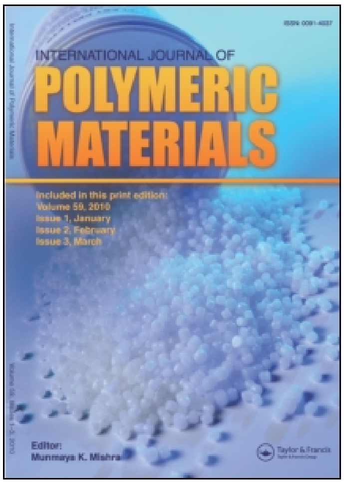

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Orientational Phenomena in Polymers

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This is a short review of 26 invited lectures presented at the 25th Europhysics Conference on Macromolecular Physics *Orientational Phenomena in Polymers* (St. Petersburg, Russia, July 6–10, 1992). The lectures encompassed a wide range of experimental and theoretical studies on the mechanisms of molecular orientation in flow and magnetic fields, in solid phase deformation, in epitaxial growth on oriented substrates, as well as mechanical behavior and resulting properties. The fine structure, the nature and role of defects along with the fracture of oriented polymers were considered. New ways for producing high performance polymer materials were discussed. A great deal of attention was given to the study of a very fast-moving area of electrical conductivity and the formation of polymer systems with nonlinear optical properties.

KEY WORDS Orientation mechanisms, structure/property relationships, defects, fracture.

INTRODUCTION

The Conference has dealt with recent developments in the field of perfect alignment of macromolecules to promote the production of polymer materials with enhanced mechanical, thermal, optical, electrical, and other properties. Different rigidity of macromolecules determines the various routes towards producing perfectly oriented macromolecular systems. It is well known that flexible molecules have a tendency to coil in a quiescent melt and solution, as well as in solidified amorphous polymers or to fold during crystallization from the melt and solution. In this case one should provide the transition from a statistical coil to an extended chain or, in the solid phase, from a folded state to an oriented one. In contrast to flexible molecules, rigid ones preserve their rod-like shape in all physical states, and one should only rotate the chains to align them in a desired direction. Besides, there are other types of macromolecules with alternating flexible and rigid or mesogene fragments in the main or side chain. This defines the singularity in the behavior of macromolecules in orienting fields. During the past decades, various routes towards producing perfectly oriented systems of different type of polymers have been developed, including the flow- or pressure-induced crystallization from the melt or solution, drawing of solidified semicrystalline or amorphous polymers, solid-state extrusion and orienting macromolecules in electric, magnetic or other fields.

The aim of this review is to survey the invited lectures presented at the Conference to compare the different approaches and to assess the progress.

THE MECHANISMS OF MOLECULAR ORIENTATION

General approach

The mechanisms of molecular orientation were a subject of many presentations. In particular, Prof. A. Ziabicki (Institute of Fundamental Technological Research, Warsaw, Poland) gave *a theoretical analysis of the kinematics and dynamics of chain orientation in two cases: (i) during elongation flow of a fluid polymer and (ii) on plastic deformation of a solid polymer.* It has been shown that in pseudo-plastic systems (cold drawing of fibers, solid-state extrusion, calendering, etc), orientation is controlled by the strain in the system. On the other hand, fluid-state processing (fiber spinning, film casting, extrusion, and injection) is controlled by the strain rate rather than the strain extent. In a fluid composed of highly mobile macromolecules, orientation is a result of competition between the orienting effect of the flow field and the disorienting effect of Brownian motion. Which of the mechanisms is to be preferred depends on the molecular structure of the polymer. Fluid flow and plastic deformation provide two extreme ideal mechanisms of orientation. In real systems, a combination of deformation and deformation-rate effects can be expected. The orientation-stress behavior was considered for some special cases, including melts and solutions of flexible-chain polymers, nematics and suspensions of rigid rods, and the conclusions were compared with commercial processes for linear PE, UHMWPE, nylon-6, Kevlar, and PBT. It is evident that the strongest fibers are manufactured either from rigid molecules wet-spun from nematic dopes (PBT, Kevlar), or from flexible UHMWPE gel-spun and drawn in the plastic state up to high draw ratios. Processing of semi-rigid polymers consists in the spinning from isotropic solutions or melts followed by drawing in the plastic state (copolyamides and copolyesters: Technora, Nomex, and Vectra).

