Macromolecules **1994,** *27,* 3162-3165

Dynamic Mechanical and Spectroscopic Study of Ionomer Blends Based on Carboxylated or Sulfonated Flexible Polystyrene and Rigid Poly(diacetylenes) with Functional Side Groups

C. D. Eisenbach* and J. Hofmann

Makromolekulare Chemie II and Bayreuther Institut für Makromolekülforschung (BIMF), Universität Bayreuth, D-95440 Bayreuth, Germany

W. J. MacKnight

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

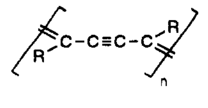
Received December 12, 1993; Revised Manuscript Received March 24, 1994[⊗]

ABSTRACT: The dynamic mechanical and infrared spectroscopic investigation of ionomer blends of poly(diacetylene)- and polystyrene-based ionomers has shown that miscibility of this usually incompatible polymer pair can be achieved through ion–ion interactions between the blend components. Microphase separation is prevented through ionic contacts generated during the blend formation; a schematic model of mixing in the blends is proposed.

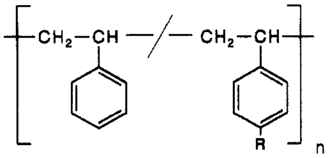
Introduction

The generally limited miscibility of two polymers, which is predominantly related to the unfavorable low entropy of mixing of macromolecules, can be considerably improved—if not even overcome—if specific interactions between the two components provide a negative enthalpy of mixing. One very encouraging route to achieve miscibility of otherwise immiscible polymer pairs is to take advantage of ion–ion or acid–base interactions of specifically modified polymers.[1-5]

The concept of inducing miscibility of different polymers through ionic interactions has been applied to a pair of random-coil and rodlike polymers[6] which—compared to flexible polymer blends—are even more unlikely to mix since the segregation is further enhanced by the preference of the rodlike component for an anisotropic phase.[7-9] In our recent study[10] of the miscibility of poly(diacetylene) ionomers with polystyrene-based ionomers, differential scanning calorimetry (DSC) and transmission electron microscopy (TEM)[11] data have revealed that the compatibilization of a true rigid-rod polymer such as poly(diacetylene) with random-coil polymers is possible by an ionic interaction. The precursor polymers for the ionomer blends were poly(5,7-dodecadiyne-1,12-dicarboxylic acid) (P12DCAH) or poly(10,12-docosadiynylene diisonicotinate) (P22DPy) as the rigid-rod polymer component and poly(styrene-*co*-4-vinylbenzoic acid) [P(S-*co*-4VBAH)] or poly(styrene-*co*-4-styrenesulfonic acid) [P(S-*co*-SSH)] as the flexible matrix.



	R
P12DCAH	$(CH_2)_3COOH$
P22DPy	$(CH_2)_9OOC$-  N



	R
(PS-co-4VBAH) (26 mole-% 4VBAH)	COOH
(PS-co-SSH) (9 mole-% SSH)	SO_3H

In this paper, the study of the anionic ionomer blend of the triethylammonium ionomers P12DCA$^-$$(C_2H_5)_3HN^+$ of the poly(diacetylene) and P[S-*co*-4VBA$^-$$(C_2H_5)_3HN^+$] of the styrene-4-vinylbenzoic acid copolymers, as well as the acid–base ionomer blend P(S-*co*-SS$^-$)/P22DPyH$^+$ of the sulfonated polystyrene and poly(diacetylene), has been complemented by dynamic mechanical thermal analysis (DMTA) and Fourier transform infrared (FTIR) spectroscopy. The DMTA data are more sensitive to phase behavior on an intimate scale (down to at least 50-Å dimension) than DSC analysis, and the FTIR spectra allow the direct investigation and quantification of specific interactions, especially in the acid–base blends where compatibility occurs with the formation of new (ionic) groups.[5,12]

