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Macrolattice formation in amorphous associating polymers

Yi. Shen
Exxon Research & Engineering Company, Annandale, New Jersey 08801
and Department of Physics, The City University of New York, New York, New York 10036

C. R. Safinya and L. Fetters
Exxon Research & Engineering Company, Annandale, New Jersey 08801

M. Adam
Centre d'Etudes Nucléires de Saclay, 91191 Gif-sur-Yvette, France

T. Witten
James Franck Institute, University of Chicago, Chicago, Illinois 60637

N. Hadjichristidis
Department of Chemistry, University of Athens, 10680, Athens, Greece

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We report on high-resolution synchrotron x-ray scattering studies of melts of a series of linear polyisoprenes with highly polar sulfozwitterion groups at one end. Studies were carried out for six different molecular weights between 2200 and 28 000. For low molecular weights between 2200 and 4650, we observe a lattice with the symmetry of a triangular array of cylinders. The lattice ordering is strong; the nominal domain size exceeds 5000 Å. A structural phase transition to a cubic (bcc) lattice with long-range order is observed to occur for melts with molecular weights between 4650 and 14 000. The lattice spacing increases over the molecular range between 83 Å (for $M_w = 2200$) and 224 Å (for $M_w = 28\,000$). In contrast to usual block copolymers, for these copolymers the long-range order sets in at extremely small volume fraction of ionic species, less than 1%.

I. INTRODUCTION

Bulk polymer fluids normally show no distinctive spatial order; their scattering structure factor is featureless at length scales comparable to the macromolecular size.[1] But modifications to the polymers can induce strong spatial ordering. The best known examples to date are "diblock" polymers in which two immiscible polymer chains are joined end to end. These diblocks phase separate locally to form spatially periodic domain structures with unit cells as large as the polymer coils.[2,3] The type of domain structure is apparently controlled by the proportion of each species in the diblock molecule: equal proportions yield lamellar domains while progressively unequal proportions yield the bicontinuous double diamond structure,[4,5] cylindrical, or spherical domains.[3] The domains in these latter cases may be thought of as micelles, with the minority species at the center and the majority tails radiating away from it.

The forces responsible for the ordered arrangement of these micelles are not well understood. Accordingly, it is of great interest to know what conditions are required for ordering. The mere assembly of several chains to make a micelle does not suffice to produce ordering. The case of star polymers illustrates this point. Fluids of star polymers with up to 18 arms show only the weakest short-range order,[6] and no sign of solidlike properties in their mechanical properties.[7] Likewise, "ionomers," which are polymer chains with ionic groups attached at sparse intervals, are known to form well-defined ionic micelles.[8–10] But only moderate short-range order occurs in these systems, even when the constituent polymers are virtually identical,[11] with ions only at the ends. Their x-ray structure factor shows a single broad peak.

We report here a strongly contrasting behavior in melts of polymers tipped with the zwitterion $N^+(CH_3)_2(CH_2)_3SO_3^-$. We have observed well-defined three- and two-dimensional crystal structures with five Bragg peaks. In contrast to block copolymers, these systems switch from spherical to cylindrical domains at an extremely small volume fraction of ionic species—less than 1%.

Similar ordering has recently been reported in other strongly incompatible polymer systems. By putting a short sequence of strongly polar monomers at the end of a nonpolar backbone, short-range order of apparently lamellar or cylindrical type has been observed by scattering and microscopy.[12,13] The distinctive feature of our results is the clear-cut long-range order. The regularity of our domains allows us to deduce detailed information about the domains which was not previously obtainable. It also gives new information about the conditions necessary for long-range order. The ordered state we report should produce distinctive rheological behavior. Indeed such behavior was reported in a previous report[7] using the same materials we study.

The structures that we have found for these melts are analogous to those found in both thermotropic and lyotropic crystalline systems. For example, for low molecular weights, we find a crystalline phase consisting of cylindrical aggregates organized on a two-dimensional hexagonal lattice. This phase is structurally similar to the hexagonal phase of thermotropic discotic liquid crystals,[14] or the hexagonal phase of multicomponent lyotropic liquid crystals consisting of surfactants in solution.[15]

The paper is organized as follows. Section II gives the details of the samples and the x-ray scattering spectrometer used for the studies. Section III discusses the chemical structure of the polymer melts used. We present and discuss the experimental scattering results in Sec. IV.

