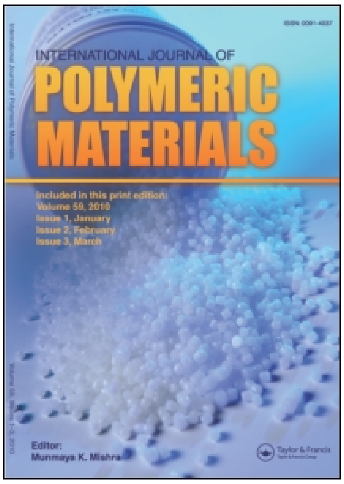

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International Perspectives

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INTERNATIONAL PERSPECTIVES

One of the goals of this journal is to facilitate communication in the international community of polymer scientists and technologists. To this end the *International Journal of Polymeric Materials* will periodically include reports of the Regional Editors covering important activities and developments in their respective regions.

The following report of activities in the U.S.S.R. and EASTERN EUROPE was prepared by G. E. Zaikov.

POLYMERS IN EASTERN EUROPE

Nineteen eighty-nine marked the Thirtieth Anniversary of the establishment of the Division of Polymers and Composite Materials, within the framework of the Institute of Chemical Physics of the U.S.S.R. Academy of Sciences in Moscow. To celebrate this event, a Conference was held October 19–21, 1989, at which the Division's achievements over the last thirty years were discussed.

Created in 1959 on the initiative of Academician N. N. Semyenov, who later became Director of the Institute, the first head of the Division was A. M. Markevich. In the early 1970s, he was succeeded by Academician N. S. Enikolopov; and since 1988, A. A. Berlin has been in charge of the Division. At present, about 700 people, including fifty doctors of science and 250 doctoral candidates, are engaged in work at the Division.

The Division of Polymers and Composite Materials is unique in its approach to studying problems. Chemical kinetics (as one of the major research methods), the study of process mechanisms, and the development of techniques to influence the process are used to improve the quality of the products. This report is an overview of presentations made by the Division's leading researchers covering major achievements in various fields of chemistry and the physics of polymers.

Macrokinetics of the Reactor for Fast Chemical Reactions

A. A. Berlin

Macrokinetic characteristics of fast chemical reactions in turbulent miscible flows of reagents are analyzed in this work. Three conditions for the process in a tubular reactor equipped with a central inlet for the catalyst—one of the reagents—are identified, namely: turbulent flow, quasi plug-flow, and intermediate. Also identified are areas where these conditions can exist depending on the flow rate, geometry of the reactor and that of the mixing arrangements.

This paper describes the possibilities for determining the effective constants of chemical reaction rates and hydrodynamic parameters proceeding from the analysis of the effect of the geometry factors of the reactor on the product yield. The operation of the reactor with multi-step and continuous inlet of the reagents along the axis is considered. Various techniques for removal of the reaction heat and the relevant temperature fields are analyzed, that is: cooling of the initial reagents (autothermal regime), boiling of the reaction system, and heat removal through the external wall. The effect of the mass- and heat-transfer limit and the possibility of process control by changing the ratio of effective coefficients of mass- and heat-transfer are shown. Shown here, parameters of molecular-mass distribution of the product are calculated for the reaction of polymerization, the wide possibilities for its control by means of changing conditions—initial temperature, pressure in the reactor, flow rates—reactor design, choice of solvents, and distribution of the catalyst. These approaches and analyses of specific chemical processes allowed the researchers to develop the methods and calculate the optimal design for the reactor and conditions for carrying out the reactions.

At present, a unique energy- and material-saving technology, having no counterpart anywhere else in the world, of fast chemical and petrochemical reactions (polymerization and oligomerization of butylenes, isobutylene; chlorination of ethylene, divinyl, and raw rubber; hydrochlorination of ethylene, and sulfuric acid; alkylation by isobutane butylenes, sulfuration) is being developed in the Soviet Union. This technology is based on the use of a Tubular Reactor of a substantially small size, without mixing arrangements and cooling systems. It operates at conditions providing high production rates and good-quality products.

The application of the new technology makes it possible to:

a. *reduce* operating area;

b. *substantially increase* total productivity two- to fourfold;

c. *reduce* amount of metal per reactor and reactor size 100-fold and more and, respectively, *increase* specific productivity 1000-fold and more;

d. *decrease* energy consumption 20% to 30%;

e. *reduce* input of raw materials 15% to 20% and the catalyst one and one-half to twofold;

f. *reduce* amount of attending personnel;

g. *decrease* water consumption and effluent of harmful wastes.

This method is protected under fifteen author's certificates and six patents in major market economy countries.

The Turbulent Reactor has passed the qualification requirements and is now used in many operations of the chemical and petrochemical industries.

Solitones in the Physics of Polymers

L. I. Manevich

A complete investigation of physical properties of condensed media includes the analysis of its spatially heterogeneous equilibrium states—in terms of mechanics or thermodynamics—as well as small and large deviations from equilibrium. Small deviations are described in terms of collective excitations, i.e., oscillatory or relaxation modes (of solving linearized equations), while the account of weak non-linearity is carried out using the theory of disturbances, and results in some transformation of these modes and weak interaction among them. However, there are also non-linear effects which fail to be identified by the theory of disturbances; these effects are described by solutions of solitone type which correspond to structural defects (spatially non-uniform equilibrium states) and localized dynamic disturbances. In this case, the direct analysis of equilibrium equations (motion equations) turns out to be a challenging task, even in the case of low-molecular substances and especially polymers. However, the situation changes drastically if the hierarchy of interactions typical for polymeric bodies is taken into account and, as a result, introduction of relevant small parameters becomes possible. It has been shown with respect to the orthorhombic crystal of polyethylene that the account of these parameters allows development of a number of asymptotic theories permitting an analytical investigation.

