Nanophase-Separated Synchronizing Structure with Parallel Double Periodicity from an Undecablock Terpolymer

Jun Masuda, Atsushi Takano, Yutaka Nagata, Atsushi Noro, and Yushu Matsushita[*]

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-8603 Japan
(Received 27 September 2005; published 29 August 2006)

A new nanophase-separated structure with parallel double periodicity has been identified for an undecablock terpolymer in bulk. The polymer includes two long poly(2-vinylpyridine) (*P*) chains on each end, with five short polyisoprene (*I*) and four short polystyrene (*S*) chains at the center. This polymer exhibits a hierarchical lamellar structure with two crystallographic periods: 88 nm and 16 nm. The 88 nm period includes one thick *P* lamella and five thin *I-S-I-S-I* lamellae, of extremely high orientation.

The hierarchical nature of materials can be seen in materials of many classes including the hard crust of the surface of Earth [1], soft biological materials such as muscles and collagen [2,3], synthetic organic materials such as dendrons and macrocyclic molecules [4,5], and inorganic materials such as minerals and metal oxides [6]. It is well established that hierarchy can be defined by the relationship of space and time with respect to components within the material.

Complex organic polymers could be useful as soft materials because they exhibit many characteristic self-assembled structures on a mesoscopic length scale, where a variety of functions are involved [7]. Among these complex polymers, block and graft copolymers are typical examples exhibiting periodic nanophase-separated structures in the spatial range from several nanometers to several hundred nanometers. In recent years these copolymers have been the subject of intense investigation since their mesoscopic patterns can be easily controlled through adjustment of molecular parameters, such as molecular weight [8,9], composition [10,11], and chain connectivity [12].

Observation of hierarchical structures from a block copolymer system was first reported by ten Brinke *et al.* [13,14], where the complex structure with a two length scale was observed for a block copolymer and low molecular weight compound which can be weakly connected by intermolecular interactions. The structure was reported to have two different kinds of periodicity, for example, one is a regular lamellar period from the block copolymer, while the other is the short period formed by the bound low molecular weight compound within a lamella whose repeating direction is perpendicular to that of the former lamellae. On the other hand, the structures with double length scale periodicity were predicted by theoretical calculations using a self-consistent theory for a multiblock copolymer system [15] and a linear-alternating nonablock copolymer system [16]. The structural change with tem-

perature (also known as the interaction parameter), was predicted and argued. However, the number of short lamellar phase was fixed at one and possible variations were not discussed in those theories.

In fact, we recently observed that an undecablock copolymer of the *SISISISIS* type, having two long tail polystyrene (*S*) blocks and nine short blocks, merely exhibits the hierarchical lamellar structure whose repeating unit is composed of one thick *S* lamella and thin *I-S-I* three-layered lamellae, though the quality of the long-range ordering and the degree of orientation were fairly poor [17]. In this Letter, we present a study of lamellar organization in a new system composed of a different undecablock polymer, *PISISISISIP*, where the end poly(2-vinylpyridine) (*P*) blocks are incompatible with both the *I* and *S* blocks. The current study is of a much broader scope than the work reported in Ref. [17] in several respects below.

First, the design and use of the new polymer is a rational one, based on the following qualitative consideration of interactions involved in such a system. That is, *P* is highly incompatible with the adjacent component *I* [18]; therefore, by adopting this design we create a well-oriented lamellar structure different in detail from that observed in Ref. [17], although the structure observed therein also of double periodicity. Second, we propose a geometric model, which rationalizes the observation. The model is based on the counting of possible conformations of the constituent polymer molecules that are associated with a given number, *N*, of centered, short lamellae formed by the *I* and *S* blocks. It is proposed that the observed lamellar structure with *N* of 5 is consistent with the model which allows the largest number of conformations when *N* equals five. Third, this geometric model is further used in a general analysis of a range of block polymers of $P\text{-}(IS)_n\text{-}I\text{-}P$ structures with *n* varying from 1 to 7 in terms of their tendency to form center *N*-layered lamellar structures, where *N* ranges from 3 to 15. This analysis leads to

predictive results, with the implication that we can control and design the complex hierarchical structures having double periodicity by this simple method.