Experimental Section

The triethylammonium blend was prepared by dissolving a mixture of the triethylammonium ionomers P12DCA$^-$$(C_2H_5)_3HN^+$ and P[S-*co*-4VBA$^-$$(C_2H_5)_3HN^+$] in a saturated aqueous triethylamine solution followed by evaporation of the water and excess triethylamine. The acid–base blend P(S-*co*-SS$^-$)/P22DPyH$^+$ was prepared by first dissolving P(S-*co*-SSH) and P22DPy separately in chloroform in stoichiometric amounts of interacting acidic ($-SO_3H$) and basic (pyridyl) groups; then the polymer(diacetylene) solution was added dropwise to the stirred solution of the sulfonate polystyrene, and the gellike layer on top of the $CHCl_3$ was removed. All blends were dried at 60 °C for 3 days under vacuum. The details of the synthesis and sample preparation have been described previously.[10]

Dynamic mechanical thermal analysis (DMTA) was done on a Polymer Laboratories DMTA at 4 °C/min and a frequency of 1 Hz similar to that described in the literature.[4] Samples were prepared by compression molding at 150 °C under vacuum for 10 min; the brittleness of the materials prevented the preparation of a standard sample size. Transition temperatures are given as the peak in tan δ.

Infrared absorption was measured using an IBM IR/32 FTIR spectrometer at a resolution of 1 cm^{-1} averaged over 64 scans. Transparent and clear films were made by compression molding at 150 °C in a manner similar to that described in the literature.[5]

Results and Discussion

The thermal analysis data of both the DMTA and DSC for the precursor triethylammonium ionomers as well as the "acid" and "base" polymers and for the triethylammonium ionomer blend as well as the acid–base blend are

---

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1994.

0024-9297/94/2227-3162\$04.50/0

Table 1. DSC[10] and DMTA Data of the Triethylammonium Ionomers PS-*co*-4VBA$^-$(C$_2$H$_5$)$_3$HN$^+$ of Poly(styrene-*co*-4-vinylbenzoic acid) (26 mol % 4-Vinylbenzoic acid) and P12DCA$^-$(C$_2$H$_5$)$_3$NH$^+$ of Poly(5,7-dodecadiyne-1,12-dicarboxylic acid) and of the Corresponding Anionic–Anionic Ionomer Blend and of Poly(styrene-*co*-4-styrenesulfonic acid) (PS-*co*-SSH; 9 mol % Styrenesulfonic Acid), Poly(10,12-docosadiynylene diisonicotinate) (P22DP$_Y$), and the Acid–Base PS-*co*-SS$^-$/P22DP$_Y$H$^+$ Blend

	T_g/°C	
	DSC	DMTA
PS-*co*-4VBA$^-$(C$_2$H$_5$)$_3$HN$^+$	101	142
P12DCA$^-$(C$_2$H$_5$)$_3$NH$^+$	0	56
PS-*co*-4BVA$^-$(C$_2$H$_5$)$_3$HN$^+$/P12DCA$^-$(C$_2$H$_5$)$_3$HN$^+$ (4.5/1, w/w)	89	125 (123)
PS-*co*-SSH	114	126
P22DP$_Y$	80[b,c]	90[b,d]
PS-*co*-SS$^-$/P22DP$_Y$H$^+$ (4.4/1 w/w)	109	110 (118)[a]

[a] T_g calculated from the experimental T_g's of the corresponding blend components by using the Fox equation $1/T_g = w_1/T_{g1} + w_2/T_{g2}$ where w is the weight fraction of the corresponding component in the blend. [b] Melting temperature T_m = 113 °C. [c] Mesophase–isotropic melt transition at 128 °C. [d] Mesophase–isotropic melt transition at 125 °C.

