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## Thermotropic Liquid-Crystalline Properties of Viologens Containing 4-n-alkylbenzenesulfonates†

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Article

# Thermotropic Liquid-Crystalline Properties of Viologens Containing 4-n-alkylbenzenesulfonates <sup>†</sup>

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<sup>†</sup> This article is dedicated to the memory of Dr. Ananda M. Sarker (1952–2018): deceased on 30 August 2018.

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**Abstract:** A series of viologens containing 4-n-alkylbenzenesulfonates were synthesized by the metathesis reaction of 4-n-alkylbenzenesulfonic acids or sodium 4-n-alkylbenzenesulfonates with the respective viologen dibromide in alcohols. Their chemical structures were characterized by Fourier Transform Infrared, <sup>1</sup>H and <sup>13</sup>C Nuclear Magnetic Resonance spectra and elemental analysis. Their thermotropic liquid-crystalline (LC) properties were examined by differential scanning calorimetry and polarizing optical microscopy. They formed LC phases above their melting transitions and showed isotropic transitions. As expected, all the viologen salts had excellent stabilities in the temperature range of 278–295 °C as determined by thermogravimetric analysis.

**Keywords:** viologens; 4-n-alkylbenzenesulfonic acids; metathesis reaction; ionic liquid crystals; thermotropic; smectic phase A; differential scanning calorimetry; polarizing optical microscopy; thermogravimetric analysis

## 1. Introduction

The 1,1'-dialkyl-4,4'-bipyridium salts are commonly known as viologens. They are an important class of dicationic salts and appropriately called advanced functional materials. The versatility of their applications arises from their redox properties, ionic conductivity, thermochromism, photochromism, and electrochromism [1]. These applications, to name a few, include electrochromic devices, molecular machines, organic batteries, and carbohydrate oxidation catalysts in alkaline fuel cells [2,3]. In addition, they were studied not only for the preparation of the ever-increasing class of ionic liquids with proper chemical modifications of cations and anions [4–12], but also for the preparation of ionic liquid crystals (ILCs) [7,13–24]. To mention several their chemical structures (I–VI) are given in Figure 1 as representative examples. Their LC phases are found to be dependent on both the chemical architecture of viologen moieties including dialkyl [13,17–19,23], asymmetric dialkyl [7], di(oligooxyethylene) [14,15], di(3,4,5-tri-n-alkoxybenzyl) [22], diphenyl [16,24], and 4-n-alkoxydiphenyl [24], and the chemical architecture of the anions are of varying sizes. The anions to date include bromide, iodide [14,15], <sup>−</sup>BF<sub>4</sub>, <sup>−</sup>PF<sub>6</sub> [22,24], <sup>−</sup>OTf, <sup>−</sup>SCN, <sup>−</sup>NTf<sub>2</sub>, 4-n-alkylsulfonates [24], 4-n-alkylbenzenesulfonates [16], and 3,4,5-tri-n-dodecyloxybenzenesulfonate [23]. Recently, their use in energy-related systems stemming from the unique properties of redox properties as well as LC properties of viologen moieties has given the boost for the exploration of this class of materials. Undoubtedly, this field is an active area of research for a decade or so that is manifested in a number of excellent reviews on this important topic [2,25–31].

As a continuation of our research efforts in the ILCs, herein, we describe the synthesis of a series of symmetric viologen compounds with 4-n-alkylbenzenesulfonates ( $n = 6, 7, 8, 9, 10, 12, 14, 16, 18$ ); wherein  $n$  denotes the carbon atoms in the alkyl chain), determine both their chemical structures by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra—as well as elemental analysis—and the characterization of their thermotropic LC properties by several experimental techniques, including differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). Their thermal stabilities by thermogravimetric analysis (TGA) are also included. The general structures and designations for these synthesized viologen salts, and their synthetic routes are shown in Scheme 1. The LC properties of this series of symmetric viologen salts with these anions enable one to establish the structure-property relationship of this important class of ILCs. Additionally, in contrast to other anions, reports of ILCs on these anions are relatively less studied [16].

