusoidal form. The weak segregation limit is a more complex and delicate area of the phase diagram, very relevant for processing of these materials, since most processing involves transient passage through this state. Moving away from $f = 0.5$, to asymmetric diblock copolymers, produces an array of ordered phases with different symmetry, most commonly hexagonally arrayed cylinders and BCC-ordered spheres, as well as bicontinuous phases, for certain values of f . Some of the structures that have been observed are illustrated in Fig. 9.

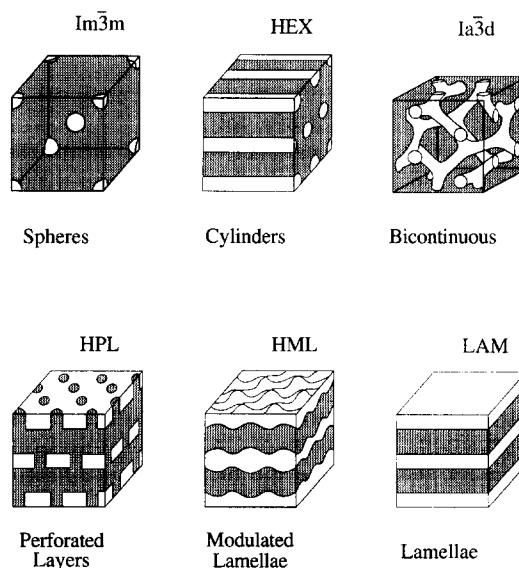


Fig. 9. Ordered microstructures observed in A-B diblock copolymer melts near the order-disorder transition. Adapted from Bates *et al.* (1994b).

Recently, several groups have seen that the phase diagram for block copolymers is asymmetric about $f = 0.5$, which would not be expected if composition and χN were the only relevant parameters. This asymmetry is particularly pronounced in the weak segregation limit (WSL) near $\chi N = 10$. The reason for the appearance of these new phases, and their asymmetric placement with respect to changes in f in the WSL, is the ability of the additional factors to influence the behavior. In the strong segregation limit (SSL), ordered-phase organization is dictated by the enthalpic drive to demix unlike segments, tempered only by classical translational entropy. Mean-field analyses are satisfactory in the SSL. In the WSL, chain stretching, chain packing and fluctuation effects come into play in addition to the classical factors. These effects require additional parameters for their description. (Bates *et al.*, 1994b). The magnitude of fluctuation corrections to mean-field theory is controlled by (Fredrickson and Helfand, 1988)

$$N = a^6 N / v^2 \quad (1)$$

where, for the time being, we are assuming that segments of both are of the same length a and same volume v . Note that $v \neq \frac{4}{3}\pi a^3$; v is a real packing volume, the occupied volume of the segment, whereas the effective segment length, a , is a chain configurational property relating the radius of gyration of the coil to N . The importance of fluctuations decreases with increasing N . A second important nonclassical parameter

$$\varepsilon = \beta_A^2 / \beta_B^2 \quad (2)$$

gauges the differences in space-filling characteristics of the two blocks A and B. β , referred to as the conformational asymmetry parameter, is defined from the ratio of the radius of gyration, $Na^2/6$, to the volume of the chain, Nv :

$$\beta^2 = a^2 / 6v \quad (3)$$

and provides a measure of the conformational vs volume-filling behavior of a polymer.

Fluctuation effects, parametrized by N , dictate the appearance of new phases for lower molecular weight polymers in the WSL. As fluctuation effects increase, the ordered system will be driven toward increasingly isotropic states, such as the cubic bicontinuous states that have recently been identified. This relieves some of the packing frustration (Seddon, 1990) experienced by low molecular weight polymers and amphiphiles in forming an ordered phase. Conformational asymmetry effects, parametrized by ε , play off against the compositional asymmetry of f in dictating interfacial curvature and therefore the morphology of micro-phase separation. A composition of $f > 0.5$ tending toward a spontaneous curvature that might lead toward a cylindrical morphology can be neutralized by a balancing conformational asymmetry, $\varepsilon > 1$, which means that the compositional majority component of the copolymer also adopts a more compact radius of

gyration per unit chain length. Thus, compositional and conformational effects are driving interfacial curvature in different directions. Phase symmetry is not dictated by copolymer composition alone.

Conformational asymmetry effects have also recently been shown to be important in determining surface segregation and phase organization in thin films of block copolymers (Sikka *et al.*, 1994). There is every reason to believe that further consideration and exploration of these trade-offs between conformation and space-filling packing, and their interactions with the classical parameters, will lead to a better understanding of phase diagrams of amphiphilic molecules, in general, and the connection between low molecular weight surfactants and block copolymers, in particular. Chemical engineers can gain practical information on the utilization and processing of these materials for a wide range of applications in pursuing such research.

Interestingly, the conformational parameter β (Helfand and Sapse, 1975) has recently appeared in a different important context, that is, in the connection between polymer molecular weight, density, chain dimensions, and melt viscoelastic properties (Fetters *et al.*, 1994). One of the principal goals of polymer science has been to relate the structure of macromolecular chains to their macroscopic properties. In the context of polymer melt rheology, dynamics and processing, the objective has taken the form of prediction of the degree to which polymer chains entangle and manifest viscoelastic rheology. In a foregoing paragraph, we mentioned the basic entanglement parameter, M_e , which is a well-tabulated quantity (Ferry, 1980) for a wide range of polymers. It is experimentally well-defined from the plateau modulus exhibited by entangled polymer melts, and given a value for M_e , or a related quantity, the reptation theories stemming from the pioneering work of de Gennes (1971) and Doi and Edwards (1978) can predict a wide range of rheological behavior (Macosko, 1994). Reptation as a physical mechanism has been vividly observed in striking experiments by Chu and co-workers (Perkins *et al.*, 1994). However, there has never been a reliable *a priori* predictor of M_e . It now appears that Fetters *et al.* (1994) have discovered one.

