Ionic Interactions in Blends of Polyamidines and Proton Donor Terminated Poly(alkylene ether)s

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Received January 18, 2005; Revised Manuscript Received June 30, 2005

ABSTRACT: 4-(Iminomethyl)phenol and 4-(iminomethyl)benzoic acid terminated aliphatic polyethers were obtained by conversion of Jeffamines with respective aromatic aldehydes. Mixtures of these polymers with polyamidines showed improved compatibility or even complete miscibility because of ionic complexes formed between the end groups of the modified polyethers and the basic amidine groups. Depending on composition and molecular weight of the components, blends with two or one glass transitions were obtained. In the case of 4-(iminomethyl)phenol terminated polyethers, deprotonation of the end groups resulted in a distinct change of the UV/vis absorption spectrum. This spectral alteration is discussed with respect to quantification of interactions in polymer blends.

Introduction

Morphology and properties of polymer blends are influenced by interactions between the components. Strong interactions such as donor−acceptor interactions, hydrogen bonds,[1] or ionic complex formation[2−4] may contribute to the formation of a fine phase morphology or even to complete miscibility on the molecular level.

Different spectroscopic methods have been used to detect and quantify interactions between the components of multiphase systems. For the detection of hydrogen bonds, IR spectroscopy has proved to be a versatile tool. Strong hydrogen bonds appear in blends, the components of which contain strong proton donor and acceptor groups. Typical polymeric proton donors used in blends investigated by IR spectroscopy are polymers based on vinyl alcohol,[5−13] vinylphenol,[14−21] and acrylic or methacrylic acid,[22] whereas polymers with pyridine,[11−13,21,22] amine, amide,[8,9] imine,[7] and carboxylic moieties, e.g. vinyl acetate,[15−18] acrylate, methacrylate,[14,19,22] and *N*-vinylpyrrolidone,[5,10] belong to the family of polymeric proton acceptors. Depending on the number of interacting groups, miscible, partly miscible, or immiscible mixtures can be obtained. Provided that the number of interacting groups is high enough, IR spectroscopy delivers reasonable results with respect to the quantity of hydrogen-bridged moieties. Miscibility facilitates determination of hydrogen bonds since accessibility of the functional groups is improved, resulting in a large quantity of hydrogen bonds. Such blend systems are also suited for other spectroscopic methods like solid-phase magic angle spinning NMR,[6] the sensitivity of which is relatively small.

Although a large number of interacting groups make the IR spectroscopic effects more distinct, the interpretation of the results may be complicated by intramolecular interactions of the single components. In this case, self- and interassociation equilibrium constants have to be taken into account.[11−14,18,19]

Polymer blends with weak interactions between the components or a small number of functional groups are usually phase separated. In such systems interactions are limited to the interface between the components. Since the interface only takes up a small volume of the whole sample, it is difficult to quantify the degree of interactions. NMR and IR techniques very often fail because of their limited sensitivity. The same problems arise if chemical reactions take place in the interface. Instead, it is attempted to draw indirect information about interactions and chemical reactions from alterations of thermal, mechanical, and rheological properties or changes in phase morphology.

More sensitive is the UV/vis absorption and emission spectroscopy that allows to quantify interactions several orders of magnitude below the concentration range of NMR and IR. One prerequisite for such measurements is the presence of chromophores that change their optical properties in dependence on the degree of interactions. At least one blend component should contain such chromophores that can be bond either as a side functional group or as a terminal group on the polymer chain.

For the investigation of polymer blends, the utilization of fluorescence probes is well established. Two different methods have frequently been used. The first method is based on the formation of chromophore dimers (excimer) which show after excitation a different fluorescence intensity than the respective monomers.[23−25] Increasing dilution of the chromophore by interdiffusion results in an alteration of the excimer/monomer fluorescence intensity ratio. This approach can directly been applied on blends with polymers possessing aromatic units as for example polystyrene[24] or poly(2-vinylnaphthalene).[23] Fluorescence inactive polymers can be labeled with appropriate chromophores, e.g., carbazole or naphthalene.[25]

The second procedure is based on a nonradiative energy transfer from a donor to an acceptor chromophore.[22,26−32] For this, the components of a polymer blend have to be labeled in a respective manner. This procedure was introduced first by Morawetz[26−29] to study compatibility of polymer blends. The extent of energy transfer depends on the degree of interdiffusion

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10.1021/ma050105s CCC: $30.25
Published on Web 08/18/2005

of chromophore-labeled polymers in the interface and has a direct influence on the fluorescence spectrum of the blend. Recently, this procedure has also been used to characterize the phase structure of diblock copolymers. For this, donor and acceptor chromophores were directly placed into the junctions between both blocks.[33]

It is a matter of common knowledge that the UV/vis absorption behavior of some chromophores depends on the degree of protonation. Such compounds are frequently used as acid−base indicators. Introduced into polymers, the absorption spectra of the chromophores may inform about the ability of the polymers to act as a proton donor or an acceptor.