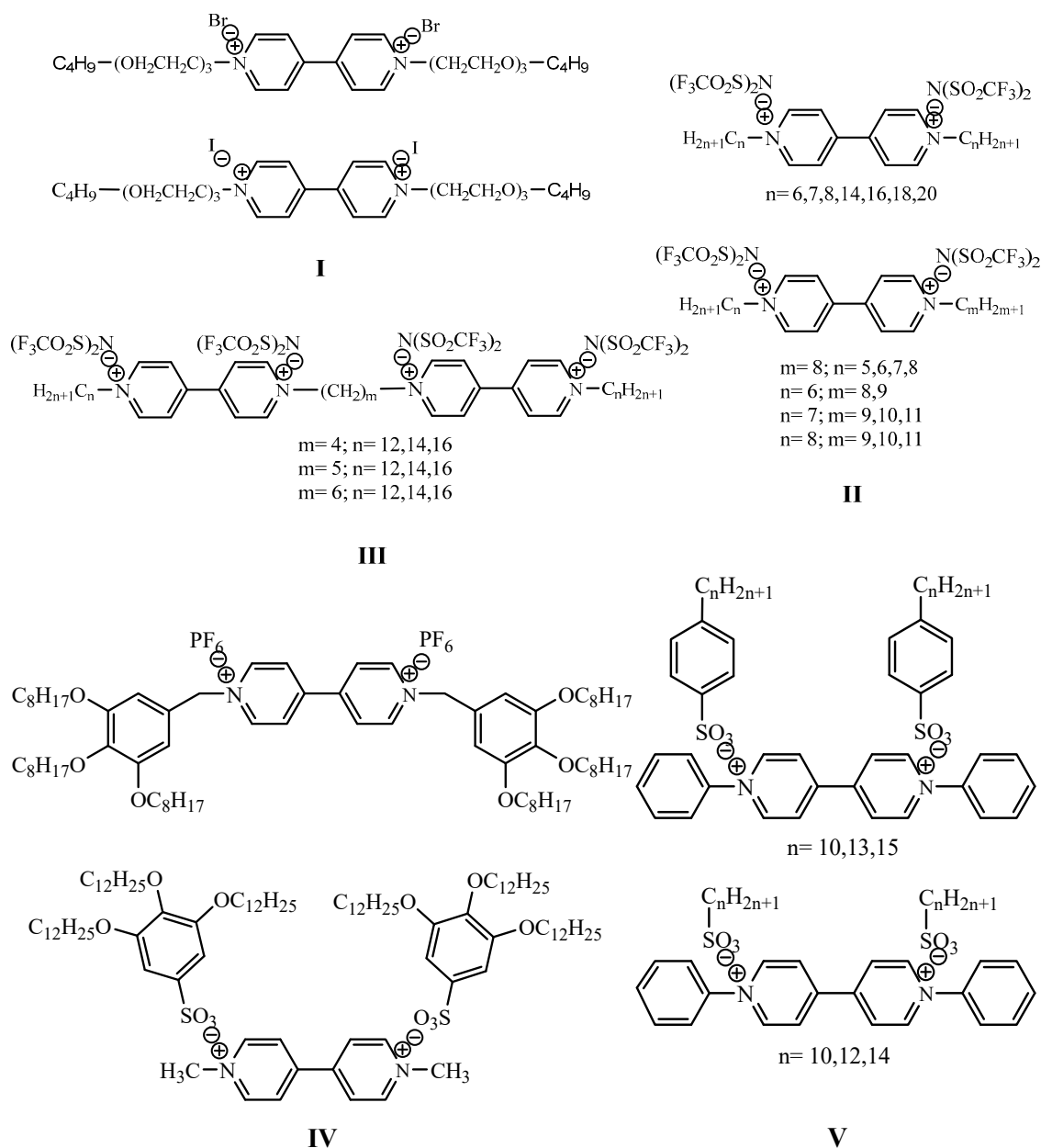
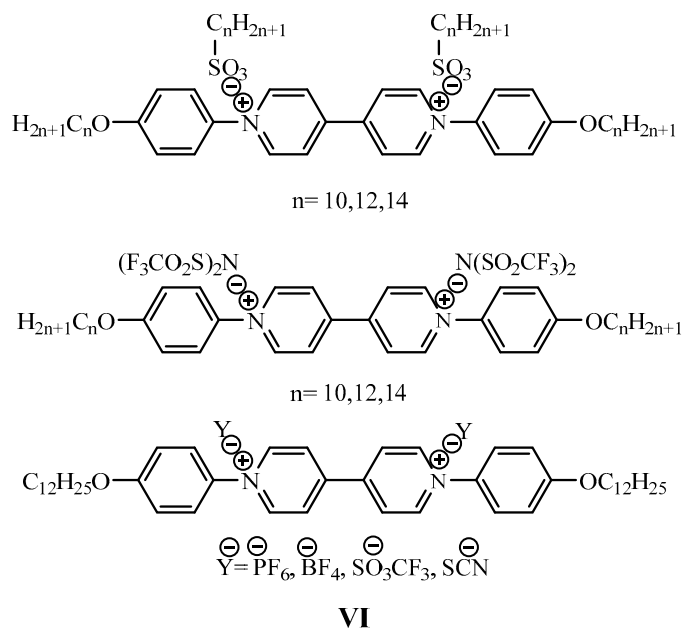
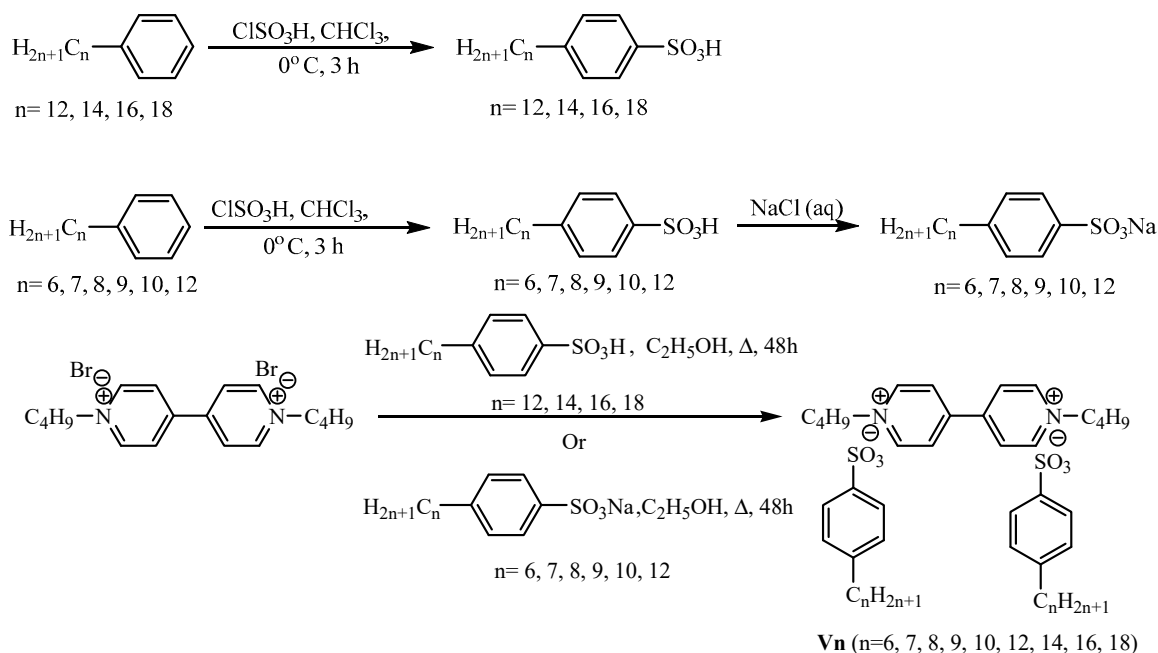


Figure 1. Cont.



**Figure 1.** Some of the representative ILCs based on viologens that exhibits smectic phases and columnar LC phases depending on their chemical architectures.



**Scheme 1.** Synthetic routes for the preparation of symmetric viologen salts containing 4-n-alkylbenzenesulfonates (Vn).

## 2. Materials and Methods

### 2.1. Instrumentation

The Fourier transform infrared (FTIR) spectra of several viologen salts were recorded with a Shimadzu IRPrestige FTIR analyser with their neat films on KBr pellets. The <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra of the symmetric viologen salts, whenever possible, in CD<sub>3</sub>OD were recorded by using VNMR 400 spectrometer operating at 400 and 100 MHz at room temperature. Elemental analysis was performed by Atlanta Microlab Inc., Norcross, GA. Differential scanning calorimetry (DSC) measurements of these salts were conducted on TA module DSC Q200 series in

nitrogen at heating and cooling rates of 10 °C/min. The temperature axis of the DSC thermograms was calibrated before use with reference standards of high purity indium and tin. Their thermogravimetric analyses (TGA) were performed using a TGA Q50 instrument at a heating rate of 10 °C/min in nitrogen. Polarizing optical microscopy (POM) studies of these salts were performed by sandwiching each of them between a standard microscope glass slide and coverslip. The salts were heated and cooled on a Mettler hotstage (FP82HT) and (FP90) controller; and observations of the phases were made between crossed polarizers of an Olympus BX51 microscope. In short, salts were heated above their clearing transitions and cooled at 10 °C/min to room temperature, with brief pauses to collect images and observe specific transitions.