Prof. H.-G. Kilian (University of Ulm, Germany) made an attempt to describe *the orientational phenomena in polymers from the general point of view using a network concept.* He considered all the polymer systems as having been “cross-linked,” for example, by crystallites, chemical bonds, entanglements or interacting molecular units. These systems were called “network-like” when the cross-links operated like junctions in a network. Then deformation is controlled by the transformation of the whole set of junctions accompanied with orientation. The simplest system is a permanent network like in polymer glasses. An affine transformation of the junction-to-junction vector ensemble leads to a well defined segmental orientation. This ensemble might be considered as a complete system of equivalent subsystems of deformation, each one locally transformed according to the law of affinity. The orientational distribution of the symmetry axes of a subsystem is given by the Kuhn–Kratky–0ka function. This function is universal and satisfies the maximum entropy principle. The orientation of rod-like fillers in a rubber network was considered. Single rods or strain-invariant clusters and their rubbery environment represent in this case equivalent subsystems of deformation. Apparently, a “network-structure” is constituted by the initially randomly oriented rod themselves. Rods or clusters are linked in the matrix by a very large number of adhesive contacts. During deformation, it is impossible to simultaneously release them to allow “free rotation”. In polymer glasses the size of equivalent subsystems is very small (probably in a range of monomer unit or Kuhn-segment). During deformation these units behave like rigid rods embedded in a quasi-isotropic continuum. Due to slippage, these rod-like elements should always be oriented along the subsystem’s symmetry axis. Orientation is fairly well described by the Oka-distribution and shows a unique dependence on strain. It was stressed that this strategy could be applied to the physics of extensive deformation in semicrystalline polymers. Crystallites were considered as subsystems embedded into a rubbery-like matrix. The proposed approach permits an adequate description of the stress-strain behavior of LDPE at different temperatures and calculate the heat evolution during the extension of the same samples, as well as the orientation function for the *a*-, *b*-, and *c*-axes of crystallites for HDPE and LDPE. A crucial point is that the supermolecular structure is transformed in such a way that the anisometric elements are not any more strain-invariant.

The mechanisms of flow-induced coil-stretch transitions from the thermodynamical point of view were also discussed by Prof. S. Frenkel (Institute of Macromolecular Compounds, St. Petersburg, Russia). The nonlinear properties of uncoiling chains, modeled by the dynamic coil-extended chain phase transition following the elongation flow, were shown to be very important for achieving a high degree of molecular extension in the process of orientational crystallization from the melt. A negative role of entanglements in the processing of ultra-high molecular weight polymers was considered. Besides, it was shown that the extension of macromolecules in flow fields is governed by the longitudinal velocity gradient of the stream, which coincides with the statement of Prof. A. Ziabicki. An unusual behavior of a solution of semi-rigid incompatible macromolecules in an elongation flow field was first observed. It was found that the addition of only a few percent of the other component to the solution of the first one drastically enhanced the degree of chain uncoiling, which can be attributed to the energetically more favorable segregation of extended macromolecules.

A study of relaxation mechanisms that (together with deformation) control the behavior of macromolecules in orienting fields is of great importance for finding a proper routes for producing perfect molecular alignment. The conformational changes in the macromolecules caused by external or internal (molecular) fields are known to change significantly their relaxation properties.

Prof. Yu. Gotlib (Institute of Macromolecular Compounds, St. Petersburg, Russia) proposed *a theory of conformational changes and molecular mobility during chain orientation in external fields and in liquid crystalline state.* The influence of external (magnetic, electric, mechanical, and others) and internal (self-consistent quadrupole) fields on relaxation properties was discussed. It was proved that the form of the relaxation spectra and the dependence of the relaxation times for different normal modes on the magnitude of the orienting field (or degree of order) were determined by the conformational and dynamic properties of the chain. The conformational changes in the quadrupole field could result in the formation of stretched conformations ("chain stiffening"). The real chains consisting of alternating rigid mesogenic groups and flexible spacers were considered. The shape and rotational diffusion coefficients were assumed to be similar for mesogenic segments and spacers in the absence of orienting field. It was shown that the chain heterogeneity caused the appearance of two branches of relaxation spectra: the acoustical and the optical ones. The anisotropy of the polymeric system in the nematic phase led in turn to the splitting of both branches into the longitudinal sub-brunch, corresponding to the shift of chain elements along a field direction, and transverse one that could by attributed to the shift in perpendicular direction. The main factors influencing on the relaxation times were discussed. It was demonstrated that the quadrupole ordering resulted in the increase of long-scale relaxation times. The behavior of short-scale (local) motions depends very strongly on the dynamical microstructure of the chain.

Behavior of flexible-chain molecules in flow fields

Prof. A. McHugh (University of Illinois, USA) who studied *in situ oriented crystal growth of high molecular weight PE and PP utilizing the seeding technique* under controlled temperature and flow conditions changed radically the generally accepted views on the mechanisms associated with this process. Crystal growth is generally ascribed to some entropic, melting point elevation effects which are believed to drive strain-induced growth of cross-linked systems. It was established that the flow-induced fiber transformation always initiates through the formation of a highly entangled, amorphous phase which anchors to the seed and then solidifies by distinct nucleation and growth mechanism induced by the stresses transmitted from the flowing solution. A modification of the Avraami equation offers a convenient basis for separately analyzing the temperature and flow rate effects. In order to study a more complicated situation in a melt flow, a special technique was developed permitting the investigation of the flow-induced crystallization and structure formation in the droplet phase of a two-phase flow. The initial crystallization rate appeared to depend on both stress and strain in a fashion suggestive more of a viscoelastic process rather than a simple nucleation and growth mechanism.