Their model is predicated on the idea that there is a relation between the sizes of the polymer coils and the degree to which they are entangled with one another. The essence of their model is that, the larger the dimensions of a chain, the greater the volume it sweeps out, and the greater the number of other chains it will encounter and with which it might entangle. This requires knowledge of the volume a chain occupies (given by M/ρ , where ρ is the polymer density) and also the volume pervaded or spanned, V_{sp} , by the random walk chain estimated as being proportional to the three-halves power of the radius of gyration of the chains. From these quantities, Fetters *et al.* (1994) estimate M_e by determining the molecular weight at which the pervaded volume of a chain is just large enough to permit there to be, on average, within

the unoccupied space within the pervaded volume, just two full chains (it takes two to entangle). This model involves the same conformational and packing parameters that were discussed in connection with block copolymers, and when these ideas are properly assembled, the resulting prediction is that

$$M_e = K\rho p^3 \quad (4)$$

where K is a numerical constant that can be estimated, and $p = \beta^{-2}$, which gives the conformational parameter the dimensions of length, sometimes termed a packing length (Witten *et al.*, 1989). Since many models of rheological properties are cast in terms of M_e , this leads immediately to property predictions such as the plateau modulus:

$$G_N^0 \sim \rho/M_e \sim p^{-3}. \quad (5)$$

Figure 10 shows how well this works for about two dozen different polymers.

It appears that these relationships apply to a very broad range of linear polymers, from rubbers to engineering thermoplastics. They should greatly assist the *a priori* prediction of the properties of new polymers by polymer modeling software packages. Accurate prediction of chain conformations leads immediately to viscoelastic property predictions. Furthermore, this packing length parameter is already appearing in other contexts, such as the packing length parameter is already appearing in other contexts, such as the packing of interfacial chains tethered to an interface (Witten *et al.*, 1989), where packing interactions result in chain stretching in the direction normal to the interface and give rise to a range of interesting properties (Halperin *et al.*, 1992).

Effects of external fields on microstructured polymers

Control of molecular orientation has always been a key component in successful polymer processing operations. Particular examples include fibers and films where strong uniaxial and biaxial extensional flows are essential to the development of good properties during processing. When the material contains larger scale, and possibly more complex and delicate, internal microstructures, such as liquid crystalline

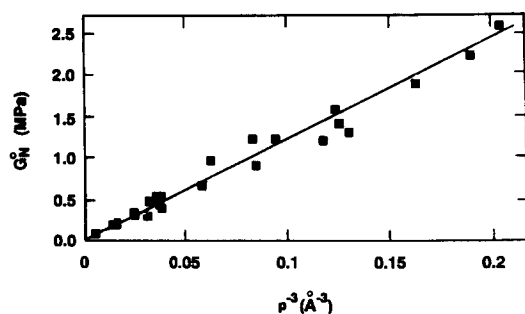


Fig. 10. Linear plot of plateau modulus vs inverse cube of the packing length, testing eq. (5). Adapted from Fetters *et al.* (1994).

polymers (Kannan *et al.*, 1993) or block copolymers (Koppi *et al.*, 1992, 1993), the opportunities for and susceptibility to processing via external fields goes up. The growing activity in a variety of chemical engineering groups on the shearing of ordered block copolymers provides good examples of the research needs and opportunities in this area.

Work in the area of shearing diblock copolymers started (Koppi *et al.*, 1992, 1993; Albalak and Thomas, 1993) with the objectives of preparing samples where the small-scale domains could be induced to form a uniform large-scale, sample-spanning orientation of the "crystallographic" planes of the microstructure, and examining structure-property relationships in these materials. Single domain samples can be used more readily for structure determination and for studying the anisotropy of properties, such as diffusion (Balsara *et al.*, 1991). We use the language of crystallography here since these efforts parallel developments of several decades ago in metallurgy in looking at multigrain materials vs single crystal materials and deducing the effects of grain boundaries on properties. We view these efforts in part as an opening of the important, and largely untouched, field of understanding the defect structure, and its implications, in microstructured polymers.

The ordered microstructures of block copolymer melts, and various other types of soft condensed matter lead to a variety of special properties. In general, the long-time relaxation behavior of ordered block copolymers follows neither a liquid-like terminal response (i.e. $G' \sim \omega^2$ and $G'' \sim \omega$) nor a truly solid-like behavior (i.e. G' independent of ω) (Bates, 1984; Rosedale and Bates, 1990). Even when the rheological properties of the polymer chains comprising each block are similar, the presence of composition gradients at the microdomain interfaces can lead to complex dynamics, including highly non-Newtonian and nonlinear rheological properties. Defects within the ordered structure of copolymer melts can also affect the relaxation behavior, and the polycrystalline nature of quench-ordered materials further complicated the dynamic response of these materials.

Techniques for producing monodomain, "single crystal" samples have been known for over 20 years (Keller *et al.*, 1970; Hadziioannou *et al.*, 1979) but a surprising array of new features and fruitful lines of research have been uncovered in the last three years. First, it has been found that lamellar-forming microstructures is simple shear can be formed into single crystal samples with very few defects (Koppi *et al.*, 1992, 1993; Winey *et al.*, 1993); however, the orientation of the lamellae can be either parallel or perpendicular to the planes of shear, depending on the material and on the temperature and deformation parameters (strain and strain rate). A variety of interesting ideas and methods are being pursued currently to understand the orientation selection mechanism in both lamellar and cylindrical samples (Morrison *et al.*, 1993; Kannan and Kornfield, 1994; Tepe *et al.*, 1995). The theory for these phenomena is only developed to

a very basic level (Fredrickson, 1994). There are parallels between these observation and phenomenon occurring in sheared suspensions of particles (Chen *et al.*, 1992).

A second new feature, that may have even more fundamental and practical significance, is that the application of shear has been shown to affect the order-disorder transition temperatures rather strongly (Koppi *et al.*, 1993; Bates *et al.*, 1994a). The basic reason for this appears to be the effect of shear on the fluctuation spectrum in the material (Cates and Milner, 1989); fluctuations tend to depress the ordering transition temperature, since fluctuations screen interactions among dissimilar segments (Fredrickson and Helfand, 1988). Shearing suppresses fluctuations and their role in depressing the transition; thus, the ordering transition temperature rises.

More generally, shearing of these materials is a prime example of the effect and utility of an external field on the properties and processing of polymers. Magnetic and electric field poling of liquid crystalline, optoelectronic and nonlinear optical polymers is an equally rich and important field of chemical engineering research (Knoll, 1993). Another general lesson from examining the opportunities in this field is the need for continuing work on the rheology and related dynamic properties of polymers with new molecular architectures. No engineering discipline is better prepared to master the delicate interplay of effects necessary to control the processing of organic materials than chemical engineering.

