

# Dyeing Behavior of Polypropylene Blend Fiber. I. Kinetic and Thermodynamic Parameters of the Dyeing System

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## SYNOPSIS

An acid dyeable polypropylene fiber has been prepared by admixing an additive to the polymer prior to extrusion. An additive has been synthesized by attaching long alkyl chains together with substituents carrying basic nitrogen to a rigid polymer backbone. The dyeing behavior of the physically modified fiber has been characterized by kinetic and thermodynamic parameters. A diffusion coefficient of the order of  $10^{-11}$  m<sup>2</sup>/s was found, indicating very fast diffusion of the dye molecules within the fiber. The measured thermodynamic parameters provide an insight into molecular interactions that are of prevailing electrostatic nature. The results have been explained in terms of the binding of dye molecules to the basic dye sites supplied to the fiber by an additive. The change of dyeability of modified fiber at about 70°C is attributable to the glass–rubber transition of the additive. From among the two models of diffusion considered, the pore model and the free volume model, the first one seems to be dominant. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

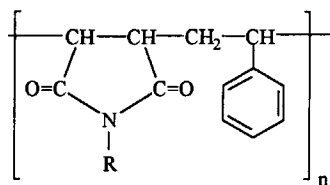
The reasons why polypropylene cannot be dyed in the bath are well known—high crystallinity and apolar aliphatic structure, which does not contain any reactive site in the molecule. The basic nitrogen additives offer an attractive means of modifying the polymer. In spite of extensive research efforts of many fiber-producing companies focused on developing an acid dyeable polypropylene fiber, no truly commercial product is available on the market at present. Journals only give a few scattered data about dyeing behavior of these fibers.<sup>1–3</sup> The cationic character of additive being transferred to the whole fiber enables the dyeability with anionic dyestuffs. Anionic dyestuffs involve established and broadened palettes of acid, reactive, and various groups of pre-metallized dyes. An attractive possibility consists in using dyes and dyeing techniques commonly employed for dyeing wool and nylon.

In our previous articles we reported physical properties of fibers and buildup of color on PP-fiber with increasing concentration of basic polymer (styrene–amine resin—Polymer A, see Fig. 1).<sup>4,5</sup> The modification has a certain unfavorable effect on spinability. Nevertheless, the worsening of spinability is not essential with the denier for which the dyeable fibers are designed: yarn for blending with wool and fibers for carpet trade. The additive affects neither the thermostability nor the light stability of the polypropylene, and it migrates from the fibers during washing neither in alkaline nor in acidic aqueous baths. The modified fibers—as compared with the nonmodified ones—show a decreased tenacity and an increased elongation, a changed sign of the electrostatic charge, and a decreased thermal absorptivity of knitted fabric.

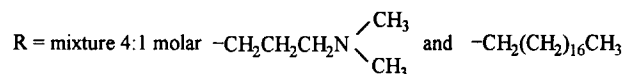
The equilibrium moisture on the fiber remains unchanged at a very low level. The wide-angle X-ray scattering showed a mild decrease in crystallinity and in the size of crystallites. The measurements of kinetics of isothermal crystallization by means of the small-angle light scattering method have shown that the additive dispersed in the polypropylene speeds up the crystallization. The additive particles

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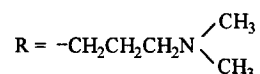
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Polymer A (partially compatible)



Polymer B (incompatible)



**Figure 1** Composition of basic polymeric additives.

cannot be seen in the fiber structure by means of the peeling technique of scanning electron microscopy: they coalesce with the polypropylene microfibrils. After dyeing the fiber with an acid dye, the particles of additive are visible; they are elongated in the direction of the fiber axis.<sup>5</sup> The polypropylene matrix remains undyed. The additive particles loosen the structure. The additive prevents an orientation of noncrystalline regions, because the birefringence decreases in the modified fiber but the orientation of crystalline regions does not change much. The technique of transmission electron microscopy of ultra-thin cross-sections shows the morphology of the additive in fiber as a transition state between the network-in-matrix type and the particles-in-matrix type. This microchannel structure indicates a partial compatibility of the polymer blend. A hypothesis has been proposed concerning the diffusion of acid ionized dye into the center of fiber through channels formed by interconnected additive particles. The dye adsorption does not increase proportionally with the concentration of additive in fiber. Beginning from a certain concentration, the dyeability increases dramatically. The fibers with 2 and 4% additive show a bad accessibility of dye sites that is connected with the ring-type dyeing of the fibers. The ring dyeing was detected by photoacoustic spectroscopy.<sup>4</sup> The fibers with 6 and 8% additive are uniformly colored through the whole cross-section.

The requirements for basic nitrogen polymeric additives for polypropylene to make it dyeable were discussed in detail by M. Ahmed<sup>3</sup> and M. Farber.<sup>6</sup> Some of these requirements are summarized below: (1) stability (thermal, oxidation); (2) compatibility;

(3) thermoplasticity; (4) basicity and polarity; (5) nonextractability; (6) noncrystallinity; (7) nontoxicity; (8) low cost; and (9) low doping.

The first three criteria are important from the point of view of processing polypropylene into the fiber as the physical mixture of additive with polypropylene being melted must get free flowing dispersion. Thermal instability can lead to crosslinking, gas formation, or discoloration, all of which are highly undesirable in fiber spinning.

The second three criteria must be satisfied to obtain fibers with high dyeing efficiency. A suitable additive should be amorphous in nature with its glass temperature below dyeing temperature to achieve adequate color yield. At the same time, the additive must be capable of withstanding extraction from fiber under scouring and dyeing conditions. To provide the preferential mass transfer of the dye from the dye bath to the fiber, the additive must contain adequate amounts of basic nitrogen and other polar groups. In this lies the heart of matter. For the maximum dyeability we wish to have the basicity high. However, a high basicity tends to produce incompatibility and poor dispersibility in a nonpolar polymer such as polypropylene. Higher amounts of the incompatible additive will act as filler and impair the physical properties of the fiber. Combination of higher polarity and lower molecular weight promising an improved compatibility and dyeability or lower additive doping can end in leachability. Compatibility, although not identical with dispersibility, appears to be parallel with it. A fine dispersion of the dye receptor in the fiber is necessary in order to have a fiber with good physical properties that can be processed at high efficiencies and dye well. A compromise in several properties must be obtained. Balancing of the polar hydrophilic basic groups with nonpolar moieties is a primary way to make an acceptable additive. Considering a perspective candidate for additive from the point of commercialization the last three requirements, especially interrelation cost doping, are important.

