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Synthesis and Characterization of New UV-curable Liquid Crystalline Diacrylates

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Abstract: A series of UV-curable liquid crystalline diacrylates were synthesized by using 4, 4′-(terephthaloyldioxy) dibenzoic acid as a mesogen unit.

Keywords: Liquid crystalline diacrylates, synthesis, mesogen unit.

The synthesis of liquid crystalline (LC) polyacrylates has been intensely investigated[1]. In particuar, a large variety of works has focused on the side-chain liquid crystalline polyacrylates. With the development of UV curing techniques, a number of liquid crystalline diacrylates monomers have been prepared, they can be photopolymerized into main-chain liquid crystalline polyacrylates[2,3]. As a mesogen unit, 4,4′-(terephthaloyldioxy) dibenzoic acid has been applied in the synthesis of the main-chain liquid crystalline polyesters and polyamides[4], but it has not been reported in the preparation of liquid crystalline diacrylates. We herein report the first synthesis of UV-curable liquid crystalline diacrylates using it as mesogen unit.

As shown in **Scheme 1**. The acid **1** was refluxed with thionyl chloride for 6 h. The crude product was filtrated and recrystallized from dry choloroform. Then it was esterified with diol to afford ester **2**. The compound **2** in THF was stirred at 0℃ while acryloyl chloride was added dropwise over 1 h, and further stirred for more 23 hours. The solution was washed with a 5% NaHCO3 solution and the product **3** was purified with column chromatography. **3b** and **3c** have liquid crystal range from DSC curves (**Table 1**).

Table 1 Thermal transitions of product **3**

Product	n	Heating		Cooling	
		1st(℃)	2nd(℃)	1st(℃)	2nd(℃)
3a	2	132.48	-	112.31	-
3b	4	120.65	169.07	94.35	127.43
3c	6	94.08	140.44	88.29	108.39

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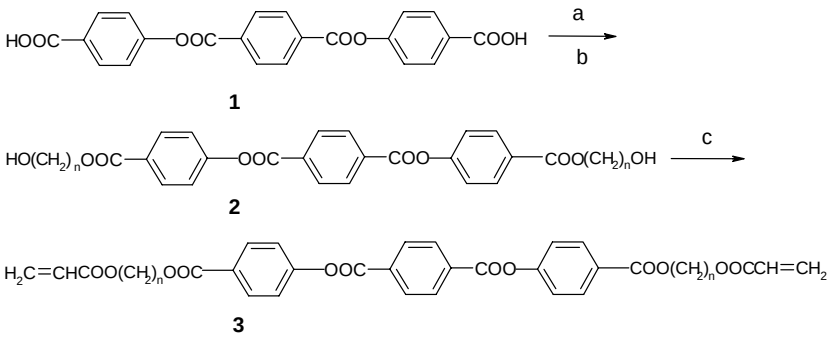
Scheme 1



a. $SOCl_2$, reflux, 6 h; b. $HO(CH_2)_nOH$, 190-200℃, 8 h; c. CH_2=CHCOCl, 0℃,24 h

References and Notes

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5. Spectral data: **3a**, IR (KBr): 1735, 1637, 1602, 1506cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$, δ ppm): 4.53 (m, 8H), 5.85 (d, 2H, J=10.4Hz), 6.14 (m, 2H), 6.43(d, 2H, J=5.2Hz), 7.32 (d, 4H, J=8.8Hz), 8.13-8.33(m, 8H); MS (APCI): *m/z* 603(M^++H); **3b**, IR (KBr): 1733, 1637, 1604, 1502cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$, δ ppm): 1.69-1.88 (m, 8H), 3.71-4.37 (m, 8H), 5.82 (d, 2H, J=9.8Hz), 6.14 (m, 2H), 6.41(d, 2H, J=5.6Hz), 7.33 (d, 4H, J=8.6Hz), 8.13-8.33(m, 8H); MS (APCI): *m/z* 659 (M^++H); **3c**, IR (KBr): 1731, 1638, 1602, 1504cm^{-1}; ^{1}HNMR (400 MHz, $CDCl_3$, δ ppm): 1.35-1.80 (m, 16H), 3.62-4.34 (m, 8H), 5.87 (d, 2H, J=10.2Hz), 6.18 (m, 2H), 6.43(d, 2H, J=5.2Hz), 7.27 (d, 4H, J=8.6Hz), 8.21(m, 8H); MS (APCI): *m/z* 715 (M^++H).

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