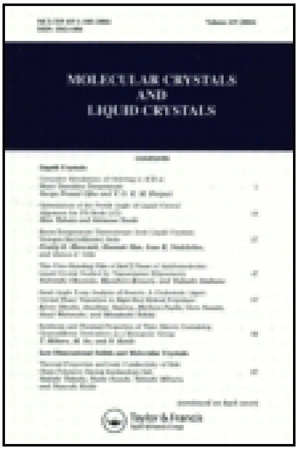

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Study of NIR-Dye Stability in Optical Film for the PDP Filter

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We have studied the thermal stability of optical film composed of transparent acrylic resin and the diimmonium dye, which is capable of absorbing intense near infrared (NIR) light from Plasma Display Panels (PDPs). After thermal aging, the color of optical film was changed and the efficiency of NIR absorption was decreased due to the deterioration of the dye. These phenomena were found to be sensitive to variations in characteristics of polymers and dyes. First of all, it was determined when the polymer resin possessed hydroxyl or carboxylic functional groups, although dyes's durability was slightly improved for the film with higher Tg polymer. These observations imply that the destructive mechanism of dye molecules is related to the effect of dye mobility and unpredictable chemical reactions between the dye and the reactive group of polymer. Additionally, we investigated the effect of solvent polarity as well as dye's rigidity on the thermal stability of the film in order to support these results.

Keywords: dye deactivation; hybrid-color film; NIR-cut dye; PDP filter; PSA(pressure sensitive adhesive)

INTRODUCTION

The PDP module radiates harmful and unprofitable lights, which are intense near infrared (NIR) light and strong electromagnetic radiation (EMI) besides the visible light. The emitted NIR is well known to cause

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malfunctions in devices such as TV remote controls and wireless microphone systems, among others. And EMI also give hazard influence on human being. Furthermore, the orange spectrum not only reduces color purity (especially red), but also interfere with improving the image qualities of PDPs. Therefore PDPs should be necessary to provide an optical filter [1] composed of special functional layers to prevent those harmful lights in the front of PDP module. In general, these layers are made of common films and are stacked together by pressure sensitive adhesives (PSAs) [2–4]. Since NIR blocking film and color compensation film are made from mixture of polymer binder with NIR-cut dye or Neon-cut dye, all mixed dyes with the polymer binder give a single film. It was named hybrid-color film which has at least three or four layers, e.g., coating layers, base film, PSA layers, and release film. Very recently, it has been attempted, however, to make multifunctional PSA film, so called color-PSA (C-PSAs), in which above dyes are dissolved in PSA. It is promising way to reduce both material cost and manufacturing cost as well because of removing one layers comparing of hybrid color film.

Until now, the various types of Neon and NIR absorptive dye for PDP color film have been reported [5–8] in many papers and patents. Among them, the most typical things are porphyrin, phthalocyanine, polymethine type, metal complex type, squarylium type, cyanine type, indoaniline type, diimmonium type, etc. Specially, the diimmonium dye is of great importance for commercial NIR blocking film because it can shield broad range of NIR region, typically from 850 to 1200 nm and it has also good solubility in most of organic solvents.

This dye, however, has some problems. It has poor stability and is easily to deteriorate in high thermal condition. Such deterioration of the dye results in the color change of the film. It is of the most important limitation factor when an optical film applies to PDPs. In the case of C-PSAs, this problem becomes more pronounced because PSA is random copolymer and has chemical functional group such as hydroxyl and carboxylic group. In fact, the durability of color film, however, is strongly dependent on the structure of dye, or coating condition, etc. Although many researchers have studied [5,7–8] the stability of the dye, none of them has focused on the destructive mechanism of the diimmonium dye in hybrid-color film or C-PSAs.

In this contribution, we demonstrate how polymer properties and dye structure have an effect on the thermal stability of the optical film. Poly (methylmetacrylate) (PMMA) and acrylic PSA were used as the polymer binder and the diimmonium dye was chosen as a NIR absorptive dye. The organization of this paper is as follows. First, we discuss the effect of dye mobility on the thermal stability for hybrid-color films. We then present results from a durability test for C-PSAs with different molecular specification such as chemical functional group and glass transition temperature. Finally, we consider the effects of organic solvent polarity as well as dye rigidity to better understand the destructive mechanism of the NIR dye molecules in polymer binder.

