

Pattern formation in polymer systems and its dynamics

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In this invited lecture, recent progress in pattern formation in polymer systems and its dynamics are reviewed with many examples. The examples are presented from large to smaller patterns together with digital image analysis (DIA) methods to treat patterns quantitatively. Examples are pattern formation on the surface of gels during volume phase transition (\sim mm), ordered banded spherulite formation from crystalline/amorphous polymer mixtures (\sim 100 μ m), pattern formation due to competition between phase separation and chemical reaction (\sim 10 μ m), and complex structure formation in polymer alloys (\sim 1 μ m). Some of the unsolved problems in each case are pointed out with some suggestions.

1. INTRODUCTION

Recently, structure formation or pattern formation in materials or biological systems is attracting much interest from the viewpoint of physics of complex systems [1, 2]. This phenomenon is related to the process where structure is formed from homogeneous multi component system. The process seems to be against the law of entropy increase but it is obeying the law of minimization of free energy. This kind of pattern formation is mostly related to some kind of phase transition and there are many studies in this field concerning to metals, ceramics, low molecular weight substance systems, and biological systems.

However, many interesting problems are left in the field of polymers, although they are very important materials in industry. Some of the reasons for this situation may be: 1) Phase transitions in polymer systems (phase diagrams for polymer alloys [3], spinodal decomposition [4], volume phase transition of polymer gels [5], etc) have been discovered only recently, 2) Digital image analysis (DIA) necessary for the analysis of pattern has been developed only recently [6, 7].

In general, pattern formation process in polymer systems is relatively slow due to the high viscosity of the systems and the scale of the pattern is large due to the long range nature of the intermolecular interaction. In a certain sense, it is just like studying metal or low molecular weight substance systems using high speed camera with high magnification power. Therefore, polymer systems

are suitable for basic studies, too.

In this invited lecture, we will review with many examples some of the development after our recent review article [8]. The examples will be presented from large to smaller patterns and they include pattern formation on the surface of gels during volume phase transition (\sim mm), ordered banded spherulite formation from crystalline/amorphous polymer mixtures (\sim 100 μ m), structure formation due to competition between spinodal decomposition and transesterification in engineering polymer alloys (\sim 10 μ m), and complex phase structure in polymer alloys (\sim 1 μ m). Structure formation in micro-phase separation of block or graft copolymers (\sim 100 nm) is one of the most exciting field. However, this is omitted due to the limitation in time and space.

2. DIGITAL IMAGE ANALYSIS (DIA)

We have recently developed a digital image analysis (DIA) method which enables us to quantitatively analyze various pattern formation in polymer systems both in real space and in wave-number (k) space [6, 7]. Table 1 shows typical examples for the application of DIA methods to polymer systems. A to J are some of the operations for DIA. E or G means where we can get excellent or good results by DIA. However, all of the matrix elements in Table 1 have not been examined yet and it is a guide for the application of DIA to polymer systems.

In most cases, photographs taken either by a

Table 1
 Pattern formation in polymer systems and applicable digital image analysis methods

	A	B	C	D	H	I	J
Crosslink structure	G				G		
Microphase separation	E	E	G	E			
Spinodal decomposition	E		G	G	E		E
Nucleation & Growth	G	E		E	E		G
IPN structure	G	G	G	G	G		
High order structure of crystalline polymers (Spherulites etc.)	E	E	E	G		G	
Liquid crystalline polymers	G	G	G		G		
Structure of polymer alloys	E	E		E			G
Structure of latex	E	E		E			
Polymer composites	G	E		E			G
Fracture surface	G	G	G			E	
Surface pattern	E					E	G

A: Two dimensional Fourier transformation (Power spectrum, Correlation function, etc.)

B: Boundary detection (Analysis of shape, Area distribution, Periphery length distribution, Compactness distribution, etc.)

C: Cross section (Periodicity analysis along a line or a circle)

D: Analysis of the state of dispersion (Voronoi polygons, Delauney triangle network, etc.)

