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Competitive Influence of Carboxylic Groups in Ionic Complex Formation of 4-Hydroxybenzylidene Alkanones with Polyamidines

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ABSTRACT: Interactions of phenolic and carboxylic group containing chromophores (hydroxyarylidene alkanones) with polyamidines were investigated by UV/vis and ^{1}H NMR spectroscopy. Because of the strong basicity of the polyamidines, deprotonation of the chromophores was observed. Deprotonation of the phenolic group is accompanied by a change of the electronic structure of the chromophore resulting in a strong bathochromic shift of the longest wavelength absorption band. Increased interactions are observed after introduction of a carboxylic group into the chromophore. It could be shown that deprotonation of the carboxylic group is favored so that the deprotonation of the phenolic group only starts after a major part of the carboxylic groups is deprotonated. In highly diluted solutions, the interaction of the carboxylic group with the polyamidine also increase the extent of deprotonation of the phenolic groups. A physical network formation is assumed that also increases the glass transition temperatures of the mixtures strongly.

Introduction

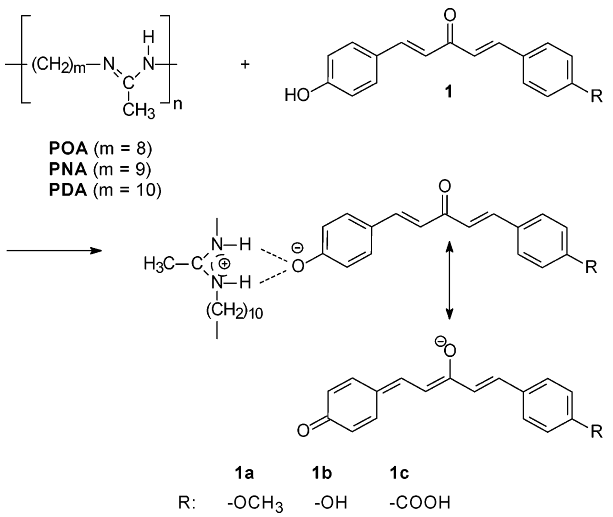
Complexes of low molecular weight compounds with polymers have been the object of intense research. On the basis of electrostatic attraction between polyelectrolytes and oppositely charged surfactants, it was possible to obtain systems with self-organization effects resulting in the formation of mesomorphic and supramolecular structures.[1−6] Other examples comprise structure formation of complexes between dendritic ionomers and polyelectrolytes.[7,8]

Nowadays, special attention is paid on optical properties of such polymeric systems.[9−11] Thunemann and Ruppelt[9,10] described supramolecular structures based on carboxylate group containing polymers and cationic low molecular weight compounds that showed electro luminescence. Behnke and Tieke[11] pointed out that coloring agents could be bonded ionically to amino group containing polymers.

Recently, we reported that aliphatic polyamidines are able to interact with proton donating compounds resulting in deprotonation of the later. It was shown that in ethanolic solution poly(1,10-decamethyleneacetamidine) (**PDA**) forms ionic complexes with different 4-hydroxybenzylidene alcanones.[12−15] Due to deprotonation, the chromophores exhibit a bathochromic shift of their longest wavelength absorption band by more that 100 nm. Additionally, third-order nonlinear optical activity was evidenced on solution cast films. The reason for the changes in optical properties is the much stronger linear π-conjugation in the deprotonated chromophore molecule and a high portion of the quinoid form (see Scheme 1).

Since the chromophore possesses two binding sites (usually two hydroxyl groups, **1b**), the noncovalent interaction with the polymer leads to ionic network formation accompanied by an increase of the glass transition temperature about 60 K.[12,13] It could be shown that the deprotonation of the second OH group of **1b** did not influence the optical behavior of the mixture significantly.[12] In other words, although the second hydroxyl group favors network formation, it is not required with respect to optical properties. This raised the idea to exchange one hydroxyl group with other functional groups possessing more or less pronounced acidity. With the aim to promote network formation, we replaced one hydroxyl group by one carboxylic group. It is known that the interactions of carboxylic groups with polyamidines are strong, resulting in almost complete deprotonation of the carboxylic groups.[16]

Scheme 1



In the present article, the competitive influence of the carboxylic group in complex formation of 4-hydroxybenzylidene alkanones with poly(1,9-nonamethylene acetamidine) (**PNA**) or poly(1,8-octamethylene acetamidine)

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(**POA**) is discussed. For this, interactions of the three different chromophores **1a**−**c** (see Scheme 1) with **PNA** in solution and with **POA** in the solid were investigated.