EXPERIMENTAL

Two types of diimmonium dyes used in this paper were synthesized at our lab. The structures of dyes are shown in Figure 1 and they are characterized by ^{1}H NMR, DSC, MS/MS, and LC/MS. Poly(methylmethacrylate) (PMMA) was used to make hybrid-color film (HC-A) as polymer binder and commercial porhyrin dye was applied as a Neon-cut dye. For the comparison of two hybrid-color film, commercialized hybrid-color film (HC-B), imported from one of Japanese companies, was also examined for this study. Three different acrylic PSAs, supported from Keomyeong Inc., were used for C-PSAs. Specifications of polymer binders studied here are summarized in Table 1.

Coating solution was coated on a transparent PET film by using a bar coater and dried at 100°C for 5 minutes. For C-PSAs, the coated film was laminated with releasing film and aged at room temperature for 7 days or 60°C for 3 days depending on nature of cross-linking agent. The thermal stability of the optical films was studied by measuring a Lamda 950 UV-Vis spectrophotometer (Perkin-Elmer). In more detail, we compared with the UV-spectrum of two above optical

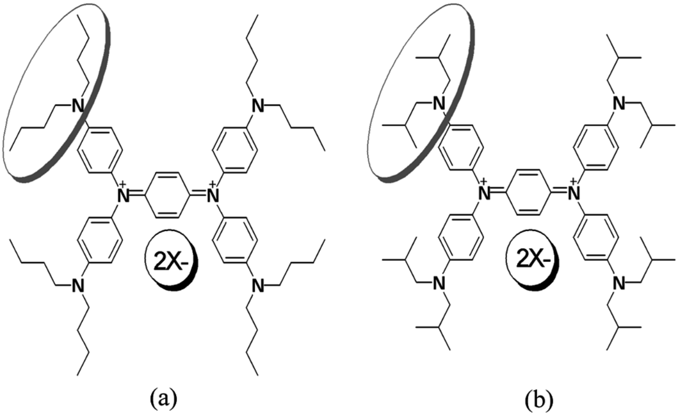

FIGURE 1 Chemical structures of diimmonium dyes. Alkyl side chain is (a) n-butyl, (b) iso-butyl. X=N(SO_2CF_3)$_2$.

TABLE 1 Specifications of Various Polymers

	Polymer	Functional group	M_n (k)	T_g (°C)
Color Film	PMMA	–	70	95
Color-PSA	K-1	–COOH	1000	–10
	K-2	–COOH	550	–45
	K-3	–OH	550	–50

films before and after thermal aging. And then color coordinates in the CIE (Commission International del'Eclairage) Yxy color space were calculated from the transmittance data.

RESULTS AND DISCUSSION

Kinetics Study of Durability for Hybrid-Color Film

Measurements were made first on aged film at 80°C for 5~500 hours to understand general features of experiment. Figure 2 presents absorption spectra of hybrid-color film (HC-A) contained with diimmonium

