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New Type of Pattern Formation in Polymer Mixtures Caused by Competition between Phase Separation and Chemical Reaction

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When two nonequilibrium phenomena, at least one of which accompanies pattern formation, proceed in a system at the same time, the resulting pattern formation could be strongly affected by the competition between the two phenomena. This coupling between nonequilibrium phenomena is very interesting to study from both the scientific and the industrial viewpoints since it may cause a new type of pattern formation; the pattern evolution could be very different in both morphology and kinetics from the individual pattern formation without competition. Although a single nonequilibrium phenomenon such as crystallization and phase separation has been extensively studied, the coupling phenomena between two nonequilibrium processes are largely unexplored. An example of such couplings is a competition between crystallization and phase separation.[1-5] Since crystallization is a transition from liquid to solid, liquid–liquid phase separation is prevented by solidification, which characterizes this coupling. Unusual pattern formations caused by the competition between these two ordering (heterogenization) phenomena in a polymer/oligomer mixture[1,2] have already been reported.

In this paper, we will demonstrate a new type of pattern evolution caused by two competing nonequilibrium phenomena: homogenization (chemical reaction) and heterogenization (phase separation). We have studied two binary mixtures of immiscible polymers between which an exchange chemical reaction occurs. In these mixtures we have found unusual pattern evolutions caused by the dynamic competition between phase demixing and chemical-reaction-induced phase mixing. Phase separation accompanies pattern formation, while an exchange reaction between chains itself does not. Phase separation in a binary mixture is driven by the difference in the interaction energy between homo- and heterocombination. Since the chemical reaction reduces a chemical difference between the two component polymers, a driving force of phase separation becomes weaker with the chemical reaction. Furthermore, the probability of collision between different kinds of polymer chains necessary for chemical reaction is determined by the local concentration, which is governed by phase separation. Thus these two phenomena are strongly coupled with each other. It should be noted that the mixture is finally homogenized since the final product of this chemical reaction is a random copolymer of the two component polymers and eventually their dissimilarity disappears by the reaction. Unlike the competition between phase separation and crystallization, both these phenomena can proceed at the same time in a liquid state without the interference from solidification. This feature characterizes the competition between heterogenization and homogenization. Thus the physical behavior is expected to be very different from the competition between solidification and phase separation.[1,2]

The samples studied were a mixture of polycarbonate (PC) and poly(ethylene terephthalate) (PET) and that of PC and polyarylate (PAr). PET and PAr belong to the group called polyester. The weight-average molecular weights (M_w) of PC, PET, and PAr were 29 000, 49 600, and 55 000, respectively. The polymers used were rather polydisperse ($M_w/M_n \sim 2$, M_n = number-average molecular weight). However, the polydispersity probably causes no serious problems in the present study, since it does not affect the essential conclusion, and furthermore chemical reaction itself also changes the molecular weight distribution of the polymers. The glass transition temperatures (T_g) of PC, PET, and PAr were 153, 79, and 203 °C, respectively. The mixture was prepared by a solvent-cast method. The cosolvents for PC/PET and PC/PAr mixtures were $CF_3CHOHCF_3$ and CH_2Cl_2, respectively. By careful experiments, both PC/PET and PC/PAr mixtures were found to be thermodynamically immiscible in the entire composition region. However, a transparent film of a mixture can be prepared by a rapid evaporation of the cosolvent far below T_g. The film prepared like this is nearly homogeneous and in a quasi-equilibrium, frozen glassy state at room temperature (below T_g). We used these thin, transparent films for measurement. The temperature jump of a sample was performed by using a temperature-controlled hot stage (Linkam TH-600). The maximum jump rate was 1.5 °C/s. This temperature jump above T_g initiated both phase separation and chemical reaction. The resulting pattern formation process was studied by direct observation using phase-contrast microscopy. The process was also recorded by a video-recording system and then analyzed by a digital image analysis (DIA) method.[6-11] The occurrence of chemical reaction was confirmed by the measurements of both infrared absorption spectra and T_g.[12]

It is well-known that a chemical reaction called transesterification occurs between PC and polyesters in the melt. This reaction is an exchange of chemical units between different polymer chains. If we express the two kinds of polyesters as –AAAAA– and –BBBBB–, the products of transesterification are something like –AABBA– and –BBAABB–. In other words, random copolymerization occurs by the reaction. This change in the chemical structures strongly affects the phase separation. In general, Flory's interaction parameter between two random copolymers A_xB_{1-x} and $A_{x+\Delta x}B_{1-(x+\Delta x)}$ is given by $(\Delta x)^2\chi_{AB}$.[13] This means that random copolymerization enhances the miscibility between two polymers having a positive χ_{AB}.

