

Novel chromotropic dyes with surface activity and a regulable color transition point derived from phenolsulfonphthalein

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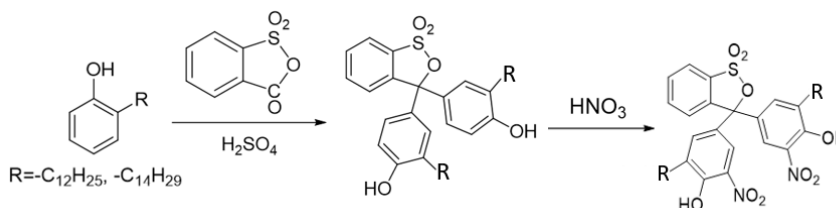
Received 06-13-2024

Accepted 07-16-2024

Published on line 07-25-2024

Abstract

Three novel compounds called 3',3''-dodecyl-2-sulfonyl phthalein (DSP), 3', 3''-myristyl-2-sulfonyl phthalein (MSP) and 3',3''-dodecyl-5',5''-nitro-2-sulfonyl phthalein (DNSP) were synthesized as functional dyes in both chemical and biological areas. The synthesized chromotropic dyes were characterized by NMR, elemental analysis and pH value tester. Also the allochronic behaviors and surface activity of the new compounds were tested mainly with the optical contact angle measurement and UV-Vis spectrophotometer. The introduction of the long chain alkyl groups into the skeleton aimed to increase the surface activity of those dyes while that of the nitro group was focused on the regulation of the color transition point (CTP). The results indicate that the target dyes show satisfying properties in not only the chromogenic performance, but also the surface activity. Therefore, it may be an effective and durable functional dye with further potential applications in the field of pH sensors, probe and coating materials.



Keywords: Phenolsulfonphthalein derivative, chromotropic dyes, surface activity, color transition point

Introduction

Dyes with discoloration properties play an important role among the functional materials in the dyestuff industry, and are widely used for the manufacturing of various equipments particularly in military, detecting and construction applications.¹⁻¹² It is well known that the demand of the biological diagnosis based mechanical and electrical life system feedback devices, implanted with pH monitoring, keeps increasing every year.^{37,15,39} However the vulnerabilities of traditional glass electrodes expose patients to big risks while the optical sensors on the basis of glass fibers are relatively safe.^{38,40} Moreover, the performances of checking and resisting electronic interference are more stable. Most pH sensors are based on dye adsorptions, and such systems will attach the dyes to the glass fibers exploiting the hydrophilic properties of these dyes. Increasing the surface activity means that the dyes will be combined more firmly with the fibers. The pH measurement inside the body will not exist without the development of an optical fiber sensor. As a result, many people become interested in the preparation of dyes which can be combined directly with plastic optical fiber. The use of the plastic optical fiber leads to a high flexibility and at the same time, they are smaller and have a lower cost. Dyes with discoloration properties control the change of color due to the change of pH, temperature, light intensity and so on. Realizing the reversible change of color anticipated for specific applications is necessary. Thus far, some chromotropic dyes such as bromophenol blue (BB) and bromocresol green (BG) are generally and extensively applied in pH sensors.^[13,14] The chromotropic phenol derived dyes such as BB and BG can appear as lactone or as quinoid structure to achieve the reversible color change under acidic or alkaline conditions. However, it was found problematic that BB and BG, as chromotropic dyes with multiple bromine atoms, are likely to be dissolved in water which means those kinds of pH sensors will not last for very long. Apart from this, those two dyes have single CTPs which leads to a limited utilization. Consequently, the research towards ideal chromotropic dyes with outstanding surface activities and a wide range of CTPs becomes necessary and urgent, which is the main purpose of this work. Recent studies have shown that phenolic hydroxyl, sulfonic groups and a conjugated structure play an important role in the discoloration performance of the molecular skeleton of phenol red. In this work, the molecular skeleton of phenol red was connected with two different molecule groups (a long alkyl chain and a nitro group) as new chromotropic dyes. The nitro group is considered as an ideal group for changing the CTPs of chromotropic dyes, because the strong electron-withdrawing ability keeps the molecular electronic balance and lowers the bond energy of the C-N making it possible to change the CTPs. Additionally, various long alkyl chains increase the hydrophobicity and lipophilicity (including dodecyl and myristyl chains), lead to a good compatibility with the organic polymer resin and increase the water resistance. Theoretically, the alkyl chains of the new structure would be hidden inside the sensors without being washed away by water and the coloring group would migrate to the material surface achieving variable colors. Based on these studies, herein, novel chromotropic dyes such as DSP, MSP, DNSP were successfully synthesized and were developed as chromotropic materials for the first time. Therefore, it may be an effective and durable functional dye with further potential applications in the field of indicators, probes and coating materials.

