critical value $C_\infty = 9$, and the more elaborate theory of Ronca and Yoon[12] also predicts order in the PTFE melt, it would be imprudent to conclude that PTFE must be ordered in the melt. Recall that all of the approximations that underpin eq 6 conspire to underestimate θ_c. Thus, while the inequality C_∞ (observed) $< C_\infty^{(c)}$ (critical) represents an unambiguous prediction of isotropy in the melt, the condition C_∞ (observed) $\gtrsim C_\infty^{(c)}$ (critical) is not immune from equivocation. Certainly, when their difference is on the order of only 20% caution is suggested both in interpreting existing data and in performing new experiments.

Thus, the lattice-model description of neat, semirigid chains yields a simple criterion for stable orientation order. The lower limit of chain stiffness can be compactly rendered as

$$C_\infty^{(c)} = [1 + \exp(-1/m)]/[1 - \exp(-1/m)] \quad (9)$$

by combining eq 6 and 8. This reduces to the result Flory[2] obtained some 30 years ago in the limit $m = 1$. The predictions of this relationship seem to be in good accord with observations. It can be most fruitfully employed to sort any homopolymer melt into isotropic ($C_\infty < C_\infty^{(c)}$), orientationally ordered ($C_\infty \gg C_\infty^{(c)}$), or borderline ($C_\infty \gtrsim C_\infty^{(c)}$) classes.

Registry No. Polyethylene, 9002-88-4; (*p*-phenylenediamine)·(terephthalic acid) (copolymer), 25035-37-4; (*p*-polyphenylene)·(terephthalamide) (SRU), 24938-64-5; poly(tetrafluoroethylene), 9002-84-0.

References and Notes

(1) This communication recapitulates an address delivered at the Symposium in honor of the late Professor P. J. Flory's 75th birthday at Stanford University in June 1985, some 2 months before his death. It is respectfully dedicated to his inspiring and celebrated contributions to the study of macromolecules.
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Sharpness of the Functionality Induced Structural Transition in Poly(styrene–isoprene) Star Block Copolymers

In a recent publication,[1] we reported on the solid-state morphology of poly(styrene–isoprene) star block copolymers having 30 wt % polystyrene outer blocks. The method of synthesis employed[2,3] enabled well-defined materials to be produced so that a systematic study of the effect of functionality (number of diblock arms) and arm molecular weight on the microstructure could be made. The most striking finding of this study was the discovery of a transition in equilibrium domain morphology from the normally observed cylindrical morphology (for this composition) to an ordered bicontinuous (OB) structure upon increasing the functionality of the star molecules. In addition, the functionality required to obtain the OB structure was found to decrease as the molecular weight of the diblock arm increased. For the samples having 10^4 molecular weight (outer) polystyrene blocks, 2- and 4-arm stars exhibited the morphology of hexagonally packed polystyrene cylinders in a polyisoprene matrix while 8-, 12-, and 18-arm stars exhibited the OB structure. In the OB morphology the polystyrene forms two distinct three-dimensional networks of short rods which are mutually interwoven but unconnected.[4]

The purpose of this work is to investigate the sharpness of this structural transition with functionality by studying the corresponding 5- and 6-arm-star copolymers. The experimental techniques utilized were transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and dynamic mechanical thermal analysis (DMTA). It was found that the 5-arm star exhibited exclusively cylindrical morphology while the 6-arm star was predominantly OB.

The star block copolymers were prepared by using the chlorosilane linking method which has been described in detail previously.[2,3] The chlorosilanes used for the linking reactions were 1-(methyldichlorosilyl)-2-(trichlorosilyl)ethane and 1,2-bis(trichlorosilyl)ethane. The pentafunctional material was synthesized from vinyltrichlorosilane and methyldichlorosilane following the procedures outlined elsewhere.[2,3] The hexafunctional linking agent was obtained from Petrarch Systems, Inc. The linking reactions were facilitated by the addition of tirethylamine following the polymerization of the isoprene segment of the diblock. It has been found[5] that the addition of amines or ethers, which are known[6] to cause disruption of poly(isoprenyllithium) aggregates, facilitates the linking event leading to the formation of star-shaped polymers.

The size exclusion chromatography measurements were done with the Waters 150C instrument with tetrahydrofuran as the mobile phase at 30 °C. The number-average molecular weights were determined in toluene at 38 °C with the Wescan membrane osmometer. The nomenclature used to describe the samples is as follows: SI 5/30/10 is a 5-armed poly(styrene–isoprene) star containing 30 wt % polystyrene outer blocks with molecular weights of 10^4. The same diblock precursor was used to prepare both the 5- and 6-arm stars for which the functionalities achieved were 4.9 and 6.0, respectively. The characterization results are given in Table I.