Polymer surfaces and interfaces

Surfaces are the regions through which materials connect and interact with their surroundings. Transmission of stress, adhesion, friction, abrasion, permeability to gases and liquids, compatibility with biological or harsh corrosive environments are all properties of polymeric materials that are dominated by the structure and characteristics of that portion of the material that finds itself within tens of nanometers of the surface. All multicomponent polymers have an important internal structure comprising interfaces that determine their properties, such as the rheology discussed in the preceding section. Furthermore, some components of multicomponent polymers may segregate preferentially to the external surfaces of the material and therefore exert an influence on surface properties disproportionate to their bulk composition (Parsonage and Tirrell, 1993). Much of modern polymer engineering research is dominated by surface and interfacial issues.

Tremendous advances have been made in the last decade in the instrumental methods to examine polymer surfaces and interfaces (Parsonage and Tirrell, 1993; Stamm, 1992). It is now possible to determine compositions and molecular ordering of polymers near surfaces with depth and lateral resolutions of the order of nanometers in the most favourable cases. Adsorption of polymers at interfaces between solids and polymer fluids can be followed from the point of

view of adsorbed amount and chain configurations on surfaces (Amiel *et al.*, 1995; Watanabe and Tirrell, 1993).

This is not the place for a thorough review of all the possible research opportunities in polymer surfaces and interfaces. However, some general commentary is in order since the potential for significant engineering research in this area is enormous. What is most needed is a shift in emphasis from the recent concentration on structure toward a focus on the properties of polymer surfaces. Engineers need to take up the direction of the development of *surface structure-property relationships* in polymers.

An excellent example of this line of work is in the study of the adhesiveness of polymer interfaces. There is currently no fundamental theory from which one can reliably predict the adhesion at a polymer interface. There is no parallel to our understanding of bulk structure-property relationships. This endeavor is challenging because adhesion is a complex property combining rheology, fracture mechanics and surface science. Brown (1991, 1993, 1994) has summarized many of the important issues. Some current attention is being focused on the adhesion at the interface between a cross-linked elastomer and a solid surface with linear chains end-anchored to the solid. The aim is to pose well-defined questions on model systems where the structure is both simple enough to model and readily determinable in sufficient detail experimentally. The basic goal in this research is to understand how the number of length of polymer chains attached to the surface enhance the adhesion by penetration into the network. Simple theory predicts linearity in adhesion enhancement with both variables (Raphaël and de Gennes, 1992). Experiments show (Deruelle *et al.*, 1995) that adhesion is indeed enhanced by polymer grafting but there is a maximum with increasing density. This problem is currently being dissected by detailed study of the degree of interpenetration between the layer and the elastomer.

Other important problems in this surface structure-property vein include: studies of shearing and other dynamic phenomena in this polymer films (Van Alsten and Granick, 1990) and near surfaces (Chakraborty and Adriani, 1992), leading to enhanced basic understanding of friction; microscopic probes of adhesion, aiming to break down adhesion phenomena into their rheological and surface chemistry components (Mangipudi *et al.*, 1994, 1995); wall slip, and related flow instabilities in exit flows of polymer fluids (Denn, 1980); biocompatibility, and learning to make polymers that are *designed for*, rather than *adapted to*, contact with tissue.

Instrumentation to advance polymer science and engineering

Significant advances in characterization methods have always paralleled the development of new polymeric materials. This is a very germane point for chemical engineers, related to our discussion in the Introduction. One can only control a process when

the desired outputs are well-measured or estimated. Generally speaking, with polymeric products, these can often be difficult-to-measure structural features or end-use properties. Instrumentation must advance as new applications are moved forward. The Stein Committee (National Research Council, 1994) categorizes the recent and potential breakthroughs in instrumental methods of polymer characterization into five main target areas: molecular characterization of the architecture of single polymer chains; characterization of the architecture of single polymer chains; characterization of solutions, melts and elastomers, especially in their dynamic properties; solid-state structure and properties; surfaces and interfaces; and characterization of biopolymers. Only a few highlights of needs and opportunities for chemical engineers will be mentioned here.

Related to the molecular characterization area, the Polymer Reactions section of this paper discussed many ways in which seemingly subtle manipulations of feature such as placement of chain branching, sequence distribution and stereoregularity can be of major technological importance for polymer products. Better means, and faster means (for process control), to measure these quantities and couple the measurements with production are very much needed. NMR and other high-speed, high-resolution spectroscopies seem most promising. Molecular weight determination, even for relatively high molecular weight polymers, is on the verge of becoming a nearly exact methodology with the continuously increasing capability of matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF). Precise molecular weights up to 100,000 have been determined along with more subtle, important features such as simultaneous end-group analysis (Belu *et al.*, 1994).

Molecular rheology is a field with a rich tradition, and an important future, in chemical engineering. The relation between molecular level structure in solutions, melts and elastomers, and their deformation and flow characteristics is essential to control properly polymer processing operations such as injection molding, fiber spinning or extrusion. Perhaps most worthy of developmental time and energy expenditure are methods that couple flow with on-line optical, scattering or imaging methodologies that operate in real time. Rheo-optics [e.g. Kannan and Kornfield (1994)], on-line neutron [e.g. Koppi *et al.* (1992, 1993)] or X-ray scattering, flow ellipsometry, and other related methods yet to be conceived, are all worthy of development to the maximum extent possible, which will not be adequate until we can see all essential fine molecular details of structure and orientation, on-line in real processing operations. There is great potential for interaction here between basic and applied research. Some of this capacity will come from instrumental development; some will come from peripheral (e.g. fast, multidimensional detectors) and software development. Scattering methods with increasingly intense sources will pay back their costs with a more

than proportional amount of unprecedented information.

New imaging methods are likely to be the dominant innovations in both solid-state and surface characterization. Among these will be scanning probe microscopies, of which scanning tunneling microscopy and atomic force microscopy are the first examples; optical, magnetic, electric field and ionic versions are in various stages of development and realization. Micromechanical analysis, combining deformation with *in situ* microscopy (Michler, 1995), will be increasingly important tools to probe complex molecular architectures.

PROCESSING POLYMERS FOR HIGH PERFORMANCE

The growth of polymers, both in volume and in number of uses, is in part related to their ease in processing. Means of processing are many and varied, tailored to their applications. The Stein Committee Report (National Research Council, 1994) has pointed to two broad areas as most significant for future advanced technology applications of polymers: health, medicine and biotechnology; and information and communications. These applications in turn suggest the importance of certain types of processing: surface modification and the development of soft, composite materials for biomedical applications; precise control of molecular orientation for optoelectronic polymers, of growing importance in information and communications.