All possible polymeric compounds as additives for PP fibers are thought and claimed in patent literature. One of them was N-(3-dimethylaminopropyl)maleimide styrene copolymer.<sup>7</sup> The configuration and molecular relaxation of an the homologous series based on N-substituted maleimide styrene copolymers were studied by R. Cubbon<sup>8</sup> and H. Block et al.<sup>9</sup> A thermal instability of these copolymers due to their rigid structure was found above 270°C. The x-ray spectra indicate that all polymers are amorphous in nature and that maleimide units form 3<sub>1</sub> helix. N-Substituents are on outer side of the back-

bone chains in the direction of the planes perpendicular to helix axis. Basic nitrogen atoms in 3-(dimethylaminopropyl) substituents, thus, are well accessible for diffusing molecules of dyes. Increase in the length of the side chain will result in a large free volume, a reduced packing density, and, thus, reduced steric hindrance to segment mobility. This kind of internal plasticization is characterized by a lower activation energy of the segmental motion and lowers the glass transition temperature. Attaching long chain hydrocarbon groups on polymer backbone offers a convenient procedure for improving compatibility of basic polymers with polypropylene. Polymers carrying polar groups together with high alkyl substituents exhibit the properties of a polymer surfactant. Uniformity of dispersion in polypropylene phase can be further improved using a low molecular emulsifier such as sodium stearate, glycerol monostearate, or methylenedistearamide. However, the phenomenon of self-plasticization may be reflected in a drastic decrease of softening point and viscosity. Alkyl acrylates, for instance, are known for being sticky from alkyl length  $C_4$  and, therefore, unsuitable for blending with polypropylene. On the other hand, in the case of N-substituted maleimide styrene copolymers after attaching octadecyl substituents the characteristics such as both glass and melting temperatures will not decrease progressively (see Table I). It is evident that the stiffened character of the main polymer chain is primarily responsible for level of thermal stability and other properties even at relatively low molecular mass.

The present work was also undertaken to investigate the role of glass-rubber transition of the additive,  $72^\circ\text{C}$ , in relation to the dyeing behavior of the modified fiber. The importance of the glass transition temperature of a textile fiber in the dyeing process is well established, namely, for polyester and polyacrylics.<sup>10-14</sup> Below  $T_g$ , the polymer chains remain frozen in their positions, which results in a very slow rate of dye diffusion, whereas in the region of  $T_g$ , the onset of polymer chain segmental mobility leads to a marked increase in the rate of dye diffusion in the fiber. In practical dyeing of synthetic fibers the difference  $T - T_g$  of at least  $50^\circ\text{C}$  is considered sufficient to obtain an adequate diffusion rate without observing ring dyeing and the difficulties accompanying it. Modified polypropylene is a somewhat different case, as not the whole fiber but only the dispersed additive particles are colored.

Because dyeing is a process, the state of equilibrium is reached after a time period. Therefore, determination of kinetic and thermodynamic parameters has a fundamental meaning for considering

**Table I** Properties of Basic Polymeric Additives

	Polymer A	Polymer B
Basic nitrogen	3.7%	4.9%
Molecular mass	4500	4300
Glass temperature	$72^\circ\text{C}$	$80^\circ\text{C}$
Melting temperature	$116^\circ\text{C}$	$125^\circ\text{C}$
Decomposition	$> 340^\circ\text{C}$	$> 340^\circ\text{C}$
Density, $20^\circ\text{C}$	$1096 \text{ kg} \cdot \text{m}^{-3}$	$1145 \text{ kg} \cdot \text{m}^{-3}$
Melt viscosity, $150^\circ\text{C}$	$398 \text{ Pa} \cdot \text{s}$	$1584 \text{ Pa} \cdot \text{s}$

the dyeing mechanism. Adsorption of dyes by fibers from aqueous solution takes place in three stages: (1) adsorption of dye at the fiber surface; (2) diffusion of dye from the surface to the interior of the fiber; and (3) interaction of a dye molecule with dye site.

The slowest rate-determining step is often the diffusion within the fiber. In some cases, the overall rate of dyeing is influenced by the value of the equilibrium surface adsorption. On the other hand, the interaction of dye molecule with dye site predetermines its equilibrium behavior. As the modified polypropylene fiber carries charged groups, dyeing with an acid dye should take place according to an ion-exchange mechanism, which should normally be described by a Langmuir-type isotherm.

## EXPERIMENTAL

### Additive

For the dye-fixing additive we used Polymer A, which was synthesized by imidation of alternating styrene maleic-anhydride copolymer ( $M_n = 3000$ ) using a mixture of 3-dimethylaminopropylamine and octadecylamine. Polymer B was also synthesized by reacting the styrene maleic-anhydride copolymer with 3-dimethylaminopropylamine in equimolar ratio. Styrene maleic anhydride copolymer was prepared by free radical initiation (0.15% benzoyl peroxide) of equimolar amounts of the monomers in xylene as diluent (20%). The polymerization was carried out under nitrogen at  $80^\circ\text{C}$  for several hours. The precipitated polymer was isolated by filtration, washed with toluene, and vacuum dried. The yield was 95% of white fine powder. The purity of commercially available maleic anhydride chips was 99.5%. The content of 3-dimethylaminopropylamine was 99%, checked by gas chromatography. Technical grade octadecylamine was vacuum distilled on a film evaporator to remove the secondary amine. The dis-

