The Mechanism of Dyeing and Phase Structure of Nylon 6 Fiber by Broad-Line ¹H NMR Spectroanalysis

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The dyeing process of nylon 6 fiber is studied by a recently developed refined broad-line ¹H nmr spectroanalysis. The spectra for samples dyed to different degrees were decomposed into three components which differ in line-width: broad, medium, and narrow, in connection to the multi-phase structure of samples. In this three-component analysis major influence of dyeing was recognized in the medium and narrow components which correspond to the noncrystalline entities in the structure. It is confirmed that the dyeing takes place in the noncrystalline regions, mostly in a noncrystalline region which is associated with a higher conformational freedom of molecules and undergoes a micro-Brownian segmental motion of molecules at higher temperatures. The effects of dyeing on the noncrystalline components differ in a wide range, depending on the kinds of dyes used, so that some dyes heighten the molecular mobility of the component but some lower.

KEY WORDS: Broad-line spectrum / Molecular mobility of noncrystalline material / Three-component analysis of spectrum /

INTRODUCTION

The dyeing process of fibers has been extensively studied but the detailed mechanism still remains obscure. For example, nobody can answer for such a simple question as to how and where the molecules of dyes are absorbed on fibers. In general, the x-ray diffraction patterns of fibers do not change appreciably by dyeing.[1,2] Hence, dyes are assumed to be absorbed only in the noncrystalline region of fibers. On the other hand, the increase of dye-accessibility is sometimes recognized when synthetic fibers such as nylon 6 fiber are annealed at high temperatures while the degree of crystallinity being heightened or held constant. Accordingly, dyes could not be assumed to be absorbed uniformly in the whole noncrystalline region. The noncrystalline material in semicrystalline polymers such as fibers does not comprise a homogeneous phase but has a wide distribution in the conformation and mobility of molecules.[3~8] The lack of universal consensus on the mechanism of dyeing will have been brought about by the failure of proper consideration of this fact. The mechanism of dyeing should be studied in terms of the detailed structure of noncrystalline material.

Some authors of this paper recently showed that a refined analysis of broad–line ¹H nmr spectra for linear polyethylene could impart us detailed information of

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the multi-phase structure of samples, particularly in regard to the noncrystalline component, depending on the mode of crystallization and the molecular weight.[4~8] The spectra were decomposed into three components: broad, medium, and narrow. These components were considered to be contributions from protons belonging to the crystalline and noncrystalline components with different molecular motions, respectively. Examining the relative mass ratios of these components and parameters which characterize each component, detailed information of the multi-phase structure of samples was obtained. In this paper we will apply a similar spectroanalysis to nylon 6 fiber in order to inquire the change of the multiphase structure of samples through dyeing with various dyestuffs.

<center>EXPERIMENTAL</center>

1. Samples and Dyeing

Nylon 6 fiber 110–30–S–100 supplied from Toray INC was scored with a nonionic surface active agent of a concentration of 2 g/l at room temperature, washed with distilled water and dried in air. Each sample was dyed at 98°C for 1hr in a dyeing bath of a dye and assistant agent, equipped a reflux condenser. Here, a cage of stainless steel mesh containing the sample was immersed in the bath and vibrated vertically by 2 cm at a frequency of 50 Hz.

After dyeing, the fiber was washed with distilled water and the degree of dyeing was determined by spectrophotometries for the dyeing bath remained and the washing water. The degree of dyeing was expressed by the weight of dye absorbed on 100 g of the fiber (owf%, % on the weight of fiber). The degree of dyeing was

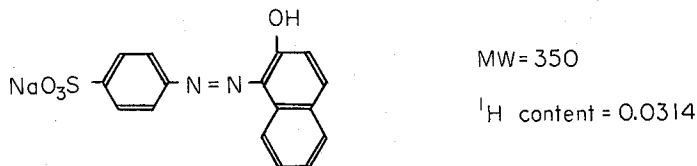<center>Table I. Samples and Conditions for Dyeing</center>

Sample	Degree of Dyeing		Dyeing assistant
	owf %[a]	m mole[b]	
A: Orange II			
A – 1	0	0	Acetic acid (2%)
A – 2	2.12	6.06	
A – 3	9.01	25.74	
B: C.I. Acid Red 14			
B – 1	2.23	4.44	Acetic acid (2%)
B – 2	3.22	6.41	
C: Neolan Red REG			
C – 1	0	0	Sulfuric acid (5%)
C – 2	3.67	6.45	Glauber salt (5%)
C – 3	5.47	9.61	
D: Celliton Fast Blue B			
D – 1	0	0	Sodium
D – 2	3.25	12.22	Laurylsulfate
D – 3	8.41	31.62	

a) weight percents of dye absorbed on fiber (based on the weight of dry fiber).
b) m mol of dye absorbed on 100 g of fiber.