Mixtures of low molecular weight chromophores with polymers are regarded as a promising alternative for polymers with covalently bonded chromophores. They are easier to prepare and possess better processability, and their properties can be tailored by changing the composition. The properties of the mixtures described here strongly depend on the interactions between the components. A better understanding of these interactions and their influence on optical, thermal, and mechanical properties may open new possibilities for the development of optical and pH sensitive materials for information storage and optical switching.

On the other hand, the alterations of the optical behavior of the chromophores in the presence of proton donor groups might be a very sensitive probe for interactions in the interface of polymer blends or composite materials. For this the chromophore has to be bonded covalently to one of the components. In the case of **1c**, this can be done with the carboxylic group side without to lose the optical sensitivity of the molecule. This will be subject of future investigations.

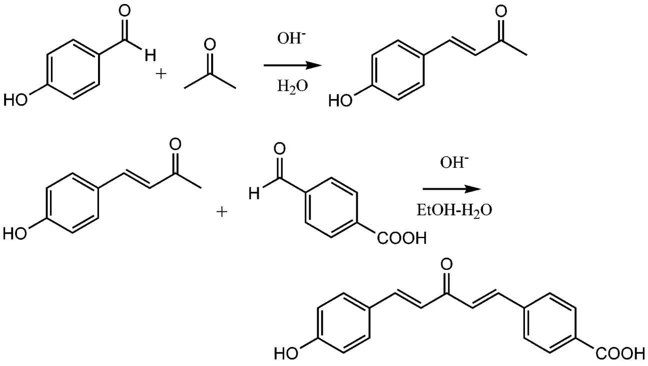
Experimental Section

Materials. *p*-Hydroxybenzaldehyde, *p*-carboxybenzaldehyde, and acetone were purchased from Aldrich and used without further purification.

Polyacetamidines. The phenol catalyzed preparation of polyacetamidines by conversion of aliphatic diamines with triethyl orthoacetate was carried out as described earlier.[17]

1-(4-Hydroxyphenyl)-5-(4-methoxyphenyl)-penta-1,4-dien-3-one (1a) and 1,5-Bis(4-hydroxyphenyl)-penta-1,4-dien-3-one (1b). Preparation of compounds **1a** and **1b** was described elsewhere.[12]

4-[5-(4-Hydroxy-phenyl)-3-oxo-penta-1,4-dienyl]-benzoic acid (1c). 1c was prepared as follows:



A solution of 2.65 g (66 mmol) of NaOH in 10 mL of water was added to a solution of 4.00 g (33 mmol) of p-hydroxybenzaldehyde in 15 mL of acetone. A precipitate was formed. The mixture was heated to 50 °C for 15 min (precipitate dissolves) and then cooled and left overnight. The mixture was diluted with water (about 80 mL) until the precipitate dissolved completely. After acidification with diluted acetic acid, a yellow oil was formed, which turned into a crystalline product within 5 min. The intermediate 4-(4-hydroxyphenyl)-but-3-en-2-one was filtered off and recrystallized from an ethanol−water (1:2 v/v) mixture. Yield: about 4 g (75%); $T_m = 108-110$ °C.

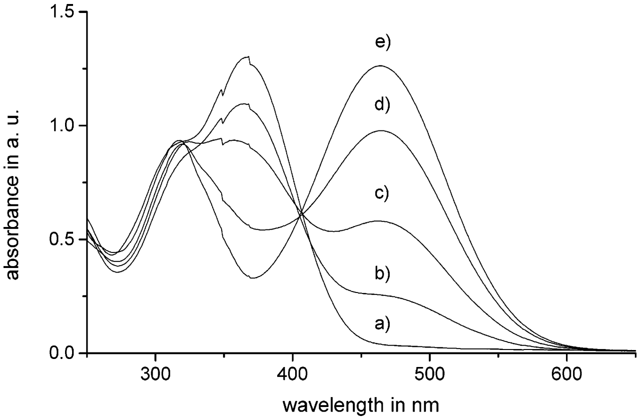


Figure 1. UV/vis spectra of **1c** in ethanol in the presence of different amounts of **PNA** (concentration of **1c**, 4.34×10^{-5} mol/L; molar amidine-chromophore ratio (a) 0, (b) 1.19, (c) 2.05, (d) 3.41, and (e) 13.64).