### 2.2. General Procedure for the Synthesis of 4-n-alkylbenzenesulfonic Acids ( $n = 12, 14, 16, 18$ )

The synthesis of 4-n-alkylbenzenesulfonic acids was carried out in accordance with the literature procedures [32,33]. The preparation of dodecylbenzenesulfonic acid from n-dodecylbenzene by using chlorosulfonic acid in chloroform was described as a typical procedure [33].

Chloroform (20 mL) was added to n-dodecylbenzene (2.26 g, 9.17 mmol) to form a colorless solution in a 50 mL flask that was placed in an ice bath. Chlorosulfonic acid (1.28 g, 11.0 mmol) was added slowly to the reaction flask over 10 min, resulting in a yellow viscous solution. The reaction mixture was stirred for 3 h inside an ice bath. At the end of the reaction, the reaction flask was taken out of the ice bath to reach the ambient temperature. The organic solvent was removed using a rotary evaporator. The product was dried overnight in vacuum to remove any residual solvent. It was then purified by washing with the excess toluene and dried again in vacuum to yield the white product (2.20 g, 73%). Similarly, 4-n-tetradecylbenzene- (2.96 g, 8.35 mmol), 4-n-hexadecylbenzene (2.69 g, 7.04 mmol), and 4-n-octadecylbenzenesulfonic (2.79 g, 6.80 mmol) were prepared from the corresponding n-alkylbenzenes with the yields of 74, 67, and 70%, respectively.

### 2.3. General Procedure for the Synthesis of Sodium 4-n-alkylbenzenesulfonates ( $n = 6, 7, 8, 9, 10, 12$ )

The modified literature procedure [34] was adopted for the synthesis of sodium 4-n-octylbenzenesulfonate, as an example, is as follows. Chloroform (20 mL) was added to n-octylbenzene (2.60 g, 13.7 mmol) to form a colorless solution in an Erlenmeyer flask that was set in an ice bath. Chlorosulfonic acid (1.90 g, 16.3 mmol) was added dropwise to the reaction flask, forming a yellow solution. The reaction mixture was stirred for 3 h in an ice bath. At the end of the reaction, the reaction flask was taken out of the ice bath to reach the ambient temperature. The organic solvent from the reaction mixture was removed using a rotary evaporator to yield the yellow viscous liquid. A saturated sodium chloride solution was carefully added to the viscous liquid on stirring to form the white precipitate of the product. It was then filtered and washed with a minimum quantity of water and excess toluene, respectively, to yield the white product (2.91 g, 9.95 mmol, 73%). Similarly, sodium 4-n-hexylbenzenesulfonate (3.02 g, 11.4 mmol), sodium 4-n-heptylbenzenesulfonate (2.91 g, 10.5 mmol), sodium 4-n-nonylbenzenesulfonate (3.00 g, 9.79 mmol), sodium 4-n-decylbenzenesulfonate (2.30 g, 7.18 mmol), and sodium 4-n-dodecylbenzenesulfonate (2.90 g, 8.85 mmol) were prepared from the corresponding n-alkylbenzenes with the yields of 75, 73, 74, 57, and 76%, respectively.

### 2.4. Synthesis of 1,1'-di-n-butyl-4,4'-bipyridinium Dibromide

This salt was prepared according to the literature procedure [18].

### 2.5. General Procedure for the Synthesis 1,1'-di-n-butyl-4,4'-bipyridinium di(4-n-alkylbenzenesulfonates) by Metathesis Reaction (V12, V14, V16, V18) Using 4-n-alkylbenzenesulfonic Acid [35]

Ethanol (35 mL) was slowly added to 1,1'-di-n-butyl-4,4'-bipyridinium dibromide (0.93 g, 2.16 mmol) in a 100 mL round-bottomed flask and heated on stirring to form a clear solution. The 4-dodecylbenzenesulfonic acid (1.50 g, 4.60 mmol) was then slowly added to the hot solution, and the reaction flask was heated to reflux for 48 h. The solvent was reduced using a rotary evaporator. Then

