Possible Impact of Polymer Morphology on the Light Stability of Ink Jet Graphics

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Abstract

The chemistry of receiving polymers greatly affects the photo-permanence of dye based ink jet images. Earlier work has shown that in some cases the dye – polymer interactions lead to varying degrees of dye aggregation that can significantly improve dye photo permanece. Factors other than the solvating power of polymer for the dye also play a role in image photo stablity. Introducing co-monomers into the polymer backbone can greatly affect the degree of observed dye aggregation and photo stability. The changes in degree of aggregation and photo stability do not necessarily correlate with each other, and a decrease in aggregation does not always lead to a similar decrease in permanence.

This report describes an attempt to relate changes in polymer morphology, as detected by thermal analysis, with dye photopermanence. Specifically, co-polymers with ionic and non-ionic segments will be evaluated to determine if differences in dye aggregation or stability correlate with the possible presence of micellular domains or other morphology characteristics of the co-polymers.

Introduction

One of the most important factors affecting the photo stability of a dye is the chemical environment in which it resides.[1] All of the factors that impact the permanence of dye-based ink jet graphics, e. g., light intensity at harmful wavelengths, humidity, oxygen, airborne pollutants, etc., must operate in an environment largely defined by the chemistry of the receiving media. The interactions between the dye and the receiving polymers used in swellable media also play a large role in determining the degree of dye aggregation, an important feature of many stable dyes.

Aggregation can significantly improve the light stability of a dye.[2] Aggregation involves two or more dye molecules interacting with each other strongly enough so that they act as a single entity. In a sense a micro-pigment is formed and enough orbital interaction occurs to alter molecular properties such as absorption or emission profiles.

Critical dye/polymer interactions that influence aggregation can be isolated from the complexities of a printed image and studied directly. Previous work from these labs demonstrated a correlation between the increased degree of dye aggregation (Acid Yellow 23) in a polyacrlamide films and the increase in photo-permanence relative to polyvinyl pyrrolidone films.[3] In this work, the dye was incorporated into the polymer formulation prior to casting a film on a glass or quartz disc. The relative amount of aggregation could also be inferred from model calculations of dye/polymer interaction energies and the results were in good agreement with the permanence of printed images.

We have since found that the introduction of certain zwitterionic co-monomers[6] into polymers that are still predominately acrylamide exhibit good photo-stability. Acrylic sulfobetaine co-polymers, acrylic co-polymers containing zwitterionic monomers, are known to adopt a polymer configuration with defined ionic and non-ionic domains.[4] Acrylamide betaines have similar properties.[5] It is proposed that this discrepancy in the photo permanence of dyed polymer and printed polymer films may be due to differences in polymer morphology and the creation or destruction of zwitterionic micelles in these co-polymers.

Experimental

Dyed Polymer Details

Acid Yellow 23 and Acid Red 52 was dissolved into aqueous solutions of the polymers under investigation at two concentrations of 2.0% and 8.0% weight per dry weight of polymer.

Coatings were applied onto 1.5" diameter quartz discs using a Headway Spin Coater Model EC 101DT-1790. Rotation speed and duration were adjusted to achieve film thicknesses of 10 microns and 2 microns. UV/Vis spectra of the resultant discs were taken using a Perkin Elmer Lambda 9 Spectrophotometer. The discs were then exposed in an Atlas Ci65 Weatherometer, installed with a Xenon arc lamp and inner and outer borosilicate filters, for 48 hours. The exposure conditions were power = 0.35 Wm^2, relative humidity = 50% and temperature = 50°C.After

exposure, final UV/Vis spectra were taken using the Lambda 9.

Printed Polymer Details

Aqueous solutions of the polymers under investigation were drawn down onto a polythene coated paper substrate using a Meyer bar so that a 20-micron coating thickness was obtained after oven drying.

Yellow, magenta and cyan color blocks were printed on the samples using a HP 970 Cxi desk jet. Initial optical density measurements on the color blocks were taken using an X-Rite TR938 Spectrophotometer. The resultant prints were exposed in an Atlas Ci65 Weatherometer, installed with a Xenon arc lamp and inner and outer borosilicate filters, for 48 hours. The exposure conditions were power = 0.35 Wm2, relative humidity = 50% and temperature = 50°C. After exposure final optical density measurements were taken with the X_rite Spectrophotometer. The percent loss in optical density ((initial-final/initial) x100) is reported.