Results and Discussion

The introduction of the long alkyl chains (usually more than 12 C) into the skeleton is aiming to increase the surface activity of those dyes while that of the nitro group was focused on the regulation of the color transition point. In this experiment, we selected dodecyl and tetradecyl groups.

In this paper, we synthesized the following three compounds, as shown in Figure 1.

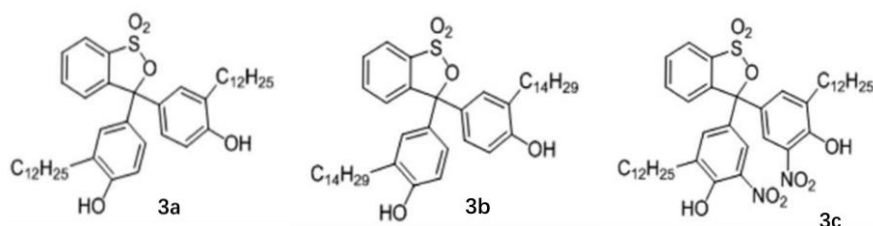
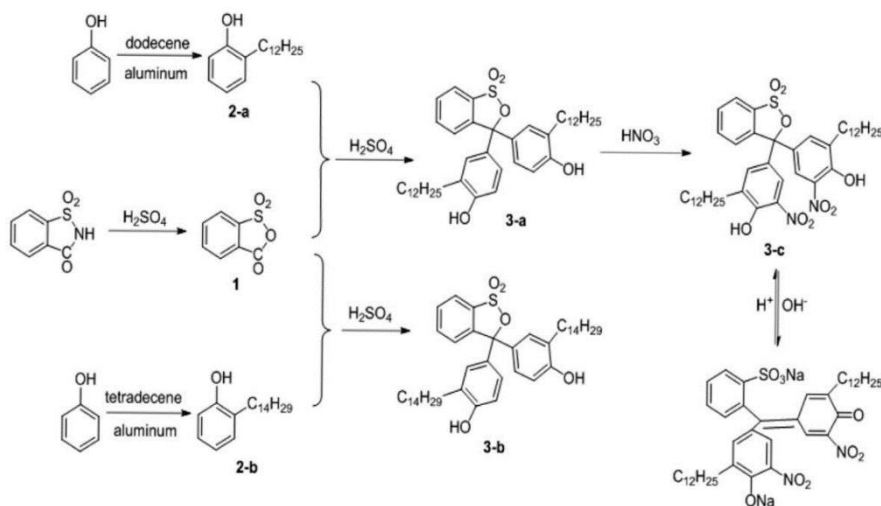


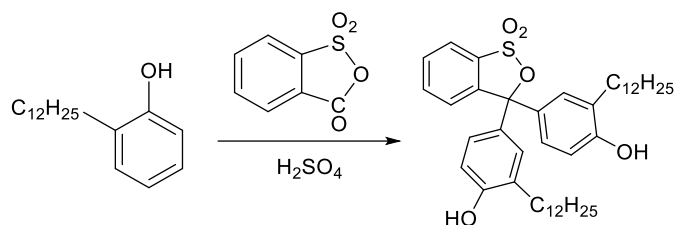
Figure 1. the structure of sulfonylephthalins **3a**, **3b**, **3c**.

The synthesis steps of the above compounds are divided into two steps, as shown in Scheme 1:



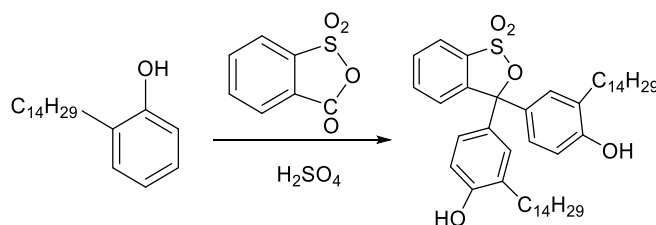
Scheme 1. Synthesis procedure of **3a**, **3b**, and **3c**.

Exploration of the synthetic conditions for **3a**: at first, we use ZnCl_2 , which is a traditional Lewis acid, in the preparation of phenol red as a catalyst for the reaction of sulfobenzoic anhydride and dodecylphenol. Unfortunately, the reaction did not take place, despite long heat times. Then, we considered that perhaps the solid-state catalyst (ZnCl_2) was not working well, so we introduced Tin(IV) chloride to catalyze the reaction. However, the results were unsatisfactory. Thus, H_2SO_4 were chosen as an Ideal catalyst in this paper due to its strong acidity and strong dehydration activity. The reaction results are shown in Table 1.

