

Model Studies Towards Alternative Cross-Linking of Unsaturated Polyesters

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Abstract: Fumaric and maleic acid esters are functionalised with propargylamine. A subsequent Pd/Cu-catalysed oxidative homo-coupling of two alkyne moieties yields the corresponding dimers. Hence, a model of an unsaturated polyester chain is cross-linked in a well-defined, metal-mediated reaction in a very high yield.

Keywords: Unsaturated polyester, cross-linking, catalytic, alkyne coupling.

INTRODUCTION

Unsaturated polyester resins are heterochain polymers, containing repeating ester groups and aliphatic double bonds in the backbone [1]. These chains are generally copolymerised in a free-radical chain-growth process, with a vinyl monomer, usually styrene, to yield the final product, a three-dimensional cross-linked network [1, 2]. Since environmental legislation becomes more and more stringent constantly reducing the amount of monomeric components, which can be used in unsaturated polyester products, the development of alternative cross-linking methods, reducing or completely avoiding possible emissions of harmful, volatile compounds, e.g. of styrene, is of particular interest.

Radical cross-linking processes do not yield very well defined products, instead they give rise to different chain lengths of the linkages, irregular, incomplete consumption of the double bonds of the polyester heterochain and direct linking of the latter. In addition, side-reactions such as homopolymerisation of styrene occur [3]. So, we opted for a well-defined metal-mediated reaction that could circumvent these problems. Further considering an unsaturation in the linkage a desirable feature, since it provides the possibility for additional cross-linking if demanded to alter the properties of the final product, the metal-catalysed coupling of alkynes is highly attractive for its wide scope [4]. Here we report a model reaction for an alternative cross-linking of unsaturated polyesters *via* functionalisation of maleic/fumaric diesters and subsequent oxidative homo-coupling of the introduced alkyne moieties.

RESULTS AND DISCUSSION

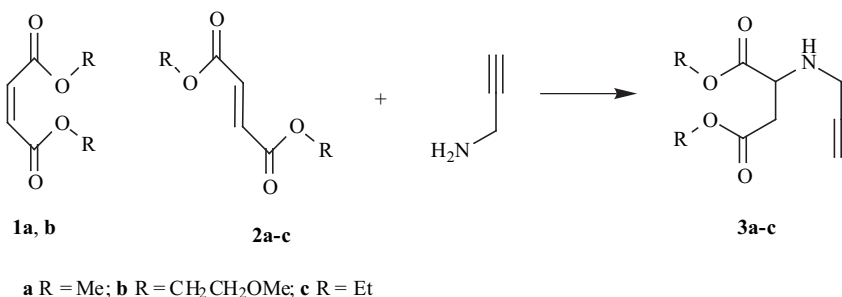
Nucleophilic addition of propargylamine to maleic acid esters (**1a**, **1b**) or fumaric acid esters **2a-c** respectively, yielded **3a-c** [5], bearing the desired alkyne function. The reactions were performed at RT, using neat compounds, and proceeded quantitatively [6], making further purification essentially superfluous. The reaction of maleic anhydride and

2-methoxyethanol [7] produced a 3:1 mixture of maleic (*cis*) **1b** and fumaric (*trans*) **2b** diester [8], an isomerisation well-documented for the preparation of unsaturated polyester chains from maleic anhydride and diols [1, 2a, 9]. Subsequent radical cross-linking using styrene favours the *trans*-type of unsaturation, thus introducing a source of inhomogeneity in the cured product [2a, 10]. This complication is eliminated here, since the addition of the propargylamine to the esters yields the racemats **3a-c** quantitatively, if somewhat slower for the *trans*-species **2a-2c**. All the double bonds are consumed, and can potentially contribute to the cross-linking *via* the introduced alkyne functionality. Using the amine in any sub-stoichiometric amount would allow a defined degree of unsaturation in the heterochain backbone to be retained. It is noteworthy that in the course of the addition reaction, the propargylamine catalyses an isomerisation of the maleic diester to the fumaric diester, which can easily be followed by nmr spectroscopy and by the visible temporary formation of fumaric diester crystals in the reaction mixture. However, this does not constitute an obstacle since the addition of the amine proceeds to completion. Various mechanisms have been proposed for this isomerisation [11].

