

# Characterization of Nafion Solutions and Films and Observation of the Casting Process Using Basic Dyes as Optical Probes

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## SYNOPSIS

The absorption spectrum of methylene blue and crystal violet (CV) in ethanol-water in the presence of Nafion exhibited metachromasy, but a little or no formation of the large aggregates of the dye was observed. This indicates that the dye molecules are bound to the surface of the micellar particles of the polymer, but the ability of Nafion to induce the aggregation of the dye is weak. The absorption spectrum of malachite green (MG) and CV was measured in a cast film of Nafion at varying ambient humidity. The spectral change with humidity indicates that the decrease in the water content of the film causes the increase of H<sup>+</sup>-ion concentration in the hydrophilic cluster of Nafion and, hence, leads to the protonation of the dyes. The absorption spectrum of a Nafion solution containing MG or CV was recorded in the process of casting. The dyes changed to the protonated form right after evaporation of most solvent from the solution. This suggests that the phase inversion occurs in the casting process. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Nafion is the trademarked name for a perfluorosulfonate ionomer manufactured by E. I. du Pont de Nemours & Co., Inc. Nafion has been proving to be an interesting and useful membrane material. Solid Nafion can be dissolved in an water-alcohol mixture at an elevated temperature under pressure.<sup>1</sup> Reconstituted films of Nafion are obtained by evaporating solvent from the solution. The condition of film preparation such as the kind of casting solvent and evaporation temperature has been examined in order to obtain good insoluble films.<sup>2,3</sup> The characteristics of Nafion solutions<sup>4,5</sup> and films<sup>6,7</sup> as well as original Nafion membranes<sup>8-12</sup> have been investigated using variety of chemical and physical methods of analyses. It has been supposed that there is a large difference in structure between Nafion polymers in solution and as a solid; the fluorocarbon phase exists as micelles surrounded by ionic groups in the solution,<sup>5</sup> whereas it forms a continuous phase including

clusters of ionic groups in solid film.<sup>9</sup> However, the structural change of Nafion from solution to solid film, which occurs in the casting of the solution, is not known in detail.

Recently, Nafion has been used as polymer matrices doped with dyes and the consequent photo-physical and photochemical properties of the dye have been studied.<sup>13-18</sup> Dye-doped Nafion films have also been studied for applications to optical sensors for metal ions,<sup>19</sup> moisture,<sup>20-22</sup> and the hydrogen ion.<sup>23,24</sup> Fluorescent dyes as probes have been incorporated in Nafion films to investigate the properties and structure of these films.<sup>25-28</sup> However, very little work has been reported on simpler methods using light-absorbing probes.<sup>29</sup>

In this work, a simple method is proposed using basic dyes as light-absorbing probes for *in situ* characterization of Nafion solutions and films and for *in situ* observation of the casting process. Such dyes are expected to report the conformation of Nafion in the solution and to function as acidity indicators in the film. The absorption spectrum of some basic dyes was measured in a Nafion solution when the concentration of Nafion was changed. It was also measured in cast films of Nafion at varying ambient