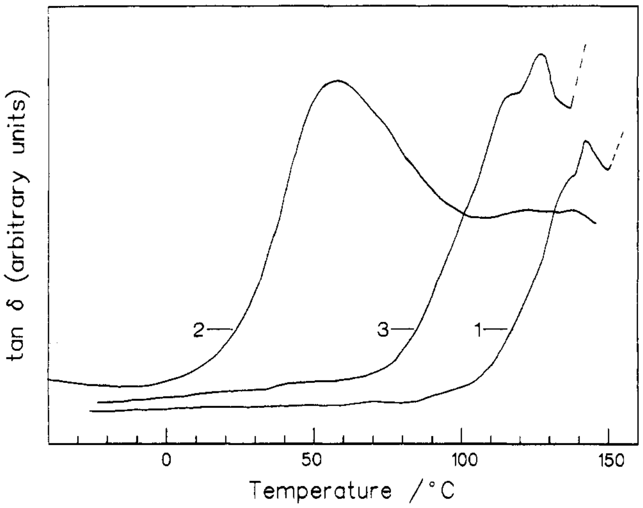


Figure 1. DMTA curves (tan δ) of PS-*co*-4VBA$^-$(C$_2$H$_5$)$_3$HN$^+$ (curve 1) P12DCA$^-$(C$_2$H$_5$)$_3$HN$^+$ (curve 2) and the ionomer blend (4.5/1, w/w; curve 3).

compiled in Table 1. The deviations between the glass transition temperatures T_g of P(S-*co*-SSH) and P22DPy measured by DSC and DMTA are due to the fact that the DMTA is sensitive to the frequency-dependent viscoelastic relaxation phenomena associated with T_g, while the DSC provides a measurement of the (pseudo) thermodynamic glass transition itself.

Figure 1 shows the tan δ curves of the triethylammonium rigid-rod and random-coil ionomer precursors and the triethylammonium ionomer blend. The occurrence of only one loss peak for the polymer blend (curve 3) with a maximum at 125 °C indicates the compatibility of the blend components on a length scale of 50 Å and is in accordance with the DSC analysis (Figure 2, curve 1).[10] The shoulder on the low-temperature side, which is also present in the loss peak of the carboxylated polystyrene ionomer, is not yet understood and might be related to a secondary (β) relaxation process. The tan δ increase at higher temperatures (dotted) is associated with thermal decomposition as confirmed by thermogravimetric analysis. There is little deviation between the experimentally observed and calculated T_g based on the Fox equation; however, in this context it has to be considered that this equation does not account for specific interactions which are expected to raise T_g above the value from the linear additivity, as was in fact observed by DSC.[10]

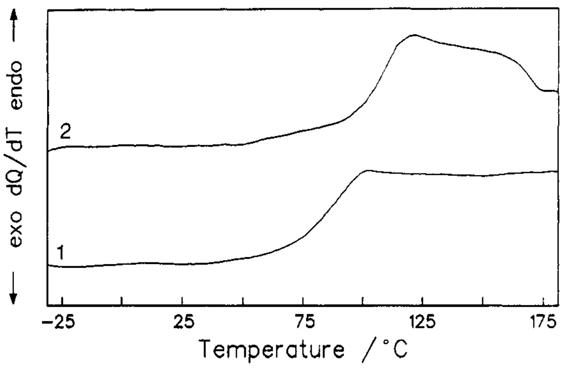


Figure 2. DSC trace (cf. ref 10) of the triethylammonium ionomer blend PS-*co*-4VBA-(C$_2$H$_5$)$_3$HN$^+$/P12DCA$^-$(C$_2$H$_5$)$_3$HN$^+$ (4.5/1, w/w), curve 1, and of the acid–base ionomer blend PS-*co*-SS$^-$/P22DPyH$^+$ (4.4/1, w/w; charge neutrality), curve 2. Heating rate 20 K/min.