There are other drivers of polymer processing technology beyond applications. Effective, new processing methods are required for each of the new molecular architectures discussed in previous sections if they are to become of real practical significance. New architectures require new means of construction; the processes will remain inextricably part of the product. Multi-component polymer blends are a rich example of this close relationship between processing and product. Polymer blends constitute over 30% of all plastics sold and this fraction continues to increase. The materials produced include high impact resistant materials, thermoplastic elastomers, polymers modified for ease of processing and blends created for the purposes of plastics recycling (Hamid and Atiqullah, 1995). Nearly all of these blends are immiscible, yet the resulting two-phase morphologies, if stable, can produce desirable properties (Utracki, 1989). The most common method for creating new polymer blends is to disperse one thermoplastic melt into another via a twin screw extruder. In these blends, the minor phase must be reduced in size to critical scale, typically microns, and stabilized against coalescence, that is, the blend must be compatibilized.

Reactive processing is increasingly becoming the optimum method for these purposes. In the broadest sense, reactive processing includes both the synthesis of high polymers from monomers and the chemical modification of polymers. To produce compatible polymer blends, reactive processing is a particularly

effective alternative (Kumpf *et al.*, 1995). Interfacial agents, typically block copolymers, are necessary for several purposes in stabilizing polymer blends: reduction of interfacial tension, enabling smaller scale dispersion of droplets; prevention of subsequent coalescence by steric stabilization; and mechanical interconnection and augmentation of adhesion between phases. One of the advantages of reactive processing revolves around the means by which the agent is delivered to the phase boundary. Mixing in a third component, the block copolymer surfactant, to the blend requires additional mixing operations and, more importantly has been shown (Nakayama *et al.*, 1993) to be less effective than making the block copolymer *in situ* by having a portion of the blend components have reactive end groups so that interfacial encounters lead to reactions that chemically link the two components into one well-suited surfactant molecule.

Twin screw extruders have gained wide acceptance for conducting reactive processing operations because of their flexibility in design, effective mixing, pumping and heat transfer. They are good current examples of continuous reactors for materials processing, particularly for new polymer products, where the volume of product produced may not be appropriate for other continuous reactor designs. Control of these polymer reactors must develop simultaneously. New analytical tools specifically designed for twin screw extruders, such as on-line rheometry, on-line spectroscopy and on-line scattering are playing increasingly important roles in closed-loop process control systems, leading to more consistent products.

CONCLUSIONS

A striking general conclusion of this survey of the field of polymers in chemical engineering, particularly when matched against a similar previous review (Tirrell, 1991), concerns the relative current importance of various sectors of the field in which we are engaged. The earlier review was dominated by transport phenomena, thermodynamics and phase separation, and interfacial behavior of polymers, generally, *physical phenomena* of polymers. While the current review attempts to be as broad as necessary to cover the field, from this survey, it is inescapable that the most important *contemporary* issues are those of *synthetic chemistry*: how to make and process new materials for new applications and valuable new end-use properties. Priorities have changes, due in large part to instrumentation advances and related significant progress in the last five years in measurement of diffusion and interfacial properties. Those fields have matured significantly. The chemistry opportunities are very well-suited to chemical engineers, often ones that are built on traditional strengths of our discipline: catalysis, precise control of processes, reaction processes that are coordinated in space and time. Others relate to our emerging strengths: biotechnology, surface science and environmental engineering. Physical phenomena are not of secondary import-

ance; rather, the current research landscape in polymers has physical phenomena and advanced synthesis inextricably connected. Self-assembly, noncovalent synthesis and reactive processing are all, in a sense, physical methods of polymer synthesis.

However, it is not just a rearrangement of priorities that have marked the last few years. A few qualitatively new features have emerged. Precision construction of supermolecular building blocks, the need for macromolecules with very uniform architecture and molecular weight, processing under orienting fields, on-line monitoring of physical and molecular property development and the continual drive toward new applications that goes hand-in-hand with new materials and improved processing are but a few of the unique aspects of the field of polymer engineering that will engage chemical engineers in intellectual and technological leadership for the foreseeable future.

Acknowledgements—The preparation of this review benefited enormously from wide-ranging discussions with many friends and colleagues. Singular among these have been very stimulating discussions with Sam Stupp whose conception of the potential of two-dimensional polymers is embodied in Fig. 5.

REFERENCES

- Alt, H. G., Milius, W. and Paclackal, S. J., 1994, Verbrückte bis(flourenyl) komplexe des zirconiums und hafniums als hochreaktive katalysatoren bei der homogenen olefinpolymerisation die molekülstrukturen von $(C_{13}H_9-C_2H_4-C_{13}H_9)$ und $(\eta^5:\eta^5-C_{13}H_8-C_2H_4-C_{13}H_8) ZrCl_2$. *J. Organomet. Chem.* **472**, 113.
- Albalak, R. J. and Thomas, E. L., 1993, Microphase separation of block copolymer solutions in a flow field. *J. Polym. Sci. Polym. Phys. Ed.* **31**, 37.
- Amiel, C., Sikka, M., Schneider, J. W. Jr, Tsao, Y.-H., Mays, J. W. and Tirrell, M., 1995, Adsorption of hydrophilic-hydrophobic block copolymers on silica from aqueous solutions. *Macromolecules* **28**, 3125.
- Anderson, A. J. and Dawes, E. A., 1990, Occurrence, metabolism, metabolic role, and industrial uses of bacterial polyhydroxyalkanoates. *Microbiol. Rev.* **54**, 450.
- Antonietti, M. and Conrad, J., 1994, Synthesis of most highly ordered liquid crystalline phases by complex formation of polyacrylic acid with cationic surfactants. *Angew. Chem. Int. Ed. Engl.* **33**, 1869.
- Antonietti, M. and Conrad, J. and Thünemann, A., 1994, Polyelectrolyte-surfactant complexes: a new type of solid, mesomorphous material. *Macromolecules* **27**, 6007.
- Archibald, D. D. and Mann, S., 1993, Template minearization of self-assembled anisotropic lipid microstructures. *Nature* **364**, 430.
- Bailey, J. E., 1995, *Chem. Engng Sci.* **50**, 4091-4108.
- Balsara, N. P., Eastman, C. E., Foster, M., Lodge, T. P. and Tirrell, M., 1991, Diffusion in microstructured block copolymer solutions. *Die Makromol. Chem. Symp.* **45**, 213.
- Bates, F. S., 1984, Block copolymers near the microphase separation temperature. 2. Linear dynamic mechanical properties. *Macromolecules* **17**, 2607.
- Bates, F. S. and Fredrickson, G. H., 1990, Block copolymer thermodynamics: theory and experimental. *Ann. Rev. Phys. Chem.* **41**, 525.
- Bates, F. S., Koppi, K. A., Tirrell, M., Almdal, K. and Mortensen, K., 1994a, Influence of shear on the hexagonal-to-disorder transition in a diblock copolymer melt. *Macromolecules* **27**, 5934.

