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Small-Angle X-ray Scattering Studies of Poly(arylethinylene): Molecular Conformation in Solution and Orientational Ordering in Rod−Coil Ionomer Blends

Dominik Winter and Claus D. Eisenbach*

University of Stuttgart, Institut für Angewandte Makromolekulare Chemie,
D-70569 Stuttgart, Germany

John A. Pople

Stanford Synchrotron Radiation Laboratory, SLAC, PO Box 4349, Stanford, California 94309

Alice P. Gast*

Department of Chemical Engineering, Stanford University, Stanford, California 94305

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ABSTRACT: Poly(pyridyl/phenyl-ethinylene) polymers of tuned rigidity/flexibility were synthesized and their molecular conformations in solution determined by small-angle X-ray scattering. These polymers were used as molecularly dispersed reinforcing components in ionomer blends with partially sulfonated polystyrene. Homogeneous ionomer blends were formed by acid−base interactions between the two blend components. Small-angle X-ray scattering revealed that in the case of rodlike or semiflexible poly(pyridyl/phenyl-ethinylenes) an elongation-induced orientational ordering is obtained. However, blend samples prepared with flexible poly(pyridyl/phenyl-ethinylene) polymers do not show any observable orientation. The orientation parameter varied systematically with the rigidity/flexibility of the reinforcing component, as did the Young modulus determined from stress−strain measurements.

Introduction

There is considerable current interest in macromolecules whose rigid conformation is tunable through careful selection of the building blocks and the type and pattern of linkages between them. Such materials have many applications in the field of varying optoelectronic properties and extended π-conjugation[1−3] as well as in the formation of novel polymer electrolytes, for example poly(*p*-phenylene).[4] A particular area of interest is found in blending rigid macromolecules with coil macromolecules to form novel materials where the interplay between the rods and the coils provides a mechanism for molecular reinforcement.[5,6]

Unfortunately, the polarizable π-electrons of such rigid-rod conjugated polymers lead to strong intermolecular interactions often rendering high molecular weight polyaryls insoluble unless suitable substituents, such as long alkyl side chains, are attached to the backbone.[7,8] A recent attempt to enhance the solubility and therefore the processability of the poly(phenylethinylene) polymers is to incorporate meta-substituted phenylene repeat units into the polymer.[9] This incorporation significantly modifies the rodlike molecular conformation of the polymer. The bent bond angle (about 120°) permits the polymer backbone to deviate from the rigid-rod conformation and to effectively adopt a coillike conformation in solution while preserving the good luminescence properties.

Such polyaromatic polymers are also of interest in view of studying the compatibility and properties of binary blends when one blend component is a random coil macromolecule and the other component is a macromolecule of quite restricted flexibility: a rigid-rod conformation being the extreme case. These polymer−polymer molecular composites of macromolecules of different flexibility are an attractive approach to composite materials with superior ultimate properties as compared to macroscopic fiber composite materials.[10] Whereas the classical theory of statistical thermodynamics of polymer multicomponent systems has predicted immiscibility between rod and coil macromolecules,[11] compatibility is possible if the interaction between the two blend components is sufficiently strong[5] and has been achieved by introducing, for example, acid−base interactions.[5,12,13] Similar observations have been made for the compatibility of nonflexible and flexible polymers where ion−dipole interactions or H-bonding promoted the miscibility.[14−17] The molecular miscibility generates a perfect molecular dispersion of the reinforcing polymer in the matrix, which is ideal for the purpose of molecular reinforcement, especially if the reinforcing polymer is a true rod as in our previous studies[5,6] as well as in this report.

Phase diagrams predicted for the ternary rod/coil/solvent system as well as of the binary rod/coil mixtures with attractive interactions between the rods and coils indicate that the presence of isotropic or anisotropic phases depends on the rod aspect ratio l/d (length l to diameter d) and volume fraction of the rod component.[5] In this context it is interesting to know if and to what extent anisotropy within the blend can be achieved by elongation of the bulk sample.

The enhancement of the unidirectional mechanical properties by orientational ordering of polymers is well-known for liquid crystalline polymers (LCP): the so-called self-reinforcing plastics. Furthermore, liquid crystalline rigid-rod polyesters or polyamides have been successfully applied as the reinforcing component in blends with flexible polyamide matrix polymers.[18,19] These systems differ from molecularly reinforced polymer−polymer composites presented here since the LCP reinforcers form anisotropic liquid crystal microphases.