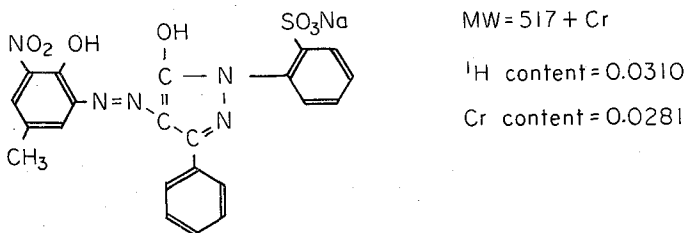Table II. Characterizations and Chemical Structure of Dyes Used

(A) Orange II (monofunctional acid dye)

MW = 350

^{1}H content = 0.0314

(B) C.I. Acid Red 14 (bifunctional acid dye)

MW = 502

^{1}H content = 0.024

(C) Neolan Red REG (metal complex dye)

MW = 517 + Cr

^{1}H content = 0.0310

Cr content = 0.0281

(D) Celliton Fast Blue 3 (disperse dye)

MW = 266

^{1}H content = 0.053

controlled by changing the concentration of dye and dyeing assistant agent. The dyes and assistant agents used are listed in Table I with owf%. The chemical structures of dyes used are shown in Table II.

2. NMR Spectroanalysis

The first derivative nmr spectra were obtained over a wide range of temperatures for the fiber samples, before and after dyeing, randomly packed in the absolutely dried state into a glass tube 18-mm in diameter with a JNM-PW-60 Spectrometer (JEOL Ltd.). The magnetic field slowly swept was modulated at 35 Hz and an amplitude of 0.3~0.5 G under a high frequency electromagnetic wave of 60 MHz. The line-width and the shape of the spectra thus obtained were first examined. Here the line-width is defined to be the field difference between the two extremes (maximum

and minimum) in spectra. Furthermore, the spectra were analyzed by a technique developed by Bergmann and Nawotki[9] and some of the authors,[4,5] decomposing into three components; broad, medium, and narrow. These components were considered to be contribution from protons belonging to the crystalline component including rigid glassy noncrystalline component, noncrystalline material associated with a local segmental motion of molecules, and noncrystalline component with micro-Brownian segmental motion of molecules, respectively. The theoretical spectrum can be expressed in three terms as a function of field intensity H.

$$y_{cal}(H) = w_b y_b(H, \Delta H_b) + w_m y_m(H, \beta_{mg}, \beta_{ml}) + w_n y_n(H, \beta_n)$$

with $\quad w_b + w_m + w_n = 1$ $\hfill (1)$

Here, the field intensity H is expressed by the deviation from the resonance center for convenience. y_b, y_m, and y_n are the elementary spectra for the broad, medium, and narrow components, respectively. w_b, w_m, and w_n designate the respective relative mass fractions. The parameters ΔH_b, β_{mg}, β_{ml}, and β_n designate the line-width and shape of the respective elementary spectra. All of the elementary spectra are normalized as

$$\int_{-\infty}^{\infty} \int_{-\infty}^{H} y_i dH = 2, \quad i = b, m, \text{ or } n \hfill (2)$$

The y_b was obtained by changing the line-width of the spectrum at $-150°C$ for a nylon 6 fiber with a very high degree of crystallinity but keeping the shape unchanged. Here, the sample with the high crystallinity was obtained from the fiber sample by removing major part of the amorphous content by immersing in 1N HCl aqueous solution at 95°C for 27 hr.