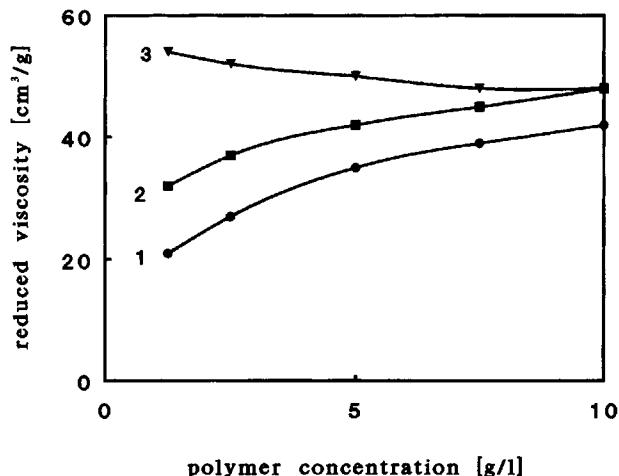
titled product was analyzed by means of nonaqueous acidimetry using salicylaldehyde as the primary amine blocking agent (purity 98%, calculated for C18). Alternating N-substituted maleimide copolymers were synthesized from the anhydride copolymer (1 mol) by reacting a 20% solution with 1 mol 3-dimethylamino-propylamine (Polymer B) or with a mixture of 0.80 mol of 3-dimethylaminopropylamine and 0.20 mol octadecylamine (Polymer A), in refluxing dimethylformamide for 6 h. The formation of anhydride groups into imide groups occurred via the stage of polymeric amidoacid. The reaction is catalyzed by the dimethylaminogroup added into the system with the dimethylaminopropylamine. After precipitation into water, the copolymers were vacuum dried in thin layer at 40°C. The estimation of acid numbers by titration of 1 g sample dissolved in 50 mL dimethylformamide with 0.1M KOH in methanol (phenolphthalein as indicator) confirmed that the conversion of maleamic groups to imide rings was 98% (acid number 3–5 mg KOH/g). It was recognized that conversion is closely related to thermal stability. If the conversion was lower than 94%, the products exhibited a loss of 4% by weight while heated at 260°C under argone for 20 min. In the IR spectra the materials showed strong imide absorption bands at 1690  $\text{cm}^{-1}$  and the absence of the 1850  $\text{cm}^{-1}$  anhydride band, present in the precursor copolymer. Titratable nitrogen content (with perchloric acid in glacial acetic acid solution), density, and other characteristic data are shown in Table I.

### Viscometric Measurements in Solution

Polymer A is a glassy, brittle powder insoluble in water, soluble in acetic acid and acetone. A clear solution can be obtained by pouring acetic acid solution into excess water. The experiments were repeated using acetone solution with various increments of hydrochloric acid. It was found that, when 60% or more basic nitrogen groups had been neutralized, the polymer became soluble in water. With the help of ultrasonic waves the finely powdered additive is even soluble in aqueous acetate buffer (0.5M  $\text{CH}_3\text{COOH}$  + 0.05M  $\text{CH}_3\text{COONa}$ ) used as the dyeing medium.

A plot of reduced viscosity vs. polymer concentration measured at 25°C in acetate buffer is shown in Figure 2. The polymer acts as a normal polyelectrolyte, for instance, the reduced viscosity is increasing with dilution (the electroviscosity effect).

In order to investigate the polymer–dye interaction, viscometric measurements were repeated in the presence of dyes. An addition of dyes causes a de-



**Figure 2** Reduced viscosity vs. Polymer A concentration: (3) reference curve for polymer; (2) Acid Orange 7, conc. 2 mmol/L; (1) Food Yellow 3, conc. 2 mmol/L.

crease in the viscosity, the effect being more pronounced for Food Yellow 3 than for Acid Orange 7. The effect of dye is to neutralize the charged nitrogen groups and, thus, decrease the electrostatic interactions between the polymer chains. Viscometric measurements were performed with a constant dye concentration of 2 mmol/l. If the concentration of polymer was decreased the dye/polymer ratio was raised resulting in a further decrease of the reduced viscosity.

### Differential Scanning Calorimetry

The thermograms were obtained using a Perkin-Elmer DSC II differential scanning calorimeter operating at a scan rate of 16°C/min and using small compressed pellets (0.5 mm thickness) of polymer. The values of temperature of glass transition  $T_g$ , melting temperature  $T_m$ , and temperature of decomposition  $T_d$  obtained are shown in Table I.

### Molecular Mass

Number-average mass was measured by vapor osmometry in dioxane solution using a Knauer osmometer.

### Viscosity of Melt

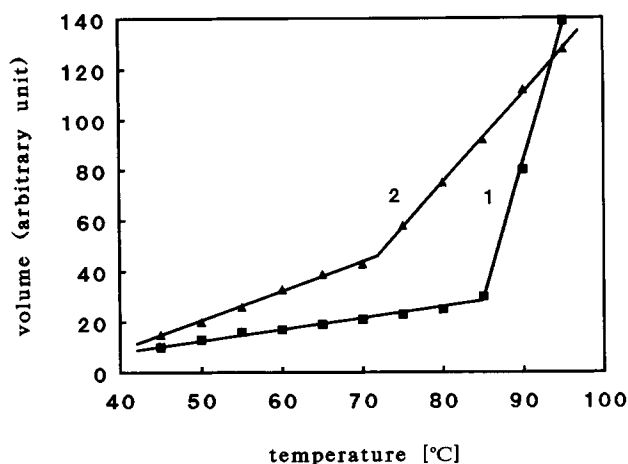
The viscosity of melted additive (150°C) was obtained using a Rheotest II in cone-plane arrangement.