The undecablock terpolymer was synthesized by a coupling reaction of a telechelic nonablock copolymer of the *ISISISISI* type with functional double bonds on both ends and a living polymer of poly (2-vinylpyridine) [17]. The desired undecablock terpolymer was isolated from the reaction mixture by a gel permeation chromatography (GPC) system since two parent polymers were included as contaminants. By careful characterization, we confirmed that the total molecular weight of the terpolymer is $339k$ with molecular weight distribution of 1.03 and the volume fractions of P, I, and S chains in bulk are 0.53, 0.26, and 0.21, respectively. The sample film for morphological observation was prepared by solvent casting from a dilute solution of THF followed by drying and annealing. The nanophase-separated structure was observed by a transmission electron microscopy (TEM) and small-angle x-ray scattering (SAXS).
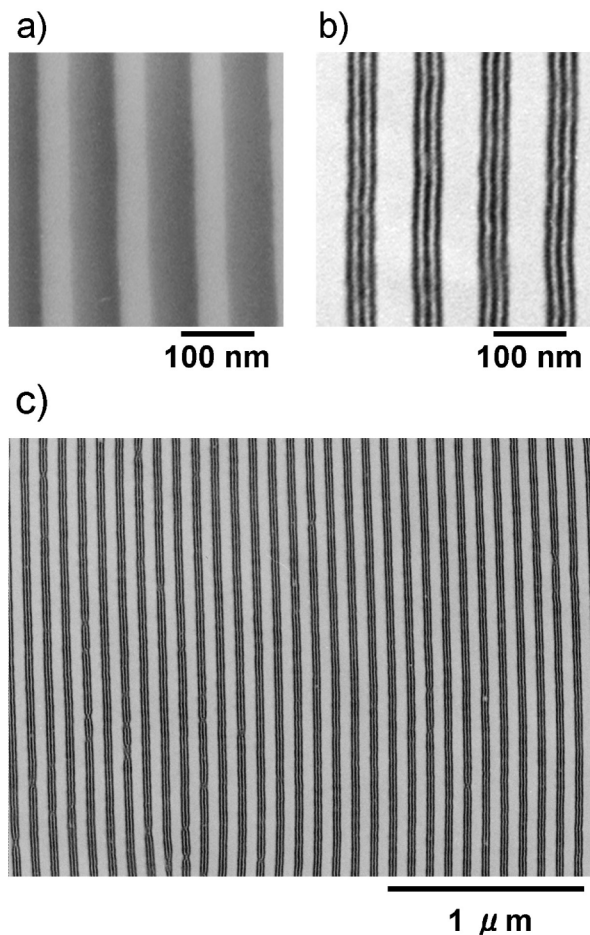

FIG. 1. Bright field transmission electron micrographs of the *PISISISISIP* undecablock terpolymer. Sample specimens are ultrathin sections cut from solvent-cast and annealed film. Ultrathin sections were stained with iodine for (a) and osmium tetroxide for (b) and (c).

Figure 1 compares the TEM micrograghs for the terpolymer specimens stained with iodine [Fig. 1(a)] and OsO$_4$ [Fig. 1(b)]. Iodine is known to selectively stain the P phase, while OsO$_4$ stains I phase effectively with negligible staining of the S phase. As seen in Fig. 1(a), the P chain forms a simple lamellar phase and it appears as if the other two components provide another simple lamellar phase. However, as seen in Fig. 1(b), the I and S chains actually phase separate into five thinner lamellae within a large-scale lamella. Consequently a very regular lamellar-in-lamellar structure along the same direction has been formed. The hierarchical lamellar structure consists of one thick P lamella and five thin lamellae, consisting of three I lamellae and two S lamellae. Thus, two interactions over hierarchically different length scales are generated simultaneously to form a synchronized structure with double periodicity from the present undecablock terpolymer. Furthermore, the very wide view of this structure at lower magnification is shown in Fig. 1(c), indicating that the degree of lamellar orientation and the periodicity of lamellae are both surprisingly high and that all of the mixed lamellar microdomains are composed of five thin lamellae. No other assembly modes can be recognized.

In Fig. 2(a), a two-dimensional x-ray diffraction pattern is displayed. It is apparent from this anisotropic pattern with high intensity dots along vertical plane, that the lamellae are regularly oriented parallel to the film surface because the sample film was set horizontally. Figure 2(b) shows a sector-averaged intensity pattern within the detector area of $\pm 5°$ from the longitudinal central line. In the intensity curve shown in Fig. 2(b), integer order diffracted peaks are seen up to at least the seventh order, reflecting a highly ordered lamellar structure with a longer repeating distance, which was estimated to be 88 nm by applying Bragg's condition. At the upper part of this figure, intensities in the lower q region and the higher q region were enlarged and compared. There is one additional peak, designated as 1̲, located between the fifth and the sixth peaks for larger lamellar structure and its higher order peaks 2̲ and 3̲ can be seen in the higher scattering range. These peaks arise from the lamellar structure in the shorter hierarchical level and the repeating distance was estimated to be 16 nm, which is a reasonable size considering the molecular weight of the short blocks.