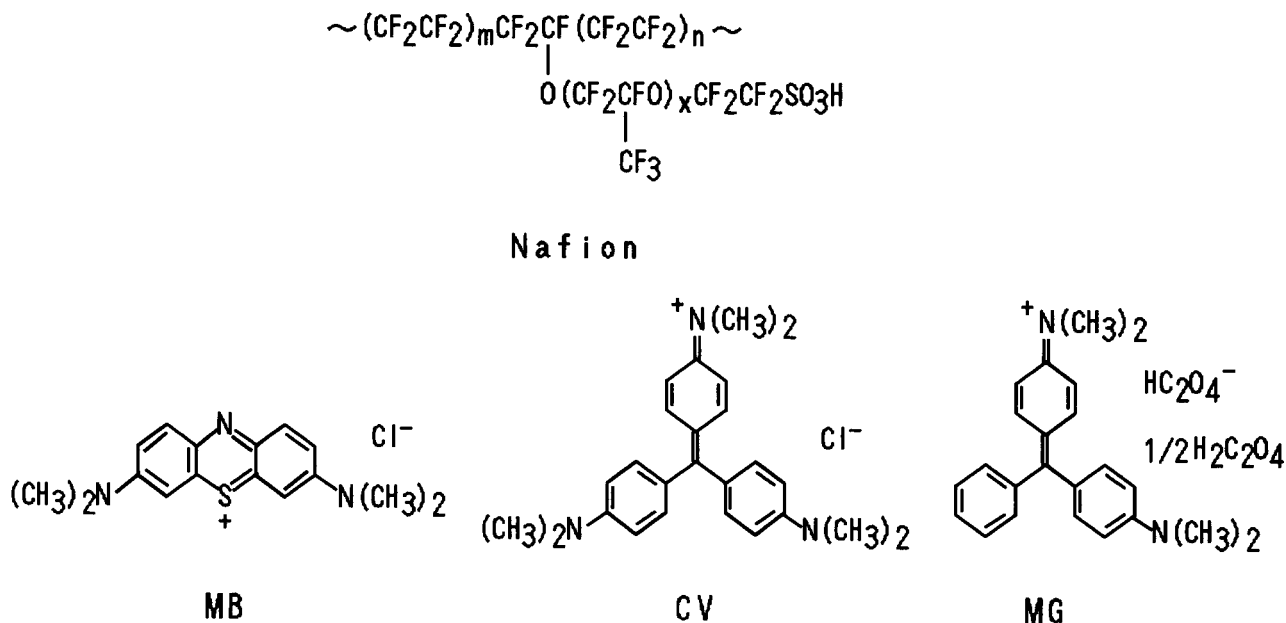
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relative humidity (RH). The water content of the film, which strongly influences the chemical properties of the polymer, could be controlled by RH. In addition, changes in the absorption spectrum of a Nafion solution containing the dyes were analyzed during solvent evaporation. These investigations offer evidence for the micellar structure of Nafion in solution, the formation of ionic clusters in solution-cast Nafion films, and the phase inversion during the casting process.

## EXPERIMENTAL

### Materials

Nafion (1100 equiv. wt.; water-alcohol solution, 5 wt %, Aldrich), methylene blue (MB) (hydrochloride, extrapure, Ishizu), crystal violet (CV) (hydrochloride, extrapure, Kishida), and malachite green (MG) (oxalate, 90%, Aldrich) were used as received. The chemical structures of Nafion and the dyes are given below:



### Measurements for Solutions

Dyes were dissolved in ethanol-water (2 : 1 v/v) at  $10^{-3}$  or  $10^{-4} M$ . Nafion, 5 wt %, corresponds to  $0.0397 M$  of sulfonate groups contained by the polymer. The 5 wt % Nafion solution was diluted with the solvent mixture to  $10^{-3}$  or  $10^{-4} M$  of sulfonate groups. Measured volumes of the dye and Nafion solutions and solvent mixture were mixed and equilibrated for more than 10 min. The concentration of the dye was held constant at  $10^{-5} M$  and the concentration of Nafion was changed from 0 to  $3 \times 10^{-4} M$  of sulfonate groups. For such an experiment, the molar ratio of monomer unit of polymer to dye (P/D) has been used frequently to describe the relative amount of polymer and dye in a solution.<sup>30,31</sup> In this study, the P/D value is also used, but it means the molar ratio of sulfonate group to dye. Absorption spectra were measured in a quartz cell ( $10 \times 10$  mm) on a Shimadzu UV-2200 double-beam spectrometer. The temperature was maintained at  $25.0^\circ\text{C}$ .

### Measurements for Films

A dye solution in ethanol-water (2 : 1 v/v) was mixed with the same volume of the 5 wt % Nafion solution. The stock solution containing 2.5 wt % Nafion and  $7.2 \times 10^{-3} M$  dye was cast on a glass plate ( $30 \times 9.5$  mm) and air-dried at room temperature. Film thickness was about  $9 \mu\text{m}$ , as calculated from the volume of the stock solution by assuming that the density of the film equals 1.0. Absorbance measurements were made under the conditions of desired RH and  $25.0^\circ\text{C}$  by using a JASCO UVIDEC-1 double-beam spectrometer equipped with an air-flow system, as described elsewhere.<sup>32</sup>

### Observation of the Casting Process

The same stock solution as used for film preparation described above was diluted twofold with ethanol.