The classification of structural defects in the polyethylene crystal includes three types: 1) cooperative twisting and deflectionally twisting deformation of domain walls; 2) stretching deformation as well as stretching and shifting deformations localized mainly on the same chain (analogous to vacancies in low-molecular crystals); and 3) linear structural defects of dislocation and distapering. In all cases, energy characteristics of structural defects have been analytically estimated, conditions for their motion have been determined, and possible applications are discussed.

Concerning the Peculiarities of Frontal Conditions of Polymerization in Reactors with Directed Radially Symmetrical Flows

S. P. Davtyan

Development of highly productive, energy-saving and ecologically sound processes for obtaining polymers and polymer-based products directly in the polymerization process requires basically new approaches to the commercial production of high-molecular compounds. One of the tangible ways of achieving this aim appears to be polymerization in high-temperature conditions with the use of exothermal reaction of polymerization in a continuous flow system. Discussed in this paper are possibilities for the implementation of frontal conditions for radical polymerization in continuous reactors of various configurations.

Radical polymerization of vinyl monomers in continuous reactors of cylindrical and spherical configuration with radially symmetrical flows and internal and external introduction of initial reagents (monomer + initiator) is considered in both stationary and non-stationary conditions. Various techniques of initiating are taken into account in setting up the task; namely: initiation at a constant rate, with one substance initiator, with two initiators differing in activation energies of their disintegration (decomposition), and alteration of initiated and thermal polymerization.

Analytical and numerical methods are used to analyze the effect of various kinetic, thermophysical, and technological factors on the yield and characteristics of the final polymer, and its thermal stability. Process efficiency is also considered.

The conditions for increasing the yield and regulating the molecular mass and polydispersity of the final polymer are identified.

Selected theoretical results are compared with the experimental data.

Main Development Trends in the Chemistry of Polymerizable Oligomers

B. I. Zapadinskii and M. N. Gusev

A steady interest in the oligomeric method of synthesizing and processing polymeric materials is explained not only by the technological advantages of this method, but also by its high sensitivity to recent technological requirements. Thus, for example, new methods of storage and transfer of information, electronics, and medicine have aroused interest in creating new types of polymerizable oligomers and their technological syntheses.

One of the obvious trends in the technology of oligomers synthesis consists in introducing the end polymerizable groups, usually when disocyanate is used, into previously prepared intermediate products using reactions which do not require any solvents, isolation and purification of the oligomer. This method is preferable technologically and environmentally, but requires a careful study of the kinetics and mechanism of the reactions and their effect on the yield and quality of the final product. Thus, the reactions of unsaturated acids with epoxy oligomers widely used in this process scheme have shown that sufficiently strong acids cause (give rise to) polymerization of epoxide, resulting in the formation of a set of oligomer-homologs and incomplete consumption of the acid.

Intensive research is being conducted to develop oligomers capable of high-rate photopolymerization to obtain protective coatings and optical articles. Oligourethane and oligocarbonate acrylates containing stabilizing groups in their oligomeric block are found to be the most promising oligomers for this purpose. In addition to selection of the oligomeric block pattern, controlled introduction of substitutes at the nitrogen atom is also very promising for regulating the properties of the articles made from oligourethane acrylates. The only feasible method to obtain the appropriate oligomers is the reaction of glycol bichloroformates or bis-phenols with N,N′-disubstituted diamines or their mixtures with unsubstituted diamines in the presence of *N*-phenylaminoethylmethacrylate.

In connection with the development of optical methods of information storage and transfer with the use of oligomers, new types of fluorine-containing oligomers are obtained, that allow reduction of the refraction factor and improvements in water stability and adhesion properties of the materials.

At present, various types of oligomers for obtaining articles with temperatures up to 370°–390° have been obtained. In the case of purely organic oligomers, an increase of thermostability of articles is always associated with increasing temperature of processing. For this reason, the application of oligomers containing siloxane, carborane, blocks etc. and/or acethylene end groups are particularly promising, since, in this case, strong intermolecular interactions develop only at the stage of the article formation.

Metallopolymer: The Present and the Future

A. D. Pomogailo

Metal-containing polymers are widely applied in many fields, particularly as metal complex catalysts.

For this reason, much attention is given to analysis of the peculiarities of interactions in the macroligand-transition metal compound systems resulting in immobilization of Me_n on polymeric carriers. The basic transformations of macroligands, such as conformation changes, structuralization processes, transformation of functional groups, destruction of the main chain, etc. have been identified. In the reacting Me_n-polymer systems, the transition metal participates inredox transformations; monomerization of dimeric and dimerization of monomeric metal complexes occur; and the geometrical pattern of the polyhedron being formed is changed. Also of importance for the application of metallopolymers in catalysis is the character of distribution of metal complexes along the polymer chain, i.e., topography of the fixed Me_n, exchange interactions, and cluster formation.

The main approaches to implementation of these processes are summarized here; the basic requirements of immobilization of metal complexes on the polymers and their structural organization as well as the trends in the development of this field are established.

In contrast to the reactions of polymer-analogous transformations with the participation of Me_n, metal polymers obtained by the methods of polymerization and copolymerization of metal-containing monomers exhibit much higher structural uniformity. These monomers are classified according to the nature of the chemical bond of the transiton metal with the organic part of the monomer. The basic ways of transforming metal monomers into metal polymers, namely, radical and ionic (including anion-coordiation) polymerizations, are analyzed.

The peculiar features of the polymerization process of these monomers are identified. The properties of the products thus formed are characterized. Non-traditional ways and means of polymerization of metal-containing monomers allowing their polymerization at any-phase states and in a wide range of temperatures have been developed. The specific features of catalysis (polymerization transformations, hydration, and oxidation) due to the effect of metal polymers are summarized.