cold water was added to dissolve the HBr acid produced in the metathesis reaction to yield the product as white precipitate. It was collected by filtration and washed with excess water until the filtrate was neutral to litmus paper to yield the white product. Finally, **V12** was washed with ether and dried in vacuum to yield (1.77 g, 1.88 mmol, 87%). IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3507, 3433, 3125, 3051, 2959, 2920, 2851, 1640, 1601, 1562, 1466, 1450, 1404, 1377, 1238, 1211, 1188, 1123, 1034, 1011, 953, 891, 841, 822, 779, 718, 694, 675, 610. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz, ppm)  $\delta$  9.24 (d, *J* = 6.8 Hz, 4H), 8.66 (d, *J* = 6.8 Hz, 4H), 7.71 (d, *J* = 8.4 Hz, 4H), 7.23 (d, *J* = 8.4 Hz, 4H), 4.74 (t, *J* = 7.6 Hz, 4H), 2.63 (t, *J* = 7.6 Hz, 4H), 2.08–2.01 (m, 4H), 1.63–1.59 (m, 4H), 1.48–1.41 (m, 4H), 1.32–1.28 (m, 36H), 1.02 (t, *J* = 7.4 Hz, 6H), 0.89 (t, *J* = 7.4 Hz, 6H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 100 MHz, ppm):  $\delta$  149.79, 145.62, 145.23, 142.42, 127.89, 126.85, 125.52, 61.61, 35.21, 33.00, 31.65, 31.14, 29.36, 29.33, 29.30, 29.16, 29.05, 28.87, 22.31, 19.03, 13.04, 12.34. Anal. Calcd. for C<sub>54</sub>H<sub>84</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>·H<sub>2</sub>O (939.40): C 69.04, H 9.23, N 2.98, S 6.83; found: C 69.03, H 9.41, N 2.97, S 6.76. Similarly, **V14**, **V16**, and **V18** were prepared by using the corresponding 4-*n*-alkylbenzenesulfonic acid with the yields of 93, 92, and 93%, respectively. Data for **V14**: <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz, ppm)  $\delta$  9.24 (d, *J* = 6.8 Hz, 4H), 8.66 (d, *J* = 6.8 Hz, 4H), 7.71 (d, *J* = 8.4 Hz, 4H), 7.23 (d, *J* = 8.4 Hz, 4H), 4.74 (t, *J* = 7.6 Hz, 4H), 2.63 (t, *J* = 7.6 Hz, 4H), 2.07–2.02 (m, 4H), 1.63–1.59 (m, 4H), 1.49–1.43 (m, 4H), 1.32–1.28 (m, 44H), 1.02 (t, *J* = 7.4 Hz, 6H), 0.89 (t, *J* = 7.4 Hz, 6H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 100 MHz, ppm):  $\delta$  149.79, 145.63, 145.23, 142.42, 127.87, 126.85, 125.51, 61.63, 35.20, 33.00, 31.64, 31.13, 29.36, 29.33, 29.15, 29.04, 28.86, 22.30, 19.03, 13.02, 12.36 (Figure S7 in the Supplementary Materials). Anal. Calcd. for C<sub>58</sub>H<sub>94</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>·H<sub>2</sub>O (995.51): C 69.98, H 9.52, N 2.81, S 6.44; found: C 70.35, H 9.58, N 2.83, S 6.39. Data for **V16**: <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz, ppm)  $\delta$  9.24 (d, *J* = 6.8 Hz, 4H), 8.66 (d, *J* = 6.8 Hz, 4H), 7.71 (d, *J* = 8.4 Hz, 4H), 7.23 (d, *J* = 8.4 Hz, 4H), 4.74 (t, *J* = 7.6 Hz, 4H), 2.63 (t, *J* = 7.6 Hz, 4H), 2.08–2.01 (m, 4H), 1.63–1.59 (m, 4H), 1.48–1.41 (m, 4H), 1.32–1.28 (m, 52H), 1.02 (t, *J* = 7.4 Hz, 6H), 0.89 (t, *J* = 7.4 Hz, 6H). Because of limited solubility in CD<sub>3</sub>OD, its <sup>13</sup>C NMR was not recorded (Figure S8). Anal. Calcd. for C<sub>62</sub>H<sub>100</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>·H<sub>2</sub>O (1051.61): C 70.81, H 9.78, N 2.66, S 6.10; found: C 70.57, H 9.81, N 2.53, S 6.04. Data for **V18**: <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz, ppm)  $\delta$  9.24 (d, *J* = 6.8 Hz, 4H), 8.66 (d, *J* = 6.8 Hz, 4H), 7.71 (d, *J* = 8.4 Hz, 4H), 7.23 (d, *J* = 8.4 Hz, 4H), 4.74 (t, *J* = 7.6 Hz, 4H), 2.64 (t, *J* = 7.6 Hz, 4H), 2.07–2.04 (m, 4H), 1.63–1.59 (m, 4H), 1.49–1.44 (m, 4H), 1.32–1.28 (m, 60H), 1.03 (t, *J* = 7.4 Hz, 6H), 0.89 (t, *J* = 7.4 Hz, 6H). Because of limited solubility in CD<sub>3</sub>OD, its <sup>13</sup>C NMR was not recorded (Figure S9). Anal. Calcd. for C<sub>66</sub>H<sub>110</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>·H<sub>2</sub>O (1107.72): C 71.56, H 10.01, N 2.53, S 5.79; found: C 71.35, H 10.14, N 2.51, S 5.72.

#### 2.6. General Procedure for the Synthesis 1,1'-di-*n*-butyl-4,4'-bipyridinium di(4-*n*-alkylbenzenesulfonates) by Metathesis Reaction (V6, V7, V8, V9, V10, V12,) Using Sodium 4-*n*-alkylbenzenesulfonate

Ethanol (35 mL) was slowly added to 1,1'-di-*n*-butyl-4,4'-bipyridinium dibromide (0.47 g, 1.09 mmol) in a 100 mL round-bottomed flask and heated on stirring to form a clear solution. Sodium 4-*n*-dodecylbenzenesulfonate (0.83 g, 2.40 mmol) was then slowly added to the hot solution, and the reaction flask was then heated to reflux for 48 h. The solvent was reduced using a rotary evaporator. Then cold water was added to dissolve the NaBr produced in the metathesis reaction to yield the product as a white precipitate. It was collected by filtration and washed with excess water until the filtrate gave the negative test with aqueous AgNO<sub>3</sub> solution to yield the white product. Finally, **V12** was washed with ether and dried in vacuum to yield (0.68 g, 0.74 mmol, 68%). Its spectral characteristics and elemental analysis were identical to those of **V12** prepared by using 4-*n*-dodecylbenzenesulfonic acid.

Similarly, in the cases of **V6–V10**, methanol (rather than ethanol) was used for this metathesis reaction for better solubility, by using the corresponding sodium 4-*n*-alkylbenzenesulfonates. Their yields were (1.77 g, 88%), (1.89 g, 93%), (1.25 g, 89%), (1.90 g, 96%), and (1.50 g, 75%), respectively. Data for **V6**: <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400 MHz, ppm)  $\delta$  9.24 (d, *J* = 6.8 Hz, 4H), 8.66 (d, *J* = 6.8 Hz, 4H), 7.71 (d, *J* = 8.4 Hz, 4H), 7.24 (d, *J* = 8.4 Hz, 4H), 4.74 (t, *J* = 7.6 Hz, 4H), 2.65 (t, *J* = 7.6 Hz, 4H), 2.09–2.01 (m, 4H), 1.63–1.57 (m, 4H), 1.50–1.41 (m, 4H), 1.36–1.30 (m, 12H), 1.04 (t, *J* = 7.4 Hz, 6H), 0.89 (t, *J* = 7.4 Hz, 6H). <sup>13</sup>C NMR (CD<sub>3</sub>OD, 100 MHz, ppm):  $\delta$  149.79, 145.62, 145.23, 142.39, 127.88, 126.84, 125.49, 61.62, 35.19, 32.99, 31.38, 31.07, 28.50, 22.22, 19.02, 12.96, 12.37, 12.36. Anal. Calcd. for C<sub>42</sub>H<sub>60</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>·H<sub>2</sub>O