## Dilatometry

The  $T_g$  value of a polymer depends, beside the method of measurement, also on the polymer impurities. In the dyeing process the  $T_g$  of textile fiber may be influenced by water, the dye, salt, acids, plasticizers employed, etc.<sup>15</sup> In order to obtain the  $T_g$  value nearer to real conditions, the dilatometry was used in water as the confining liquid.  $T_g$  of Polymer A was determined by following the change in the height of the meniscus in the capillary tube as a function of temperature while heated at a constant rate of 0.5°C/min. Correction was taken for the volume of water to get the expansion due to polymer.<sup>14</sup> The same value  $T_g = 83^\circ\text{C}$  was determined both on heating and on cooling (Fig. 3). The swelling of polymer by water was registered. When the powdered Polymer A was heated in water, it absorbed, in the temperature range of 60–70°C, approximately 60% of water with respect to its weight, becoming plastic. After cooling below 60°C, the water was released and the polymer could readily be powdered again. The dilatometry was also conducted in conventional manner, for instance, using mercury as the confining agent. The value of 72°C obtained is the same as that from the DSC measurement (Table I). The finding can be interpreted as follows: owing to the increase in temperature, such changes in the polymer chain segmental mobility occur that enable diffusion of water into the polymer. Water molecules associate with the imide groups on the main polymer chain. This makes segmental motion more difficult and, therefore, the  $T_g$  is increased. To provide the detection of  $T_g$  even more closely to dyeing conditions, the dilatometry measurement was repeated using the dyed sample suspended in acetate buffer. The value of  $T_g = 73^\circ\text{C}$  was obtained (see Fig. 3). The complex Polymer A–dye was prepared by dissolving 10 g Polymer A in 50 mL glacial acetic acid, diluting with 200 mL water, and pouring the solution into vigorously stirred solution of 5 g C.I. Acid Orange 7 in 500 mL water. The complex precipitated was then filtered and dried.

## Fibers

Both polymers A and B were tested for their suitability to act as an additive for dyeable polypropylene fiber. Six percent by weight of polymeric additive was mixed with powdered polypropylene Tatren HPF (supplied by Slovnaft, melt index 25 g per 10 min) and the blend was pelletized. The pellets were fed into a spinning machine with a spinning nozzle having 33 orifices each of 0.5 mm diameter, melt



**Figure 3** Determination of the wet  $T_g$  of Polymer A by dilatometry: (1) undyed sample in water; (2) dyed sample in acetate buffer.

spun at an extrusion rate of 1.8 kg/h, and takeup rate of 600 m/min at a temperature of the spinning head 260°C. The undrawn fibers were stretched three times while running on a hot plate (100°C, 150 m/min) to obtain multifilaments having the fineness of 120 dtex. Individual filaments had a diameter of 12  $\mu\text{m}$ . The drawn multifilaments were knitted to a tubular fabric. The fibers were purified in water containing 1 g/L pentasodium triphosphate at 60°C 30 min.

In the case of Polymer A, the stability of spinning was normal, the same as for pure PP. But processing of polypropylene blend containing incompatible Polymer B was very bad. It was not possible to prepare an undrawn fiber due to great numbers of filament breaks. Therefore, the dyeings experiments were carried out only with fiber containing Polymer A.

## Dyes

The dyeing of the modified fiber was carried out using Acid Orange 7, Food Yellow 3, Acid Yellow 11, and Acid Yellow 23. The codes and chemical structures of the dyes are given in Figure 3. These are two pairs of dyes with the same parent structure, differing in the number of acidic groups.

Before use, the fourfold crystallization from a mixture water–ethanol (1 : 1, v/v) was applied to the commercially available dyestuffs to remove neutral electrolytes.

## Dyeing and Determining the Dye Content

The dyeing of modified polypropylene fiber was carried out in acetate buffer (0.5M  $\text{CH}_3\text{COOH}$  + 0.05M

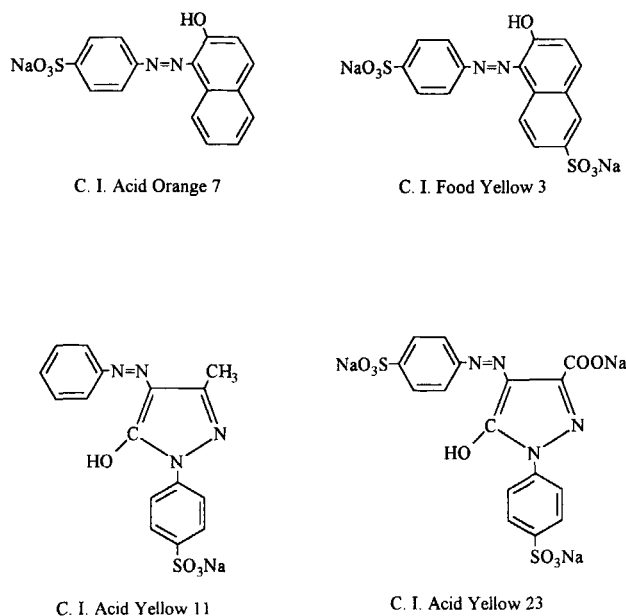


Figure 4 Chemical structure of dyes.

$\text{CH}_3\text{COONa}$ ) solution in a Linitest apparatus at  $95^\circ\text{C}$  or  $75^\circ\text{C}$  or  $85^\circ\text{C}$  under infinite dyebath conditions. The buffer had  $\text{pH} = 3.7$  at  $80^\circ\text{C}$ . The dye content in fiber was measured with a spectrophotometer. The dye was extracted from the fiber into pyridine. The extract was made up to a known volume and the absorbance of the solution was measured at the wavelength of the maximum absorption. The dye uptake was calculated from a previously constructed calibration curve.

The temperature range  $45\text{--}95^\circ\text{C}$  in  $10^\circ\text{C}$  intervals was investigated using Acid Orange 7. As we observed the change of temperature dependence of the apparent diffusion coefficient  $D$ , saturation value  $c_s$ , and standard affinity  $\Delta\mu^\circ$  at around  $70^\circ\text{C}$ , the dyeing was completed by the measurement at this temperature.