The y_n was taken as a Lorentzian, neglecting the effects of the amplitude of modulation of the main magnetic field,*

$$y_n(H, \beta_n) = 4\pi^{-1} \beta_n^{-3} H / (1 + \beta_n^{-2} H^2)^2 \hfill (3)$$

The y_m was taken as the product of Gaussian and Lorentzian distribution functions in integrated form,

$$y_m(H, \beta_{mg}, \beta_{ml}) = N \frac{\partial}{\partial H} [(\exp(-H^2/2\beta_{mg}^2)) \beta_{ml}^2 / (\beta_{ml}^2 + H^2)] \hfill (4)$$

Here, N is the normalization factor and β_{mg} and β_{ml} designate the broadness of the Gaussian and Lorentzian components, respectively.

With use of the elementary spectra cited above the parameters in Eq. (1) were determined with a Facom 230-48 computer according to the so-called simplex method so as to minimize the sum of squares of the difference between the observed and calculated spectra over the full range of H;

$$\Phi = \sum_H [y_{obs}(H) - A y_{cal}(H)]^2 \hfill (5)$$

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* Because of the smaller line-width of this component, the effect of the amplitude of modulation cannot generally be neglected. The distortion of the Lorentzian distribution function due to the amplitude of modulation was discussed in detail elsewhere, and a computational technique to take account of this effect was established.[4,5] However, since most of this work had been carried out before the establishment of the technique, the effect of the modulation amplitude is not taken account here. Nevertheless, since the amplitude of modulation used was relatively small such as 0.3~0.5 G, the results and conclusion obtained in this work will be not altered so much, if considered the effects.

Here A is a parameter which adjusts the amplitude of the spectrometry.

Thus, according to the procedure mentioned above, all spectra obtained were decomposed into three components. The line-width and second moment as well as the parameters which characterize each component were examined in connection with the phase structure of samples. Here, the second moment $\langle \Delta H_2^2 \rangle$ is defined to be the average of the squares of the deviation of the field from the center of the resonance H_0,

$$\langle \Delta H_2^2 \rangle = \langle (H - H_0^2) \rangle \tag{6}$$

RESULTS AND DISCUSSION

The change of spectrum and the line narrowing with dyeing

Figure 1 shows the spectra at different temperatures for the original and dyed samples with a mono-functional acid dye Orange II. At a temperature of 50°C below the glass-rubber transition temperature T_g of the polymer, there is recognized
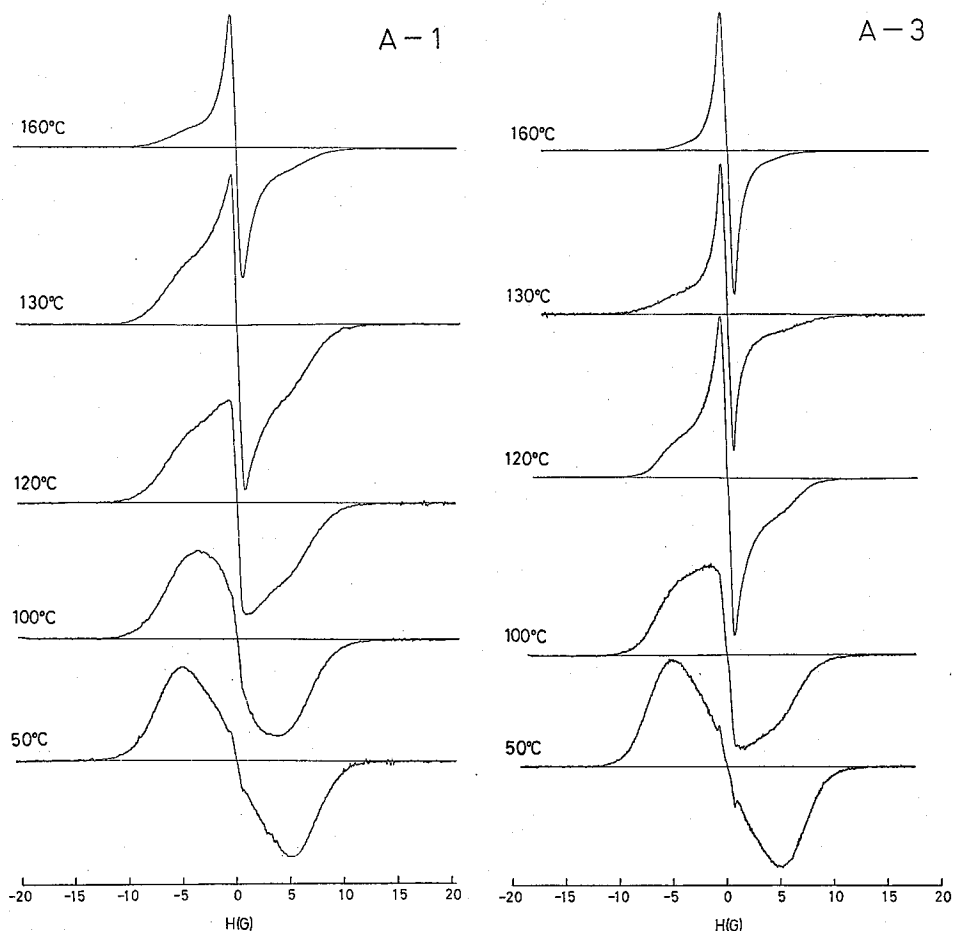

