ELSEVIER
Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polymer 45 (2004) 2507–2515
polymer
www.elsevier.com/locate/polymer

Poly(arylene-ethynylene) with tuned rigidity/flexibility as reinforcing component in polystyrene-based ionomer blends

Dominik Winter, Claus D. Eisenbach*

Universität Stuttgart, Institut für Angewandte Makromolekulare Chemie, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Received 4 August 2003; received in revised form 16 January 2004; accepted 21 January 2004

Abstract

Poly(pyridylene/phenylene-ethynylene) polymers of controlled rigidity/flexibility were synthesized and used as molecularly dispersed reinforcing components in ionomer blends with partially sulfonated polystyrene. Homogeneous ionomer blends were formed due to acid–base interactions between the two blend components. The complete protonation of the poly(pyridylene/phenylene-ethynylene) in the acid/base ionomer blends has been proven by UV–VIS absorption and emission spectroscopy. Furthermore, the complete miscibility of the blend components in the ionomer blends was revealed from DSC analysis and transmission electron microscopy. The mechanical properties of the synthesized ionomer blends were determined by stress–strain measurements. The Young modulus of the blends was found to systematically vary with the rigidity/flexibility of the reinforcing polymer i.e. the molecular conformation of the reinforcing polymers as determined by small angle X-ray scattering.

Keywords: Molecular reinforcement; Ionomer blend; Mechanical properties

1. Introduction

Polymer–polymer molecular composites are an attractive approach to composite materials with superior ultimate properties as compared to macroscopic fiber reinforced composite materials [1–4]. A significant increase in the reinforcing effect has been predicted to be achieved by reducing the diameter of the reinforcing component to atom-/to nanoscale dimensions and by simultaneously assuring a sufficiently high aspect ratio l/d (length l to diameter d) [5]. However, most polymer pairs are practically immiscible due to the unfavorably small entropy of mixing; this problem is further enhanced with decreasing flexibility of the polymers, and statistical thermodynamics predicts immiscibility between rod and coil macromolecules [6].

A requirement for miscibility in polymer–polymer blends is a sufficiently negative heat of mixing [7–11]. This may be achieved by specific interactions like hydrogen bond formation [12,13], charge-transfer complexes [14], or ionic interaction [15] as demonstrated for blends of flexible polymers. As thermodynamics of polymer multicomponent systems predict immiscibility of rod-like and random coil polymers [6,16] resulting in a phase separated system with domains of segregated rod molecules as schematically shown in Fig. 1a, compatibility may also be achieved if the interaction between the two blend components is sufficiently strong.

By introducing specific ionic interactions, e.g. acid–base interactions between the two components [17–21] molecular composites have been realized as schematically shown in Fig. 1b. Similar observations have been made for the compatibility of semiflexible and flexible polymers where Coulombic or H-bonding promoted the miscibility [22–26]. The molecular blending of rod and coil molecules can be modeled by introducing a sufficiently negative χ-parameter into Flory's original theory dealing with rods and coils [6] which leads to a theoretical model of a virtual rod approximation [17].

The molecular miscibility generates a perfect molecular dispersion of the reinforcing polymer in the matrix (Fig. 1b), which is the ideal case of molecular reinforcement, especially if the reinforcing polymer comes close to a true rod as in our previous studies [17,27] as well as in this

---

* Corresponding author. Tel.: +49-711-6854440; fax: +49-711-6854396.

E-mail address: cde@makro.chemie.uni-stuttgart.de (C.D. Eisenbach).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.01.064

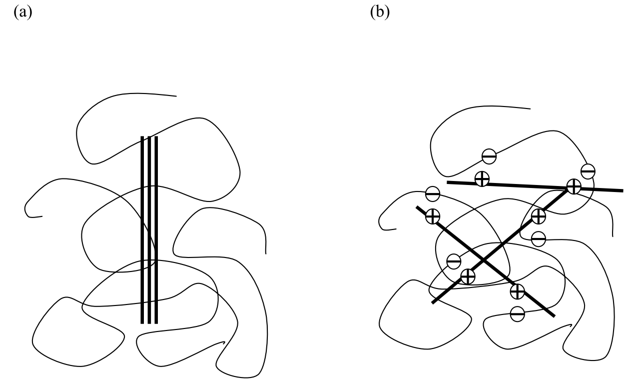


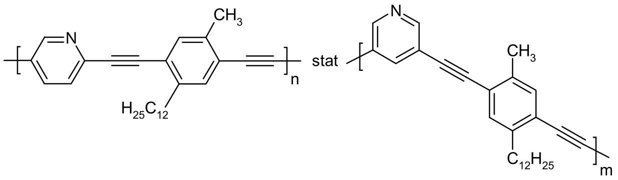
Fig. 1. Schematics of the morphology of a microphase separated mixture of rigid-rod and flexible-coil macromolecules (a) and of a molecularly dispersed mixture as achieved by ionic intermolecular rod–coil interactions (b).

report. Model studies [27,28] have successfully demonstrated the feasibility of the acid/base ionomer concept of the reinforcement of flexible matrix polymers with rod like macromolecules such as poly(*para*-phenylene) [27] or poly(*para*-arylene/ethynylene).

Semiflexible liquid crystalline rigid rod polyesters or polyamides have also been successfully applied as the reinforcing component, utilizing the excellent but anisotropic mechanical properties of the LCPs for a mechanical reinforcement of isotropic and mechanically weaker engineering plastics [4,29]. However, it must be emphasized that this is not a molecularly reinforced polymer–polymer composite in its original sense but a dispersion of microfibrills [30] since the LCP reinforcer has formed an anisotropic LC microphase whereas in our case the reinforcing components are single dispersed (rigid chain) molecules.

As the material properties of a molecularly reinforced composite material obviously depend on the rigidity/flexibility of the reinforcing polymer, it is of significant interest to determine to which extent the mechanical properties of a molecularly reinforced polymer/polymer composite material can be controlled by tuning the overall stiffness of the reinforcing polymer. This not only provides information for the design of new reinforcing polymers but also allows to estimate if and/or to what extent semiflexible worm-like macromolecules which are known and already employed in plastic materials would be suited as blend components after having been provided with suitable groups capable of strongly interacting with the matrix.