(771.08): C 65.42, H 8.10, N 3.63, S 8.32; found: C 65.29, H 8.12, N 3.55, S 8.27. Data for **V7**:  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz, ppm)  $\delta$  9.24 (d,  $J = 6.8$  Hz, 4H), 8.66 (d,  $J = 6.8$  Hz, 4H), 7.71 (d,  $J = 8.4$  Hz, 4H), 7.24 (d,  $J = 8.4$  Hz, 4H), 4.74 (t,  $J = 7.6$  Hz, 4H), 2.65 (t,  $J = 7.6$  Hz, 4H), 2.06–2.03 (m, 4H), 1.63–1.59 (m, 4H), 1.48–1.43 (m, 4H), 1.33–1.25 (m, 16H), 1.04 (t,  $J = 7.4$  Hz, 6H), 0.89 (t,  $J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 100 MHz, ppm):  $\delta$  149.79, 145.62, 145.23, 142.39, 127.88, 126.84, 125.49, 61.62, 35.18, 32.99, 31.53, 31.11, 28.81, 22.24, 19.02, 12.98, 12.36. Anal. Calcd. for  $\text{C}_{44}\text{H}_{64}\text{N}_2\text{O}_6\text{S}_2 \cdot \text{H}_2\text{O}$  (799.13): C 66.13, H 8.32, N 3.51, S 8.02; found: C 66.20, H 8.20, N 3.52, S 7.93. Data for **V8**: IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3507, 3433, 3125, 3051, 2955, 2924, 2851, 1643, 1562, 1450, 1377, 1238, 1211, 1188, 1119, 1034, 1011, 845, 690, 606.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz, ppm)  $\delta$  9.24 (d,  $J = 6.8$  Hz, 4H), 8.66 (d,  $J = 6.8$  Hz, 4H), 7.69 (d,  $J = 8.4$  Hz, 4H), 7.22 (d,  $J = 8.4$  Hz, 4H), 4.74 (t,  $J = 7.6$  Hz, 4H), 2.65 (t,  $J = 7.6$  Hz, 4H), 2.09–2.01 (m, 4H), 1.63–1.59 (m, 4H), 1.51–1.41 (m, 4H), 1.30–1.26 (m, 20H), 1.00 (t,  $J = 7.4$  Hz, 6H), 0.87 (t,  $J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 100 MHz, ppm):  $\delta$  149.79, 145.62, 145.24, 142.41, 127.89, 126.85, 125.51, 61.63, 35.20, 33.00, 31.58, 31.12, 29.11, 28.97, 28.85, 22.28, 19.04, 19.03, 13.01, 12.38. Anal. Calcd. for  $\text{C}_{46}\text{H}_{68}\text{N}_2\text{O}_6\text{S}_2 \cdot \text{H}_2\text{O}$  (827.19): C 66.79, H 8.53, N 3.39, S 7.75; found: C 66.56, H 8.73, N 3.39, S 7.76. Data for **V9**:  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz, ppm)  $\delta$  9.24 (d,  $J = 6.8$  Hz, 4H), 8.66 (d,  $J = 6.8$  Hz, 4H), 7.71 (d,  $J = 8.4$  Hz, 4H), 7.24 (d,  $J = 8.4$  Hz, 4H), 4.74 (t,  $J = 7.6$  Hz, 4H), 2.65 (t,  $J = 7.6$  Hz, 4H), 2.09–2.01 (m, 4H), 1.63–1.59 (m, 4H), 1.49–1.43 (m, 4H), 1.32–1.28 (m, 24H), 1.03 (t,  $J = 7.4$  Hz, 6H), 0.89 (t,  $J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 100 MHz, ppm):  $\delta$  149.81, 145.64, 145.23, 142.38, 127.88, 126.85, 125.51, 61.64, 35.20, 33.01, 31.61, 31.12, 29.25, 29.15, 28.99, 28.84, 22.29, 19.03, 13.00, 12.37. Anal. Calcd. for  $\text{C}_{48}\text{H}_{72}\text{N}_2\text{O}_6\text{S}_2 \cdot 2\text{H}_2\text{O}$  (873.26): C 66.02, H 8.77, N 3.21, S 7.34; found: C 66.19, H 8.62, N 2.90, S 7.94. Data for **V10**: IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3507, 3433, 3125, 3051, 2959, 2920, 2851, 1639, 1450, 1238, 1211, 1188, 1122, 1034, 1011, 845, 694, 610.  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz, ppm)  $\delta$  9.24 (d,  $J = 6.8$  Hz, 4H), 8.65 (d,  $J = 6.8$  Hz, 4H), 7.71 (d,  $J = 8.4$  Hz, 4H), 7.23 (d,  $J = 8.4$  Hz, 4H), 4.74 (t,  $J = 7.6$  Hz, 4H), 2.63 (t,  $J = 7.6$  Hz, 4H), 2.08–2.00 (m, 4H), 1.62–1.59 (m, 4H), 1.50–1.41 (m, 4H), 1.31–1.28 (m, 28H), 1.03 (t,  $J = 7.4$  Hz, 6H), 0.89 (t,  $J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 100 MHz, ppm):  $\delta$  149.84, 145.61, 145.23, 142.35, 127.86, 126.84, 125.49, 61.63, 35.18, 33.01, 31.61, 31.10, 29.27, 29.13, 29.00, 28.82, 22.28, 19.02, 12.99, 12.34. Anal. Calcd. for  $\text{C}_{50}\text{H}_{76}\text{N}_2\text{O}_6\text{S}_2 \cdot \text{H}_2\text{O}$  (883.29): C 67.99, H 8.90, N 3.17, S 7.26; found: C 67.73, H 8.90, N 3.17, S 7.26 (Figure S1–S6).

### 3. Results and Discussion

In this study, several viologen salts containing 4-*n*-alkylbenzenesulfonates (**V6–V18**) were synthesized, characterized for their chemical structures by spectroscopic methods, and further characterized for their thermotropic LC properties by DSC and POM studies. The thermal stabilities of the viologen salts were also determined by TGA.

#### 3.1. Synthesis of Viologen Salts (V6–V18)

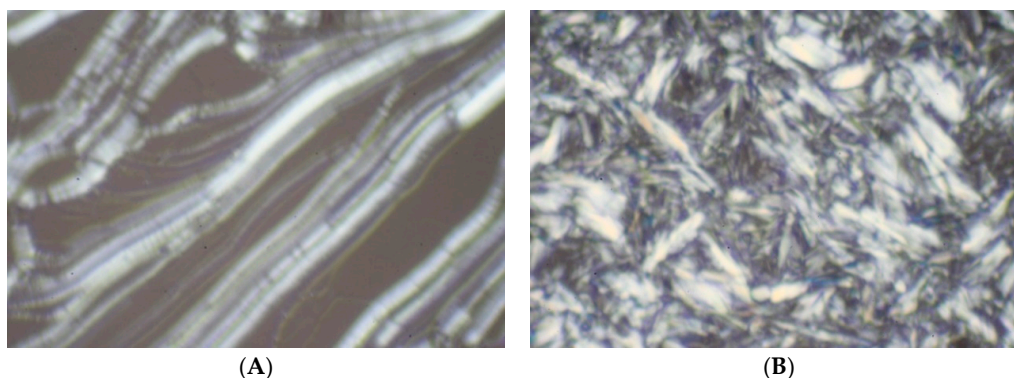
The synthetic methods of 4-*n*-alkylbenzenesulfonic acids ( $n = 12, 14, 16, 18$ ) and sodium 4-*n*-alkylbenzenesulfonates ( $n = 6, 7, 8, 9, 10, 12$ ) are shown in Scheme 1, which also includes the synthetic procedures of the viologen salts (**V6–V18**). We prepared the long alkyl chain sulfonic acids as hydrates in respectable yields, in contrast, we also prepared the short alkyl chain sodium 4-*n*-alkylbenzenesulfonates as anhydrous forms in respectable yields. Both sulfonic acids and sodium salts were successfully used in the metathesis reaction for the synthesis of **V6–V18** salts as monohydrates except **V9**, in this case, it was dihydrate from viologen dibromides. The yields of the metathesis reaction were also respectable.