Parts a and b of Figure 1 show typical pattern evolutions caused by the temperature jump from below to above T_g for PC/PET (5/5) and PC/PAr (5/5), respectively. These figures demonstrate a striking difference in pattern formation dynamics between the PC/PET and PC/PAr mixture. In the PC/PET mixture (Figure 1a), a droplet structure is formed by phase separation and then chemical reaction proceeds mainly in the interfacial region. The interface becomes diffuse with time, and eventually the system is homogenized. In the PC/PAr mixture (Figure 1b), on the other hand, the concentration fluctuation grows, then decays, and finally is homogenized. It should be noted that the pattern formation dynamics is strongly dependent on the annealing temperature T_{an} since the phase-separation and chemical-reaction speed are differently dependent on the temperature.

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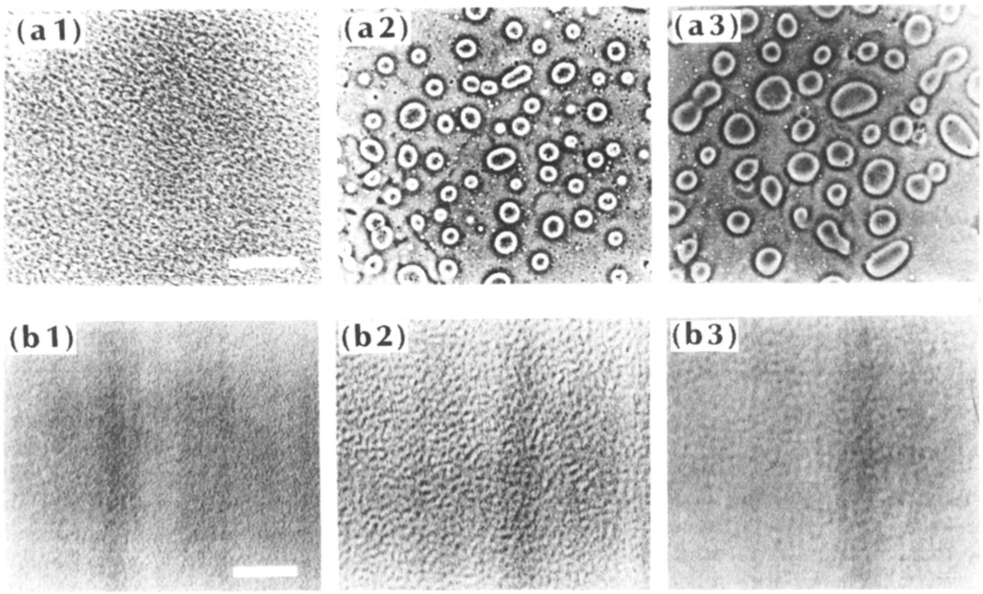

Figure 1. (a) Pattern evolution in PC/PET (5/5). T_{an} = 251 °C. (a1) 10 s, (a2) 185 s, (a3) 920 s. The bar corresponds to 100 μm. (b) Pattern evolution in PC/PAr (5/5). T_{an} = 240 °C. (b1) 10 s, (b2) 2290 s, (b3) 3020 s. The bar corresponds to 20 μm.

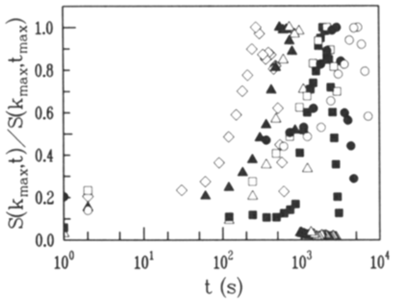

Figure 2. Temporal change in $S(k_{max})$ for PC/PAr (5/5) for various T_{an}'s: (○) T_{an} = 255 °C, (●) T_{an} = 250 °C, (□) T_{an} = 240 °C, (■) T_{an} = 235 °C, (△) T_{an} = 230 °C, (▲) T_{an} = 225 °C, (◇) T_{an} = 220 °C.