In this paper, we report the blending of novel poly(pyridylene/phenylene-ethynylene) PPyPE polymers of tuned rigidity/flexibility (Scheme 1) with partially sulfonated polystyrene and their application as reinforcing component in ionomerblends. The tuning of the possible conformation with regard to rigidity/flexibility is given by the ratio of *para*/*meta*-substituted pyridylene moieties in the macromolecule (mole fraction $n/(n+m)$ and $m/(n+m)$ in the chemical structure Scheme 1). This is directly reflected from the systematic variation of the Flory exponent that was determined by small angle X-ray scattering (Table 1) [31]. For further analysis of the polymers with respect to their function as ionomer blend components, we utilized a model compound 2,5-bis(2-(2-pyridylene)-ethynylene)-4-dodecyltoluene (**1**) (Scheme 2) representing constitutional features of the PPyPE polymers.



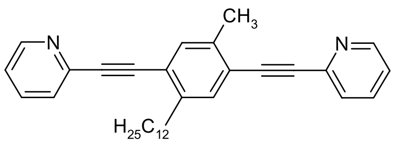
	m/(m+n)	n/(m+n)
PMPyPE	1	0
PCPyPE34	0,66	0,34
PCPyPE60	0,4	0,6
PCPyPE76	0,24	0,76
PPPyPE	0	1

Scheme 1. Chemical structure of poly(pyridylene/phenylene-ethynylenes); $n = 0$ represents the coil-like multibroken rod; the rigid rod is for $m = 0$.

2. Experimental section

2.1. Materials

The synthesis of poly(pyridylene/phenylene-ethynylenes) (PPyPE) of different rigidity/flexibility was carried out according to literature known procedures [32,33] and is described in detail elsewhere [34]. In brief, the PPyPE polymers and the model compound 2,5-bis(2-(2-pyridylene)-ethynylene)-4-dodecyltoluene (**1**) were synthesized applying the Sonogashira–Hagihara coupling reaction starting from 2,5-diethinyl-4-dodecyl toluene and 2,5- and/or 3,5-dibromo pyridine for the PPyPE polymers and 2-bromo pyridine for the model compound **1** [35] (Scheme 3). Polymers of different rigidity/flexibility were obtained by systematically varying the ratio of 2,5-/3,5-dibromo pyridine. The ratio of the two pyridine isomeric moieties within the backbone of the copolymers was determined by



1

Scheme 2. Model compound 2,5-bis(2-(2-pyridylene)-ethynylene)-4-dodecyltoluene (**1**) representing characteristic constitutional features of the PPyPE polymers.

Table 1
Structural characteristics of the five poly(pyridylene/phenylene-ethynylene) polymers studied in this work (see Scheme 1)

	$m/(m+n)$	$n/(m+n)$	$M_{n(GPC)}$ (g/mol), PD	$M_{n(VPO)}$ (g/mol), P_n	Flory exponent	Aspect ratio
PMPyPE	1	0.0	2500, 1.7	1700, 4	0.593	7
PCPyPE34	0.66	0.34	2700, 2.0	2100, 5	0.61	7
PCPyPE60	0.4	0.6	3100, 1.9	2300, 6	0.619	10
PCPyPE76	0.24	0.76	4400, 2.2	2600, 6	0.68	15
PPPyPE	0	1.0	4400, 1.9	2900, 7	0.806	45

Number average molecular weights $M_{n(GPC)}$ and polydispersity indices PD as determined by gel permeation chromatography (GPC, PS calibration), number average molecular weights $M_{n(VOP)}$ as determined by vapor pressure osmometry (VPO), and Flory exponents as extracted from SAXS patterns [31]. Aspect ratios calculated for the PPyPE polymers are based on the average length of the *para*-linked rigid segments within the polymer backbone (bond length data taken from literature [44]).

NMR-spectroscopy. Since the hydrogen in 4-position to the nitrogen of the pyridine ring generates signals, which are in case of a *meta*- or *para*-linkage well enough separated from each other, the signal intensities allow the quantitative determination of the ratio of the two pyridine isomeric moieties. This is described in detail elsewhere [34].

All PPyPE (Scheme 1) have comparable molecular weights as determined by vapor pressure osmometry and gel permeation chromatography [34] (Table 1). Since for the PPyPE polymers, the conventional GPC–polystyrene(PS)-calibration does not give the true molecular weights, the number average molecular weight of the PPyPE polymers was determined by vapor pressure osmometry, and these data together with the model compound **1** have been used for correct calibration.

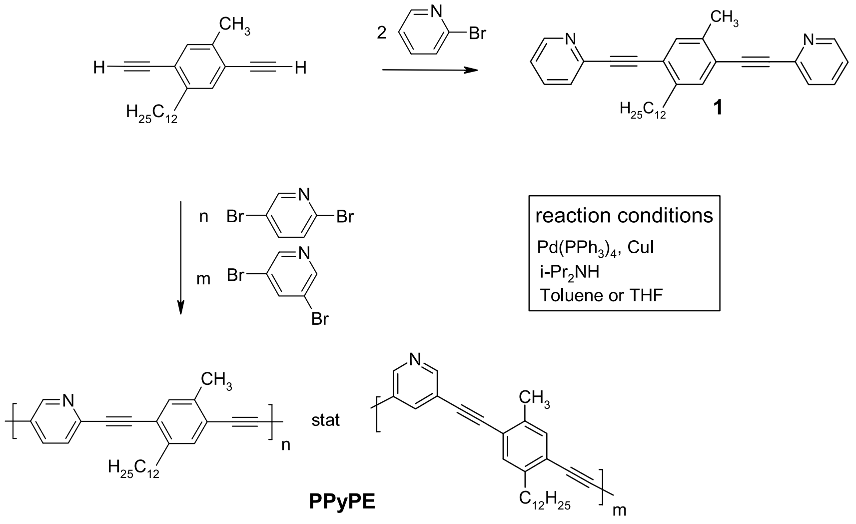
Partially sulfonated polystyrene (PS-*co*-SSH, 11 mol% arylene sulfonic acid) was used as the flexible matrix polymer. Homogeneous acid–base-ionomer blends were obtained by dropping a chloroform solution of the PPyPE (concentration between 0.2 and 0.7wt%) under stirring into a chloroform solution of PS-*co*-SSH (concentration between 1.2 and 1.8 wt%) up to equivalent amounts of the acid/base-functionalities and collecting the ionomer blend precipitate. All blends were dried at 100 °C for 2 days under vacuum.