The details of the experimental methods used for TEM, SAXS, and DMTA have been given elsewhere.[1] Briefly, the 1-mm-thick samples were prepared by slow casting from a 3 wt % solution in toluene, a nonpreferential solvent for polystyrene and polyisoprene,[7] over a period of 1 week followed by 120 °C annealing under high vacuum for 1 week. This sample preparation technique was used in order to obtain, as nearly as possible, thermodynamic equilibrium structures. Thin sections for TEM were obtained by cryoultramicrotomy at −110 °C followed by osmium tetraoxide vapor staining. SAXS patterns were obtained with a Kratky camera equipped with a Braun one-dimensional position-sensitive detector. The SAXS data were corrected for sample absorption, wire sensitivity, and parasitic scattering. Slit-length desmearing was done by using Vonk's FFSAXS Version 3 program.[8] Mechanical analysis was performed with a Polymer Labs DMTA in the single-cantilever mode at a frequency of 1 Hz and a scan rate of 5 °C/min.

The electron micrograph in Figure 1a shows that sample 5/30/10 has the domain morphology of polystyrene cylinders in a polyisoprene matrix as evidenced by the axial and longitudinal cylindrical projections seen to the right

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Table I
Star Block Copolymer Characteristics

sample	polystyrene segment $M_n \times 10^{-4}$ [a]	polystyrene segment M_w/M_n [a]	diblock copolymers $M_n \times 10^{-4}$ [b]	diblock copolymers M_w/M_n [a]	wt % polystyrene [d]	star block copolymers $M_n \times 10^{-5}$ [b]	star block copolymers M_w/M_n [a]	star block copolymers f [c]
5/30/10	1.04	1.05	3.36	1.04	30	1.65	1.03	4.9
6/30/10	1.04	1.05	3.36	1.04	30	2.00	1.03	6.0

[a] Via size exclusion chromatography. [b] Via membrane osmometry. [c] Star functionality: $f = M_n(\text{star})/M_n(\text{arm})$. [d] NMR composition is actually 30.9 wt % PS. The series of materials in ref 1 varied from 29 to 31 wt % PS.

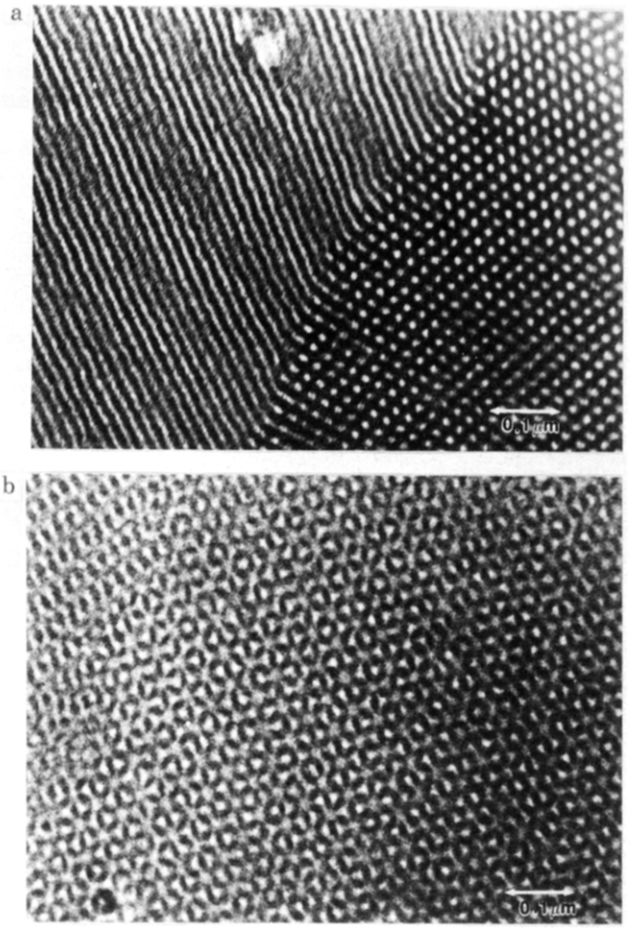

Figure 1. (a) Bright-field TEM micrograph of sample 5/30/10 showing highly ordered cylindrical morphology. (b) Bright-field TEM micrograph of sample 6/30/10 showing the (111) projection of the OB morphology.

