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Microphase Structure of Block Ionomers. 1. Study of Molded Styrene–4-Vinylpyridinium ABA Blocks by SAXS and SANS

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ABSTRACT: The bulk morphology of 4-vinylpyridinium-*b*-styrene-*b*-4-vinylpyridinium ABA block ionomers with short ionic blocks has been studied by small-angle X-ray scattering (SAXS) as a function of the length of both A and B blocks. A broad asymmetric intensity maximum is observed for each sample and is interpreted as arising from correlation between phase-separated ionic domains on a paracrystalline lattice. The length of the ionic segments is found to have a much stronger effect on the average characteristic distance than that of the nonionic ones. Comparison of spherical, cylindrical, or lamellar morphologies of the ionic domains points to a pseudocubic arrangement of elongated or flat large multiplets. The morphology of the nonionic precursors of some of the above materials has been studied by small-angle neutron scattering (SANS). The shapes of the scattering patterns were found to be generally similar to those of the corresponding ionic materials except for peak positions and relative widths.

Introduction

Ionic aggregation in ion-containing polymers, specifically ionomers, has been the subject of extensive interest in the last 20 years.[1-7] Ion pairs tend to aggregate in media of low dielectric constant, and the presence of these ionic aggregates modifies the properties of polymers profoundly; thus, it is of continuing interest to elucidate the relationship between the structure of the aggregates and the physical properties of the materials. Most studies have

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concentrated on polymers containing pendant ionic groups placed randomly along the polymer chain, the classical ionomers, in which two types of structures have been postulated: multiplets and clusters.[1] Unfortunately, the structure of the aggregates has proven to be extremely elusive. To date, there is no unanimity on the size and shape of the aggregates, on their distribution, or on their internal structures, in spite of the large number of studies devoted to the topic.

In the last few years, considerable attention has been devoted to the halatotelechelics, both of the two-arm and three-arm variety, in which a single group is placed at the ends of each polymer chain.[8-12] Depending on the valency of the cation used to neutralize the sulfonic or carboxylic group, either small independent chains or longer chains with regularly spaced ionic groups are formed. Although the ion content is very low, ionic aggregation takes place, as shown by thermal mechanical and structural studies. SAXS and other structural techniques have shown[11,13-15] that the ionic domains are small and of the multiplet type, i.e., with complete microphase separation between ionic and nonionic moieties. The size of these and, therefore, the functionality of the cross-links are a function of the relative size of the ionic groups and of the organic monomers. They are organized in liquidlike order with an average distance of the order of the end to end distance of the coiled prepolymer. Infinite lamellae[16] and small platelets[17] have also been proposed in some cases.

From a review on block copolymers where at least one of the blocks is ionic,[18] it appears that very little has been published on the morphology of block copolymers containing both ionic and nonionic sequences. Most of the knowledge is inferred from studies of the enhancement of physical properties of multiblock thermoplastic elastomers via the incorporation of ionic groups into the aggregating blocks. Polyurethane- and ionene-based elastomers have been particularly studied in this respect.[19-21] Morphological data on three-phase ionic block copolymers were also published along with the corresponding mechanical studies.[22,23] The effect of the ionic sequence on the mechanical properties is quite drastic. Broadening of the rubbery plateau and increase in modulus and tensile strength are among the effects observed. From the morphological point of view, the major finding of the above studies is that phase separation is enhanced by the incorporation of ionic sequences. In some works,[21,22] SAXS and electron microscopic evidence suggests that the size of the microphase-separated regions increases upon ionization of the block. In samples ionized in the solid state, aggregation of ionic domains to form bigger particles has been observed.[22] It must be mentioned, however, that the materials used in the above studies were all characterized by relatively complex morphologies even in the nonionic states.

Very recently, AB, ABA, and star block ionomers were prepared in different laboratories.[24-29] These are characterized by long nonionic block(s) and relatively short ionic sequence(s). The morphology of these materials does not seem to have been investigated, but some studies of their mechanical properties were conducted. In general, the same findings as mentioned above for the other ionic block copolymers were reported. For example, a thermomechanical investigation[29] of ionomers based on styrene midblocks (1000 units) with very short ionic end blocks (ca. 10–50 units) has shown, not unexpectedly, that the properties of the block copolymers differ markedly from those of the random copolymers of the same ion content. For the nonionic materials, the thermal and dynamic mechanical behavior observed is characteristic of normal block copolymers with longer sequences. Thus, samples having 24, 35, or 46 4-vinylpyridinium (4-VP) units showed an extended rubbery plateau on the storage modulus curves, indicating phase separation. For the ionic materials, a shoulder appeared on the low-temperature side of the polystyrene glass transition peak on the loss tangent curves, which was related to the glass transition of the water-plasticized ionic domains. All samples exhibited an extended rubbery plateau in the storage modulus curves, more so than was seen in the nonionic materials.