#### 3.2. Thermotropic LC Properties of 4-*n*-alkylbenzenesulfonic Acids ( $n = 12, 14, 16, 18$ ) by DSC and POM [36–40]

Sodium 4-*n*-alkylbenzenesulfonates ( $n = 6, 7, 8, 9, 10$ ) showed melting transitions, that is, solid to isotropic transitions with high melting enthalpies at relatively high temperatures, as expected. Their melting peaks were at 296, 285, 275, 263, and 261 °C, respectively, as determined by DSC at a heating rate of 10 /min. Their thermal stability was in the range of 413–429 °C as determined by TGA at



a heating rate of 10 °C/min in nitrogen. In contrast, 4-n-alkylbenzenesulfonic acids ( $n = 12, 14, 16, 18$ ), as hydrates showed LC phases at relatively low melting temperatures and also showed isotropic transitions at high temperatures. Their melting peaks were at 40, 47, 52, and 65 °C, respectively, as determined by DSC at a heating rate of 10 °C/min, and isotropic peaks were at 134, 150, 144, and 141 °C, respectively. Figure 2 shows the LC phases of  $n = 12$  and  $n = 18$  sulfonic acids as examples. Their thermal stability was relatively low: as expected, there was 15% of water at about 130 °C.



**Figure 2.** POM textures of (A) 4-n-dodecylbenzenesulfonic acid at 100 °C and (B) 4-n-octadecylbenzenesulfonic acid at 110 °C displaying oily streaks and bâtonnets textures of SmA phases (magnification 400 ×).

### 3.3. Thermotropic LC Properties of (V6-V18) by DSC and POM [36–40]

Figure 3 displays the DSC thermograms of **V6** in the heating and cooling cycles. The first heating cycle clearly shows two endotherms. In conjunction with POM, the large endotherm corresponded to crystal–LC transition,  $T_m$ , at 185 °C, and the small endotherm corresponded to LC–isotropic transition,  $T_i$ , at 202 °C. In the first cooling cycle, it showed an exotherm that corresponded to the isotropic transition to LC transition. The absence of LC-crystallization exotherm in the first cooling cycle and the crystal-LC transition in the second heating cycle suggested it remained in the LC state and subsequently went to isotropization at 213 °C. Thus, it was found that **V6** showed the LC phase that underwent isotropic transition at high temperature. The DSC thermograms of **V7** were essentially identical to those of **V6** and hence the similar interpretations, suggesting that it also showed a  $T_m$  at 185 and a  $T_i$  at 199 °C. It went to isotropization at 214 °C in the second heating cycle. Like **V6**, **V7** formed a LC phase and an isotropic phase (Figure S10).

Figure 4 shows the DSC thermograms of **V8** in its heating and cooling cycles. In the first heating cycle, it showed three endotherms that were related to the crystal–LC phase ( $T_m$ ) at 181, LC–LC transition at 199, and LC–isotropic transition at 238 °C. In the first cooling cycle, isotropic–SmA, SmA–SmX, and SmX–crystalline transitions occurred at 227, 194, and 127 °C, respectively. Figure 5 shows the DSC thermograms **V9** in its heating and cooling cycles. In the first heating cycle, it showed the  $T_m$  at 178 and  $T_i$  at 268 °C. In between  $T_m$  and  $T_i$  there were two additional endotherms that were presumably related LC–LC transitions. In the first cooling cycle, the isotropic–SmA, SmA–crystal and crystal–crystal transition occurred at 250, 161, and 39 °C, respectively. The features for DSC thermograms of **V10–V18** in their heating and cooling cycles were essentially identical (Figure S11–S14). For example, **V10** showed  $T_m$  at 174 wherein it transformed into a LC phase and  $T_i$  at 202 °C as a small endotherm in the first heating cycle. In the first cooling cycle, the isotropic–LC transition was not detected in its DSC thermogram, but it was detected by POM studies. However, the LC–crystal transition was detected in the first cooling cycle and verified with POM studies. It did not show the crystal–crystal transition at low temperature, but **V12–V18** did show additional endotherms as these transitions at low temperatures. Figure 6 shows the DSC thermograms of **V18** in its heating and cooling cycles, which are the representative thermograms for **V10–V16**. Figure 7 shows the photomicrographs of **V8**, **V9**, **V10**, and **V12** taken at specified temperatures suggestive of their SmA phases (Figure S15).

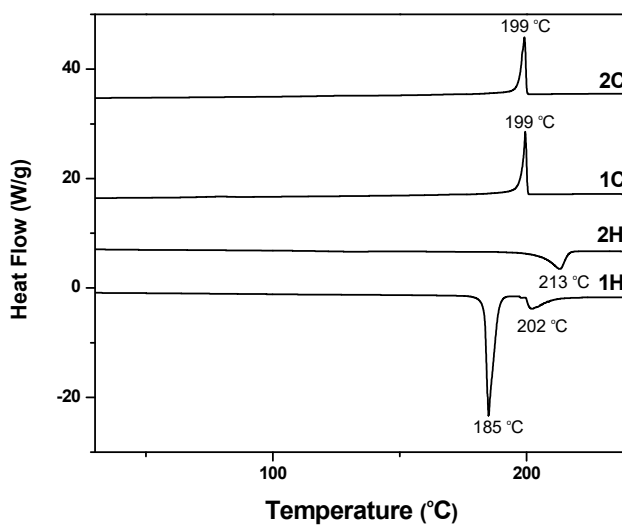


Figure 3. DSC thermograms of V6 obtained at heating and cooling rates of 10 °C/min in nitrogen.