Figure 2 shows the temporal change in the scattering peak intensity $S(k_{max},t)$ (k_{max} = the wave number giving the scattering peak) in the PC/PAr mixture, which is obtained from the power spectrum of the two-dimensional Fourier transformation of an image by a DIA operation.[6,7] We can clearly see that the scattering intensity, namely, the amplitude of the concentration fluctuation, shows the maximum at a certain time t_{max} for all the T_{an}'s. t_{max} decreases with an increase in T_{an}. This is probably because the chemical-reaction speed increases more rapidly with an increase in T_{an} than the phase-separation speed. This problem will be discussed later in more detail. The temporal change in the characteristic wavelength of the concentration fluctuation, λ_{max}, is also studied. We find that λ_{max} is almost independent of time and only slightly increases in the late stage. This behavior implies the phase-separation process can be described by Cahn's linear theory;[14] in other words, the phase separation is in the so-called initial stage. This conclusion is also supported by the behavior of the concentration distribution function $P(\phi)$ shown in Figure 3, which can be obtained by a DIA operation.[8,9,11] $P(\phi)$ keeps an almost Gaussian shape throughout the process and only the width of the distribution becomes broad in the intermediate stage, reflecting the enhancement of the concentration fluctuation by phase separation. This behavior is characteristic of an initial, linear regime of spinodal decomposition.[9]

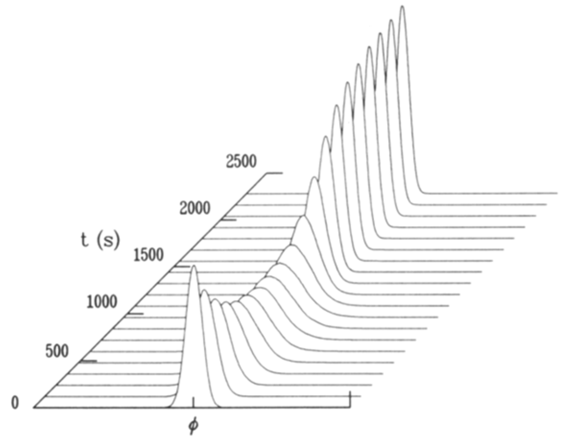

Figure 3. Temporal change of $P(\phi)$ for PC/PAr (5/5) at T_{an} = 245 °C.

It is unusual that the linear regime of phase separation lasts for such a long period. This behavior may be explained by the fact that the random copolymerization proceeds so quickly compared to the phase separation, and thus the driving force for phase separation (the interaction parameter) is weak even in the initial stage. In this case the amplitude of the concentration fluctuation is likely small, and therefore the higher-order nonlinear terms of the concentration fluctuation are negligible. Thus we can safely assume that the chemical reaction proceeds almost homogeneously in space for the PC/PAr mixture.

Here we discuss the difference in pattern evolution dynamics between the PC/PET and PC/PAr mixtures. The pattern evolution dynamics under the competition is likely dominated by the relation between the chemical-reaction speed and the phase-separation speed, as follows. When the chemical reaction proceeds much faster than the phase separation, the former is not localized in the entire process and proceeds almost homogeneously. This is because the chemical reaction continues to reduce the driving force of phase separation and a large concentration fluctuation is never established. This is likely the case for the PC/PAr mixture. On the other hand, when the phase separation proceeds much faster than the chemical reaction, a domain structure is first formed by the phase separation, and then the chemical reaction proceeds mainly at the domain interface because only around the interface do the different polymers encounter with a high probability. Thus the system is slowly homogenized by the reaction localized at the interface. This is likely the case for the PC/PET mixture.

Next we describe pattern evolution dynamics caused by a competition between chemical reaction and phase separation more quantitatively. For simplicity, we analyze the behavior on the basis of Cahn's linear theory,[14] which is valid in the initial stage of spinodal decomposition. The free energy of the system is given by the following equation

$$\Delta F/kT = (1/V)\int [f(r) + \kappa(\nabla\phi)^2]\, dr$$

The equation of motion is given by

$$\partial\phi/\partial t = MkT[(\partial^2 f/\partial\phi^2)\nabla^2\phi - 2\kappa\nabla^4\phi]$$

where M is the mobility and dependent on T_g. For binary polymer mixtures, f is given by the equation according to the Flory–Huggins lattice theory[15,16]

$$f = (\phi/n)\ln\phi + ((1-\phi)/n)\ln(1-\phi) + \chi_{12}\phi(1-\phi)$$

where ϕ is the volume fraction of polymer 1, n the degree of polymerization, and χ_{12} Flory's interaction parameter between components 1 and 2. In this case[17–19]

$$\kappa = a^2/[36\phi(1-\phi)] + \chi_{12}a^2/18$$

$$\partial^2 f/\partial\phi^2 = 1/(n\phi(1-\phi)) - 2\chi_{12}$$

Here we consider the mixture of two copolymers composed of A and B units, $A_{c_0+\Delta c}B_{1-c_0-\Delta c}/A_{c_0-\Delta c}B_{1-c_0+\Delta c}$. To simplify the problem, we ignore the temporal change in the degree of polymerization n. Suppose that the mixture is initially A/B (1/1) ($c_0 = {}^1/_2$ and $\Delta c = {}^1/_2$). We define the concentration of segment A as c and the interaction parameter between segments A and B as χ_{AB}. Then the behavior is described by

$$\partial c/\partial t = MkT[((1/n)(\Delta c)^{-2} - 2\chi_{AB})\nabla^2 c - (a^2/18)((\Delta c)^{-2} + 2\chi_{AB})\nabla^4 c]$$