Table 1. Optimization of the reaction conditions for the synthesis of **3a**

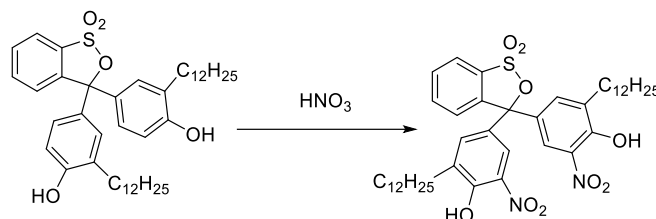
S.No	Compound1(mmol)	Compound2a(mmol)	Acid(mmol)	Temp(°C)	Time(h)	Yield(%)
1	22	48	(98%V/V H ₂ SO ₄) 36	100~110	5	40
2	22	48	(98%V/V H ₂ SO ₄) 36	100~110	6	40
3	22	48	(98%V/V H ₂ SO ₄)36	110~120	5	41
4	22	50	(98%V/V H ₂ SO ₄)40	120~130	5	39
5	22	50	(98%V/V H ₂ SO ₄)40	130~140	5	36
6	22	52	(98%V/V H ₂ SO ₄)50	140~150	5	35
7	22	48	ZnCl ₂ ,36	100~110	5	-
8	22	48	ZnCl ₂ ,36	100~110	6	-
9	22	48	ZnCl ₂ ,36	110~120	5	-
10	22	50	ZnCl ₂ ,40	120~130	5	-
11	22	50	ZnCl ₂ ,40	130~140	5	-
12	22	52	ZnCl ₂ ,50	140~150	5	5
13	22	48	SnCl ₄ ,36	100~110	5	-
14	22	48	SnCl ₄ ,36	100~110	6	-
15	22	48	SnCl ₄ ,36	110~120	5	-
16	22	50	SnCl ₄ ,40	120~130	5	-
17	22	50	SnCl ₄ ,40	130~140	5	7
18	22	52	SnCl ₄ ,50	140~150	5	7

For the synthesis of **3b**, concentrated sulfuric acid was also chosen as catalyst, and the reaction results are shown in Table 2.

Table 2. Optimization of the reaction conditions for the synthesis of **3b**

S.No	Compound1(mmol)	Compound2b(mmol)	(98%V/V H ₂ SO ₄) (mmol)	Temp(°C)	Time(h)	Yield(%)
1	5.5	12	18	110~120	3	41
2	5.5	12	18	130~140	4	42
3	5.5	12	18	150~160	5	40
4	5.5	13	20	110~120	3	41
5	5.5	13	20	130~140	4	42
6	5.5	13	20	150~160	5	42

Once we introduced the donor group on the phenol red skeleton, we were curious to see what would happen to the reintroduction of the electron-withdrawing nitro group, as a typical electron-withdrawing group. The optimization of the nitration reagent is shown in Table 3.

Table 3. Optimization of the nitration reagent of **3c**

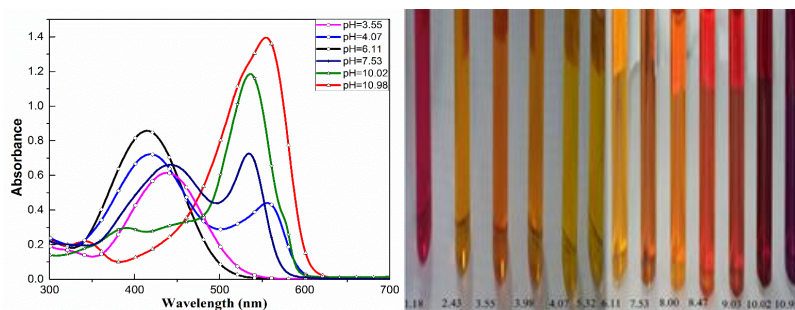
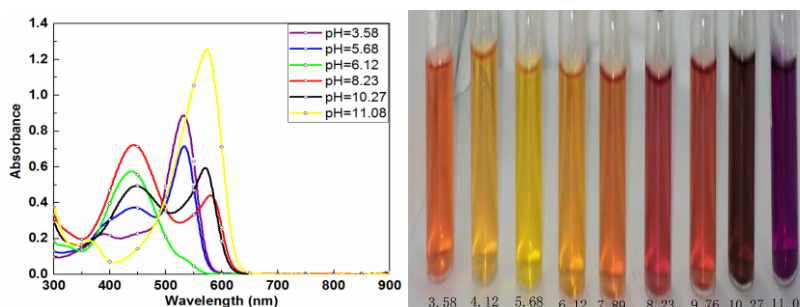
reagent	Ratio (v/v/v)	Yield (%)
nitric acid 98%, sulfuric acid, acetic anhydride	1/0.05/10	15
nitric acid 65%, sulfuric acid, acetic anhydride	1.5/0.05/10	4
nitric acid 98%, sulfuric acid	1/0.05	0

The nitration reaction is sensitive to temperature and can be performed at room temperature, but since the reaction is exothermic, it needs to be carried out in a constant temperature water bath at 25 °C. The results are shown in Table 4.

