

<Research Paper>

Calculation and Analysis of Hydrophobicity of the Dyes Synthesized for Unmodified Polypropylene Fibers Using Molecular Descriptors

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Abstract— In order to analyze numerically the hydrophobicity of the new dyes synthesized for unmodified pure polypropylene fibers, the octanol-water partition coefficient (logP), which is one of molecular descriptors representing hydrophobicity of organic compounds, was obtained by a semi-empirical method using Chem3D software. For the dyes of higher logP than around 5, the affinity of the dyes towards unmodified polypropylene fiber was substantial. In contrast to the new dyes for polypropylene, conventional disperse dyes have logP values lower than 5 and exhibited poor affinity.

Keywords: hydrophobic dye, disperse dye, polypropylene, logP, molecular descriptor

1. Introduction

It has been generally considered that it was impossible to dye polypropylene fibers at any dyeing systems because of the extreme hydrophobicity of the fiber¹⁻³. To have strong affinity to the hydrophobic fibers like polypropylene, dyes also need to have comparable hydrophobicity. Previous studies showed that the dyeing of polypropylene fibers without any physical and chemical modifications was possible at the established process by super hydrophobic dyes having long alkyl substituents which imparted significant hydrophobicity to the dyes⁴⁻⁷.

As a successive study, logP values were calculated in order to express the hydrophobicity of the dyes numerically by a semi-empirical method using Chem3D software. The logP is one of molecular descriptors representing hydrophobicity of organic compounds. Theoretical meaning of the logP originates from the partition coefficient of an organic compound between two different liquid phase, 1-octanol and water(Eq. (1))⁸. However, recently the logP values can be calculated conveniently by many computer softwares semi-empirically such as Chem3D.

$$\begin{aligned}\log P &= \log K_{ow} = \log \frac{[C]_{\text{octanol}}}{[C]_{\text{water}}} \quad \dots\dots \text{Eq. (1)} \\ &= \log [C]_{\text{octanol}} - \log [C]_{\text{water}}\end{aligned}$$

In this regards, the logP values of the dyes, synthesized for polypropylene in the previous studies, were calculated by Chem3D and analyzed numerically in terms of relationship between hydrophobicity of dyes and affinity of them towards pure polypropylene fibers.