II. EXPERIMENTAL TECHNIQUE

The high-resolution x-ray scattering studies were carried out on the Exxon beam line X10A at the National Synchrotron Light Source (NSLS). An 18-kW Rigaku rotating anode x-ray generator was also used in the early stages of the investigation. The experimental layout is shown schematically in Fig. 1. The out-of-plane resolution which was achieved by using slits was set at 0.005 Å^{-1} described in terms of the half width at half maximum (HWHM) of the Gaussian resolution function. The in-plane resolution was achieved by the combination of the monochromator which consists of a double-bounce Ge(111) crystal, and a flat Ge(111) crystal as an analyzer. This configuration yields a sharp in-plane Lorentzian resolution function with a width of 0.0002 Å^{-1} (HWHM), and allows us to measure domain sizes as large as 5000 Å.

The sample cell containing the polymer melts had a cylindrical volume which was 1 mm thick with a circular cross section of diameter 10 mm. The 1 mm thickness is approximately the $1/e$ absorption length for these melts for the 8-keV photons used in the experiments.

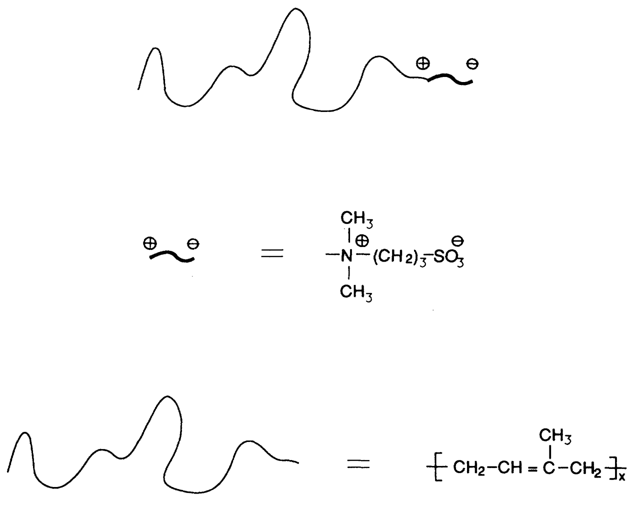

FIG. 2. A schematic zwitterionic polyisoprene molecule. The polyisoprene is represented by the thin wiggly lines and the zwitterionic sulfo-head group by the short thick line.

III. EXPERIMENTAL SYSTEMS

The high-resolution x-ray scattering studies were carried out on six zwitterionic polyisoprene melts with molecular weights (M_w) of 2200, 3850, 4650, 14 000, 23 000, and 28 000. The zwitterionic polyisoprene polymers were prepared by reacting the amine-functionalized polymers with propane sultone. For these polymers, the zwitterion end groups cause aggregation in hydrocarbon solvents for polyisoprene. A schematic configuration of the molecule is shown in Fig. 2. The description of the polymer preparation, characterization, and functionalization conditions is given elsewhere.[16] For our purposes, we point out that all of the zwitterionic polyisoprenes had near monodisperse molecular weight distributions.

The polymer chains were measured by size exclusion chromatography (SEC) in tetrahydrofuran, and low-angle laser light scattering in tetrahydrofuran and cyclohexane