In this report we describe investigations of the elongational response of a series of rod/coil ionomer blends

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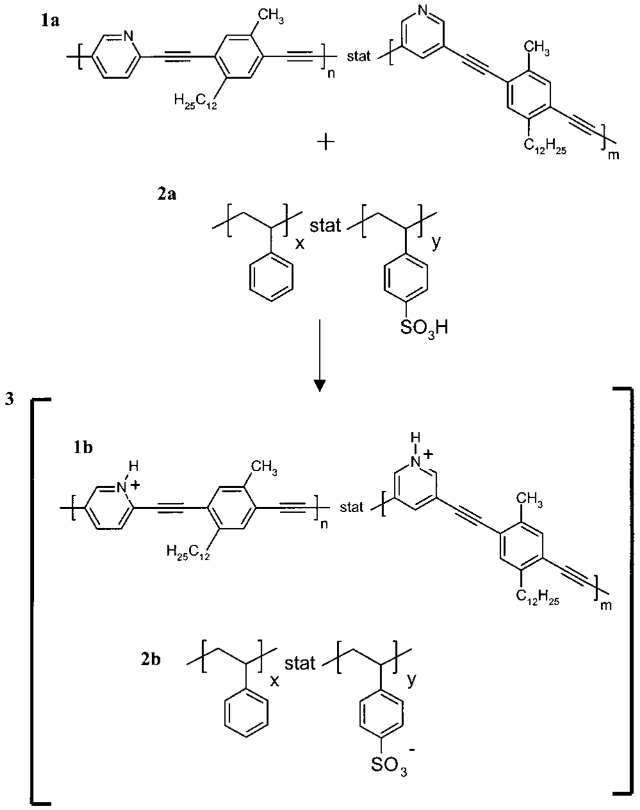
Scheme 1. Chemical Structures of the Blend Components Poly(arylethinylene) (PPyPE) Rod (1a) and Sulfonated Polystyrene Coil (2a; $y/(x + y) = 0.11$) Employed in the Formation of the Acid/Base Ionomer Blends 3 (Stoichiometry of Pyridyl and Sulfonic Acid Groups) Composed of Rod Polycation (1b) and the Coil Polyanion (2b)



having varying rod rigidity. We begin by characterizing the solution conformations of poly(pyridyl/phenyl-ethinylene) polymers (PPyPE) of different rigidity/flexibility (**1a** in Scheme 1) by small-angle X-ray scattering (SAXS). The rigidity/flexibility is tuned by varying the number of meta linkages (m-linkages) at the pyridyl moiety, i.e., by the mole fraction $n/(n + m)$ of the para linkages. We then report model studies of rod−coil ionomer blends (**3** in Scheme 1). We investigate the elongation induced orientational ordering of poly(arylethinylenes) of different rigidity in rod−coil ionomer blends and relate the orientational order seen on the molecular scale to the rigidity of the reinforcing polymer.

Experimental Section

Materials. The synthesis of poly(pyridyl/phenyl-ethinylenes) (PPyPE) of different rigidity/flexibility was carried out according to existing procedures for phenyl-ethinylene polymers.[3,9] In brief, the PPyPE polymers were made via the Heck coupling reaction starting from 2,5-diethinyl-4-dodecyl toluene and 2,5- and/or 3,5-dibromopyridine; details will be described elsewhere.[20] All PPyPE have nearly identical molecular weights as determined by vapor pressure osmometry and gel permeation chromatography. Partially sulfonated polystyrene (11 mol % arylsulfonic acid) (PS-*co*-SSH) was used as the flexible matrix polymer. Homogeneous acid−base ionomer blends were obtained by mixing a chloroform solution of the PPyPE with PS-*co*-SSH up to equivalent amounts of the acid/base functionalities and collecting the ionomer blend precipitate followed by drying at 100 °C at high vacuum. The investigation of the miscibility of the blend components determined by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) as well as by UV/fluorescence spectroscopy, and further details of the blend formation and sample preparation for the strain experiments are also described elsewhere.[21]

The stress−strain measurements were carried out with an Instron 4301 at 150 °C.

For the solution scattering experiments, spectroscopic grade tetrahydrofuran was purchased from Aldrich and used without further purification. The sample cells were filled with 1 wt % concentration solutions.

Sample Environments. Solution samples were mounted in a solution cell holder manufactured at SSRL that has an active path length of 1 mm. The cell is enclosed from all sides to prevent solvent loss, and the probe beam passes through two 25 μm thickness mica windows. All solution scattering data were collected at room temperature.

Uniaxial extension of the solid blend samples was performed in a device manufactured at the Stanford Synchrotron Radiation Laboratory (SSRL) specifically for tensile testing, which held the samples in situ in the probe beam. The samples were clamped between two steel jaws in an oven environment with mica windows for transmission of the X-ray beam. The oven temperature was remotely programmed between room temperature and 120 °C, controlled to within ±1 °C. The separation of the jaws was controlled remotely by a stepper motor which extended the samples smoothly at extension rates between available limits of 0.05 and 1000 mm/min. All experiments reported here were conducted at a temperature of 120 °C.

