

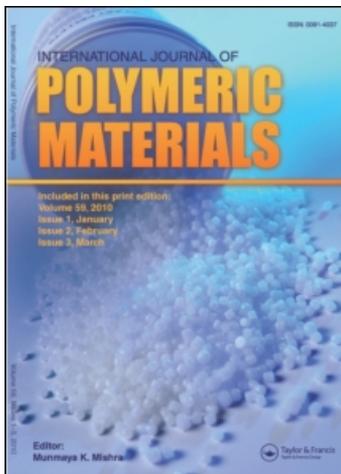
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Polymer Dynamics and Rheology

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Advances in five topics of Polymer Dynamics and Rheology are reviewed; Thread-like Secondary Structures of Surfactants and Ovalbumin, Polymer Chain Entanglement, Polyelectrolytes and Rigid Polymers, Electro-Rheology, and Rheo-Optics.

We consider five topics from the "Polymer Dynamics and Rheology" session in this review.

THREAD-LIKE SECONDARY STRUCTURES OF SURFACTANTS AND OVALBUMIN

Amphiphilic surfactant molecules form micelles of various shapes in solution. In some cases, a very long thread-like structure is formed and the solution becomes a viscoelastic liquid or even an elastic gel.

Imae and Hashimoto (4208, E1615) has been studying the structure and properties of such systems and reported the spinnability and viscoelasticity of aqueous solutions of alkyltrimethylammonium salicylates (C_n TASal; $n = 14$ and 16), alkyldimethylamine oxides (C_n DAO; $n = 14, 16$, and 18) and oleyldimethylamine. The viscoelastic behavior varied with the concentration and was classified in three types: a gel, a Maxwell-model type viscoelasticity with only one relaxation time, and a polymer-like viscoelasticity similar to that of an entangled polymer, usually in the decreasing order of the concentration; the salt concentration also affected the structure and properties of the solution. The spinnability was examined by drawing up a glass rod from the material. The thread of a gel was thick and exhibited a cohesive fracture. The viscoelastic liquid formed thinner thread and broke in a ductile manner. An extensive list in the abstract includes the shape of micelles as observed with an electron microscope or the light scattering method and the types of viscoelasticity and the spinnability at various concentrations. Apparently, the viscoelastic liquids are composed of rod-like micelles and gels tend to include board-like vesicles.

Nemoto, Shikata *et al.* (4211, E1616) measured with the forced Rayleigh scattering method the diffusion coefficient of a dye-tagged molecule of cetyltrimethylammonium bromide (CTAB) in an aqueous solution containing sodium salicylate (NaSal). It is well-known that that CTAB molecules together with the salicylate ion form a thread-like micelle and the solution is viscoelastic. The diffusion coefficient, D , varied with the concentration in the same way as τ^{-1} where τ is the maximum viscoelastic relaxation time. The diffusion coefficient was too large for the diffusion of thread-like micelles. Obviously the mechanism of stress relaxation is different from that of entangled polymers and is not due to the reptational motion of thread-

like micelles. The relaxation mechanism is still not very clear.

The molecules of ovalbumin form a similar thread-like structure in aqueous solution at low salt concentrations and the solution is viscoelastic. Under some conditions, the linear structure exists even at high concentrations and gives transparent gels different from those due to the heat denaturation. Chiba and Matsumoto started a detailed study of such solutions (4217, E1618) including light scattering, small angle x-ray scattering, and rheology. They observed very strong non-Newtonian behavior of the viscosity in steady shear flow at concentrations higher than 0.03%. The non-Newtonian behaviour was such that the stress remained almost constant over the range of shear rate from 10^{-2} to 10^1 s^{-1} ; the behavior may be classified as pseudoplastic with an yield stress. They also observed that the solutions of low concentrations changed from Newtonian to non-Newtonian in repeated runs of measurements, which is contrary to the observation for ordinary aggregated systems. The SAX data indicated that aggregates of two or more molecules existed in the range of 0.5–1.0%. They proposed the possibility of an ordered structure of particles as the origin of the yield stress. However, the concentration may be too low for an ordered structure due to the repulsive interaction of spherical particles and the origin of the observed phenomenon is not yet clear.

POLYMER CHAIN ENTANGLEMENT

The problem of polymer chain entanglement is always one of the major topics in the polymer dynamics and rheology session.