A 3.87 g (26 mmol, 10% excess) sample of *p*-carboxybenzaldehyde was dissolved in a solution of 2.81 g (70 mmol) of NaOH in 15 mL of water. This solution was added to a solution of 3.80 g (23 mmol) of 4-(4-hydroxyphenyl)-but-3-en-2-one in 15 mL of ethanol. A precipitate was formed. The mixture was heated to 50 °C for 15 min (precipitate dissolves), then cooled and left overnight. The mixture was diluted with 30 mL of water, and acidified with diluted acetic acid. Yellow crystals precipitated. The product **1c** was filtered off and recrystallized from an ethanol−water (1:2 v/v) mixture. Yield: about 3 g (45%). Data for **1c**: $T_m = 260-262$ °C; ^1H NMR (CD_3OD) δ (ppm) = 8.07 (d, H_1), 7.81 (d, H_2), 7.79 (d, H_6), 7.78 (d, H_3), 7.60 (d, H_7) 7.37 (d, H_4), 7.08 (d, H_5), 6.85 (d, H_8).

Measurements. UV measurements were recorded on a Cary 100 Varian spectrophotometer on ethanol solutions (l = 10 mm).

^1H NMR spectra were recorded on a Bruker DRX 500 NMR spectrometer operating at 500.13 MHz for ^1H. CD_3OH was used as solvent and tetramethylsilane (TMS) as internal standard. In the titration experiments a **PNA** solution in CD_3OH (0.08 and 0.008 mol repeating unit/L, respectively) was added in 25 μL portions to 1 mL of chromophore solution (0.01 and 0.001 M of **1c** in CD_3OH, respectively) directly placed in a NMR tube.

DSC measurements were performed on a Perkin-Elmer DSC 7 at a heating rate of 20 K/min in the temperature range −30 to +180 °C.

Results and Discussion

As shown earlier, aliphatic polyamidines are basic enough to be able to deprotonate chromophores of type **1**. Upon deprotonation strong changes in their absorption behavior are observed. As an example, UV/vis spectra of **1c** in the presence of different amounts of **PNA** are shown in Figure 1. Two absorption bands are seen, the intensities of which alter in opposite directions. The absorption band at 370 nm belongs to the structure with a protonated phenolic group, whereas the band of the deprotonated structure appears at 460 nm. The deprotonation of the carboxylic group has no influence on the UV/vis spectrum of **1c**. The spectral behaviors of compounds **1a** and **1b** are very similar.[12]

The influence of the degree of deprotonation on the absorption behavior allows one to record the titration curves of **1a**−**c** by UV/vis spectroscopy. The absorbance of the maximum at 460 nm serves as a measure for the degree of deprotonation. In Figure 2, the respective titration curves of **1b** with NaOH and **PNA** are shown. As expected, the deprotonation proceeds at much lower base concentrations when the stronger base NaOH was used as a titrator. In both cases, a distinct excess of base is required to achieve complete deprotonation. This is not typical for strong bases, such as NaOH, but can be explained by the high dilution of the titrant (concentration of **1b** = 3.58×10^{-5} mol/L). In such highly diluted

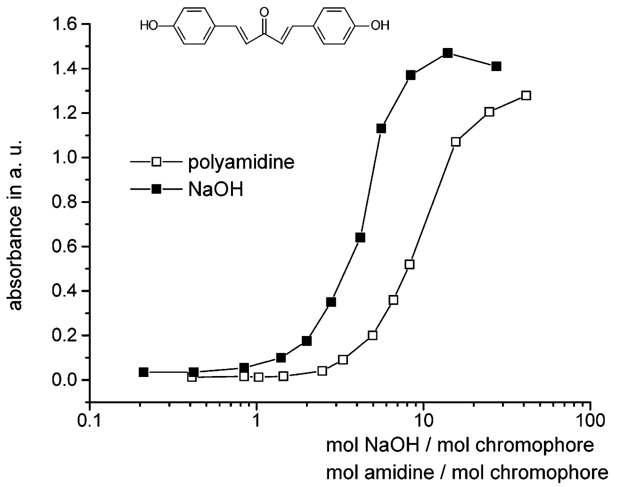


Figure 2. UV/vis titration curves of **1b** (absorbance measured in the maxima at about 470 nm in dependence on NaOH and **PNA** added; concentration of **1b** = 3.58×10^{-5} mol/L).