2.2. Methods

Transmission electron microscopy (TEM) studies have been conducted on a LEO 912 Ω electron microscope with an accelerator voltage of 120 kV. Microtomed samples were prepared from compression molded specimen (170 °C, 5 min). The experimental procedure was similarly as described elsewhere [17].

Stress–strain measurements were carried out with an Instron 4301 (Automated Materials Testing System) in a temperature controlled environment. Measurements were conducted at 150 °C. Samples were again prepared by compression molding (170 °C, 5 min) as were the samples for TEM investigation.

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 focused, collimated X-ray source with a flux of 10^{10} photons on a spot size of ~0.5 mm (vertical) × 1 mm (horizontal), monochromated by a 1 1 1 Si crystal to a wavelength of $\lambda = 1.488$ Å. For the solution scattering experiments, spectroscopic grade tetrahydrofuran (Aldrich) was used without further purification. The sample cells were filled with 1% weight concentration



Scheme 3. Synthesis of poly(pyridylene/phenylene-ethynylene) (PPyPE) and 2,5-bis(2-(2-pyridylene)-ethynylene)-4-dodecyltoluene (**1**).

solutions. Further details about the sample preparation and data collection in the SAXS experiments are described elsewhere [31].

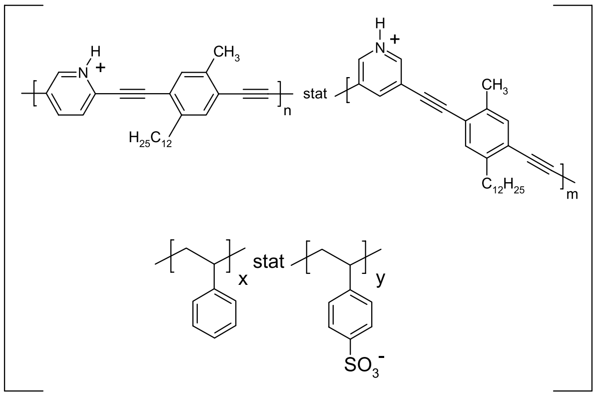
3. Results and discussion

Since the pattern and type of linkages in a polyarylene molecule determine its overall conformation, macromolecules based on arylene moieties in the constitutional unit are ideally suited models with designed and controlled rigidity/flexibility.

By varying the ratio of *para* to *meta* linkages of the pyridine moiety incorporated in the poly(arylene-ethynylene) (Scheme 1), molecules of different rigidity/flexibility are obtained. A rigid rod molecule is generated if only *para* linkages are present; the introduction of *meta* linkages provides a kink, and with increasing number of kinks the structure will ultimately be reminiscent to a flexible coil molecule. The degree of polymerization of all poly(arylene-ethynylene) employed in this work was relatively low on purpose: by keeping the contour length below the persistence length (which based on poly(arylene) data is estimated to be in the range of 13–20 nm [36]), the ideal model of a rod-shaped molecule is realized for the exclusively *p*-linked PPPyPE; by introducing and successively increasing *m*-linkages, the copolymer PCPyPE and finally the all-*m*-linked PMPyPE represent molecules of similar contour length but different conformational flexibility.

Considering the phenylene constitutional unit with *p*-ethynylene-linkages, the molecule with all *m*-linkages at the pyridine moiety may also be described as multiple broken rod with pyridylene–ethynylene–phenylene–ethynylenen–pyridylene adopting a coil conformation [31,37]. Thus in variation of the percentage of *meta* pyridine linkages from 0 to 100%, molecular conformations varying from rod-like (poly(*para*-pyridylene/phenylene-ethynylene), PPPyPE) to those of a well solvated coil (poly(*meta*-pyridylene/phenylene-ethynylene), PMPyPE) are obtained (Table 1).

In the blend formation of the poly(pyridylene/phenylene-ethynylenes) with sulfonated polystyrene from solution, quantitative proton transfer from the styryl sulfonic group to the pyridylene group takes place resulting in a poly(pyridylenium/phenylene-ethynylene) multiplication and polystyrene sulfonate polyanions (Scheme 4).



Scheme 4. Acid/base polymer/polymer polyelectrolyte as resulting from proton transfer of polystyrene sulfonic acid to poly(pyridylene/phenylene-ethynylene) (stoichiometry of pyridylene and sulfonic acid groups).

The complete protonation of the poly(pyridylene/phenylene-ethynylene) in the acid/base ionomer blends with sulfonated polystyrene has been proven by UV–VIS absorption and emission spectroscopy. As expected from their conjugated structure, the optical properties of the PPyPE polymers depend on the electronic properties of the conjugated arylene–ethynylene-π-electron system and therefore on the extension of the conjugated system [32, 37–39], and also on the type and number of substituents attached to the polymer backbone [39] as well as the type of the arylene constitutional unit [33,40]. Due to the pyridine moiety incorporated into the polymer backbone, the optical properties of the PPyPE polymers are further affected by the degree of protonation, which renders the optical spectroscopy a valuable tool in determining the degree of protonation of the PPyPE polymers within the ionomer blends.