Iwata and Tanaka discussed their local knot model of entanglement based on computer simulation of entangled ring polymers (4244, 4247, E1627, E1628). The local knot is defined in their theory as the part of the chain where the Gauss integral, a topological measure of the entanglement between a pair of chains, remains finite over a certain period. They expect that many local knots exist in an array along an entangled chain and move along the chain without passing each other like particles with repulsive forces. With this concept, they had theoretically exhibited that polymer chains move in a manner similar to that predicted by the reptation model of de Gennes. The reptation motion may be most ideally realized in the motion of entangled ring polymers. The purpose of the present report was to observe by simulation the existence and characteristic motion of the local knot. The array of local knots was actually observed and they exhibited the expected features; the life-time of a local knot was longer than the disengagement time of chain from the tube and the local knots exerted a repulsive force upon each other. The diffusion coefficient of the local knot evaluated from the simulation was in good agreement with the theory. Incidentally, the mean-square displacement of an entangled ring polymer varied in proportion to $t^{0.85}$ over a wide range of time, t . This result of simulation has not been explained theoretically at this moment.

Nemoto, Osaki *et al.* (1261, 4250, E1629) studied the dynamic viscoelasticity, the stress relaxation, and the diffusion of polystyrene molecules in dibutyl phthalate at concentrations 13%, 18% and 40% over a wide range of molecular weight of the polymer. The rate of change with molecular weight of the longest relaxation time or

the diffusion coefficient varied greatly at the molecular weight equal to M_e , the entanglement molecular weight. On the other hand, the longest relaxation time was always about 15% of the diffusion time, i.e., the average time for the polymer chain to diffuse a distance corresponding to the radius of the coil. They found that the diffusion coefficient varied in proportion to $M^{-2.5}$ at high molecular weights. This result is in contrast with the widely accepted result, $M^{-2.0}$, for semidilute solutions, concentrated solutions, and polymers melts. They asserted that many reported data for solutions were in better agreement with $M^{-2.5}$ than with $M^{-2.0}$. The difference may be of some importance; a lot of studies have been devoted to elucidate the origin of discrepancy between the observed $M^{3.5}$ dependence of the relaxation time and the $M^{3.0}$ dependence due to the reptation theory. Most of the modified or refined theories have given $M^{-2.0}$ dependence for the diffusion coefficient. Theoreticians may have to invent some other way of refining theories if they accept the above-mentioned result.

One of the most elaborate models for refining the reptation theory is the Configuration-Dependent Constraint Release model of Watanabe and Tirrell. The Constraint Release is a major concept in modifying the tube model and implies the effect on the chain motion of the motion of tube itself caused by the motion of surrounding chains which form the tube constraint. The rate of change of chain orientation is given by the product of the rates of reptation and CR, considered as independent processes at the early stage of the theory. The CDCR model takes account of the possible effect of coupling between two processes. Watanabe, Kotaka *et al.* (4253, E1630) showed that the CDCR model was much better than the simple CR model in describing the complex modulus and the complex dielectric coefficient of polyisoprene with bimodal molecular weight distribution. On the other hand, the model probably predicts that the diffusion coefficient of polymer is proportional to M^{-2} , contrary to the report of Nemoto *et al.* mentioned above.

The following reports by Adachi, Kotaka *et al.* in the spring session includes interesting measurements on model polymers for studying the entanglement dynamics: Dielectric Normal Mode Process of Guest Polyisoprene in Polybutadiene (1246); Dielectric Normal Mode Process of 2-Arm Star-Like cis-Polyisoprene (1247); Dielectric Normal Mode Process of Isoprene in Butadiene-Isoprene-Butadiene Block Copolymer (1248).

POLYELECTROLYTES AND RIGID POLYMERS

The viscoelasticity of flexible polyelectrolyte seems to be a very difficult problem. Takahashi, Noda *et al.* has been studying the viscoelasticity of solutions of well-characterized polyelectrolytes with a traditional method for entangled ordinary polymers: to examine the effect of varying molecular weight, concentration, and salt concentration on the zero-shear viscosity, and the steady shear compliance. Results for poly(N-methyl-2-vinylpyridinium chloride) were reported this year (4265, E1634). At high salt concentrations, the solution properties resembled those of non-ionic polymers as expected. However, the results at low salt concentrations were very complicated. For example, the steady shear compliance was proportional to

$M^{-2}c^{-2.5}$ at 0.1 M salt concentration but it did not follow such a power law at 0.01 M. One of the difficulties in viscoelasticity of polyelectrolyte solutions is the limited range of frequency attained; in contrast with the case of ordinary polymers, the method of reduced variables cannot be employed to extend the range of measurements. Measurements over a wider frequency range covering the rubbery plateau region for example may be very valuable and a cooperation of groups with different apparatuses may be effective in solving the difficulty.