Fig. 1. Broad-line spectra at different temperatures for samples dyed with Orange II. A-1: undyed original sample, A-3: sample dyed to a dyeing degree of 9.01 owf%.
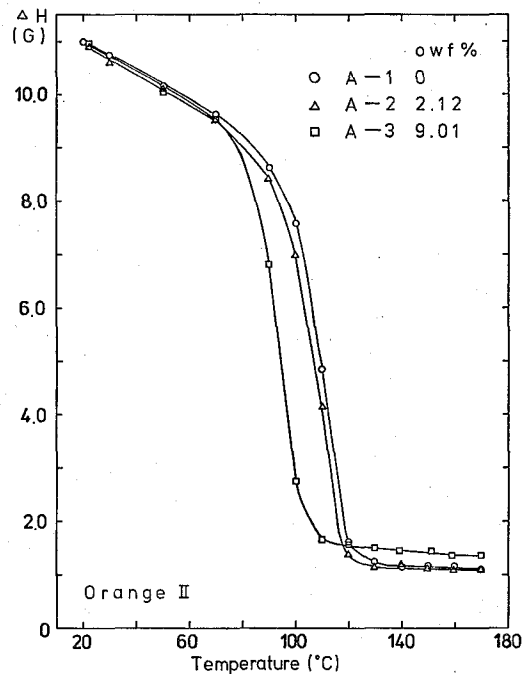
(322)

Fig. 2. Line-width of spectrum against temperature for samples dyed with Orange II to different degrees. A-1: ○, original undyed sample. A-2: △, 2.12 owf%. A-3: □, 9.01 owf%.
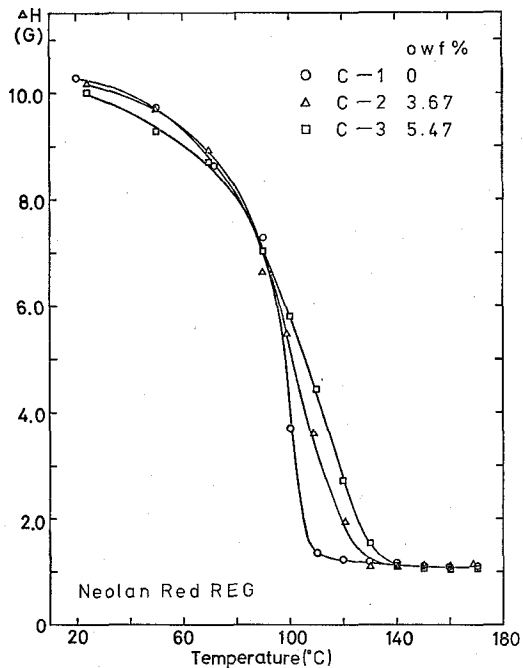

Fig. 3. Line-width of spectrum against temperature for samples dyed with Neolan Red REG. C-1: ○, original undyed sample. C-2: △, 3.67 owf%. C-3: □, 5.47 owf%.

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no appreciable difference in spectra between the original and dyed samples. The spectra for the both samples are very broad and alike, indicating that all components are in the rigid state. However, as the temperature rises beyond 100°C, the spectrum for the dyed sample becomes narrower than the original sample. This effect of dyeing is distinctly recognized in Fig. 2, where the line-width of spectra ΔH for samples dyed to different degrees is plotted against temperature. It is seen that the temperature at which the narrowing of spectrum becomes pronounced shifts to lower temperatures with increasing amount of dyestuff absorbed. Accordingly, it is concluded that the glass transition temperature of the fiber sample is lowered by dyeing with this dye. Similar lowering of T_g was recognized for samples dyed with bifunctional acid dyes such as C.I. Acid Red 14.