In this equation chemical reaction modifies Δc, and thus Δc is a function of time. Provided $\Delta c(t) = \Delta c\exp(-Kt)$ (K = the reaction constant), the temporal change in the scattering function $S(q,t)$ is given by the following relations:

$$S(q,t) = S(q,\infty) + [S(q,0) - S(q,\infty)]\exp(2R(q,t))$$

$$R(q,t) = -MkTq^2[((1/2Kn)(\Delta c)^{-2}\exp(2Kt) - 2\chi_{AB}t) + (a^2/18)((1/(2K))(\Delta c)^{-2}\exp(2Kt) + 2\chi_{AB}t)q^2]$$

Qualitatively, the sign of $\partial R(q,t)/\partial t$ determines whether the system becomes more heterogeneous or more homogeneous. It should be noted that the sign of $\partial R(q,t)/\partial t$ is largely determined by the sign of ($\chi_{AB} - (1/2n)(\Delta c(t))^{-2}$). Initially Δc is large (close to ${}^1/_2$), and accordingly $\partial R(q,t)/\partial t$ is always positive for a certain region of q. Thus, the concentration fluctuation grows as in the usual spinodal decomposition. In this process, random copolymerization due to the chemical reaction occurs simultaneously with phase separation, and consequently $\Delta c(t)$ monotonously decreases with time. If the relation $\chi_{AB} < (1/2n)(\Delta c(t))^{-2}$ is satisfied for $t < t_{lin}$ (t_{lin} = the time of a change from the linear to the nonlinear regime), the system becomes homogeneous again within the linear regime. That is, when the chemical reaction proceeds faster than the phase separation, the behavior can be described by this linear theory. On the other hand, when the chemical reaction proceeds much slower than the phase separation, the phase separation mainly proceeds and enters in the late stage where a sharp interface between the phases is formed. Namely, the relation $\chi_{AB} = (1/2n)(\Delta c(t))^{-2}$ is never satisfied in the linear regime, and thus $\partial R(q,t)/\partial t$ is positive for $t < t_{lin}$. Accordingly the system enters into the intermediate or late stage of spinodal decomposition within a short time before the chemical reaction proceeds. After the formation of the interface, the chemical reaction proceeds mainly at the interface. This regime is beyond the above linear theory. A strongly nonlinear problem must be solved to get a complete physical picture for this case.

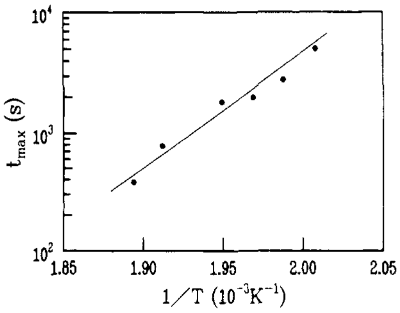

Figure 4. Temperature dependence of t_{max} for PC/PAr (5/5).

In the above theory, the maximum time for the scattering intensity, t_{max}, is approximately given by the condition $\chi_{AB} = (1/2n)(\Delta c)^{-2}\exp(2Kt_{max})$. To check this relation, we plot $\log t_{max}$ against $1/T$ for the PC/PAr mixture in Figure 4. The almost linear relation between these two quantities supports the prediction of the above theory, provided that the reaction constant K represents the Arrhenius-type activation process.

The difference in pattern evolution behavior between the PC/PET and PC/PAr mixtures is likely caused by the difference in mobility M due to the large difference in T_g between PET and PAr. The rate of the chemical reaction K estimated from the activation energy for each elementary reaction is on the order of 10^{-3}/min for both the PC/PET and PC/PAr mixtures. Thus the pattern formation is more likely governed by the mobility M determined by ($T_{an} - T_g$) rather than by the rate of the chemical reaction K. It should be mentioned that the difference in the thermodynamic driving force for phase separation (χ_{AB}) between these two mixtures is another factor to be considered.

The pattern formation dynamics is also strongly dependent on the initial composition in both the PC/PET and PC/PAr mixture. The behavior can be qualitatively explained by the difference in T_g among the mixtures: With an increase in the content of PC, T_g of the mixture increases and thus a phase-separation speed becomes slower. The details including the composition dependence of the morphological characteristics of phase-separated patterns will be published elsewhere.