Table 4. Optimization of the reaction temperature of **3c**

Temp(°C)	Yield(%)
0	0
10	10
25	16
50	0

CTPs analysis. UV-Vis spectra were recorded from 300 to 900 nm using a UV-7500 UV-Vis spectrophotometer (Keda Instruments, China). In this study, 5.5×10^{-4} mol/L dye/ethanol solutions (0.10 mL) were taken into 10 mL volumetric flasks, and then different pH aqueous solutions were added into the volumetric flasks to make sure that the dye solutions have the same concentration at a different pH.¹⁷ The UV-Vis absorption spectra are a significant analytical approach for the investigation of the discoloration performance, which can indicate the color change point (pH) and the color at different pH. The products **3a**, **3b** and **3c** showed a considerable sensitivity in color change. As shown in Figures 2 and 3, the gradient color of **3a** and **3b** is attributed to the change of pH (1-11). However, the color of **3c** (Figure 4) is quite different due to the introduction of the nitro group, which changed the color from yellow to blue as the change of pH (6.12~8.00). The CTPs of **3a** and **3b** became higher because of the introduction of an electron-donating group increasing the pKa of the molecule. However, the dye **3c**, with the electron-withdrawing nitro group, showed the opposite result. Figure 2 suggests that **3a** shows a different color at a different pH, and that it can be used in conditions with a wide range of pH, while **3c** can be used in a precision test for the pH. The introduction of an electron donor group (such as alkyl) and an electron withdrawing group (such as nitro group) can make the CTP of the chromotropic dyes move. The electron withdrawing group makes it move to the acidic direction, controlling the CTPs.¹⁸⁻²²

**Figure 2.** The UV-Vis spectra and photograph of DSP at different pH.**Figure 3.** The UV-Vis spectra and photograph of MSP at different pH.

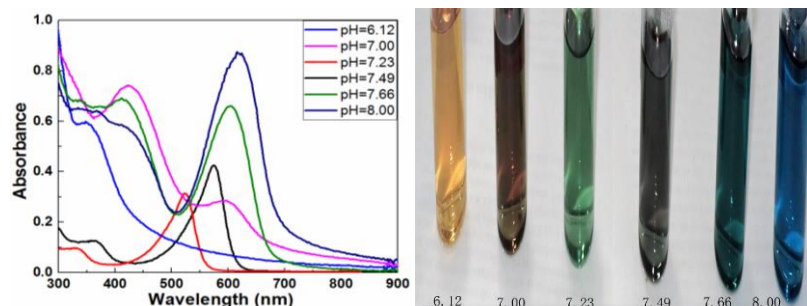


Figure 4. The UV-Vis spectra and photograph of DNSP at different pH.

Surface activity analysis. Because there are two hydrophobic alkyl groups and a hydrophilic sulfonic group and a hydroxyl group, the compounds show some surface activity. Therefore, the following experiments were carried out.

The surface tension was recorded on the OCA 40 optical contact angle measuring instrument (Dataphysics, Germany). For DSP, the solutions were 3.75×10^{-6} , 3.75×10^{-5} , 7.50×10^{-5} , 1.12×10^{-4} , 1.50×10^{-4} , 3.75×10^{-4} , 7.50×10^{-4} , 1.12×10^{-3} , 1.50×10^{-3} , 1.88×10^{-3} , 3.75×10^{-3} , 7.50×10^{-3} , 1.12×10^{-2} , 1.50×10^{-2} , 1.88×10^{-2} , 3.75×10^{-2} mol/L, for MSP the solutions were 1.00×10^{-5} , 1.67×10^{-5} , 3.34×10^{-5} , 1.67×10^{-4} , 3.34×10^{-4} , 6.72×10^{-4} , 8.00×10^{-4} , 1.67×10^{-3} , 3.34×10^{-3} , 4.00×10^{-3} , 6.72×10^{-3} , 1.67×10^{-2} , 3.34×10^{-2} , 4.00×10^{-2} mol/L and for DNSP the solutions were 4.00×10^{-6} , 8.00×10^{-6} , 1.20×10^{-5} , 1.60×10^{-5} , 2.00×10^{-5} , 1.00×10^{-4} , 1.60×10^{-4} , 3.20×10^{-4} , 8.00×10^{-4} , 1.20×10^{-3} , 1.60×10^{-3} , 3.20×10^{-3} , 1.20×10^{-2} , 1.60×10^{-2} mol/L. The experiments were performed at 25 °C using the optical contact angle measuring instrument to measure the surface tension. The blank of a deionized water solution is 72 mN/m.²³⁻²⁸ From Figure 5, it can be noted that there are small differences among the synthesized dyes' cmc and the values are shown in Table 5.

