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# Salami pattern formation during phase separation induced by polymerization of 2-chlorostyrene in the presence of polystyrene

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## Abstract

Development of morphological structures during phase separation induced by radical polymerization of 2-chlorostyrene in the presence of polystyrene was studied with an electron microscope. No stirring of the mixture was made. Domain structure changed significantly with initial monomer composition within a narrow range. Salami domains similar to those observed in high-impact polystyrene (HIPS) formed at certain initial compositions, notwithstanding that production of graft polymers, which was known to play an essential role of the salami structure formation in HIPS, was negligible in this system. An explanation for the mechanism of salami pattern formation was proposed.

*Keywords:* Polymerization-induced phase separation; Salami structure; Polymer blend

It is known that a wide variety of morphological structures forms during phase separation induced by polymerization or cross-linking reaction [1–4]. Salami structure of high-impact polystyrene (HIPS) is especially interesting because of duality of the structure. HIPS is obtained by polymerization of styrene monomer in the presence of polybutadiene. Detailed mechanism of the salami structure formation in HIPS has not been fully understood because of its complexity, but it has been experimentally revealed that production of graft polymers by attacking of polystyrene radicals onto double bonds of polybutadiene and stirring of reacting mixture play essential roles in its formation [2]. Then arises a question whether salami pattern formation has to be accompanied by production of graft polymers. In this communication we show experimental results of phase separation induced by radical polymerization of 2-chlorostyrene in the presence of polystyrene, as an evidence that salami pattern forming without graft reaction.

Previously rather simple morphological structures were observed in phase separation induced by polymerization of 2-chlorostyrene (2CLS) in the presence of polystyrene (PS) [5,6]. Phase being rich in the polymerization product, poly(2-chlorostyrene) (P2CLS), formed spherical domains (droplets) initially, and these spherical domains continued to coarsen with keeping their spherical shape or coagulated into continuous domains, depending on temperature. Formation of these spherical domains in the initial stage of phase separation was explained as follows. In the time scale of our observation of phase separation, the advance of radical polymerization is expressed by the increase in the number (namely, concentration) of the polymer product having roughly constant average molecular weight. Thus, the process in which polymerizatiion reaction induces phase separation can be illustrated by using a phase diagram of three component system shown in Fig. 1. With the advance of polymerization reaction, a point representing a composition of the mixture moves from a point A to a point B along a line parallel to the side connecting two apexes 2CLS and P2CLS. When the composition reaches an intersection with the coexistence curve, the mixture is destabilized and undergoes phase separation. When the intersection is located on the PS-rich side of the coexistence curve as shown here, the P2CLS-rich phase becomes a minor phase according to the lever rule and forms spherical domains in the sea of PS-rich phase [6].

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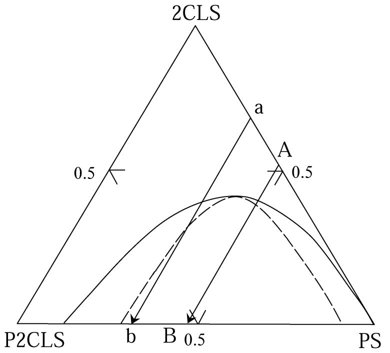

Fig. 1. Phase diagram of 2-chlorostyrene(2CLS)/poly(2-chlorostyrene) (P2CLS)/polystyrene (PS) mixture calculated by the Flory–Huggins theory. The solid line denotes binodal line and the broken line denotes spinodal line. Molecular weights of P2CLS and PS are $2.6 \times 10^5$ and $5.0 \times 10^4$, respectively. Values of the interaction parameters used in the calculation are given in the text. Composition changes along line AB with the advance of polymerization.

Since, the P2CLS-rich side of the coexistence curve forms a much more acute angle with the line AB than the PS-rich side does, a range of location of the initial point A within which the line AB intersects with the PS-rich side of the coexistence curve is wider than a range within which the line intersects with the P2CLS-rich side. As a result, a quite limited range of the initial composition leads to phase separation at a concentration on the P2CLS-rich side. This is why only P2CLS-rich droplets were initially observed in the previous study. In other words, in order to observe a novel morphological structure, it is necessary to destabilize a mixture at a concentration on the P2CLS-rich side (as shown by a line ab) or very close to the critical point.