Model studies applying a model compound **1** representing characteristic constitutional features of the polymers (Scheme 2) and *p*-toluene sulfonic acid were performed in order to determine the degree of protonation achievable within the PPyPE polymers. A solution of **1** in deuterated chloroform was treated with *p*-toluene sulfonic acid and the resulting change in the chemical shifts of the pyridylene-proton signals initiated by the protonation of the pyridylene–nitrogen was monitored by NMR-spectroscopy [41]. We observed that the change in chemical shift depends linearly on the amount of acid added reaching a limiting value for 2 equiv. of acid added. Hence, with *p*-toluene sulfonic acid, both pyridylene units of **1** can be quantitatively protonated. The same experiment was performed and monitored by UV–VIS-absorption and -emission spectroscopy. The change in the absorption and emission spectrum of **1** upon addition of *p*-toluene sulfonic acid is shown in Fig. 2a and b. The absorption and emission spectra steadily change with the protonation of the pyridylene-unit; the spectrum of the 100% protonated **1** distinctly differs from the spectrum of the non-protonated species.

Partially protonated **1** displays spectra composed of the corresponding spectrum of the protonated and the non-protonated species with the ratio being related to the obvious equilibrium of the two isolated chromophores. In this context it has to be mentioned that here, in contrast to the NMR experiment, a higher number of equivalents of acid has to be added to obtain the fully protonated **1**; this is to some extent an effect of different sample concentrations and will be described in detail elsewhere [41].

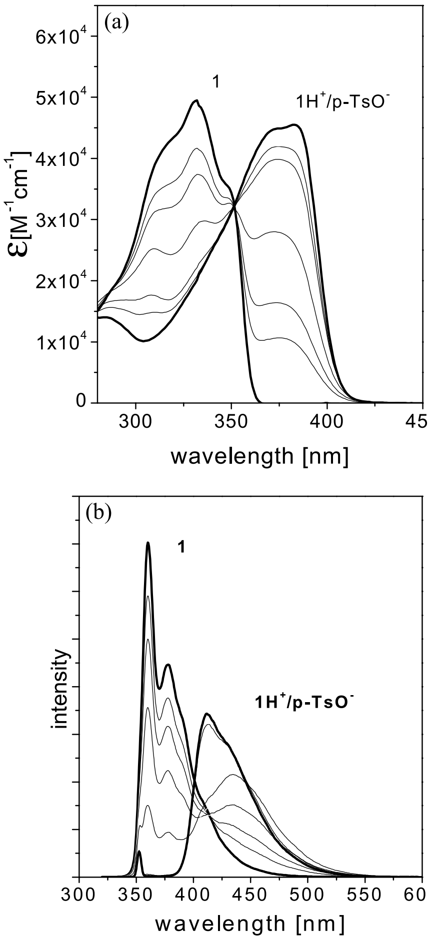


Fig. 2. UV–VIS-absorption (a) and emission (b) spectra of **1**/1H$^+$ with varying degree of protonation (solution spectra in chloroform; *p*-toluenesulfonic acid *p*-TsOH as protonating agent); the mole ratio *p*-TsOH/pyridylene of the depicted absorption spectra is 0 (**1**), 1, 2, 4, 9, 14, 24 (1H$^+$) and for the emission spectra 0 (**1**), 1, 2, 4, 10, 20 and 70 (1H$^+$).

Since the PPyPE polymers contain the same constitutional unit as **1**, optical spectroscopy can be also applied the determine the degree of protonation of the PPyPE polymers. The change in the poly(pyridylene/phenylene-ethynylene) absorption and emission spectra in chloroform solution upon addition of *p*-toluene sulfonic acid is exemplarily illustrated for the rigid PPPyPE by the series of spectra depicted in Fig. 3a and b.

Again, this model study shows that the absorption and emission spectra steadily change with the protonation of the pyridylene moiety, and that the spectrum of the protonated polymer distinctly differs from the spectrum of the non-protonated polymer. As observed for the model compound **1**, the spectra of the partially protonated polymer species is composed of the spectra of the corresponding protonated and non-protonated species, indicating the presence of an equilibrium between two isolated species The polymer behaves as if it is composed of isolated chromophores [32]. Therefore, quantitative protonation is indicated by the presence of only one absorption or emission band, which is red-shifted to the corresponding absorption or emission band of the non-protonated polymer. Hence, this optical characterization can be applied in investigating the degree of protonation of the PPyPE polymers in the ionomer blends. The protonation equilibrium and further spectroscopic aspects will be discussed in detail elsewhere [41].

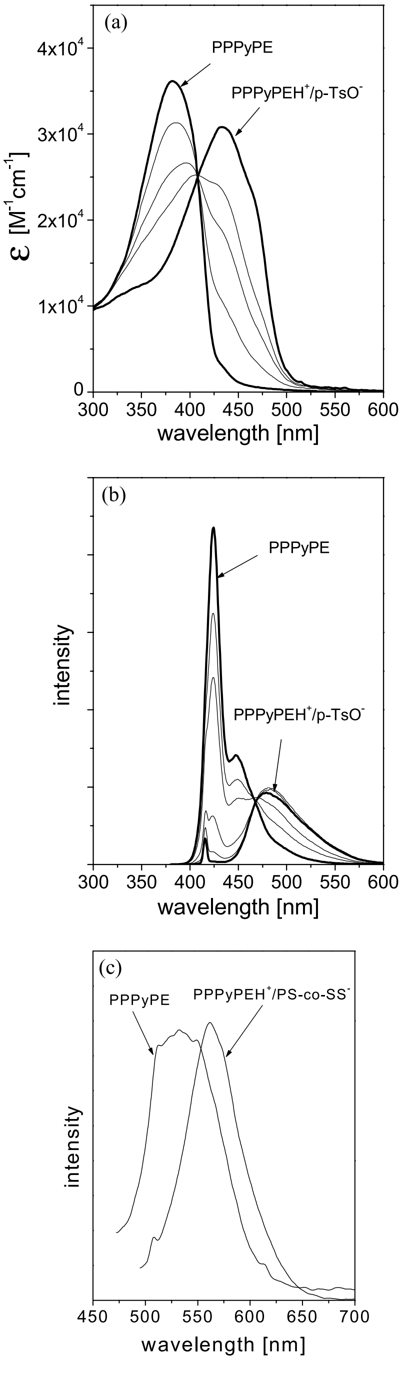


Fig. 3. UV–VIS-absorption (a) and emission (b) spectra of PPPyPE/PPPyPEH$^+$ with varying degree of protonation (solution spectra in chloroform; *p*-toluenesulfonic acid *p*-TsOH as protonating agent), the mole ratio *p*-TsOH/pyridylene of the depicted absorption spectra is 0 (PPPyPE), 1, 4, 8, 40 (PPPyPEH$^+$) and for the emission spectra 0 (PPPyPE), 4, 8, 26, 64, 140 (PPPyPEH$^+$); (c): UV–VIS-emission spectra of PPPyPE and PPPyPEH$^+$/PS-*co*-SS$^-$ (solid state spectra).