Related to their surface activity, the dyes were added to polymers to test if they can improve the materials' hydrophilicity. In this study, two materials polyvinyl chloride (PVC) and poly caprolactone (PCL) were chosen as they are quite commonly used. The polymer/dye films were obtained from a slow drying in air of the solutions of the polymer and dye dissolved in THF with a mass ratio of 1:10 (dye: polymer). The contact angles of water were recorded on the OCA 40 optical contact angle measuring instrument (Dataphysics, Germany) and are shown in Figure 6. As compared with the blank polymer film, the films with dyes show a much better hydrophilicity. Because of the long alkyl chain and the hydroxy group, the dyes can assemble neatly on the surface with the alkyl group oriented inside and the hydroxy group oriented outside.²⁹⁻³¹

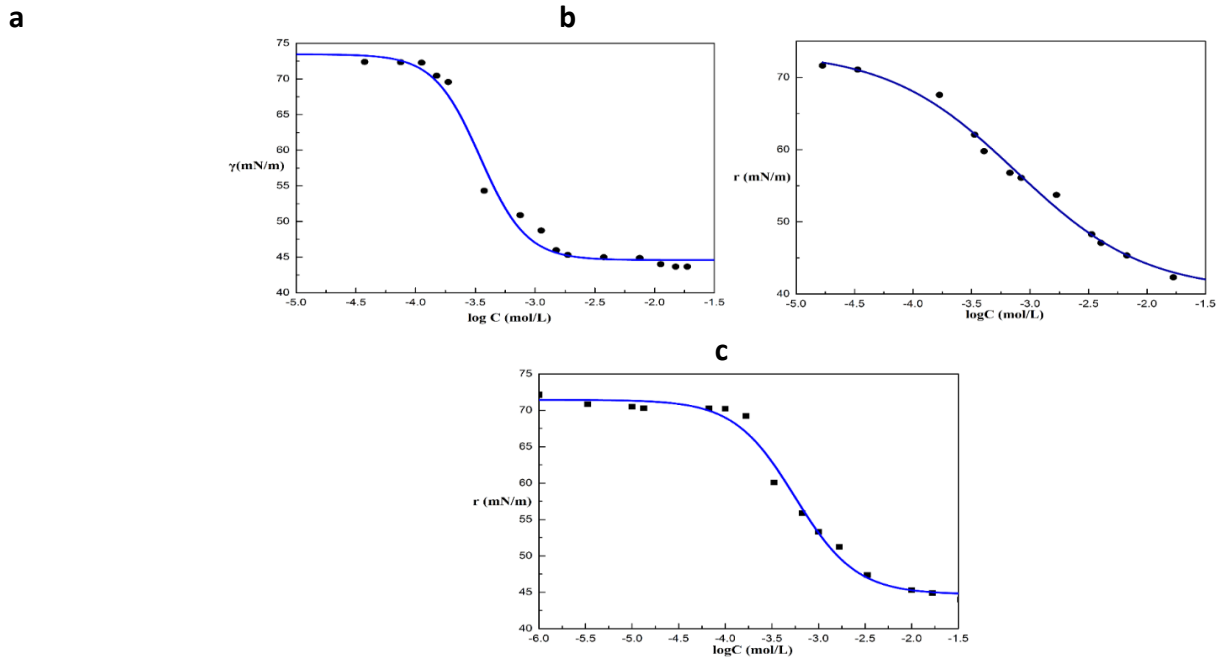


Figure 5. The γ -log C Curve of Dyes in Water Solution (a: DSP; b: MSP; c: DNSP).

Table 5. The Critical Micelle Concentration of Synthesized Dyes

Dye	cmc (mol/L)
DSP	$3.47 \cdot 10^{-4}$
MSP	$5.62 \cdot 10^{-4}$
DNSP	$3.12 \cdot 10^{-4}$