H: Concentration distribution

I: Three dimensional representation of images

J: Intercorrelation between images

E: Excellent results

G: Good results

camera, optical microscope, or electron microscope are put into computer by a drum scanner or via. TV camera and image processor. Each image is represented either by a 256×256 , 512×512 , or 1024×1024 pixel block of 8-bit or 10-bit resolution depending on the situation. Experimental details are presented elsewhere [6, 7].

3. PATTERN FORMATION ON THE SURFACE OF GELS

It is known that there appears complex wrinkle on the surface of gel when shrunken gel is immersed in swelling solvent [9]. The size of the wrinkle increases gradually with time. Figure 1 shows typical pattern evolution on the surface of gel during the swelling process where 2 mm thick shrunken acrylamide gel adhered to glass substrate is put into water [10]. The average size of the wrinkle is in the order of mm~cm which

is observable with the naked eye and the pattern changes in the order of one day.

For the quantitative analysis of the pattern, power spectra of the two dimensional Fourier transformation (2DFT) of the photographs were calculated. The power spectra had spinodal ring like structure and the averaged structure factor $S(R)$ during the swelling process is shown in Figure 2 [10]. In the $S(R)$, we can define k_{\max} where $S(k)$ shows a maximum in the early stage of swelling. There appears sub-maximum in the late stage and we can also define k_{sub} . On the k - t plain in the Figure 2, the temporal changes in k_{\max} and k_{sub} are also plotted. In the initial stage, the shape of $S(k)$ is not so sharp. However, the main peak abruptly becomes narrower with the appearance of the subpeak. There is a $2k_{\max} \sim k_{\text{sub}}$ relationship indicating that the subpeak corresponds to the second-order higher

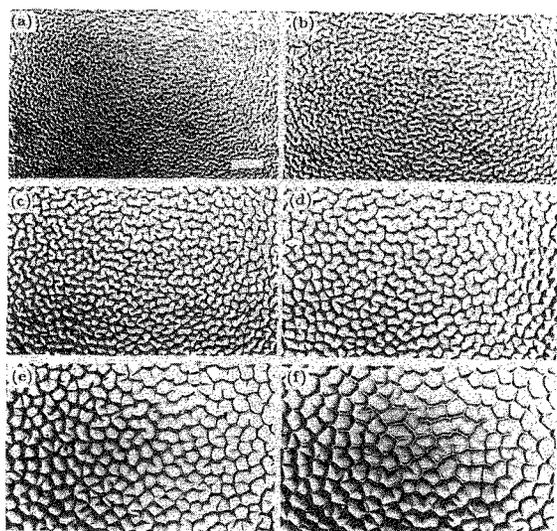


Figure 1. Pattern evolution on the surface of gel during the swelling process [10]. (a) to (f) correspond to the patterns observed at swelling times $t = 1800, 3600, 7200, 14400, 28800,$ and 63000 s, respectively. The white bar corresponds to 10 mm.

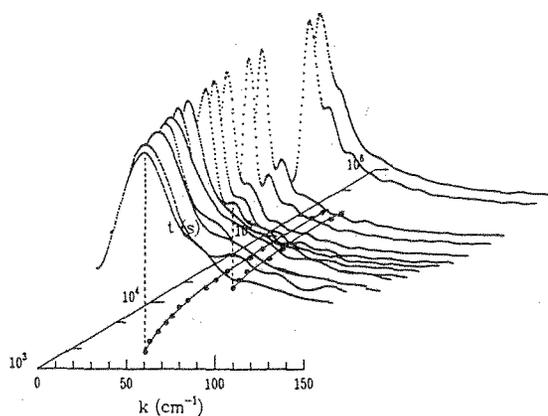


Figure 2. Temporal change in the structure factor $S(k)$ for the gel during the swelling process [10]. On the k - t plain, the temporal changes in k_{\max} and k_{sub} are also indicated.

harmonics originating from the regularity of the pattern. By comparing the photographs in the Figure 1 and the structure factor $S(k)$ in the Figure 2, we can find a transition in the pattern where there appears a subpeak in the $S(k)$. In the