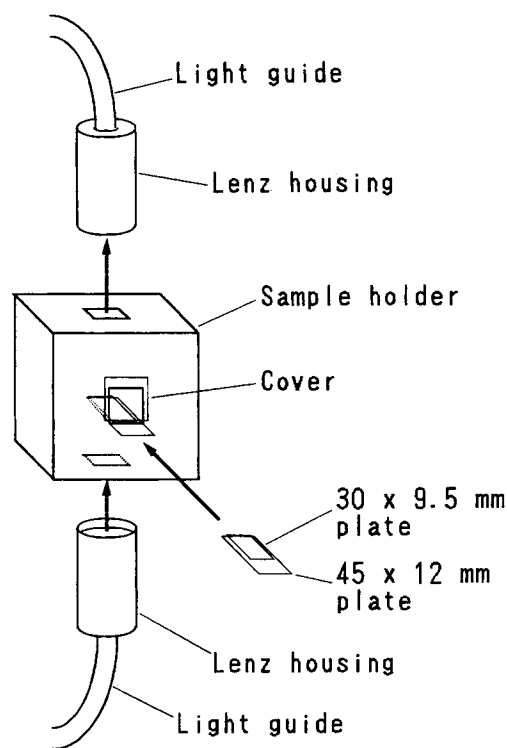
The resulting solution, 0.05 mL, was cast on top of two glass plates, which consisted of an upper plate (30 × 9.5 mm) and a lower plate (45 × 12 mm). The plates were carefully inserted horizontally into a sample holder, as shown in Figure 1. The lower plate served as a carrier for the upper plate. The front opening was sealed with a cover. The solvent was evaporated slowly and its vapor went out through the upper opening of the holder. Uniform evaporation of the solvent occurred in almost the whole process of casting except just before the completion of drying. The holder was temperature-controlled by circulating water at 20.0°C. Light from a 250 W halogen lamp passed through color temperature-converting filters and was focused into a light guide for illumination. Light from a lens housing that was fixed under the sample holder was shed on the back of the sample. The transmitted light was collected by another lens housing that was fixed over the sample holder. The collected light was conducted by a light guide and analyzed by an Unisoku USP-500 multichannel photodetector. The spectrum of the transmitted light through the two glass plates without solution was used as a reference. After dark and reference spectra were measured, spectra of the solution were measured at intervals of 10 s to 20 min until the solution was completely dried. The absorption spectra of the solution were obtained by calculation from these spectra.

## RESULTS AND DISCUSSION

### Characterization of Nafion Solutions

An obvious color change is observed when cationic dyes are bound to polyanions. This phenomenon called metachromasy is useful to study the nature of the interactions between the Nafion polyelectrolyte and the dye. MB and CV were chosen as dyes for this study because the metachromasy of these dyes is dramatic and well characterized.<sup>30,31</sup>

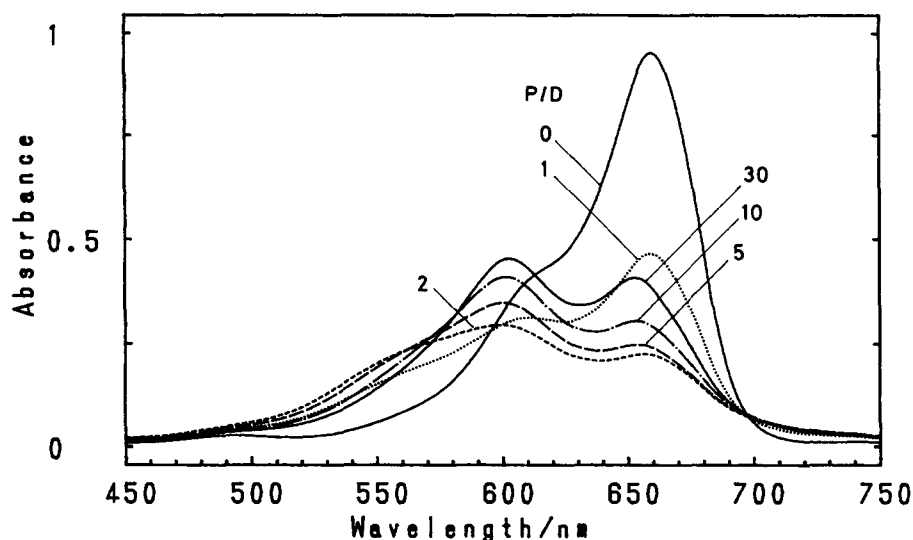
The absorption spectra of MB in the presence of Nafion are shown in Figure 2. The absorption spectrum of MB in a solution without Nafion is characterized by a strong peak at 664 nm corresponding to monomeric MB and a slight shoulder at 610 nm corresponding to dimeric MB.<sup>33</sup> As Nafion was added to the solution up to P/D of 2, the band for the monomer decreased, while the band for the dimer relatively increased and a shoulder near 550 nm corresponding to the higher aggregate of MB appeared.<sup>34</sup> As P/D increased from 3, the band for the higher aggregate diminished and the bands for the