We reported about aliphatic polyamidines which proved to be strong organic bases. In mixtures with different phenolic group containing chromophores, the formation of ionic complexes was observed.[34−38] Because of deprotonation, the chromophores exhibited a bathochromic shift of their longest wavelength absorption band by more than 100 nm. Additionally, third-order nonlinear optical activity was evidenced on solution-cast films. The reason for these changes in optical properties is the much stronger linear π-conjugation in the deprotonated chromophore molecules.

The strong alterations observed in the UV/vis absorption spectra of a phenolic group containing chromophores after deprotonation make these kinds of compounds to potential probe molecules for acid−base interactions. It is intended to utilize the sensitivity of the absorption behavior of chromophores in response to deprotonation to quantify interactions in polymers and polymer blends. This article estimates the potential of Schiff's bases introduced into polymers to act as probe for specific acid−base interactions in polymer mixtures. This group can easily be introduced into polymers by conversion of amino functional groups with benzaldehydes. Exemplarily, the preparation of 4-(iminomethyl)-phenol and 4-(iminomethyl)benzoic acid terminated aliphatic polyethers and their mixtures with an aliphatic polyamidine with the structure $-[(CH_2)_8-N{=}C(CH_3)-NH-]$ are investigated in solution and in bulk.

Experimental Section

Materials. 4-Hydroxybenzaldehyde, 4-formylbenzoic acid, ethanol, and methanol were purchased from Aldrich and used without further purification. Polymeric diamines Jeffamine D-2000 and Jeffamine ED-600 from Huntsman were dried by heating at 80 °C for several hours in a vacuum prior to use.

Model Compounds. 4-(Isobutyliminomethyl)benzoic acid **1a**: A mixture of 4-formylbenzoic acid (0.01 mol), isobutylamine (0.0105 mol), and methanol (10 mL) was refluxed for 2 h. Then, solvent, excess isobutylamine, and water formed during the reaction were distilled off. The resulting product was dried under vacuum at 100 °C. Yield: 95%.

Data for **1a**: ^{1}H NMR (DMSO-d_6) δ (ppm) = 0.93 (d, 6H, CH_3); 1.92 (m, 1H, CH); 3.43 (d, 2H, CH_2); 7.85 (d, 2H, H_{Ar} *meta* to COOH); 8.00 (d, 2H, H_{Ar}); 8.39 (s, 1H, CH=N); 13.15 (br, 1H, COOH).

^{13}C NMR (DMSO-d_6) δ (ppm) = 20.62 (CH_3); 29.26 (CH); 68.66 (CH_2); 127.94 (C_{Ar} *meta* to COOH); 129.73 (C_{Ar} *ortho* to COOH); 132.45 (C_{Ar} *para* to COOH); 139.91 (C_{Ar} *ipso* to COOH); 160.15 (CH=N); 167.07 (COOH).

4-(Isobutyliminomethyl)phenol **1b**: A mixture of 4-hydroxybenzaldehyde (0.01 mol), isobutylamine (0.01 mol), and ethanol (10 mL) was refluxed for 3 h. The resulting product was poured into cold water. After precipitation, the product was filtered off, dried, and recrystallized from ethanol. Yield: 72%.

Data for **1b**: ^{1}H NMR (DMSO-d_6) δ (ppm) = 0.90 (d, 6H, CH_3); 1.86 (m, 1H, CH); 3.32 (d, 2H, CH_2); 6.80 (d, 2H, H_{Ar} *ortho* to OH); 7.55 (d, 2H, H_{Ar}); 8.15 (s, 1H, CH=N); 9.81 (s, 1H, OH).

^{13}C NMR (DMSO-d_6) δ (ppm) = 20.57 (CH_3); 29.28 (CH); 68.55 (CH_2); 115.40 (C_{Ar} *ortho* to OH); 127.65 (C_{Ar} *para* to OH); 129.51 (C_{Ar} *meta* to OH); 159.61 (C_{Ar} *ipso* to OH); 159.92 (CH=N).

Polymers. Schiff's base terminated poly(oxyalkylenediamine)s **4**: The preparation of **4** was carried out by conversion of amino group terminated polyethers (Jeffamine D-2000 and Jeffamine ED-600) with 4-hydroxybenzaldehyde or 4-formylbenzoic acid, respectively. As an example, the synthesis of **4a** is described in the following: To a solution of 12 g (0.02 mol) of Jeffamine ED-600 in 40 mL of ethanol, 4.8 g (0.032 mol) of 4-formylbenzoic acid was added. The mixture was stirred for 1 h at 45 °C. Then the temperature was raised to 65 °C, and after 3 h the reaction was completed. The solvent was distilled off, and the product was obtained as a yellowish viscous liquid. **4b**−**d** were synthesized correspondingly. The degree of conversion was determined by NMR spectroscopy from end-group signal intensities and UV/vis spectroscopy using extinction coefficients of model compounds.

Data for **4a**: ^{1}H NMR (DMSO-d_6) δ (ppm) = 0.95−1.08 (H_2); 1.15 ($H_{1'}$); 3.2−3.7 ($H_{4'}$, H_5, H_6, H_7); 3.5 (H_8), 7.80 (H_{11}); 7.98 (H_{12}); 8.39 (H_9).