A new standpoint on the mechanism of *shish-kebab formation during high speed spinning of semi-dilute solutions* of UHMWPE in paraffin oil was given by Prof. A. J. Pennings (University of Groningen, The Netherlands). It was demonstrated with scanning and transmission electron microscopy that a macrofiber is composed of a bundle of rather loosely assembled elementary fibrils. These fibrils appeared to have a shish-kebab morphology at intermediate winding speeds and resemble strings of beads at take-up velocities around 1000 m/min and higher. It was suggested that the entanglement network in these solutions breaks up, under the action of an elongation flow field, into fluid-like fibrils in a craze-like manner via the mechanism of Taylor's meniscus instability. In a subsequent stage these fibrils solidify in an oriented way, giving rise to shish-kebab structures with uniform diameters and virtually of infinite length.

The observations of the melt flow singularities presented in the lecture of Prof. A. Keller (Bristol University, UK) open up new possibilities for the improvement of processing technologies for flexible-chain polymers. The study of melt extrusion of PE as a model substance at the moderately above the usual solidification temperature has shown that there is a narrowly defined temperature window, $\pm 1\,^{\circ}$C around 150°C, where the extrusion pressure has a sharp minimum at a constant shear rate or the extrusion rate has a sharp maximum at a constant extrusion pressure. The observed behavior must facilitate the processing of high molecular weight materials where otherwise the flow instabilities would make the processing difficult or altogether impossible. This effect was found to be caused by the flow-induced coil-stretch transitions, the influence of the chain extension being critical for both the strain rate and the molecular weight. The phase transition induced can be of two kinds, possibly in the sequence: a mobile metastable phase with liquid crystal characteristics which could be the hexagonal phase in PE and the final stable crystal (orthorombic in PE) with filamentous morphology. It was suggested that it was the former which, in its transient form, was responsible for the window effect in extrusion, while the latter for the variety of morphological features. Extrusion under the conditions defined above has a potential for creating a special morphology, "self-composites" in particular, that may provide advantageous properties of both filamentous extrudates and injection moulded objects.

The behavior of flexible-chain molecules under the combined action of elongation flow and high pressure usually occurring in the injection molding was analyzed in the lecture of Prof. F. Balta-Calleja (Instituto de Estructura de la Materia, Madrid, Spain). The study focused on the influence of the processing parameters and molecular characteristics on the chain orientation during the filling process of a mold. It was shown that the application of high pressures (more than 2 kbar) leads to a pressure-induced crystallization effect which freezes-in the molecular orientation within the mold. The results obtained for linear PE at a critical molecular weight of about 10^5 evidence for a pronounced enhancement of orientation to $\langle \cos^2 f \rangle = 0.95$, as revealed by WAXS, and $\Delta n = 45 \times 10^3$, obtained from birefringence measurements. The thermostability of the best oriented samples appeared to be very high. The orientation derived from real time WAXS patterns using synchrotron radiation starts dropping slightly at about 125°C. The shish-kebab morphology was observed, and it was pointed out that the shish-fibrils were preferentially formed where high orientation occurred, i.e. in zones around the central axis of the mold at melt temperatures of about 150°C.

Other methods of orienting macromolecules

Polymers with mesogenic moiety in the main chain or side group are known to arrange themselves into smectic, nematic or cholesteric domains. Isotropic liquid crystal polymers can be considered as microcomposite materials in which the individual domains, usually of colloidal dimensions (10–10^3 nm), are oriented randomly. Polymers exhibiting thermotropic or lyotropic mesomorphism are readily oriented in flow fields. This property of liquid crystalline polymers is widely used for producing polymers with extreme parameters. The applications of polymers with the liquid-crystalline order are already numerous and steadily growing. Thus, the control of the physical properties of such systems depends on the ability to translate the molecular and colloidal anisotropy into a macroscopic anisotropy. Besides, it is of great importance to understand the mechanisms of formation and the fine structure of these domains.

Stimulating results in this field were presented by Dr. G. Lieser (Max-Planck Institute for Polymer Research, Mainz, Germany) who had investigated *structuring warm-like chains with attached flexible side chains in the lyotropic liquid-crystalline state in the absence of external force fields*. When these molecules undergo the transition from a dilute into an anisotropic solution, they arrange themselves in a nematic state of order with the chain ends (giving rise to defects) randomly distributed throughout the sample. Usually, an energetically favorable nematic-smectic phase transition occurs in low molecular weight liquid crystal solutions with increasing dwell time, which diminishes the defect concentration. The chain ends are then assembled at interlamellar surfaces reducing the Gibbs free energy. This effect is not expected to be realizable in polymer systems in which the chain ends vary significantly. However, the experimental evidence showed that the warm-like polymers investigated (e.g. soluble diacetylene, PPP, PcPS) are also able to concentrate their defects in the areas between the lamellae of the highest degree of order. Polarizing and electron microscopy showed a decrease of disclination density for two weeks.

As was mentioned above, high orientation can be produced in a number of liquid crystalline systems by applying flow fields (extrusion, spinning, etc.). However, in limited systems successful alignment of anisotropic domains has not been easy to achieve.