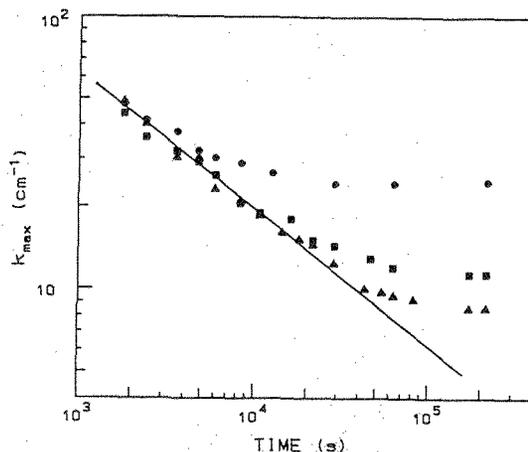


Figure 3. Temporal change in k_{\max} for the gels with different initial thickness [10]. \bullet ; 1.00 mm, \blacksquare ; 2.15 mm, \blacktriangle ; 2.65 mm. The solid line in the figure has a slope of $-1/2$.

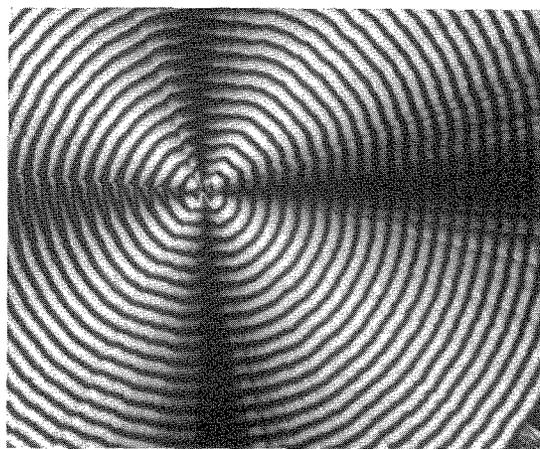


Figure 4. An example of banded spherulite from PCL/PVB = 98/2 mixture crystallized at 42°C observed under polarizing microscope. The bar corresponds to $200\ \mu\text{m}$.

late stage, the pattern is a honeycomblike structure.

Figure 3 shows the temporal change in k_{\max} for the gels with different initial thickness [10]. In all the gels, the initial time dependence of k_{\max} can be well expressed by $k_{\max} \sim t^{-1/2}$. At longer times, the growth rate slows down and the pattern relaxes to the final equilibrium state. In ev-

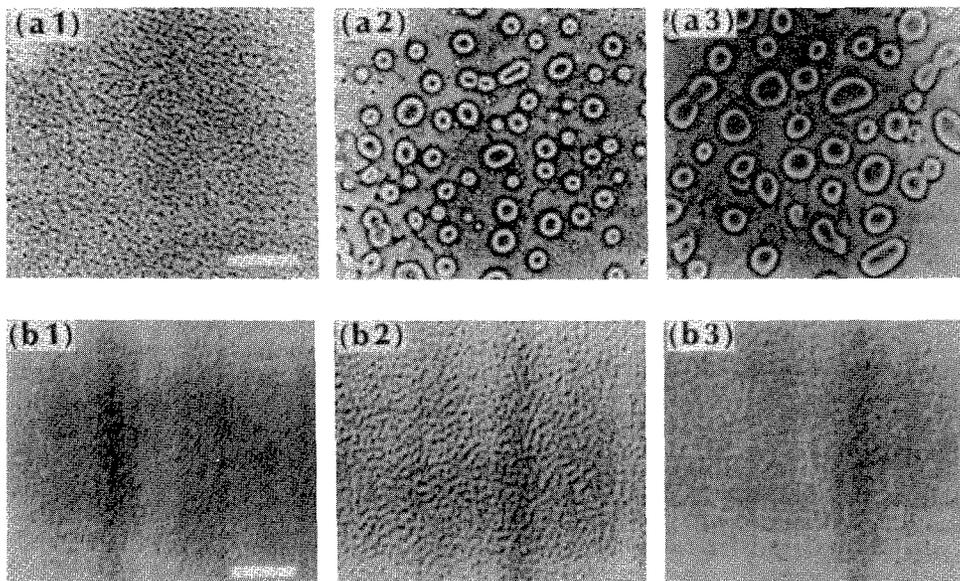


Figure 5. (a) Pattern evolution in PC/PET = 5/5 at 251° C. (a1) 10 s, (a2) 185 s, (a3) 920 s. The white bar corresponds to 100 μm . (b) Pattern evolution in PC/PAr = 5/5 at 240° C. (b1) 10 s, (b2) 2290 s, (b3) 3020 s. The white bar corresponds to 20 μm . All the images were taken by phase contrast microscope [18].

ery case, the crossover time from the exponent of $-1/2$ to the exponent of 0 coincides well with the times for the morphological change.