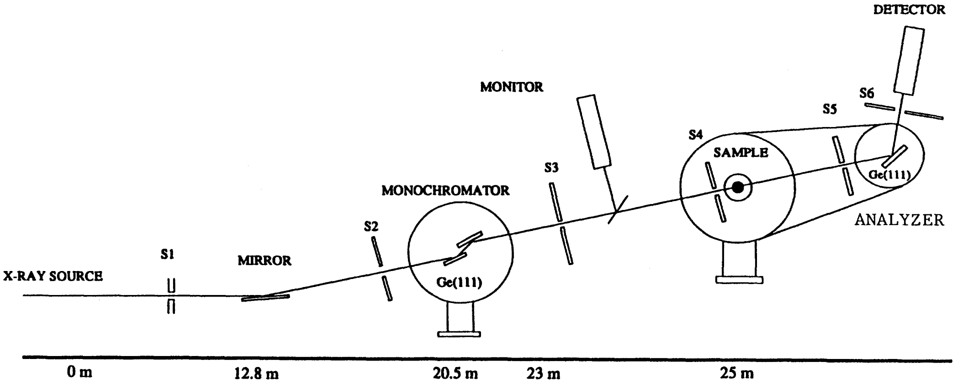

FIG. 1. The experimental layout at the NSLS beam line X10A. The x-ray beam was focused in the horizontal plane by an upstream bending mirror and then monochromated by a double-bounce Ge(111) crystal. The analyzer was a single-bounce Ge(111) crystal. The out-of-plane resolution was achieved by three sets of slits (S1, S3, S5). S1 and S3 define the spot size at the sample position. S2, S4, and S6 are primarily used to cut out stray air scattering.

TABLE I. Tabulation of the experimental results and some relevant parameters. The molecular weights of the six samples are listed in the first column, followed by the corresponding end-to-end distances and radii of gyration of the polyisoprene melts. The fourth column indicates the lattice spacings measured by the x-ray experiment, followed by the aggregation numbers deduced from the molecular weights and the lattice spacings. The last column shows the thickness of the space occupied by the polyisoprene tails for the two-dimensional hexagonal lattices shown schematically in Fig. 2.

M_w	R_0 (Å)	R_g (Å)	Lattice Spacing (Å)	Aggregation numbers	Shell thickness (Å)
2200	38	15.5	81	1.4 molecule/Å	36.5
3850	50	20.5	96	1.14 molecule/Å	43
4650	55	22.5	102	1.06 molecule/Å	46
14 000	96	39	156	75 molecule/aggregate	
23 000	123	50	204	101 molecule/aggregate	
28 000	135.5	55	224	110 molecule/aggregate	

with a chromatrix KMX-6 photometer at $\lambda=633$ nm (Table I). The refractive index increment needed for the molecular weight calculations was measured for each of the samples in the same solvents using a chromatrix KMX-16 differential refractometer at $\lambda=633$ nm. Samples were prepared by spooning the viscous polymer melt into the samples holders with a spatula. After the x-ray synchrotron experiments were carried out we checked for radiation damage to our samples (via SEC) which we found to be undetectable.

IV. RESULTS AND DISCUSSION

In the synchrotron x-ray scattering studies two distinct structures with long-range order were observed. For the three lower-molecular-weight samples, we find a two-dimensional hexagonal lattice while the latter three molecular weight melts exhibited a three-dimensional cubic lattice. The appropriate crystallographic mosaic scans showed that all six melts consisted of randomly oriented crystalline domains.

Figure 3 shows, on a logarithmic intensity scale versus αq (α is a rescaling factor), typical scattering profiles for longitudinal scans through the first five lattice reflections for the three smaller molecular weight samples. The profiles of the samples with molecular weights of 3850 and 4650 have been shifted by $\alpha=1.19$ and 1.26, so that their first peak overlaps with the profile for the sample with a molecular weight of 2200. The peaks can be indexed on a two-dimensional hexagonal lattice of tubes where the peaks correspond to the (10), (11), (20), (12), and (30) reflections of the lattice. The lattice spacings which are tabulated in Table I are 81, 96, and 102 Å for the samples with molecular weights of 2200, 3850, and 4650, respectively. The resolution-limited peak widths indicate that the crystalline domain sizes are of order 5000 Å and probably larger. Increasing the molecular weight has little effect other than to shift the scattering pattern to lower q because of the increase in the lattice spacing.

The observed diffraction suggests a two-dimensional lattice formed by the close packing of tubular aggregates, as shown in Fig. 4. A stacking of the dipolar head groups forms the core of the tubelike structure with the relatively stretched polyisoprene tails forming the outer shell. Molecular mechanics calculations[17] also suggest that tubelike structures would result in an energetically favorable aggregate. As we show in Fig. 4, in a tube structure, the dipoles attached to the head groups arrange themselves in an antiparallel configuration thus minimizing the electrostatic interactions. The scattering (form factor) is proportional to the square of the relative electron density difference of the polyisoprene chain region and the head group core region that contains the zwitterions. From Fig. 3, we see that the first minimum in the scattering occurs at $q \geq 0.24$ Å^{-1}. This minimum in the form factor is consistent with a cylindrical region for the head group region with a diameter of about $\pi/0.24 \sim 13$ Å, which corresponds to the size of zwitterions attached at