Some success can be attained by application of strong magnetic and electric fields. Prof. S. Stupp (University of Illinois at Urbana-Champaign, USA) reviewed the salient features of *magnetic orientation in main chain nematic polymers* including faster kinetics after mesophase aging, the synergistic effect of surfaces, and the rapid disorientation of monodomains at zero field. The last feature has interesting theoretical implications and could be indicative of nematic-isotropic fluctuations in nematic polymers. Notable results have been demonstrated on application of magnetic orientation to a guest-host system enabling to process the advanced materials filled with dye molecules with nonlinear optical properties. Dye molecules orient extensively to form a macroscopic system guided by the molecular field of nematic domains as well as by magnetic and electric fields. This orientation was shown to triple the second order nonlinear optical susceptibilities of solid films. Prof. S. Stupp also exhibited a unique possibility of molecular sheet initiation from specially synthesized supramolecules which can assemble into single crystals.

The generation of perfect alignment of dispersed species such as dyes with anisotropic optical properties can be also attained by incorporating them in the flexible-chain host polymer subjected further to conventional drawing, as Dr. C. Bastiaansen convincingly demonstrated in his presentation. It was shown that the most promising host polymer could be UHMWPE produced by gel-crystallization due to its extremely high drawability. The orientation mechanism of dichroic dyes in the host material was discussed. Besides, a mathematical procedure was presented to derive the (apparent) transition moment of dyes from the experimental data.

One of the alternative techniques for producing highly oriented polymer systems is *polymerization of monomers pre-ordered by the physical contact with a highly anisotropic substrate*. Excellent examples of this approach were displayed in a lecture of Dr. U. Gedde (Royal Institute of Technology, Stockholm, Sweden) brightly illustrated with a color video film following the process of polymerization of mesogenic vinyl ethers spread on oriented rubbed polyimide films. The resulting polymers were completely transparent and exhibited an ordered (S_A) structure with high orientation. The properties of the films strongly depend on the chemical structure of the original mesogenic monomer and on the polymerization temperature.

Highly anisotropic substrates can also be used for epitaxial growth of polymers leading to a perfect alignment of macromolecules. While epitaxial polymer growth on inorganic substrates was investigated earlier, the use of organic or polymeric substrates has been developed only recently. As was pointed out by Prof. J. C. Wittmann (Institute Charles Sadron, Strasbourg, France) aromatic compounds, which are characterized by almost endless possible variations in the chemical, physical, and crystallographic properties, are especially promising for application. Organic substrates provide the possibility to monitor the crystallographic interactions with the deposited layers and very often lead to outstanding orientations of many crystalline polymers. Prof. J. C. Wittmann also addressed new options on using polymeric layers oriented by uniaxial drawing or transfer friction as very suitable substrates for epitaxial growth for a remarkably wide range of deposited materials of differing chemical composition or physical properties. A simple and surprisingly versatile method was developed for orienting a wide variety of crystalline and liquid crystalline materials, including polymers, monomers, and small organic and inorganic molecules. The focus of the lecture was on ultrathin PTFE layers (about 10 nm) produced simply by sliding the polymer at controlled temperature, pressure and speed against a smooth solid support such a glass slide. Materials grown on this coated surface from the solution, melt, vapor phase or polymerized on it from gaseous monomers showed a remarkable degree of alignment. It is much higher than that attained by epitaxial growth on a polymeric substrate oriented by conventional tensile deformation.

ORIENTATION OF POLYMERS IN A SOLID STATE

Amorphous polymers and condis crystals

Since the majority of commercial polymer films and fibers, when processed, are subjected in a solid state to tensile drawing aimed at the improvement of their mechanical, thermal, optical, and other properties, it is very important to understand the details of macromolecular orientation. A number of invited lectures presented at the conference were concerned with this problem.

Prof. L. Monnerie (Ecole Supérieure de Physique et de Chémie Industrielle de Paris, France) considered *the orientation of solid amorphous polymers above the glass-rubber transition temperature* T_g as a result of the competition between the chain orientation due to the stretching and the chain relaxation from the elastic strength to recover the isotropic chain conformations. Interesting data were obtained with IR-spectroscopy, enabling to understand the molecular mechanisms and to define the most convenient processing conditions (strain rate and temperature) as well as molecular characteristics. A study of the orientation and chain relaxation of polystyrenes with hydrogenated and deuterated blocks made it possible to follow the behavior of each block individually; faster relaxation of the chain ends relative to the center was established. It was also shown that two polymers of different chemical nature (PMMA and PS) displayed various chain relaxation when stretched at a temperature higher than their T_g by the same ΔT, with PMMA samples oriented better than PS ones. On the contrary, they behaved identically when the stretching temperature was chosen in such a way that the monomer friction coefficients were identical. On this basis some improvements of the Doi–Edwards model were suggested:

(i) it was proved that the shortest relaxation time (local relaxation) did not depend on the molecular weight between the entanglements but it was controlled by the monomer friction coefficient,

(ii) the second relaxation process (chain retraction inside the deformed tube) has to be made self-consistent by considering the effect on the surrounding chains which retract too,

(iii) there is an anisotropic orientational coupling effect between a chain segment and its oriented environment.

As for the behavior of compatible blends, the stretching experiments showed that each component had its own relaxation time and different orientation, but there was a coupling effect which can be assigned to the variation in the friction coefficient due to specific interactions between the two polymer species making the systems compatible.