On the other hand, when dyed with other kinds of dyes the effect on the spectrum is somewhat different. In Fig. 3, the line-width of spectrum for samples dyed with a metal complex dyes Neolan Red REG is plotted against temperature. As can be seen in the figure, in this case the temperature at which the narrowing of spectrum begins is not changed so much with dyeing, but the narrowing of spectrum with increasing degree of dyeing becomes slower and the temperature at which the narrowing terminates becomes higher. The narrowing of spectrum for the sample with an owf % of 5.47 terminates at 140°C about 30° higher than for the original sample.

In Fig. 4, the temperature dependency of the line-width is shown for samples dyed with a disperse dye Celliton Fast Blue B. In this case the line-width over the
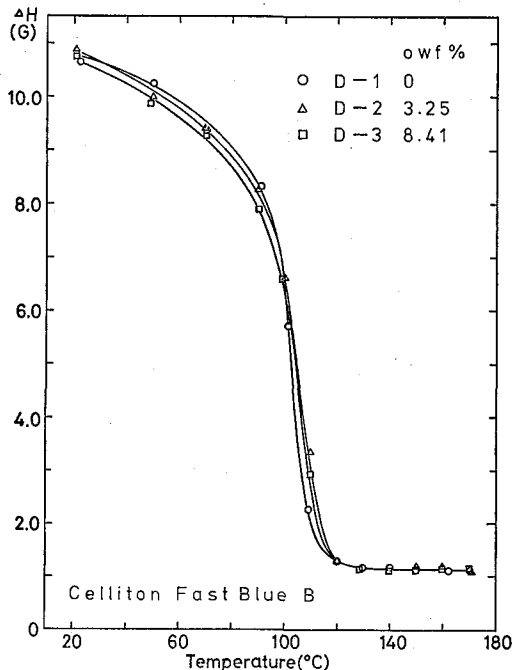

Fig. 4. Line-width of spectrum against temperature for samples dyed with Celliton Fast Blue B. D-1: ○, original undyed sample. D-2: △, 3.25 owf%. D-3: □, 8.41 owf%.

wide range of temperatures is hardly altered with dyeing. Only recognized is that the ΔH-temperature curve shifts slightly to higher temperatures on the contrary to the case of other dyes.

The results cited above indicate the change of the phase structure of the nylon 6 fiber upon dyeing, depending strongly on the kind of dyes. We next inquire the change of the phase structure accompanying dyeing with different kinds of dyes in more detail with use of the three-component analysis of spectrum in connection with the change of each component of the spectrum.

Three-component analysis of spectrum for the dyed fibers

The broad, medium, and narrow components of spectra are apt to be considered as contributions from the crystalline component, noncrystalline materials with a restricted segmental motion of molecules, and noncrystalline component with
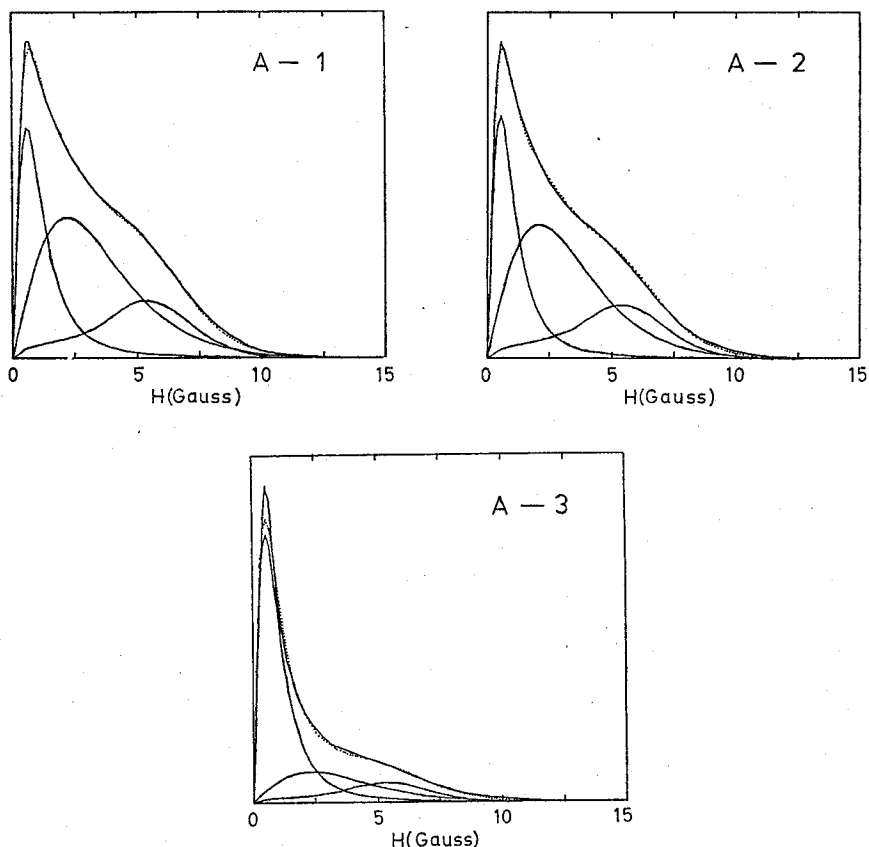