Selective Dimerization and Polymerization of Olefins on Zygler-natta Catalysts

G. P. Belov

Here, the current understanding of selectivity in catalytic reactions of transformation of low olefins (ethylene and propylene) into valuable dimeric and polymeric products is assessed on the basis of literature data and experiments made by the author.

Ways of increasing the selectivity of the dimerization and oligomerization of ethylene and propylene are discussed, using the example of selective catalytic dimerization of ethylene developed in the Institute of Chemical Physics Department of the U.S.S.R. Academy of Sciences. The industrial process of butene-I production evolved from collaboration of the Soviet Union and a number of countries abroad.

Also, possibilities are considered for selective production of polyethylene and polypropylene characterized by narrow molecular weight distribution.

Epoxide Polymeric Matrices: Approaching the 1990s

B. A. Rosenberg

Analysis of scientific and practical achievements in the field of epoxide polymers; availability and relatively low cost of raw materials used for their production; and exclusive flexibility of this class of polymers' meeting various requirements of technology and, at the same time, providing high level of operating characteristics of composite materials based on these polymers have led to a conclusion that the 1990s will witness a consistent interest of the researchers in this area of polymeric materials and the priority role of epoxide-adhesive (binding) materials in the production of high-strength composite materials with average thermostability to 250°C.

In the last decade, the Department of Polymers and Composite Materials of the Institute of Chemical Physics, U.S.S.R. Academy of Sciences, has made a major contribution toward understanding of the process of structure formation and properties of epoxide polymers. Detailed investigations of the kinetics and mechanism of epoxide oligomers' solidification processes with the use of various solidifying agents resulted in the development of the theory of the reactions of nucleophilic addition to the epoxide ring. The molecular structure of epoxide polymers has been established and the theory of the formation of topological structure of epoxide polymeric networks has been developed Also, the peculiarities of structural organization and properties of epoxide polymers in glassy state and their performance as matrices in composite materials have been established.

Analysis of the present state of epoxide polymeric matrices in terms of degradation mechanism of composites shows that the key problem in increasing the strength of fiber-strengthened composite materials consists in increasing the plasticity and impact strength of epoxide matrices. Possible approaches to investigating this problem are considered.

Much attention is given to the processes of obtaining the heterophase epoxide polymeric matrices upon solidification of epoxide compositions containing reactive oligomers or polymers as additivies resulting in phase separation. The mechanism of phase separation in solidified systems is discussed, the approaches to regulating the volume part of heterophase, as well as the function of distribution of heterophase particles according to sizes and adhesion strength of dispersion phase particles' adhesion to the matrix, that is parameters determining the modifying effect of additives are formulated.

The application of liquid crystalline epoxide oligomers capable of orientation in an electromagnetic field seems to be promising for increasing the rigidity and strength of epoxide polymeric matrices.

Guidelines to improve the technological properties of epoxide compositions yielding very strong composites based on these epoxide compositions are formulated.

Mechanisms of Destruction of Reinforced Plastics

S. L. Bazhenov and A. A. Berlin

This paper contains an overview of the authors' works relative to destruction mechanisms of unidirectional reinforced plastics upon static loading. The peculiarity of reinforced plastics destruction consists in the variety of mechanisms of their destruction. This makes the formulation of the matrix criteria and prediction of the material behaviour on the basis of standard tests very difficult. Failure caused by elongation may result from the inability of fibers to sustain loads, growth of the crack associated with some technological flaws, or longitudinal cracking.

Failure due to the insufficient load-carrying ability of fibers is typical for composites based on glass and carbon fibers embedded in rigid matrices. In considering the effect of cracks, it is necessary to take into account the local separation of fibers from the matrix at the crack end or the matrix plasticity.

Boundary Layer in Organic Composites

V. I. Irzhak

The paper presents the experimental data allowing evaluation of the thickness and properties of the interphase layer in organic composites, as well as of the role of this layer in the initial stage of the failure of organic composites.

Analysis of the kinetics of the reinforcement in the torsion pendulum experiment using the thread with various types of reinforcement and correlation with the kinetics of chemical transformation in the process of solidification leads to a conclusion that the rigidity of the thread with unidirectional fibers characterizes the rigidity of the interphase layer.

Microscopic investigation of model composites consisting of monofibers in the matrix film has shown that the cracks resulting from their deformation are localized in the interphase layer. The fiber, on the other hand, remains intact up to relatively large sizes of cracks which are formed inside the matrix. It is consequently the interphase layer where the initial cracks are formed and where the failure of organic composite is initiated. Therefore, the properties of the interphase layer play a decisive role at this stage of destruction.

Some Non-traditional Methods of Processing Polymeric Materials

E. V. Prut

The effect of temperature and time regimes on the production of materials with required characteristics upon two-stage drawing and extrusion in the solid state is analyzed. Isotactic polypropylene was chosen as the object to be studied.

1. The mechanism of polypropylene deformation is considered.

2. It is shown that the two-stage drawing results in films with the modulus of elasticity equal to ~35 GPa. This equals 75% of the theoretical value. The effect of the drawing rate of the first and second stages on the maximum draw ratio and elastic modulus are studied.

3. The dynamics of the extrusion process in the solid state is studied. The peculiar features of the process in the stable and unstable states are discussed and a criterion proposed to treat these problems.

4. Degradation of the polymer in the critical regimes of extrusion are also investigated.

Conducting Polymers: Problems and Perspectives

V. M. Kobryanskii

Conducting polymers which possess a set of interesting electrophysical and electrochemical characteristics have recently attracted a great deal of attention. A possibility to use these polymers for sources of electricity, photo convertors (transformers), semiconductors and even substitutes of non-ferrous metals is here demonstrated. In 1987, H. Naarmann obtained polyacetylene with conductivity equal to $1.5 \cdot 10^{5}\,0\,\mathrm{m}^{-1}\,\mathrm{cm}^{-1}$ which exceeds copper conductivity two times in terms of mass unity. However, the practical application of most of these polymers is limited due to their poor stability.

