Synthesis of New Functionalized Cyclopentadienes To Reach Reversible Bonding between Two Substrates

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Abstract: Reversible adhesive bonding of polymer films requires new reactive chemical compounds that permit easily broken bonds between two polymer layers. This work describes the synthesis of such new molecules possessing two reactive moieties, the cyclopentadiene-terminated thiol and the cyclopentadiene-terminated amine in 50% and 70% yields, respectively, from the known, corresponding alcohol.

Key words: polymers, functional cyclopentadienes, adhesive bonding, adhesive

Adhesive bonding is nowadays a technology used in all fields of industry to assemble two substrates. However, disassembling can be an important aspect of manufacturing if the entire life cycle of the product is considered. For example, recycling or repairing a component requires the bond to be easily broken. In this context a good adhesive must create strong adhesion between two substrates, but the bonds must also be removable so that the forces are low enough to avoid collateral damage. One solution is to incorporate onto the solid surfaces specific chemical groups that are able to react and to generate reversible bonds. In particular we are interested in employing self-assembly chemistry and non-isothermal plasma chemistry. Self-assembly chemistry consists of adsorbing thiols, which contains specific functional groups, onto gold surfaces.1–3 The non-isothermal plasma chemistry (i.e., plasma polymerization4–6) entails the aminolysis reaction of amines, which contains the desired functional groups, with maleic anhydride pulsed plasma polymer functionalized surfaces.7 Recently, we demonstrated that diene-functionalized surfaces, obtained using both the aforementioned methods, could offered interesting properties due to the thermally reversible chemistry of the Diels–Alder reaction.8 In this study, we describe the synthesis of such new molecules possessing two reactive moieties, the diene-terminated thiol 1 and diene-terminated amine 2. These new molecules should be able to react with alkenes via the Diels–Alder reaction, but it should also be possible to immobilize these new molecules on gold surfaces via the thiol functionality or on maleic anhydride plasma polymer functionalized surfaces via the amine functionality. In future works, the smart interface obtained between an alkene-functionalyzed surface and a diene-functionalyzed surface should permit adhesion between any kind of solid surfaces to be controlled in a reversible and ‘on-demand’ fashion according to the reversibility of the Diels–Alder chemistry.9

Cyclopentadiene-terminated thiols or amines are rarely described10–12 and consequently a good synthetic method for these reactive species would be welcome. The length of the chain must be between 11 and 16 carbons in order to reach (a) optimal auto-assembling of these chains in monolayers and (b) optimal accessibility of the cyclopentadiene groups in the plasma polymer thin film; we have chosen a C11 chain. The synthesis of these two compounds 1 and 2 required soft reaction conditions and reactions were carried out at 0 °C to room temperature to avoid possible dimerization of the cyclopentadiene moiety. They were obtained from the common, known alcohol 3,13 which was synthesized by nucleophilic substitution of 11-bromoundecan-1-ol (4) with sodium cyclopentadienide. Alcohol 3 was a 57:43 isomeric mixture of the 2′-isomer 3a and the 1′-isomer 3b of the cyclopentadiene moiety (Scheme 1) and this isomer distribution is similar to that for methylcyclopentadiene.14,15

Scheme 1

The 1H NMR data of the isomers 3a and 3b was close to those of the corresponding methylcyclopentadiene isomers, which have already been published.14,16 In the 2′-substituted major isomer 3a, the 5′-CH3 signal appeared
as a sextuplet \((J = 1.5 \text{ Hz})\) due to coupling with \(H_1', H_3',\) and \(H_4' \) cyclopentadienyl protons and with the chain 11-CH_{2}; the 11-CH_{2} signal appeared as a quadruplet \((J = 1.6 \text{ Hz})\) of triplets \((J = 7.6 \text{ Hz})\) due to coupling with the 10-CH_{2} and long-range coupling with the cyclopentadienyl protons 5'-CH_{2} and H1'. In the minor isomer 3b, the 5'-CH_{2} was only coupled with H2', H3', and H4' cyclopentadienyl protons and appeared as a quadruplet, and 11-CH_{2} was only long-range coupled with H2' and appeared as a doublet of triplets. Of note is the fact that the final thiol 1 and amine 2 have the same isomer distribution 1a/1b, 2a/2b, respectively (Scheme 1).

The synthesis of the thiol-functionalized cyclopentadiene was achieved in two steps from the alcohol 3 (Scheme 2). The first step was the nucleophilic substitution of the alcohol function with thioacetic acid under Mitsunobu conditions\(^{17}\) to give the thioacetate 3a in 95% yield. Lithium aluminum hydride reduction of the thioacetate function gave the final thiol 1 in 65% yield.

Scheme 2

The amine-functionalized cyclopentadiene was obtained in three steps from the alcohol 3 (Scheme 3). Mesylation of the alcohol gave quantitatively the mesylate 6, which provided the azide 7 by substitution with sodium azide in \(N,N\)-dimethylformamide\(^{18}\) in good yield (79% from 3). The reduction of the azide 7 with lithium aluminum hydride gave easily the amine 2 in 95% yield.

Scheme 3

We have here described the easy synthesis of two undecane chain molecules functionalized at both the ends with reactive moieties. The cyclopentadiene moiety at one end was respected by the reaction sequence and the reactive functions amine or thiol were formed at the second end of the chain. Thiol 1 and amine 2 were also obtained from the known alcohol 3 in ca. 50% and 70% yields, or from 11-bromoundecan-1-ol (4) in 35% and 50% yields, respectively.

