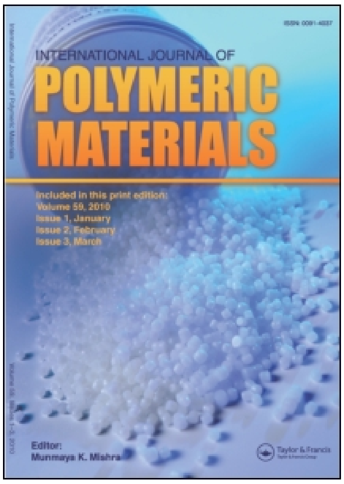

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Yoshiyuki Suetsugu[a]
[a] Polymer Research Laboratory, Idemitsu Petrochemical Co., Ltd., Ichihara, Chiba, Japan

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Polymer Engineering and Technology

YOSHIYUKI SUETSUGU

Polymer Research Laboratory, Idemitsu Petrochemical Co., Ltd., Anesaki-kaigan, Ichihara, Chiba 229-01 Japan

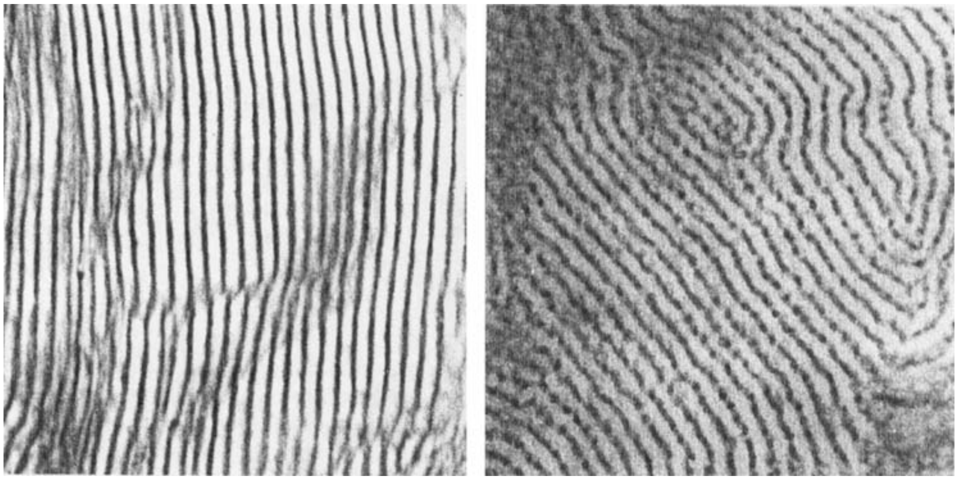
Several topics have been selected from among the presentations at the sessions on Processing in Polymer Alloys, High-Performance Polymers and Polymer Engineering and Technology. These are: mesh-like structure in block copolymer/homopolymer mixtures, ordered tricontinuous double-diamond structure of triblock copolymers, size of dispersed phases in polymer blends and in reactive processing, and polymer ionics in block-graft copolymers having poly(ethylene oxide) as graft chains.

1. CONTINUOUS STRUCTURES OF BLOCK COPOLYMERS AND BLENDS

1.1. Mesh-like Structure

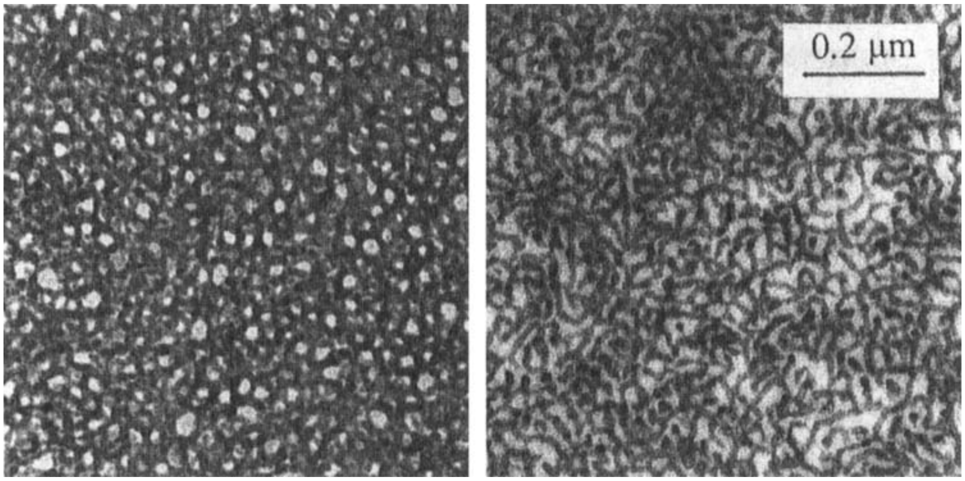
AB block copolymers and blends of AB block copolymer/A homopolymer typically take spherical, cylindrical and lamellar microdomain structures depending upon the volume ratio of the chains of A and B polymers. Recently the formation of bicontinuous structures was reported at the intermediate composition required for the cylindrical and lamellar structures.