Since the PPPyPEH$^+$/PS-*co*-SS$^-$ ionomer blends are insoluble in common solvents, the comparable optical characterization of the blends had to be performed in solid state. The emission spectrum of the solid film of the PPPyPEH$^+$/PS-*co*-SS$^-$ ionomer blend gives a single fluorescent band only ($\lambda_{\text{max,E}} = 563$ nm with $\lambda_{\text{exc}} = 420$ nm) which distinctly differs from the emission spectrum of the bulk PPPyPE (Fig. 3c). Based on the results obtained for the model compound **1** and the PPPyPE in solution as described above, this is a clear spectroscopical evidence that complete proton transfer has taken place during the ionomer blend formation (stoichiometry of pyridylene and sulfonic acid groups); the same results have been obtained for the other systems where the poly(pyridylene/phenylene-ethynylenes) of tuned rigidity have been employed with the only difference that the absorption as well as emission band maxima varied with the mole fraction of *m*-linkages [41].

The complete miscibility of the blend components in the ionomer blends with sulfonated polystyrene (PPyPEH$^+$/PS-*co*-SS$^-$) as compared to a phase-separated blend with pure polystyrene (PPyPE/PS) has been first investigated by DSC analysis. The comparison between the DSC curves of the PPPyPEH$^+$/PS-*co*-SS$^-$ blend (curve 3a/b, Fig. 4) with the curves of the employed blend components (curves 1 and 2a/b, Fig. 4) shows for the ionomer blend a single glass transition at around $T_g = 117$ °C (curve 3b, second heating) which is in between the glass transition of the PS-*co*-SSH matrix polymer (curve 1; $T_g = 125$ °C) and the PPPyPE reinforcer polymer (curve 2b, second heating; $T_g = 39$ °C); due to the matrix-rod ionic interactions, the T_g temperature-range of the ionomer blend is broader than that of the pure matrix polymer (compare curves 1 and 3, Fig. 4).

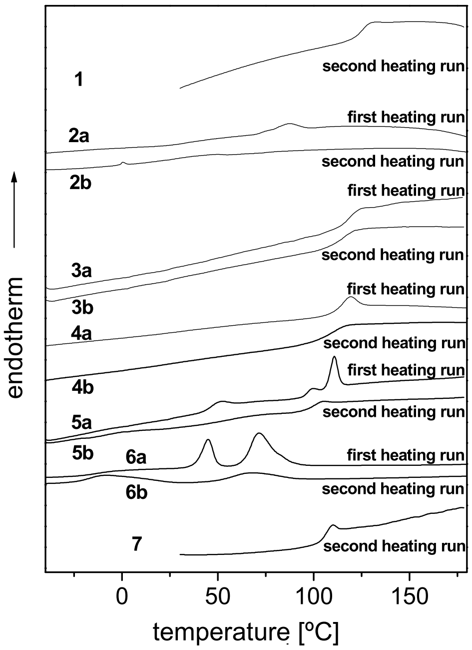


Fig. 4. DSC curves of sulfonated polystyrene PS-*co*-SSH (11 mol% sulfonation (SSH), curve 1), of the poly(pyridylene/phenylene-ethynylene) PPPyPE (curves 2a/b, first/second heating), of the stoichiometric acid–base blends PPPyPEH$^+$/PS-*co*-SS$^-$ (curve 3) and PMPyPEH$^+$/PS-*co*-SS$^-$ (curve 4), of the PMPyPE/PS mixture (curves 5a/b, first/second heating; same PMPyPE-weight fraction (27 wt%) as for the ionomer blend curve 4) as well as of the poly(pyridylene/phenylene-ethynylene PMPyPE (curve 6) and of polystyrene (curve 7).

For comparison and in order to clarify the necessity of rod-coil intermolecular ionic interactions for molecular blending, the DSC curve of the blend of PMPyPE with PS-*co*-SSH is contrasted to the DSC-curve of the mixture of PMPyPE with polystyrene (PS). Again, the PMPyPEH$^+$/PS-*co*-SS$^-$ ionomer blend exhibits a single glass transition (curve 4b, second heating, Fig. 4; $T_g = 109$ °C) only, which is in between the glass transitions of the blend components (matrix polymer, curve 1, $T_g = 125$ °C; PMPyPE, curves 6, T_g around -10 °C; Fig. 4). In contrast to this, the DSC curve of the PMPyPE/PS blend shows multiple transition features (curves 5a/b, Fig. 4) to be expected for an immiscible blend: The DSC trace is reminiscent to the various phase transitions of the PMPyPE polymer (T_g around -10 °C and endothermic transitions at higher temperature, compare curves 6a/b, Fig. 4) and exhibits also a the strong enthalpy relaxation peak of the glass–rubber transition of polystyrene (around 106 °C, compare curve 5a and curve 7, Fig. 4). The multiple transition peaks of the PMPyPE polymer phase in the phase-separated PMPyPE/PS blend are attributed to the melting of different crystallites of partially crystalline PMPyPE microphases which may be related to constitutional and chain length distribution effects; this has been discussed elsewhere [34].