- Bates, F. S., Schulz, M. F., Khandpur, A. K., Förster, S., Rosedale, J. H., Almdal, K. and Mortensen, K., 1994b, Fluctuations, conformational asymmetry and block copolymer phase behavior. *Faraday Discuss. Chem. Soc.* **98**, 1.
- Belu, A. M., Hunt, M. O., DeSimone, J. M. and Linton, R. W., 1994, End-functionalized polymers. 2. Quantification of functionalization by time-of-flight secondary ion mass spectrometry. *Macromolecules* **27**, 1905.
- Bird, R. B., Curtiss, C. F., Armstrong, R. C. and Hassager, Ole, 1987, *Dynamics of Polymeric Liquids, Vol. 2: Kinetic Theory*. Wiley, New York.
- Brown, H. R., 1991, Adhesion between polymers. *Ann. Rev. Mater. Sci.* **21**, 463.
- Brown, H. R., 1993, Effects of chain pull-out on adhesion of elastomers. *Macromolecules* **26**, 1666.
- Brown, H. R., 1994, Chain pullout and mobility effects in friction and lubrication. *Science* **263**, 1411.
- Cao, G. and Mallouk, T., 1991, Topochemical diacetylene polymerization in layered metal phosphate salts. *J. Solid State Chem.* **94**, 59.
- Cates, M. E. and Milner, S. T., 1989, Role of shear in the isotropic-to-lamellar transition. *Phys. Rev. Lett.* **62**, 1856.
- Chakraborty, A. K. and Adriani, P. M., 1992, Glassy relaxation at polymer-solid interfaces. *Macromolecules* **25**, 2470.
- Chen, L. B., Zukoski, C. F., Ackerson, B. J., Hanley, H. J. M., Straty, G. C., Barker, J. and Glinka, C. J., 1992, Structural changes and orientational order in a sheared colloidal suspension. *Phys. Rev. Lett.* **69**, 688.
- Chien, J. C. W., Tsai, W. M. and Rausch, M. D., 1991, Isospecific polymerization of propylene catalyzed by racethylenebis(indenyl)methylzirconium "cation". *J. Am. Chem. Soc.* **113**, 8570.
- Coates, G. W. and Waymouth, R. M., 1995, Oscillating stereocontrol: a strategy for the synthesis of thermoplastic elastomeric polypropylene. *Science* **267**, 217.
- Creel, H. S., Fournier, M. J., Mason, T. L. and Tirrell, D. A., 1991, Genetically directed syntheses of new polymeric materials. Efficient expression of a monodisperse copolypeptide containing fourteen tandemly repeated-(AlaGly)_nProGluGly-elements. *Macromolecules* **24**, 1213.
- Dangani, R., 1992, Nanostructured materials promise to advance range of technologies. *C & E New* 23 Nov., 23.
- Davis, M. E., 1993, Organizing for better synthesis. *Nature* **364**, 391.
- de Carvalho, A. B., Gloor, P. E. and Hamielec, A. E., 1989, A kinetic mathematical model for heterogeneous Ziegler-Natta copolymerization. *Polymer* **30**, 280.
- de Carvalho, A. B. M., Gloor, P. E. and Hamielec, A. E., 1990, A kinetic mathematical model for heterogeneous Ziegler-Natta (co)polymerization. Part 2: stereochemical sequence length distributions. *Polymer* **31**, 1294.
- Decher, G., Lvov, Y. and Schmitt, J., 1994, Proof of multilayer organization in self-assembled polycation-polyanion molecular films. *Thin Solid Films* **244**, 772.
- Decher, G. and Schmitt, J., 1992, Fine-tuning of the film thickness of ultrathin multilayer films composed of consecutively alternating layers of anionic and cationic polyelectrolytes. *Progr. Colloid Polym. Sci.* **89**, 160.
- de Gennes, P. G., 1971, Reptation in the presence of fixed obstacles. *J. chem. Phys.* **55**, 572.
- Denn, M. M., 1980, Continuous drawing of liquids to form fibres. *Ann. Rev. Fluid Mech.* **12**, 365.
- Deruelle, M., Marciano, Y., Hervet, H., Léger, L. and Tirrell, M., 1995, Adhesion energy between polymer networks and solid surfaces modified by polymer attachment. *Faraday Discuss.* **98**
- DeSimone, J. M., Guan, Z. and Elsbernd, C. S., 1992, Synthesis of fluoropolymers in supercritical carbon dioxide. *Science* **257**, 945.
- DeSimone, J. M., Maury, E. E., Menciloglu, Y. Z., McClain, J. B., Romack, T. J. and Combes, J. R., 1994, Dispersion polymerizations in supercritical carbon dioxide. *Science* **265**, 356.