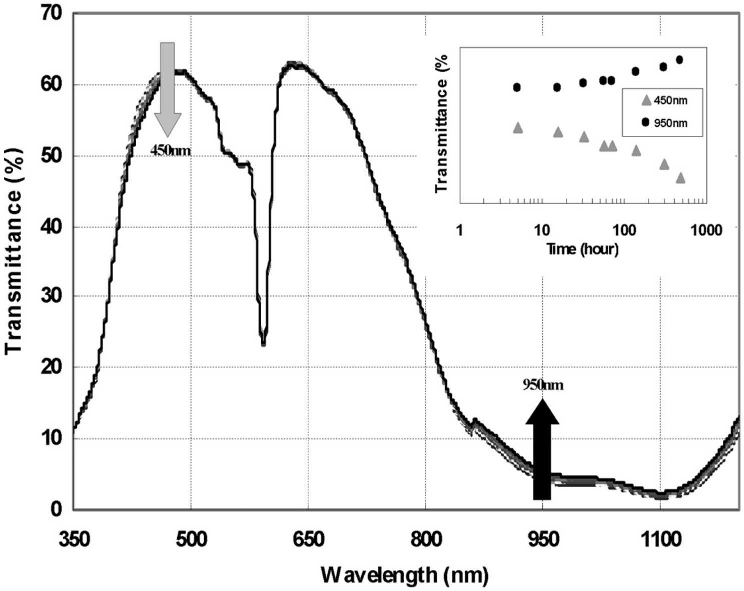

FIGURE 2 Absorption spectra of the hybrid-color film aged at 80°C for 5~500 hours. Inset: transmittance profile at 450 nm and 950 nm along the aging time.

dye, as shown in Figure 1(a), and PMMA with molecular weight of 70,000 g/mol. No obvious change of spectrum shape was observed around 590 nm where Neon-cut dye can absorb light. Two substantial changes, however, were found both shorter wavelength (450 nm) and NIR regions (800∼1200 nm). One is that transmittance was gradually decreased around 450 nm with aging time, and the other is that it was increased at NIR region. This implied that the efficiency of NIR blocking slightly declined during the aging process. The inset showed clearly that the transmittance profile moved opposite way in two regions along the aging time. For the diimmonium dye, no thermal changes are observed in DSC spectra up to 230°C (not shown here), indicating the diimmonium dye itself is thermally stable at 60∼100°C, typical temperature for thermal durability test. Therefore we believe that two above changes might be originated from physicochemical interaction between the dye and its surrounding molecules.

We have also studied the temperature dependence of dye deactivation for the hybrid-color films. Deactivation rate, transmittance at 950 nm versus aging time, was increased with aging temperature, as shown in Figure 3(a) for HC-A and Figure 3(b) for HC-B. Although similar trend was obtained, sharply different behavior can be found at 100°C. Whereas rate of the dye deactivation (slope of the curve) for HC-B gradually decreased after 100 hours, it continuously increased for sample HC-A, even around 500 hours. This implies that there are certain differences in physicochemical properties between two samples around 100°C. Since overall shape of absorption spectra for both films are almost identical (not shown here), we assume that same type of diimmoium dyes were used for both films. Therefore we ignore the effect of dye and consider only the effect of polymer to explain our intriguing finding.

One of key parameters governing thermo-physical properties of polymer is Glass Transition Temperature (T_g) through which the polymer change from a glassy (hard) state into a liquid (rubber-like) state [9]. Since differences in viscoelastic parameters around T_g can be directly related to the mobility of both polymer and dye molecules, large difference in thermal stability of the film might be also expected. This proposed explanation was further probed by measuring weight-loss of the film with temperature using thermo-gravimetric (TG) measurement [10], as shown in Figure 4. Apparently, first weight loss was found to be occurred below 100°C for HC-A, but over 100°C for HC-B. We believe this result is directly related with T_g of the film because the mechanical strength of polymer must be weakened dramatically at 100°C for HC-A, and thus mobility of dye might be also increased.