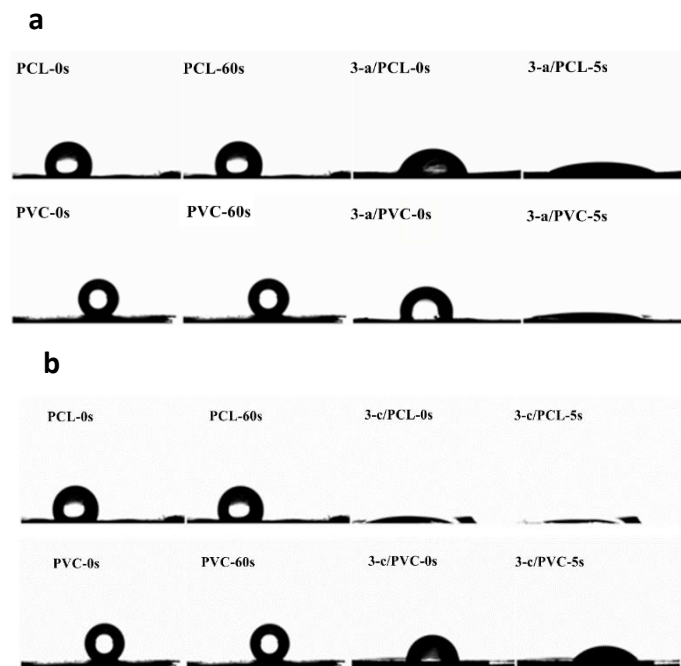


Figure 6. The Changes of Water Contact Angle with the Adding of Dye in the Different Polymer (a: DSP; b: DNSP.)

Water-resistance analysis. The polymer/dye films were obtained from a slow drying in air of the solutions of polymer and dye dissolved in THF with a mass ratio of 1:10 (dye: polymer).³²⁻³⁵ The films were put into 10 mL thermostatic pure water (parallel experiments at 35 °C and 50 °C were conducted). The water was poured out and another 10 mL thermostatic pure water was added into the tube every ten minutes. The poured water was measured by a UV-visible spectra photometer. With the same principle as mentioned above, the quantitative calculation of the dyes released from the films was performed. The quantitative calculation of the photolytic dyes can be made according to the Lambert-Beer's law ($A=KC$). In the cumulative % release amount-time graph, the ordinate of the graph is $\sum C_i/C_0\%$ and the abscis is time (min). The maximum absorption wavelengths for DSP, MSP, DNSP and phenolsulfonphthalein were measured at 413 nm, 440 nm, 400 nm and 458 nm, respectively. Phenolsulfonphthalein was chosen as comparison in this experiment to test if the synthesized dyes have a better water resistance performance than the skeleton compound (phenolsulfonphthalein). From Figure 7 and Figure 8, it can be seen that the water resistance performance of the synthesized dyes in PVC and PCL are much better than that of the phenolsulfonphthalein. In the dye/PCL system, the cumulative release of DSP and MSP is no more than 2% and that of DNSP is no more than 3.5%, however that of phenolsulfonphthalein is almost 20%. In the dye/PVC system, the cumulative release of DSP and MSP is no more than 3% and that of DNSP is no more than 5.5%, however that of phenolsulfonphthalein is almost 25%.

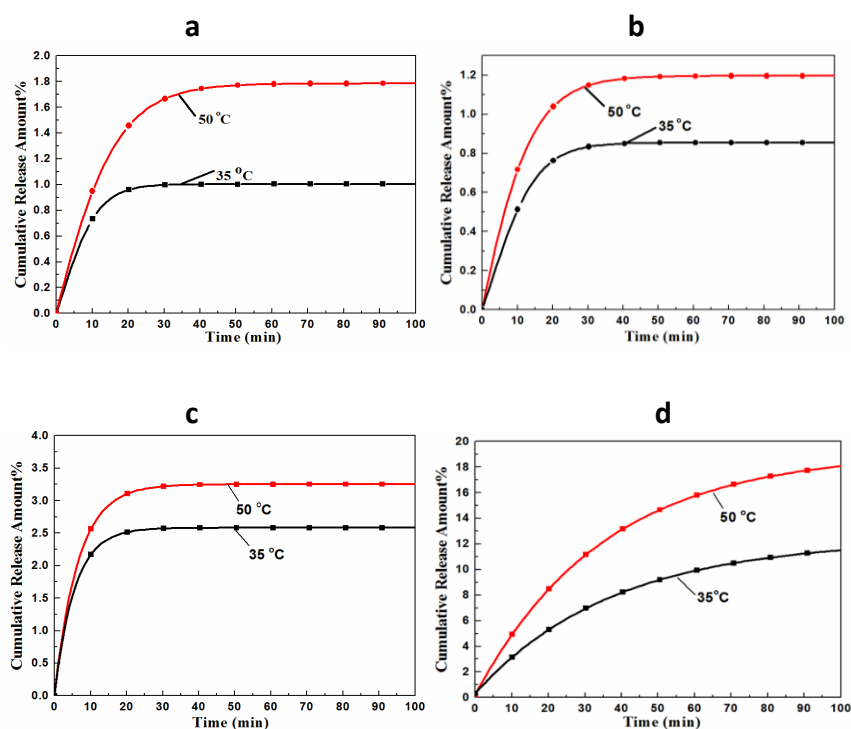


Figure 7. Dye/PCL System Cumulative % Release - Time Curve (a: DSP; b: MSP; c: DNSP; d: Phenolsulfonphthalein).