Small-Angle X-ray Scattering. Small-angle X-ray scattering was performed on beamline 1-4 of the Stanford Synchrotron Radiation Laboratory (SSRL) at the Stanford Linear Accelerator Center (SLAC) in Stanford, CA. The facility offers a collimated X-ray source with a flux of 10^{10} photons on a spot size of ~0.5 mm (vertical) × 0.8 mm (horizontal), monochromated by a 111 Si crystal to a wavelength of $\lambda = 1.488$ Å. The 16 bit SAXS data were collected on 2-dimensional image plates with a 1600 × 1600 array of 50 μm square pixels over a period of 30 min. The sampled range of the scattering vector q (where q is magnitude of the scattering vector: $|\mathbf{q}| = 4\pi \sin \theta/\lambda$ for photons scattered through an angle of 2θ) was $0.008 < q < 0.11$ Å^{-1}, which gave a reciprocal space resolution of 3.675×10^{-4} Å^{-1} per pixel. These data were corrected for background scattering and scattering from the relevant sample environment. One-dimensional radial and azimuthal profiles of the data were acquired by integration routines.

Results and Discussion

Since the pattern and type of linkages in a polyaryl molecule determine its overall conformation, macromolecules based on aryl moieties in the constitutional unit are ideally suited for controlling the rigidity/flexibility by molecular design. The orientation induced by elongation of a given macromolecular species in a molecular polymer−polymer blend is related to the flexibility of the matrix polymer and to the interaction between the blend components. We have previously demonstrated the effectiveness of the rod molecule as a reinforcing component within a polymeric matrix during stretching using a polydiacetylene−polyurethane elastomer polymer−polymer molecular composite.[22] By varying the ratio of para to meta linkages at the pyridine moiety in the poly(arylethinylene), molecules of different rigidity/flexibility are obtained.[9] A strictly para linkage molecule produces a rigid rod, and the introduction of meta linkages provides greater flexibility to the structure and will ultimately result in a flexible coil molecule. By the variation of the ratio of the p-/m-linkages at the pyridine moiety, the conformation can be changed from rigid-rod or wormlike characteristics to random coil characteristics. Considering the phenylene constitutional unit with p-linkages, the molecule with all m-linkages at the

Table 1. Characterizing Moments of the Five Poly(pyridyl/phenyl-ethinylene) (PPyPE) Polymer Solutions (1 wt % in THF) Studied in This Work[a]

polymer[b]	$n/(m+n)$[c]	M_n [g/mol]	P_n	Flory parameter ν
PMPyPE	0.0	3200	8	0.593
PCPyPE66	0.34	2100	5	0.61
PCPyPE40	0.6	2300	6	0.619
PCPyPE24	0.76	2600	6	0.68
PPPyPE	1.0	2900	7	0.806

[a] *n* and *m* represent the chemical composition of the poly(arylethinylene) with regard to the p- and m-linkages of the pyridyl unit. Number-average molecular weights M_n and degree of polymerization P_n are determined by vapor pressure osmometry, and Flory parameters are extracted from SAXS patterns. [b] In the acronym for the PPyPE polymers with differing p- and m-pyridyl linkage content, PPPyPE and PMPyPE stand for the all p- or all m-linked polymers. For the p-/m-copolymers PCPyPE the additional figures give the mol % p-linkages of the pyridyl moiety. [c] Mole fraction of p-linked repeat units in PPyPE (see **1a** in Scheme 1).

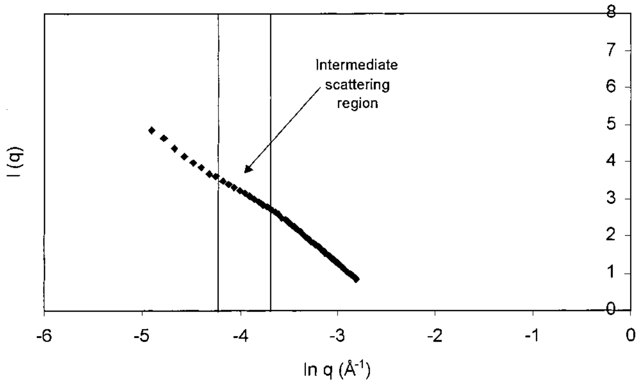


Figure 1. Scattering profile from PPyPE polymers in dilute solution (sample PCPyPE40), indicating the intermediate scattering region from which the Flory parameters were determined.

pyridine moiety may be described as a multiply broken rod with m-pyridylethinylphenylethinyl−m-pyridyl (cf. **1a** in Scheme 1 for $n = 0$) adopting a coil conformation. This is evident from the chemical structure of the poly(arylethinylene) (**1a** in Scheme 1 and Table 1).

Conformation Studies of Dilute Solutions. The conformation of constitutionally homogeneous and heterogeneous poly(arylethinylenes) in dilute solution was inferred from the logarithmic dependence decay of the small-angle X-ray scattering intensity in the intermediate scattering region (Figure 1). The scaling exponent reflects the dimensionality of the scattering units. Thus, for an intensity decay of the form $I(q) \sim q^{-1}$, the scattering implies a one-dimensional scattering unit. In this study we understand this to represent a rodlike molecule in solution. Larger scaling exponents do relate to a larger fractal dimension and therefore an increasingly coillike molecular conformation. We express this dimension in terms of the Flory exponent ν, which appears in the scattering decay as $I(q) \sim q^{-1/\nu}$ in the intermediate region of the scattering profile.