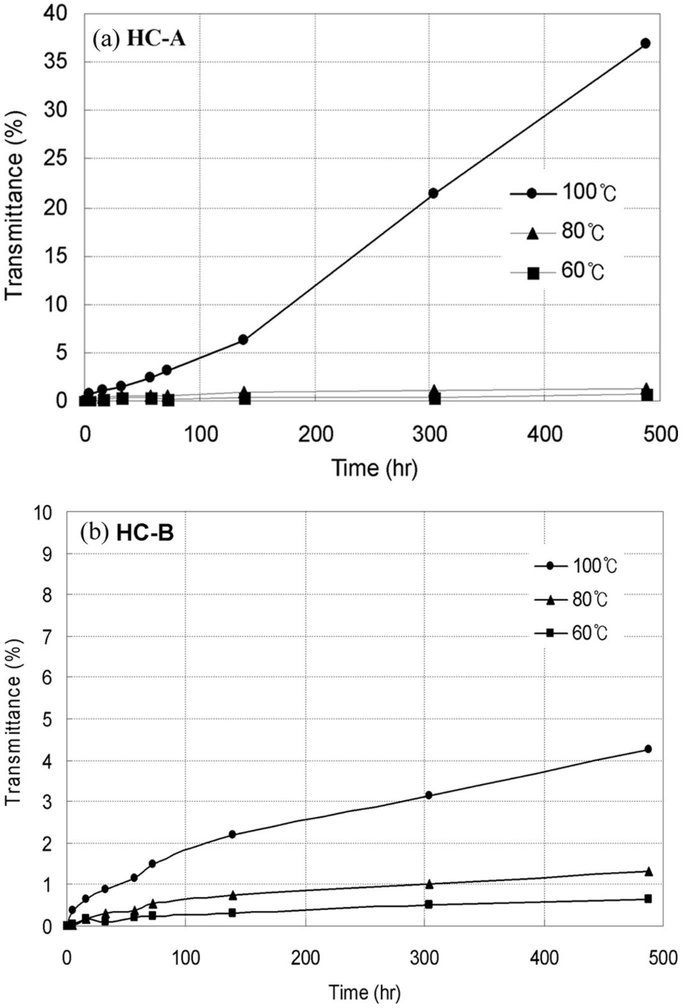

FIGURE 3 Variation in transmittance at 950 nm with aging time for hybrid-color films (a) HC-A: film made using diimmonium dye and PMMA (b) HC-B: commercial film. Results are shown for three aging temperature.

Here, we have to consider the effect of dye mobility driven by change in mechanical properties of polymers on thermal stability of the dye. First, we attempted to explain the general feature of dye deactivation rate and special behavior at 100°C for HC-A using collision theory based on Arrhenius Eq. [11],

$$k = A \cdot e^{-\frac{Ea}{RT}} \tag{1}$$

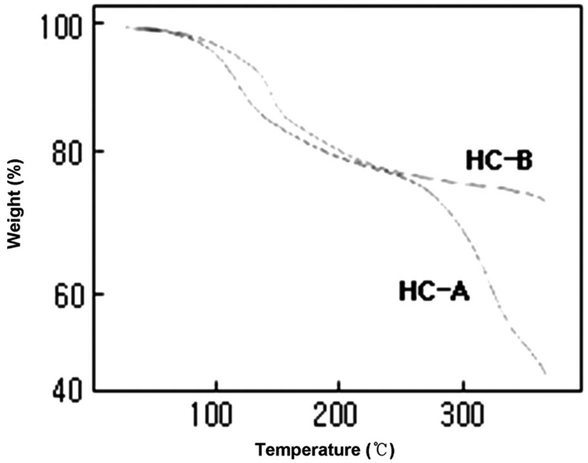

FIGURE 4 Experimental TG curves for hybrid-color films.

where k is rate constant, A is a collision coefficient, Ea is activation energy, R is gas constant, and T is temperature. The rate constant of chemical reaction is proportional to temperature, the frequency with which the reactions collide with each other, and also to the probability that the collision is sufficiently energetic for a reaction to occur. Higher temperature means greater the proportion of vigorous encounters, according to the Boltzmann distribution [11].

Therefore most of chemical reaction fastened at higher temperature. The analysis of collision coefficient, however, is more complicated. Two contributions must be considered. The first factor is the transport property and second one is geometric configuration of reactive molecules. The transport property is determined by how easily the reactive sites come together. In the case of dye and polymer system, the mobility of reactive sites, which means a collision probability, becomes more pronounced at rubbery (liquid-like) state. This is the reason for why the role of thermo-mechanical characteristics of polymer is important. This postulation is well consistent with our observation, as shown in Figure 3. The second factor takes care of the local properties of the reaction, such as the orientations necessary for reaction and the details of how close they must come.

DURABILITY TEST FOR C-PSAs

Before discussing the dye deactivation mechanism in more details, we turn our focus on C-PSAs which is quite new applicable area for NIR cut film. They are different in some way from hybrid-color film, especially, existence of chemical functional group. Industrially, adhesives are well known for their role in the assembly of diverse items as furniture, automobiles, and aircraft. PSA is less known but equally important industrial application for the use of adhesives in the assembly of electronic component. Differences of industrial adhesives are that this segment has certain specific requirements included ease of use, rapid cure for thermoset and reliability in manufacturing and in the properties of the resulting component. Among them, reliability and durability tests are most stringent for the electronic devices [1]. Moreover, C-PSAs will be the most important factor for PDP filter market in near future because it is effective way not only to simplify the PDP filter structure, but also to reduce overall manufacturing cost of the PDP filter.