Thus, the feature of the newly found hierarchical lamellar structure was precisely clarified. In Fig. 3 possible molecular conformations of molecules in this lamellar structure were schematically represented. The undecablock terpolymer must satisfy two conditions (i) I chains adjacent to long P chains must possess a bridge conformation since S as well as I is evidently incompatible with P and (ii) the densities of the chains within thin lamellae must not change appreciably to retain constant segment density for both the I and S phases.

As previously mentioned, an undecablock copolymer of the *SISISISISIS* type predominantly forms the "three-layered structure," while the present terpolymer does not.
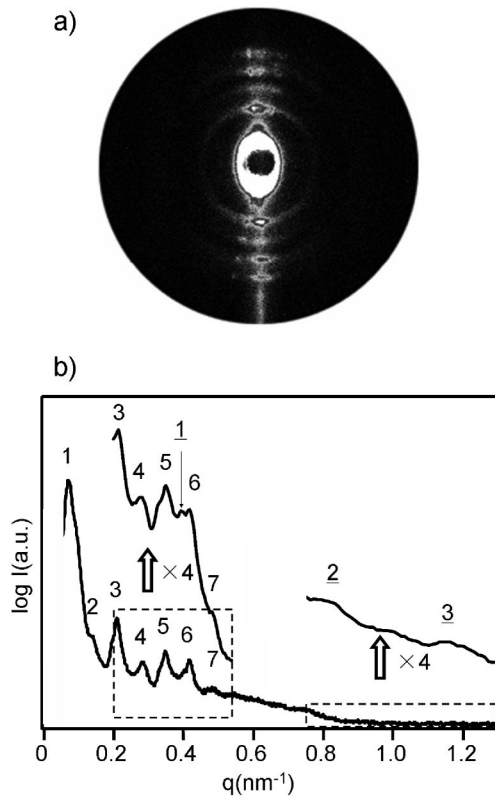
FIG. 2. Small-angle x-ray scattering intensities. Film specimen is placed horizontally and x-ray incidents parallel to the film surface. (a) is a two-dimensional map on an imaging plate and this figure shows that lamellar orientation is extremely high. (b) shows the sector-averaged intensities within the sectors along the vertical line as a function of $q(= 4\pi \sin\theta/\lambda)$, where λ is the wavelength of x-ray and 2θ is the scattering angle.

These results are directly related to the condition (i), because mixing of the S chains of the terpolymer into the P phase is inhibited, while any of the short S chains in the copolymer can be mixed into the thick S lamellae of the long chains. Accordingly, all of the S chains must be squeezed into one centered thin lamella in the "three-layered structure" which could cause instability in the structure in opposition to the condition (ii) because of the increase in segment density for the S phase. Therefore, it is reasonable to expect that if the copolymer has three thin lamellae, the terpolymer should have five thin lamellae. As a result, the effect of long-range interaction for two component system is somewhat vague, while two competing interactions over long and short ranges are separated out for the present terpolymer.

Figure 3 also shows the "nine-layered structure" in 3(c). It becomes unfavorable for the terpolymer to realize condition (ii) if the number increases from five. The number of short chains at the centered S layer becomes low for the seven-layered and nine-layered structures, since the molecules having loop-type conformations are hard to reach the center of thin layers as expressed in Fig. 3(c) so that these structures are actually inhibited.
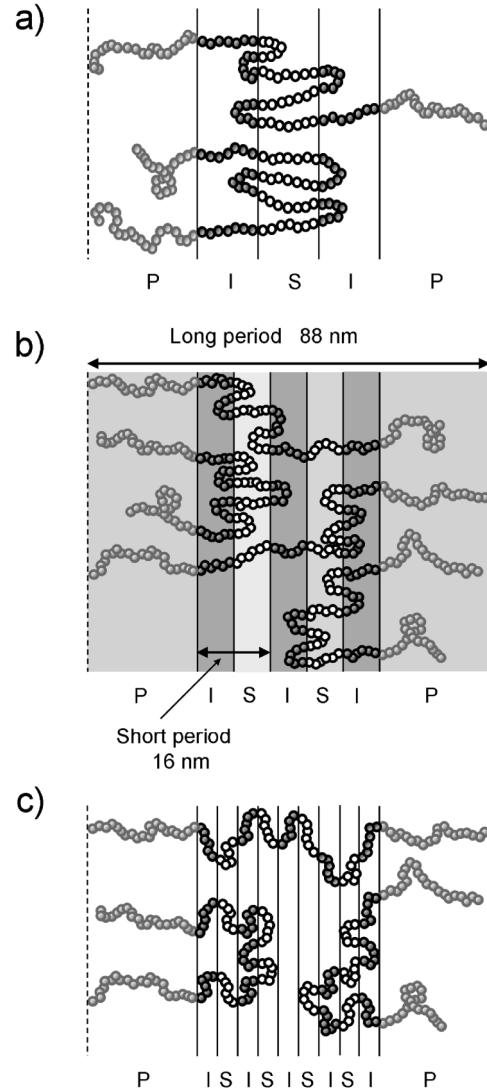

FIG. 3. Possible molecular conformations of the undecablock terpolymer in lamellar nanophase-separated (a) three-layered, (b) five-layered, and (c) nine-layered structures.