^{13}C NMR (DMSO-d_6) δ (ppm) = 17.2 (C_2); 18.8 ($C_{1'}$); 64.8 and 65.3 ($C_{4'}$); 70.0 (C_8); 72−76 (C_5, C_6, C_7); 127.75 (C_{11}); 129.54 (C_{16}); 129.69 (C_{12}); 134.78 (C_{10}); 139.12 and 139.17 (C_{13}); 159.57 and 159.67 (C_9); 167.65 (C_{14}).

Data for **4b**: ^{1}H NMR (DMSO-d_6) δ (ppm) = 0.95−1.05 (H_2); 1.11 ($H_{1'}$); 3.2−3.7 ($H_{4'}$, H_5, H_6, H_7); 3.5 (H_8), 6.78 (H_{18}); 7.53 (H_{17}); 8.16 (H_{15}).

^{13}C NMR (DMSO-d_6) δ (ppm) = 17.3 (C_2); 19.2 ($C_{1'}$); 64.7 and 65.2 ($C_{4'}$); 70.0 (C_8); 72−76 (C_5, C_6, C_7); 115.45 (C_{18}); 127.50 and 127.56 (C_{16}); 129.69 (C_{17}); 159.39 and 159.48 (C_{15}); 159.90 and 159.93 (C_{19}).

Data for **4c**: ^{1}H NMR (DMSO-d_6) δ (ppm) = 0.95−1.1 (H_2); 1.15 ($H_{1'}$); 3.2−3.7 ($H_{4'}$, H_5, H_6, H_7); 7.77 (H_{11}); 7.96 (H_{12}); 8.37 (H_9).

^{13}C NMR (DMSO-d_6) δ (ppm) = 17.3 (C_2); 18.7 and 18.8 ($C_{1'}$); 65.2 and 65.3 ($C_{4'}$); 72.4 and 72.6 (C_7); 74−75 (C_5, C_6); 127.66 (C_{11}); 129.04 (C_{16}); 129.46 (C_{12}); 134.28 (C_{10}); 139.23 (C_{13}); 159.39 (C_9); 167.34 (C_{14}).

Data for **4d**: ^{1}H NMR (DMSO-d_6) δ (ppm) = 0.95−1.07 (H_2); 1.10 ($H_{1'}$); 3.2−3.7 ($H_{4'}$, H_5, H_6, H_7); 6.78 (H_{18}); 7.53 (H_{17}); 8.16 (H_{15}).

^{13}C NMR (DMSO-d_6) δ (ppm) = 17.2 (C_2); 19.0 and 19.1 ($C_{1'}$); 65.0 and 65.2 ($C_{4'}$); 72.4 and 72.6 (C_7); 74−75 (C_5, C_6); 115.26 and 115.28 (C_{18}); 127.50 (C_{16}); 129.43 and 129.46 (C_{17}); 159.06 (C_{15}); 159.81 (C_{19}).

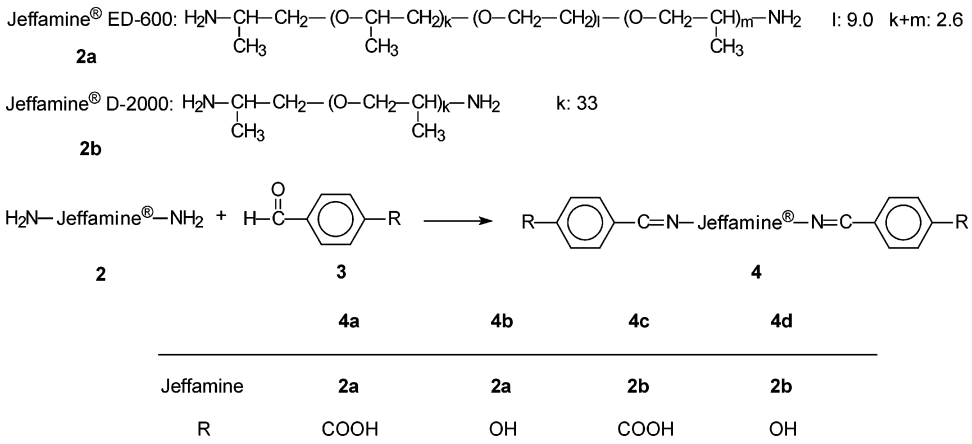
Poly(1,8-octamethyleneacetamidine) **5**: The phenol-catalyzed preparation by conversion of aliphatic diamines with triethyl orthoacetate was carried out as described earlier.[39] Two samples of different molecular weight (**5a**: M_n(NMR) = 1300 g/mol; **5b**: M_n(NMR) = 3400 g/mol) were prepared.

Measurements. DSC measurements were performed on a Q 1000 (TA Instruments) at a scanning rate of ±20 K/min in the temperature range −80 to 80 °C (program cycle: heating, cooling, heating). The glass transition temperatures were determined from the second heating scan by using the inflection point method.