Fig. 5. Three-component analyses of spectra at 130°C for samples A-1, A-2, and A-3. The description of the samples is given in Table I and in the legend for Fig. 2.
The decomposed components are the narrow, medium, and broad components, respectively from the left. The dotted line which is mostly superposed on the experimentally observed spectrum indicates the composite curve of the three components.

(325)

micro-Brownian segmental motion of molecules, respectively. At low temperatures, however, the broad component also comprises a contribution from a noncrystalline component in the rigid glassy state in addition to contribution from the crystalline component. Accordingly, correspondence of the three components of spectra to the morphological phase structure of samples is not simple. However, as previously reported,[8] at temperatures between 120 and 160°C the broad component of spectrum for nylon 6 fibers well corresponds to the morphological crystalline material in the structure, and the noncrystalline material contributes either in the medium or narrow component. In a lamellar crystalline structure of polymers such as linear polyethylene, the medium and narrow components at room temperature represent the noncrystalline components in the interfacial and interzonal regions in the structure, involving only local segmental motion and micro-Brownian segmental motion, respectively.[5] In the fiber structure, however, the correspondence of the medium and narrow components to the morphological structure is obscure. Nevertheless, it is believed that in this range of temperature the medium component corresponds to a noncrystalline material, of which molecular conformational freedom is severely restricted by the presence of fibrilar crystallites. On the other hand, the narrow component is thought to correspond to a noncrystalline material, involving micro–Brownian segmental motion of molecules. Actually at these temperatures the mass fraction of the broad component is in good accordance with the degree of crystallinity obtained from other techniques such as x-ray diffraction technique. Therefore, we focus attention to the three-component analysis of spectra carried out at 130°C for the dyed fibers.

Figure 5 demonstrates the three-component analysis of spectra at 130°C for samples dyed with Orange II to different degrees. The dotted line and the solid line, which represent the composite curve of the three components decomposed and the experimentally observed spectrum, respectively, are well coincident with each other for all samples, showing rationality of the analysis, independent of dyeing. Such three-component analysis was satisfactorily carried out for all samples dyed with different dyes.

The results of three-component analysis at 130°C for samples dyed with Orange II, Neolan Red REG and Celliton Fast Blue B are summarized in Figs. 6 and 7. Here, w_b, w_m, w_n and ΔH_b, ΔH_m, ΔH_n, and $\langle \Delta H_2{}^2 \rangle_m$ are plotted against the amount of dye absorbed (owf %). Here, the second moment of medium component $\langle \Delta H_2{}^2 \rangle_m$ is considered in addition to ΔH_m, because the elementary line of this component contains two parameters (β_{ml} and β_{mg}) so that only the line-width can not characterize the line shape.