On the other hand, the viscosity of solutions of polyelectrolyte molecules of rigid structure can well be described by the theory based on the entanglement of rod-like molecules. Sato, Teramoto *et al.* have been studying solution properties of a polysaccharide, xanthan. Three molecules of this polymer form a rigid helical structure in solutions. They degraded a raw sample using an ultrasonic method and fractionated to obtain samples of various molecular weights and with very narrow molecular weight distributions. They exhibited that the viscosity over wide ranges of molecular weight and concentration can be described with this theory provided that the effect of partial flexibility was considered at high molecular weights (4268, 4271, E1635, E1636). In the case of the rigid polyelectrolyte, the varying salt concentration did affect the phase transition point between the isotropic and liquid crystalline phases but did not affect the viscosity in the isotropic phase. This fact may imply that the viscosity of solutions of rigid polymers is determined only by hydrodynamics of the solvent and the topological constraint among the polymer molecules. The situation is simpler not only for flexible polyelectrolyte but also than for ordinary polymers, for which the segmental friction coefficient changes with varying concentration.

ELECTRO-RHEOLOGY

Some fluids change their rheological properties, the viscosity above all, when an electric field is applied. Electro-rheology is widely studied in Japanese companies; such a fluid may be employed in mechanical systems such as the damper of an automobile; a servo-system with such a material may be employed in robot fingers that can pick up an egg. Fluids which show a marked electro-rheological effect have mostly been liquids with dispersed solid particles, and polymer solutions are rare.

Tanaka, Koyama *et al.* studied the electro-rheology of a 15% solution of a copolymer, poly(vinylidene fluoride-trifluoro ethylene), in dimethyl formamide (4274, E1637). An electric field of 0.4 MV m^{-1} was applied to the fluid in a capillary viscometer. The increase of viscosity was low, typically 4%, in the first run of the experiments, even though the electric field was applied for a long time before the run. The effect increased with repeated runs, i.e., the flow under an electric field, and the viscosity increased as much as four times when the frequency of the field was 7 Hz. A vibration of the meniscus was observed and its frequency was different from that of the electric field. Interesting hystereses were observed in various combinations of the periods of applications of electric field and shear.

RHEO-OPTICS

Among a few papers in the rheo-optics, the following two gave new aspects of its application.

Noda, Dowrey *et al.* from the USA showed the wide applicability of their two-dimensional correlation analysis of dynamic infrared dichroism (4223, E1620). The IR dichroism of a certain wave number is caused by the orientation of a certain portion of the molecule in a deformed material. In an oscillatory deformation, the IR signal may exhibit a time lag with respect to the deformation because of the time lag in the motion of that portion. Their method is to calculate the correlation of oscillating signals at different wave numbers at a fixed frequency of deformation and to make a correlation map at each frequency. This corresponds to the correlation of the change of orientation of various parts of the molecule. The method will be very effective in studying the detailed molecular mechanisms of various rheological phenomena.

Inoue, Osaki *et al.* revealed that the dynamic birefringence, i.e., the birefringence under oscillatory deformations, is convenient for studying the glass-to-rubber transition behavior of amorphous polymers (4256, E1631). The method is actually a revival of the studies done in 1960s and 70s; the difference is that now it is much easier to perform at higher frequencies, over a wider range, and more quickly. From the data of complex dynamic Young's modulus and strain-optical coefficient for a plasticized polystyrene, they exhibited that the relaxation spectrum in the glass-to-rubber transition zone was composed of two components with different stress-optical coefficients and that the two components varied to the different degrees with varying temperature. The component at longer times could be described with a bead-spring segment theory with each segment composed of about 10 monomer units.

References which appear in brackets in the text are page numbers from the conference proceedings, published in Japanese by the Society of Polymer Science Japan, in: *Polymer Preprints Japan*, **39** (1990). Following E denotes the English abstract page numbers.