The Flory exponents for the five rod−coil polymers in dilute (1 wt %) solution as a function of the proportion of para/meta linkages at the pyridine moiety of the PPyPE molecules (i.e., the rodlike nature of the molecule) are shown in Table 1. As seen from the table, the largest Flory parameter (approaching unity) comes from the PPPyPE solution, indicating that this molecule has the most rodlike conformation. This is consistent with the synthesis, as this molecule possesses 100% para linkages in its structure. For the other solutions the Flory exponent decreases with increasing proportion of meta linkages, again consistently with expectation, as the conformation of the molecule in solution becomes ever more coillike. The lowest value of the Flory parameter, $\nu = 0.593$, for PMPyPE is essentially the same as the Flory parameter for a polymer coil in a good solvent, $\nu = 0.6$, and indicative of a flexible, swollen structure. Thus, varying the percentage of meta pyridine linkages from 0% to 100% (corresponding to a variation of the mole fraction of the *p*-pyridyl linkages $n/(n + m)$ from 1 to 0, as Table 1), we have demonstrated molecular conformations spanning from rodlike to those of a well-solvated coil.

Measurement of the radius of gyration R_g is determined from the Guinier region, where the Guinier region is defined as the portion of the scattering curve showing a linear relationship between the logarithm of the intensity and the square of the scattering vector and is located at the innermost portion of the scattering profile. A Guinier region was observed for the PPPyPE sample only. From this we determined a measure of the radius of gyration R_g from the relationship

$$R_g = \sqrt{\frac{3\ln(I_0/I_q)}{q^2}} \qquad (1)$$

In eq 1, I_0 is the scattering intensity at zero scattering angle and I_q the intensity within the region studied. The radius of gyration $R_g = 12.3 \pm 0.1$ nm and is comparable to the theoretical contour length of 11.0 nm for a degree of polymerization $P_n = 7$ (Table 1), which indicates that the persistence length is greater than 11 nm. This is in turn confirmed by the experimentally determined value of the Flory parameter $\nu = 0.81$, which is within the range of parameters characteristic of rodlike particles.

Orientation Studies of Uniaxially Deformed Blends. Since the macromolecules with tuned rigidity/flexibility contain the pyridyl base unit, a sulfonated polymer was chosen as the acidic coil polymer for the formation of the acid/base ionomer blends (Scheme 1).

In the blend formation from solution, we have verified spectroscopically quantitative proton transfer from the styryl sulfonic group (**2a** in Scheme 1) to the pyridyl group,[23] resulting in a poly(pyridinium/phenyl-ethinylene) rod polycation (**1b** in Scheme 1) and coil polyanion (**2b** in Scheme 1).

The miscibility of the components in the ionomer blend with sulfonated polystyrene as compared to a phase-separated blend with pure polystyrene is illustrated in the transmission electron micrographs (Figure 2). The images of the poly(arylethinylene)/polystyrene blend (Figure 2a) clearly revealed the phase-separated morphology for the noninteracting system; further analysis by taking electron energy loss spectra (EELS) from the domains and the matrix by applying the element specific imaging technique (ESI) showed the presence of nitrogen in the circular domains only, and ESI pictures coinciding with the elastic bright field images were obtained. In contrast to this, the poly(arylethinylene)/sulfonated polystyrene acid−base ionomer blends (**3** in Scheme 1) with the strong attractive interactions between the two blend components showed a grainy morphology over 1−3 nm length scales in the high-resolution (20 nm) bright field image (Figure 2b).

Orientation studies were performed by loading the samples into the tensile testing device described above,