#### Leachability of Additive from Fiber

As the additive becomes soluble in water when protonated, the question of its leachability from fiber must be solved before starting the dyeing experiments. The modified fiber was treated with a blank dyebath at  $95^\circ\text{C}$  and  $\text{pH} = 3.5$  in the dyeing apparatus, and the additive exuded into the bath was detected UV spectrophotometrically. The kinetics of exudation is pictured in Figure 5. One-thirtieth of additive originally present in the fiber migrates out. The results may be explained in such a way that at initial stages of washing a small amount of ad-

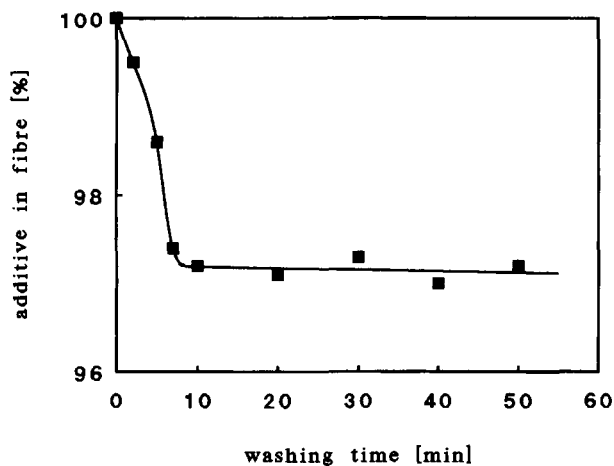


Figure 5 Migration of additive from modified fiber.

ditive settled on the surface is rinsed off and no migration from the interior of the fiber takes place.

#### Determination of Thermodynamic Parameters of the Dyeing System

The sorption isotherm is the fundamental characteristic describing the equilibrium, expressing the relation between the dye concentration on fiber and in bath at equilibrium. In our experiments, the state of equilibrium was achieved after 4–5 h, depending on temperature. Examples of sorption isotherms of Acid Orange 7 and Food Yellow 3 are presented in Figure 6.

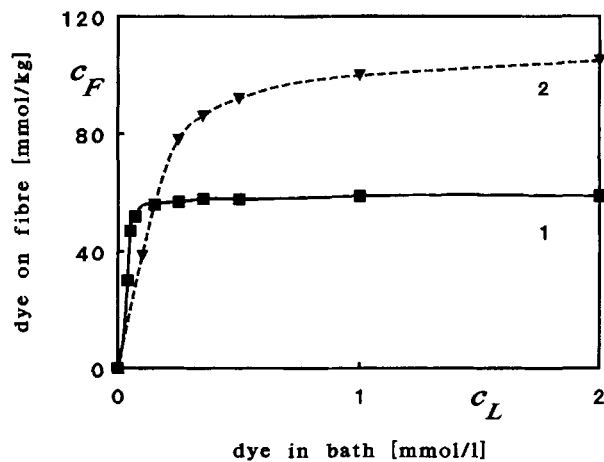


Figure 6 Sorption isotherms of Acid Orange 7 and Food Yellow 3 on modified PP fiber: (2) Acid Orange 7; (1) Food Yellow 3.

The sorption isotherm may be expressed in the form

$$c_F = \frac{c_S \cdot K \cdot c_L}{1 + K \cdot c_L} \quad (1)$$

where  $c_F$  = concentration of dye in fiber,  $c_L$  = concentration of dye in bath,  $c_S$  = saturation concentration, for instance, the maximum concentration of dye in fiber that can be achieved,  $K$  = equilibrium constant.

The equilibrium constant can be used for calculation of the standard affinity  $\Delta\mu^0$  following eq. (2):

$$\Delta\mu^0 = -RT \cdot \ln K \quad (2)$$

The standard affinity of a dye for a given substrate has a fundamental effect on dyeing properties, such as power of exhaustion, leveling properties, and suitability for application in a mixture of dyes. The standard enthalpy  $\Delta H^0$  of dyeing is calculated from eq. (3):

$$\ln K = -\frac{\Delta H^0}{RT} + \text{const.} \quad (3)$$

To determine  $\Delta H^0$ ,  $\ln K$  is plotted against  $1/T$ , and entropy  $\Delta S^0$  is calculated from eq. (4):

$$\Delta\mu^0 = \Delta H^0 - T \cdot \Delta S^0 \quad (4)$$

The thermodynamic quantities  $\Delta\mu^0$ ,  $\Delta H^0$ ,  $\Delta S^0$ , and saturation concentration  $c_S$  for four acid dyes are shown in Table II.

The values  $\Delta\mu^0$ ,  $\Delta H^0$ , and  $\Delta S^0$  determined in this way have not exact thermodynamic meaning because the experiments were realized in a heterogeneous system. Another problem is the substitution of activities by concentrations. Nevertheless, the value of these "quasi" thermodynamic quantities lies in the possibility of comparing the behavior of different dyes on the same fibrous material and, thus, allowing

conclusions to be drawn about the mechanism of dyeing.

### Determination of Kinetic Parameters of Dyeing

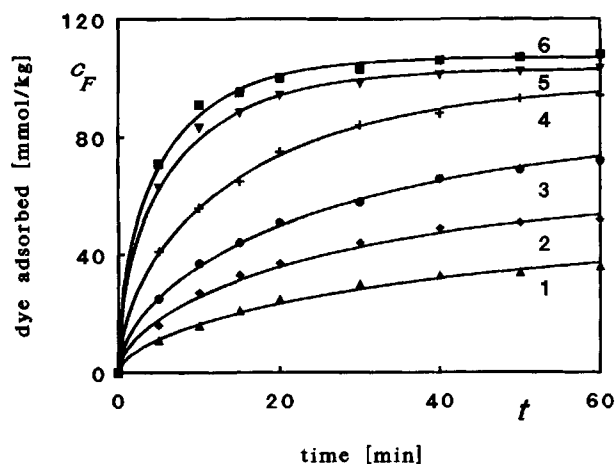
The rate of dyeing can be characterized by the diffusion coefficient  $D$ , and activation energy of diffusion  $\Delta E$ . Direct information about diffusion coefficient is obtained from scanning of the concentration profile, for instance, determining the dependence of dye concentration upon the distance from the fiber surface. The technique, however, cannot be applied to the modified polypropylene fiber because of the relatively inhomogeneous substrate. The diffusion of dye into a fiber of circular cross-section from an "infinite" dye-bath (i.e., one in which no appreciable change in concentration of dye occurs during dyeing) conforms to Hill's equation. For a fiber of radius  $R$

$$\frac{c(t)}{c(\infty)} = 1 - \sum_{n=1}^{\infty} \frac{4}{\beta_n^2} \exp\left(-\beta_n^2 \cdot \frac{D \cdot t}{R^2}\right) \quad (5)$$