Polymers Used:

PAM = Polyacrylamide
Co-PAM 1 = Polyacrylamide / betaine copolymer
Co-PAM 2 = Polyacrylamide / betaine terpolymer
PVP = Polyvinyl pyrroloidone K90
Gelatin = Acid treated pig skin gelatin

Thermal Analysis

Glass transition temperatures were attained using a TA Instruments Q1000 DSC. Each sample was subjected to two temperature ramps (-60°C to 250°C @ 100°C/min) the first to ensure complete desiccation of the sample, the second to ascertain the Tg.

Results

Thermal Analysis

Table 1. DSC Results.

Sample / Tg°C	#1 Tg	#2 Tg
Co-PAM1 @ pH6	46	193
Co-PAM1 @ pH5	100	192
Co-PAM1 @ pH4	61	192
Co-PAM1 @ pH3	53	191
Co-PAM2	-----	183
PAM	-----	165

Thermal analysis of acrylamide betaine copolymer (Co-PAM 1) films found two distinct glass transitions, a pH dependent Tg that varied from 45 to 100, and a higher temperature pH independent Tg that at 193 C. This is consistent with the presence of defined micelle formation.

There is no evidence for micelle formation in Co-PAM2.

Printed Films – Light Stability

Figure 1 shows the dye loss from color blocks printed on polyethylene coated paper coated with the various polymers. The acrylamide homo -polymer (PAM) is difficult to print on but provides excellent light fastness. The acrylamide betaine co-polymers (Co-PAM) gives much better print quality than PAM and exhibits excellent light stability.
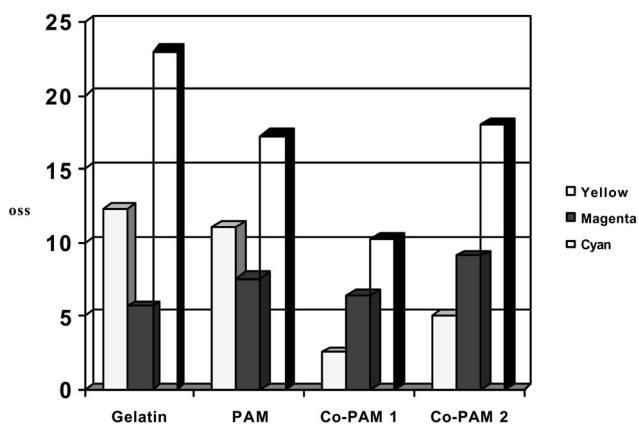

Figure 1. Optical Density Loss of Printed Polymer Films after Xenon Aging.

Dyed Film Aggregation

The effects of aggregation on UV/Vis spectra is seen readily with AR 52, see figure 2. One can clearly see the absorption due to dye aggregation as a separate peak or shoulder at ~ 530 nm. The acrylamide homopolymer has the largest degree of aggregation. Somewhat surprisingly, in light of the printed sample results, Co-PAM 2 displays almost the same negligible degree of aggregation as PVP. Figure 2b illustrates the change in the ratio of aggregate to monomer absorption as the dye concentration increases in the strongly aggregating PAM.
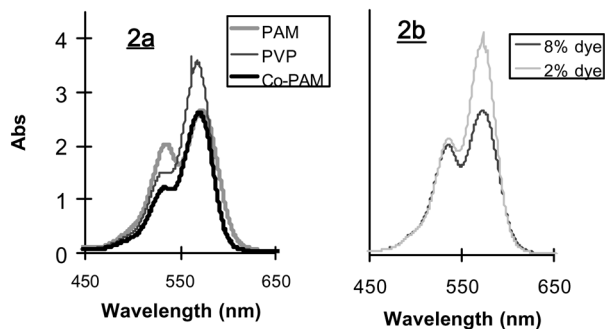

Figure 2. Absorption spectra of PAM, PVP and Co-PAM 2 films with 8% AR 52 (Fig 2a). Absorption spectra of PAM film with 2% and 8% AR 52 (Fig. 2b).