It appears that a detailed quantitative investigation of the effect of the presence of ionic sequences on the morphology of block copolymers is lacking.

This paper contains a report of the first experimental data on the structure of the block copolymers based on nonionic middle blocks and short ionic end blocks. The structure is explored as a function of both the length of the middle block and the length of the end block. An exploration of other relevant parameters is left for future publications.

Experimental Section

Materials. The preparation of the materials has already been described elsewhere.[29] Thus, only a summary of the procedure will be given here. The block copolymers were synthesized by sequential anionic copolymerization. A specially designed polymerization line allows the synthesis of series of ABA block copolymers with identical middle-block length and different end-block lengths. Four different series of samples have been prepared with polystyrene middle blocks of molecular weight ranging from 20 000 to 100 000 (200–1000 units) and with vinylpyridine end blocks ranging from 1000 to 5000 (10–50 units). For one series, the polystyrene block was perdeuterated in order to provide a good contrast for the SANS studies.

The vinylpyridine content of the resulting copolymers was determined by FTIR for the hydrogenated samples containing less than 10 mol % of vinylpyridine and by H NMR for the other hydrogenated samples. Nonaqueous titration of the vinylpyridine segments by perchloric acid was done for all samples except for the series with a polystyrene block of molecular weight 100 000 since gelation occurred after only a few milliliters of titrant had been added. The molecular weight of the polystyrene middle block was determined by gel permeation chromatography (GPC). The resulting precision on the number of repeat units per block is of the order of 5%. The polydispersity index was found to vary from 1.1 to 1.3 for the samples used in this study. A description of the materials studied is given in Table I, along with a tabulation of the results discussed below.

The nonionic copolymers were compression molded at about 130 °C and soaked in 80/20 (v/v) absolute ethanol/methyl iodide solution for 3 days under reflux in order to quaternize fully the 4-VP units. Under these conditions, the polystyrene matrix is swollen by the methyl iodide. The samples were then dried and remolded at about 140 °C. The disappearance of the 1414-cm^{-1} 4-VP IR band was taken as evidence of complete quaternization. Some samples were not compression molded before quaternization. Instead, the powder, obtained by precipitation of THF solutions of the polymers in water or ethanol/water mixtures, was directly soaked in the methyl iodide mixture. The quaternized powder was then dried and molded.

Scattering Experiments. SAXS experiments were conducted at LURE, Orsay, France, on the D22 beam line. Synchrotron radiation was provided by the DCI storage ring. A description of the spectrometer has been published.[30] It is a specialized spectrometer equipped with a double-crystal, fixed exit monochromator providing a beam of narrow energy range (resolution $\leq 0.1\%$) tunable from 4 to 15 keV (3–0.8 Å). The size of the beam at the sample is about 1 mm^2. The experiments were done under vacuum. The scattered radiation was detected with a gas-filled one-dimensional position-sensitive detector with a resolution of 135 μm. All samples were studied in the angular range from $q = 0.004$ to 0.14 Å^{-1} ($q = 4\pi \sin \theta/\lambda$; θ is one-half the scattering angle) with $\lambda = 1.55$ Å. Some samples were also studied in the

Table I
Morphological Parameters Obtained Assuming Spherical Domains on a Body-Centered Cubic Macrolattice

sample[a]	vol % endblock[b]	d,[c] Å	R, Å	$d' = d - 2R$, Å	calcd $\langle r_0^2 \rangle^{1/2}$ of free ps chain, Å	N	S/N, Å^2
Ionic Materials							
10-200-10	13.2	212	61	90		390	121
20-200-20	23.7	291	102	87	110	880	148
48-200-48	43.2	427	182	63		2100	200
9-480-9	5.36	245	52	141		270	127
17-480-17	10.0	336	88	160	170	660	148
48-480-48	23.7	630	220	192		3600	170
12-960-12	3.69	384	72	240		530	125
24-960-24	7.2	520	122	276	240	1200	150
35-960-35	10.5	680	182	316		2800	150
46-960-46	13.4	1000	290	420		9000	120
Nonionic Materials							
10-530-10	3.75	200	38	124		140	130
22-530-22	7.79	270	64	142	180	300	170
53-530-53	16.6	500	150	200		2000	180
PI-PS-PI[d]							
500-5000-500	16	1000	260	480	450	950	900