NMR spectra were recorded on a Bruker DRX 500 NMR spectrometer operating at 500.13 MHz for ^{1}H and at 125.75 MHz for ^{13}C. DMSO-d_6 was used as solvent and reference (δ(^{1}H) = 2.50 ppm, δ(^{13}C) = 39.60 ppm). Quantitative ^{13}C NMR spectra were obtained using inverse gated decoupling, 30° ^{13}C pulses, and a relaxation delay of 7 s.

UV/vis spectra were recorded on a Lambda 800 spectrophotometer (Perkin-Elmer, Germany). Solution spectra were obtained with a 1 cm thick cuvette. Dip coating films on quartz were prepared with a dipping speed of 500 mm/min from THF solutions (polyamidine 0.5 wt %, varying chromophore concentrations). Titration experiments were carried out in a sealed cuvette by adding a concentrated solution of the base. The

Scheme 1



resulting dilution of the samples was corrected by applying an appropriate factor for each spectrum.

Results and Discussion

Two amino group terminated poly(oxyalkylenediamine)s (**2a**: Jeffamine ED-600; **2b**: Jeffamine D-2000) were converted with para-substituted benzaldehydes **3** according to Scheme 1. As a result, Schiff's base functionalized polyoxyalkylenes **4** were obtained. The degree of conversion could be determined by NMR spectroscopic terminal group analysis. Figure 1 shows the respective ^{1}H NMR spectra of Jeffamine ED-600 and its conversion products with 4-formylbenzoic acid (**4a**) and 4-hydroxybenzaldehyde (**4b**). The conversion proceeded smoothly without significant side reactions. Typical amino group signals of the Jeffamine appearing at 0.9 ppm ($H_2N-CH(CH_3)$) and 2.9 ppm ($H_2N-CH(CH_3)$) strongly decrease after conversion. The formation of Schiff's bases could be concluded from the aromatic signals by using model compounds **1a** and **1b**.

To prevent that unconverted benzaldehyde may disturb further measurements, reactions were carried out

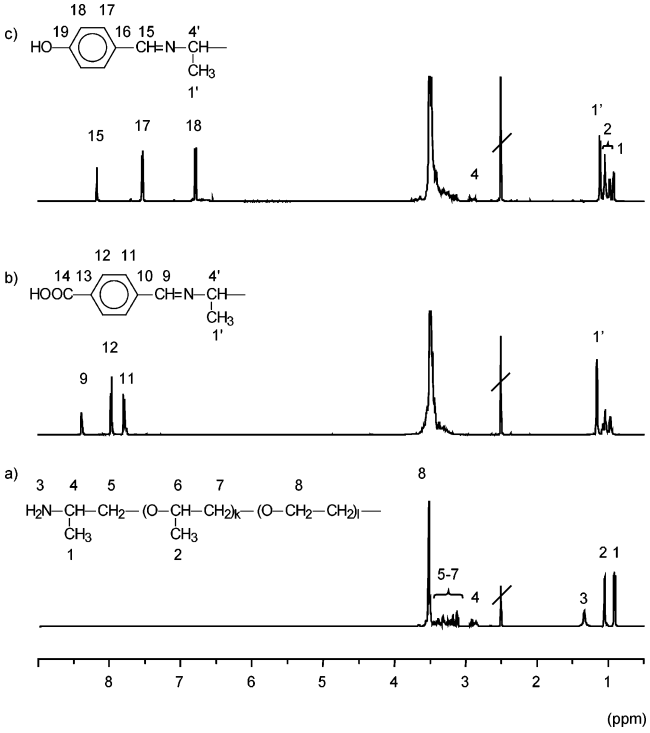


Figure 1. ^{1}H NMR spectra (in DMSO-d_6) of (a) **2a**, (b) **4a**, and (c) **4b**.

Table 1. Degree of Terminal Group Conversion (*X*) for Polymers 4

sample	4a	4b	4c	4d
X(NMR), %	79[a]	74[b]	75[a]	78[b]
X(UV/vis), %	52	55	56	75

[a] By ^{13}C NMR (±3%). [b] By ^{1}H NMR (±1%).

in excess of the amino group terminated polymers. Therefore, amino group signals are still present after reaction whereas the aldehyde signals are negligible. For polymers **4b** and **4d**, the degree of terminal group conversion was determined by ^{1}H NMR spectroscopy using the signal intensities of formed C*H*=N– and residual $H_2NCH(CH_3)$ groups. In the case of the carboxy terminated polymers **4a** and **4c**, a shift of the terminal group signals occurred due to protonation of the amino groups, resulting in signal overlap with main-chain signals. This hampered terminal group analysis by ^{1}H NMR. Instead, quantitative ^{13}C NMR was used in evaluating the intensities of the methine carbon signal of =N–*C*H(CH_3)– and H_2N–*C*H(CH_3)–. Additionally, the degree of conversion was determined by UV/vis spectroscopy by using the extinction coefficient of model compounds **1a** and **1b** (see Table 1). The results obtained by NMR and UV/vis spectroscopy differ to some extent distinctly. Because of the specific of NMR techniques used, the conversions determined by NMR are assumed to be more accurate than those determined by UV.