It is first seen that both of w_b and ΔH_b (the mass fraction and the line-width of the broad component) do not change with dyeing. This is in good consistence with the fact that the x-ray diffraction pattern of the fiber is not changed with dyeing, indicating that dyes do not penetrate in the crystalline region upon dyeing under usual conditions. A very small lowering of the line-width is recognized for samples dyed with a metal complex dye Neolan Red REG. However, this will not be due to the penetration of the dyes into the crystalline region but due to a lowering of
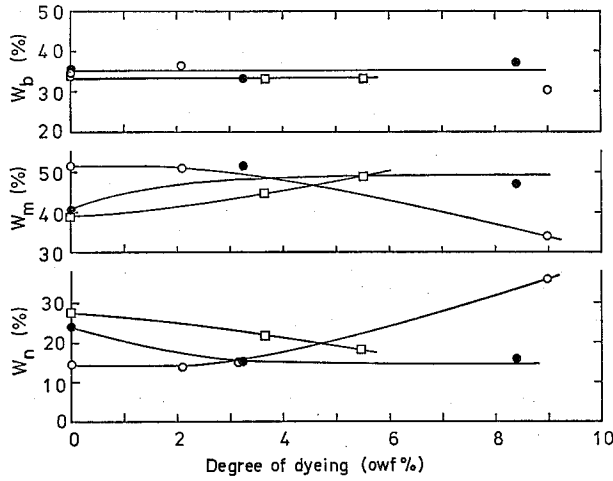
Fig. 6. Mass fractions of the three components for spectra at 130°C against the degree of dyeing for samples dyed with different dyes. Open circles, squares, and closed circles indicate data for samples dyed with Orange II, Neolan Red REG and Celliton Fast Blue B, respectively.
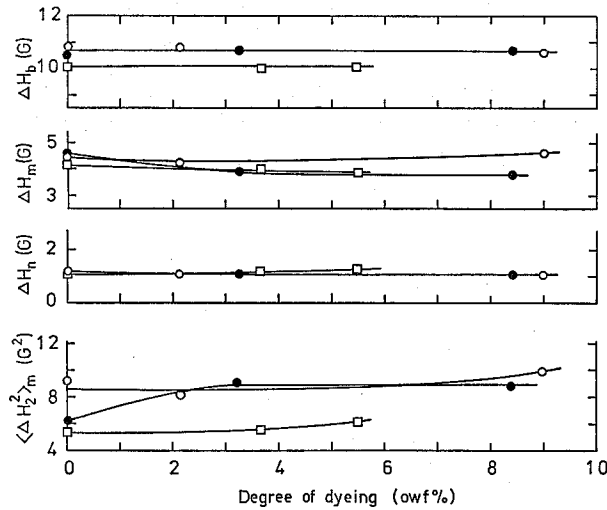

Fig. 7. The line-widths and second moment for three components for spectra at 130°C against the degree of dyeing for samples dyed with different dyes. The symbols for data are the same as in Fig. 6.

crystallinity caused by the rather severe condition for dyeing, where the sample has been treated at 95°C in the dyeing bath including 5% sulfuric acid as a dyeing assistant agent.

On the other hand, the mass fractions and molecular mobilities for the two noncrystalline components are greatly altered by dyeing, depending on the kind of dyes as well as the degree of dyeing. When dyed with Orange II, both of the medium

and narrow components do not change appreciably until a dyeing degree of 2 owf% but with further dyeing the mass fraction of the medium component decreases whereas the narrow component increases. This result implies that this dye acts as a plasticizer and heightens the molecular mobility of the noncrystalline entities, as a result of breaking of hydrogen bondings in the polymer through reactions with amino end-groups or amide groups.

On the contrary, when dyed with the metal complex dye, the medium component increases whereas the narrow component decreases with increasing degree of dyeing. The slight increase of $\langle \Delta H_2{}^2 \rangle_m$ as well as ΔH_n is also recognized with increasing degree of dyeing, implying lowering of molecular mobility in the noncrystalline regions. These results may be due to the fact that this metal complex dye is not only an acid dye but it has a functional group which could form a coordinate bond with the polymer molecules.

Similar increasing of the medium component as well as decreasing of the narrow component are also recognized with increasing degree of dyeing when dyed with the disperse dye. This result suggests that the disperse dye not only acts as a plasticizer but the mode of dyeing is rather complicated as assumed sometimes[10] that the dye molecules react with amide groups in the molecules of the polymer forming hydrogen bonding.

CONCLUDING REMARK

In this paper we have inquired the change of the multiphase structure of nylon 6 fiber with dyeing by various kinds of dyes with use of a recently developed nmr spectroanalysis. It has been found that the change of the phase structure differs in a wide range, depending on the kinds of dyes used. The mechanism of dyeing is very complicated and many problems are remained still unsolved. Nevertheless, the refined nmr analysis technique used in this work has proven to be very useful to elucidate the mechanism of dyeing. We expect further studies along this line by many investigators.

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