This paper proposes and develops a concept that conductivity and stability of conducting polymers is limited by defects which result from disordered domains of the solid phase. For the most highly ordered polyacetylene polymerized on metal complex catalysts the mechanism of defects formation can be explained as follows. Polyacetylene is insoluble. For this reason, two parallel processes take place in the course of polymerization: growth of the polymer chain and formation of the solid phase. When the chain growth speed exceeds the rate of crystallization, then conformation defects are being formed. Chemical defects, as a rule, are secondary and are formed at the sites of conformation defects at the expense of the chemical reactions which follow. The ratio of the rate of chain growth and crystallization can be regulated by choosing the structure of the catalytic center and the medium viscosity. Experiments have shown that in the case of acetylene polymerization, an increase in the medium viscosity may result in a sharp improvement of polyacetylene quality.

Physical Aspects of Loosely Cross-linked Hydrogels' Swelling

S. A. Dubrovskii and K. S. Kazanskii

Physical aspects of the behaviour of loosely cross-linked acrylamide-based polyelectrolite hydrogels upon their swelling in water and mineralized aqueous solutions (the swelling degree up to 3.10^4 ml/g) are here considered. A group of "key" dependencies which can be most efficiently employed for qualitative evaluation of hydrogels and quantitative characteristics of their molecular structure are identified. First of all, these include the dependencies of swelling on pH, ionic force, concentration of some "specific" ions, external pressure and the modulus of elasticity and degree of swelling. Possibilities for theoretical description of these dependencies and prediction of hydrogels' efficiency in practical application are analyzed. The applicability of the Gaussian approximation to hydrogels in the indicated scale of swelling is discussed.

Also discussed are anomalies in the dynamics of supergels' swelling due to the deformations appearing on the surface of the swelling sample caused by tangential stresses. The phenomenon in question is explained, and the critical conditions of its implementation are formulated.

Microheterogeneity of Amorphous Polymers

I. M. Bel'govskii

Microscopic fluctuations of density and chemical composition of the polymer, finely divided filler and porosity give rise to local fluctuations of the substance electronic density. Their topology is reflected in spatial distribution of intensities of diffused light. Measurement and processing of the diffused light are important, though ambiguous, with regard to statistical characteristics of microheterogeneity, namely, correlation radii and mean-square amplitude of fluctuations, r_{corr} and $\langle \Delta^2 \rangle$.

Unambiguous interpretation of the light diffusion data can be obtained by additional measurement of the same statistical parameters of the medium but with a different averaging degree. For this purpose, the spatial correlation of intensity in diffused light upon illumination of the object by a thin laser beam is employed. It is much easier technically to replace the spatial scanning of the diffusion field by uniform rotation of the test sample while the monitor is stationary.

The photoflow of the monitor is time-fluctuating following the changing interference picture. By studying the spectral composition of fluctuations of the photoflow $S(\omega)$ it is possible to obtain valuable statistical characteristics of diffusion medium with a higher degree of averaging.

$$-\frac{1}{\omega}\frac{d_1 S(\omega)}{d\omega} = Cf\left(\left|\frac{\omega}{\bar{\Omega} \times \bar{k}}\right|\right)$$

where $f(r_{ik}) = \langle \Delta_i^2 \Delta_k^2 \rangle$ is the correlation function of the squares of fluctuations of polarizability, $S(\omega)$ is the spectrum of the photoflow power, $\omega = 2\pi\nu$ is the angular velocity, C is the constant, $\bar{k}$ is the vector of diffusion, and Ω is the vector of the angular velocity of the sample rotation.

Dynamic Theory of Polymeric Melt. Reptation as Dynamic Phase Transition

V. G. Rostiashvili

Dominisis-Peliti type functional producing time-correlation functions of the polymeric chain system reacting with Edwards-Hamiltonian function are obtained. Expressions in Gaussian approximation for correlators and susceptibilities are obtained. The interaction of the test chain with the polymer medium is expressed by a nonlinear equation for the lateral coefficient of autodiffusion. It has been shown that this equation can be solved in conformity with the localized state, the length of localization playing the role of the order parameter. The theory is adequate for the tube model within the range of long chains. The expression for the tube thickness has been derived from the chain characteristics.

The idea of the primitive chain is developed with the use of the expression for tangent susceptibility. The Edwards-Doi diffusion equation for the primitive chain is derived.

Cases were also considered for 1) the frozen test chain environment medium, and 2) the medium behaving similarly to the test chain. The dependencies of the tube thickness on the concentration of the system and the length of Kuhn segment of the chains are discussed in detail.

Realization of Strength of Fibers in Unidirectional Reinforced Plastics

E. S. Zelinskii, Yu. A. Gorbatkina, A. M. Kuperman,
L. V. Puchkov, and R. A. Turusov

The idea of using high-strength glass fibers as reinforcing elements bound with each other by polymeric matrix belongs to A. K. Burov (1900–1957), a talented scientist and architect. As far back as the 1940s, A. K. Burov, G. D. Andreevskaya, and M. V. Klassen-Neglyudova developed the principles of obtaining nonwoven glass-reinforced plastics developing the ideas proposed by the school of Ioffe, Griffits *et al.* Strict orientation of fibers and protection of their surface from damage made it possible to increase the materials' strength by two to three times, as compared with glass-cloth-based laminates.

