

Electronic Supplementary Information

Covalent modification of reduced graphene oxide by chiral side-chain liquid crystalline oligomer via Diels-Alder reaction

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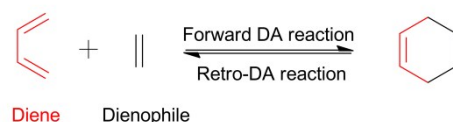
Synthesis of CSLCO

The liquid crystalline monomer cholesteryl 4-(allyloxy)benzoate (M_1) was prepared according to previously reported synthetic method.¹ It showed the following phase transition: Crystalline (112 °C), chiral nematic (240 °C), and isotropic fluid, the detailed chemical parameters of M_1 were as follows, IR (KBr, cm^{-1}): 3057(=CH), 2971-2860(-CH₃, -CH₂-), 1703(C=O), 1645 (C=C), 1604, 1493(Ar-), 1271, 1173 (C-O-C). ¹H NMR (600 MHz, CDCl₃, δ): 7.99-7.98 (d, 2H, Ar-H), 6.92 (d, 2H, Ar-H), 6.05 (m, 1H, CH₂=CH-), 5.44-5.41 (t, 2H, CH₂=CH-), 5.32-5.31 (m, 1H, =CH- in cholesteryl), 4.59-4.58 (d, 2H, -OCH₂-), 2.03-0.67 (m, 44H, cholesteryl-H). 4-(10-undecen-1-yloxy) benzoic acid (M_2) was synthesized according to reference,² the detailed chemical parameters of M_2 were as follows, (mp=128 °C). IR (KBr, cm^{-1}): 3080(=CH); 2930, 2852(-CH₂-); 2678, 2557(COOH); 1754,1684(C=O); 1641(C=C);1602,1508(Ar-).4'-hydroxy-[1,1'-biphenyl]-4-yl4-(undec-10-enyloxy)benzoate (M_3) was synthesized according to reference,^{3,4} Crystalline (173 °C), nematic (207 °C), and isotropic fluid, the detailed chemical parameters of M_3 were as follows, IR (KBr, cm^{-1}): 3412 (-OH), 2921, 2849 (-CH₂-), 1754, 1695 (C=O), 1642 (C=C), 1602, 1508 (Ar-). ¹H NMR (600 MHz, CDCl₃, δ): 1.29-1.36 (10H, m, CH₂=CHCH₂(CH₂)₅-); 1.73-1.78 (2H, m, -CH₂CH₂COO-); 2.02-2.06 (2H, m, CH₂=CHCH₂-); 2.37-2.60 (2H, m, -CH₂CH₂COO-); 4.85-5.02 (2H, m, CH₂=CH-); 5.13 (s, 1H, -OH); 5.77-5.86 (1H, m, CH₂=CH-); 6.84-8.26 (12H, m, Ar-H). CSLCO was synthesized according to reference.⁵ M_1 , M_2 and M_3 were added to polymethylhydrogensiloxane (PMHS, Aldrich). After the addition of platinum

catalyst, the polymerization was carried out at 80 °C under nitrogen protection with magnetic stirring until the infrared spectra showed no Si-H absorption peak at 2166cm⁻¹.⁶ The polymer solution was dried over anhydrous magnesium sulfate and filtered, then, furoyl chloride was dissolved in tetrahydrofuran (THF) and added dropwise to the solution of polymers at 25 °C. The mixture was stirred at room temperature under dry air for 3 h, then heated to 65 °C and kept for 10 h in an oil bath to ensure that the reaction finished. The solution was poured into a beaker filled with 100mL of methanol, the crude product was obtained by filtration and recrystallized from ethanol.⁷ The chiral side-chain liquid crystalline oligomer (CSLCO) was obtained.

Diels-Alder Reaction

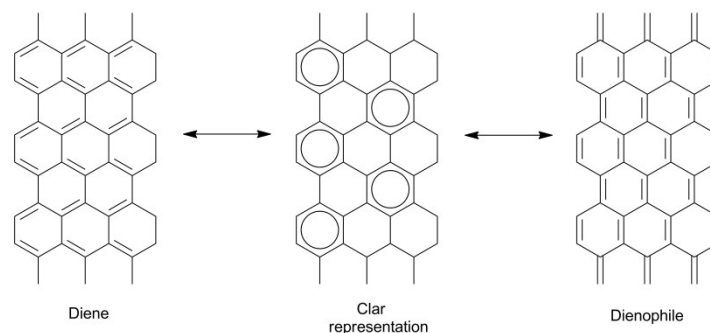
The forward reaction leads to the formation of a six-membered ring via simultaneous creation of two new σ -bonds and one new π -bond and the loss of three π -bonds; alternatively, the process may be viewed as a change in hybridization in which four sp^2 carbon atoms become sp^3 hybridized.⁸



SCHEME 1. Schematic representation of the Diels-Alder reaction between a Diene (1,3-Butadiene) and Dienophile (Ethylene), illustrating the Diels-Alder cycloaddition and cycloreversion reactions in their simplest form

Canonical Resonance Structures of Graphene

In contrast to fullerene and carbon nanotubes, which always act as the dienophile in [4 + 2] cycloaddition due to their curvatures, 2-dimensional graphene and its derivatives are able to behave as both diene and dienophile.^{9,10}



Scheme 2. Resonance Forms of Graphene: Graphene as Diene and Dienophile

The reasons for the necessary of M_1 and M_2

The reasons for using M_1 are that M_1 has wide liquid crystalline range (from 112 °C to 240 °C) and the chemical structure possesses high stability for lack of reactive functional groups. The extra spacer in M_1 is used to broaden the liquid crystalline range of M_1 . The reasons for using M_2 are as following, There is long hydrocarbon chain in the molecular structure of M_2 compared with M_1 , the main purpose of using M_2 is to bring some flexibility to CSLCO. Meanwhile, M_2 has carboxyl group, which makes R_2 have good compatibility. Based on the above analysis, both M_1 and M_2 are necessary in this study.

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