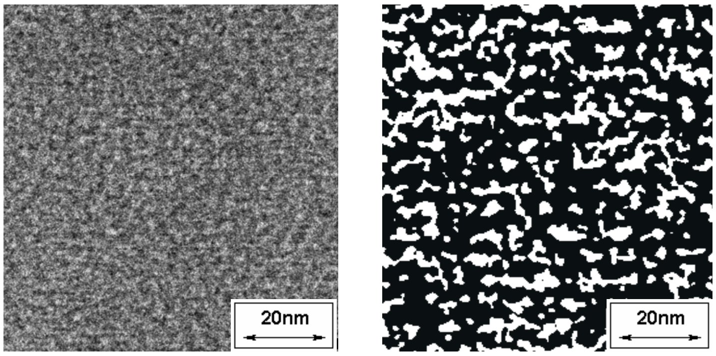
This microphase separated system of poly(pyridylene/-phenylene-ethynylene) domains dispersed in PS matrix which results from the lack of interacting groups and thus the incompatibility of the blend components has been visualized by TEM [31].

As it is already inferred from the DSC traces of the PPPyPEH$^+$/PS-*co*-SS$^-$ and PMPyPEH$^+$/PS-*co*-SS$^-$ ionomer blends, the high resolution TEM bright field images of microtomed specimen showed no evidence of heterogeneity, indicating the complete miscibility through attractive ionic interactions (Fig. 5a1 and b1); the granular texture does not reflect a heterogeneity but is typically obtained for homogeneous amorphous materials observed in phase contrast [17,31].

The molecular dispersion of the poly(pyridylene/phenylene-ethynylene) polycations in the polystyrene sulfonate matrix was further revealed from nitrogen net element specific image (ESI) TEM (Fig. 5a2/b2). The bright areas on black background represent enrichment of the element nitrogen in a nitrogen-free matrix. Since the element nitrogen is only present in the poly(pyridylene/phenylene-ethynylene) blend component, these bright areas can only be associated with molecularly dispersed poly(pyridylene/phenylene-ethynylene) molecules; this is in agreement with the angström-to-nanoscopic dimensions of the size and shape of the polycations. In this context it is interesting

a1/a2)

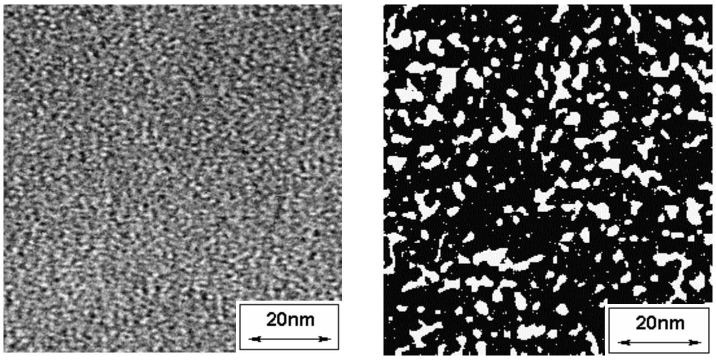
PPPyPEH$^+$/PS-co-SS$^-$



bright-field-TEM **ESI(N)-TEM**

b1/b2)

PMPyPEH$^+$/PS-co-SS$^-$



bright-field-TEM **ESI(N)-TEM**

Fig. 5. Transmission electron micrographs bright field images (bright-field-TEM, a1/b1) and nitrogen net element specific images (ESI(N)-TEM, a2/b2) of the stoichiometric acid-base ionomer blends PPPyPEH$^+$/PS-*co*-SS$^-$ and PMPyPEH$^+$/PS-*co*-SS$^-$ (27 wt% poly(pyridylene/phenylene-ethynylene) blend component); magnification: 125,000 × .

to note that the ESI(N)-TEM of the PPPyPEH$^+$/PS-*co*-SS$^-$ ionomer blend infers anisotropic orientation of the rod-like polycations (Fig. 5a2) which is not seen for the coil-like PMPyPEH$^+$ polycations in the PMPyPEH$^+$/PS-*co*-SS$^-$ ionomer blend (Fig. 5b2). Such a texture would be in accordance with theory which predicts anisotropic one phase ionomer blends when the volume fraction of the rod-component (of a given length i.e. aspect ratio) exceeds a certain value [17], and the development of such anisotropy has actually been observed in poly(*p*-phenylene) reinforcer based ionomer blends with both variation of the length and volume fraction of the poly(*p*-phenylene) component [42].

3.1. Stress–strain measurements

The reinforcement in the polymer–polymer composites due to the rigid rod PPPyPE or the semiflexible, copolymers PCPyPE is evident from the comparison of the stress–strain curves of the sulfonated polystyrene matrix polymer PS-*co*-SSH and the blends with poly(pyridylene/phenylene-ethynylene) (Fig. 6). The values obtained for the Young modulus E of each blend are also given. Due to the brittleness of the materials at ambient temperature, stress–strain measurements were conducted at 150 °C, i.e. above the glass transition temperatures T_g of the polymer blends and blend components.

With the rigid rod poly(*para*-pyridylene/phenylene-ethynylene) in the blend, the elastic modulus increased from 0.28 MPa of the sulfonated polystyrene matrix polymer (curve 1, PS-*co*-SSH) to 7.7 MPa (curve 6, PPPyPEH$^+$/PS-*co*-SS$^-$), while for the blend with the relatively flexible coil-like poly(*meta*-pyridylene/phenylene-ethynylene) (curve 2, PMPyPEH$^+$/PS-*co*-SS$^-$) no increase of the modulus as compared to the modulus of

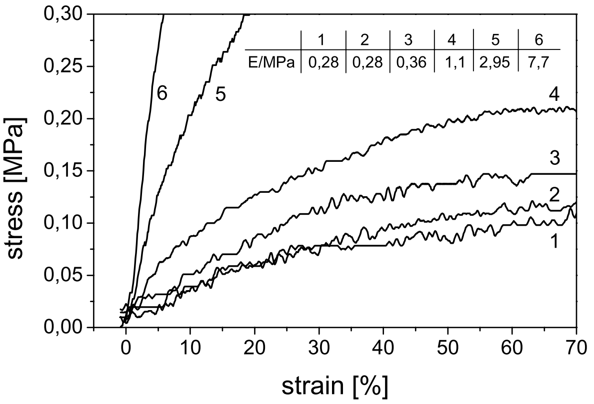


Fig. 6. Stress–strain curves of PS-*co*-SSH (curve 1) and of the acid-base ionomer blends PMPyPEH$^+$/PS-*co*-SS$^-$ (curve 2), PCPyPE34H$^+$/PS-*co*-SS$^-$ (curve 3), PCPyPE60H$^+$/PS-*co*-SS$^-$ (curve 4), PCPyPE76H$^+$/PS-*co*-SS$^-$ (curve 5), PPPyPEH$^+$/PS-*co*-SS$^-$ (curve 6) containing 27% reinforcer. The Young moduli *E* as determined from the initial slope are inserted.

the pure matrix polymer was detected. This enhancement of the mechanical properties can directly be related to the stiffness of the reinforcing polymer, since the formation of an ionomer network which might also contribute to the overall reinforcement is present in both cases.