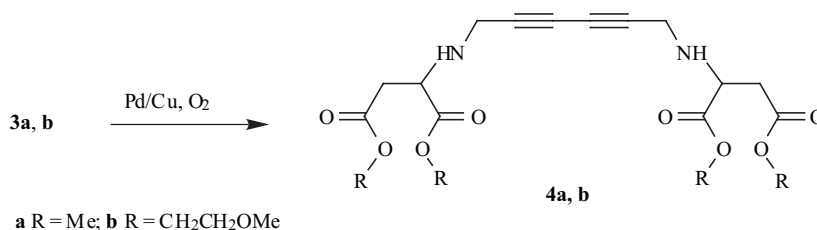
Attempts to dimerise **3** under standard Hay conditions [4] or with Cu(OAc)₂/MeCN [12] failed. However, in presence of air, the PdCl₂(PPh₃)₂/CuI/amine mixture is a very effective system for the catalytic oxidative homo-coupling of terminal alkynes to the corresponding diynes [13] and thus, the target compounds **4** were obtained in very high yields (94-96%) [14]. Control runs confirmed that the combination of Pd, Cu and O₂ is crucial for the success of the coupling reaction. Recently an anaerobic variant of this reaction has been reported, but it fails when acetyl or phenylsulphonyl groups are present [15].

The reaction is easily monitored by proton nmr spectroscopy, the terminal alkyne hydrogen disappearing and the doublet of the corresponding methylene group collapsing being the obvious features. The carbon nmr spectra unambiguously confirm the structure of the target compounds **4**, revealing a characteristic shift and loss of multiplicity for the signals of the alkyne carbons as well as the loss of a long range coupling for the adjacent methylene

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Scheme 1.



Scheme 2.

group in comparison to the corresponding spectra of compounds **3**.

In summary, we demonstrated that a Pd/Cu catalysed oxidative coupling of alkynes provides a potential alternative for the cross-linking of unsaturated polyester chains, once the latter have been functionalised quantitatively by facile nucleophilic addition of propargylamine to the maleic/fumaric ester units. The procedure presents a synthesis of structurally well-defined products in high yield in a one-pot reaction. Various disadvantages of radical copolymerisation pathways that introduce inhomogeneities into the cured product are thus avoided and emission of vinyl monomer is eliminated altogether, a distinctive plus in times of environmental awareness and legislative restrictions.