**Figure 1** Schematic drawing of the sample holder and the optical components.

monomer and dimer increased. The absorption spectra of CV in the presence of Nafion are shown in Figure 3. The absorption spectrum of CV in a solution without Nafion is characterized by a peak at 592 nm and a shoulder around 550 nm. As Nafion was added to the solution up to a point (P/D = 2), a peak at 552 nm rose at the expense of the 592 nm peak. The absorption spectrum did not change over the P/D range of 2–5. As P/D increased further, the spectral change reversed slowly. It has recently been demonstrated that the CV monomer, dimer, and trimer are characterized by a peak at 590 nm and a shoulder near 550 nm, a peak at 545 nm, and a peak at 520 nm, respectively.<sup>35</sup> Therefore, it can be said that with increasing P/D value the absorption spectrum of the monomeric dye was converted to that of the dimer form and then gradually reverted to the original one.

Because the above results for the Nafion–cationic dye system are similar to those observed for systems with ordinary polyanions, the interpretation for the metachromasy in the latter systems<sup>36</sup> is applicable to the system of this study. Since sulfonate groups of Nafion have strong acidity, Nafion dissociates to form polyanion. Consequently, it is proposed that by adding Nafion to a solution of cationic dyes the dye molecules were held sufficiently close together

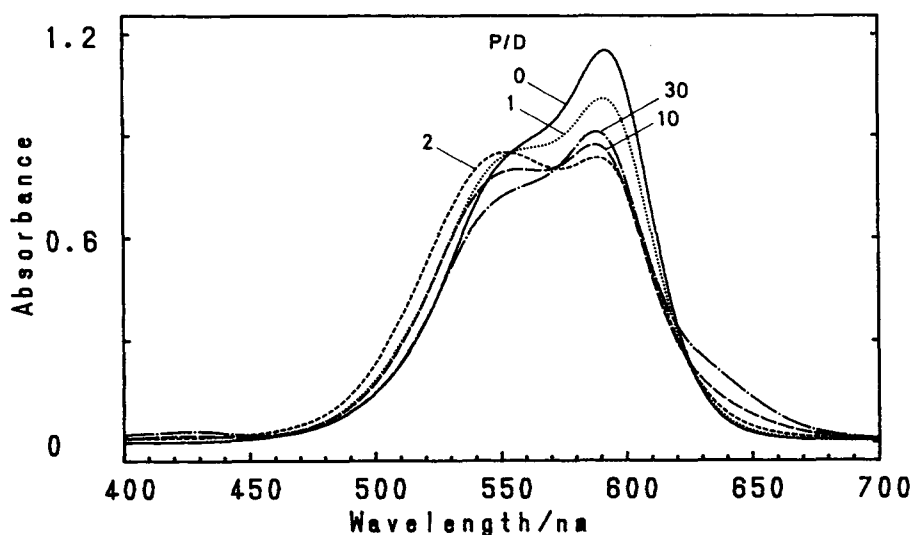


**Figure 2** Absorption spectra of MB in ethanol-water in the presence of Nafion. MB:  $10^{-5}M$ .

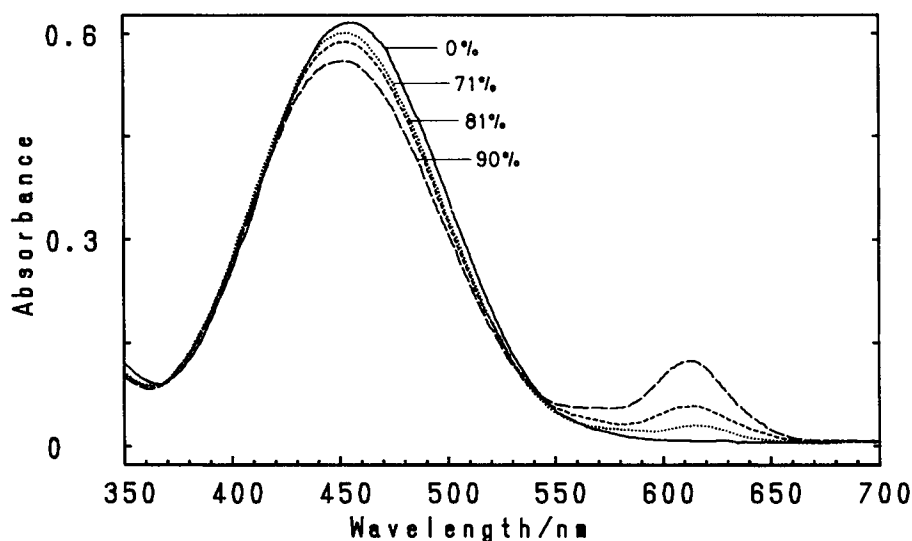
on the surface of the polyanion to allow them to interact, forming dimers and higher aggregates, and that in the presence of a large excess of the polyanion the dye molecules exist mainly in the monomer form because they are distributed over the excessive binding sites. From the above results, the stacking of the dye occurs most strongly within a few P/D values after 2 for both dyes, which is in good conformity with the results with ordinary polyanions.<sup>30,31</sup> This indicates that most of sulfonate groups of Nafion are in contact with the solution and are able to interact with the dye molecules.