This view further implies that the varying reinforcement effect as determined for the other samples containing the poly(*co*-pyridylene/phenylene-ethynylene) copolymers (PCPyPE) of varying *m*-pyridylene linkages (see Scheme 1), could be related to differences in the stiffness of the poly(pyridylene/phenylene-ethynylene) blend components. Consequently considering the Flory exponent being correlated to the fraction of *para*-linkages [31], the Young modulus of the ionomer blend is directly proportional to the conformational structure of the reinforcer molecule; this is shown in Fig. 7.

In order to correlate the anisotropy and therefore the rigidity/flexibility of the reinforcing PPyPE polymer with the mechanical properties of the reinforced ionomer blend, the Halpin–Tsai equations [2] can be taken into account. The Halpin–Tsai equations are a set of empirical relationships that enable the property of a composite material to be expressed in terms of the mechanical properties of both the matrix and the shape-anisotropic reinforcing component (e.g., glass or carbon fibers) together with their volume fraction and the geometry (aspect ratio) of the reinforcer. Accordingly, in a composite material consisting of randomly oriented rod-like macromolecules in an amorphous coil polymer matrix, the blend modulus is directly correlated with the aspect ratio (polymer length *l* to diameter *d*) of the reinforcing rod polymer [43].

The aspect ratios of the PPPyPE and PMPyPE homopolymers as well as of the PCPyPE copolymers as compiled in Table 1 were obtained by using literature known bond length data [44]. The calculations are based on the assumption, that the alkyl-side chains do not contribute to the overall molecule diameter. In order to account for the interruption of the rigid-rod geometry by the *m*-linkages, the semiflexible PCPyPE and flexible PMPyPE polymers were considered as 'broken rods'. For the sake of simplicity and since the main reinforcing effect may be attributed to the average length of the rigid-rod between *m*-linkage break points, the average length of only *para*-linked rod-like segments within the copolymers, was taken for the calculation of the aspect ratio of the copolymer. Thus considering the aspect ratio as being correlated to the fraction of *para*-linkages [31], the Young modulus of the ionomer blend is found to be directly proportional to the aspect ratio of the reinforcer molecule, as predicted by theory; this is shown in Fig. 8. In this context, it is also worthwhile to mention that the glass transition temperature of the poly(pyridylene/phenylene-ethynylenes) scales (decreases) with the content of *m*-pyridylene-linkages in the same way [34] as does the reinforcement effect in the ionomer blends.

Further studies investigating the elongation induced orientational ordering of the reinforcing PPyPE polymers of different rigidity/flexibility within the ionomer blends were performed applying SAXS. Ionomer blend samples were strained to about 300% elongation and the degree of orientational ordering induced was monitored. While for the

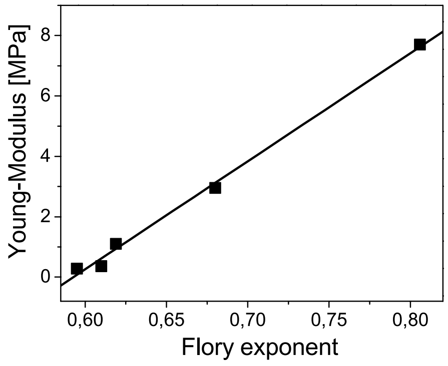


Fig. 7. Young modulus as determined from the stress-strain curves of the poly(pyridylene/phenylene-ethynylene)/polystyrene sulfonate ionomer blends (see Fig. 6) vs. the Flory exponent of poyl(pyridylene/phenylene-ethynylene) as determined by SAXS.

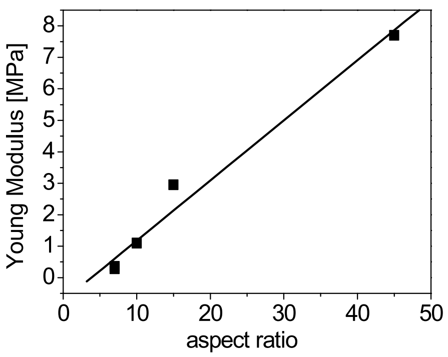


Fig. 8. Young modulus as determined from the stress–strain curves of the poly(pyridylene/phenylene-ethynylene)/polystyrene sulfonate ionomer blends (see Fig. 6) vs. the aspect ratio of poyl(pyridylene/phenylene-ethynylene) as calculated (see Table 1).

not strained samples no orientational ordering was observed indicating isotropy, the strained ionomer blend samples displayed orientational ordering phenomena. The degree of orientational ordering varied hereby systematically with the rigidity/flexibility of the PPyPE reinforcing polymer: with the ionomer blend containing the rod-like polymer PPPyPE display the highest order of orientation while for the ionomer blend with the coil-like polymer PMPyPE no orientational ordering was observed. Since the degree of orientation of the reinforcing polymers was measured at high elongation values while the Young-Modulus was determined at low elongation values, i.e., in a practically unoriented state of the reinforcing macromolecules, the correlation between molecular architecture and bulk material properties is meaningful [31].