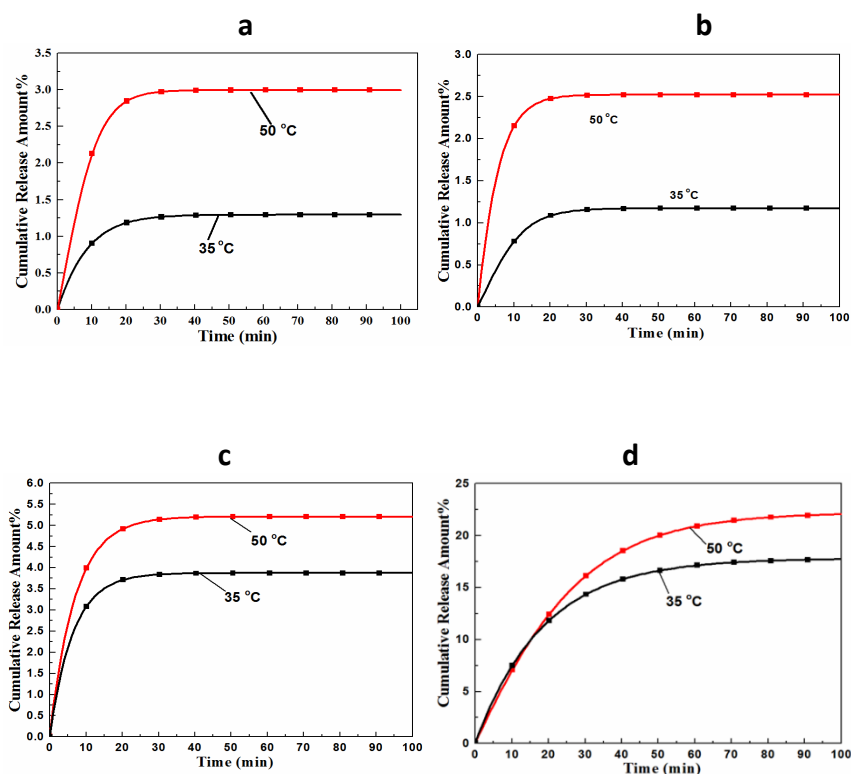


Figure 8. Dye/PVC System Cumulative % Release - Time Curve (a: DSP; b: MSP; c: DNSP; d: Phenolsulfonphthalein).

Conclusions

In summary, three functional chromotropic dyes such as 3', 3''-dodecyl-2-sulfonyl phthalein, 3', 3''-myristyl-2-sulfonyl phthalein and 3', 3''-dodecyl-5', 5''-nitro -2-sulfonyl phthalein have been synthesized using saccharin and phenol as raw materials and all the products were well characterized. The result indicated that

1. The color of DSP and MSP with gradient changes of color is attributed to the change of pH (1-11), while the color of DNSP shows quite different behaviour due to the introduction of the nitro group, which changed from yellow to blue as the change of pH (6.12~8.00). The electron withdrawing group makes it move to the acidic direction achieving the purpose of controlling the CTPs.
2. There are two hydrophobic groups (long alkyl chains) and hydrophilic groups (sulfonic group and hydroxyl group) leading to some surface activity and small differences among the synthesized dyes' cmc.
3. The existence of the long chain alkyl group and hydroxyl group makes it possible that the dyes can assemble neatly on the surface of the polymer with the alkyl group oriented inside and the hydroxy group oriented outside to improve the polymers' hydrophilicity.
4. The water resistance performance of the synthesized dyes in PVC and PCL are much better than that of phenolsulfonphthalein because of the introduced functional groups.

Experimental Section

General. ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 101 MHz in $\text{DMSO-}d_6$. The chemical shifts (δ) are reported in ppm units relative to TMS as an internal standard for ^1H NMR and $\text{DMSO-}d_6$ for ^{13}C NMR spectra. Coupling constants (J) are reported in hertz (Hz) and multiplicities are indicated as follows: s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet); Elementar Analyzer Vario EL was obtained by VARIOEL III (Elementar); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; All the reagents were purchased from commercial sources (J&K Chemic, TCI, Acros, SCRC, HEOWNS), and used without further purification.