The deformation behavior of filled amorphous glassy polymers with network structure of different nature was under examination in a lecture of Prof. H. Meijer (University of Eindhoven, The Netherlands). Two model systems were used for investigation: (i) miscible blends of two thermoplastics and (ii) epoxy resins. Their microscopic structure at a length scale of 50–300 nm was controlled by addition of different amounts of non-adhering core-shell-rubber particles of constant diameter. The first system's network derived from entanglements could be varied systematically by changing the relative volume fraction of one component. The other one based on the cross-links could be set by selecting various epoxide monomer molecular weights. The theoretical maximum draw ratio that could be obtained experimentally showed that the characteristic length scale of the material microstructure was below a certain value, namely the critical matrix ligament thickness between the added particles. This thickness appeared to increase with increasing network density independent of the nature of the network (entanglements or cross-links). A simple model was presented based on an energy criterion to account for the phenomenon of critical ligament thickness.

Interesting aspects of *the behavior of a new class of flexible macromolecules (linear polyorganosiloxanes and polyphosphazenes) during uniaxial stretching* were discussed by Prof. Yu. Godovsky (Karpov Institute of Physical Chemistry, Moscow, Russia). In spite of the absence of mesogenic groups in the main chain and in the side chains, these polymers appear to be able to form thermotropic mesophases. Unlike the mesophase of conventional liquid crystalline polymers, that of the above molecules can be regarded as a highly disordered crystal with a high molecular mobility (condis crystals). Uniaxial stretching of amorphous films is accompanied by the stress-induced mesophase producing self-reinforced stretched samples. On heating, the melting of the mesophase domains leads to isotropization of the stretched mesophase networks and, as a consequence, to a large decrease in the sample length (supercontraction). The isotropization temperature for stretched mesophase elastomers may be a hundred degrees higher than for the same elastomers in the nonstretched state, making possible the operation of the self-reinforcement mechanism even at very high temperatures.

Semicrystalline polymers

In contrast to amorphous polymers, the complex morphology of semicrystalline polymers, significantly depending on the molecular characteristics and crystallization conditions, complicates the analysis of orientational phenomena. It is clear that the initial morphology drastically influences the production of oriented polymers. Despite a great deal of attention given to the development of orientation in semicrystalline polymers, some questions still remain open to argument. For instance, stretching of semicrystalline polymers is often considered as affine deformation of a network formed by physical entanglements of macromolecules or by crystallites.

In reality, the matter is much more complex, because of a large variety of morphological forms of the starting materials, as was once again proved in the lecture of Prof. D. Bassett (University of Reading, UK) by the highly qualified *electron microscopic study, with lamellar resolution, of the morphology of banded spherulites of PE uniaxially drawn* at 80°C. The conclusion was drawn that circular bands transform to increasingly eccentric ellipses to 30% extension but thereafter they extend less than for an affine change and show inhomogeneous response. Even at 30% extension, the internal microstructure shows the deformation not to be strictly affine. It becomes more inhomogeneous with increasing draw ratio. Inhomogeneity becomes evident in the differences between the textures along major and minor axes of deformed spherulites. The greatest deformation occurs towards the outside of the spherulites along radii parallel to the draw direction; orthogonal radii show the least change at low draw ratios. There is no evidence for interspherulitic yielding, and the presents of comparatively undeformed segments or caps within a more highly drawn matrix is much less than for drawing at room temperature, as it was observed in the earliest studies of Hay and Keller. The changes caused by deformation reduce the melting point of lamellae, the more so the greater the associated increase of the Gibbs free energy. Inhomogeneous deformation can, therefore, be reflected in a spatial variation of the melting point, which was clearly demonstrated in the fascinating annealing experiments, by the significant difference in the behavior of the dominant and subsidiary lamellae earlier discovered by Bassett on both deformation and annealing.

The origin of the oriented structure on necking, which is of primary importance for the understanding of the structure/property relationships, was studied in detail by Prof. H. Zachmann (University of Hamburg, Germany) on PET using deuteron NMR with samples, in which either only the benzene rings or the ethylene groups were deuterated. With the help of NMR, WAXS, and SAXS techniques it was possible to separately identify the orientation of the benzene rings, the ethylene groups, and chains of four different degrees of mobility. It was established that in the amorphous neck samples the orientation functions of the benzene rings, ethylene groups and of all kinds of chains showing different mobilities are identical. Furthermore, in these samples it is the benzene ring axis that is preferentially oriented parallel to the draw direction. The annealing of the oriented amorphous samples is known to drastically change their structure and lead to crystallization with the formation of the folded lamellar structure. In the annealed samples a parallelization of the benzene ring planes was shown occur not only in the crystals but also in the amorphous regions. The least mobile amorphous chains (probably taut tie molecules) have almost the same high orientation as the chains in the crystals, while the more mobile amorphous chains (probably loops) are less well oriented. For these chains, the orientation function of the ethylene groups was smaller than that of the benzene rings. This was interpreted as being due to the bents in the loops formed by the ethylene groups rather than the benzene rings.