Complete conversion of the amino groups can be achieved when an excess of benzaldehyde was used. In this case, NMR signals of unconverted aldehyde are visible.

The proton donor groups (OH and COOH) at the chain ends of the modified poly(oxyalkyleneamine)s are potentially able to interact with weak Lewis or Brønsted basic compounds. Self-association of the carboxylic groups, formation of hydrogen bonds with the ether linkages in the polymer, and interactions with unreacted amino groups can be assumed. A clear indication that such interactions exist is the distinctly increased viscosity of the modified polymers at room temperature. Whereas the unmodified ones possess very low viscosities like low molecular weight liquids, the viscosity of the proton donor group terminated polymers is increased very distinctly. Their consistency is comparable with that of honey. Even the viscosity of modified Jeffamine ED-600 (**4a** and **4b**; $M_n \approx 800$ g/mol) is much higher than that of the unmodified Jeffamine E-2000 (**2b**; $M_n \approx 2000$ g/mol).

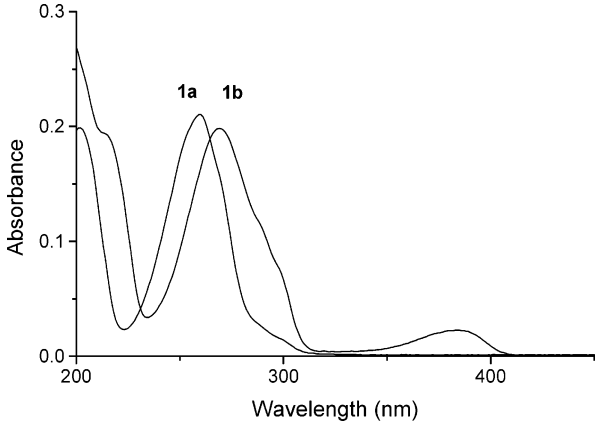
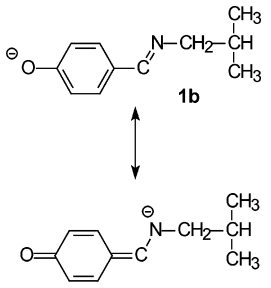


Figure 2. UV/vis spectra of model compounds **1a** and **1b** in methanol, $c = 1 \times 10^{-5}$ mol/L.

Scheme 2



Schiff's bases are known to have characteristic absorption bands in the UV/vis region. UV/vis spectra of the two model compounds **1a** and **1b** that represent the structures of the terminal groups in the polymers **4** are shown in Figure 2. In both cases strong absorption bands are visible in the UV region which can be assigned to $\pi-\pi^*$ and $n-\pi^*$ transitions. The respective absorptions of the Schiff's base terminated polymers appear exactly at the same position as those of the model compounds. Obviously, these absorptions are not sensitive enough to be used as probe for interactions between the terminal groups and the ether linkages in the polymer which are assumed to be polar interactions or hydrogen bonds.

To check whether stronger interactions with bases leading to deprotonation of the terminal groups (OH, COOH) influence the UV/vis absorption of the Schiff's base, an excess of NaOH was added to the model compounds. In the case of the carboxylic group containing model compound **1a** no influence upon deprotonation was observed, whereas in the case of the hydroxy group containing compound **1b** strong changes in the spectrum could be detected. After deprotonation, the absorption bands at 270 and 380 nm disappeared, and it raised a new strong absorption band at 330 nm. The differences between both compounds can be explained by the stronger linear π-conjugation in the deprotonated state of **1b**, resulting in a higher contribution of the quinoid-like structure as shown in Scheme 2. In the case of the carboxy group containing compound **1a** delocalization of the negative charge is less pronounced.

These observations encouraged us to utilize this effect in polymeric mixtures of the 4-(iminomethyl)phenol terminated polymers **4b** and **4d** with poly(1,8-octamethyleneacetamidine), **5**. The latter has proved to be a strong organic base. UV/vis spectra of mixtures of both polymers in solution showed that with increasing content of amidine groups a progressive deprotonation of the 4-(iminomethyl)phenol moiety occurred (Figure 3).

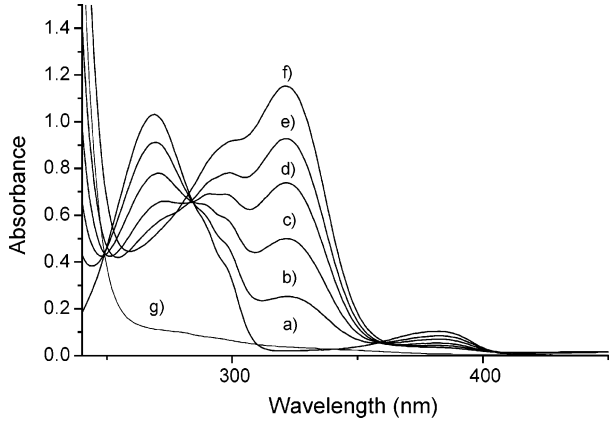


Figure 3. UV/vis spectra of **4d** in methanol in the presence of different amounts of polyamidine **5** [chromophore concentration = 5.3×10^{-5} mol/L; ratio amidine/chromophore: (a) 0.0, (b) 3.83, (c) 7.22, (d) 11.9, (e) 18.3, (f) 42.5, (g) spectrum of polyamidine **5**, $c = 2.27 \times 10^{-3}$ mol/L]. Spectra a–f are corrected by the absorption of the polyamidine.