The aggregate absorption is less shifted for AY 23 than for AR 52. The change in the absorption spectra with increasing aggregation is seen as a change in shape of the absorption band and a shift in λmax, Figure 3. The observed peak is actually a composite of both the monomer absorption near 435 nm and the aggregate absorption closer to 420 nm. Again, the PAM has the highest degree of aggregation, λmax shifted most to the blue.

The amount aggregation of AY 23 induced by Co-PAM 1 is not as obvious. Figure 3b shows the change in absorption in the co-polymer upon change in dye concentration. The λmax shifts only 4 nm, in PAM the shift is 8 nm, PVP has no shift. While difficult to assess, there does seem to be less aggregation of AY 23 in Co-PAM 2 than PAM, but more than seen in PVP.
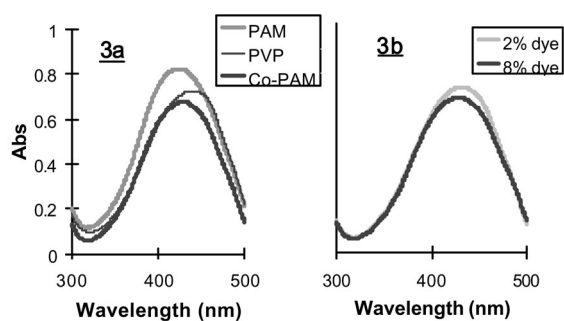

Figure 3. Absorption spectra of PAM, PVP and Co-PAM 1 films with 8% AY 23 (Fig 3a). Absorption spectra of Co-PAM 1 film with 2% and 8% Ay 23 (Fig. 3b).

Dyed Film Light Fastness

Table 2 shows the xenon aging results of the AY 23 samples. As in the printed samples, both the PAM and the co-polymer displayed excellent permanence, while the PVP sample is bleached. Certainly the PAM results can be explained by aggregation. The Co-PAM sample showed a moderate degree of aggregation and whether the stability can be attributed to this effect alone, or is in part due to other polymer/dye interactions, needs to be further investigated.

Table 2. Absorbance of AY 23 After Xenon Aging.

	Abs initial	Abs 24 hr	Abs 48 hr
2%, PAM	1.14	1.03	0.97
8%, PAM	0.82	0.75	0.66
2%, Co-PAM 1	0.72	0.69	0.61
8%, Co-PAM 1	0.68	0.62	0.54
2%, PVP	0.72	0.0	xx

The xenon aging results for AR 52 are shown in Table 3, Abs measured at the maximum ~ 350 nm. As expected, the PAM samples were very stable, the PVP samples very unstable. The 8% dye formulation in the Co-PAM is extremely photo labile. This is in contrast with results from printed samples, but perhaps consistent with the lack of aggregation seen above. Despite this lack of aggregation the 2% formulation in Co-PAM exhibits photo-stability similar to the PAM homo -polymer that has a large degree of aggregation.

Table 3. Absorbance of AR 52 After Xenon Aging.

	Abs initial	Abs 24 hr	Abs 48 hr
2%, PAM	4.0	Xx	2.5
8%, PAM	2.6	1.6	1.2
2%, Co-PAM 2	2.9	1.5	0.8
8%, Co-PAM 2	2.6	0.7	0.1
2%, PVP	3.0	0.2	Xx
8%, PVP	3.6	0.2	xx

Figure 4 displays the loss of absorption over time for the 8% PAM sample and the Co-PAM formulations.
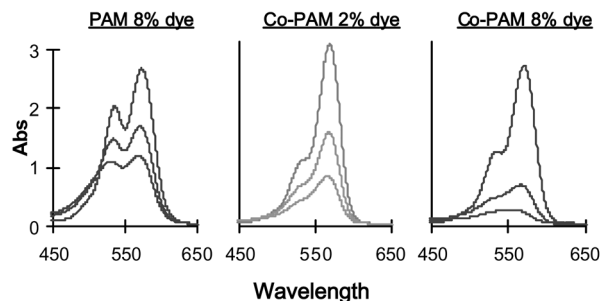

Figure 4. Absorbance loss of AR 52 from PAM and CoPAM 2.