Some controversial points in the development of orientation of semicrystalline polymers in a solid state were emphasized by Prof. V. Marikhin (Ioffe Physico-Technical Institute, St. Petersburg, Russia). One is, in his opinion, the structural rearrangement of the initial morphology into a fibrillar one, which is typical of oriented polymers. The data analysis permitted the conclusion that the model of unfolding macromolecules with their subsequent recrystallization in the orienting field is preferrable to that proposed by Peterlin. The drawing includes two stages different in their nature and obeying different physical laws: (i) solid phase chain-folded–extended chain transition in a neck region and (ii) plastic deformation of the newly built fibrillar structure from a natural up to an ultimate draw ratio. Although the draw ratio in the neck region makes up only a few tens percent of the ultimate one, the most important details of the oriented structure are formed at this drawing stage and have a "genetic" affinity to the parameters of lamellar morphology. This approach makes one pay a great deal of attention to the formation of a special type of initial structure with convenient molecular characteristics and to establishing strictly prescribed drawing conditions for each stage of the process. The optimal initial morphology, from this point of view, can be that of single crystal mats, polymers crystallized from semi-dilute solutions (gel-technology) or small isotropic spherulites composed of small folded crystallites connected by a great amount of tie molecules. The latter occurs in the quenching of the polymer melt.

The great role of the initial morphology in the achievement of high molecular orientation was also mentioned by Dr. S. Chvalun (Karpov Institute of Physical Chemistry, Moscow, Russia) who confirmed that the single crystal mats of UHMWPE could be drawn to a very high draw ratio (DR = 200). UHMWPE films characterized by a structure close to that of single crystal mats with a low concentration of entanglements in the initial samples also displayed a high deformability. Such films could be obtained via short-term swelling in organic solvents at high temperatures followed by polymer crystallization or via reactor powder cold compression followed by drawing.

Prof. T. Kanamoto (Science University of Tokyo, Japan) also shared this standpoint and considered *the initial morphology, molecular weight, the drawing technique and conditions as the matters of primary importance for achievement of highly oriented state.* Convincing evidence for the influence of the thermal prehistory and the drawing technique on the polymer drawability was demonstrated in the experiments with PBI samples. The maximal draw ratio attained under conventional drawing was by a factor of 8 less than that achieved for the samples with a modified initial crystal structure and drawn by solid-state coextrusion followed by tensile drawing. As was emphasized by Prof. T. Kanamoto, this technique gives a unique possibility to orient the reactor powder of ultrahigh molecular weight polymers and to use their specific morphology for producing superdrawn films and fibers with a draw ratio up to 80–800, depending on the catalyst properties and polymerization temperature.

In the oriented state as well as in unoriented one, all polymers have a heterogeneous structure which controls their behavior. Because of this, the structure/property relationships are of paramount interest for studies of polymeric materials, and the knowledge of morphology permits the production of polymers with prescribed properties.

STRUCTURE OF ORIENTED POLYMERS

As was pointed out by Prof. V. Marikhin, oriented polymers have *two levels of heterogeneity (micro- and macrofibrils), both resulting from the necking due to recrystallization of the initial structure.* It was emphasized that whatever the initial state or orienting technique, the longitudinal heterogeneity (long period) of microfibrils, which is their intrinsic feature, is also formed during the necking and cannot be avoided even at ultrahigh drawing rate. The disordered regions of microfibrils consist mostly of tie molecules of different length having predominantly a crankshaft structure with a great amount of 2g1-type kinks. During the drawing, the difference in the tie molecule lengths decreases due to the deletion of defects. Those that can not be deleted are accumulated on the former long period boundaries. The possibility of avoiding these defects and of achieving the theoretical properties was discussed.

The internal structure of disordered microfibrillar regions in UHMWPE samples oriented from single crystal mats up to a draw ratio of 200 was also a subject of a close examination by Dr. S. Chvalun discussed this question in connection with the long disputed paradox of the longitudinal crystallite size excess over the long period. In contrast to the widely spread opinion, this effect should be attributed to the linear diffraction on separate *trans*-tie-molecules bridging the adjacent crystallites in microfibrils rather than to the contribution to the diffraction pattern from long three-dimensional crystalline bridges. The volume fraction of linear systems was estimated from the X-ray crystallinity determined by the total intensities of 110 and 002 reflexes and appeared to be equal to 75% chains involved in the crystallites. This explains the high quality of ultradrawn UHMWPE.

NEW TECHNOLOGIES AND MECHANICAL PROPERTIES OF ORIENTED POLYMERS

Oriented polymers find many applications in engineering and industry due to their extraordinary mechanical properties together with low density, chemical resistance, ease of processing, etc. The achievement of extreme mechanical properties of polymers in the oriented state has been presented by many invited speakers who pioneered in this field. During the past decade, impressive progress has been made in the enhancement of mechanical properties of polymers, flexible-chain ones in particular, using different routes of processing.