2. Experimental

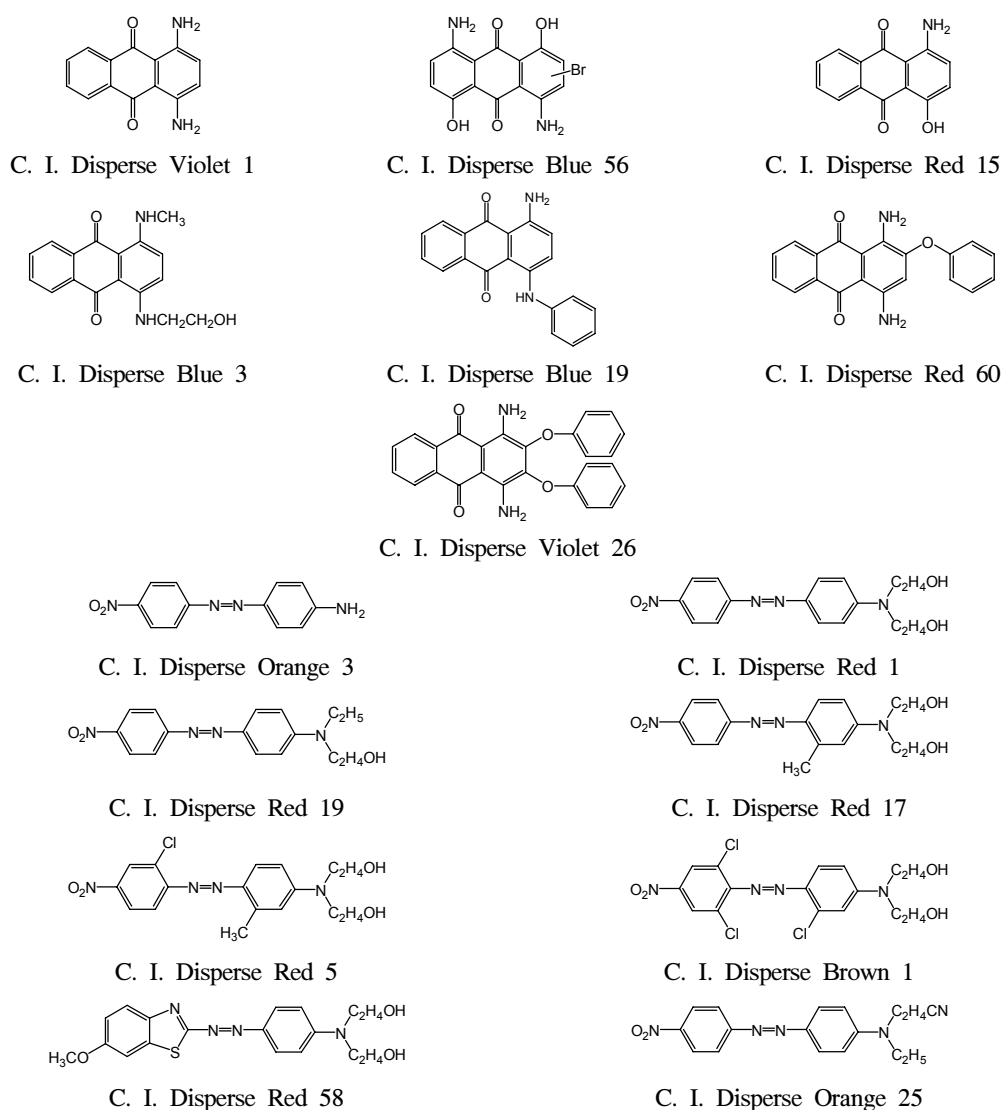
2.1 Materials

The unmodified pure polypropylene fabrics (plain weave, 120g/m²) were used for dyeing experiments after scouring with acetone. The dyes are divided into two groups; one is a new group synthesized in the previous studies for pure polypropylene fibers, which has long alkyl substituents in order to impart extreme hydrophobicity (Fig. 1), and the other is a conventional disperse dye group for regular polyester fibers which comprises 7 anthraquinoid dyes and 14 azo dyes (Fig. 2).

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Color	Chromophore	Chemical structure	R :
Blue	Anthraquinone		-CH ₃ -CH ₂ CH ₃ -CH ₂ CH ₂ CH ₂ CH ₃ -CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ -CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃
Orange	Disazo		-CH ₃ -CH ₂ CH ₃ -CH ₂ CH ₂ CH ₃ -CH ₂ CH ₂ CH ₂ CH ₃ -CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ -CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃
Yellow	Monoazo		-CH ₃ -CH ₂ CH ₃ -CH ₂ CH ₂ CH ₃ -CH ₂ CH ₂ CH ₂ CH ₃ -CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃

Fig. 1. Chemical structures of alkyl-substituted dyes.



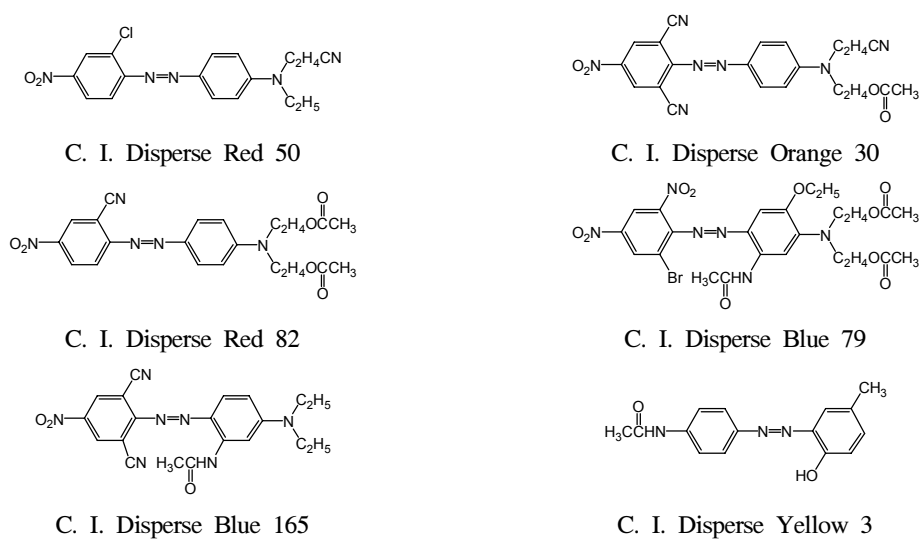


Fig. 2. Conventional disperse dyes.