Figure 5. shows three absorption spectra of C-PSAs after aging at 80°C for 500 hours. Diimmonium dye (Fig. 1(a) and three different acrylic PSA used. PSA are typically random copolymers of a long side-chain acrylic (n-butyl acrylate or 2-ethyhexyl acrylate) with a short side-chain acrylic. In more details, the role of methyl acrylate chains can control T_g, and acrylic acid or 2-hydroxyethyhexyl acrylate chains improve mechanical properties of PSA.

One can see that deactivation of diimmonium dye is more pronounced for all three C-PSAs comparing to hybrid-color films. However, no substantial difference was found between K-1 and K-2. Those two PSAs have same functional group, but different molecular

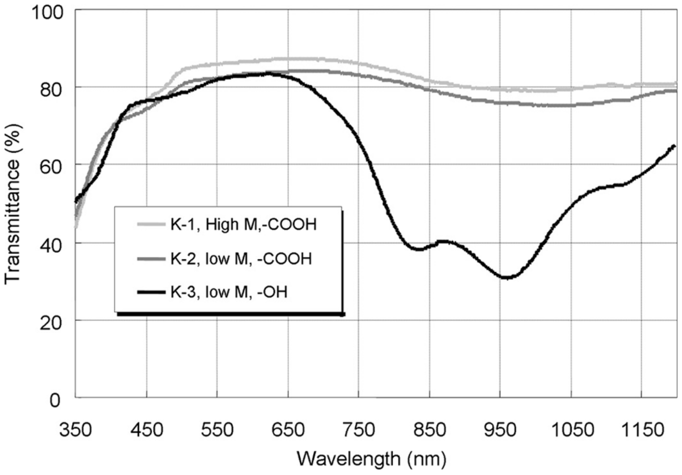

FIGURE 5 Absorption spectra of the C-PSAs aged at 80°C for 500 hours.

weight. On the contrary, K-2 and K-3 shows sharply different behavior. Even though difference in molecular weight and thus T_g do not affect significantly on dye deactivation, the role of type of functional group is quite substantial. The implication of the above results is that the effect of functional group is much more complex than had been suspected. In any case, however, it is believed that chemical interaction between dye and polymer is predominant prior to the effect of dye mobility only if the polymers have reactive functional group.

INTERPRETATION OF DYE DEACTIVATION

In previous section, we demonstrated how polymer matrix affects on the thermal stability of diimmonium dye. It has been shown that driving force for the dye deactivation is quite different, depending on existence of chemically reactive group. In the case of hybrid-color film, although overall deactivation rate is relatively slow due to small amount of reactive site of polymer, mobility of dye plays a role in determining the deactivation rate. On the contrary, the deactivation rate of C-PSAs became faster in which effect of chemical environment, specifically strength of polarity, dominates over the dye mobility. Note that K-1 and K-2 are more polar nature than K-3. The features that dominated in determining dye deactivation rate are summarized in Figure 6.

This proposed explanation can be further verified by attempting to see if structural change in dye molecules can also influence on their

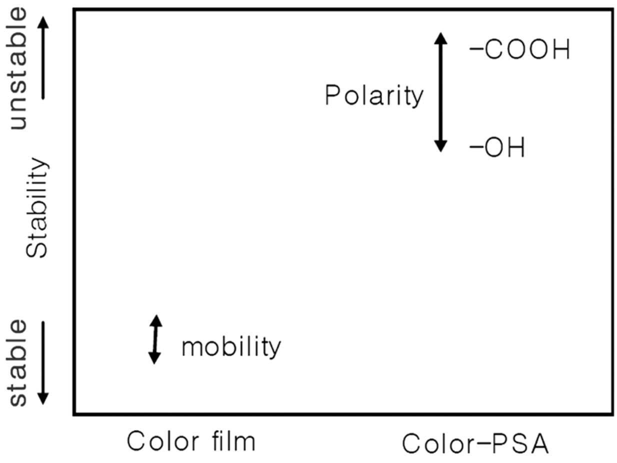

FIGURE 6 Factor dominating the dye deactivation for color film and C-PSAs.