S. Koizumi, H. Hasegawa *et al.*, Kyoto University (3566, ES1399), reported a newly observed "mesh"-like structure in a mixture of styrene-butadiene block copolymer (K-Resin®, KR-03, Phillips Petroleum Co.; 76 wt% styrene and 24 wt% butadiene; number- and weight average molecular weights 80,000 and 157,000 respectively) and polystyrene homopolymer (TS23, TOSOH Co.; number average molecular weight and polydispersity index 2,800 and 1.05 respectively). Styrene-butadiene block copolymer (SB) and polystyrene (PS) were mixed in different ratios and dissolved in toluene. Film specimens of ca. 0.3 mm thick prepared by casting 5.0 wt% solution were observed by small angle X-ray scattering (SAXS) and transmission electron microscope (TEM). Bragg spacing representing the lamellar thickness increased by the addition of polystyrene homopolymer up to a composition of ca. 80/20% (SB/PS), and sharply dropped at a composition of 70/30 indicating the structural change. Figure 1 shows the electron micrographs of the ultrathin sections of the specimens. The dark regions correspond to polybutadiene microphases stained with osmiumte troxide, and the bright region polystyrene. Lamellar structure of 90-10 blend is exhibited in Figure 1(a). Similar observations were made for 100/0 and 80/20 blends. Figure 1(b) and (c) demonstrate the edge and through views of 70/30 mixture. In the edge view, Figure 1(b), the morphology resembles lamellar. However, the dark striations were not solid lines but rather consisted of an array of dark spots



(a) 90/10 mixture

(b) 70/30 mixture: Edge view



(c) 70/30 mixture: Through view

(d) 60/40 mixture

Figure 1. Transmission electron micrographs of KR03/TS23 mixtures.

of polybutadiene. Morphology in the through view, Figure 1(c), was significantly different from the lamellar. There can be seen spot-like bright polystyrene microphases dispersed in polybutadiene matrix. In other words, the microdomain structure was composed of altering layers of solid PS sheets and mesh-like PB sheets with the holes filled with PS. In this structure, PS phase is continuous in three dimensions but PB phase is continuous only in two dimensions. This may be called a "mesh"-like structure. At 60/40 mixture, Figure 1(d), the polybutadiene microphase formed a flexible cylindrical structure crosslinked to form a three-dimensional percolation network in polystyrene matrix. This is a bicontinuous network structure or a "strut" structure.

1.2. Tricontinuous Double-diamond Structure

Y. Mogi, K. Mori *et al.*, Nagoya University (3593, ES1408), reported the "ordered tricontinuous double-diamond (OTDD)" structure of ABC type triblock copolymer. Poly(isoprene-b-styrene-b-2-vinylpyridine) with different center block contents and narrow molecular weight distributions (Mw/Mn = 1.03 ~ 1.05) were prepared by anionic polymerization. Number average molecular weights were in the range of ca. 6,000 ~ 10,000. Casted films were prepared from dilute solution of THF and dried under vacuum. These were then annealed at 120°C for 10 days. Morphology was observed under TEM after OsO_4 staining. When the volume ratio of polyisoprene (I), polystyrene (S) and poly(2-vinylpyridine)(P) was roughly 1:1:1, three-phase-four-layer-lamellar (TPFLL) structure was formed; piling the lamellar in S-P-S-I order. The new structure was observed at a volume ratio of 1:2:1 (I:S:P). Three dimensionally tricontinuous structure, as shown in Figure 2, was observed. Mutually interpenetrated diamond frames of the end blocks (I and P) were embedded