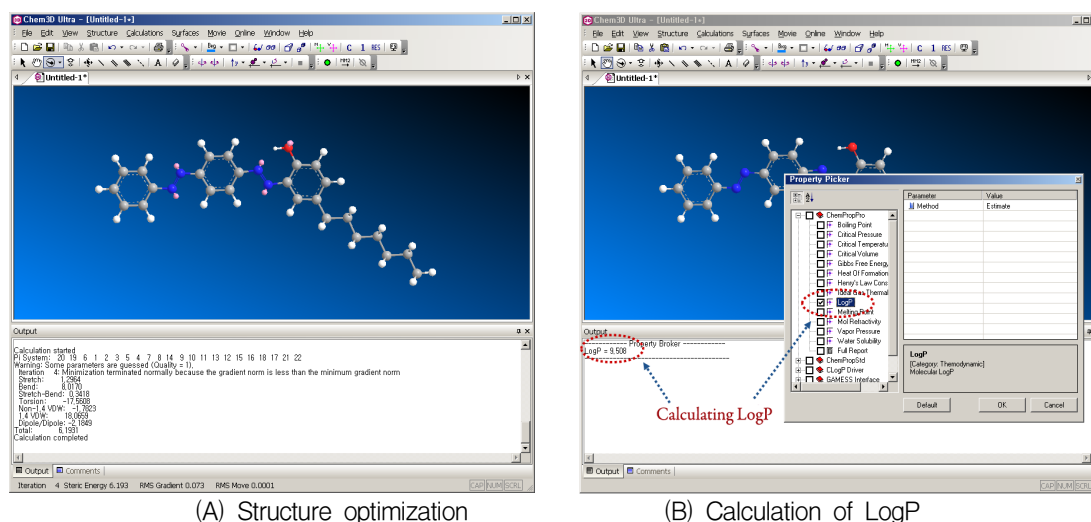


Fig. 3. Calculation of LogP values using Chem3D Ultra.

All dyes were purified by general purification methods. The surfactant used for dispersion of dyes was didodecyldimethyl ammonium bromide (DDDMAB).

2.2 Preparation of dye dispersion

Certain amount of dyes was dissolved in 50ml tetrahydrofuran and mixed with the solution of DDDMAB (2 weight ratio to dye amount) dissolved in 50ml tetrahydrofuran. The mixture was heated under reduced pressure and then dried under vacuum for 24 hours to remove the tetrahydrofuran entirely. In this procedure, the uniform mixture of dyes and dispersant(DDDMAB) was prepared. The 1 hour exposure in an ultrasonic apparatus after the addition of water to this mixture makes uniform

and stable dye solution by the dispersing activity of DDDMAB⁹⁻¹¹). This solution was finally used for dyeing.

2.3 Dyeing

The unmodified polypropylene fibers (1.0g) were dyed with basically 5% owf dyes at a liquor ratio of 50:1.

The temperature of dyebath was elevated to 13 0°C at a rate of 2°C/min and maintained at the temperature for 60 minutes.

The dyed materials were reduction-cleared in an aqueous bath comprising sodium hydroxide (2g/l), sodium hydrosulfite (2g/l), and nonionic surfactant (5g/l) at 60°C for 10 minutes.

2.4 Measurement of color strength

The color strength of dyed fabrics was measured by a color measurement instrument (*Spectrophotometer CM-3600d, Konica Minolta*) and expressed by K/S values at the maximum absorption wavelength of each dyes. The measurement was carried out with 10° standard observer under standard light D_{65} .

2.5 Calculation of logP

In order to calculate the logP of dyes, the chemical structures were drawn using ChemDraw Ultra 10.0 and then the structure files were imported into Chem3D Ultra 10.0. The chemical structure of the opened dye was optimized by the process *MM2 Minimize Energy* (Fig. 3, (A)). Minimum RMS Gradient was set to 0.100. After the structure optimization, the logP of *ChemPropPro* at the *Compute Properties* menu was selected and calculation was carried out (Fig.3, (B)).