4. Conclusions

The study of the series of rod-coil ionomer blends based on poly(pyridylene/phenylene-ethynylene) of tuned rigidity/flexibility as blend component with sulfonated polystyrene has demonstrated that the mechanical properties of a molecularly reinforced blend material can be controlled by varying the rigidity/flexibility of the reinforcing polymer component. Stress–strain measurements showed, that a significant reinforcement effect of almost a factor of 30 was achieved when the blends were made with rigid rod polymer but the mechanical properties of the flexible matrix polymer remained unchanged upon blending with the flexible Poly(pyridylene/phenylene-ethynylene). The Young modulus of the blends was found to systematically vary with the rigidity/flexibility of the reinforcing polymer.

Information about the molecular conformation of the reinforcing polymers in solution obtained by small angle X-ray analysis, allowed to directly relate the change of the mechanical properties of the ionomer blends to the overall chain stiffness, i.e. to the rod/coil character of the reinforcing polymers.

These findings open interesting perspectives for the design of novel materials with controlled mechanical properties based on molecular rod/coil ionomer blends; this will be emphasized in future studies.

Acknowledgements

We acknowledge the support in small angle X-ray scattering by Dr John A. Pople, Stanford Synchrotron Radiation Laboratory, Stanford University and Prof. Dr A.P. Gast, Massachusetts Institute of Technology. The support in transmission electron microscopy by Dr R. Thomann, University of Freiburg, is gratefully acknowledged. Dominik Winter would also like to thank the Fonds der Chemischen Industrie for a fellowship.

References

[1] Kardos JL, Raisoni J. Polym Engng Sci 1975;15:183.
[2] Halpin JC, Kordos JL. Polym Engng Sci 1976;16:344.
[3] Hwang WF, Wiff DR, Benner CL. J Macromol Sci Phys 1983;B22:231.
[4] Takayanagi M, Ogata T, Morikawa M, Kai T. J Macromol Sci Phys 1980;B17:591.
[5] An ideal representation of such a component would be a rigid-rod macromolecule.
[6] Flory PJ. Macromolecules 1978;11:1138.
[7] Li L, Chan CM, Weng LT, Xiang ML, Jiang M. Macromolecues 1998;31:7248.
[8] de Meftahi MV, Frechet JMJ. Polymer 1988;29:477.
[9] Radzilowski LH, Stupp SI. Macromolecues 1994;27:7747.
[10] Zhang L, Huo F, Wang Z, Wu L, Zhang X, Hõppener S. Langmuir 2000;16:3813.
[11] Dormidontova E, Brine G. Macromolecues 1998;31:2110.
[12] Robeson L, McGrath JJ. Polym Engng Sci 1977;17:300.
[13] Pierce E, Kwai T, Min B. J Macromol Sci Chem 1984;A21:1181.
[14] Rochigues-Parada JM, Percec V. Macromolecules 1986;19:55.
[15] Eisenberg A, Smith P, Zhou ZL. Polym Engng Sci 1982;22:1117.
[16] Ballauf M. Angew Chem Int Ed Engl 1989;28:253.
[17] Noolandi J, Shi ACh, Hofmann J, Eisenbach CD. Macromolecules 1999;32:1463.
[18] Eisenbach CD, Hofmann J, Fischer K. Macromol Chem Rapid Commun 1994;15:117.
[19] Eisenbach CD, Hofmann J, MacKnight VJ. Macromolecules 1994;27:3162.
[20] Tan LS, Arnold FE, Chuah HH. Polymer 1991;32:1376.
[21] Weiss RA, Shao L. Macromolecules 1992;25:6370.
[22] Cowie JMG, Nakata S, Adams GW. Macromol Symp 1996;112:207. Fifth European Symposium on Polymer Blends.
[23] Weiss RA, Shao L, Lundberg RD. Macromolecules 1992;25(23):6370.
[24] Tang WL, Thompson B, Coleman MM, Painter PC. Polym Prepr (Am Chem Soc, Div Polym Chem) 1990;31(1):541.
[25] Tson L, Hara M. Polym Prepr (Am Chem Soc, Div Polym Chem) 1996;37(1):390.
[26] Hara M, Parker GJ. Polymer 1992;33:4650.
[27] Eisenbach CD, Datko A, Göldel A, Hofmann J, Lehmann T, Winter D. Polym Prepr, Am Chem Soc Div Polym Chem 1998;39/1:715.
[28] Eisenbach CD, Fischer K, Hofmann J. Polym Prepr, Am Chem Soc Div Polym Chem 1995;36/1:795.
[29] Kricheldorf HR, Wahlen LH. Macromolecules 1997;30:2642.
[30] Cimecioglu AL, Weiss RA. Macromolecules 1995;28:6343.
[31] Winter D, Eisenbach CD, Gast AP, Pople JA. Macromolecules 2001;34:5943.
[32] Swager TM, Gil CJ, Wrighton MS. J Phys Chem 1995;99:4886.
[33] Moroni M, Le Moigne J. Macromolecules 1994;27:562.
[34] Eisenbach CD, Winter D. J Polym Sci, Chem Ed 2004; 42, in press.
[35] Sonogashira K, Tohda Y, Hagihara N. Tetrahedron Lett 1975;4467.
[36] Vanhee S, Rulkens R, Lehmann U, Rosenauer C, Schulze M, Köhler W, Wegner G. Macromolecules 1996;29:5136.
[37] Pang Y, Li J. Macromolecules 1998;31:6730.
[38] Tour JM, Pearson DL, Schumm JS. Macromolecules 1994;27:2348.
[39] Wautelet P, Moroni M, Oswald L, Le Moigne J, Pham A, Bigot JY, Luzzati S. Macromolecules 1996;29:446.
[40] Yamamoto T, Honda K. Macromolecules 1998;31:7.
[41] Eisenbach CD, Winter D, Kramer HEA. Macromolecules; submitted.
[42] Datko A, Eisenbach CD. In preparation.
[43] Eisenbach CD, Fischer K, Hofmann J, MacKnight WJ. Macromol Symp 1999;100:105.
[44] Morrison RT, Boyd RN. Lehrbuch der Organischen Chemie, 3rd ed. Weinheim: VCH; 1986.