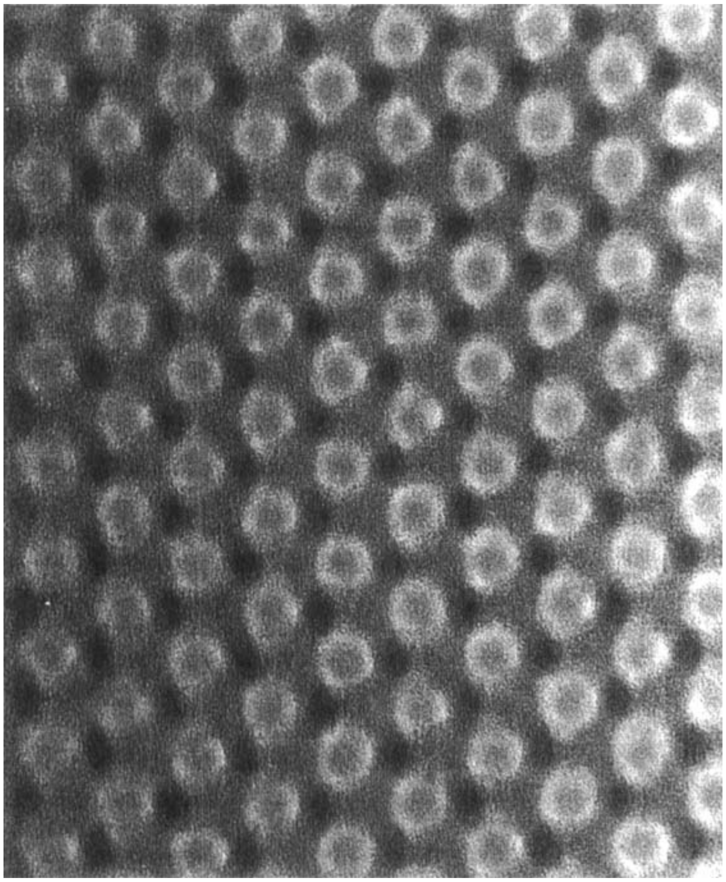


Figure 2. Transmission electron micrograph of poly(isoprene-b-styrene-b-2-vinylpyridine).

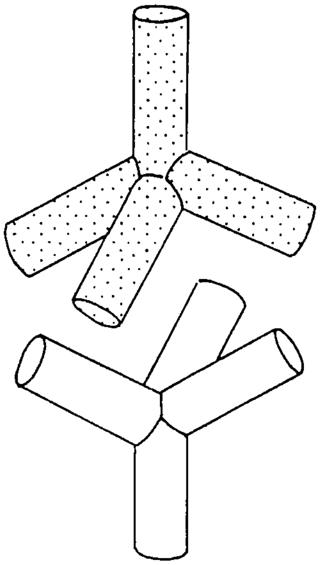


Figure 3. Schematic diagram of ordered tricontinuous double diamond structure.

in S matrix as shown in Figure 3. This new structure was named as the ordered tricontinuous double-diamond (OTDD) structure. The phase transition from TPFLL to OTDD occurred when the volume fraction of the center block exceeded 0.45.

2. DISCRETE STRUCTURES IN BLENDS

2.1. Dispersed Particle Size

S. Maeda *et al.*, Ube Industries and T. Masuda, Kyoto University (3623, ES1419), studied the morphology control in various incompatible polymer blends; polyamide-6 (PA)/styrene-acrylonitril copolymer (SA), PA/PS, PA/polypropylene (PP) and PS/PP. Composition of the blends was varied from 90/10 to 10/90. Brabender type mixer was used to prepare the blends. Rotor speed; 30, 60 and 90 rpm. Blending temperature; 235, 250 and 265°C for PA blends, 200 and 250°C for other blends. It turned out that the size of the dispersed phase, r_n, can be expressed as,

$$r_n \propto \gamma_{12} f \sigma^{-1/2}, \qquad f = \phi^{2/3}$$

where γ_{12} denotes the interfacial tension, f corresponds to the probability of the collision of the dispersed particles, ϕ the fraction of the dispersed phase and σ the shearing stress. The relation between $\gamma_{12} f/r_n$ and σ is shown in Figure 4. The above equations were found to be valid for all blends prepared at various temperature and blend ratios. The size of the dispersed phase of poly(ethylene terephthalate)/ethylene-propylene rubber and polyamide/ethylene-propylene rubber blends prepared by a co-rotating twin screw extruder was previously reported elsewhere.