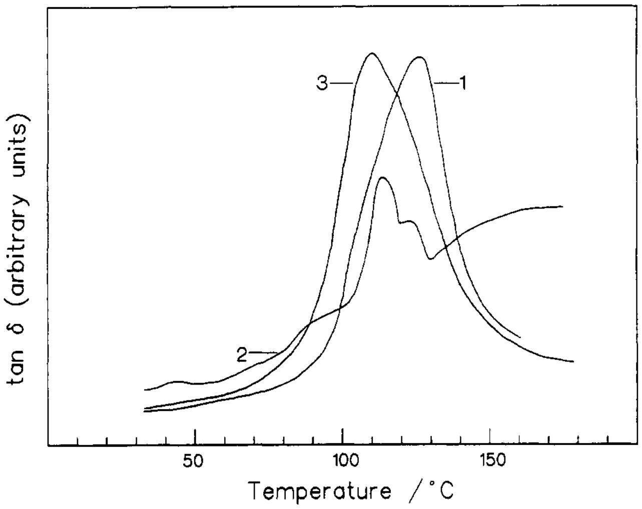


Figure 3. DMTA curves (tan δ) of PS-*co*-SSH (curve 1), P22DP$_Y$ (curve 2), and the blend (4.4/1, w/w; curve 3).

The results of the dynamic mechanical measurements of the acid–base ionomer blend and of the corresponding blend precursors are shown in Figure 3. The behavior of the loss curve of the polydiacetylene P22DPy (curve 2) is very similar to the DSC trace[10] and the loss at around 90 °C reflects motions accompanying the glass transition, whereas the maxima at 113 and 125 °C are associated with diffuse first-order transitions, i.e., crystalline–liquid crystalline (LC) and LC–isotropic melt transitions. Again, the blend shows only a single but relatively broad loss peak with a maximum at 110 °C, which infers that this acid–base blend consists of a single phase on a scale of 50 Å, too; this is in agreement with the DSC analysis as well (Figure 2, curve 2).[10] The deviations between the experimentally observed and calculated T_g illustrate the effect of ionic interactions on T_g as has already been addressed above.

The comparison of the IR spectrum of the acid–base blend with those of the precursor polymers in the region where the sulfonate group exhibits characteristic bands clearly reveals that the sulfonic acid group formed sulfonate anions in the blend (Figure 4). Characteristic bands of the sulfonic acid vibrations at 906, 1102, 1178, and 1350 cm^{-1} present in P(S-*co*-SSH) (spectrum 1) have decreased or disappeared in the blend (spectrum 3), and the blend exhibits new bands at 1008, 1123, and 1250 cm^{-1}, with the latter two being characteristic of the sulfonate anions (cf.

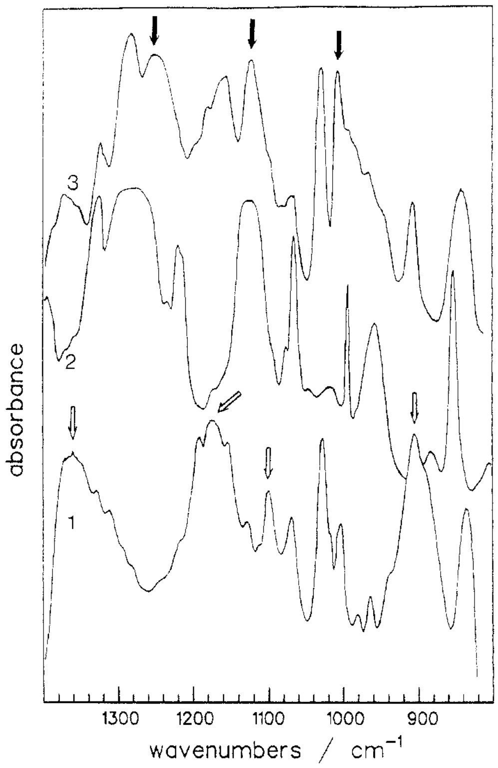


Figure 4. IR absorption spectra of PS-*co*-SSH (curve 1), P22DPy (curve 2), and the acid–base blend (4.4/1, w/w; curve 3) from 1400 to 800 cm^{-1}. Appearing and disappearing bands are shown by filled and unfilled arrows.