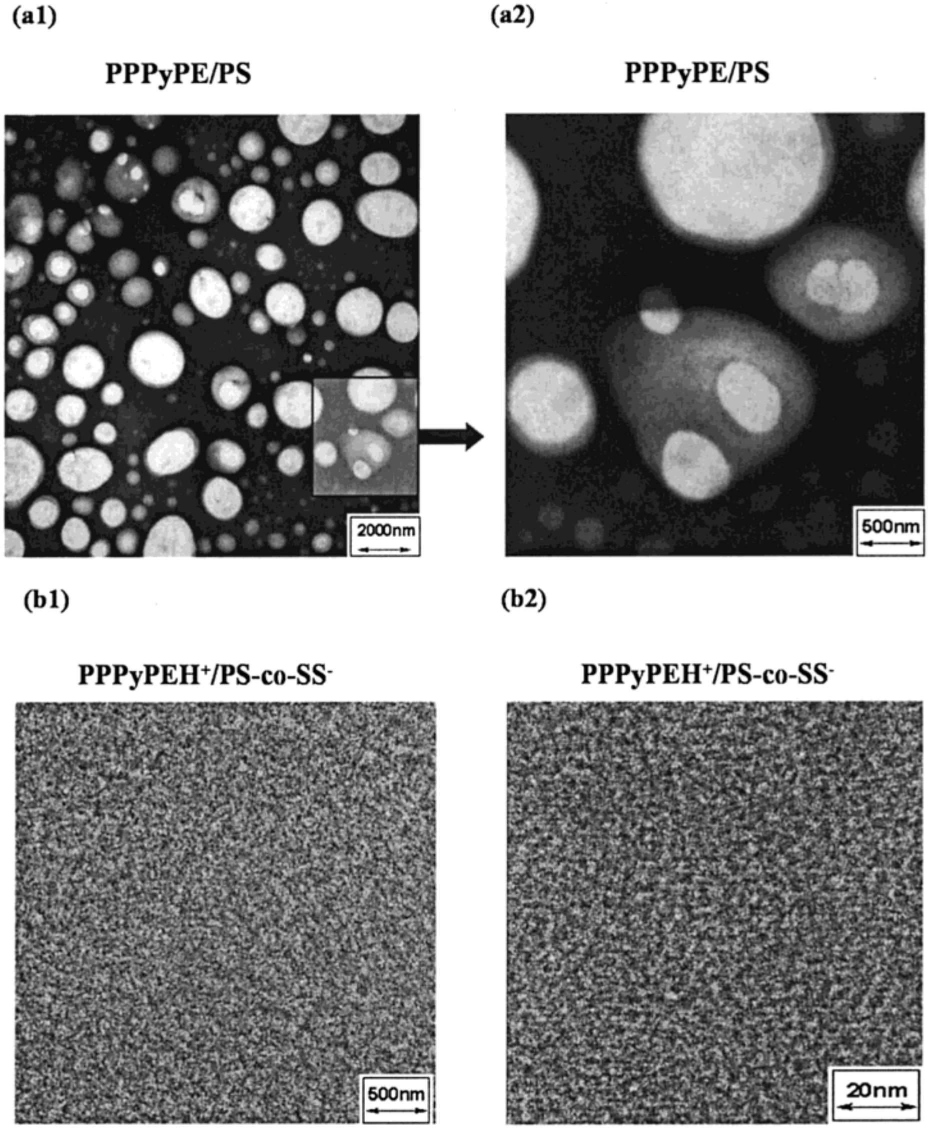


Figure 2. Transmission electron micrographs bright field image of a blend of para-linked poly(pyridyl/phenyl-ethinylene) (PPPyPe) with polystyrene (a1/2) and of the acid−base ionomer blend PPPyPEH$^+$/PS-*co*-SS$^-$ (b1/2) with sulfonated (11 mol % sulfonation) polystyrene (PS-*co*-SSH); weight fraction PPPyPE 27% in both cases, i.e., stoichiometry of acid/base groups in the ionomer blend; magnification: (a1): 900×; (a2): portion of (a1), 4×; (b1): 9000×; (b2): 125 000×.

heating the sample to 120 °C, straining it at 120 °C followed by cooling the strained sample to room temperature, and then collecting X-ray scattering data in situ at ambient temperature with the sample held under tension. (The straining device did not have the ability to prevent or monitor relaxation of the extended structure during the 30 min data collection period.) Successive SAXS images were collected, and no progressive changes were seen between them. This indicates either that there was no significant reorganization of the structure at any time after the extension or that such reorganization was completed over a time scale much shorter than 30 min.

To quantify the degree of molecular orientation in the strained samples, orientation parameters were calculated from the SAXS patterns. SAXS reveals information about the polymer structure on a scale of ∼100−1000 Å, in this case of comparable order to R_g. The anisotropy of the scattering at a given q vector in the SAXS pattern is related to the macroscopic orientational ordering of the scattering units at the corresponding reciprocal length scale in the polymer.

To describe the anisotropy within the system, we employ a distribution function $D(\alpha)$ denoting the probability of finding a structural unit (in this case a polymer rod or coil) at an angle α to the extension axis. The orientation distribution function $D(\alpha)$ completely characterizes the orientational order as a sum of orthogonal harmonic functions and can be written as[24]

$$D(\alpha) = \sum (4n + 1)\langle P_{2n}(\cos \alpha)\rangle P_{2n}(\cos \alpha) \qquad (2)$$

with the globally averaged amplitude terms $\langle P_{2n}(\cos \alpha)\rangle$ being utilized here to describe the overall state of orientational order. These coefficients can be extracted directly from the SAXS patterns using the azimuthal distribution of the intensity function at a fixed value of the magnitude of the scattering vector q and a model for the scattering of a perfectly aligned system:

$$\langle P_2\rangle = \frac{\langle P_2^{\mathrm{I}}\rangle}{\langle P_2^{\mathrm{m}}\rangle} \qquad (3)$$

where $\langle P_2^{\mathrm{I}}\rangle$ is the normalized coefficient calculated from the SAXS patterns and $\langle P_2^{\mathrm{m}}\rangle$ is the coefficient calculated from the model. In this case the model for a single unit is assumed to be an infinitely long rod (in physical terms this translates to the assumption of a rod length $l \gg q_{\min}{}^{-1}$), so that the orthogonal components of the scattering model are simplified to[25]

$$\langle P_{2n}(\cos \alpha)\rangle^{m} = \frac{(2n)!}{(-1)^{n}2^{2n}(n!)^{2}} \tag{4}$$

and thus $\langle P_2^{\mathrm{m}}\rangle = -{}^{1}\!/_{2}$, $\langle P_4^{\mathrm{m}}\rangle = {}^{3}\!/_{8}$, and $\langle P_6^{\mathrm{m}}\rangle = -{}^{5}\!/_{16}$.