Polystyrenes of two different molecular weights were used in this work. PS with weight average molecular weight $M_w = 3.79 \times 10^4$ and polydispersity indices $M_w/M_n = 1.01$ was purchased from Toso Co. Ltd. and PS with $M_w = 5.0 \times 10^4$, $M_w/M_n = 1.06$ was purchased from Pressure Chemical Co. 2-Chlorostyrene monomer was a product of Tokyo Kasei Co. and purified by distillation under reduced pressure. Ten percents by weight of di(*n*-butyl) phthalate (DBP) was added to a sample mixture so as to reduce the viscosity at high monomer conversions. DBP of reagent grade (purity $> 98\%$) was purchased from Tokyo Kasei Co. Radical polymerization of 2-chlorostyrene was initiated by raising temperature without the aid of initiator. Methods of sample preparation were the same as those used in a previous work and details were given in Ref. [5].

Polymerization reaction and phase separation were made at 130 °C. No stirring of a sample mixture was made during polymerization and phase separation. Morphological structures of phase separated domains were observed with a scanning electron microscope JEOL JSM-T220 in the following way. After a sample was allowed to undergo phase separation in a thermostat controlled to ±0.03 °C for a desired period, it was taken out and quenched rapidly to room temperature to fix its phase-separated domain structure. Backscattered-electron image of a microtomed surface of the quenched sample was observed.

As molecular weight of PS increases, the critical point shifts toward apex 2CLS and an appropriate initial composition range becomes even narrower (See Fig. 1). Thus selection of proper molecular weight is also of great importance for reducing the difficulty in finding a novel morphological structure. In order to roughly estimate appropriate range of molecular weight and initial composition, we calculated coexistence curves on the basis of the Flory–Huggins theory. For simplicity, we neglected DBP in these calculations. For the interaction parameter between PS and P2CLS $\chi_{P2CLS-PS}$ we used a value evaluated from molecular-weight dependence of cloud point curves of P2CLS/PS mixtures: $\chi_{P2CLS-PS} = 0.0078 - 1.63/T(\mathrm{K})$ [7]. For the other interaction parameters, we assumed $\chi_{2CLS-P2CLS} = 0$ and $\chi_{2CLS-PS} = \chi_{P2CLS-PS}$. For molecular weight of P2CLS, we used $M_w = 2.6 \times 10^5$, which was the experimental value of the product polymerized in the presence of an equal amount of PS having $M_w = 5.0 \times 10^4$,

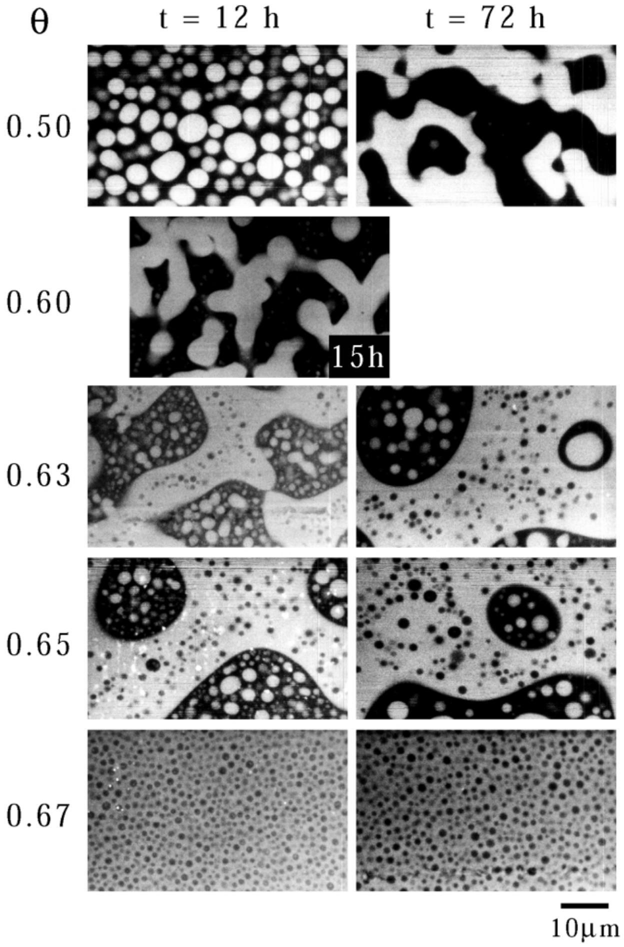

Fig. 2. Scanning electron micrographs of domain structures formed at time *t* during phase separation induced by radical polymerization of 2-chlorostyrene in the presence of polystyrene of molecular weight $5.0 \times 10^4$ for several initial monomer compositions *θ*. Darker part corresponds to polystyrene-rich phase.