The dominating direction in the work of the laboratory set up by A. K. Burov was realization of the initial strength of the fibers in RPs, eliminating or diminishing probability of fibers' damage. For this reason, the first problem to face is the determination of the fibers' properties: their initial strength, elasticity modulus, presence of defects, study of the effect of dispersion strength and the length of monofibers in a cluster (bunch) (thread, braid) on the strength of RPs. As a result of this study it has been found that the latter can be determined by the value of microplastic strength, since the fibers start degrading there at the critical length (Gurland-Rosen model) depending on the limit of the matrix fluidity and the elasticity modulus rather than distribution of defects (scale factor).

Also of great importance, in addition to properties of fibers and matrix, is the interaction of these components. The authors developed the method and devices for the determination of adhesion strength of polymers directly to the surface of fibers, which allowed them to evaluate the effect of time-temperature conditions of the adhesion compound formation, modification of the fibers' surface and of other factors on the strength of the fiber bonding with the matrix. They found the correlation dependencies between this value and the RP strength upon various types of loading.

The technology of unidirectional, material formation, which is the major element in the articles made from reinforced plastics, can decisively affect their properties. The following conditions were found to be oligatory:

- elimination or decreasing of fibers' damage in the process of winding;
- formation of a bundle with regular hexagonal interposition of fibers up to the contact with the surface of the frame, which results in an increase of the fibers' volume content from 60%–65% to 80%–85%, and, in the case of thermal profiling of organic fibers, to 95%–98%;
- decreasing the matrix porosity from 4%–5% to 0.5%–1.5% due to variously impregnating the reinforcing materials with bonding agents;
- optimization of temperature-time conditions of thermal processing upon solidification and cooling of articles in order to decrease the residual stress.

The work done in this direction resulted in the theory of mechanical phenomena in solidification of polymers and composites.

Ways of creating materials with higher thermal stability and impact elasticity (strength) based on thermal plastic matrices, as well as with rather high specific strength upon drawing from the use of highly oriented polyethylene fibers, are to be found with the help of the approaches developed.

Plastic State of Polymeric Glasses. Concept, Problems, Perspectives

S. N. Rudnev, O. B. Salamatina, and S. I. Nazarenko

It has been found that when external mechanical forces act on polymeric glasses, the latter assume a metastable structurally excited state saturated with plastic defects having elevated internal energy. This state is the plastic state of the solid. Many physical and chemical processes in the solid polymer are determined by the structure and the properties of the plastic defects. The kinetics of their accumulation and decay under stress determines the development of plastic deformations in polymers and their mixtures, which also occurs during fatigue, experiments, impact loads and other types of mechanical loadings. There are indications that plastic defects also act as centers of many chemical reactions in solid polymers.

This paper also deals with kinetic and structural aspects of plastic defects, including their geometry. An attempt was made to trace a linkage of the chemical structure and flexibility of polymer chains with the character of the defects and behaviour of the latter. Fundamental and applied directions of the science in which the plastic state of polymers may be of importance are considered.

Structural and Micromechanical Foundations of Strength and Plasticity of Filled Polymers

V. A. Topolkareva, N. V. Gorbunova, I. L. Dubnikov,
and Yu. M. Tovmasyan

Thermoplastic polymers subjected to the orientational process of deformation are characterized by their ability to retain high plastic deformations after introduction of solid fillers. Structural and micromechanical aspects of high plasticity of the filled composites are investigated here using as a model the analysis of deformation micromechanisms of filled linear polyolefins. Deformed stress state of the filled polymer is shown to be determined by deformation properties of matrix polymer packing efficiency of composite cross section, and the conditions of formation and development of micropores in the system. Also analyzed are the factors controlling the strength of the filled material. These factors are: deformation properties of the polymer, the content and distribution of the filler in the composite, the size of inclusions and their size distribution, and the strength of the interface.

It was found that high strength and plastic properties of the composite are obtained with the use of matrix which gain in strength on deformation and inclusions of optimal size. The optimal size of inclusions depends on the type of polymer and adhesion between the particles and the matrix, and is determined by the local stress level which decreases with an increase of the inclusions' size. An increase in the adhesion interaction results in increasing strength of the composite. However, excessive bonding to the surface of the interface causes certain limitation of plastic deformations and embrittlement of the material.

Stage Process of Suspension Polymerization

A. M. Markevich

When chemical reactions proceed in solutions, the reaction medium often appears to be a poor solvent of the reaction product and accumulation of this product causes oversaturation of the solution and precipitation of the new phase. Thus, a dispersed system is formed, which is often observed in polymerization processes when the polymer formed precipitates the reaction medium and the concentration of such suspension increases in the course of the experiment.

Now we consider the process of suspension formation in radical polymerization which is initiated by a free radical. Initially, there is only a solution of the monomer which does not contain any solid phase. At the moment of introduction of an initiator, the chain reaction of polymerization starts. At the initial stage of the chain growth when polymerization rate and concentration of the products being formed are still low these particles—both alkyl radicals and inactive products of their recombination—are in solution. In the course of the process, both the polymerization rate of all the products—alkyl radicals and inactive products—and their concentration grow, leading to oversaturation of the solution and formation of seeds of the new solid phase of the polymer. The structure of these seeds involves all the reaction products which reached a certain degree of polymerization, including the free radicals. These radicals are rigidly fixed in the suspension particles and, unlike the emulsion particles, each suspension particle contains quite a great number of such active particles. Further growth of the suspension particles is due both to capture of new reaction products from the solution and the reaction of occluded radical chain growth. This reaction becomes the major route of macromolecule formation. Thus, the process passes from the homophase stage into the heterophase.

A change in the reaction medium, the formation of suspension, causes a change in the reaction mechanism, and, in the first place, the reaction of the chain rapture. If at the first stage (the homogeneous stage) the radical in solution exhibits mobility, and collision of two particles is determined by the diffusion coefficient in the liquid, then in the heterogeneous stage the mobility of the radical, and hence the rate of recombination of these particles, is retarded. Respectively, the reaction rate decreases. The lifetime of the radical is growing, as well as the average polymerization rate of macromolecules. All these phenomena create the conditions for the synthesis of the high-molecular product.