These arguments should provide important reasons for the present observation that the "five-layered structure" was uniquely observed. In short, the assemblies other than this manner might be suppressed during the formation of the structure and actually transformed into this structure to reduce the free energy of domain formation.

It is worthwhile to compare the predominance of the number of sublayer for the general multiblock terpolymer of the $A(BC)_n BA$ type. Here we simply count the number of ways of distribution of molecules within a multilayered structure so as to search the layer number to minimize Boltzmann's factor. The numbers were investigated in a simple counting method and the results are compared with n up to 7 in Table I and the relative fraction, f, of the possible ways for every N-layered structures is compared in Fig. 4, where N denotes the number of short lamellae. One finds the system favors the three-layered structure

TABLE I. Comparison of the numbers of the possible ways for N-layered structures formed by multiblock terpolymers of the $A(BC)_nBA$ type.

n N	1	2	3	4	5	6	7
3	2	4	8	15	30	59	123
5		3	9	27	83	229	701
7			6	20	68	218	773
9				15	50	160	616
11					43	128	483
13						119	431
15							420
Total	2	7	23	77	274	913	3547

when n equals 2 [19], and the five-layered structure becomes the most favorable in the case n equals 3. Its superiority over the other layered structures lasts up to n equals 6, the present undecablock terpolymer with n of 4 being included, then seven-layered structure becomes favorable when n equals 7, which is actually heptadecablock terpolymer.

These results are very interesting because it means we can control and design the complex hierarchical structures having double periodicity by this simple method on the basis of the present molecular design. The present result for undecablock terpolymer is quite consistent with this very simple estimation. As mentioned above, no theoretical works have been given on this matter; however, a theoretical argument will appear soon [20].

In summary, we have succeeded in forming a nanophase-separated synchronizing structure with parallel double periodicity by preparing an undecablock terpolymer of the $ABCBCBCBCBA$ type, where the component A is strongly incompatible with the component B. The degree
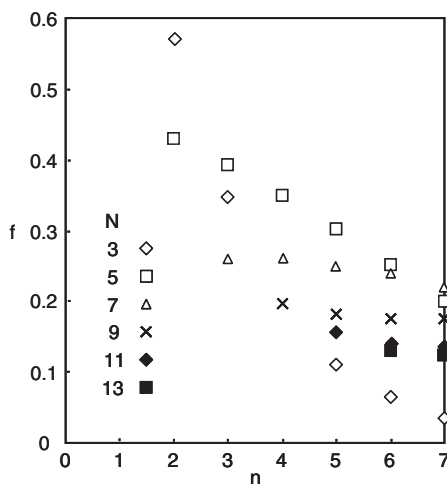

FIG. 4. Variation of relative fraction, f, for the N-layered structures as a function of n for multiblock terpolymers of the $A(BC)_nBA$ type. The actual counted numbers of possible ways are shown in Table I.

of lamellar orientation is extremely high and the long-range ordering is excellent for the complex lamellar structure formed by the present terpolymer due to two competing interactions over different length scales. Furthermore, a model was proposed to predict the number of short lamellae for general multiblock terpolymer of the $A(BC)_nBA$ type with n varying from 1 to 7. The present experimental result is consistent with the predicted one based on this model, and it can be applicable to the current multiblock terpolymer series.

*Corresponding author.
Tel: +81-52-789-4604
Fax: +81-52-789-3210
Email address: yushu@apchem.nagoya-u.ac.jp
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[18] According to the recent neutron scattering experiments based on poly (isoprene-d_8-block-2-vinylpyridine) with M of 4k (by SEC) at the temperature up to 220 °C, we were not able to reach the disordered state under the condition employed. This result means that χ_{IP} is much more higher than χ_{IS} and χ_{SP}. (Unpublished data.)
[19] An experiment was carried out recently on a hexablock terpolymer of the $PISISI$ type, where the length of P chain is much longer than the others, and a 3-layered structure was observed. This molecule is similar to the $P(IS)_2IP$, that is, with n of 2 for the present case, though it is not comparable exactly. (Unpublished data.)
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