and we assumed it independent of molecular weight of PS. Coexistence curve calculated for molecular weight of PS $= 5.0 \times 10^4$ was shown in Fig. 1. Similar calculations were made for several other molecular weights of PS and two molecular weights used in this work were chosen on the basis of their results.

Fig. 2 shows phase-separated domain structures forming during phase separation induced by polymerization of 2CLS in the presence of PS of $M_w = 5.0 \times 10^4$ for different initial compositions $\theta$ ($\equiv$2CLS/(2CLS + PS) by weight). Darker parts in the scanning electron micrographs correspond to PS-rich domains. At $\theta = 0.50$, as reported previously [5], droplets of P2CLS-rich phase initially formed and these droplets coagulated into continuous domains in a later period. Similar morphological change from droplets to continuous domains occurred at $\theta = 0.60$ as well, but continuous domains of P2CLS-rich phase formed much earlier than at $\theta = 0.50$ (they formed in a period between 48 and 72 h at $\theta = 0.50$ [5]).

When $\theta$ increased by 0.03, the development of morphological structure changed drastically. At 12 h both P2CLS-rich and PS-rich phases formed continuous domains, and there were many droplets inside respective continuous domains. There were some narrow necks in PS-rich continuous domain. These necks were eventually broken in the subsequent coarsening process and salami-like domain structures formed as shown by the electron micrograph at 72 h. The salami structure also formed when the initial composition increased to $\theta = 0.65$. Continuous domains of PS-rich phase, which preceded the salami structure in the case of $\theta = 0.63$, were not observed.

At $\theta = 0.67$, droplets of the PS-rich phase formed in the P2CLS-rich sea phase, which is a reversal of the pattern observed at $\theta = 0.50$, $t = 12$ h. The growth of each PS-rich droplet was quite slow, and the morphological change to continuous domains was not observed. At compositions larger than $\theta = 0.70$, inhomogeneous structure was not observed by the electron microscope, and any growth of light intensity was not detected in the time-resolved light scattering experiments, indicating that no phase separation occurred at these initial compositions.

In the experiments using PS molecular weight $M_w = 3.79 \times 10^4$, similar variations of morphological structure development with the initial monomer composition were observed as shown in Fig. 3. At monomer compositions up to $\theta = 0.53$, droplets of the P2CLS-rich phase initially formed. At $\theta = 0.55$ bicontinuous domains containing small droplets inside emerged. Similar bicontinuous domains emerged in an early period at $\theta = 0.60$. These PS-rich continuous domains broke into discrete spherical regions in a later period, resulting in formation of the salami structure. At $\theta = 0.62$ droplets of PS-rich phase without inside structure formed in the P2CLS-rich sea phase.

Both series of observations for different molecular weights of PS showed that with decreasing initial 2CLS content the initial domain structure changed in the order of P2CLS-rich droplets in PS-rich background sea, bicontinuous domains, and P2CLS-rich droplets in PS-rich background sea, if the fine structure inside each domain was neglected. In addition, the corresponding morphological structures were observed at smaller initial compositions when molecular weight of PS decreased. These results are consistent with those expected from Fig. 1. With increasing the initial composition $\theta$, the locus of composition change due to polymerization, namely the line AB, in Fig. 1 approaches the side connecting two apexes 2CLS and P2CLS, which causes a shift of the intersection of the line AB and the coexistence curve from the PS-rich side to the P2CLS-rich side of the coexistence curve. Consequently, the ratio of volume of the P2CLS-rich phase to the total volume increases with $\theta$. It is well known that the above mentioned three patterns of domain structures emerge depending on the ratio of volume of the phase in phase separation of non-reacting systems [6]. It is also noted that the morphological pattern significantly changed within a small range of $\theta$ as expected from Fig. 1.