It has been reported that the band for the higher aggregates of MB appears as a distinct peak in

aqueous solutions of polyanions with a polyethylene backbone, but appears only as a slight shoulder in those of polyanions with a polystyrene backbone.<sup>30</sup> The spectral trend of the latter is similar to that in the Nafion-MB system. Any band for the trimer or higher aggregates of CV was not observed with Nafion, whereas a metachromasy band near 510 nm has been observed in aqueous solutions of several linear polyanions.<sup>31</sup> Thus, it can be said that Nafion is unable to cause the strong aggregation for both dyes. It has been suggested that the flexibility of polyanions is an essential factor for the high aggregation of bound dye.<sup>30</sup> It seems that the Nafion polyelectrolyte is incapable of exerting an effective



**Figure 3** Absorption spectra of CV in ethanol-water in the presence of Nafion. CV:  $10^{-5}M$ .



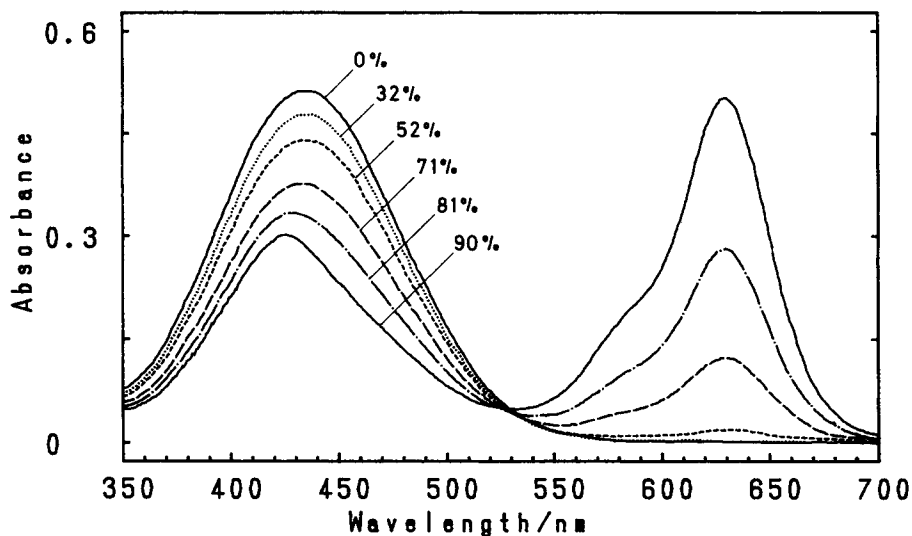
**Figure 4** Absorption spectra of a Nafion film containing MG at a concentration of  $2.9 \times 10^{-2} \text{ mol kg}^{-1}$  (dye/polymer: 0.0134 wt/wt) measured at varying RHs.

conformation change of the polymer chain because of the strong hydrophobic interaction between the fluorocarbon chains.

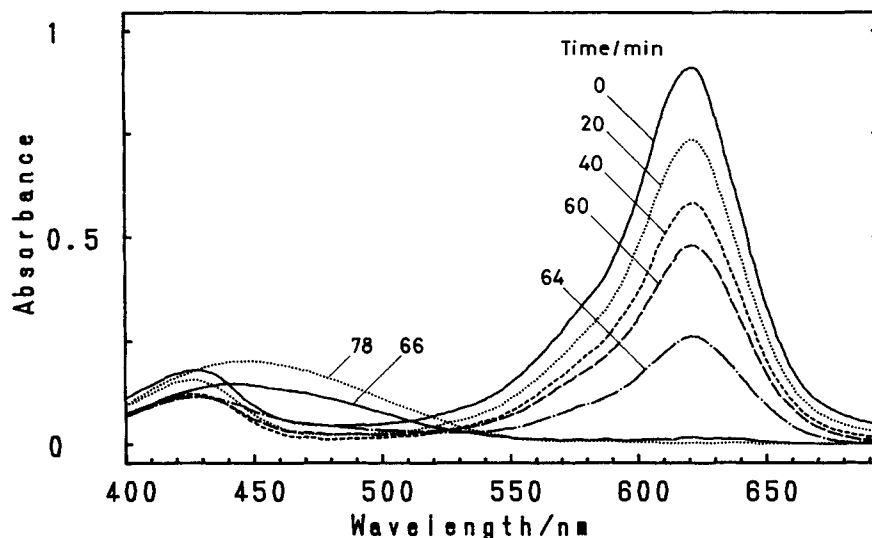
It has been suggested that the Nafion polymer in solution does not form a coil, in which the solvent-polymer contact is all along the polymer chain, but forms a particlelike micelle, in which the solvent-polymer contact is at the surface of the particle.<sup>5</sup> The effective contact of the sulfonate groups with solution and the poor ability of conformation change of the polymer chain coincide well with the micelle-like structure of the polymer.