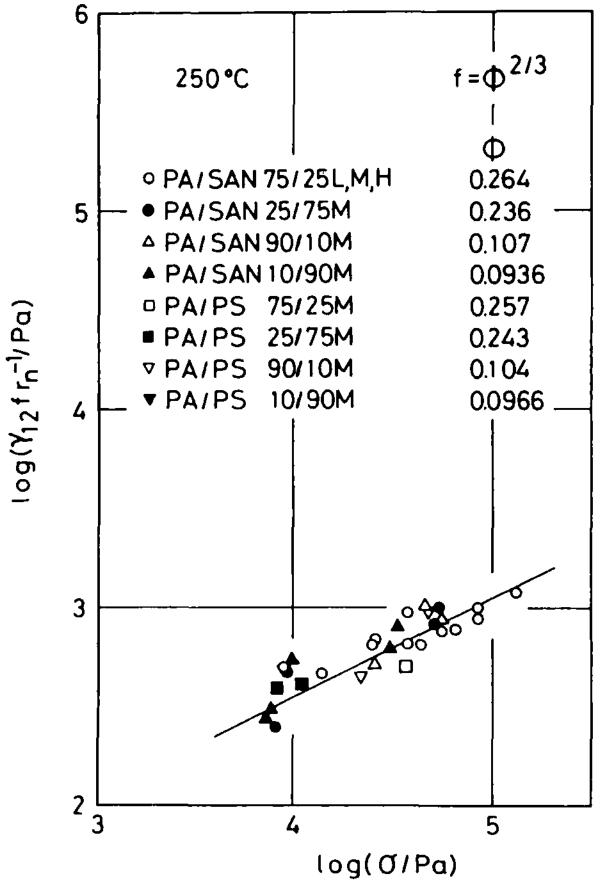


Figure 4. Relationship between $\gamma_{12} f r_n^{-1}$ and σ for various polymer blends.

$$r_n = \frac{\gamma_{12}}{\sigma\eta_m}\left(\frac{\eta_d}{\eta_m}\right)^{\pm 0.84}$$

where η_m and η_d denote the matrix viscosity and the dispersed drop viscosity respectively.

K. Kakugo, T. Nishio *et al.*, Sumitomo Chemical Co., (3623, ES1420) studied the morphology control of polyamide alloys in reactive processing. They interpreted the size of the dispersed phase with the interfacial area occupied by copolymer molecules. Reactive processing of maleic anhydride grafted PP/polyamid-6 (PA6) alloy (35/65 mixture) and reactive compatibilizer grafted polyphenylene ether (PPE)/PA6 alloy (49/51 mixture) were carried out by twin screw extruder. The amount of the graft copolymer formed during the extrusion process was determined by successive extractions with xylene and then trifluoroethanol for PP/PA6, and with chloroform and then trifluoroethanol for PPE/PA6. The size of the dispersed phase decreased more

