

Phase Transitions and Ordering Processes
— Research Accomplishments of Hashimoto Polymer Phasing Project —

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The Hashimoto Polymer Phasing Project (*HPPP*) conducted basic research on the mesoscopic structures of complex liquids (soft-condensed matters) in order to elucidate the space-time organization of their structures via phase transitions and to control their self-organized structures, in either non-equilibrium or equilibrium states, as novel structures in new materials. “*Polymer Phasing*” has been coined to refer to the studies of the mesoscopic pattern formation via *phase* transitions and *phase* separation in multiphase *polymer* systems, as a model for complex liquids; the pattern-formation processes were manipulated by applying various external fields to the systems at particular *phases* of the self-organization processes.

The complex liquids primarily explored were polymer blends, block copolymers, gels, ionic colloidal dispersions in water, and nano-metal colloids created or incorporated in nano-space self-organized by polymers. The phase transitions included not only the single-phase-multiphase and liquid-solid phase transitions but also the sol-gel transition. A “*complex phase-transition*” in which more than two transitions occur simultaneously or at different times was also studied as a self-organization process giving rise to a rich variety of novel patterns. The self-organization processes associated with these transitions are typically *non-linear* and *non-equilibrium*. The processes, the mechanisms, and the patterns were explored as an important research subject for modern science. Furthermore the project studied how external fields such as shear flow, stationary or moving temperature gradients, chemical reaction, etc. affect the self-organization processes of the systems as a challenging problem in *open non-equilibrium* systems.

The space-time organization processes were explored *in situ* and *in real time* as much as possible in order to unveil basic physics underlying the processes and to discover novel structures for new materials. The processes were explored over a wide range of time and space (several Angstroms to several ten micrometers) by simultaneous applications of various real-space analyses (various conventional optical microscopies,

laser scanning confocal microscopy(LSCM), transmission and scanning electron microscopy, element specific transmission electron microscopy (ESTEM), and scanning probe microscopy) and Fourier-space analyses (static and dynamic light scattering, small- and ultra-small-angle X-ray scattering (SAXS and USAXS, respectively), small- and ultra-small-angle neutron scattering (SANS and USANS, respectively) and SAXS using Synchrotron Orbital Radiation as an incident X-ray source (SOR-SAXS). The project studied polymers and colloidal particles also from a view point that they provide extremely good model systems for elucidating non-linear and non-equilibrium problems, because their fundamental length and time scales are large and long: large structures evolve more slowly with time in these systems than in their low molecular weight counterparts[1]. The non-linear and non-equilibrium processes were also analyzed theoretically with computer simulations based upon the time-dependent Ginzburg-Landau equations as a non-linear time evolution equation. Some representative research outputs of the project will be listed below.

The project has for the first time succeeded in constructing 3D digital images for phase-separating binary polymer mixtures with nearly equal phase volume and nearly equal molecular weights[2-7]. The images were found to be bicontinuous and to have characteristics of “*sponge-like*” structure found for microemulsions[5,8,9]. The sponge-like structure was verified to be applicable also to the phase-separating structures of binary critical mixtures of simple liquids whose phase-separating structures have not been directly observed so far as a function of time[10]. The research thus contributed to the field of critical phenomena, especially in identifying the real-space structure corresponding to the *scaled structure factor* underlying the dynamical scaling hypothesis[1,11,12]. The structures has been analyzed on the basis of differential geometry, and the results successfully yielded local mean and Gaussian curvatures of the interface between the coexisting phases and their distribution function as a function of time[13-15], information which may be important for further advance of mathematical physics on interface dynamics[15,16]. The sponge-like structure was quantitatively explained theoretically on the basis of time-dependent Ginzburg-Landau (TDGL) equation with hydrodynamic interactions[16] by using 3D computer simulations[5,10,17-19]. The method established for constructing 3D image analyses were successfully applied to other systems such as the gyroid structure found for block copolymers[20,21], the porous glass created by the sol-gel transition of silica systems[22,23], etc.