where  $Dt/R^2 = Fo$  is the Fourier number for cylinder. The term  $\beta_n$  stands for the  $n$ -th positive root for the equation  $Jo(\beta_n) = 0$ ,  $Jo(x)$  is the zero order Bessel function of the I-st type,  $R$  is fiber diameter,  $t$  is time of dyeing. Thus,  $c(t)/c(\infty)$  is related to  $Dt/R^2$ . A small weight of material is dyed in a large volume of dye solution for a prolonged time and the amount of dye adsorbed is determined to give the value of  $c(\infty)$ . Another set of dyeing operations is then carried out for a much shorter time, and  $c(t)$  is determined. For a given set of experimental data  $c(t)$  vs.  $t$ , the diffusion coefficient  $D$  was then calculated by using a nonlinear regression procedure. The diffusion coefficient  $D$  determined in this way has an apparent meaning only because the overall amount of the dye exhausted by the fiber at a certain time of dyeing represents an integral of concentration profile. For kinetic measurements, the fibers were pretreated in a blank dyebath for 5 min before start-

**Table II Saturation Concentration  $c_S$  and Affinity  $\Delta\mu^0$ , Enthalpy  $\Delta H^0$ , and Entropy  $\Delta S^0$  for Dyeing Equilibrium**

Dye C.I.	$c_S$ [mmol/kg]	$\Delta\mu^0$ [kJ/mol]	$\Delta H^0$ [kJ/mol]	$\Delta S^0$ [kJ/mol · K]
Acid orange 7	110	-7.04	-16.5	-0.101
Food yellow 3	65	-12.15	-16.9	-0.028
Acid yellow 11	128	-4.60	-49.8	-0.123
Acid yellow 23	42	-11.59	-21.9	-0.028



**Figure 7** Dyeing rate curves for different concentrations of Acid Orange 7 in the bath: (1) 0.10 mmol/L, (2) 0.15 mmol/L, (3) 0.25 mmol/L, (4) 0.50 mmol/L, (5) 1.00 mmol/L, (6) 2.00 mmol/L.

ing the dyeing experiments. The fiber/liquor ratio was 1 : 2000.

Typical dyeing curves for samples of different dye concentrations in bath are shown in Figure 7 for data obtained at 95°C. The diffusion coefficient is not constant: it was found to depend on the concentration of the dye in bath (see Fig. 8).

The activation energy of diffusion,  $\Delta E$ , was then calculated from the temperature  $T$  dependence applying the Arrhenius equation (6):

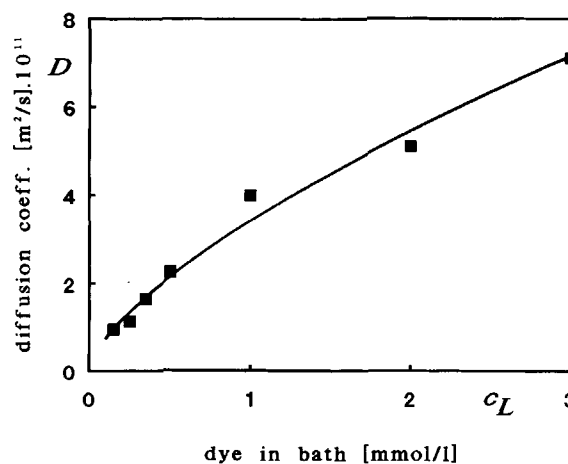
$$\ln D = \ln D_0 - \frac{\Delta E}{RT} \quad (6)$$

The  $\Delta E$  values of four acid dyes at the concentration of 0.25 mmol/L are listed in Table III.

## RESULTS AND DISCUSSION

An important conclusion about the nature of sorption and binding of acid dyes on cationically modified polypropylene fiber may be drawn from experimental findings. The equilibrium distribution of dyes between the bath and fiber is governed by the Langmuir isotherm. The shape of sorption isotherm suggests that the sorption occurred on a finite number of identical sites. At the same time, an adsorption of dyes in a nondissociated form like disperse dyes or a mechanism of creating aggregates of dye on fiber seem to be improbable.

Supposing that the dye sites are basic amino groups, the additive supplied 127 mmol/kg such sites



**Figure 8** Variation in diffusion coefficient with concentration of Acid Orange 7 in bath, 95°C.

to the fiber. At the dyeing conditions, 86 and 100% of dye sites are accessible for Acid Orange 7 and for Acid Yellow 11, respectively. The disulfonated dyes exhibited lower occupation of the dye places. In the case of Food Yellow 3, the accessibility is only 52%, whereas Acid Yellow 23 gives a value of 34%. The second sulfonic group attached to the dye molecule thus causes a dramatical decrease in the saturation value (Table II). There is convincing evidence that the interactions operating in bonding of dye on fiber are of the Coulombic type. Ionic interactions are the main source of affinity of dyeing. Acid Orange 7 has the affinity of  $-7.04$  kJ/mol; after supplying the second sulfonic group into the dye (Food Yellow 3) the value decreases to  $-12.15$  kJ/mol. From the point of view of practical dyeing, it may be recommended to be careful in building of a compound shade using a mixture of monosulfo- and disulfonated dyes.

The negative sign of affinity suggests a spontaneous character of the dyeing process. The overall value of affinity is given by the sum of two contributions: the enthalpic gain and the entropic gain. The action of these contributions is antagonistic. A de-

**Table III** Diffusion Coefficient  $D$  and Activation Energy  $\Delta E$  for Dye Concentration of 0.25 mmol/L

Dye C.I.	$D$ [m <sup>2</sup> /s]	$\Delta E$ [kJ/mol]
Acid orange 7	$7.59 \cdot 10^{-11}$	47.0
Food yellow 3	$5.98 \cdot 10^{-11}$	53.5
Acid yellow 11	$6.34 \cdot 10^{-11}$	54.5
Acid yellow 23	$5.93 \cdot 10^{-11}$	49.2



crease in entropy acted adversely against dye sorption. The entropy decrease is due to the change of the state of freedom between the dye in solution and that fixed on a dye place. However, the enthalpy gain is dominant. An exothermic character of process suggests a prevailing contribution of ionic as well as other intermolecular bonding between dye and polymeric additive dispersed in the fiber. The dyeing can generally be described as an enthalpy-driven reaction.