It should be noted that a complete description of the orientation function can be obtained from the scattering data between the azimuthal angles of $\alpha = 0$ and $\alpha = \pi/2$. Thus, the results presented here, determined from the complete azimuthal range of $0 < \alpha < 2\pi$, are averaged results from the four quadrants.

For a complete description of the orientation function, the infinite series of these Legendre polynomials is required; nevertheless, a first-order approximation to the orientation is obtained from the first-order term, the amplitude coefficient of which is $P_2(\cos \alpha)$. In this work the poly(pyridyl/phenyl-ethinylene) system under observation can be described as a uniaxial matrix of axially nonpolar units, and therefore the first-order coefficient to the polynomial series provides an adequate description of the overall orientation function. Additionally, the dimension of the sample illuminated by the incident beam is large in relation to the scattering units (1 mm, cf. 100 Å), and therefore the SAXS patterns provide orientational order parameters that are averages for the scattering units. Thus, the orientational order in this study will be defined according to $\langle P_2\rangle(\cos \alpha)$.

Two-dimensional SAXS patterns were collected for each of the five blend samples first in the quiescent state and then held in the probe beam at full strain. Full strain for all samples was 300% extension, with the exception of the coil molecule sample PMPyPEH$^+$/PS-*co*-SS$^-$, which was strained to 500% extension.

There was no observable diffraction ring within the scattering vector range investigated, $0.01 < q < 0.11$ Å^{-1}, and therefore no obvious feature in reciprocal space on which to focus the orientation study. Therefore, the azimuthal intensity profiles were collected at a variety of q vectors: for each sample 13 adjacent q ranges are analyzed. Figure 3 shows five of the 13 azimuthal intensity profiles collected for the rod molecule sample PPPyPEH$^+$/PS-*co*-SS$^-$ strained to 300% extension. There is clearly a dependence of anisotropy on scattering vector: no orientation is observed at the smaller scattering angles, and the anisotropy, and therefore orientation, only becomes apparent at the larger scattering angles, which correspond to the smaller length scales within the polymer.

Figure 4 shows the global orientation parameter calculated from each of the 13 azimuthal intensity traces extracted from the SAXS pattern for the five rod–coil molecule samples held under strain at 300% extension. The trace exhibiting the highest degrees of elongation induced orientation corresponds to the rodlike PPPyPEH$^+$/PS-*co*-SS$^-$ sample, as shown in the figure. The highest level of orientation for this sample corresponds to the smallest length scale of scattering unit and is relatively modest: $\langle P_2\rangle = 0.146 \pm 0.01$. The development of orientation with scattering vector is clearly visible from Figure 4. It is possible to identify the beginning of quantifiable orientation as developing between the scattering vectors of $q = 0.044$ Å^{-1} and $q = 0.051$ Å^{-1}, corresponding to a development of orientation within the sample beginning at length scales ~13 nm. The figure shows a similar effect for all other samples in which anisotropy was observed.

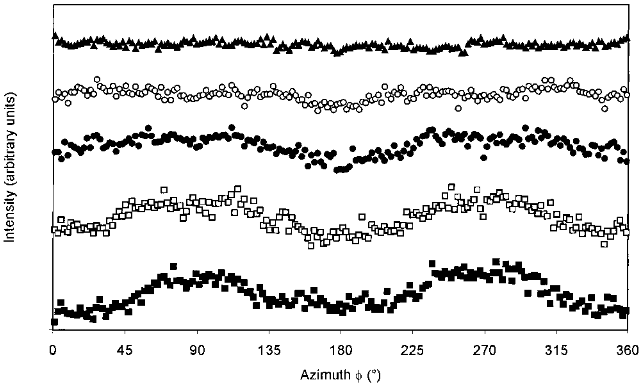


Figure 3. Profiles of intensity against azimuthal angle extracted from SAXS patterns for a poly(pyridyl/phenyl-ethinylene) ionomer blend sample containing only para linkages at the pyridine moiety (PPPyPEH$^+$/PS-*co*-SS$^-$) strained to 300% extension for various q ranges (Å^{-1}): $0.103 < q < 0.110$ (■); $0.0809 < q < 0.0882$ (□); $0.0588 < q < 0.0662$ (●); $0.0368 < q < 0.0441$ (○); $0.0147 < q < 0.0221$ (▲). Intensities are in arbitrary units and not comparable from one profile to another: the profiles are displaced along the ordinate for clarity.