- Dotson, N., Galván, R., Laurence, R. L. and Tirrell, M., 1995, *Polymerization Process Modelling*. VCH Verlagsgesellschaft mbH, Weinheim.
- Dougherty, M. J., Kothakota, S., Fournier, M. J., Mason, T. L. and Tirrell, D. A., 1993, Synthesis of a genetically engineered repetitive polypeptide containing periodic selenomethionine residues. *Macromolecules* **26**, 1779.
- Eisenbach, C. D., Haarer, D. and Schmidt, M., 1995, Macromolecular chemistry and physics 1994. *Acta Polym.* **46**, 1.
- Ferry, J. D., 1980, *Viscoelastic Properties of Polymers*, 3rd Edition. Wiley, New York.
- Fetters, L. J., Lohse, D. J., Richter, D., Witten, T. A. and Zirkel, A., 1994, Connection between polymer molecular weight, density, chain dimensions, and melt viscoelastic properties. *Macromolecules* **27**, 4639.
- Firouzi, A., Kumar, D., Bull, L. M., Besier, T., Sieger, P., Huo, Walker, S. A., Zasadzinski, J. A., Glinka, C., Nicol, J., Margolese, D., Stucky, G. D. and Chmelka, B. F., 1995, Cooperative organization of inorganic-surfactant and biomimetic assemblies. *Science* **267**, 1138.
- Flory, P. J., 1969, *Statistical Mechanics of Chain Molecules*. Wiley-Interscience, New York.
- Floyd, S., Choi, K.-Y., Taylor, T. W. and Ray, W. H., 1986a, Polymerization of olefins through heterogeneous catalysis. IV. Modeling of heat and mass transfer resistance in the polymer particle boundary layer. *J. Appl. Polym. Sci.* **31**, 2231.
- Floyd, S., Choi, K.-Y., Taylor, T. W. and Ray, W. H., 1986b, Polymerization of olefins through heterogeneous catalysis. III. Polymer particle modeling with an analysis of intraparticle heat and mass transfer effects. *J. Appl. Polym. Sci.* **32**, 2935.
- Floyd, S., Heiskanen, T., Taylor, T. W., Mann, G. E. and Ray, W. H., 1987, Polymerization of olefins through heterogeneous catalysis. VI. Effect of particle heat and mass transfer on polymerization behavior and polymer properties. *J. Appl. Polym. Sci.* **33**, 1021.
- Förster, S., Khandpur, A., Zhao, J., Bates, F. S., Hamley, I. W., Ryan, A. J. and Bras, W., 1994, Complex phase behavior of PI-PS diblock copolymers near the order-disorder transition. *Macromolecules* **27**, 6922.
- Fréchet, J. M. J., 1994, Functional polymers and dendrimers: reactivity, molecular architecture and interfacial energy. *Science* **263**, 1710.
- Fredrickson, G. H., 1994, Steady shear alignment of block copolymers near the isotropic-lamellar transition. *J. Rheol.* **38**, 1045.
- Fredrickson, G. H. and Helfand, E., 1988, Rheology of homogeneous block copolymers near the microphase separation transition. *J. chem. Phys.* **89**, 5890.
- Galli, P., 1994, The breakthrough in catalysis and processes for olefin polymerization: innovative structures and a strategy in the materials area for the twenty-first century. *Prog. Polym. Sci.* **19**, 959.
- Galván, R. and Tirrell, M., 1986a, Orthogonal collocation applied to analysis of heterogeneous Ziegler-Natta polymerization. *Comp. Chem. Eng.* **10**, 77.
- Galván, R. and Tirrell, M., 1986b, Molecular weight distribution predictions for heterogeneous Ziegler-Natta polymerization using a two-site model. *Chem. Engng Sci.* **41**, 2385.
- Graessley, W. W., 1974, The entanglement concept in polymer rheology. *Adv. Polym. Sci.* **16**, 1.
- Gun, J. and Sagic, J., 1986, On the formation and structure of self-assembling monolayers. *J. Colloid Interface Sci.* **112**, 457.
- Hadziioannou, G., Mathis, A. and Skoulios, A., 1979, Obetention de "monocristaux" de copolymères triséquences styrène/isoprène par cisaillement plan. *Colloid Polym. Sci.* **257**, 136.
- Haensler, J. and Szoka, F. Jr, 1993, Polyamidoamine cascade polymers mediate efficient transfection of cells in culture. *Bioconjugate Chem.* **4**, 372.