The duration of the first stage of polymer synthesis is usually very short and is not practically observable. Meanwhile, a product of lower molecular weight is formed at this stage. The amount of this product is always small, as compared with the main mass of the final product. Depending on the specific conditions of the experiment, this low-molecular product can be localized in the main mass of the polymer in the form of separate inclusions, which adversely affect the quality of the final product.

A good object for studying stages of the polymerization process was found to be the reaction of synthesis of polytetrafluoroethylene, because this reaction is not complicated by any side reactions like isomerization, the reaction of chain transfer, etc. The transition of one stage into another can be substantially delayed in the experiments in aqueous solution at low concentration of tetrafluoroethylene in the conditions of constant initiation rate. The first stage is characterized by low and time constant reaction rate and by the fact that the moment of transition into the heterogeneous stage is exactly fixed.

The study of the kinetics of tetrafluoroethylene polymerization has shown that when the structure of the suspension particles is sufficiently formed, the mobility of occluded fluoroalkyl radicals in this structure is equal to zero. For this reason, the reaction of recombination becomes possible only in the course of the chain propagation reaction, when every event of this kind shifts the active site of the radical by the double length of the C–C bond.

The stage-like character of the suspension polymerization which was demonstrated in the experiments with tetrafluoroethylene should occur in analogous syntheses of other polymers. At high concentrations, the homophase stage becomes abruptly shorter and may be practically unnoticable. However, this stage always contributes to the process kinetics and the picture of the molecular-mass distribution of the product.

Possibilities and Problems of a Polymerization Filling Method

L. A. Novokshonova and F. S. D'Yachkovskii

In recent years, the Department of Polymers and Composite Materials has engaged in research to develop the scientific foundations of a polymerization method for introducing fillers in polyolefins and other thermoplastics. The method is based on the idea of polymerization of the corresponding monomer, or a mixture of monomers, on the fillers surface' having fixed metal-complex catalysts. This approach includes development of methods of activating the surface of the fillers of various nature by metal-complex catalysts, the study of the kinetics and macro-kinetics of the polymerization process on the surface of the fillers, characteristics of the structure and physico-mechanical properties of polymerizationally filled polyolefins (properties of olefins filled by polymerization process).

One of the major key features of the structure of polymerizationally filled materials appears to be attainment of uniform distribution of filler particles in the polymeric matrix even at high degrees of filling. Analysis of the effect of the particle size (degree of dispersion) of the filler on the micro-deformation processes allowed the identification of criteria for realization of plastic properties of filled composites based on various polyolefin matrices.

Complex investigations allowed formulation of synthetic possibilities and determination of promising trends in application of the polymerizational method of filling. First, fillers and reinforcing elements can be introduced into super-high-molecular polymers with very limited fluidity; this cannot be done using ordinary mixing methods.

Composite materials based on super-high-molecular polyethylene (SHMPE) and coolene (named COMPONOR) exhibit a more unique combination of properties—much higher rigidity and wear resistance—than SHMPE by itself. In addition, high-impact strength, anti-adhesion and anti-friction properties, and retention of plasticity even at high degrees of filling have also been achieved. A method of synthesis of filled isotactic polypropylene with the use of various inorganic fillers, as well as methods of synthesis of impact resistant, non-hardening filled polypropylene with the use of vanadium catalysts have been developed. A number of new materials based on filled polyolefins with specific properties have been obtained. These include: lower combustibility, electroconductive, magnitoactive, heat conducting (with desirable dielectric properties), and heat insulation materials.

This polymerization method opens up new perspectives for directed regulation of the structure and properties of the intermediate polymeric layer at the interface "filler-matrix" and thus of the physico-mechanical properties of the composite material as a whole. It should be noted that possibilities are great for the synthesis of polymer-polymer compositions in order to modify the properties of the polymer.

Some technological versions of processes for obtaining polymers filled through the polymerization process have been developed: a suspension method in the medium of the solvent, in the liquid monomer (in the case of propylene), and in the gas-phase version.

Fundamental Problems of Catalysis of Polymerization Processes

F. S. D'Yachkovskii, L. A. Novokshonova and
V. I. Tsvetkova

The Department of Polymers and Composite Materials is widely engaged in studying the polymerization of olefins in the presence of organometallic catalysts, including the development of new catalytic systems, the kinetics of the processes of homo- and co-polymerization of olefins in the liquid and gas phases and processes proceeding also in the medium of the liquid monomer. As a result of work performed in recent years, the concept of lability of the Ti-C bond towards the ligand environment—the presence of donors or acceptors of electrons in the coordination or external spheres was substantiated experimentally and quantum-chemically. Principles of synthesis of highly efficient catalytic systems on organic and inorganic carriers have been formulated on the basis of recently developed concepts.

Investigation of the kinetics of polymerization of olefins and elementary constants of the main intermediate stages has resulted in development of mathematical models of these processes which take into account kinetic non-uniformity of the active sites and mass- and heat-transfer in the catalysis seed. Methods for calculating molecular-mass distribution of polyolefins being synthesized have been developed in relation to distribution of sites according to their activity.

Study of the mechanism of stereospecific action of complex catalysts confirms the enantiomorphous model of isotactic polymers formation, and quantitative estimates of the degree of stereospecificity of catalytic systems. Using these approaches, the non-uniformity of active sites in terms of stereospecificity has been studied and the model of two-step formation of the polymeric chain microstructure has been confirmed. Activity and stereospecificity have been found to increase at the moment of fixing the organometallic catalysts on the surface of the laminated carrier—graphite.

Studies have also been carried out to establish linkage between synthesis conditions and polymer properties. Ways of regulating the granulometric composition of the polymer, its density and branching have been developed. The mathematical model of the synthesis of isotactic polypropylene in the reactor in liquid propylene with the classifying choice of polymeric particles has been investigated.