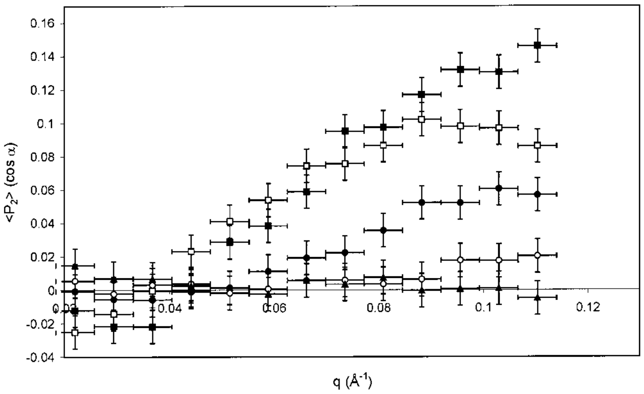


Figure 4. Orientation parameter as a function of scattering vector for five poly(pyridyl/phenyl-ethinylene) ionomer blend samples of varying compositions: PPPyPEH$^+$/PS-*co*-SS$^-$ (■); PCPyPE24H$^+$/PS-*co*-SS$^-$ (□); PCPyPE40H$^+$/PS-*co*-SS$^-$ (●); PCPyPE66H$^+$/PS-*co*-SS$^-$ (○); PMPyPEH$^+$/PS-*co*-SS$^-$ (▲). All samples were strained to 300% extension, except the PMPyPEH$^+$/PS-*co*-SS$^-$ sample (lowest trace) that has been strained to 500%.

For the most rigid polymer PPPyPEH$^+$/PS-*co*-SS$^-$, this observation can be directly related to the dimension of the polymer rod molecule (PPPyPE). The overall length of the molecule calculated from its number-average molecular weight (M_n), assuming a rigid rod (Table 1) is about 11 nm and in good accord with the length scale associated with the onset of quantifiable orientation within the ionomer blend. This suggests that within the ionomer blend strain-induced orientational ordering of the molecularly dispersed reinforcing polymers occurs, resulting in the development of an anisotropic phase, as illustrated in Figure 5.

Comparing the results of Figure 4 between samples, it is notable that the sample containing no para but only meta linkages at the pyridine moiety does not exhibit any observable orientation, even at an extension of

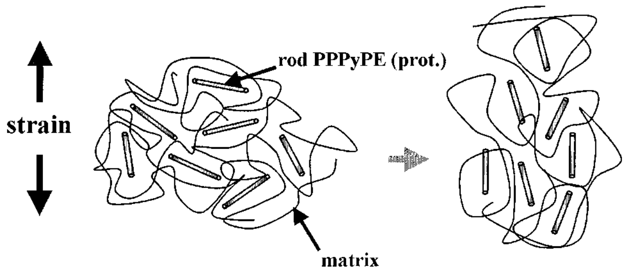


Figure 5. Schematic diagram of the elongation-induced orientational ordering of rod polymers in rod–coil blends.

500%. This demonstrates that no degree of preferential alignment can be induced in the coillike molecules by the application of a macroscopic uniaxial strain to the bulk material. This also implies that the degree of orientation observed in the other samples should be related to the increasing stiffness, i.e., to the proportion of para linkages at the pyridine moiety of the ultimately rodlike molecule. Figure 4 supports this implication, since the degree of orientation realized is a function of the parallel (*p*-pyridyl) bond linkage in the molecule structure and therefore of the rodlike character of the reinforcing polymer. That is to say the more rodlike nature of the polymer, the higher the orientation that can be induced by the stress field. This is demonstrated in Figure 6, where the maximum orientation achieved in each of the samples is plotted as a function of the proportion of para linkages at the pyridine moiety.

The rod/coil character of the reinforcing polymers, as reflected from the Flory exponent that was determined by small-angle X-ray scattering (Table 1), can also be taken into account. The Flory exponent varies systematically with the rigidity imparted by the para-to-meta linkage ratio and can be correlated with the maximum orientation achieved in each of the corresponding blend samples.

Of further interest is the effect that these molecular level conformational and orientational trends may have on the material properties of the bulk. In a preliminary investigation of this, and in order to complement the above results, we measured Young's modulus for each of the samples in the same series of ionomer blends. Figure 6b shows a comparison between the Flory parameter ν of the rod–coil molecules in dilute solution with the Young's modulus E determined from stress–strain measurements for the blend samples, both expressed as a function of the mole fraction of *p*-pyridyl linkages. Once again an interesting positive correlation is seen between E and ν, as with the orientation parameters compared to ν.