- Haggan, J., 1995, Concern for environment is shaping research in catalysis. *C & E News* 10 July, 25.
- Halperin, A., Tirrell, M. and Lodge, T. P., 1992, Tethered chains in polymer microstructures. *Adv. Polym. Sci.* **100**, 31.
- Hamid, S. H. and Atiqullah, M., 1995, Role of blending technology in polyethylene recycling. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **C35**, 495.
- Helfand, E. and Sapse, A. M., 1975, Theory of unsymmetric polymer-polymer interfaces. *J. chem. Phys.* **62**, 1327.
- Horton, A. D., 1994, Metallocene catalysis: polymers by design? *Trends Polym. Sci.* **2**, 158.
- Huang, J. and Rempel, G. L., 1995, Ziegler-Natta catalysts for olefin polymerization: mechanistic insights from metallocene systems. *Prog. Polym. Sci.* **20**, 459.
- Hutchinson, R. A., Chem, C. M. and Ray, W. H., 1992, Polymerization of olefins through heterogeneous catalysis. X. Modeling of particle growth and morphology. *J. Appl. Polym. Sci.* **44**, 1389.
- Imrie, C. T., 1995, Supramolecular chemistry and liquid crystalline polymers. *Trends Polym. Sci.* **3**, 22.
- Jackson, D. E. and Srienice, F., 1994, Novel methods to synthesize polyhydroxyalkanoates. *Ann. N. Y. Acad. Sci.* **745**, 134.
- Jansen, J. F. G. A., de Brabander-van den Berg, E. M. M and Meijer, E. W., 1994, Encapsulation of guest molecules into a dendritic box. *Science* **266**, 1226.
- Kabanov, V. A. and Zevin, A. B., 1984, A new class of complex water-soluble polyelectrolytes. *Makromol. Chem. (Suppl.)* **6**, 259.
- Kaminsky, W., Engehausen, R., Zoumis, K., Spaleck, W. and Rohrman, J., 1992, Standardized polymerizations of ethylene and propene with bridged and unbridged metallocene derivatives: a comparison. *Makromol. Chem.* **193**, 1643.
- Kaminsky, W. and Steiger, R., 1988, Polymerization of olefins with homogeneous zirconocene/alumoxane catalysts. *Polyhedron* **7**, 2375.
- Kannan, R. M. and Kornfield, J. A., 1994, Evolution of microstructure and viscoelasticity during flow alignment of a lamellar diblock copolymer. *Macromolecules* **27**, 1177.
- Kannan, R. M., Kornfield, J. A., Schwenk, N. and Boeffel, C., 1993, Rheology of side-group liquid-crystalline polymers: effect of isotropic-nematic transition and evidence of flow alignment. *Macromolecules* **26**, 2050.
- Keller, A., Pedemonte, E. and Wilmouth, F. M., 1970, Macrolattice from segregated amorphous phases of a three block copolymer. *Nature* **225**, 538.
- Kim, Y. H. and Webster, O. W., 1990, Water-soluble hyperbranched polyphenylene: a unimolecular micelle? *J. Am. Chem. Soc.* **112**, 4592.
- Knoll, W., 1993, Optical properties of polymers, in *Structure and Properties of Polymers* (Edited by E. L. Thomas), Chap. 8; *Materials Science and Technology* (Edited by R. W. Cahn, P. Haasen and E. J. Kramer). VCH Verlagsgesellschaft, Weinheim.
- Koppi, K. A., Bates, F. S., Almdal, K., Colby, R. H. and Tirrell, M., 1992, Lamellae orientation in dynamically sheared diblock copolymer melts. *J. Phys. II (France)* **2**, 1941.
- Koppi, K. A., Bates, F. S. and Tirrell, M., 1993, Shear-induced isotropic-to-lamellar transition. *Phys. Rev. Lett.* **70**, 1449.
- Kumpf, R. J., Wiggins, J. S. and Pielartzik, H., 1995, Reactive processing of engineering thermoplastics. *Trends Polym. Sci.* **3**, 132.
- Kwon, Y. K., Chvalun, S., Schneider, A.I., Blackwell, J., Percec, V. and Heck, J. A., 1994, Supramolecular tubular structures of a polymethacrylate with tapered side groups in aligned hexagonal phases. *Macromolecules* **27**, 6129.
- Layman, P., 1994, Europe looks to 'new perspectives' in polymers. *C & E News* 31 Oct.
- Lehn, J.-M., Mascal, M., DeCian, A. and Fisher, J., 1992, Molecular ribbons from molecular recognition directed self-assembly of self-complementary molecular components. *J. Chem. Soc. Perkin Trans.* **461**.
- Leiber, L., 1980, Theory of microphase separation in block copolymers. *Macromolecules* **13**, 1602.
- McAuley, K. B., Macgregor, J. F. and Hamielec, A. E., 1990, A kinetic model for industrial gas-phase ethylene copolymerization. *A.I.Ch.E.J.* **36**, 837.
- McGrath, K. P., Fournier, M. J., Mason, T. L. and Tirrell, D. A., 1992, Genetically directed syntheses of new polymeric materials. Expression of artificial genes encoding proteins with repeating (AlaGly)₃ProGluGly-elements. *J. Am. Chem. Soc.* **114**, 727.
- McHugh, M. and Krukons, V. J., 1986, *Supercritical Fluid Extraction—Principles and Practice*. Butterworths, Boston, MA.
- Macosko, C. W., 1994, *Rheology: Principles, Measurements and Applications*. VCH, Poughkeepsie, New York.
- Mangipudi, V., Pocius, A. V. and Tirrell, M., 1994, Direct measurements of molecular level adhesion between poly(ethylene terephthalate) and polyethylene films: Surface and interfacial energies. *J. Adhesion Sci. Tech.* **8**, 1251.
- Mangipudi, V., Pocius, A. V. and Tirrell, M., 1995, Direct measurement of the surface energy of corona treated polyethylene using the surface forces apparatus. *Langmuir* **11**, 19.
- Mao, G., Tsao, Y., Davis, H. T., Hessel, V., Ringsdorf, H. and Tirrell, M., 1993, Self-assembly of photopolymerizable bolaform amphiphile mono- and multilayers. *Langmuir* **9**, 3461.
- Mao, G., Tsao, Y.-H., Davis, H. T., Hessel, V., Ringsdorf, H. and Tirrell, M., 1995, Interactions, structure and stability of photoreactive bolaform amphiphile multilayers. *Langmuir* (in press).
- Mao, G., Tsao, Y.-H., Davis, H. T., Hessel, V., Ringsdorf, H. and Tirrell, M., 1994, Monolayers of bolaform amphiphiles: influence of alkyl chain length and counterions. *Langmuir* **10**, 4174.
- Maoz, R., Yam, R., Berkovic, G. and Sagiv, J., 1995, Third-level self-assembly and beyond: polar hybrid superlattices via post-assembly intercalation into multilayer matrices. *Thin Films* **20**, 41.
- Messersmith, P. B. and Stupp, S. I., 1992, Synthesis of nanocomposites: organoceramics. *J. Mater. Res.* **7**, 2599.
- Michler, G. H., 1995, Electron microscopic techniques for direct investigation of micromechanical mechanisms in polymers. *Trends Polym. Sci.* **3**, 124.
- Mobley, D. P. (ed.) 1994, *Plastics from Microbes: Microbial Synthesis of Polymers and Polymer Precursors*. Hanser, Munich.
- Monnier, A., Schüth, F., Huo, Q., Kumar, D., Margolese, D., Maxwell, R. S., Stucky, G. D., Krinshnamurty, M., Perloff, P., Firouzi, A., Janicke, M. and Chmelka, B. F., 1993, Cooperative formation of inorganic-organic interfaces in the synthesis of silicate mesostructures. *Science* **261**, 1299.
- Morrison, F. A., Mays, J. W., Muthukumar, M., Nakatani, A. I. and Han, C. C., 1993, Shear-induced morphological structures in triblock copolymers. *Macromolecules* **26**, 5271.
- Mourey, T. H., Turner, S. R., Rubinstein, M., Fréchet, J. M. J., Hawker, C. J. and Wooley, K. L., 1992, Unique behavior of dendritic macromolecules: intrinsic viscosity of polyether dendrimers. *Macromolecules* **25**, 2401.
- Nagel, E. J., Kirillov, V. A. and Ray, W. H., 1980, Prediction of molecular weight distributions for high density polyolefins. *Ind. Engng Chem. Prod. Res. Dev.* **19**, 372.
- Nakahama, A., Inoue, T., Guégan, P. and Macosko, C. W., 1993, Compatibilizers for melt blending: premade vs. reactively formed block copolymers. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **34**, 840.
- National Research Council, 1994, *Polymer Science and Engineering: The Shifting Research Frontiers*. National Academy Press, Washington, DC.