From k_{max} , we can define a wavelength λ_{max} ($= 2\pi/k_{\text{max}}$) which is the characteristic size of wrinkles. Temporal change of λ_{max} can be expressed as $\lambda_{\text{max}} \simeq t^{1/2}$. This means that the pattern evolution is due to the diffusion of swelling solvent into the gel from the surface. In this case, one side of the gel is adhered to the glass substrate and the swelling is possible only from the other side of the gel. The pattern is formed due to the buckling of the surface of gel caused by the compressive force [9]. There is a maximum in the crossing angle between the folds and it is 120° [11]. This angle is corresponding to minimize the local elastic energy. This kind of research may be only possible through DIA.

4. BANDED SPHERULITE FORMATION FROM CRYSTALLINE/AMORPHOUS POLYMER MIXTURES

When crystalline polymers such as polyethylene are crystallized from melt, they form spherulites and there often appears concentric banded structure depending on the crystallization condition. The banded structure is caused by the growth of twisted lamellae during crystallization. We found when crystalline polymers like poly(ϵ -caprolactone) (PCL) were mixed with amorphous polymers having miscibility with crystalline polymers, the crystallization behavior was changed drastically [12]. In PCL case, the nucleation frequency is suppressed very much and there appear banded spherulites which are not observed in homopolymers. Recently, it is shown that these phenomena can be observed with addition of very small amount of amorphous polymers [13].

Figure 4 shows an example of banded spherulite of PCL ($\bar{M}_w \cong 70000$)/poly(vinyl butyral) (PVB,

$\bar{M}_w \cong 116000$) = 98/2 crystallized at 42° C observed under polarizing microscope. The bar in the photograph corresponds to 200 μm . With addition of only 2 % PVB, the crystallization behavior of PCL is greatly changed. The size of the spherulites can be in the range of several mm's observable with the naked eye due to the suppression of nucleation. For homopolymers, The average size of spherulite is in the range of several μm 's. The pitch of the banded spherulite is in the range of 50 μm which is abnormally large compared to polyethylene (\sim several μm 's) and it is not observed for PCL homopolymer. The structure of the banded spherulite can be also analyzed with DIA and some of the results are published elsewhere [14, 15].

The size of the pitch is dependent on the molecular weight for each polymer, crystallization temperature, and amount of amorphous polymer in the mixture. It seems that PVB is suppressing the nucleation of PCL crystals and it is between the lamellae of PCL causing strain at the crystal surface of PCL to twist the lamellae. However, detailed mechanism of the phenomena is still unknown and more intensive study is necessary to solve this kind of pattern formation.

5. STRUCTURE FORMATION DUE TO COMPETITION BETWEEN SPINODAL DECOMPOSITION AND CHEMICAL REACTION

It is known that there appears interconnected structure when a polymer blend in its miscible state is rapidly brought into the spinodal region of the phase diagram of the blend. The other characteristic of the spinodal decomposition is the continuous change of concentration during phase separation. Spinodal decomposition of polymer blends with phase diagrams has been one of the most actively studied subject in polymer physics [4, 16, 17]. However, it is found that in some cases, there is a new type of pattern formation in polymer systems caused by competition between phase separation and chemical reaction [18].