The phenomena described in this paper show interesting possibilities of new types of pattern formation caused by a competition between nonequilibrium phenomena. Furthermore, they provide us with a possibility to control an interface structure of a polymer mixture; this may have practical importance. Finally it should be stressed that much care should be paid to check the thermodynamic miscibility of binary polymer mixtures under the influence of transesterification. To unambiguously check the miscibility, it is very important to study the dynamics of competitive pattern evolution.

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Registry No. PET (SRU), 25038-59-9.

CORRECTIONS

Burak Erman and Lucien Monnerie*: Theory of Elasticity of Amorphous Networks: Effect of Constraints along Chains. Volume 22, Number 8, August 1989, pp 3342–3348.

Equations 23, 28, 29, 31, 40, and 41 of ref 1 should be corrected as

$$\frac{\rho_\lambda}{\rho_{*\lambda}} = 1 + \frac{\left(\dfrac{\sigma_\lambda}{\rho_\lambda}\right)^2\left(\dfrac{\eta_0}{\eta_\lambda}\dfrac{\rho_\lambda}{\rho_0} - 1\right) + \left(\dfrac{\sigma_\lambda}{\rho_\lambda}\right)\left(\dfrac{\eta_0}{\eta_\lambda}\dfrac{\sigma_\lambda}{\sigma_0} - 1\right)}{\left(1 + \dfrac{\sigma_\lambda}{\rho_\lambda}\right)^2} \tag{23}$$

$$\frac{\sigma_\lambda}{\rho_\lambda} = \lambda_x{}^{-2}\kappa_G[1 + (\lambda_x{}^2 - 1)\Phi] \equiv \lambda_x{}^{-2}h(\lambda_x) \tag{28}$$

$$h(\lambda_x) \equiv \kappa_G[1 + (\lambda_x{}^2 - 1)\Phi] \tag{29}$$

$$B_x = h(\lambda_x)\kappa_G(1 - \Phi)(\lambda_x{}^2 - 1)/[\lambda_x{}^2 + h(\lambda_x)]^2 \tag{31}$$

$$\dot{B} \equiv \frac{\partial B}{\partial \lambda^2} = B\left\{(\lambda^2 - 1)^{-1} - 2[\lambda^2 + h(\lambda)]^{-1} + \frac{\kappa_G}{h(\lambda)}\frac{[\lambda^2 - h(\lambda)]\Phi}{[\lambda^2 + h(\lambda)]}\right\} \tag{40}$$

$$\dot{D} \equiv \frac{\partial D}{\partial \lambda^2} = B\left[h(\lambda)^{-1} - \frac{\lambda^2\kappa_G\Phi}{h(\lambda)^2}\right] + \frac{\lambda^2\dot{B}}{h(\lambda)} \tag{41}$$

The $g(\alpha)$ vs α^{-1} curves given in Figure 5 of the paper are not noticeably affected by the corrections, provided that the κ_G values are suitably rescaled. Hence, the qualitative predictions and conclusions given in the original manuscript remain unchanged.

The figures given in refs 2 and 3 comparing experimental data with predictions of the theory based on ref 1 are not significantly affected by the correction provided that the κ_G and $[f^*]_{ph}$ parameters are suitably rescaled. As an example, Figure 1 of ref 2 is replotted in terms of the corrected expression. The $[f^*]_{ph}$ and κ_G parameters required for the fit have been changed from 0.15 MPa and 3.0 to 0.135 MPa and 5.6, respectively.

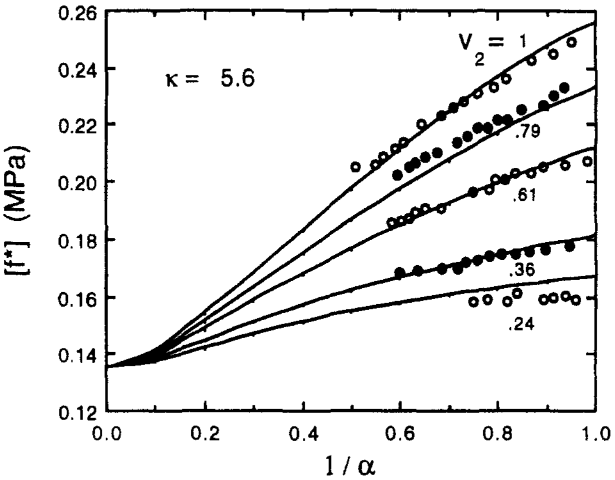

Figure 1. Figure 1 of ref 2 replotted according to the corrected expressions.

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