The project conducted basic research on the effect of applied field on polymer blend systems as a challenging problem concerning *open non-equilibrium* systems. It constructed a versatile rheo-optical apparatus which really enables simultaneous

measurements of rheology, transmission optical images, and light scattering under shear flow[24]. The apparatus was specially designed so as to cover a wide range of stress, weak image contrast and weak scattering intensity, thus useful for rheo-optical studies of most complex liquids. Unique non-equilibrium structures, such as the string structure and the shear-induced phase-separated structures, and their relationships with rheological properties were illuminated using this apparatus[25-29]. Stationary and moving temperature gradients were applied to a polymer blend system and to block copolymers, respectively. The former system led us to discover the Soret-effect-induced phase separation and convection[30], even above the critical temperature of the system in the absence of the temperature gradient, and the latter systems to create “superlamellae”, macroscopically aligned almost perfect lamellar stack as large as $2 \times 2 \times 6 \text{ mm}^3$ [31,32]. Such “superlamellae” show how we can control the final structure of a material by manipulating the self-assembling process.

High resolution SAXS analysis was applied to explore nature of order-disorder transition (ODT) of block copolymer[33] by using a USAXS apparatus constructed in the project[34]. The analysis led us to discover for the first time a narrow biphasic region, where ordered and disordered phases coexist at thermal equilibrium, at around the ODT temperature[35,36]. The experimental finding was theoretically interpreted as a consequence of the thermal-fluctuation-induced first-order phase transition based upon the Fredrickson-Helfand-Binder[37,38] and Hohenberg-Swift (HS) theories[39,40]. Moreover various anomalies, such as large-length-scale density fluctuations, specific volume, etc., were found in the biphasic region[41], which will illuminate further new physical problems to be explored in the system which belongs to so called *Brazovskii universality class*[42]. The studies will be important not only in the field of block copolymers but also in other fields of physical science. The discoveries on the fluctuation-induced disordered structure (D_F) and on nucleation of highly anisotropic grains of lamellae in the disordered matrix were found to be theoretically predictable[43] by using 2D computer simulations[44] based on the TDGL theory for the block copolymer developed by Ohta-Kawasaki[45] and on the renormalization group theory developed by HS[39].

The project elucidated a mechanism of the thermoreversible order-order transition between BCC-sphere and Hexagonal-cylinder in block copolymer[46], the principle of which may be applied to manipulate nano-structures with a controlled orientation. A tracer diffusion coefficient of block copolymer molecules was measured using the forced Rayleigh scattering method in order to obtain very basic information concerning dynamics of the molecules in the ordered state[47]. Blends of two block

copolymers such as *A-b-B* and *A-b-C* were studied in order to clarify the self-organization via the complex phase-transition. The project elucidated that a control of intermolecular interaction between B and C block polymers strongly affects the self-organization process and structure[48]. The project has succeeded for the first time in visualizing single synthetic polymer molecules thorough atomic-force-microscopic (AFM) studies of polystyrene-*block*-poly(methyl methacrylate)[49]. Microphase-separated structures developed in a monolayer of a block copolymer was also observed for the first time with AFM[50], the results of which may be useful to control nanoscopic-scale surface patterns of materials.

Polymer gels, primarily chemical gels, were studied not only from a view point of unveiling their internal structures for a deeper unstanding of their intriguing physical properties as a soft matter but also from a view point of elucidating a self-organization process via a chemical reaction of the system comprised of monomers (M), crosslinkers (C), solvent (S) as a reaction medium, and initiator (I) for the reaction. The project elucidated intriguing hierarchy structure developed in macroscopically homogeneous poly(N-isopropylacrylamide) gel prepared via the chemical reaction, as described above. It especially visualized for the first time a sponge-like structure composed of the network-rich and network-poor phases with an average spacing of ca. 10 μm [51]. The SANS, USANS, and SOR-SAXS studies further revealed that the network-rich phase is comprised of a fractal-like structure composed of microgels of ca. 300 nm which contain tight networks and which are linked to other microgels by loose networks[52]. The heterogeneous structure are shown to strongly affect physical properties of the gels such as transparency, swelling and deswelling behavior, deformation behavior, etc. The heterogeneities were proposed to be attributable to the following counter-balancing effects: the reaction between M and C promotes concentration fluctuations of the resulting polymers on one hand and growth of the fluctuations induced by the reaction is limited by the pinning effects of crosslinks on the other hand. The reaction-induced fluctuations may be a consequence of energetic interactions between M and S and between C and S playing an increasingly important role, against translational entropy of the systems, on the thermodynamic state of the system. This concept may provide a key to manipulate the heterogeneities of the gels and their physical properties.