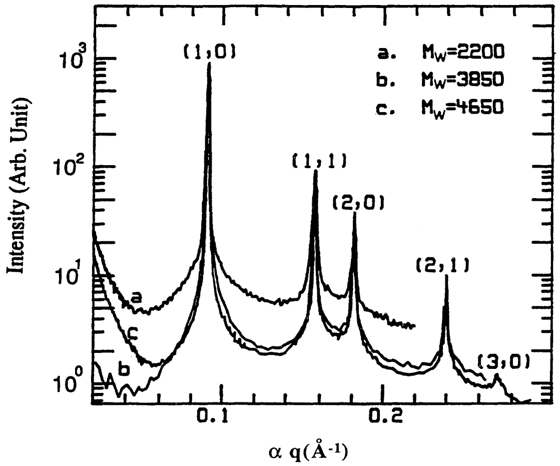

FIG. 3. The x-ray scattering profiles of the polycrystalline samples with molecular weights of 4650, 3850, and 2200. The figures are plotted on a logarithmic intensity scale (with arbitrary units) vs the rescaled scattering vector αq in Å^{-1}. The profiles of the samples with molecular weights of 3850 and 4650 have been shifted by a factor α to make the first peak positions overlap ($\alpha=1.00$, 1.19, and 1.26 for the samples with molecular weights 2200, 3850, and 4650, respectively). The peaks are resolution limited and indexed on a two-dimensional hexagonal lattice. The peaks correspond to the (10), (11), (20), (12), and (30) reflections.

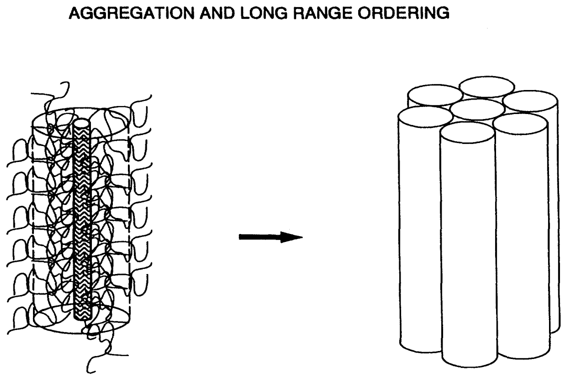

FIG. 4. A schematic representation of the formation of two-dimensional lattices of the close-packed tubular aggregates. The tubelike aggregate has a polar core region where the zwitterionic heads reside surrounded by the polyisoprene tails which are relatively stretched out.

one end.[18] Although the polydispersity of the radius is expected to be small, the powder averaging of the scattering intensity smooths out the minima.

The domain sizes that were observed for these lower-molecular-weight samples were normally larger than our spectrometer resolution. However, in one instance for the sample with $M_w = 2200$, the initially prepared sample had domain sizes less than our resolution. The width of the scattering profile for this sample, which is shown as the solid curve in Fig. 5, was substantially broader than our resolution. For these lower-molecular-weight samples, we found that annealing the sample, which consisted of keeping the melt at high temperatures ($T \sim 120\,^{\circ}\mathrm{C}$) for one or two days, would result in a still unoriented sample, but consisting of much larger domain sizes. The dashed curve in Fig. 5 is the profile for the annealed sample which gives resolution-limited peaks.

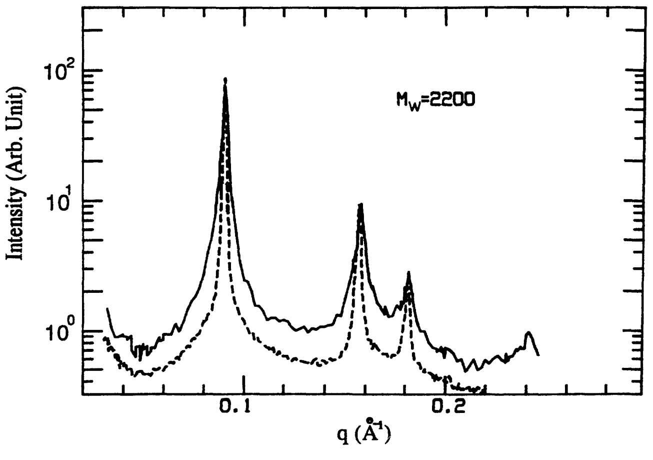

FIG. 5. X-ray scattering profiles plotted on a logarithmic intensity scale (with arbitrary units) vs q (Å^{-1}); the solid curve is the scattering profile of the sample with molecular weight of 2200 before the annealing process and the dashed curve after annealing at about 390 K for four days.