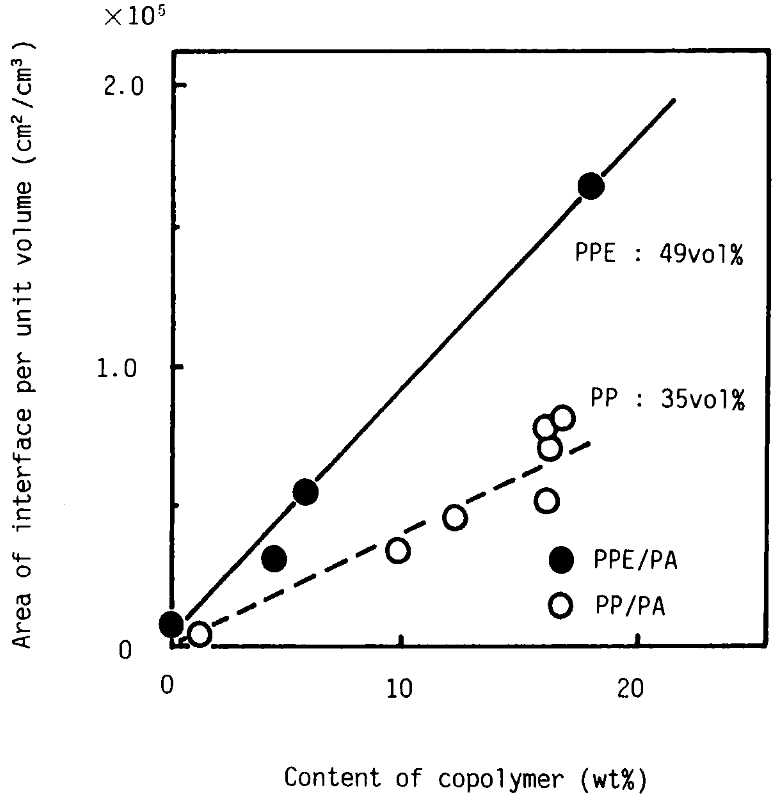


Figure 5. Relationship between the content of extracted copolymer and the surface area of dispersed phase per unit volume for PPE/PA and PP/PA.

than 20 times in diameter as the content of copolymer formation progressed in the extrusion process. Graft copolymer of these polymer alloys were found to be present at the interface between the dispersed phase and the PA matrix. It was found that the interfacial area calculated from the size of the dispersed phase increased linearly with the content of copolymer formed as indicated in Figure 5. It should be noted that a single graft copolymer molecule always occupies 520 Å^2 for PPE/PA6 and 570 Å^2 for PP/PA6 respectively at the interface.

3. POLYMER IONICS

3.1. Poly(ethylene Oxide) Grafted Polymer

It is well known that an amorphous poly(ethylene oxide) (PEO) containing alkali metal shows high ionic conductivity. PEO is liquid-like in the low molecular region in which high ionic conductivity may be expected. It is, however, a crystalline polymer. A key to the practical use of PEO as a conductive material is to improve the mechanical strength as well as the conductivity.

Y. Isono, S. Annen *et al.*, Nagaoka University of Technology (3590, ES1407), prepared poly(styrene-b-*p*-hydroxystyrene-[g-ethylene oxide]-b-styrene)s. Poly(styrene-b-tert-butoxystyrene-b-styrene) was anionically synthesized followed by the elimination of a tert-butyl group with HBr. Phenolic hydroxy group was then converted to potassium oxide. Ethylene oxide was finally anionically polymerized with potassium oxide as initiator. Number average molecular weights of PS, PHS and PS blocks were 47,000, 31,000 and 50,000 respectively in the backbone triblock copolymer. PEO chains were grafted onto the centre block. Films cast from 1,4-dioxane solutions showed clear microdomain structures dependent upon the composition ratios; lamellar structure for 20-30% of PEO, cylindrical structure of PS in PEO matrix for 40-50% of PEO, and spherical structure of PS in PEO matrix for greater than 50% of PEO. In the block-graft copolymer, grafted chains tend to form a matrix at rather low composition. These structures were preserved after the addition of $LiClO_4$ or $LiClO_4$/PEO oligomer (M = 600). Crystallization of PEO was restrained by the grafting or the addition of Li salt. This is very important because amorphous PEO is necessary for polymer ionics. When the degree of polymerization of a graft chain exceeded a critical value, typically about 40, such an effect was not observed. The samples with 40-60% of PEO were found to possess high storage modulus, 10^7-10^9 dyne/cm^2 up to 100°C. These showed high ionic conductivity as expected; 60% PEO sample showed $10^{-4.5} - 10^{-4}$ S/cm at 40-80°C. The 1:1 blend of this and PEO oligomer $10^{-3} - 10^{-1.5}$ S/cm at 40-80°C.