The project investigated aqueous dispersions of ionic colloidal particles from the view point of phase transitions and self-organization of the particles via phase transitions. In other words we focused on the phase behavior of the particles as supermolecules rather than focusing on detailed behavior of the particles as colloids. The ordered phase, the disordered phase, the order-disorder coexistence phase, and the gas-liquid coexistence

phase were found in the space determined by the physical parameters C_s , σ_e , and ϕ (C_s : salt concentration, σ_e : effective charge density of the particles, ϕ : particle concentration)[53-56]. Self-organization processes of the particles from the shear-induced disordered state as an initial state were explored in the order-disorder coexistence phase[57] and the gas-liquid coexistence phase by using LSCM and USAXS[53]. The former and latter processes are regarded as those involving the order-disorder transition and the macrophase separation, respectively. The intriguing structures found suggest existence of *net* attractive interactions among the particles. The project found also similarities of the order-disorder transition and macrophase separation processes in the colloidal systems to those found in block copolymers (ODT) and polymer blend (phase separation). The nature of the electrostatic interactions of the systems was also explored[58-60].

The project conducted basic research to create novel nanoscopic-scale structures via “*nanoprocessing*” with an aim to develop new materials. Selective degradation of one of the phases of the so called gyroid structure formed by block copolymers enabled us to create the unique materials containing regularly spaced networks of holes (“*nano-channels*”)[61]. The selective degradation was found to provide a fundamental method which enables an unequivocal identification of the complex bicontinuous morphology having Ia $\bar{3}$ d space group symmetry. The surface of the channels was able to be coated with metals such as nickel through a nonelectrolytic metal plating[61].

The project succeeded in preparing Pd particles having ca. 4nm in diameter coated with a few polyisoprene (PI)-*block*-poly(2vinylpyridine) (PVP) block copolymer molecules[62]. This particles were introduced into nano-phases composed of PI and PVP formed by PI-*block*-PVP block copolymers. This process involves self-organization of a mixture composed of the Pd particles coated with PI-*block*-P2VP block copolymers, another PI-*block*-P2VP block copolymer forming a matrix for the particles, and a solvent during solvent evaporation. The project succeeded in manipulating the distribution of the Pd particles across the interface between the PI nanophase and the PVP nanophase by controlling molecular weight of PI-*block*-PVP block copolymers coating Pd metals and those forming the nano-phases (note that two block copolymers can have different molecular weights)[63]. The nano-metal-particles can be either localized near the interface or near the middle of the PVP nanophase or they can be uniformly distributed in the PVP phase.

Nano-metal particles of Pd were directly formed by a reduction of ion-polymer complexes between PI-*block*-PVP block copolymers and Pd ions at high concentrations of block copolymer in benzyl alcohol where the nanophases are formed via microphase

separation, prior to the reduction. The reduction created the Pd nanoparticles aligned in the middle of the PVP nanophases[64]. The manipulation of the system utilizes the principles of self-organization via various fundamental physico-chemical processes: microphase separation under the influence of the metal ions, chemical reaction giving rise to the selective reduction of metal ions in the concentrated polymer field of the PVP phase, and organization of metal atoms into nanospheres via diffusion-coalescence in the viscous matrix of the PVP polymer phase. The self-organization of metal atoms into nano-metal clusters itself involves many intriguing physical processes which deserve further investigation: diffusion-coalescence of metal atoms into clusters, adsorption of the metal atoms and clusters to and desorption of them from PVP, repelling of the metal clusters from the PVP brushes and stabilization of the metal clusters in the middle of the PVP nanophase.

In order to extend the results obtained by conventional TEM for a number of polymer systems studied in frame of the project's research, element specific imaging with ESTEM and electron energy loss spectroscopy (EELS) were applied to further study their structural features. In this context the morphology of the above described PI-*block*-PVP block copolymer system was investigated with respect to the amount of Pd nanoparticles contained in the system. It turns out that a high Pd particle content prevents microphase separation of the block copolymer [65]. Quantitative analysis of the OsO₄ staining procedure of a polystyrene-*block*-PI block copolymer was also conducted with ESTEM and EELS. The results obtained with this new technique suggested that the staining process leads to a crosslinking of the PI phase [66].

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