[a] Numbers indicate end-block length-middle-block length-end-block length, with lengths in numbers of monomer units. [b] Calculated with $\rho_{PS} = 1.05$ g/cm^3 and with $\rho_{P(4\text{-VP}\cdot\text{MeI})} = 1.6$ g/cm^3 for the ionic materials, taken as equal to mol % for the nonionic materials. [c] Body center to corner of cube. [d] By interpolation from experimental data from ref 31.

range from $q = 0.01$ to 0.34 Å^{-1} with $\lambda = 1.48$ Å. The resulting I vs q curves were corrected for incident beam decay, sample thickness, and transmission. The optics of the experimental setup was such that no desmearing of the curves was necessary. The background scattering from a polystyrene homopolymer or an empty sample holder was subtracted. The q resolution is of the order of 0.0004 Å^{-1}.

SANS experiments were conducted at Laboratoire Lêon Brillouin (LLB), Saclay, France, on the PACE spectrometer. This instrument is equipped with a mechanical monochromator tunable from 4 to 20 Å with a resolution of 10%. The scattered neutrons were detected with a multidetector made of 30 concentric rings. The cold neutron beam was provided by the Orphêe reactor. Experiments were done with a beam of neutrons of 7 Å. The angular range studied was from $q = 0.011$ to 0.12 Å^{-1}. The resulting I vs q curves were corrected for incident beam decay, sample thickness, and transmission. The background scattering from an empty sample holder was subtracted. Inhomogeneities in the sensitivity of the cells of the detector were accounted for by normalization of the resulting curves with the flat background signal of a water sample. The q resolution is of the order of 0.003 Å^{-1}.

Results and Discussion

Figure 1 shows typical data plotted as scattered intensity I versus q of X-rays for ionic material and of neutrons for similar nonionic material. Note first the striking similarity between the scattering profiles before and after neutralization. All samples show one broad intense main peak and either weak evidence of second- and third-order peaks best revealed in logarithmic plots or pronounced asymmetry on the high-q side. In the latter case, a simple deconvolution assuming a symmetric main peak yielded the additional peaks. However, the secondary peaks are too broad and their intensity too weak to be able to determine precisely their position. Whether the material is quaternized in the powder state or in the molded state does not affect the scattering pattern. The position of the main peak is a strong function of the end-block length and also, but to a lesser extent, of the middle-block length. In some cases, a small upturn is seen at very low q values in a range too limited to perform a Guinier analysis. No correlation could be made between the occurrence of the upturn and the architecture of the samples.

For the nonquaternized samples studied by SANS, it was found that the intensity at high scattering angle varies as q^{-4}. This indicates that the scattering pattern is due to a phase separation with sharp boundary and not to a correlation hole effect in a monophasic sample where the intensity would decrease as q^{-2}[31]. Since the nonionic materials were phase separated, we concluded that this should be true for the ionic ones also, given the higher driving force for phase separation present in the latter.

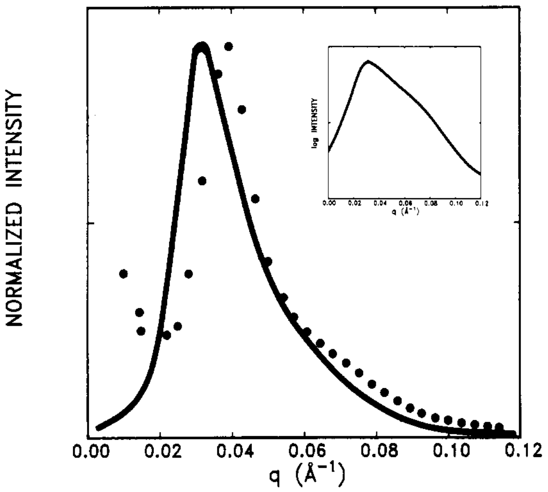

Figure 1. Scattering patterns of ionic material (9-480-9) by SAXS (line) and of nonionic material of similar architecture (10-530-10) by SANS (circles). The normalization factors are different.

The attribution of the first peak to the first maximum of the form factor for spherical domains leads to radii 5–10 times larger than the fully stretched length of the ionic blocks. For this reason, the first peak is interpreted as a interparticles correlation factor, most likely for a paracrystalline or a highly distorted lattice. In addition, the results of an ongoing study showed that upon preferential swelling of the polystyrene phase with a nonpolar solvent the peak moves to a lower angle, as would be expected from a correlation signal.