At lower concentration, the equilibrium is strongly shifted in favor of the fiber. For instance, the concentration 0.25 mmol/L Acid Orange 7 in the bath corresponds to 80 mmol/kg (i.e., 320-fold higher) dye on fiber. Dyeing to dark shades can be expected to be accompanied by a high exhaustion of dye from bath.

A coefficient of diffusion of the order of  $10^{-11}$  m<sup>2</sup>/s was found, indicating that the diffusion of the dye molecules into polymer is very fast. No marked difference was seen between the four dyes in this respect. The values are much higher than those for the diffusion of acid dyes into wool.<sup>16,17,22</sup> Such rapid diffusion is reflected in dyeing from finite dyebath, for example, 2% dye o.w.f., where exhaustion comes to equilibrium within 6 min at 100°C and pH = 3.5. The diffusion coefficients were found to depend very much upon the concentration of dye present in the dyebath. From the different initial slopes of dyeing curves presented in Figure 7, it may be presumed that the rate-limiting step does not consist in the adsorption on the surface of the fiber in the concentration range examined.<sup>18</sup> If a quick saturation of the fiber surface occurred with subsequent diffusion inside, one would expect the rate of dyeing independent of dye concentration in early stages of dyeing.

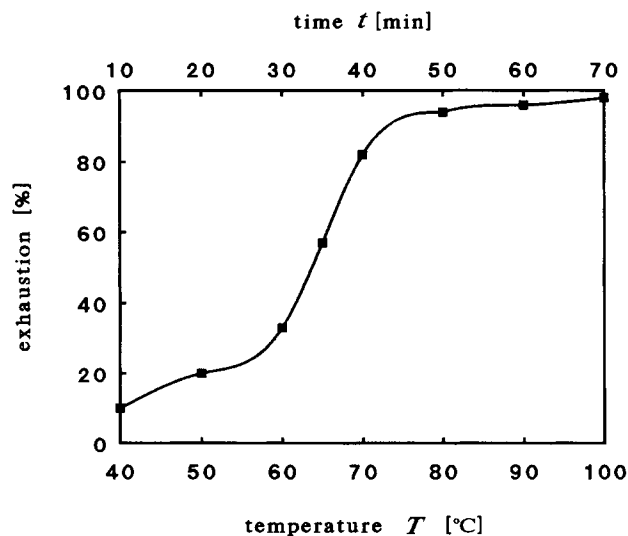
As it is evident that the binding of a disulfonated dye occurs at two points, the question arises as to how this bonding occurs, whether on the same polymer chain or between two distinct macromolecules. The latter mechanism represents the crosslinking. If the crosslinking took place, the viscosity would increase. The viscosity measurements did not confirm such a dye polymer interaction. On the other hand, an addition of Food Yellow 3 even led to a considerable viscosity reduction indicating an ionic screening effect (Fig. 2). The similarity of values of both the diffusion coefficients and activation energies of diffusion also indicates that the dye double ions do not cause any transient crosslinking.

In practical dyeing the fibrous material is put into the stirred dyeing bath at lower temperature. The temperature is gradually increased and the dye is

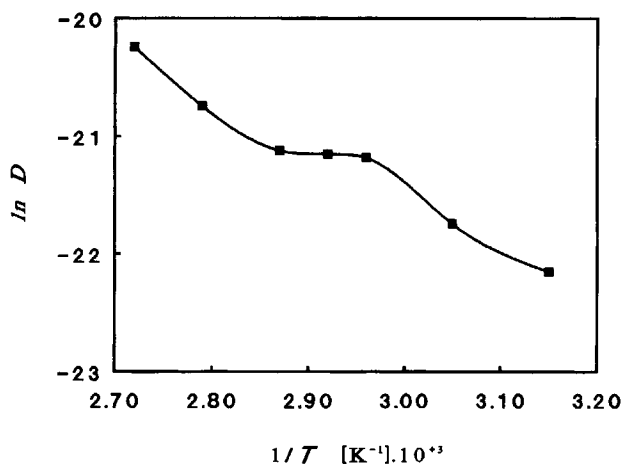
exhausted onto the fiber. The exhaustion curve of finite dyebath (2% on the weight of fiber of C.I. Acid Orange 7, liquor ratio 50 : 1) onto modified polypropylene fiber is pictured in Figure 9 for the rate of heating 1°C/min.

The exhaustion of dye from bath exhibits a peculiarity in the range of 60–70°C. There seems to be an additional effect besides that of temperature. It may be due to breaking down of dye aggregates in solution or due to the changes in the structure of fiber. But the simple acid dye, Acid Orange 7, does not aggregate in any great extent, only forming a dimer at temperatures below 40°C.<sup>20</sup> The picture resembles that of dyeing of acrylic fiber where the break at 80°C is suggestive of a change in the amorphous structure as the polymer passes through the glass transition temperature.<sup>21</sup>

The change in dyeability within a narrow temperature range has been reflected in the apparent diffusion coefficient measured under infinite dyebath conditions. In Figure 10, the temperature dependence is plotted as the logarithm of diffusion coefficient  $\ln D$  against the inverse of absolute temperature of dyeing in order to prove whether the Arrhenius equation is valid. Figure 10 shows that there is no linear relationship that would be expected if the process were characterized by a single activation energy. The relationship consists of two approximately linear branches connected by a transition area, implying the change in mechanism of diffusion. The transition area is characterized by a sudden decrease in activation energy of diffusion.