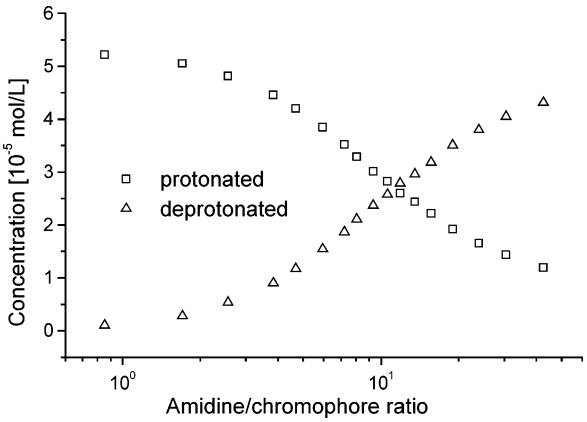


Figure 4. Titration curves of **4d** calculated from the UV/vis spectra after addition of different amounts of polyamidine **5**.

The polyamidine has an absorption in the same range as the chromophore (see spectrum g in Figure 3). Therefore, the observed spectra were corrected by subtracting a polyamidine reference spectrum of appropriate concentration. At polyamidine-to-chromophore ratios smaller than 20, this procedure worked very well as indicated by the isosbestic point. At higher ratios deviations from the isosbestic point were observed which might be caused by small differences between applied polyamidine concentrations in the titration experiment and those used to obtain the reference spectra.

The degree of deprotonation could be calculated by approximating superpositions of the spectra of the completely protonated and unprotonated polymer. The respective titration curve is shown in Figure 4.

For comparison purposes, **4b** and **4d** were also titrated with NaOH, which is a stronger base than polyamidine **5**. A characteristic point in Figure 4 is the intersection of both curves were 50% of chromophore is neutralized ($P_{50\%}$). The position of this point reflects how easy the chromophore can be deprotonated by the respective base. For the titration of **4b** and **4d** with polyamidine **5** and NaOH, respectively, the positions of $P_{50\%}$ are summarized in Table 2. In the case of NaOH, $P_{50\%}$ does not depend on the molecular weight of the modified Jeffamine. Obviously, the accessibility of the

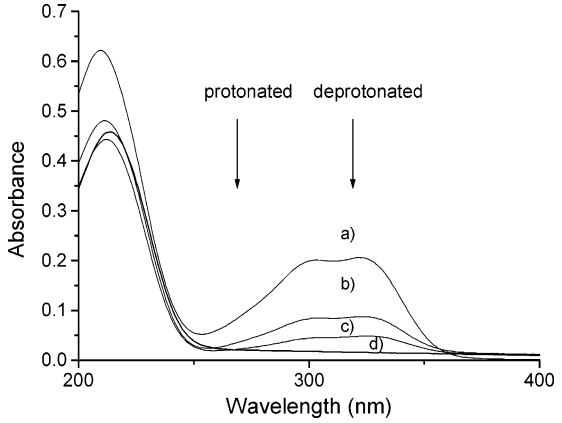


Figure 5. UV/vis spectra of solution-cast films of blends of **4d** and **5b** at different amidine/chromophore ratios: (a) 4.3, (b) 9.33, (c) 21.4, and (d) pure **5b**. The arrows indicate where the absorptions of the protonated and the deprotonated form have to be expected.

Table 2. Base/Chromophore Ratios ($P_{50\%}$) at Which 50% of the Chromophore Is Neutralized

sample	$P_{50\%}$ NaOH/chromophore (mol/mol)	$P_{50\%}$ amidine/chromophore (mol/mol)
4b	2.3	6.9
4d	2.2	10.0

terminal groups by NaOH is comparable, showing that the molecular weight of both polymers is not high enough for shielding effects. Titration with the polyamidine **5** gives a completely different picture. A distinct excess of base is needed to achieve the same degree of deprotonation as with NaOH. This can be explained by the lower basic strength of the amidine moiety but also by a reduced accessibility of the interacting groups in a system with two polymers. Here the influence of the molecular weight of the modified Jeffamine becomes evident.

UV/vis spectra of the mixtures of **4d** and polyamidine **5** in bulk were also obtained from dip-coated films (Figure 5). For the film preparation, both polymers were dissolved together in THF and cast under defined conditions on quartz plates. The procedure ensured that films with comparable thickness were obtained. The ratio amidine to chromophore (mol/mol) in the films varied from 21.4 to 4.3. The spectra clearly show that in each case even at the lowest amidine-to-chromophore ratio of 4.3 (spectrum a) no protonated species are detectable. That means ionic complex formation occurs to a high extent. In solution at the same ratio, protonated species appear in large quantities and are even detectable at distinctly higher amidine chromophore ratios. The lower extent of complex formation in solution can be explained by additional interactions with the solvent which have a remarkable influence at the low concentrations chosen for UV/vis measurements.