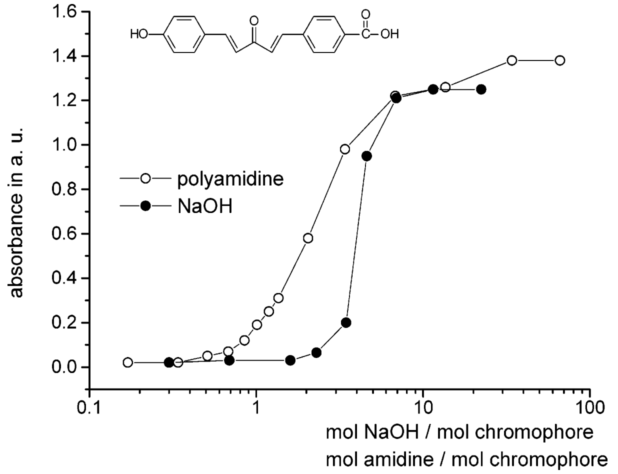


Figure 3. UV/vis titration curves of **1c** (absorbance measured in the maxima at about 460 nm in dependence on NaOH and **PNA** added; concentration of **1c** = 4.34×10^{-5} mol/L).

systems the competing interactions with the solvent (ethanol) reduces the activity of the base strongly.

The titration curves of the carboxylic group containing chromophore **1c** are shown in Figure 3. In contrast with **1b**, the deprotonation of the phenolic group of **1c** with NaOH is retarded. At a NaOH/chromophore ratio of about 1.5 (mol/mol) the deprotonation of the phenolic group of **1c** is negligible whereas in the case of **1b** deprotonation already starts at a ratio distinctly below 1. This can be explained by the presence of carboxylic groups which are stronger acidic than phenolic groups. If NaOH is added to the solution, the base is first consumed by the neutralization of the carboxylic groups with no influence on the UV/vis absorption. Significant deprotonation of the phenolic groups only starts after the majority of carboxylic groups is neutralized.

The shape of the curve obtained for the titration of **1c** with **PNA** was completely unexpected. In contrast with **1b**, deprotonation of the phenolic groups starts at much lower base concentrations (amidine) and occurs even easier compared with the NaOH titration curve. It is reasonable to assume that this behavior is caused by the competing interaction of the phenolic and the carboxylic groups with the polymer. An explanation for this behavior will be given later.

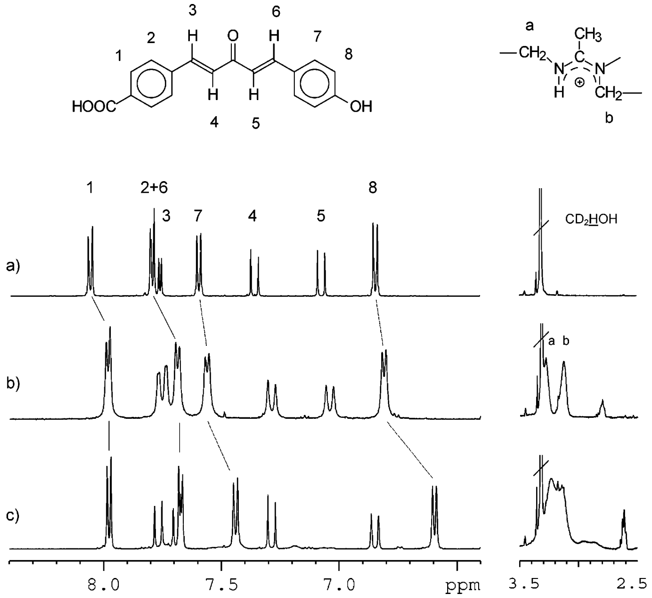


Figure 4. ^{1}H NMR spectra of **1c** in CD_3OD in the presence of **PNA**: (a) pure sample; (b) equimolar sample; (c) sample with distinct excess of amidine groups.

The UV/vis spectroscopy gives only information about the degree of deprotonation of the phenolic group of **1c**. Conclusions as to the deprotonation state of the carboxylic group can only be drawn indirectly since its deprotonation does not influence the UV/vis spectrum.

Simultaneous information about both groups can be obtained by NMR spectroscopy. In Figure 4, ^{1}H NMR spectra of **1c** in the presence of different amounts of **PNA** are shown. It can be seen that the position of the signals of the aromatic group protons H^1, H^2, H^7, and H^8 strongly depend on the amount of base in the system. With increasing degree of deprotonation a distinct high-field shift of these signals is observed. Comparing the three spectra shown in Figure 4, it is obvious that the behavior of the H^1 and H^2 signals differs from that of H^7 and H^8. The proton signals at the carboxylic group side (H^1 and H^2) change their position already at relatively low amidine concentrations, whereas a distinct shift of the proton signals at the phenolic side is only seen at higher amounts of **PNA** added. This reflects the different deprotonation behavior of the carboxylic and the phenolic groups.