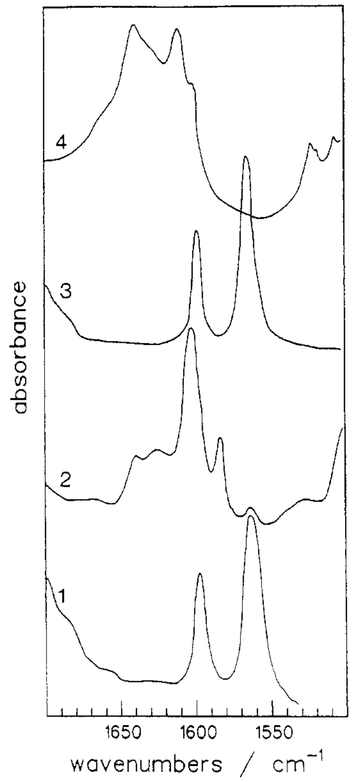


Figure 5. IR absorption spectra of P22DPy (curve 1) and of the acid–base blend PS-*co*-SS$^-$/P22DPyH$^+$ (4.4/1, w/w; curve 2) in comparison with the spectra of an isonicotinic acid ethyl ester (curve 3) and its salt with *p*-toluene sulfonic acid (curve 4; mole ratio 1:1) from 1700 to 1500 cm^{-1}.

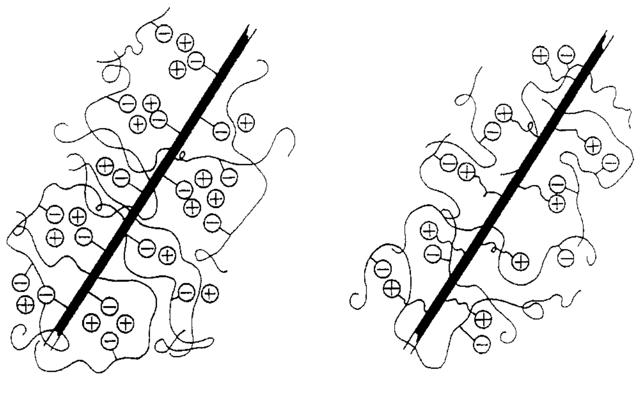

a, b,

Figure 6. Schematic diagram of a model of mixing in (a) the triethylammonium blend through ion clusters and (b) the acid–base blend through sulfonate–isonicotinium ionic interactions. The thick solid line represents a portion of the poly(diacetylene) rod, and the thinner coiled lines represent the flexible polymer: (⊖) anionic groups; (⊕) cationic moieties.

ref 5); the new bands do not originate from the poly(diacetylene) blend component (see spectrum 2). In this context it has to be pointed out that the quantitative analysis of the S–O stretching peak at 906 cm^{-1} following the procedure given in the literature[5] suggests that most of the sulfonic acid groups present have transferred a proton to the isonicotinic ester side group in the blend.

The formation of the isonicotinium acid ester counterion by proton transfer from the sulfonic acid group of the sulfonated polystyrene to the isonicotinate side group of the poly(diacetylene) is confirmed by comparison of the spectra of the poly(diacetylene) blend precursor polymer and of the acid–base blend with the spectra of the model compounds isonicotinic acid ethyl ester and its salt with *p*-toluenesulfonic acid (Figure 5). The characteristic peak of the pyridine ring at 1563 cm^{-1} in the poly(diacetylene) (spectrum 1) has almost disappeared in the spectrum of the blend, where the new bands of the isonicotinium cation appear at 1640 cm^{-1} and hydrogen bonding at 1625 cm^{-1} (spectrum 2), which have no counterpart in either of the blend precursors; this is in agreement with the differences in the spectra of the model compounds (cf. ref 5).