**Characterization of Nafion Films**

Because the chemical properties of Nafion depend critically on the water content, measurements should be carried out in an environment of controlled RH. Figure 4 shows the visible absorption spectra of an MG-mixed Nafion film, which were recorded after equilibrium with air streams of different RHs. A large peak at 457 nm appears in the spectrum recorded at 0% RH. As RH increases, this peak is diminished and shifts to a shorter wavelength. A new peak develops at 614 nm at a higher RH than

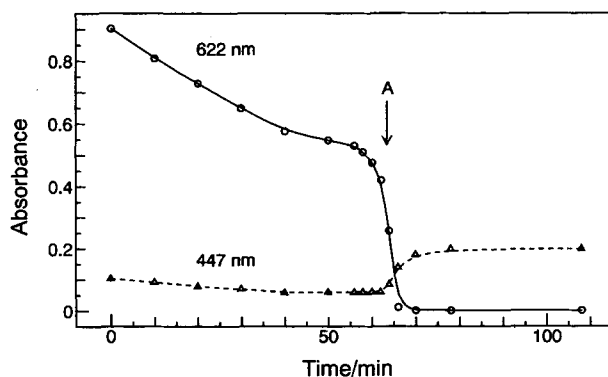


**Figure 5** Absorption spectra of a Nafion film containing CV at a concentration of  $2.9 \times 10^{-2} \text{ mol kg}^{-1}$  (dye/polymer: 0.0118 wt/wt) measured at varying RHs.



**Figure 6** Absorption spectra of a solution containing Nafion and MG measured at intervals during solvent evaporation. Initial concentration: Nafion, 1.25 wt %; MG,  $3.6 \times 10^{-4} M$  (dye/polymer: 0.0134 wt/wt).

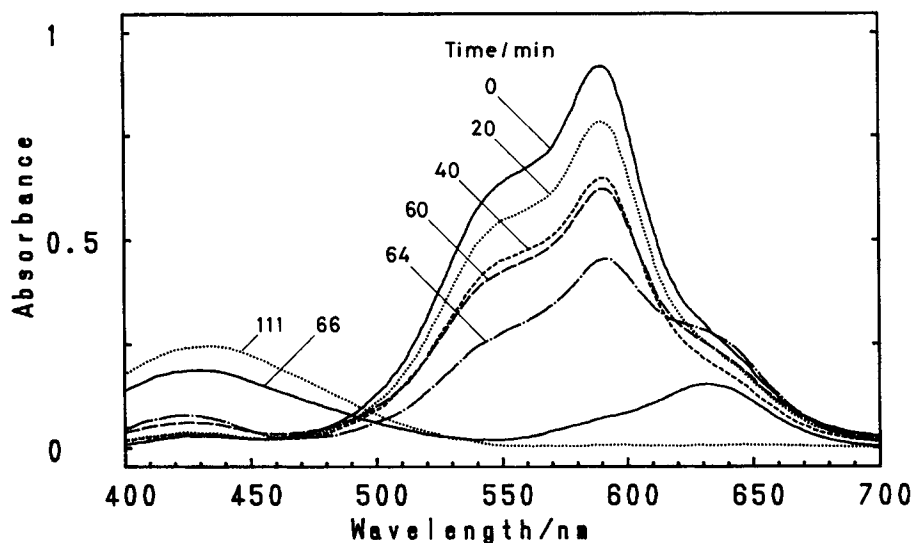
71%. The monocation  $MG^+$  is in equilibrium with the protonated dication  $MGH^{2+}$  in acidic solutions. The absorption maxima are 430 and 618 nm for  $MG^+$  and 450 nm for  $MGH^{2+}$ .<sup>37</sup> Consequently, the above spectral change is the result of the interconversion between  $MG^+$  and  $MGH^{2+}$ .  $MG^+$  is present at higher RHs than 71% but absent in the lower RH range. On the other hand,  $MGH^{2+}$  is the main species at 0% RH and decreases with increasing RH. In strongly acidic solutions, e.g., concentrated sulfuric acid, the carbonium ion  $MGH_2^{3+}$  is formed; the absorption maximum is 434 nm.<sup>38</sup> However,  $MGH_2^{3+}$  is absent even at 0% RH, taking into account its absorption maximum, which should appear at a fairly shorter wavelength than that of the observed peak.



