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Przedmowa

II Konferencja p.t. Teoria Agregacji i Koagulacji odbyła się w Warszawie 9-10 czerwca 1989 r. W Konferencji wzięło udział około 30 uczestników krajowych oraz goście zagraniczni: Prof. I.Gutzov i Dr S.Stoyanov z Bułgarskiej Akademii Nauk w Sofii oraz Doc. Jürn Schmelzer z Uniwersytetu w Rostocku (NRD). Referaty przedstawiane były w języku angielskim lub polskim (z angielskim opisem materiału ilustracyjnego).

W niniejszym tomie publikujemy teksty 8 referatów nadesłanych przez uczestników. Prof. Gutzov dostarczył jedynie streszczenie, a Dr Stoyanov nie dostarczył do chwili zamknięcia zeszytu żadnych materiałów. Tytuły publikowanych materiałów nie zawsze odpowiadają tytułom referatów przedstawianych na Konferencji.

Dużą pomoc w organizowaniu Konferencji okazali Dr Michał Kość i p. Anna Godlewska, bez których Konferencja nie mogłaby się odbyć. Dr Kość przygotował program naukowy Konferencji i redagował nadesyłane do publikacji materiały. Pani Ania dbała o logistyczną stronę Konferencji i przepisywała część nadesłanych do publikacji tekstów.

Organizator Konferencji

Prof. dr hab. Andrzej Ziabicki

Warszawa, styczeń 1990

Spis treści

Theory of Aggregation and Coagulation II,
Warsaw, 9-10 June 1989,
Polymer Physics Laboratory,
Institute of Fundamental Technological Research PAS

ABSTRACTS

Graph-like Models of Polymer Gelation

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Polymer gelation (in crosslinking polymerization, vulcanization or in other aggregation processes) has been extensively analyzed by using essentially graph-like models. The models were either statistical (Markovian) in nature (e.g. Flory-Stockmayer theory) or kinetic ones (e.g. based on the Smoluchowski coagulation equation). All these models produce the same size distribution of aggregates for the so called random tree-like systems where Flory's principle of equal and conversion independent reactivity of functional groups is obeyed and intramolecular links are neglected.

There were numerous attempts to modify the random tree-like models in order to incorporate the two important features of real polymerization systems: (i) substitution effect that alters reactivity of functional groups and (ii) intramolecular cyclization. For the first feature, rigorous, but different results were obtained from the statistical and kinetic models. Incorporation of cyclization was much more complicated and only approximate solutions of the problem are known.

In this work, it is shown on simple examples that cyclization plays much more important role than substitution effect and that the influence of the two features on, say, conversion at gelation, cancel each other to some extent.

The reasons for differences between statistical and kinetic models in dealing with substitution effects are also discussed. It is shown that the sample space and probability function for the two models are different. The models used for aggregation processes are compared with two random graph evolution models (Erdös-Renyi and f-graph models).

DIFFUSION AND AGGREGATION IN WET SPINNING OF VISCOSE FIBERS

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In wet spinning of viscose fibers into a coagulation bath take place: diffusion of the components of the bath into viscose jets, neutralization of the bath and (eventually) change of the chemical composition of the polymer. In viscose jets occurs separation into liquid phases and solidification of gel fibers.

The studies concerned effects of the concentration of sulfuric acid and zinc sulfate in the coagulation bath in various temperatures on the rate of solidification of viscose, the course of the spinning process and physico-mechanical properties of the resulting fibers.

The studies were performed on a tyre-cord viscose dope produced by "Chemitex-Wiston" Man-Made Fiber Works in Tomaszów Mazowiecki The measurements of solidification rates were carried out in a flat model system, under microscope with magnification 100 x. The coagulation baths contained sulfuric acid, zinc sulfate, sodium sulfate and a modifier. The concentration of acid was changed in the range of 80-145 g/l, that of zinc sulfate - in the range of 20-50 g/l. Spinning of fibers was performed on a laboratory spinning machine at the speed of 30-40 m/min.

In all cases studied, solidification was accompanied by formation of large "finger like" pores, and the solidification rate parameter Ξ for the solid phase varied in the range of $(2.5\text{-}25.45)\ 10^{-10}\ m^2/s$, and for pores in the range of $(5.13\text{-}47.89)\ 10^{-10}\ m^2/s$.

Fibers formed in various coagulation baths exhibited different swelling behavior. E.g. primary swelling of fibers formed at low acid concentration was of the order of 200%, and increased to ca. 700% at acid concentration 145 g/l.

Stability of the spinning process markedly increased with concentration of sulfuric acid, while deformability of gel fibers and tenacity of drawn fibers increased with reduction of acid concentration and with an increase of zinc sulfate content in the coagulation bath. The degree of crystallinity of drawn and stabilized fibers markedly increases when acid concentration in the coagulation bath is reduced; the increase of longitudinal dimensions of crystallites is less evident.