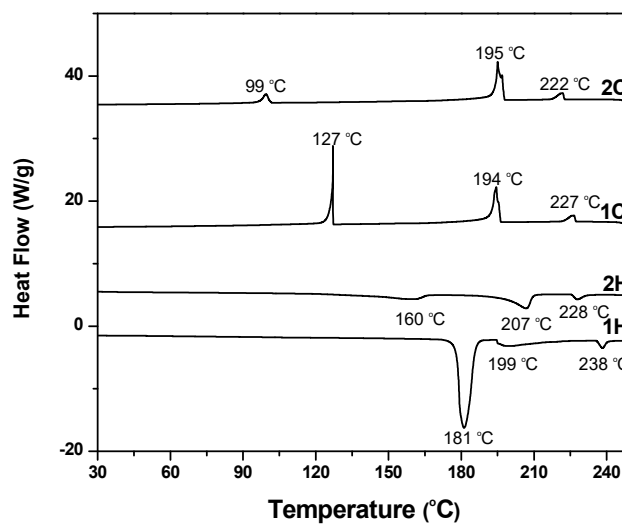


Figure 4. DSC thermograms of V8 obtained at heating and cooling rates of 10 °C/min in nitrogen.

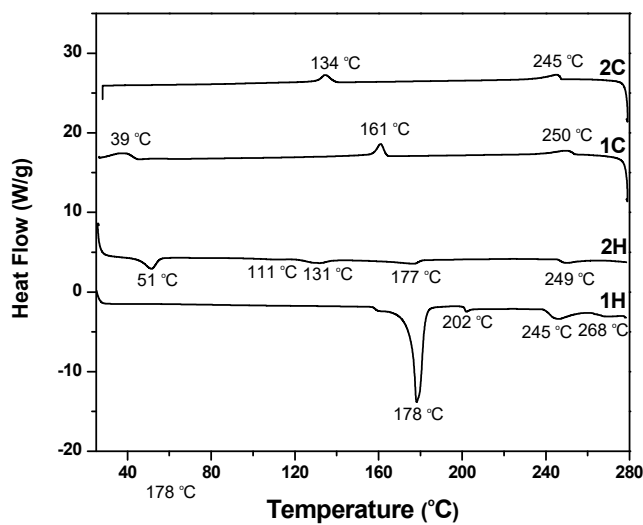


Figure 5. DSC thermograms of V9 obtained at heating and cooling rates of 10 °C/min in nitrogen.

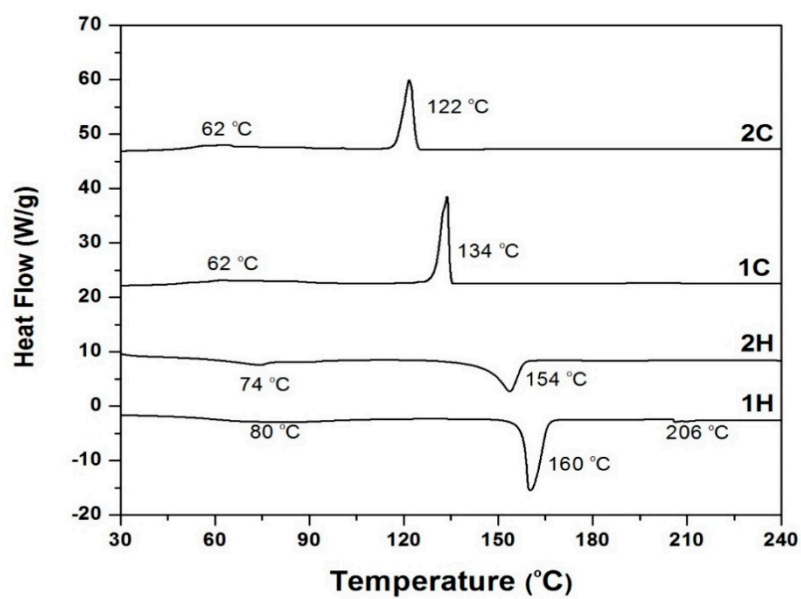


Figure 6. DSC thermograms of V18 obtained at heating and cooling rates of 10 °C/min in nitrogen.

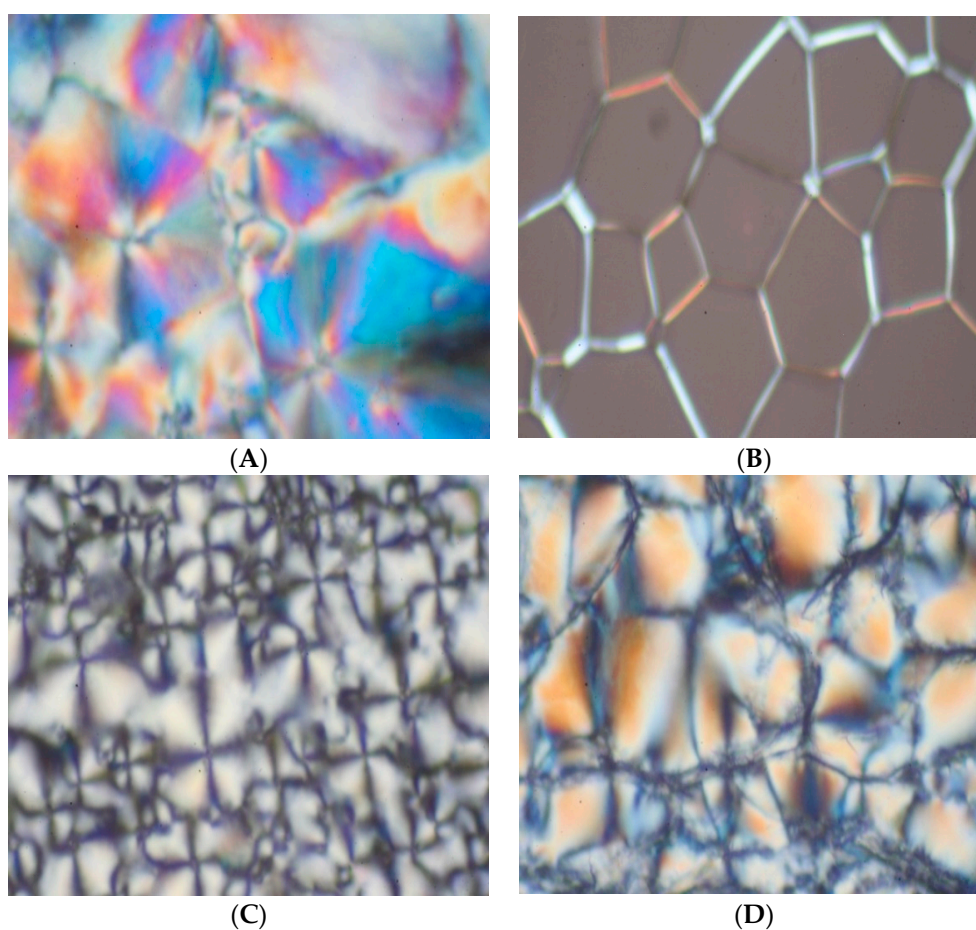


Figure 7. Typical textures observed by polarizing optical microscopy studies, revealing Schlieren or focal conic textures of (A) V8 at 230 °C (B) V9 at 260 °C (C) V10 at 190 °C (D) V12 at 200 °C on heating suggestive of their smectic A LC phases (magnification 400 ×).