Provided the chemical shifts of the completely protonated ($\delta_{\alpha=0}$) and the completely deprotonated chromophore ($\delta_{\alpha=1}$) are known, it is possible to calculate the degree of deprotonation α for both groups from the actual chemical shifts:

$$\alpha = \frac{\delta_{\alpha} - \delta_{\alpha=0}}{\delta_{\alpha=1} - \delta_{\alpha=0}} = \frac{[A^-]}{[A^-] + [AH]}$$

$[A^-]$ and [AH] are the molar concentrations of the particular deprotonated and protonated group, respectively. Here, $\delta_{\alpha=0}$ was determined from a saturated solution of the chromophore and $\delta_{\alpha=1}$ from a solution with a 5-fold molar excess of the base.

Because of the low sensitivity of NMR spectroscopy, the measurements had to be carried out at higher concentrations than the UV/vis measurements. Figure 5 shows the calculated α values of **1c** in dependence on the chromophore/amidine ratio at a chromophore con-

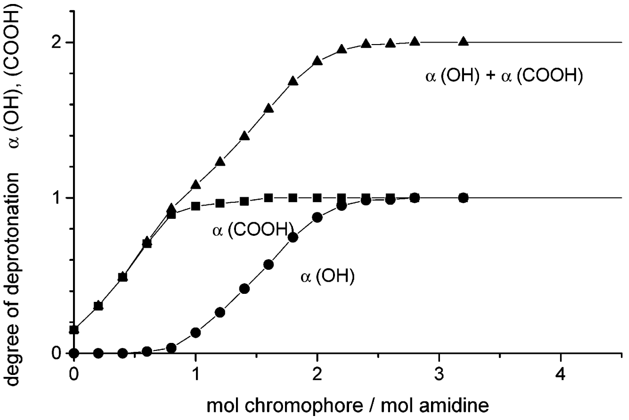


Figure 5. ^{1}H NMR titration curves of **1c**, with **PNA** as titrator (concentration of **1c**, 1×10^{-2} mol/L).

centration of 1×10^{-2} mol/L. The curves clearly show that the deprotonation of the carboxylic groups starts first and that of the less acidic phenolic groups subsequently. In the pure chromophore solution without base, about 15% of the carboxylic groups are already deprotonated by self-dissociation. Complete deprotonation of the whole chromophore is reached at about equimolar ratio (chromophore/amidine = 2).

Additional measurements showed that at higher dilution (1×10^{-3} mol/L) the self-dissociation of the carboxylic groups is more pronounced (α approximately 75%) and that deprotonation of the phenolic group starts already at distinctly lower base concentration (chromophore/amidine approximately 0.4). Furthermore, complete deprotonation (COOH and OH) was only observed if a distinct excess of base (approximately 100%) was added to the solution. These observations are in good accordance with the results obtained by UV/vis spectroscopy.

As mentioned above, UV/vis titration of the carboxylic group containing chromophore **1c** proved that the phenolic group is easier deprotonated by **PNA** than by NaOH. This can be explained by the polymeric nature of **PNA**. As approximated from the NMR results, one has to assume that the carboxylic group of **1c** is completely dissociated at the concentration commonly used for UV/vis measurements. As soon as **PNA** or NaOH is added to the solution of **1c**, the free protons are neutralized. In the case of **PNA**, proton absorption results in a positively charged polymer chain that is assumed to form immediately ionic complexes with the anions of **1c** by electrostatic attraction. In the vicinity of the polymer, the local concentration of amidine groups is much higher than average resulting in an earlier deprotonation of the phenolic group of **1c**. In other words, the carboxylic group of **1c** favors the approach of the chromophore to the polymer and subsequently also the deprotonation of the phenolic group.

The interactions of the chromophores with the polymer also influence the thermal behavior of the mixtures in bulk. Mixtures of **1a**, **1b**, and **1c** with poly(octamethyleneacetamidine) (**POA**) were prepared by casting from ethanolic solutions. After complete evaporation of the solvent, deeply red films were obtained, the thermal properties of which were investigated by DSC. DSC scans of all mixtures showed pronounced glass transitions which were strongly dependent on their composition. The results are demonstrated in Figure 6. In each case a strong increase in T_g upon addition of chromophore is observed. Since the rodlike chromophores are completely soluble in the polymer, they contribute to a molecular reinforcement of the matrix polymer, resulting in reduced mobility of its chain segments and eventually in increased T_g. The differences between the three compounds can be explained by the nature of their functional groups.