A different structure is observed for the samples with molecular weights of 14 000, 23 000, and 28 000. Figure 6 shows, on a logarithmic intensity scale versus αq, typical scattering profiles for longitudinal scans through the first five lattice reflections for the three larger molecular weight samples. The profiles for the samples with molecular weights of 23 000 and 28 000 have been shifted by $\alpha = 1.31$ and 1.44, so that the first peaks of all three samples overlap. The peaks can be indexed on a three-dimensional body-centered-cubic (bcc) lattice where the reflections correspond to the (110), (200), (211), (220), and (310) reflections (we are indexing on a cubic lattice). The peaks are resolution limited, indicating that the order is long range over macroscopic distances. Table I tabulates the expansion of the lattice as the molecular weight increases from 156 Å at $M_w = 14\,000$, to 224 Å at $M_w = 28\,000$. An important feature to note is that the Bragg peaks are sitting on top of a very large thermal diffuse scattering (TDS) component. This is in striking contrast to usual solids where the TDS component is many orders of magnitude smaller than the Bragg components. The main reason for the difference arises from the very large lattice spacing ~ 200 Å, about two orders of magnitude larger than the lattice spacing of an ordinary solid. Since the ratio of the intensities of the Bragg to TDS components is proportional to N,[19] the number of unit cells in the scattering volume, the TDS component is amplified in systems with very large lattice spacings. In principle, by analyzing the TDS component of the scattering one will obtain the Debye-Waller factor which is in turn related to the elastic constants of the lattice. The same behavior has been recently observed in

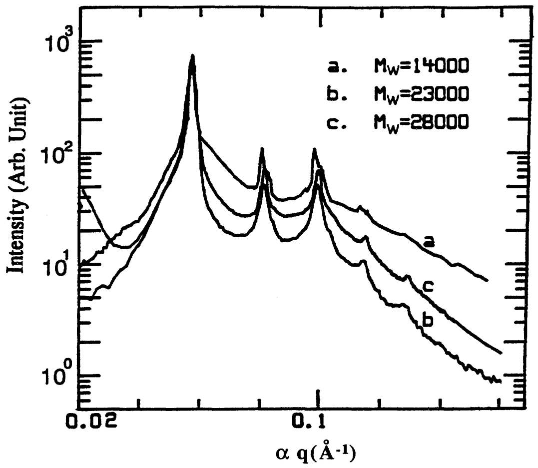

FIG. 6. The scattering profiles of the samples with molecular weights of 14 000, 23 000, and 28 000, plotted on a logarithmic intensity scale vs the rescaled scattering wave vector αq. The profiles of the samples with molecular weights of 23 000 and 28 000 have been shifted to make the first peak positions overlap ($\alpha = 1.00$, 1.31, and 1.44 for the samples with molecular weights 14 000, 23 000, and 28 000). The peaks are resolution limited and can be indexed on a body-centered-cubic lattice. They correspond to the (110), (200), (211), (220), and (310) reflections of a bcc lattice.

the (bcc) phase of charged polystyrene spheres (polyballs) suspended in water, where the long-range order is obtained due to the electrostatic repulsion.[20]

Another important feature in the powder patterns of these melts is that the (200) second peak has relatively low intensity compared to the third (211) reflection. The first five reflections can be indexed according to the reflections either for the simple-cubic or bcc lattice. If the lattice were simple cubic, the second and third peaks would correspond to the (110) and (111) reflections. In a powder sample, the multiplicity factor for each peak [arising from the fact that for example the (hkl) and $(\bar{h}kl)$ reflections are positionally degenerate in reciprocal space], would then favor the bcc over the simple-cubic structure because the ratio of the third to second reflection peaks is larger for the bcc (24/6) than for the simple cubic (8/12). Thus the relative intensities indicate that the lattice is most probably bcc.