**Figure 9** Dye uptake of modified PP fibers at different temperatures, Acid Orange 7, 2% on the weight of the fiber.



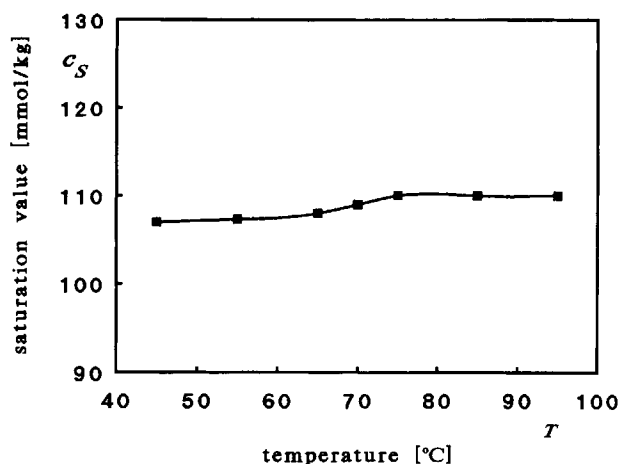
**Figure 10** Temperature dependence of diffusion coefficient of Acid Orange 7.

If the glass transition temperature played a role, the free volume of the fiber would decrease rapidly below  $T_g$ , and, therefore, the number of accessible dye sites would be expected to decrease markedly with decreasing temperature. However, the saturation values calculated from the Langmuir sorption isotherms are not much lowered at 45–65°C as compared to those for the temperature range of 75–95°C (see Fig. 11). Thus, modified polypropylene fiber can be dyed even at 45°C. Nevertheless, the time period required to reach the equilibrium lasted 12 h at this temperature.

The affinity of dyeing increases with decreasing temperature, as expected for an exothermic process, however, the affinity increases until the temperature 68°C exhibits a sharp change in slope dependence (Fig. 12).

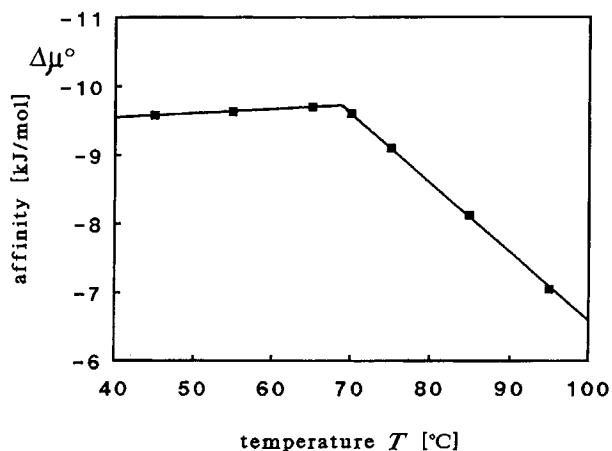
The monitoring of the temperature changes of both kinetic and thermodynamic parameters describing the dyeing process may serve as an indirect method for determining the transition temperature related to dyeing— $T_D$ . The temperature changes in the dyeability of modified polypropylene fiber used may be explained in terms of the interaction of dye-additive and molecular relaxation in polymer additive.

Essentially, two models have been formulated to explain the mechanism of dye migration in textile fibers, namely, the rigid pore matrix model and the dynamic free volume model.<sup>21</sup> The pore model was suggested for dyeing natural hydrophilic fibers such as cellulose, wool, and silk fibers. According to this model, the water-swollen textile fiber can be regarded as a solidified sponge, a rigid matrix in which there is a maze of interconnected pores. The pores are filled with water and the dye enters from the



**Figure 11** Temperature changes of saturation value of Acid Orange 7.

bath liquid into the pores and penetrates the fiber by diffusing along these water-filled channels. The second free volume model is suggested in dyeing synthetic hydrophobic fibers—polyamide, polyacrylonitrile, and polyester fibers—which do not absorb water to a great extent. It describes the dyeing kinetics as a diffusion of dye molecules through amorphous parts of the polymer matrix. Below  $T_g$  the polymeric material behaves as rigid body or glass. In this region dyes can move only through the pores and cracks in the polymer. Above the  $T_g$ , the migration is linked to the amount of free volume available (the volume that is not occupied by the chains of the polymer itself). The larger the free volume, the greater is the probability that suitable voids will open periodically, through which the dye molecules can move.



**Figure 12** Temperature variations of standard affinity of Acid Orange 7.

Modified polypropylene has been successfully dyed even below  $T_g$ . Discussing the possibilities of the free volume below  $T_g$  of additive we must consider that the side octadecyl substituents cause the decrease of density, which represents the increasing of polymer backbone distance (see Table I). Moreover, the protonation of basic nitrogen atoms by acetic acid can also induce an increase of interchain distances due to electrostatic repulsion forces and, at the same time, the higher polarity supports the water swelling. Furthermore, Coulombic forces between protonated neighboring groups can enforce the straightening up of the polymer chain. All that may be a plausible explanation of the good accessibility of dye sites over the whole temperature range.

## CONCLUSION

An acceptable additive for acid dyeable polypropylene was synthesized by attaching long alkyl chains together with substituents carrying basic nitrogen atoms to a polymer backbone. The long alkyl chains that are favorable for good dispersibility and compatibility of the additive with polypropylene matrix can, however, adversely act by decreasing the softening point. For such effect not to occur, a rigid polymer backbone should be used.

A modified polypropylene capable of being dyed in aqueous dye bath is now available with the saturation limit of 110–120 mmol of monosulfonated dye per kg of fiber. Because the fiber carries a limited number of binding sites, the dye can be doped into the bath at a concentration lower than that corresponding to the bend of isotherm if the detention of dye in the bath should be avoided. In the case of monosulfonated dyes, the doping could be lower than approximately 80 mmol dye/kg fiber. Considering that the dyes have molecular mass of 350 or greater, it is apparent that a dyeing using 3% o.w.f. of dye of commercial purity can be accompanied by a satisfactory exhaustion.

The equilibrium sorption of ionic dyes by fibers containing fixed charged groups has been investigated by many researchers.<sup>16,17</sup> In this context it may be noticed that the normal types of polyamides have

a content of binding sites of 30–60 mmol/kg, the acrylics 45–60, and for wool the value 800 has often been mentioned. The acid dyeable polypropylene Meraklon D produced by Montecatini through the 60s and 70s possessed the sorption capacity of 310 mmol/kg.<sup>1,19</sup>

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