Discussion

As mentioned in the introduction, zwitterionic acrylates and acrylamide co-polymers can adopt configurations in which a separate ionic domain, or micelle, can exist within a nonionic domain. These two configurations obviously provide two very different chemical environments. This was seen with Co-PAM 1, but not Co-PAM 2, a softer terpolymer similar to Co-PAM 1.

Co-PAM 1 did provide print stability better than either the highly aggregating PAM or the non-aggregating Co-PAM 2. It is tempting to ascribe some of the stability of the dye in Co-PAM 1 to the presence of separate zwitterionic domains. It is possible that the highly ionic micelles allow efficient penetration of the ink to allow good printing characteristics while the dye is forced into aggregates by the acrylamide. Another possibility is that the dye resides predominately in the zwitterionic regions and is stabilized by interactions with the cation/anion pair comprising the betaine.

Rayonette exposures of AR 52 in solution offer some support for the latter scenario. Addition of soluble betaines, e.g., trimethylammoniummethylcarboxylate, improved the

light stability of aqueous solutions of the dye. Cationic or anionic species, added separately or together, did not provide the same improvement. No dye aggregation was observed in any of the samples.

The behavior of AR 52 in Co-PAM 2 is, however, startling in at least two other aspects; the apparent lack of aggregation in a polymer that tended to give good light fastness when used as a receiving coating, and the remarkable difference in photo-stability between the high and low concentrations.

Similar behavior was noted previously for PVOH films dyed with AY 23, less than expected aggregation (although AY 23 aggregation can be hard to assess) and a concentration dependent stability. Here again the lower dye concentration was more stable.

It appears that stability factors other than aggregation are operative here, the ionic nature of Co-PAM 2 and the hydrogen bond network of PVOH. The higher dye loadings in Co-PAM 2 may be enough to overwhelm the influence of the zwitterionic side chains, it may even alter the manner in which the dye is solvated by the polymer.

However, changes in polymer morphology may also play a role, especially in the PVOH example. It could be surmised that tight hydrogen bonds set up a specific configuration of the PVOH film that is not disturbed in the printing process. Preformulation with a high concentration of dye may prevent this configuration from forming. The dyed film would then become a poor model for a printed article and evidence for or against aggregate formation in the dyed film may not apply.

This is of course highly speculative and the necessary further investigations are planned.

Conclusion

The morphology of the receiving polymer may in fact play an important role in dye light fastness; micelle formation in Co-PAM 1, a tight network of hydrogen bonding in PVOH. This configuration is set up when the polymer is cured during the coating process. The coating formulation, however, and conditions employed in film cure can impact the morphology. If, in the case of Co-PAM 1, the process of printing does not destroy the micelles, these two domains will continue to exist and impact the subsequent chemistry of the dye. Other factors, however, might be operative as the monophasic Co-PAM 2 also provides good print photo stability without showing signs of aggregation in the dyed film. The difference in photo permanence between the Co-PAM 2 print samples and the dyed film samples at high concentration do bring into question the validity of dyed films as a model for printed images.

References

1. A. Lavery, et. al , Proc. NIP 14, pg. 123= (1998).
2. R. Stieger, P. A. Brugger, Proc. NIP 14, pg. 114 (1998).
3. A. Naisby, et. al. Proc. NIP 18, pg. 749 (2002).
4. M. Ehrmann et. al. , Macromolecules, 25, pg. 2553 (1992); ibid., Macromolecules, 26, pg. 988 (1993).
5. D.J. Liaw, et. al., Polymer, 41, pg. 6123 (2000).
6. Wo 030376641 A2

Biography

Andrew Naisby is a Scientist in the Applications Laboratory of Ciba Specialty Chemicals Corporation in Tarrytown, New York (USA). Supervising Ciba's ink jet media laboratory his primary line of work is developing photo stable polymers for ink jet. He has over nine years experience in the formulation of media coatings and printing inks and holds several patents in this area.

Mr. Naisby holds an Honours Degree in chemistry from the Bristol, England University.