stability. Structural change is another way to control dye mobility and reactivity. As mentioned earlier, local properties of the reaction, such as the orientations necessary for reaction, is one of key issues in determining reaction rate. Therefore introducing rigid and bulky side group might be helpful for thermal stability of the dye. We examined this effect by replacing n-butyl (Fig. 1(a).) with iso-butyl (Fig. 1(b)) and the results are summarized in Table 2. While no difference was observed for C-PSA, durability of the hybrid-color film was slightly increased when iso-butyl group applied. Note that since durability of hybrid-color film is quite good even after 500 hours, this small increment in stability is still meaningful. However, for C-PSAs, the effect of functional group is sufficiently large enough to ignore structural change of dye. These results are consistent with our postulation, as discussed in Figure 6.

Finally, it remains to rationalize these behavior and to identify the dye deactivation mechanisms. In fact, the common limitation of organic dyes, especially those with long-wavelength absorption bands, is their susceptibility to chemical and photochemical degradation. It is well known [7] that the reason for enhanced reactivity is an inherent and small HOMO-LUMO energy gap, which means that the dyes are potentially reactive with nucleophiles and electrophiles.

Another possible way of deactivation route is the dye aggregation, which includes multichromophoric interactions that alter the color. Understanding these two possibilities for dye deactivation is very important for developing new product like C-PSAs, because the way of approaching to overcome durability problem is strongly dependent on detailed mechanism of deactivations. For this purpose, we investigated the effect of solvent polarity on absorptive behavior of the diimmonium dye. Instead of looking at aged film, dye solutions with different solvent polarity were compared.

Figure 7 presents absorption spectra of diimmonium dye solutions with different solvents. By varying solvents from toluene, ethylacetate

TABLE 2 Difference in Color Coordinates After Thermal Aging for 500 hours at 80°C. Note that Smaller Δ y, x Means Higher Stability

	Hybrid-color film		C-PSAs	
Polymer	PMMA	PMMA	K-3	K-3
Dye	n-Butyl	Iso-Butyl	n-Butyl	Iso-Butyl
Δ y	0.004	0.001	0.016	0.017
Δ x	0.002	0.000	0.009	0.008

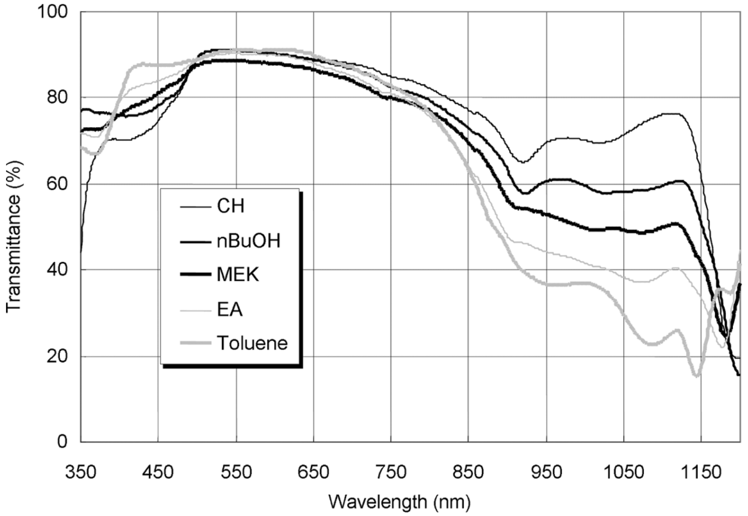

FIGURE 7 Absorption spectra of dye solutions with different solvents. (CH: cyclohexanone, nBuOH: n-butyl alcohol, MEK: methyl ethyl ketone, EA: ethyl acetate).