The shapes of the scattering patterns obtained by SANS for the three nonionic samples were similar to the patterns obtained by SAXS for quaternized samples of similar molecular architecture. The main differences lie in the peak positions and relative widths, which are compared in Table II. These results show that on quaternization the peak moves to lower angles, indicating larger characteristic lengths, and that it becomes wider. The larger line

Table II
Peak Positions and Relative Widths

sample[a]	q_{max}, Å^{-1}	$q_{1/2}/q_{max}$[b]
Ionic Materials (SAXS)		
9-480-9	0.032	0.71
17-480-17	0.023	0.80
48-480-48	0.012	0.70
Nonionic Materials (SANS)		
10-530-10	0.038	0.48
22-530-22	0.029	0.46
53-530-53	0.016	0.60

[a] Numbers have the same meaning as in Table I. [b] Width at half-height divided by q_{max}.

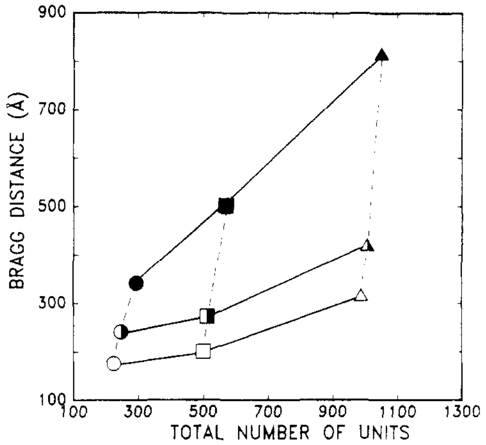

Figure 2. Bragg distance (d_{Bragg}) versus total number of repeat units in the chain. Middle blocks: 200 styrene units (circles), 480 styrene units (rectangles), 960 styrene units (triangles). End blocks: ca. 10 VP units (open symbols), ca. 20 VP units (half-filled symbols), ca. 50 VP units (filled symbols). Solid lines connect samples of similar numbers of VP units; dashed lines connect samples of identical number of styrene units.

width indicates a greater dispersity in either the distances between the scattering centers or their size; it could also be due to a decrease in the ordering of the macrolattice. But no dramatic changes occur in the morphology.

The application of Bragg's law to the first peak gives a characteristic distance, d_{Bragg}, which is directly proportional to the distance, d, center to center between scattering centers. This distance is plotted for the ionic materials in Figure 2 as a function of total number of units in the chain. The precision on d_{Bragg} is of the order of 5%. Dotted lines connect results for constant middle-block lengths, while solid lines connect points for samples with similar end-block lengths. It is clear that the end block has a far stronger effect than the middle block. This very strong effect of the end blocks on d_{Bragg} is also observed with the nonionic materials. This suggests that the end blocks are in a rather extended conformation.

With the Bragg distance and the volume content of the two components, it is possible, by using simple crystallographic, geometric, and space-filling calculations, to compute the morphological parameters for different shapes of the scattering units arranged on different paracrystalline lattices. This has been done for spherical domains arranged on simple cubic, body-centered cubic, face-centered cubic, and hexagonal close-packed lattices; for cylindrical domains arranged on a hexagonal close-packed lattice; and for lamellar domains. For the spherical and cylindrical morphologies, the continuous phase is assumed to be polystyrene. For all morphologies, complete phase separation and negligible interphase thickness have been assumed, a reasonable assumption in view of the very high driving force for phase separation between ionic and nonionic segments, evidenced by the q^{-4} dependence of the scattering intensity. Parameters calculated for these morphologies include the radius, R, of the sphere or of the cylinder, the shortest distance, d, center to center, and d', the surface to surface distance between the spheres or the cylinders. In the case of the spheres, the number, N, of chain ends inside the sphere has also been calculated. For the lamellar morphology, the specific parameters were the thickness of the styrene phase and of the vinylpyridine or vinylpyridinium phase. Another parameter that was calculated for all morphologies is the contact area, S/N, defined as the interphase area divided by the number of covalent interblock links present in this area.