Typical examples are shown in Figure 5 for pattern evolution in polycarbonate (PC, $\bar{M}_w = 29000$)/poly(ethylene terephthalate) (PET, \bar{M}_w

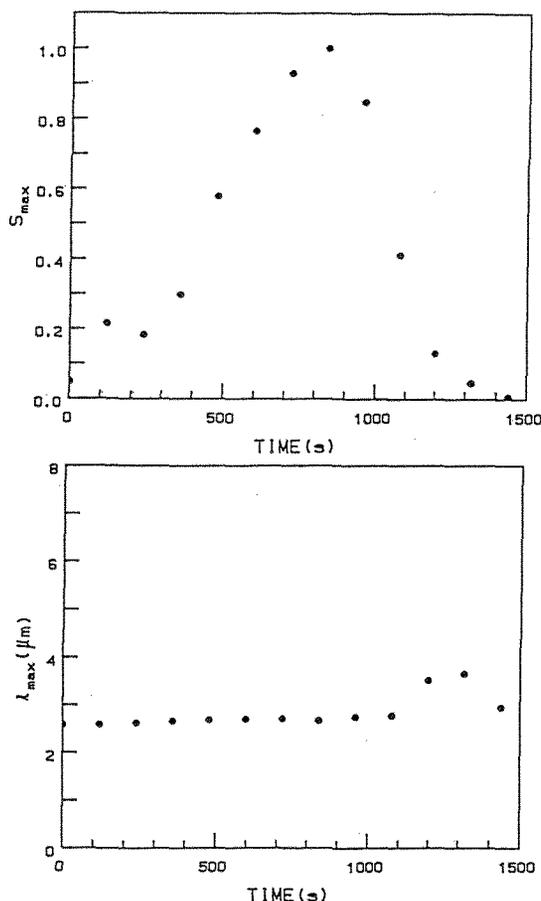


Figure 6. Temporal changes in S_{\max} and λ_{\max} for PC/PAr = 5/5 annealed at 250° C.

= 49600) = 5/5 and PC/polyarylate (PAr, $\bar{M}_w = 55000$) = 5/5 [18]. In these cases, PC/PET and PC/PAr are not miscible in thermodynamical sense [19, 20]. However, they can be brought into semi-miscible state by casting and subsequent rapid evaporation of co-solvent. The photographs were taken while the blends were annealed at 251° C for PC/PET and at 240° C for PC/PAr. In the initial stage, there appear spinodal decomposition like pattern. However, the pattern becomes droplet like for PC/PET and then the pattern itself disappears for enough annealing. For PC/PAr, the spinodal like pattern is once enhanced and then disappears. The same type of behavior were observed at annealing temperature around 250° C.

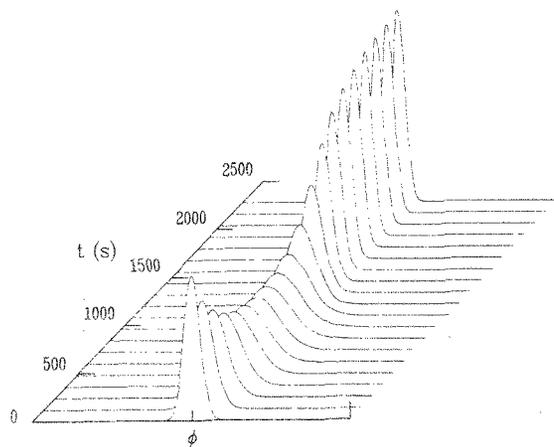


Figure 7. Temporal change of light intensity distribution for PC/PAr = 5/5 at 245° C. [18].

To study the pattern evolution in PC/PAr, power spectra of 2DFT at each annealing time at 250° C were calculated. The results were all spinodal ring like and the Figure 6 shows temporal change of S_{\max} and λ_{\max} . λ_{\max} is almost constant during the process and S_{\max} increases in the initial stage and then decreases. To prove that there is occurring spinodal decomposition in PC/PAr, light intensity distribution of phase contrast microscope images was calculated and it is shown in the Figure 7 [18]. Since phase contrast microscope is detecting the refractive index difference in the sample, the light intensity distribution is proportional to the concentration distribution function of the system [21]. The distribution starts to broaden in the initial stage corresponding to spinodal decomposition and then it becomes sharper. The latter means that the system is becoming homogeneous again. This homogenization is due to chemical reaction between PC and PAr and it is called transesterification. In PC/PAr, the spinodal decomposition and transesterification are balanced and in PC/PET, the phase separation is faster than transesterification. Therefore, the pattern is determined by the balance between the two mechanisms. Since PC, PET, and PAr are typical engineering plastics and their combinations are engineering polymer alloys, this kind of study has significance in