Chemical Modification of Polymers in the Solid Phase Under the Action of Strain Stress

S. A. Vol'fson

More than twenty years ago, Academician N. S. Enikolopov *et al.* were the first to carry out investigations in the field of synthesis and chemical modification of polymers in the solid phase under high pressure and simultaneous deformation using a device called the "Bridgeman's anvil." In the course of these investigations, some anomalous features of processes presenting one of the types of mechano-chemical reactions were identified.

Recently, it has been established experimentally that many of these processes can be reproduced in less exotic conditions. Strain deformations in the solid can be obtained with the use of powder materials and traditional equipment for processing plastics, that is, single- and double-screw extruders equipped with mixing elements, various types of mixers. Substantially less efforts are to be made in the mixing equipment, as compared with pressures of 5 kilobar to 20 kilobar used in Bridgeman's anvils.

Anomalous features of processes of this type also include absence or weak dependence of the reaction rate on the temperature, which allows the process to proceed at room temperature. In addition to energetic advantages, it is also possible to decrease the contribution of reactions of degradation and cross-linking typical of such processes proceeding in polymeric melts at high temperatures.

The absence of solvents and dilutents simplifies the processing of products. In a number of cases, it is possible to unify several stages within one process, for example, grinding of the polymer due to the effect of the strain during crystallization, chemical modification and introduction of a filler. The grinding process is followed by the formation of the virgin surface, which is chemically active at that moment.

One of the reactions studied is amination of polyvinylchloride in the reaction with solid amine (hexamethylenediamine). The introduction of polar modifying groups into polypropylene is the process alternative to high-temperature modification in melt.

Computerized Modelling of Structure, Dynamics and Chemical Reactions in Solids

E. F. Oleinik, M. I. Kotelyanskii and M. A. Mazo

The present paper summarizes the intermediate results of the work carried out in computerized modelling of physical and chemical processes in solid polymeric and non-polymeric bodies over the last four to five years. This work was performed in the Laboratory of Polymers' Structure at the Institute of Chemical Physics of the U.S.S.R. Academy of Sciences.

The following three problems are considered:

1. Modelling of the structure, dynamics, glass transition upon cooling and response to the external mechanic force of the ordinary atomic two-dimensional Lennard-Jones glass;
2. Dynamics of three-dimensional polyethylene crystals with and without defects of substitution;
3. Modelling of the simple chemical reaction A + A, AA in two-dimensional atomic Lennard-Jones glass in the conditions of external hydrostatic pressure.

In all cases, modelling was performed in the framework of the method of molecular dynamics with the time step of $\sim 10^{-14}$ sec.

The ordinary atomic glass 'system I) consisted of two kinds of atoms differing in mass and diameter, with an approximately equal number of particles of various kinds. Such a system is not available for crystallization and remains amorphous in the entire temperature range of the presence of the liquid and solid glasslike state.

When the computer-obtained liquid is cooled, the diagram $V - T$ at $T = 0.28$ exhibits a break point which is interpreted as a sign of the system glass transition. Below this temperature of glass transition T_g the mobility abruptly decreases, the diffusion of particles ceases, while the radius of the shift correlation for all pairs of particles abruptly increases.

While passing through T_g the system does not change its local geometrical structure (the coordination numbers, the composition of the coordination spheres), but substantially changes the interatomic dynamics.

The construction of the Voronoy polyhedrons for each particle allows one to obtain the quantitative characteristic of local free volume V_f per particle and to make an attempt to correlate V_f with the mobility of each particle, for example, with its mean-square shift (r^2 in time.

In terms of the current free-volume approach, the local mobility of the particles in glass and the liquid near T_g is closely connected with the available local free volume.

The result obtained in modelling differs in principle from the generally adopted viewpoint. The graph $r^2 - V_f$ practically shows no difference in the mobilities of the particle with small and large V_f. This is also the case for longer lifetimes of the system (~100 psec), though in this time interval in the system, on the average, a substantial diffusion is observed and the macro-coefficient of diffusion increases with the general macroscopic free volume of the system.

The result obtained suggests that the free-volume concept of molecular/atomic mobility in amorphous bodies is correct at the macrolevel upon averaging according to the great number of particles. However, it is not applicable at the atomic (molecular) level when the mobility of particles is of a collective character.

Analysis of the dynamics of the system shows that under the external mechanical driving force in the glassy state, the vortecies take place and their propagation results in the macroscopic plastic flow of the entire system. It is also important to note that the rotational modes of vibrations are seen as the form of thermal mobility of the system particles in the absence of the external force. The centers of these vibrational rotones later become the centers of vortecies responsible for the plastic flow.

The modelling of the microcrystal consisting of 17 $CH_3—(CH_2)_{10}—CH_3$ type chains was carried out in the second case. The density and geometrical structure of the system made it possible to identify the features of the chains in the crystal at low temperatures and near the melting point. In the latter case, the intensive large-scale rotations of the molecules as the whole around the axis were demonstrated; that is, the rotone state of the system at the stage preceding its melting was obtained. This result agrees with the experiment described in the literature. This experiment deals with the structure of *n*-parafins in premelting. Substitution of some hydrogen atoms in $—CH_2$-groups of chains by other, more voluminous substitutes ($—CH_3$ or —Cl, for example), markedly affects the local dynamics of the chain and the free volume near the new group. Despite the appearance of geometrical irregularity (defect of packing), the free volume near the new group decreases, i.e., the local compression of the system occurs.

It is well known that amorphous systems has macroscopically larger free volume as compared with the crystalline state.

Analysis of the local density near the defects of substitution shows that the excessive free volume when it "passes" from the crystalline state to the solid amorphous state should be determined by the set of defects which are probable, arranged in certain order in the chain.