Flash chromatography: silica gel (Merck 60, 230–400 mesh). TLC: Al-roll silica gel (Merck 60, F_{254}). Mp: Kofler hot bench, corrected. IR spectra: Bruker IFS 66/s infrared spectrophotometer. \(^{1}H\) and \(^{13}C\) NMR (400 MHz and 100.6 MHz, respectively, 295 K) spectra: Bruker Avance 400, TMS (\(\delta = 7.00\)) \(^{13}\)C NMR as internal references; numbering of products in assignments as shown in Scheme 1. Microanalyses were carried out by the Service Central de Microanalyses du CNRS, F-69390 Vernaison.

11-(Cyclopenta-1,4-dienyl)undecan-1-ol (3a) and 11-(Cyclopenta-1,3-dienyl)undecan-1-ol (3b)\(^{13}\)

Using the literature procedure\(^{13}\): yield: 69%; ratio 3a/3b = 57:43. IR (neat): 3340 (br), 3059, 2925 (s), 2853 (s), 1694, 1465, 1353, 1134, 984, 929, 897, 810, 723, 675 cm\(^{-1}\). IR spectra: Bruker IFS 66/S infrared spectrophotometer. \(^{1}H\) and \(^{13}C\) NMR (400 MHz and 100.6 MHz, respectively, 295 K) spectra: Bruker Avance 400, TMS (\(\delta = 7.00\)) \(^{13}\)C NMR as internal references; numbering of products in assignments as shown in Scheme 1. Microanalyses were carried out by the Service Central de Microanalyses du CNRS, F-69390 Vernaison.
(C11, a), 43.2 (C11, b), 125.6 (C1’, a), 126.1 (C2’, b), 130.3, 132.4 (C3’, C4’, a), 147.4 (C2’, a), 150.3 (C1’, b), 196.0 (CO, a + b).

Anal. Caled for C30H48O4S: C, 73.41; H, 10.27; S, 10.89. Found: C, 73.4; H, 10.2; S, 10.9.

11-(Cyclopenta-1,4-dienyl)undecane-1-thio (1a) and 11-(Cyclopenta-1,3-dienyl)undecane-1-thiol (1b)

To a soln of 5a, b (1.56 g, 5.3 mmol) in anhyd Et2O at 0 °C under argon, was added portionwise LiAlH4 (0.623 g, 16 mmol, 3 equiv). The mixture was stirred at 0 °C for 30 min and then at r.t. for 1 h. Solid Na2SO4·10 H2O (3.2 g) was added and the mixture was stirred for 30 min and then at r.t. for 1 h. The mixture was filtered through Celite and the filtrate was dried (MgSO4) and evaporated. Crude 1a, b was purified under argon by flash chromatography (argon-saturated cyclohexane–CH2Cl2, 7:3) to give pure 1a, b (0.86 g, 65%) as colorless crystals; ratio 1a/1b 57:43; mp 25–27 °C. The product was unstable and must be stored under argon at 0 °C.

IR (neat): 3058, 2925 (s), 2893 (s), 2365, 1611, 1446, 1364, 1264, 977, 947, 928, 897, 809, 740, 675, 633 cm⁻¹.

11-(Cyclopenta-1,4-dienyl)undecane-1-thio (1a) and 11-(Cyclopenta-1,3-dienyl)undecane-1-thiol (1b)

To a stirred mixture of K2CO3 (3.2 g, 0.023 mol, 1.1 equiv) in anhyd Et2O (15.4 ml) at 0 °C, was added dropwise a soln of 1a, b (11.1 g, 42 mmol) in anhyd Et2O. After stirring for 30 min at 0 °C, solid Na2SO4·10 H2O (25 g) was added portionwise with stirring and then aq 2.5 M NaOH (4 mL) was added dropwise. The mixture was filtered through Celite and the filtrate was dried (MgSO4) and evaporated. Crude 7a, b as a greenish resin (14 g). It was purified by flash chromatography (cyclohexane–CH2Cl2, 1:1) to give pure 7a, b (13.1 g, 79%, from 3a, b) as a colorless resin; ratio 7a/7b 57:43.

IR (neat): 3059, 2926 (s), 2854 (s), 2905 (s), 1602, 1464, 1366, 1349, 1258, 977, 947, 928, 897, 809, 723, 675, 633 cm⁻¹.

11-(Cyclopenta-1,4-dienyl)undecane-1-thio (1a) and 11-(Cyclopenta-1,3-dienyl)undecane-1-thiol (1b)

To a stirred mixture of LiAlH4 (6.4 g, 0.168 mol, 4 equiv) in anhyd Et2O (0.15 l) at 0 °C, was added dropwise a soln of 1a, b (11.1 g, 42 mmol) in anhyd Et2O. After stirring for 30 min at 0 °C, solid Na2SO4·10 H2O (25 g) was added portionwise with stirring and then aq 2.5 M NaOH (3 mL) was added dropwise and the mixture was stirred for 0.5 h. The mixture was filtered through Celite and the filtrate was dried (MgSO4) and evaporated to give pure amine 2a, b (9.4 g, 95%) as greenish crystals; mp 30–32 °C; ratio 2a/2b 57:43.

IR (neat): 3321, 2981, 2922 (s), 2851 (s), 1557, 1466, 1342, 1372, 1398, 1068, 979, 947, 929, 897, 809, 722, 675 cm⁻¹.

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(14) Korenevsky, V. A.; Sergeyev, N. M. *J. Am. Chem. Soc.* 1972, 94, 8586; add ca. 0.16 ppm to the δ values.