Prof. I. Ward (University of Leeds, UK) well known for his progressive research work on the elaboration of techniques for producing high modulus polymers presented *an overall survey of the present state of the art in solid phase deformation of PE and related polymers.* Fiber processing was considered together with hydrostatic extrusion and a recent dye-drawing technology. It was explained that the further development for melt-spun and drawn PE has been advanced by the investigation of processes for surface treatment and radiation cross-linking to provide better fiber-resin adhesion for composites and improved creep behavior, respectively. Further increase of tensile strength is possible through an understanding of its dependence on the molecular weight and scale factor. Combined physics and engineering efforts at Leeds University has produced a combination of the hydrostatic extrusion and dye-drawing mechanisms. This yielded a continuous dye-drawing process enabling to produce biaxially oriented pipes with excellent impact strength and long-term strength characteristics, where ductile rather than brittle failure is observed. Other significant property changes include improved chemical resistance, which relates to lower solubility and diffusion of liquids and gases. A great deal of attention was given to practical application of polymers with enhanced mechanical properties (cables, water and gas pipes, biomedical prostheses, composites, etc).

Irrespective of the fact that the values of elastic modulus close to the theoretical estimates were obtained for PE comparatively long ago, the strength characteristics still remain inferior to those predicted by theory. Over the past decade, however, a considerable progress has been made in this field. The first breakthrough in producing strong PE fibers was made by the invention of the surface-growth technique and the development of gel-technology. Further advance was achieved by the improvement of these processes.

Prof. A. Pennings reported on the possible increase of tensile strength (up to 7 GPa) in a two-step process involving *high speed spinning from semi-dilute UHMWPE solution and drawing*. Prof. V. Marikhin emphasized the importance of finding an optimal temperature-force drawing regime for producing strong polymeric materials taking into account the kinetic approach. It was pointed out that drawing is always a competition of two processes: (i) the strengthening of the material due to alignment of macromolecules under the action of orienting stress and (ii) the loss of strength due to molecular relaxation and molecular scissions caused by thermal fluctuations. *Optimization of the multistage zone drawing technique* can yield UHMWPE films with a tensile strength of 7 GPa for the drawn gel-crystallized samples and about 10 GPa for the drawn solution-crystallized filaments.

Two-stage zone drawing of single crystal mat samples also provides UHMWPE films of ultrahigh modulus (from 120 to 200 GPa) and tensile strength (from 2.5 to 5 GPa), as was shown by Dr. S. Chvalun. UHMWPE samples with enhanced mechanical properties were also obtained by Prof. T. Kanamoto through *solid state extrusion followed by conventional drawing from the reactor powder or single crystal mats.* The highest tensile strength attained in this case was about 6 GPa, while the elastic modulus was close to the theoretical one. One can conclude from the forgoing, that the developed theory of molecular orientation and the progress in the experimental techniques allow one not only to produce superstrong and superstiff lab-scale samples but also implement the commercial production of polymeric materials with enhanced properties. The most promising results were obtained for linear ultrahigh molecular weight polyethylenes. Nevertheless, even for this material there is still a considerable discrepancy between the theoretical and attainable tensile strengths. Thus, there is much room for further research efforts and for processing improvement.

DEFECTS AND FRACTURE OF ORIENTED POLYMERS

Knowledge of the fine structure of oriented polymers and a clear understanding of the distribution of external forces over the structural elements in stressed polymers are of primary importance for the further progress in this field.

These problems were thoroughly considered in the presentation of Prof. H. Kausch (Swiss Federal Institute of Technology, Lausanne, Switzerland) who, following the pioneering research of S. Zhurkov, gave *direct evidence for the chain loading and scission with IR-, ESR-, and Raman-spectroscopy.* A static model of stress transmission was confirmed by the data obtained. It was, however, emphasized that the stress transfer is an eminently dynamic process (single crystals are an exception). It is controlled by a constant struggle between internal friction to impose axial stresses on the chains and fibrils and internal relaxation reducing elastic stresses by segmental slip and/or conformational changes. Four cases were analyzed: (i) static stresses imposed on and maintained by a highly but not totally extended chain, (ii) static and dynamic loading of highly oriented UHMWPE fibers, (iii) dynamic loading of coiled chains up to chain scission, and (iv) static and dynamic stress transfer of chains at an interface. The calculations showed that the annihilation of a kink in a highly but quasi-statically loaded kinked segment is much more probable than bond scission, i.e. macromolecular segments break up only if there are no more kinks to relax. The energy released at the moment of chain scission can be very high (e.g. 870 KJ/mol, as was calculated for polyamide segments of 6 nm length with elastic modulus of 200 GN/m^2; if this energy was to be confined within the volume of a segment, it would constitute an energy density of 764 MJ/m^3). Chain scission events, therefore, can be discussed in terms of microexplosions, as S. Zhurkov and his colleagues suggested. It was shown that the undisputable fact of the multiple molecular scissions under mechanical loading of polymers is in itself neither proof nor even indication that macroscopic stress relaxation, deformation and fracture are a consequence of the chain breakage.