This striking similarity in the correlation of the orientation parameter of the PPyPE molecules with strain and of the Young modulus of the blends with the Flory parameter ν as a measure of the flexibility of the PPyPE molecules suggests that these effects all have a common molecular origin. As ν increases from 0.6 toward the ideal value of 1.0 for a true rod, the PPyPE molecules change from a coiled conformation to a rodlike anisotropic shape. As the rigidity of the PPyPEH$^+$ polycation increases, it becomes aligned more and more parallel to the stretching direction due to its increasing shape anisotropy (i.e., decreasing flexibility). Similarly, as the blend is elongated, a rodlike PPyPEH$^+$ molecule represents an obstacle for the relaxation of the sulfonated polystyrene matrix, and this obstruction is increased for polyethinylaryl blend components of greater

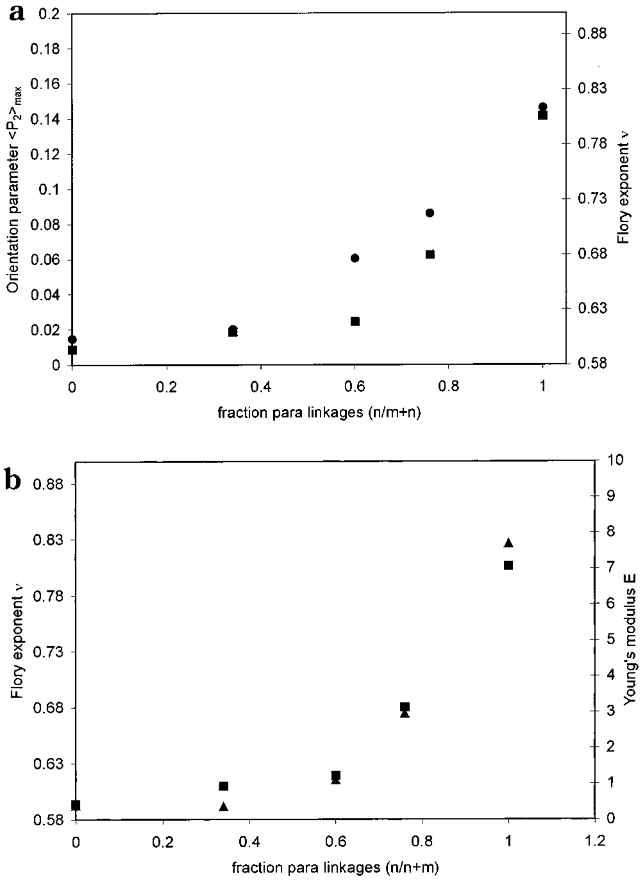


Figure 6. (a) Maximum orientation (●) observed in azimuthal profiles of SAXS patterns from strained PPyPEH$^+$/PS-*co*-SS$^-$ ionomer blends and Flory exponent (■) from SAXS experiments on PPyPE polymers in dilute solution as a function of the mole fraction of para linkages at the pyridine moiety of the PPyPE molecules. (b) Flory exponent (■) from SAXS experiments on PPyPE polymers in dilute solution and Young's modulus (●) of the bulk material from PPyPEH$^+$/PS-*co*-SS$^-$ ionomer blends of as a function of the number of para linkages at the pyridiene moiety of the PPyPE molecules.

rigidity. Thus, while the orientation parameters cannot be directly associated with the values of Young's modulus, the possibility of molecular architecture influencing bulk material parameters remains an area of great interest and forms our directive for further study in these materials.

Conclusions

This study has shown that the small-angle X-ray scattering technique lends itself as a valuable tool in the extraction of meaningful structural parameters of these rod–coil ionic polymer materials. Characterization of the reinforcing polymers in dilute solution reveals the conformation of the molecules: the sample with 100% *p*-pyridine linkages was the most rigid, as expected, and the rigidity of the conformation decreased with increased proportion of meta linkages, again in accordance with expectation. The radius of gyration of the molecules with only para linkages of the pyridine moiety was 12.3 nm: close to the theoretically calculated contour length for $P_n = 7$ (11.0 nm), supporting the rodlike nature of the all para-linked pyridine molecules.

The study of the series of rod–coil ionomer blends based on poly(pyridyl/phenyl-ethinylene) of tuned rigidity/flexibility as blend component with sulfonated polystyrene demonstrated that a formerly isotropic blend can be transferred in sample exhibiting directional anisotropy. With small-angle X-ray scattering monitored strain experiments we were able to show that for rigid-rod and semiflexible reinforcing polymers a quantifiable degree of orientation of the reinforcer is induced by an elongation of the blend material. The orientation parameter for a given strain varies systematically with the rigidity/flexibility of the reinforcing polymer, reaching a maximum for the ideal rigid rod polymer of $\langle P_2 \rangle \sim 0.15$ at 300% strain. No orientation is observed for the blend sample containing the flexible reinforcing polymer poly(meta-pyridyl/phenyl-ethinylene).

Comparisons between orientation parameters and Flory exponents revealed that higher degrees of orientation were achievable from blends where the molecular components were more rigid in conformation. Comparisons between Young's modulus values determined from stress−strain experiments and Flory exponents determined from SAXS experiments indicated a strong positive correlation between the reinforcement effect and the rigidity of the reinforcing molecules. These findings open interesting perspectives for the design of novel materials with anisotropic properties based on molecular rod/coil ionomer blends; this will be emphasized in future studies.

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