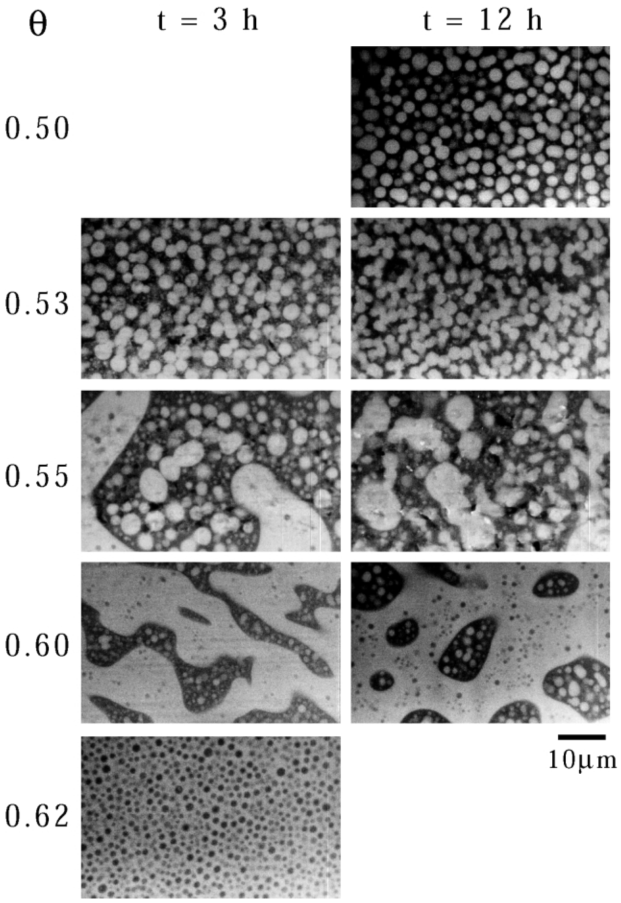

Fig. 3. Scanning electron micrographs of domain structures formed at times $t$ during phase separation induced by radical polymerization of 2-chlorostyrene in the presence of polystyrene of molecular weight $3.79 \times 10^4$ for several initial monomer compositions $\theta$.

Since polystyrene has not double bond as polybutadiene has, graft polymer is scarcely produced during polymerization of 2CLS. This indicates that the salami pattern of this system formed through a mechanism different from that working in HIPS. The salami structure consists of droplets of two widely different sizes, and to find out the origin of the bimodal distribution of domain size is probably essential for understanding the mechanism of the salami pattern formation. An important clue has been given by computer simulation. A difference between polymerization-induced phase separation and ordinary phase separation lies in the fact that in the polymerization-induced phase separation quenching depth (distance from binodal line) and viscosity of the system increases with time. Computer simulation on the basis of a model taking into account these characteristics of polymerization-induced phase separation has shown that droplets of bimodal size distribution are generated under certain conditions [8]. The same mechanism is considered to work in the formation of the salami pattern of the present experiments.

In this communication, it was shown that salami pattern formed during phase separation induced by radical polymerization of 2-chlorostyrene in the presence of polystyrene, where grafting reaction rarely occurred. The result indicates that salami pattern formed through different mechanism from that in HIPS, and consequently suggests a method of generating the salami structure in a wider variety of polymer blends.

## References

[1] Inoue T. Progr Polym Sci 1995;20:119.
[2] Fischer M, Hellmann GP. Macromolecules 1996;29:2498.
[3] (a) Harada A, Tran-Cong Q. Phys Rev Lett 1996;76:1162. (b) Harada A, Tran-Cong Q. Macromolecules 1997;30:1643.
[4] Kim JY, Chou CH, Palffy-Muphoray P, Mustafa M, Kyu T. Phys Rev Lett 1993;71:2232.
[5] Okada M, Fujimoto K, Nose T. Macromolecules 1995;28:1795.
[6] Okada M, Sun J, Tao J, Chiba T, Nose T. Macromolecules 1995;28:7514.
[7] Kwak KD, Okada M, Nose T. Polymer 1991;32:864.
[8] Okada M, Masunaga H, Furukawa H. Macromolecules 2000;33:7238.