**Figure 7** Absorbance vs. time curves during solvent evaporation for a solution containing Nafion and MG. See the caption of Figure 6.

Figure 5 shows the visible absorption spectra of a CV-mixed Nafion film, which were recorded similarly to MG. A large peak at 437 nm appears in the spectrum recorded at 0% RH. As RH increases, this peak diminishes and shifts to a shorter wavelength. A new peak develops at 631 nm at a higher RH than 52%. The monocation  $CV^+$  is in equilibrium with the protonated dication  $CVH^{2+}$  and doubly protonated trication  $CVH_2^{3+}$  in acidic solutions. The absorption maxima in aqueous solutions are 590 nm for  $CV^+$ , 635 and 420 nm for  $CVH^{2+}$ , and 434 nm for  $CVH_2^{3+}$ .<sup>39</sup> Consequently, the above spectral change is the result of the interconversion between  $CVH^{2+}$  and  $CVH_2^{3+}$ .  $CVH_2^{3+}$  monotonously decreases with increasing RH. In contrast,  $CVH^{2+}$  is absent in the low RH region but is formed above 52% RH.  $CV^+$  is absent at 90% RH in the Nafion film, judging from the wavelength of its absorption maximum, which is fairly shorter than that of the observed peak.

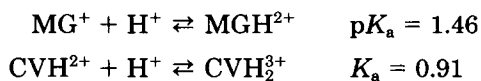
The RH dependence of the absorption spectra of Nafion films containing MG or CV is caused by the interconversion between different cationic forms of the dye. It has been proposed that ionizable groups and adsorbed water form clusters in Nafion films.<sup>9</sup> It has been reported that the number of water molecules contained in the cluster is highly dependent on the amount of water present in the film.<sup>10</sup> Because most of sulfonate groups in the cluster probably dissociate at a low water content, the  $H^+$ -ion concentration in the cluster increases with decreasing water content. Since the water content of Nafion films in-



**Figure 8** Absorption spectra of a solution containing Nafion and CV measured at intervals during solvent evaporation. Initial concentration: Nafion, 1.25 wt %; CV,  $3.6 \times 10^{-4} M$  (dye/polymer: 0.0118 wt/wt).

creases with RH, it is concluded that the variation in water content changes the  $H^+$ -ion concentration in the cluster and results in the protonation and deprotonation of the dye. Similar results have been reported for MB<sup>16,40</sup> and rhodamine 6G<sup>18</sup> in Nafion film.

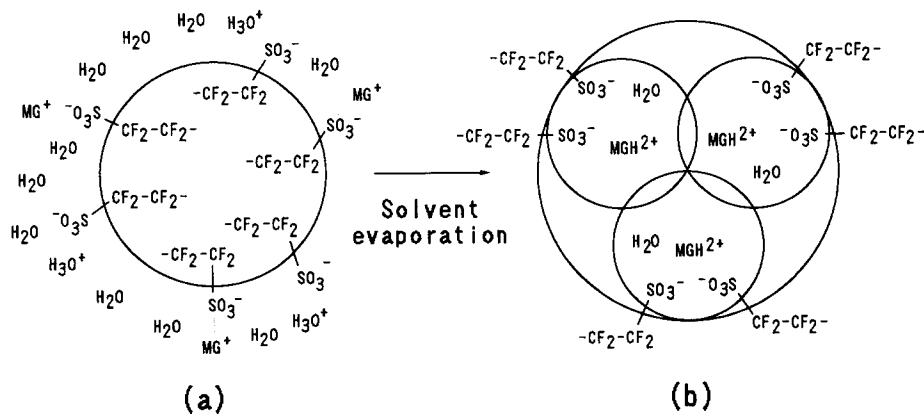
This interpretation for the interconversion between cationic forms of the dyes permits evaluation of the acidity function,  $H_0$ , of Nafion films at a few RHs. The equilibrium constants of the protonation have been estimated as shown below<sup>37,39</sup>:



The  $H_0$  value of Nafion is evaluated from these constants to be fairly lower than 0.91 at 0% RH and between 1.46 and 0.91 at 90% RH. It has been reported that the acidity in Nafion film is very strong in the completely dry state,<sup>12</sup> but the absence of the carbonium ion of MG at 0% RH described above suggests that the acidity in Nafion film is not so strong at 0% RH. It seems that Nafion allowed to stand under a dry air stream is not absolutely dry but contains some water.