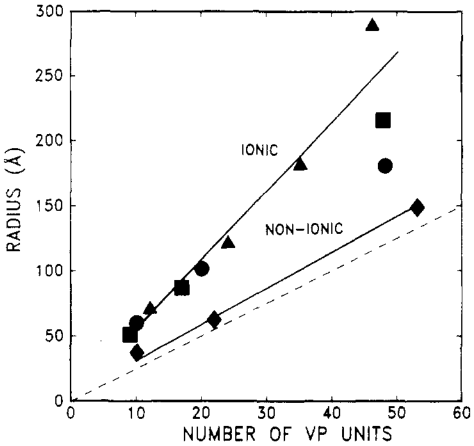

Figure 3. Calculated radius of spherical domains (bcc lattice) as a function of the number of units per end block. Ionic materials: middle blocks of 200 (circles), 480 (rectangles), and 960 styrene repeat units (triangles). Nonionic materials: middle block of 530 styrene repeat units (diamonds). The dashed line indicates the fully stretched zigzag length of the end blocks taking 2.5 Å per repeat unit.

For the case of the spherical domains, all the lattices examined gave similar results. Since the body-centered cubic lattice is a common one for block copolymers, this was selected to exemplify the results. Table I gives the different morphological parameters for the spheres. It must be pointed out that due to the presence of an upturn at low angles in some cases the precision on the morphological parameters decreases as the distance between the domains increases. Figure 3 shows the radius of the scattering center, R, as a function of the number of VP units for the various middle-block chain lengths. It is seen very clearly that, except for the longer VP blocks, R is a linear function of the number of units in the end block and is independent of the number of units in the middle block. On this figure, the dashed line represents the fully stretched zig-zag length of the VP blocks assuming 2.5 Å per repeat unit. It can be seen that while the nonionic materials have radii of the order of the extended length, the ionic materials have radii twice as large as this value. This problem will be covered later. The linear relation between the radius and the molecular weight of the end blocks is very different from what has been found in regular block copolymers, where a 2/3 dependence is observed.[32]

The free distance d' between the spheres is given in column 5 of Table I. It is evident that d' is a function of both the middle-block and the end-block lengths. For comparison, the end to end distance of the corresponding free polystyrene chain is also given in the table as $\langle r_0^2\rangle^{1/2}$. It is clear that d' is in some cases very different from $\langle r_0^2\rangle^{1/2}$. It should be pointed out that d', while undoubtedly related to the end to end distance of a free chain, need not, by any means, be identical with it since the chain can reach nonnearest neighbors, loop back onto the same aggregate, or not use the shortest path between aggregates. The dimensions of the polystyrene chains can only be determined by SANS experiments with selective deuterations, which is the subject of an ongoing study. The number of chains, N, which is emanating from a domain is, in some cases, much higher than is observed in normal block copolymers, as can be seen from Table I. The contact surface area, S/N, which is remarkably constant for the ionic materials, is in all cases considerably lower than the typical values reported for regular block copolymers, where the contact surface area was observed to depend on molecular weight.[32]

The analysis of the data on the basis of a cylindrical morphology gave results similar to the spherical models, the only difference being that the radii are no longer higher than the extended length of the end blocks but equal to this value. However, based on our knowledge of block copolymers, it would be surprising to observe cylindrical domains for all samples studied here, especially those of low vinylpyridinium content, and no discontinuity in the morphological properties was found which would suggest a different morphology for some of the samples. Finally, the lamellar model was rejected due to the unreasonable results obtained from the space-filling calculations.

One explanation for the very high radius values is that the domains are not spherical; they might be deformed to produce domains with at least one dimension equal or smaller than the extended length of the end block. Thus, small cylindrical or flat domains might be formed. These domains might very well arise from an attempt by the system to reorganize during the quaternization. The physical conditions in which this reaction was conducted probably allow only very limited morphological reorganization which, would require a chain end to diffuse through polystyrene from one aggregate to another. This implies that the system is not in its thermodynamic equilibrium state. Keeping the same macrolattice parameters and volume of domains as was obtained for the spheres but changing the shape from perfect spheres to small cylinders or disks would result in considerably smaller dimensions in two directions or one direction, respectively. For example, for short cylinders with an arbitrary length to radius ratio of 6, the radius of the cylinders would be 60% of the radius obtained for the spherical model. With the elongated domain on a cubic macrolattice, the morphological parameters determined for the spheres still hold quite well. The functionality N of the domain remains the same, and the free distance d' between the domains also remains essentially the same, on the average. The contact surface area S/N becomes higher but still much lower than for regular block copolymer systems. Finally, even if the radius value R is reduced, if the length to radius ratio of the short cylinders is the same from one material to the other, the linear relation between the radius and the molecular weight of the ionic block would still hold.

Another possible explanation to account for the high value of the radii could be a very high dispersity in end-block chain length. We have at this time no practical way to measure this value. However, although this dispersity might be partially responsible for the phenomenon, we believe that it is unlikely to be high enough to explain it alone.