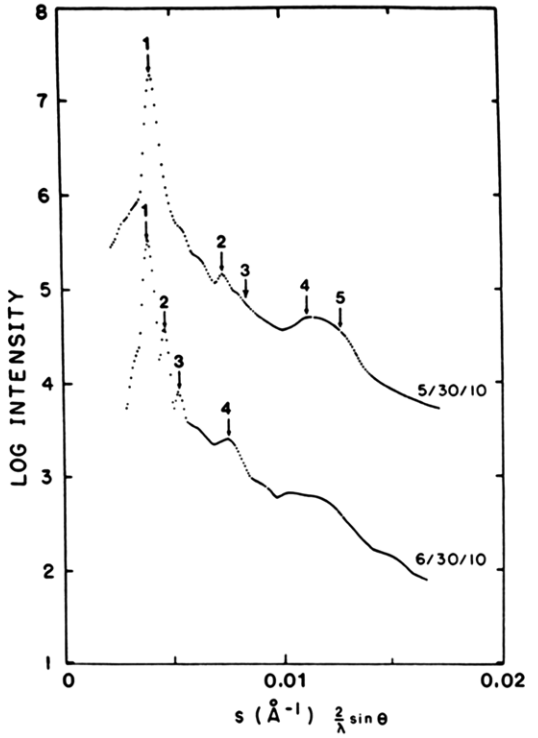

Figure 2. SAXS profiles for samples 5/30/10 and 6/30/10.

and left of the grain boundary, respectively. This is the same morphology observed previously[1] for samples 2/30/10 and 4/30/10. Sample 6/30/10, however, exhibits a distinctly different morphology as exhibited in Figure 1b. This is the same morphology seen previously for samples 8/30/10, 12/30/10, and 18/30/10, which we have referred to as the ordered bicontinuous (OB) structure.[1] While no OB structure was seen by TEM for sample 5/30/10, it was observed that a small number of grains (<10%) in the 6/30/10 sample exhibited cylindrical morphology. It should be remarked that Figure 1b shows only one of the many high-contrast, high-symmetry projections observed for the OB morphology, the detailed structure of which is the subject of another paper.[4]

The transition from the cylindrical to the OB structure is clearly evident in the SAXS patterns shown in Figure 2. Sample 5/30/10 (for which the SAXS intensities have been shifted upward by 2 orders of magnitude) exhibits two well-defined lattice peaks with the corresponding spacings in the ratio 1.00/0.58 as expected for hexagonally packed, cylindrical morphology. In addition, there is a much broader peak at higher angles which is due to the combination of the higher order (4th and 5th) cylindrical lattice peaks (whose predicted positions are marked by arrows) and the cylindrical form factor scattering. In contrast, sample 6/30/10 shows three distinct low-angle lattice peaks with the corresponding spacings in the ratio 1.00/0.83/0.73, as observed previously for the OB morphology.[1] Furthermore, an additional, somewhat broader, interference peak (labeled 4) is present at approximately the same position as the second lattice peak of sample 5/30/10. This peak likely arises from a combination of the fourth-order OB reflection and the second-order cylindrical reflection since both structures are known to be present in sample 6/30/10.

It has been observed that the star copolymer samples possessing the OB structure have a Young's modulus in the plateau region (−40 to +50 °C) about an order of magnitude larger than samples having cylindrical morphology.[1] This increased modulus was attributed to enhanced polystyrene continuity in the OB structure, which also manifests itself as a yield point during uniaxial extension. Detailed analysis of the mechanical properties of these star copolymers is the subject of a future paper.[9] The DMTA results of Figure 3 show that sample 6/30/10 has a plateau modulus about 7 times that of sample 5/30/10, consistent with the morphological transition observed by both TEM and SAXS.

In conclusion, the transition in equilibrium domain morphology from cylinders to ordered bicontinuous for the

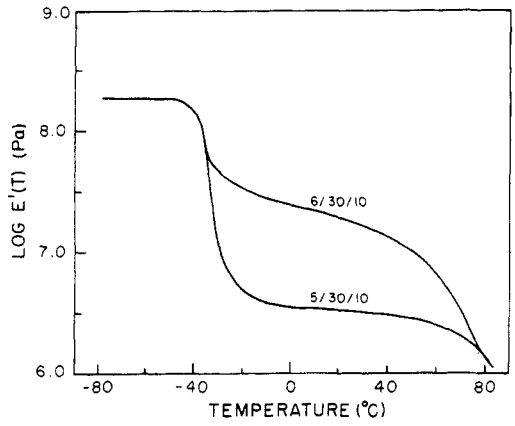

Figure 3. DMTA results for samples 5/30/10 and 6/30/10.

samples described herein is remarkably sharp, occurring at 6 arms as evidenced by TEM, SAXS, and DMTA.

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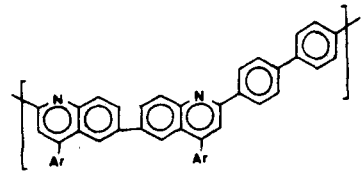
CORRECTIONS

Dirk M. Sutherlin and J. K. Stille*: Rigid-Rod Polyquinolines with Extended Aryl Ether Pendent Groups: An Approach to Solubility Enhancement. Volume 18, Number 12, December 1985, p 2669.

Structure **22** in Scheme VI (p 2671) is correctly represented as follows:



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