The first experiments on MD-modelling of chemical reaction in crystal have shown that in conditions of hydrostatic compression, reactions proceed faster in areas of higher local density.

The heat of the reaction between two particles is diffused quickly and cannot initiate the following reaction near the previous one.

At present, analysis of the ordinary chemical reaction in the solid amorphous body considered at the beginning of the present paper is being performed.

Modifications of Polymers in the Solid Phase Affected by Shift Deformation (Strain)

S. A. Vol'fson

Reactions in the solid phase have never been given much attention in the chemistry and technology of high-molecular compounds. The early 1960s, however, marked a period of great interest in radiation chemistry of solids or plasmic modification of the surface of polymers to add some specific properties to the latter. In classical mechanochemistry, interest in solid polymers as objects for research surfaced sporadically but did not result in any consistent conception.

About twenty five years ago, Academician N. S. Enikolapov initiated research on the effect of high pressure in combination with deformations. This work was carried out within the framework of studying extreme effects on high-molecular compounds in the Department of Polymers and Composites at the Institute of Chemical Physics of the U.S.S.R. Academy of Sciences. The so-called "Bridgeman's anvil" was used as an experimental installation, since it makes possible creation of rather high pressures.

Despite the fact that these experiments gave interesting results on transformations of the structure and chemical activity of polymers, the unique conditions of the experiments did not allow prediction of any real implementation of these results in practice.

However, the situation changed drastically after discovery of powderlike polyethylene of low density from the melt upon cooling and simultaneous effect of deformation stress (Enikolopov, Nikol'skii, Nepomnyashchii *et al.*). Availability of the experimental equipment and the simplicity of the experiment considerably widened the scope of research and the number of its participants. The unusualness of the phenomenon observed, and the discovery of "synergism" upon grinding of various mixtures and filled polymers attracted a great deal of attention. At that time, there were ideas about a possible high chemical activity of the formed powderlike particles following the analogy of grinding the minerals. However, an alternative hypothesis about a possible activating effect of even relatively small (deformations) and pressures, as compared with Bridgeman's anvils, appeared to be more fruitful. A number of experiments with the use of various types of mixers and laboratory extruders confirmed that the chemical reaction with the involvement of powderlike solid components is possible without the melting-crystalization transition.

It should be noted that the possibility of carrying out these reactions on inorganic substances, in principle, was established in the framework of classical mechanochemistry. Some research works on the reactions of organic substances are known; but this trend was never considered as a perspective one in terms of technology. It should be stressed that, traditionally, classical mechano-chemistry operates with doses of mechanical energy disregarding types of mechanical action. N. Enikolopov and his school emphasized the shifting effect as the most "merciful" towards macromolecular chains from the point of view of degradation effect, as compared with the impact, vibro, ultrasound and other methods.

The problem of qualitative identification of the forms of mechanical effect on polymeric materials is a fundamental one and requires a careful experimental verification.

Numerous experiments performed on Bridgeman's anvils, mainly with low-molecular substances (Zharov, Zhorin *et al.*), allowed N. Enikolopov to propose an hypothesis about the anomalous process of chemical reactions in these conditions. He noted that reagents interact at a high rate due to effective shift in thin layers, reaction rate is independent of temperature, catalytic effects are absent, and possible directions of reactions may differ from those observed in the liquid phase.

A number of research teams in the ICP, Institute of the Synthesis of Polymeric Materials (the U.S.S.R. Academy of Sciences), and other institutions are engaged in experimental verification of this hypothesis. Equipment of the experiment consists of mixers of various types, ball mills, vibrators, and laboratory extruders specially designed at the Institute of Chemical Physics. Improvement of experiment equipment is of crucial importance for transition from qualitative to strictly quantitative results. So far, the major principle in choosing the appropriate experiment equipment is intuition; and very often, the depth of the reagents' transformation is the only criterion of the efficiency of equipment operation.

The wide scope of investigations carried out over the last four to five years has enabled the identification of the most promising directions, such as reactions of complex-formation (complexing), etherification, substitution, and polyaddition. In recent years, our laboratory, in collaboration with the laboratories headed by E. Prut and P. Butyaghin, Institute of the Synthesis of Polymeric Materials, has carried out a number of experiments with the use of various experimental equipment in the area of solid phase chemical reactions involving polymeric substances.

Data on the reactions of chlorination of low-density polyethylene by hexachloroethane have been published (A. Zelenetskii and M. Knunyants). Research on modification of polypropylene by polar compounds is being carried out. In both cases, the degree of grafting was equal to 1% to 2%.

The reaction of amination of polyvinylchloride (A. Solovyeva *et al.*) is also of significant interest. When this reaction proceeds in solution, dehydrochlorination and cross-linking of the polymer occurs. We found the conditions in the solid phase when the degree of amination reaches 20% and the polymer retains solubility. Though this reaction was first developed as a model one, it resulted in interesting outcomes. For example, it has been shown that the aminated PVC exhibits good ion-exchange properties and can be employed accordingly.

The reaction of complex-formation of melamine with cyanuric acid (A. Zelenetskii) is of practical importance. The tests performed on the laboratory plant have shown certain possibilities for the implementation of the process with a great saving of energy and, what is more important, with a complete elimination of the powder material penetration into the atmosphere, which previously greatly polluted the environment. Unfortunately, the tragic earthquake in Armenia delayed the implementation of this ecologically sound process.

A. Solovyeva *et al.* proposed an unusual process for obtaining metal microparticles fixed on a solid surface. This method consists in complexing of metals from oxides and some salts by ammonium bicarbonate in the solid phase and then in metal reduction in the form of cluster particles of 100 A, to 1000 A in size.

In general, the development of this new scientific trend promises much interesting news in pure and applied science.