We point out that the observation of a bcc lattice, which is normally what is observed whenever cubic order is established in copolymers, is not entirely understood. The bcc phase of charged polyballs suspended in solution occurs because of the longer-range Coulombic forces, and in the absence of these forces one obtains the usual close-packed structures. In the melts that we have studied we do not expect to have long-range forces present and based only on excluded volume effects we might expect a close-packed structure. However, the self-assembled aggregates that order into the bcc lattice in our systems are not hard spheres, but rather consist of partially stretched polymers with complicated near-neighbor interactions which are not entirely understood at present.

A set of samples of the same high molecular weights was also investigated at temperatures above about 80 °C. The result is plotted in Fig. 7. The comparison is between the scattering patterns of the sample with $M_w = 23\,000$ at room temperature (solid curve) and after warming up (dashed curve). We see that the peak positions have shifted and broadened which is indicative of a different structure with essentially short-range positional order. The "peak" positions are consistent with what one would find in a sample that contained a local face-centered-cubic structure. We found that once the disordered structure set in, the cubic lattice did not reappear at room temperature even after several days. The same trend was observed for the samples with molecular weights of 14 000 and 28 000. This is in contrast to what we found for the low-molecular-weight samples which always exhibit the long-range tubular structure, and seems to suggest that the long-range cubic structure that is found for the high-molecular-weight samples at room temperature may not be the ground state of the system.

The aggregation number and the corresponding lattice spacing for all of the six samples are tabulated in Table I. For the low-molecular-weight melts consisting of a two-dimensional lattice of tubular aggregates, the aggregation number is close to 1 per Å of length along the cylinder (see Fig. 4). For the high-molecular-weight samples with a bcc lattice, the aggregation number is around 100 per aggregate (see Table I). The aggregates which close pack to form the bcc lattice are formed by a core of the sulfonate groups and a shell of the polyisoprene tails. From Fig. 6, we see that the first minimum in the scattering occurs at $q \sim 0.12$ Å^{-1}. This minimum may be interpreted as that of the form factor for spherical domains with a diameter size of about $\pi/0.12 \sim 26$ Å.[18] To satisfy the electrostatic energetics, a large number of dipoles are not likely to aggregate into a spherical object. A more likely shape for the aggregates would consist of an approximately disk-shaped core for the zwitterionic end groups with a diameter of approximately 26 Å.

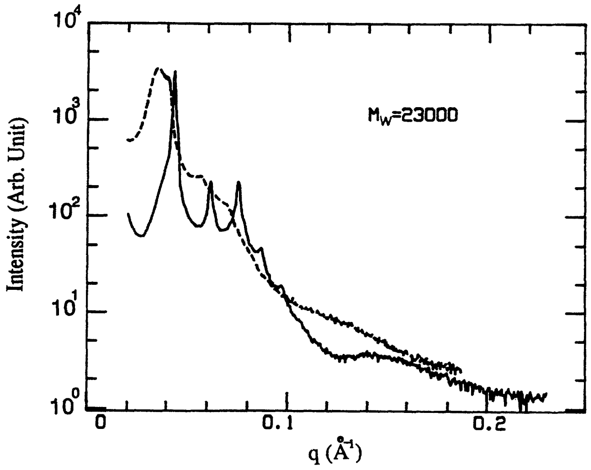

FIG. 7. The scattering profiles of the zwitterionic polyisoprene with molecular weight equal to 23 000 before (solid curve) and after (dashed) annealing at about 390 K for four days.

To summarize, we have used high-resolution synchrotron x-ray scattering techniques to elucidate the structure of polymer melts tipped at one end with a highly polar sulfozwitterionic group. We have found that for low molecular weights less than 5000, the polymer aggregates into a tabular structure with the tubes close packed on a two-dimensional hexagonal lattice with crystalline order. For larger molecular weights (> 14 000), the aggregates form a body-centered-cubic lattice with long-range order. In contrast to usual block copolymers, for these copolymers the long-range order sets in at extremely small volume fraction of ionic species, less than 1%.

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