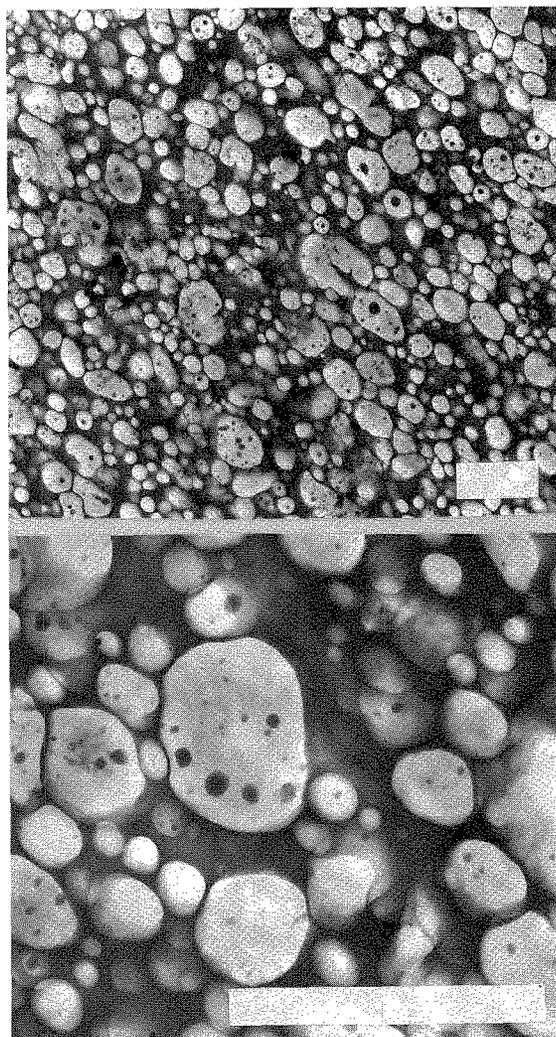


Figure 8. Example of complex phase structure observed under electron microscope for engineering polymer alloy composed of PPE/PA (Ultanyl KR 4520 from BASF). The white bar corresponds to 2 μm . (Photographs from Bridgestone Corp.)

practical problems. The same type of pattern formation may be observed for PC/poly(butylene terephthalate) (PBT) and so on.

6. COMPLEX PHASE STRUCTURE FORMATION IN POLYMER ALLOYS

Polymer alloys and blends are one of the most intensively studied topics in the field of polymer science and engineering. There are at least 15000 literatures on polymer alloys between 1967

to 1991 excluding patents [22]. They show very complex phase structures since they are generally multi-component and multi-phase materials. To obtain optimum physical properties, it is necessary to control the phase structure. There are at least 3000 literatures related to the phase structure of polymer alloys.

Figure 8 is an example of complex phase structure observed under electron microscope for engineering polymer alloy composed of poly(phenylene ether) (PPE)/polyamide (PA). The white bar corresponds to 2 μm . Here, the matrix is PA and the islands are PPE. The structure is dependent on the extrusion condition, small amount of compatibilizer, and so on. In order to analyze these structures, various DIA techniques shown in Table 1 are necessary. However, there is no standard to treat these structures at present and VAMAS (Versailles Project on Advanced Materials and Standards) on Polymer Blends group has started to do research on these problems. One of the problems may be to study the correlation between physical properties and structures [23, 24]. Some of the results will be reported in the near future.

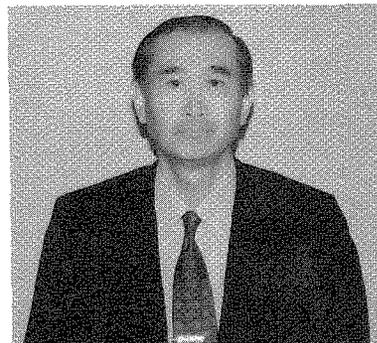
7. CONCLUSION

As shown in the above examples, studies on pattern formation in polymer systems and its dynamics are progressing very rapidly and very extensively from basic studies to practical studies. We would like to welcome newcomers to this field with physics, chemistry, materials science & engineering, and many other backgrounds.

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