Synthesis of product 3a. Products **1**,¹⁵ **2a** and **2b**¹⁶ are obtained according to the references. Product **1** (4.005 g, 22.13 mmol) concentrated sulfuric acid (2.0 mL, 36 mmol) and product **2a** (12.676 g, 48.17 mmol) were added in a 100 mL three-necked flask with a reflux condensation at 100~110 °C for 5 h in an oil bath protected by N_2 . The reaction mixture was obtained and then purified by flash column chromatography (ethyl acetate/hexane 3:1) and recrystallized in an ether-petroleum ether system. Product **3a** was obtained as red powder in 40% yield with a melting point of 233.5~235.5 °C and can be dissolved in many organic solvents such as ethyl acetate, ethanol, ether and so on. The NMR spectrum and elemental analysis of **3a** ^1H NMR (400 MHz, DMSO) δ 8.87 (s, 2H), 8.01 (d, J 7.1 Hz, 1H), 7.66 (t, J 6.5 Hz, 2H), 7.31 (d, 1H), 7.14-6.59 (m, 6H), 1.72-0.47 (m, 50H) ^{13}C NMR (101 MHz, DMSO) δ 157.94, 155.11, 134.43, 133.62, 129.68, 126.65, 126.44, 126.40, 119.26, 119.18, 118.56, 115.99, 115.71, 37.15, 32.02, 32.01, 30.77, 30.72, 29.60, 29.56, 29.27, 27.71, 22.61, 21.26, 14.28. Elem. Anal. found: C 74.71, H 9.03, S 4.65; calculated: C 74.74, H 9.04, S 4.64.

Synthesis of product 3b. Product **1** (1.012 g, 5.56 mmol) concentrated sulfuric acid (1 mL) and product **2b** (4.178 g, 13.13 mmol) were added in a 100 mL three-necked flask with a reflux condensation at 110~120 °C for 3 h in an oil bath protected by N_2 ^[36]. Compared with **3a**, the product **3b** was afforded as dark red powder in 41% yield with a melting point of 222.1~226.7 °C through the same purification method and also has the same solubility property. The NMR spectrum and elemental analysis of **3b** ^1H NMR (400 MHz, DMSO) δ 8.83 (s, 2H), 8.03 (d, J 7.5 Hz, 1H), 7.88-7.53 (m, 2H), 7.52-7.25 (m, 1H), 7.17 – 6.58 (m, 6H), 1.72-0.43 (m, 58H) ^{13}C NMR (101 MHz, DMSO) δ 157.84, 155.08, 134.43, 133.65, 129.68, 126.80, 126.44, 126.40, 119.26, 119.18, 119.14, 115.69, 115.41, 36.95, 31.89, 31.84, 29.77, 29.62, 29.60, 29.56, 29.27, 27.71, 27.49, 22.61, 21.26, 14.31, 14.28. Elem. Anal. found: C 75.54, H 9.45, S 4.28; calculated: C 75.56, H 9.44, S 4.29.

Synthesis of product 3c. The mixture consisting of product **3a** (5.012 g, 7.26 mmol) tetrachloromethane (30.0 mL), 2 drops of concentrated sulfuric acid, acetic anhydride (7.5 mL) and fuming nitric acid (0.8 mL, 2.2 equivalent) was stirred at room temperature for 1 h and was then added 20 mL saturated NaOH aqueous solution after removing the tetrachloromethane. Meanwhile the system began to change to blue as the product **3c** turning to its quinone structure (sodium salt) in the solution and subsequently was washed with petroleum ether and extracted with ethyl acetate. The product of sodium salt of **3c** was gained as blue-green powder in 38% yield with a melting point >300 °C and can be dissolved in ethyl acetate, ethanol, acetone and so on. The NMR spectrum and elemental analysis of **3c**. ^1H NMR of sodium salt (400 MHz, DMSO) δ 7.93 (d, J 7.8 Hz, 1H), 7.53 (t, J 7.5 Hz, 1H), 7.51-7.39 (m, 2H), 7.37 (s, 1H), 7.33-7.12 (m, 2H), 7.05 (d, J 11.9 Hz, 1H), 1.72-0.46 (m, 50H). ^{13}C NMR of sodium salt (101 MHz, DMSO) δ 172.34, 170.61, 170.56, 157.81, 155.90, 155.65, 155.06, 133.54, 129.66, 129.65, 126.63, 126.33, 124.71, 124.52, 119.23, 119.11, 115.65, 115.35, 114.35, 36.99, 36.88, 31.87, 31.84, 31.48, 29.79, 29.60, 29.30, 29.25, 27.68, 27.52, 22.58, 21.35, 21.34, 21.17, 21.15, 21.04, 21.01, 18.88, 14.41, 14.40, 14.17, 14.13, 14.06. Elem. Anal. found: C 66.15, H 7.71, N 3.59, S 4.11; calculated: C 66.13, H 7.74, N 3.59, S 4.11.

Supplementary Material

^1H NMR, ^{13}C NMR and IR data for the title compounds.

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