Kinetics of Formation of Thermodynamically Stabilized Colloidal Dispersions

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Due to the large surface to volume ratio colloidal dispersions show a general tendency to separate into different bulk phases. However, in particular, in micellar solutions thermodynamic factors exist which prevent an unlimited growth and result in a time independent relatively monodisperse distribution of a large number of micelles.

In this contribution a kinetic description of this process will be presented which represents a modification of the theory of Ostwald ripening in elastic media developed in cooperation with I.Gutzov (Sofia) in the last years.

Effects of Mechanical Constraints on Orientation Distributions of Polyethylene Crystallites during Melting

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A further attempt was made to experimentally verify the nucleation theory and its prediction concerning dependence of the melting temperature on the orientation of crystallites.

Changes of orientation distributions of (110) and (200) planes during melting of drawn ultra-high molecular weight polyethylene were investigated. The samples drawn to various extensions in the state of dried gel were prepared according to the procedure by Smith and Lemstra. Melting of these samples was performed by stepwise increase of temperature in specially designed X-Ray diffraction camera. Constant length, freely shrinking and constant load regimes were investigated. It was confirmed that changes of orientation are dependent on the mechanical conditions applied to the sample. The results indicate that in the case of strained molecules in all applied regimes of mechanical conditions there is a region of temperatures at which melting is accompanied by narrowing of crystal orientation distribution. The narrowing of crystal orientation during melting in shrinking regimes confirmed presumably the mechanism of selective melting theoretically predicted by Ziabicki.

A diffraction line corresponding to the hexagonal phase was observed during melting.

Effect of Impingement on the Rotational Diffusion Coefficient of Rigid Rods

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Suspensions (solutions) of rigid, rodlike molecules form, in the range of higher concentrations, liquid-crystalline (nematic) structures. These structures are controlled by flow field, intermolecular interactions and interaction with external fields (magnetic, electrostatic).

A non-linear theory describing behaviour of flowing, concentrated solutions of rigid rods with dipole interactions (described by a mean-field, Meier-Saupe model) and interactions with external fields, has been presented. Effects of flow, external fields and concentration have been analyzed and discussed.

An Influence of Various Fields on Diffusion Limited Aggregation Process

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Diffusion limited aggregation (DLA) process [1,2] on a square lattice has been simulated. The Eden cluster-producing algorithm [3] (in which a small test particle is diffusing around the cluster and selecting perimeter site by hitting it during a diffusion process) has been effectively used. It has been shown that such rather simple algorithm enables to simulate a broad variety of diffusion limited aggregation, mostly by changing appropriately the rules of simulation involved. By means of such modifications three types of so called DLA clusters have been formed (in fact, in this way a whole class of DLA structures can be obtained):

- pure (or typical) DLA clusters [4],
- DLA clusters with attracting interface (or attracting perimeter sites),
- DLA clusters formed by random walk [5] with superimposed drift [6].

The number of perimeter sites, their average distance from the origin as well as the fluctuations of that distance have been investigated as a function of the number of cluster particles.
An attempt has been made to determine the number of cluster particles from which the aforementioned quantities are "well established" i.e. the stationary state in the aggregation process may be reached.
The so called Hausdorff-Besicovitch dimensions [7] of the above mentioned DLA structures have been obtained from the adequately chosen rules having a form of scaling laws [8].

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Diffusion of Single Elements and Steric Constraints in Kinetic Theory of Nucleation and Crystallization

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Translational and rotational diffusion equation is solved for long-range diffusion effects in the kinetic theory of nucleation and crystallization. Analytical formula for effective rate constants is proposed. Boundary conditions, adequate to reversible reaction of cluster growth, and accounting for steric constraints of the reaction, are used. Uniaxial single elements involved in the process are considered.

Substantial depression of concentration of single elements at the cluster boundary is predicted, and it is controlled by chemical rate constants, translational and rotational diffusion of single elements, supercooling, and steric constraints. The effective rate constants are derived as controlled by reduced chemical rate constant of single elements, and tolerance angle of steric constraints.

Rate reduction factor, responsible for the effects of long-range diffusion at steric constraints present, is defined, and applied for the kinetic model of nucleation and crystal growth. Example computations are performed for a wide range of the model variables, and rate reduction effects several orders of magnitude are predicted. The ranges of dominating role of particular kinetic and steric variables are discussed.

Void Formation and Microfracure of Strained Metals

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A theory of vacancy-microvoid formation in uniaxially strained metals is presented. The continuum coupled nucleation theory has been applied and essentially extended by using a modified Ziabicki approach to the coupling of both homogeneous and heterogeneous mechanisms; the effect of strain on the free energy of formation of vacancy clusters was also taken into account. Three models of clusters are considered - spherical, double-lens and in the shape of spherical trihedron. Conventional microfracture criterion for origination of a critical cluster (microcrack nucleus) is proposed from which the corresponding critical strain can be found.