#### Observation of the Casting Process

Figure 6 shows the absorption spectra of a Nafion solution containing MG, which were measured in



**Figure 9** Schematic view of phase inversion upon evaporating the solvent from a solution containing Nafion and MG.

the process of casting. A peak at 622 nm dramatically decreases with time. A peak at 430 nm also decreases with time up to about 65 min and then a new peak at 447 nm appears. The peaks at 622 and 430 nm are characteristic of  $MG^+$ . The peak at 447 nm is due to  $MGH^{2+}$ . As shown in Figure 7, the absorbance at 622 nm decreases slowly with time up to about 60 min (point A) and then decreases abruptly and becomes nearly 0 at about 70 min. On the other hand, the absorbance at 447 nm decreases slowly with time up to point A and then begins to increase. Point A probably corresponds to the point when almost all solvent is evaporated from the solution. It is clear that  $MG^+$  begins to change to  $MGH^{2+}$  right after point A. The diminution of the peak due to  $MG^+$  before point A is not due to the consumption of  $MG^+$  but is probably the result of dye concentration on the micellelike particles of Nafion. It is concluded from these facts that  $MG^+$  is changed to  $MGH^{2+}$  after the solution is dried almost completely.

Similar changes can be observed in the absorption spectra of a Nafion solution containing CV, as shown in Figure 8. A peak at 590 nm and a shoulder at about 550 nm, which correspond to  $CV^+$ , decrease with time. As soon as these peaks fade away, a shoulder at 630 nm becomes pronounced. Concomitantly, a peak at 436 nm begins to increase. The peak at 630 nm disappears soon after its growth. The peaks at 630 and 436 nm correspond to  $CVH^{2+}$  and  $CVH_2^{3+}$ , respectively. The peak due to  $CV^+$  diminishes slowly with time up to a point (point A) corresponding to the approximate completion of solvent evaporation and then decreases rapidly, in a similar manner to  $MG$ . The diminution of this peak before point A is probably because of the concentration of  $CV^+$  on the Nafion particles. Thus, it is concluded that  $CV^+$  changes to  $CVH_2^{3+}$  via  $CVH^{2+}$  after most of the solvent is evaporated from the solution.

Because the change of the cationic state of the dye results from change in the  $H^+$ -ion concentration, as concluded in the previous section, it is expected from the above results that a large change in  $H^+$ -ion concentration occurs in the process of casting. Until most of solvent is evaporated from the solution, the  $H^+$ -ion concentration around the dye molecules is not so high but the monovalent cation is not protonated. On complete drying, however, the  $H^+$ -ion concentration suddenly increases so that the divalent and trivalent cations are produced.

When the solution is dried up to a point, the fluorocarbon chain material dispersed in the hydrophilic phase is converted to a continuous phase,

i.e., the phase inversion occurs (Fig. 9). Reconstituted films dried at room temperature have ionic clusters, although the fluorocarbon phase is not completely continuous.<sup>6</sup> The ionic clusters formed in these films are smaller in size<sup>6</sup> but are expected to have the same function as those present in the original film.

In solution, the dye molecules are bound to the surface of the micellar particles of the polymer. The sulfonate groups of Nafion extend out into the solution and are associating counterions, i.e.,  $H_3O^+$  and the cationic dye molecule. As the solvent is evaporated, a large particle is formed from small particles and grows more and more, which results in the concentration of the dye. Before phase inversion, the sulfonate groups of Nafion contact the solution and the dye molecules bound to the Nafion particle are subject to the  $H^+$ -ion concentration in the bulk solution [Fig. 9(a)]. When the phase inversion occurs, the associated counterions are incorporated into the ionic cluster but a large fraction of solvent molecules are excluded from the ionic cluster. The sulfonate groups and their counterions form clusters in a hydrophobic matrix comprising the fluorocarbon chains of the polymer. The dye molecules are subject to the  $H^+$ -ion concentration in the cluster, which is much higher than that in the bulk solution [Fig. 9(b)]. Thus, it is concluded that the phase inversion causes the sudden change of the cationic form of the dye from the monovalent to the divalent or trivalent one.

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