(EA), methyl ethyl ketone (MEK), n-butyl alcohol (n-BuOH) to cyclohexanone (CH), it is clearly seen that transmittance was gradually decrease around 450 nm and it increase at NIR region. These trends are same as what we saw in Figure 2. Above order is not directly corresponds to solvent polarity. Snyder Polarity Index [12] for Toluene, EA, MEK, n-BuOH, and CH are 2.4, 4.3, 4.7, 4.0, and 4.5, respectively. Note that more polar solvent such as water (9.0) and acetic acid (6.2) could not be tested because the diimmonium dye is insoluble. Although one can see that the dye performance is much better in non-polar solvents (toluene), the question of why n-BOH and CH deviated from the straight line in Figure 8 is still remain. One possible explanation is a role of hydroxyl group. Assuming that the hydroxyl groups interact directly with either ammonium site of the dye or its counter anion, the dye could be easily deactivated. This assumption is very similar situation as C-PSAs. For the case of cyclohexanone, it can be explained by enolization or keto-enol tautomerism, where a hydrogen atom attached to the α-carbon atom of carbonyl compound moves to the carbonyl oxygen atom. The position of equilibrium for tautomerism depends on molecular structure. The equilibrium constant for cyclohexanone is 2.0×10^{-4}, which is 100 times higher than that of MEK of 2.0×10^{-6}. This difference may be resulted from structural effect [13], indicating enough amount of hydroxyl group to be reacted with

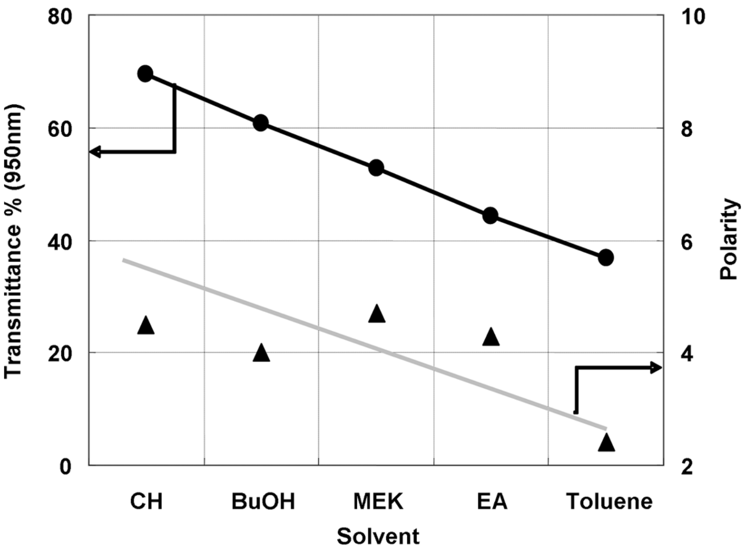

FIGURE 8 Variation in transmittance at 950 nm and snyder polarity index for diimmonium dye solutions.

dye molecules could be existed in cyclohexanone. Another important finding is existence of isobestic point around 500 nm in Figure 7.

If one absorbing species, X, is converted to another absorbing species, Y, during the course of a chemical reaction and the spectra of X and Y cross each other at any wavelength, then every spectrum is recorded. When this chemical reaction will cross at that same point, it is called an isobestic point. The existence of an isobestic point is good evidence that only two principal species are present [14].

Therefore it is believed that the origin of abortive peak around 450 nm is new species produced by chemical reaction between dye and its surrounded molecules. Although we conjecture the deactivation of diimmonium dye mainly attributed to chemical interaction, instead of dye aggregation, the precise way in which the behavior of this dye deactivation can be related quantitatively to the overall performance of NIR-cut films must be further studied.

CONCLUSIONS

The thermal stability of the hybrid-color film and C-PSAs for PDP filter was studied by observing absorptive characteristics of diimmonium dye. After thermal aging, a color was changed and the absorption ability of NIR was decreased because of the deterioration of the dye. Such deterioration of the dye was found to be sensitive to variations in characteristics of polymer binders. Although the effect of dye mobility is quite important, it has been found that existence of chemical functional group can overwhelming the mobility effect on thermal durability of NIR films. The detailed mechanism is not clarified yet, but new approach such as dye encapsulation [7] is the subject of current study.

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