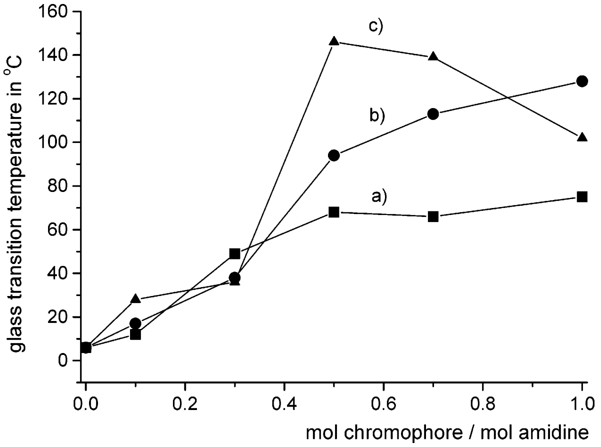


Figure 6. Glass transition temperatures of **PMA**/chromophore mixtures in dependence on their composition: (a) **1a**; (b) **1b**; (c) **1c**.

Generally, the influence of the chromophores to the glass transition behavior is very strong. From our earlier investigations, it has been known that the deprotonation of phenol group containing chromophores by polyamidines is much higher in the solid state than in solution, but not complete.[13] Deprotonation of carboxylic groups, however, proceeds quantitatively.[16] In the case of **1a**, it is assumed that in the bulk mixture with **POA** the degree of deprotonation of the single phenolic group is high at low chromophore concentration, but it diminishes with increasing chromophore content. That means, that at high chromophore concentrations near the equimolar ratio (chromophore/amidine = 1.0) some chromophore molecules are not demobilized by complexation. This explains the strong increase in T_g at low chromophore contents and the leveling off at equimolar ratio (Figure 6a).

An additional contribution to enhancement of T_g can be expected by cross-linking. Chromophore **1b** with two phenolic groups is assumed to form a physical network with **POA** by ionic complex formation. Because of this, mixtures of **1b** and **POA** possess distinctly higher T_g values (Figure 6b) than mixtures of **1a**. For **1b**, the equimolar ratio is already reached at a chromophore/amidine ratio of 0.5. At this ratio, maximum network formation is assumed. Further increase in T_g at higher chromophore/amidine ratios is attributed to the different contributions of decreasing network formation and increasing reinforcement by the rodlike chromophores.

The strongest influence on T_g is seen for chromophore **1c** (Figure 6c). The addition of **1c** to **POA** results in an increase of T_g from 7 °C for pure **POA** to 146 °C at equimolar ratio (chromophore/amidine = 0.5). At higher chromophore contents a decrease of T_g can be observed. It is reasonable that this is caused by the presence of the carboxylic group.

One can assume that the interactions of the carboxylic groups with the amidine groups are almost quantitative over the whole composition range investigated. That means that at equimolar ratio about 50% of the amidine groups are occupied by carboxylic groups and a certain part of the remaining amidine groups by hydroxyl groups. This reflects a high degree of physical cross-linking. With increasing amounts of chromophore, the bonded hydroxyl groups are more and more replaced by carboxylic groups because of their higher acidity. Eventually, a completely un-cross-linked associated side chain polymer with free hydroxyl groups is formed at a chromophore/amidine ratio of 1. In the case of chromophore **1b**, a certain amount of cross-links beside completely unassociated molecules has to be assumed at this ratio since both phenolic groups are equal. This explains the higher T_g of the mixture with **1b** at high chromophore concentrations compared to the mixture with **1c** which is assumed not to be cross-linked.

Conclusions

It could be shown that the interactions of polyamidine chromophore mixtures both in solution and in bulk are strongly influenced by the incorporation of a carboxylic group into the chromophore molecule. Because of the pronounced acidity of the carboxylic group, the chromophore is stronger bonded to the polymer that also results in an improvement of the thermal stability of the mixture. The change in UV/vis absorption caused by deprotonation of the phenolic group is not effected by the interactions of the carboxylic group. In solution, these interactions even contribute to strengthen this optical effect. The incorporation of the carboxylic group also opens the possibility to bond the chromophore covalently to a polymer. This will be subject of future investigations.

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