Macroscopic fracture of solid polymers is known to result from the main crack propagation across a loaded sample. This occurs when the submicrocracks attain a critical concentration and start to coalesce. The origin of submicrocracks is a key issue in the understanding of the fracture mechanism. Whether they appear due to molecular scissions or the rupture of macromolecules is only a consequence and not an independent cause of fracture is still open to question. If a submicrocrack is indeed formed following molecular scissions, the question arises as to which mechanism governs this process. The most disputable problem in the kinetic theory of fracture concerns the nature of an elementary act of fracture, and it was discussed in detail by Prof. S. Frenkel. Two controversial mechanisms were considered: (i) thermofluctuation rupture of a single chemical bond in the overstressed molecular segments and (ii) explosion-like fracture of separate microregions of significant volume ($10 \times 10 \times 10$ nm) resulting from gigantic thermofluctuations (dilatons) arising from inelastic phonon scattering. It was pointed out that the attribution of the fracture activation energy calculated from the mechanical tests and its relationship with that of a single chemical bond in the macromolecular backbone still remain unclear.

Application of the general theory of defects in solids to structural imperfections inherent in polymers tested by Dr. N. Pertsev (Ioffe Physico-Technical Institute, St. Petersburg, Russia) opens up a new understanding of the behavior of semicrystalline polymers on drawing. The focus of this lecture was on the defects that relate to the scale of transverse sizes of macromolecules (subdivided into conformational and crystallographic defects) and to the level of lamellae and macrofibrils, due to their important role in drawing. The generation and behavior of the defects was considered in the frame of the disclination model that is being intensively developed at the Ioffe Institute. The major advantage of the disclination approach is a quantitative estimation of the energetic benefit of generation, migration and elimination of various defects. It was deduced from the topological stability of an elementary conformational defect that a number of gauche-conformers in disordered microfibrillar regions should be regarded as "excess" defects. These residual defects can not be removed locally, in contrast to the majority of conformational defects of opposite sign annihilating with each other. The number of excess defects per chain is predetermined by the conformations of folds in the lamellae of an unoriented polymer and is usually about 3 defects per chain segment. Under usual drawing conditions the stress field in a stretched polymer does not create any driving force for their diffusion through the crystallite into the neighboring disordered layer in the microfibril. As a result, possible formation of a regular system of chain twist boundaries inside a microfibril is emphasized. The slippage of microfibrils during stretching was analyzed in terms of the dislocation model.

CONDUCTING POLYMERS

Chain orientation has been found to drastically enhance not only various mechanical properties of polymers but also the electrical conductivity, often by as much as two orders of magnitude. The fast-moving area of electrical conductivity is a new branch of polymer science and engineering. It was opened up by the discovery that the conjugated polymer polyacetylene (PA) could be rendered electrically conductive through doping with iodine vapor. The initial finding was rapidly followed by the realization that many other conjugated polymers could be doped to become electronically conductive, such as polythiophene, polypyrrole, poly(*p*-phenylene), etc. The ultimate level of conductivity was established to be widely varied through chemical modifications, the choice of dopant and by the change in the morphology during processing, the degree of order and chain alignment being of major significance. Despite the appearance of many new stable and processible conductive polymers synthesized all over the world, the interest in polyacetylene has not died because of its extreme conductivity, both theoretical and achievable, and due to the latest advances in the synthesis of more stable materials.

One of the major problems for the preparation of oriented polyacetylene is its insolubility and infusibility, but it can be overcame by several methods. Prof. H. Shirakawa (University of Tsukuba, Japan), who was the first to discover on electrical conductivity in PA, presents a *review of preparative methods for orienting conducting polymers with a focus on PA*. *Cis*-PA films are known to be more drawable than *trans*-PA ones. In this study a high degree of molecular orientation was achieved by mechanical drawing of free-standing *cis*-films in which the 85% *cis*-isomer content was attained by low-temperature polymerization developed by the author. A promising alternative route for producing oriented PA films was proposed with LC as an oriented solvent during PA polymerization. Macroscopic orientation of the nematic solution could be attained by gravity flow or magnetic field. The technique provides highly oriented PA films, whose electrical conductivity was about 10^4 S/sm upon iodine doping.

Prof. P. Smith (University of California Santa Barbara, USA) was also concerned with conjugated polymer orientation. Besides the preparation of oriented conjugated materials directly from intractable and insoluble conjugated macromolecules by mechanical means (PA, poly(*p*-phenylene), polythiophene, polypyrrole), a great deal of attention was given to *possibilities of chemical modification of conjugated molecules aimed at making them soluble and processible*. It was possible to realize the preparation of oriented, conjugated polymer products by producing non-fully conjugated (and therefore more flexible) precursor macromolecules. An easily abstracted leaving group was initially attached to the monomer. The latter was subsequently polymerized into the "precursor" polymer. The reduced or absent conjugation in this precursor polymers allowed for processing and orientation by conventional routes (solution- or melt-spinning). Leaving group abstraction might occur either during or after orientation, resulting in highly conjugated, and no longer processible polymeric materials. The alternative route for rendering conjugated polymers in the processible ones was shown to be realizable through the attachment of permanently affixed side groups. Due to the increased entropy associated with these, (mostly flexible) side groups, the relatively stiff, substituted conjugated polymers might also be processed by conventional routes.

It was emphasized that PANI holds special prominence in the field of conducting polymers due to its good processibility in the unsubstituted form and its high environmental stability.