

Synthesis of Novel Monomeric Dyes with Anthraquinone Residue

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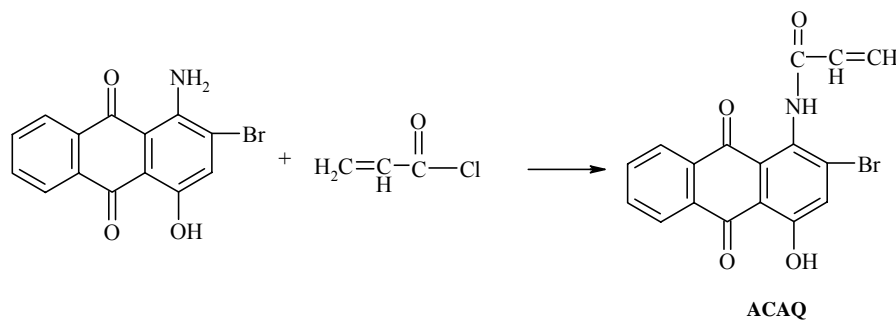
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Abstract: Two novel polymerizable dyes with anthraquinone residue have been prepared, and their structures were characterized by FTIR, ¹HNMR and EA.

Keywords: Polymerizable dye, anthraquinone residue, synthesis, characterization.

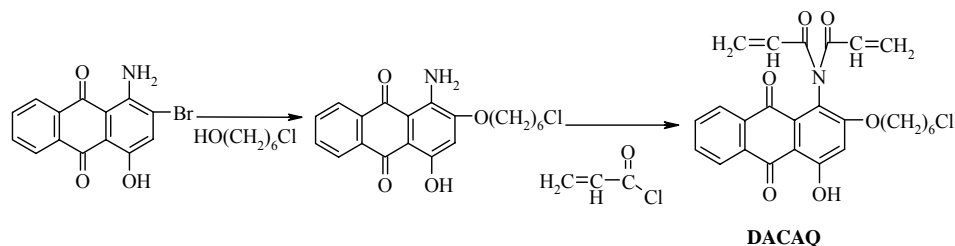
How to improve the light fastness of dyed polymers has attracted attention in recent years, and many researchers have put effort to study the factors which affected fade of dyed polymers^{1,2}. Since conventional dyed polymers, which were normally produced by mixing molecular dye with other polymer ingredients, easily fade or change their color and may lose their mechanical properties when exposed in sunshine. Self-colored polymers, which are prepared by reacting polymerizable dye and other comonomers, have been widely used in the past for their special properties such as high fluorescence, photo- and thermo-stability and good resistance to wet and solvent³⁻⁵. Various of monomeric dyes have been synthesized to prepare self-colored polymers with good utilization properties⁶⁻⁸. In this paper, two polymerizable dyes with anthraquinone residue were synthesized and their structures were characterized by ¹HNMR, FTIR and EA. The synthetic route of 1-acrylamido-2-bromo-4-hydroxyanthraquinone (ACAQ) is as shown in **Scheme 1**.

Scheme 1



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Scheme 2



A solution of 1-amino-2-bromo-4-hydroxyanthraquinone (2.0 g) and triethylamine (7.0 mL) in THF (185 mL) were cooled to 0-5 °C in nitrogen atmosphere, and acryloyl chloride (freshly distilled, 7 mL in 20 mL THF) was dropwise added to the mixture. After stirring for 4 h at 0-5 °C and 24 h at 25 °C, the mixture was filtrated and washed with THF, and the filtrate was concentrated in *vacuo*. The product was purified by column chromatography using the mixture of petroleum ether and acetone (8:1, volume ratio) as the eluent.

Analytical data of ACAQ: red crystal, mp 167.0-168.0 °C. E. A. Calcd. for $C_{17}H_{10}NO_4Br$ (%) C 54.85, H 3.76, N 2.69. Found: C 54.58, H 3.77, N 2.69. IR(KBr) (cm^{-1}): ν 3290 (OH); 3421(N-H); 1672 (C=O, acrylamido), 1530 (N-H)), 1260 (C-N), 1714 (C=O, anthraquinone); 1635 (C=C), 1600, 1529 (aromatic ring) cm^{-1} . 1H NMR (300 MHz, $CDCl_3$, ppm): 13.387 (s, exchangeable, N-H), 7.64 (s, 1H), 7.79 (m, 2H), 8.21 (d, 1H, $J=7.48Hz$), 8.31 (d, 1H, $J=7.88Hz$), 6.75 (d, 1H, $J=17.27Hz$), 6.52 (dd, 1H, $J=17.27, 10.44Hz$), 6.17 (d, 1H, $J=10.44Hz$). UV-Vis: λ_{max} : 479 nm.

The synthesis of 1-N, N-diacryloyl amino-4-hydroxy-2-[6-chlorohexyl]oxyanthraquinone(DACAQ) is shown as **Scheme 2**.

A solution of 6-chlorohexanol (8.0 g), 1-amino-2-bromo-4-hydroxyanthraquinone (13.0 g), anhydrous potassium carbonate (13.8 g) and KI (0.5 g) in DMSO (200 mL) were charged into a flask equipped with a stirrer and a thermometer. After stirring for 7 h at 110 °C, the mixture was poured into cold water (800 mL) with vigorous stirring. The crude product was collected and purified by column chromatograph using the eluent of the mixture of cyclohexane, acetone and dichloro methane (4:1:1, volume ratio).

The synthetic procedure is the same as that of 1-acrylamido-2-bromo-4-hydroxyanthraquinone except that 1-amino-2-bromo-4-hydroxyanthraquinone was replaced by 1-amino-4-hydroxy-2-[6-chlorohexyl]oxyanthraquinone and the eluent was changed to the mixture of cyclohexane and acetone (4:1, volume ratio).

Analytical data of DACAQ: red crystal, mp 112.0-113.0 °C. E. A. Calcd. for $C_{26}H_{24}NO_6Cl$ (%) C 64.86, H 4.98, N 2.91. Found: C 64.49, H 5.12, N 2.89. IR (KBr) (cm^{-1}): ν 3290 (OH); 3064 (=C-H) ; 2868, 2943(CH_2); 1647, 1261(CON(R_2)), 1720(C=O), 1580, 1514(aromatic ring) cm^{-1} . 1H NMR (300MHz, $CDCl_3$, ppm): 7.43 (s, 1H), 7.77 (m, 2H), 8.23(m, 2H), 9.20 (s, 1H, O-H), 5.80(d, 1H, $J=10.0Hz$), 6.39(d, 1H, $J=17.50Hz$), 6.12(dd, 1H, $J=17.50, 10.0Hz$), 5.86(d, 1H, $J=10.50Hz$), 6.50(d, 1H, $J=17.50Hz$), 6.40(dd, 1H, $J=17.50, 10.50Hz$), 4.16-4.21(m, 4H), 1.50-1.98(m, 8H). UV-Vis: λ_{max} : 473 nm.

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Received 8 September, 2003