It must be kept in mind that the morphological parameters reported here are indirect and have been calculated on the basis of stoichiometry. They are thus extrapolation values for completely phase-separated and perfectly shaped domains. It is therefore not possible to explain the large radii by the presence of polystyrene entrapped in the ionic domains or by a fuzzy surface. The presence of a third component (water, etc.) also cannot account for the high values of the radii since very high contents would be necessary to lower the radii significantly. For example, to obtain an increase of the radius by a factor of 2, one would need to incorporate ca. 700 vol % of a third component.

We have so far only considered the main peak from the scattering patterns obtained. We mentioned earlier the presence of smaller secondary peaks on many patterns. However, these are very broad and not intense, so their position is poorly defined. Furthermore, they can originate from higher order Bragg reflections or be related to the form factor of the ionic domains. For these reasons, it is not possible to use them to differentiate between the different models. Rather, one can say that they are compatible with the proposed model.

Conclusion

The morphology of ABA block ionomers has been studied by small-angle scattering. The length of the ionic blocks was found to have the stronger effect on the average characteristic distance between phase-separated regions, thus suggesting a high extension for these blocks. An analysis of the data based on spherical domains arranged on a cubic lattice resulted in values of the radii which were completely independent of the styrene block (matrix block) and proportional to the first power of the molecular weight of the ionic block. The distance between the domains was calculated to be roughly of the order of the root mean square of the polystyrene middle block, as expected. Other morphological parameters obtained were very different in magnitude from what is usually obtained with regular nonionic block copolymers.

It seems, however, that the exact shape of the domains might not be spherical but somewhat elongated or flat. This could arise from some kind of rearrangement of the morphology during the ionization in the swollen state. It is believed that the system investigated is not in its equilibrium state. A study of solvent-cast samples of the same polymers by scattering and microscopy techniques, which shows different morphologies, is in progress, as is a study of polystyrene middle-block conformation in molded samples by SANS.

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Registry No. ((Styrene)(4-vinylpyridine))·methyl iodide (copolymer), 107082-96-2.

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Variable-Density Model of Polymer Melt Surfaces: Structure and Surface Tension

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ABSTRACT: A variable-density lattice model is developed for the prediction of structure and thermodynamic properties at free polymer melt surfaces and polymer melt/solid interfaces. The model combines ideas from Scheutjens and Fleer's interfacial theory of polymer solutions and from the equation of state theory of Sanchez and Lacombe. Its derivation is based on the thermodynamic concept of availability. The model is implemented to study free surfaces of macromolecular liquids. The variation of surface tension with chain length and temperature is accurately predicted. The relative magnitude of enthalpic and entropic contributions to surface tension is correctly assessed. Surface tension values, obtained by using the Sanchez–Lacombe equation of state parameters, are lower than experimental, mainly because long-range segment–segment interactions are not accounted for in the lattice model. The density profile at a free surface is sigmoidal and approximately 15 Å thick for all chain lengths. Sparse, perpendicularly oriented chain tails protrude into the highly attenuated surface region. Chains are flattened immediately below this region. As one moves further into the melt, conformations narrow down to their asymptotic unperturbed characteristics, over a length roughly equal to the root mean squared end-to-end distance of chains.

1. Introduction

The surface and interfacial properties of polymers, in the condensed amorphous state, are important in a variety of technical areas. The role of polymers is becoming increasingly significant in manufacturing mechanical components with controlled friction and wear characteristics, in manipulating the wettability of surfaces by aqueous and organic fluids, and in developing new biocompatible materials. The science and technology of lubrication relies heavily on the interfacial behavior of polymers, as most lubricants are macromolecular liquids. The quality of products obtained through polymer-processing operations, such as extrusion and film blowing, is profoundly affected by surface-related dynamic phenomena (e.g., melt fracture[3]).

To judiciously select and efficiently design materials for these and similar applications, we need to understand the relationships between polymer chemical structure and macroscopically manifested interfacial properties at the molecular level. Adsorptive segment–solid interactions, or the lack thereof in polymer/gas systems, as well as entropic constraints at a phase boundary, cause the conformation of polymer chains to deviate from what it is in the bulk. Perturbations in local structure, in turn, govern thermodynamic, transport, mechanical, and optical properties in the interfacial region.

The adsorption of polymers from solution on solid surfaces has been studied in considerable detail. A concrete and particularly successful lattice model for this situation was developed by Scheutjens and Fleer.[1] Much

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