3. Results and Discussion

3.1 Affinity of alkyl-substituted dyes towards polypropylene

Affinity of the alkyl-substituted dyes toward unmodified polypropylene fiber was presented in Fig. 4 according to the length of alkyl substituents⁴⁻⁷. As the length of alkyl substituents increased, the dyeability toward polypropylene fiber tends to be

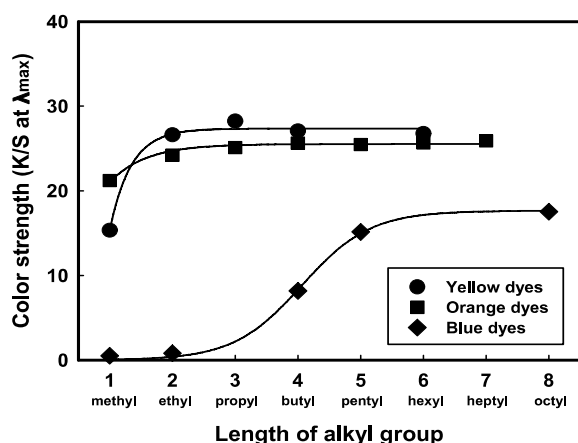


Fig. 4. Color strength of alkyl-substituted dyes onto polypropylene fabrics at 130°C for 1 hour⁴⁻⁷. (λ_{max} : Yellow dyes 420nm, Orange dyes 370nm, Blue dyes 600nm)

improved dramatically for all the dyes. This can be explained that the hydrophobicity of dyes is significantly increased according to the length of alkyl substituents. Therefore, in order for polypropylene fibers to be dyed, the super hydrophobic dyes which is much more hydrophobic than conventional disperse dyes are necessary.

3.2 LogP (hydrophobicity) of the alkyl-substituted dyes and its relationship to affinity towards polypropylene

In order to evaluate numerically the hydrophobicity of the alkyl-substituted dyes, the logP values were calculated by Chem3D software and summarized at Table 1.

As expected, the logP (hydrophobicity) increased with the length of alkyl-substituted. From the Table 1, it can be known that one methylene unit ($-\text{CH}_2-$) increases 0.417 logP value. Using these logP values, the relationship between logP values of the dyes and affinity towards polypropylene was established and shown in Fig. 5. From the result of Fig. 5, it became clear that the logP (hydrophobicity) values should be higher than around 5 in order for dyes to have commercially acceptable affinity towards unmodified polypropylene, which makes deep color with K/S value higher than 15. Disazo and monoazo dyes of this experiment show relatively higher logP values than anthraquinoid dyes. This is because that the monoazo and disazo chromophores are more hydrophobic than anthraquinoid chromophore having two ketone and two secondary amine groups which are relatively hydrophilic.

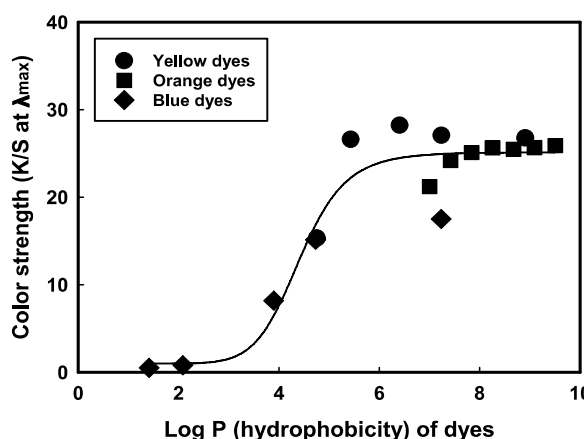


Fig. 5. Relationship between color strength on polypropylene and LogP values of alkyl-substituted dyes.

Table 1. logP values of alkyl-substituted dyes

Color	Chromophore	Alkyl group substituted		LogP
Blue	Anthraquinone	Methyl	-CH ₃	1.414
		Ethyl	-CH ₂ CH ₃	2.089
		Butyl	-(CH ₂) ₃ CH ₃	3.896
		Pentyl	-(CH ₂) ₄ CH ₃	4.730
		Octyl	-(CH ₂) ₇ CH ₃	7.234
Orange	Disazo	Methyl	-CH ₃	7.004
		Ethyl	-CH ₂ CH ₃	7.422
		Propyl	-(CH ₂) ₂ CH ₃	7.839
		Butyl	-(CH ₂) ₃ CH ₃	8.256
		Pentyl	-(CH ₂) ₄ CH ₃	8.674
		Hexyl	-(CH ₂) ₅ CH ₃	9.091
Yellow	Monoazo	Heptyl	-(CH ₂) ₆ CH ₃	9.508
		Methyl	-CH ₃	4.755
		Ethyl	-CH ₂ CH ₃	5.431
		Propyl	-(CH ₂) ₂ CH ₃	6.404
		Butyl	-(CH ₂) ₃ CH ₃	7.238
		Hexyl	-(CH ₂) ₅ CH ₃	8.907