The complete deprotonation of the chromophore in the films indicates a good miscibility of the polymers in bulk. Since all chromophores are accessible by the amidine groups, phase separation can only occur in the length scale of the dimension of one polyether chain. If larger domains occurred, some chromophores would not be accessible since they have to be situated inside the polyether phase.

DSC measurements should reveal whether miscibility occurs in the mixtures investigated. The unmodified Jeffamines **2a** and **2b** are not miscible with polyamidine **5** over the whole composition range as evidenced by DSC measurements (not shown here).

Table 3. Glass Transition Temperatures of Modified Jeffamines and Polyamidine

sample	T_g [°C]	sample	T_g [°C]
2a	not detectable[a]	**4c**	−54.3
2b	−71.0	**4d**	−54.7
4a	−25.4	**5a**	8.5
4b	−34.8	**5b**	−6.3

[a] Crystalline melting point at −15 and −9 °C.

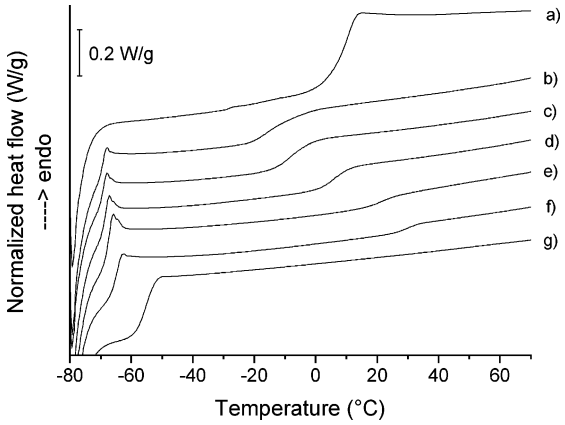


Figure 6. DSC traces of mixtures of **4d** and **5b**. Mass fraction of polyamidine: (a) 1.0, (b) 0.5, (c) 0.45, (d) 0.37, (e) 0.29, (f) 0.17, and (g) 0.0.

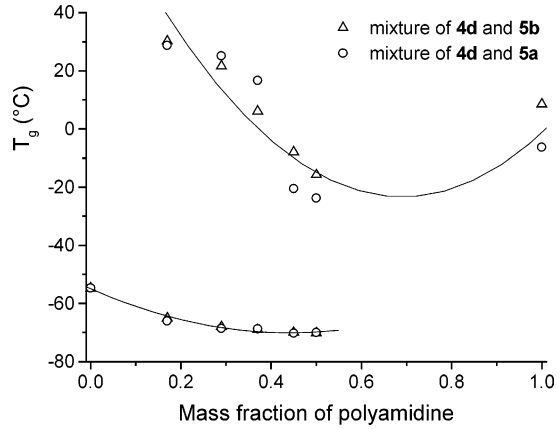


Figure 7. Glass transition temperatures of mixtures of **4d** and **5** in dependence on composition.

DSC measurements were carried out on blends of the modified Jeffamines **4a**−**d** with polyamidine **5**. For comparison purposes, two polyamidines with different molecular weight were used (**5a**: M_n = 1300 g/mol; **5b**: M_n = 3400 g/mol). The mixtures were prepared by dissolution of the components in THF and subsequent evaporation of the solvent. The DSC traces of the single components only show glass transitions reflecting their amorphous character. The glass transition temperatures are summarized in Table 3.

As an example, DSC traces of blends of **4d** and **5b** are shown in Figure 6. The respective plot T_g vs blend composition is shown in Figure 7. Figure 7 also contains values of blends with **5b** possessing a higher M_n than **5a**.

Over the whole composition range, two T_g could be found showing that the blend components are not miscible on the molecular level. However, the very distinct increase of the upper T_g with increasing Jeffamine (**4d**) content over the T_g of the pure polyamidine

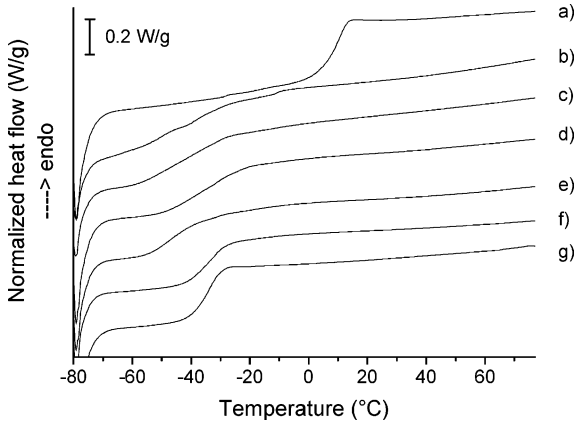


Figure 8. DSC traces of mixtures of **4b** and **5b**. Mass fraction of polyamidine: (a) 1.0, (b) 0.5, (c) 0.45, (d) 0.37, (e) 0.29, (f) 0.17, and (g) 0.0.