Conclusions

The dynamic mechanical study of the ionomer blends of rigid-rod and random-coil polymers has confirmed that miscibility of this usually incompatible polymer pair can be achieved on a size scale less than 50 Å through ion–ion interactions, and this result is in full agreement with the recent study of these systems by DSC.[10] However, the infrared spectroscopic measurements of the acid–base ionomer blend and its precursor polymers revealed that sulfonate anions and isonicotinium cations are formed in the blend through proton transfer from the sulfonic acid group of the sulfonated polystyrene to the isonicotinate side group of the poly(diacetylene), and almost all of the functional groups interact with each other either through proton transfer or hydrogen bonding. This means that every single rigid-rod macromolecule interacts with the random-coil polymer on a length scale of the poly(diacetylene) monomer repeating unit, which means a mixing on a molecular scale. The miscibility of rigid-rod and random-coil polymers in ionomer blends can be understood as being caused by the immobilization of both blend components through ionic contacts generated during the blend formation from solution; this prevents even microphase separation since the ionic cross-links are simultaneously increased and locally fixed with solvent evaporation. A schematic model of mixing in the blends is shown in Figure 6 for a portion of a poly(diacetylene) rod. This model shows that the one-phase system is a consequence of, in particular, the regular and dense sequence of potential interacting groups along the poly(diacetylene) chain and of the relatively short sequences of polystyrene between interacting groups (cf. ref 14). Further experiments and theoretical considerations will elucidate whether the observed compatibility of the rigid-rod/random-coil ionomer blend is based on true equilibrium thermodynamics, i.e., acid–base equilibria and Coulombic interactions, and/or to which extent the achieved miscibility is a frozen-in nonequilibrium structure; in any case, the high number of potential interacting ionic groups between both blend components is of crucial importance.

Experiments are currently underway to further test the potential of the enhancement of polymer miscibility of rigid-rod and random-coil polymers through ionic interactions with the objective of the realization of molecularly reinforced macromolecular systems.

Acknowledgment. Financial support of this work by the German Science Foundation (SFB 213, University of Bayreuth) is gratefully acknowledged. We thank J. Neil for assistance in the dynamic mechanical measurements. Financial support was also provided by the University of Massachusetts Materials Research Laboratory, NSF DMR-9023848.

References and Notes

(1) Murali, R.; Eisenberg, A. In *Structure and Properties of Ionomers*; Pineri, M., Eisenberg, A., Eds.; D. Reidel Publishing Co.: Dordrecht/Holland, 1987; p 307 and references cited therein.
(2) Vollmert, B.; Schoene, W. *Angew. Makromol. Chem.* **1971**, *19*, 157.
(3) Smith, P.; Eisenberg, A. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 223.
(4) Douglas, E. P.; Sakurai, K.; MacKnight, W. J. *Macromolecules* **1991**, *24*, 6776.
(5) Sakurai, K.; Dougles, E. P.; MacKnight, W. J. *Macromolecules* **1992**, *25*, 4509.
(6) Hofmann, J. Diploma Thesis, University of Bayreuth, Bayreuth, Germany, 1992.
(7) Flory, P. J. *Macromolecules* **1978**, *11*, 1138.
(8) Gupta, A. K.; Benoit, H.; Marchal, E. *Eur. Polym. J.* **1979**, *15*, 285.
(9) Ballauf, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 253.
(10) Eisenbach, C. D.; Hofmann, J.; Fischer, K. *Macromol. Rapid Commun.* **1994**, *15*, 117.
(11) Ribbe, A.; Göldel, A.; Hofmann, J.; Eisenbach, C. D. in preparation.
(12) Tannenbaum, R.; Rutkowska, M.; Eisenberg, A. *J. Polym. Sci., Pt. B* **1987**, *25*, 663.
(13) Weiss, R. A.; Agarwal, P. K.; Lundberg, R. D. *J. Appl. Polym. Sci.* **1984**, *29*, 2719 (1984).
(14) Brereton, M. G.; Vilgis, T. A. *Macromolecules* **1990**, *23*, 2044.