3.3 LogP (hydrophobicity) of conventional disperse dyes

The reason why new hydrophobic dyes having long alkyl-substituents were synthesized in this study is that there was no effective dyes among conventional disperse dyes for unmodified polypropylene. With the conventional disperse dyes, it was not possible to obtain deep color dyeings of polypropylene. To clarify this, the logP values of 21 disperse dyes comprising 7 anthraquinoid and 14 azo dyes were calculated as the same method mentioned above and listed at Table 2. Unlike the alkyl-substituted dyes, the conventional disperse dyes have logP values lower than 5.

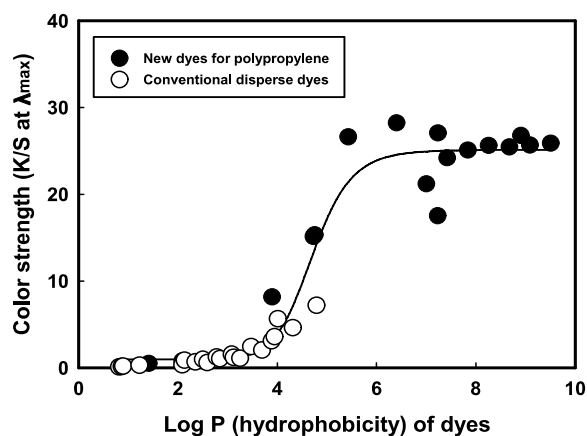

Fig. 6. Relationship between color strength on polypropylene and LogP values of alkyl-substituted and conventional disperse dyes.

Table 2. logP values of conventional disperse dyes

Chromophore	Dyes	Log P
Anthraquinone	C. I. Disperse Violet 1	0.814
	C. I. Disperse Blue 56	0.864
	C. I. Disperse Red 15	1.227
	C. I. Disperse Blue 3	0.896
	C. I. Disperse Blue 19	3.082
	C. I. Disperse Red 60	2.351
	C. I. Disperse Violet 26	3.888
Azo	C. I. Disperse Orange 3	2.589
	C. I. Disperse Red 1	3.253
	C. I. Disperse Red 19	2.088
	C. I. Disperse Red 17	2.503
	C. I. Disperse Red 5	3.122
	C. I. Disperse Brown 1	3.945
	C. I. Disperse Red 58	4.791
	C. I. Disperse Orange 25	3.695
	C. I. Disperse Red 50	4.314
	C. I. Disperse Orange 30	2.135
	C. I. Disperse Red 82	2.780
	C. I. Disperse Blue 79	4.013
	C. I. Disperse Blue 165	2.846
	C. I. Disperse Yellow 3	3.476

In order to apply the logP values to affinity towards polypropylene fiber, the conventional disperse dyes were plotted together with alkyl-substituted dyes in Fig. 6.

While the alkyl-substituted dyes exhibited very high affinity towards polypropylene fiber, the 21 conventional disperse dyes showed very low affinity and color strength towards polypropylene fiber. It is considered that even though conventional disperse dyes can be said to be generally hydrophobic, they are still not enough to dye polypropylene fiber with high color yield.

4. Conclusion

In order to analyze numerically the hydrophobicity of the new dyes synthesized for unmodified pure polypropylene fibers, the octanol-water partition coefficient (logP) was obtained.

For the dyes of higher logP than around 5, the affinity of them towards unmodified polypropylene fiber was substantial. In contrast to the new dyes for polypropylene, conventional disperse dyes have logP values lower than 5 and exhibited poor affinity. This result means that even though conventional disperse dyes can be said to be generally hydrophobic, they are still not enough to dye polypropylene fiber with high color yield and need to be more hydrophobic with logP value at least 5.

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