- Parkhe, A.D., Fournier, M.J., Mason, T.L. and Tirrell, D. A., 1993, Determination of the chain-folding pattern in the crystalline domains of the repetitive polypeptide $\{(AlaGly)_3\ GluGly(GlyAla)_3\ GluGly\}_{10}$ by FTIR studies of its blends with a ^{13}C -enriched analogue. *Macromolecules* **26**, 6691.
- Parsonage, E. E. and Tirrell, M., 1993, Polymer surfaces and interfaces with other materials, in *Structure and Properties of Polymers* (Edited by E. L. Thomas), Chap 14; *Materials Science and Technology* (Edited by W. Cahn, P. Haasen and E. J. Kramer). VCH Verlagsgesellschaft, Weinheim.
- Perkins, T. T., Smith, D. E. and Chu, S., 1994, Direct observation of tube-like motion of a single polymer chain. *Science* **264**, 819.
- Raphaël, E. and de Gennes, P.-G., 1992, Rubber-rubber adhesion with connector molecules. *J. phys. Chem.* **96**, 4002.
- Reisch, M. S., 1995, Plastics, *C & E News* 22 May, 30.
- Ringsdorf, H., 1994, From molecules, macromolecules and supramolecular systems. *Supramol. Sci.* **1**, 5.
- Roberts, G. G., 1990, *Langmuir-Blodgett Films*. Plenum Press, New York.
- Rosedale, J. H. and Bates, F. S., 1990, Rheology of ordered and disordered symmetric poly(ethylenepropylene)-polyethylene diblock copolymers. *Macromolecules* **23**, 2329.
- Savage, P. E., Gopalan, S., Mizan, T. I., Martino, C. J. and Brock, E. E., 1995, Reactions at supercritical conditions: applications and fundamentals. *A.I.Ch.E. J.* **41**, 1723.
- Scheirs, J., Burks, S. and Locaspi, A., 1995, Developments in fluoropolymer coatings. *Trends Polym. Sci.* **3**, 74.
- Schmeal, W. R. and Street, J. R., 1971, Polymerization in expanding catalyst particles. *A.I.Ch.E. J.* **17**, 1188.
- Schmeal, W. R. and Street, J. R., 1972, Polymerization in catalyst particles. Calculation of molecular weight distribution. *J. Polym. Sci. Polym. Ed.* **10**, 2173.
- Schmitt, J., Grünewald, T., Decher, G., Pershan, P. S., Kjaer, K. and Lösche, M., 1993, Internal structure of layer-by-layer adsorbed polyelectrolyte films: a neutron and X-ray reflectivity study. *Macromolecules* **26**, 7058.
- Seddon, J. M., 1990, Structure of the inverted hexagonal (HII) phase, and non-lamellar phase transition of lipids. *Biochim. Biophys. Acta* **1031**, 1.
- Shaffer, K. A. and DeSimone, J. M., 1995, Chain polymerizations in inert, near- and supercritical fluids. *Trends Polym. Sci.* **3**, 146.
- Sikka, M., Singh, N., Bates, F. S., Karim, A., Satija, S. and Majkrzak, C. F., 1994, Surface segregation in model symmetric polyolefin diblock copolymer melts. *J. Phys. II (France)* **4**, 2231.
- Sinn, H. and Kaminsky, W., 1980, Ziegler-Natta catalysis. *Adv. Organomet. Chem.* **18**, 99.
- Spaleck, W., Antberg, M., Rohrmann, J., Winter, A., Bachmann, B., Kaprof, P., Behm, J. and Herrmann, W. A., 1992, High molecular weight polypropylene through specifically designed zirconocene catalysts. *Angew. Chem. Int. Ed. Engl.* **31**, 1347.
- Stamm, M., 1992, Polymer interfaces on a molecular scale: comparison of techniques and some examples. *Adv. Polym. Sci.* **100**, 357.
- Stupp, S. I., Son, S., Lin, H. C., Li, L. S., 1993, Synthesis of two-dimensional polymers. *Science* **259**, 59.
- Tepe, T., Schulz, M. F., Zhao, J., Tirrell, M., Bates, F. S., Mortensen, K. and Almdal, K., 1995, Variable shear-induced orientation of a diblock copolymer hexagonal phase. *Macromolecules* **28**, 3008.
- Tirrell, M., 1991, Polymer science in chemical engineering. *Adv. Chem. Eng.* **16**, 321.
- Tirrell, J. G., Fournier, M. J., Mason, T. L. and Tirrell, D. A., 1994, Biomolecular materials. *C & E News* 19 Dec., 40.
- Tomalia, D. A., 1994, Starburst/cascade dendrimers: fundamental building blocks for a new nanoscopic chemistry set. *Adv. Mater.* **6**, 529.
- Tomalia, D. A. and Dvornic, P. R., 1994, What promise for dendrimers? *Nature* **372**, 617.
- Turro, N. J., Barton, J. K. and Tomalia, D. A., 1991, Molecular recognition and chemistry in restricted reaction spaces. Photophysics and photoinduced electron transfer on the surfaces of micelles, dendrimers, and DNA. *Acc. Chem. Res.* **24**, 332.
- Urry, D. W., Peng, S. Q. and Parker, T. M., 1992, Hydrophobicity-induced pK shifts in elastin protein-based polymers. *Biopolymers* **32**, 373.
- Utracki, L. A., 1989, *Polymer Alloys and Blends*. Hanser, New York.
- Vaia, R. A., Ishii, H. and Gianellis, E., 1993, Synthesis and properties of two-dimensional nanostructures by direct intercalation of polymer melts in layered silicates. *Chem. Mater.* **5**, 1694.
- Van Alsten, J. and Granick, S., 1990, Shear rheology in a confined geometry. Polysiloxane melts. *Macromolecules* **23**, 4856.
- Van Santen, R., 1995, *Chem. Engng Sci.* **50**, 4027-4044.
- Voit, B. I., 1995, Dendritic polymers: from aesthetic macromolecules to commercially interesting materials. *Acta Polym.* **46**, 87.
- Watanabe, H. and Tirrell, M., 1993, Measurement of forces in symmetric and asymmetric interactions between diblock copolymer layers adsorbed on mica. *Macromolecules* **26**, 6455.
- Whitesides, G. M., Mathias, J. P. and Seto, C., 1991, Molecular self-assembly and nano-chemistry: A chemical strategy for the synthesis of nanostructures. *Science* **254**, 1312.
- Wild, F. R. W. P., Wasiucione, M., Huttner, G. and Brintzinger, H. H., 1985, *ansa*-Metallocene derivatives. VII. Synthesis and crystal structure of a chiral *ansa*-zirconocene derivative with ethylene-bridged tetrahydroindenyl ligands. *J. Organomet. Chem.* **288**, 63.
- Wimberger-Friedl, R., 1995, The assessment of orientation, stress and density distributions in injection-molded amorphous polymers by optical techniques. *Prog. Polym. Sci.* **20**, 329.
- Winey, K. I., Patel, S. S., Larson R. G. and Watanabe, H., 1993, Interdependence of shear deformations and block copolymer morphology. *Macromolecules* **26**, 2442.
- Wirth, J. G., 1994, Polymer research and development in the 1990s—the challenge of high added value materials. *Prog. Polym. Sci.* **19**, 947.
- Witten, T. A., Milner, S. T. and Wang, Z.-G., 1989, in *Multi-phase Macromolecular Systems* (Edited by B. M. Culbertson). Plenum, New York.
- Zukoski, C. F., 1995. *Chem. Engng Sci.* **50**, 4073-4079.