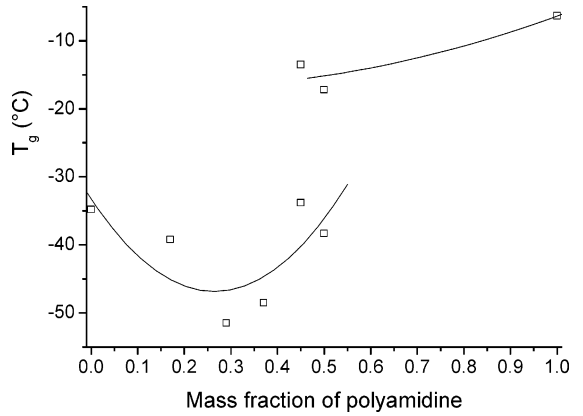


Figure 9. Glass transition temperatures of mixtures of **4b** and **5a** in dependence on composition.

indicates that strong interactions between the components must occur, resulting in a reduced mobility of the polyamidine chain. Because of the relatively low content of proton donor groups in the modified Jeffamine, this effect is more pronounced in blends with low polyamidine contents where the complexation of the amidine group is higher. Comparing the curves of blends based on polyamidine **5a** ($M_n = 1300$ g/mol) and **5b** ($M_n = 3400$ g/mol), one can conclude that the influence of the molecular weight of the polyamidine is negligible. Blends of the carboxy terminated Jeffamine **4c** with polyamidine **5a** and **5b** show similar tendencies.

Different results were obtained for blends based on the modified Jeffamines **4a** and **4b** which possess lower molecular weights compared to **4c** and **4d**. Because of the higher content of proton donor groups in the polymers stronger interactions has to be assumed in blends with polyamidine **5**. These stronger interactions have an influence on the glass transitions, which are found to be less pronounced than in blends of **4c** and **4d** (see Figure 8). Furthermore, two distinct glass transitions could only be detected in the medium concentration range. At lower polyamidine contents only one T_g was visible or the second one only appeared very weak. For blends based on **4b** and **5a**, the dependency of T_g on the blend composition is shown in Figure 9. Blends of the carboxy terminated Jeffamine **4a** show similar behavior.

It is assumed that blends of modified Jeffamines with polyamidines at least at low polyamidine contents are completely miscible whereas in the medium concentration range phase separation occurs.

The miscibility partly observed is in accordance with the above-mentioned formation of ionic complexes in solid films concluded from UV/vis measurements.

Conclusions

The smooth conversion of amino groups with aromatic aldehydes has proved to be an easy way to introduce proton donor groups such as phenolic and carboxylic groups at the chain end of Jeffamines. Another advantage of this reaction is the formation of an azomethine grouping which makes the polymer sensitive for UV/vis spectroscopic investigations. Especially, 4-(iminomethyl)phenol terminated polyethers obtained by the conversion with 4-hydroxybenzaldehyde are to be emphasized since the UV/vis spectra of which are sensitive to deprotonation. This opens the possibility to quantify interactions in blends with polymers possessing proton acceptor groups. In the case of 4-(iminomethyl)benzoic acid terminated polyethers obtained by conversion with 4-formylbenzoic acid, such a sensitivity does not exist.

It has been shown by DSC that in blend with aliphatic polyamidines the functionalized Jeffamines show improved miscibility. Because of their pronounced basicity, polyamidines form ionic complexes with the terminal groups of the modified Jeffamines. In the case of 4-(iminomethyl)phenol terminated Jeffamines it was indicated by UV/vis measurements that these complex formation was quantitative in a certain composition range. Although it has not been proved, it can be assumed that 4-(iminomethyl)benzoic acid terminated Jeffamines show such strong interactions as well since the acidity of carboxylic acid groups is even stronger than that of phenolic groups.

We regard mixtures of 4-(iminomethyl)phenol terminated Jeffamines with polyamidines as a model blend system, from which quantitative information about the interactions between the blend components are available. This blend system is compatible in a certain composition range, so that the interactions occur in a sufficiently high extent. Because of the high UV/vis sensitivity of these interactions, it should be possible to quantify these interactions even at much lower concentrations. Therefore, this approach is not limited to blend systems with high compatibility as described her. In fact, it could be used in blends with a pronounced two-phase structure where these interactions only occur in the interface.

Generally, for the incorporation of 4-(iminomethyl)-phenol groups into polymers, polymer analogous reactions can be used provided that the polymer possess amino terminal or side groups. Alternatively, copolymerization with 4-(iminomethyl)phenol group containing monomers widens the variety of polymer structures available for this purpose.

The second blend component should have functional groups with pronounced basicity ($pK_a > 9$) such as amidine, amine, imine, or guanidine groups which are able to deprotonate the above-mentioned chromophore. Also here, copolymerization with monomers bearing this group can provide suitable polymers with various content of interacting groups.

Investigations on heterogeneous blends based on such polymers including polymers with other chromophores sensitive to interactions are in progress.

Acknowledgment. The authors thank the Scientific and Technical Research Council of Turkey (Tubitak) and

the Deutsche Forschungsgemeinschaft (DFG) for financial support.

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MA050105S