The thermodynamic properties of phase transition temperatures of **V6–V18** determined from DSC measurements and POM studies are compiled in Table 1.

**Table 1.** Thermodynamic properties of phase transition temperatures of **V6–V18** obtained from DSC measurements and POM textures. Phase transition temperatures (°C) and their enthalpy changes (J/g) were taken at a scanning rate of 10 °C/min from the first heating and cooling cycles.

Identification	Phase Transition Temperature (Enthalpy Change) °C (J/g)
V6	Cr 185 (85.4) SmA 202 (14.3) I I 199 (−26.9) SmA
V7	Cr 185 (84.0) SmA 199 (24.1) I I 204 (−27.7) SmA
V8	Cr 181 (83.0) SmX 199 (12.7) SmA 238 (3.2) I I 227 (−3.3) SmA 194 (−17.9) SmX 127 (−12.4) Cr
V9	Cr 178 (85.8) SmX 202 (1.2) SmX 245 (10.6) SmA268 (1.7) I I 250 (−5.0) SmA 161 (−7.0) Cr 39 (−7.6) Cr
V10	Cr 174 (84.2) SmA 202 (1.2) I I – SmA 148 (−71.8) Cr
V12	Cr 56 * Cr 169 (79.5) 206 (0.8) I I – SmA 145 (−58.3) Cr 54 Cr
V14	Cr 68 * Cr 164 (81.5) SmA 195 (20.9) I I – SmA 159 (−3.4) SmX 126 (−37.2) Cr 88 (−1.0) Cr 66 (−8.2) Cr
V16	Cr 75 * Cr 157 (81.3) SmA 205 (2.3) I I – SmA 160 (− 4. 2) SmX 113 (−29.4) Cr 73 (−20.0) Cr
V18	Cr 80 * Cr 160 (82.9) SmA 206 (2.2) I I – SmA 134 (−60.5) Cr 62 ( −20.2) Cr

Cr-Crystal, I-Isotropic, SmA-Smectic A, SmX-Unidentified smectic phase. \* Too broad transition.

The thermotropic LC properties of this new series of viologen salts are remarkable in the sense that they showed isotropic transitions below their decomposition temperatures. These results were presumably related to the flexible n-butyl groups lined to the viologen moieties. Note here that diphenylviologens containing the long alkylbenzene sulfonates ( $n = 10, 13$  and  $15$ ) do form SmA phases until their decomposition temperatures, that is, they do not show the isotropic transitions because of the presence of the more rigid phenyl groups attached to the viologen moieties [16,35]. The short alkylbenzenesulfonates with  $n = 6$  and  $8$  do not form LC phases [16,35]. In addition, guanidinium alkylbenzene sulfonates with even alkyl chain lengths  $n = 8$  or higher do form smectic LC phases [34]. This study along with other reports (vide supra) indicate that n-alkylbenzenesulfonates are an interesting class of counterions that may be exploited for the synthesis of ILCs including viologens—a versatile class of functional materials.

### 3.4. Thermal Stabilities of Viologen Salts (V6–V18)

The thermal stabilities of the viologen salts were studied by TGA and determined as the temperature (°C) at which a 5% weight loss for each of the salts occurred at a heating rate of 10 °C/min in nitrogen. Despite the presence of flexible alkyl chains both in the viologen moieties and the benzenesulfonate moieties, TGA thermograms of some of these salts (**V10–V18**), as shown in Figure 8, show relatively high thermal stabilities that are in the temperature range of 285–292 °C. On the one hand, these temperatures slightly increase at a gradual pace with the increase of carbon numbers in the alkyl chain. On the other hand, these temperatures (278–282 °C) for **V6–V8** gradually decrease with the decrease in carbon numbers in the alkyl chain, except for **V9** (295 °C) (Figure S16).

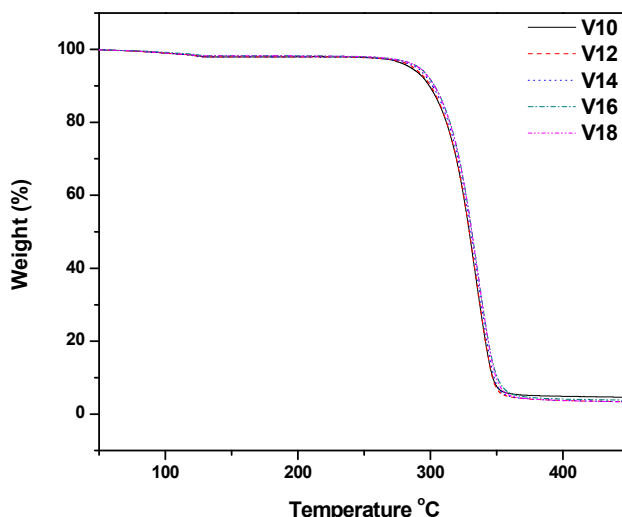


Figure 8. TGA thermograms of V10–V18 obtained a heating rate of 10 °C/min in nitrogen.

#### 4. Conclusions

A new series of viologens with 4-n-alkylbenzenesulfonates were prepared by the metathesis reaction of viologen dibromide with 4-n-alkylbenzenesulfonic acids or sodium-4-n-alkylbenzenesulfonates in alcohols. The chemical structures of these salts were established using spectroscopic techniques and elemental analysis. Their thermotropic LC properties as determined by DSC and POM suggested that they exhibited crystal–LC transitions and LC–isotropic transitions; and showed Schlieren or focal conic textures indicative of their SmA phases. They had good thermal stability. These results suggest that they belong to a class of ILCs that have practical implications.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4352/9/2/77/s1>, Figures S1–S7:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of V6–V14, Figures S8 and S9:  $^1\text{HNMR}$  spectra of V16 and V18, Figures S10–S14: DSC thermograms of V7, V10, V12, V14 and V16, Figure S15: POM texture of V18, Figure S16: TGA thermograms of V6–V9.

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