ACKNOWLEDGEMENTS

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- Compound **3a**: ¹H-NMR (C₆D₆, RT, 400 MHz, δ [ppm]): 3.73 (t, 1 H, NCH, ³J=6.0 Hz), 3.37 (s, 3 H, OMe), 3.32 (s, 3 H, OMe), 3.27 (d, 2 H, HCCCH₂N, ⁴J=2.4 Hz), 2.56 (m, 2 H, NCHCH₂CO), 2.05 (t, 1 H, HCCCH₂N, ⁴J=2.4 Hz), 1.98 (s, br, 1 H, NH). ¹³C-NMR (C₆D₆, RT, 100 MHz, δ [ppm]): 172.5, 170.0 (COOCH₃), 80.7 (dt, HCCCH₂N, ²J=50 Hz, ²J=8.3 Hz), 70.8 (dt, HCCCH₂N, ¹J=249 Hz, ³J=4.2 Hz), 55.5 (d, NCHCH₂, ¹J=138 Hz), 50.5, 50.2 (q, OCH₃, ¹J=146 Hz), 36.7 (dt, NCHCH₂CO, ¹J=131 Hz, ²J=4.2 Hz), 35.9 (tt, HCCCH₂NH, ¹J=140 Hz, ²J=4.2 Hz, ³J=4.2 Hz). Boiling point: 99°C/0.2 mm. HRMS (ESI⁺) calcd. for C₉H₁₄NO₄ 200.0923; found 200.0925.
- Compound **3b**: ¹H-NMR (C₆D₆, RT, 400 MHz, δ [ppm]): 4.10-4.03 (m, 4H, COOCH₂CH₂), 3.79 (t, 1 H, NCH, ³J=6.0 Hz), 3.28 (d, 2 H, HCCCH₂N, ⁴J=2.4 Hz), 3.19-3.10 (m, 4H, COOCH₂CH₂), 3.01 (s, 6 H, OMe), 2.64 (m, 2 H, NCHCH₂CO), 2.21 (s, br, 1 H, NH), 1.90 (t, 1 H, HCCCH₂N, ⁴J=2.4 Hz). ¹³C-NMR (C₆D₆, RT, 100 MHz, δ [ppm]): 172.0, 169.6 (s, COOCH₃), 81.0 (dt, HCCCH₂N, ²J=50 Hz, ²J=8.3 Hz), 71.1 (dt, HCCCH₂N, ¹J=248 Hz, ³J=4.2 Hz), 69.9, 69.3 (t, COOCH₂CH₂, ¹J=148 Hz), 63.0, 62.7 (t, COOCH₂CH₂, ¹J=147 Hz), 57.4 (q, OCH₃, ¹J=141 Hz), 55.6 (d, NCHCH₂, ¹J=138 Hz), 37.0 (dt, NCHCH₂CO, ¹J=131 Hz, ²J=4.3 Hz), 35.9 (tt, HCCCH₂NH, ¹J=139 Hz, ²J=4.3 Hz, ³J=4.3 Hz). HRMS (ESI⁺) calcd. for C₁₃H₂₂NO₆ 288.1447; found 288.1461.
- Compound **3c**: ¹H-NMR (C₆D₆, RT, 400 MHz, δ [ppm]): 3.88 (m, 2 H, COOCH₂CH₃), 3.84 (m, 2 H, COCH₂CH₃), 3.74 (t, 1 H, NCH, ³J=6.2 Hz), 3.23 (d, 2 H, HCCCH₂N, ⁴J=2.4 Hz), 2.55 (m, 2 H, NCHCH₂CO), 1.96 (s, br, 1 H, NH), 1.86 (t, 1 H, HCCCH₂N, ⁴J=2.4 Hz), 0.87 (t, 3 H, OCH₂CH₃, ³J=7.2 Hz), 0.86 (t, 3 H, OCH₂CH₃, ³J=7.2 Hz). ¹³C-NMR (C₆D₆, RT, 100 MHz, δ [ppm]): 171.9, 169.4 (s, COOCH₂CH₃), 80.9 (dt, HCCCH₂N, ²J=48.6 Hz, ²J=8.0 Hz), 70.9 (dt, HCCCH₂N, ¹J=247 Hz, ³J=4.2 Hz), 60.0, 59.5 (t, OCH₂CH₃, ¹J=147 Hz), 55.7 (d, NCHCH₂, ¹J=137 Hz), 37.1 (dt, NCHCH₂CO, ¹J=130 Hz, ²J=4.3 Hz), 36.0 (tt, HCCCH₂, ¹J=139 Hz, ²J=4.3 Hz, ³J=4.3 Hz), 13.9 (q, OCH₂CH₃, ¹J=137 Hz). Boiling point: 112°C/0.2 mm.
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- E*); *E/Z* = 1/3. ^{13}C -NMR (C_6D_6 , RT, 100 MHz, δ [ppm]): 164.1 (s, COO, *Z*), 163.6 (s, COO, *E*), 132.9 (d, =CH, $^1J=168$ Hz, *E*), 129.0 (d, =CH, $^1J=167$ Hz, *Z*), 69.1 (t, COOCH₂CH₂, $^1J=138$ Hz), 63.1 (t, COOCH₂CH₂, $^1J=149$ Hz), 57.3 (q, OCH₃, $^1J=143$ Hz). Boiling point: 115-118 °C/0.02 mm. HRMS (ESI⁺) calcd. for C₁₀H₁₆O₆Na 255.0845; found 255.0838.
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- [17] Compound **4a**: ^1H -NMR (C_6D_6 , RT, 400 MHz, δ [ppm]): 3.66 (t, 2 H, NCH, $^3J=6.0$ Hz), 3.34 (s, 6 H, OMe), 3.27 (s, 6 H, OMe), 3.20 (m, 4 H, CCCH₂N), 2.51 (m, 4 H, NCHCH₂), 2.02 (s, br, 2 H, NH). ^{13}C -NMR (C_6D_6 , RT, 100 MHz, δ [ppm]): 172.2, 169.8 (s, COOCH₃), 75.5 (t, CCCH₂N, $^2J=8.6$ Hz), 67.8 (t, CCCH₂N, $^3J=4.3$ Hz), 55.6 (d, NCHCH₂, $^1J=141$ Hz), 50.7, 50.2 (q, OCH₃, $^1J=147$ Hz), 36.8 (dt, NCHCH₂CO, $^1J=130$ Hz, $^2J=4.3$ Hz), 36.6 (dt, CCCH₂NH, $^1J=141$ Hz, $^2J=4.3$ Hz). HRMS (ESI⁺) calcd. for C₁₈H₂₅N₂O₈ 397.1611; found 397.1609. Compound **4b**: ^1H -NMR (C_6D_6 , RT, 400 MHz, δ [ppm]): 4.13 (m, 4 H, COOCH₂CH₂), 4.06 (t, 4 H, COOCH₂CH₂, $^3J=4.9$ Hz), 3.70 (dt, 2 H, NCH, $^3J=7.2$ Hz, $^3J=6.2$ Hz), 3.30 (d, 4 H, CCCH₂N, $^3J=6.2$ Hz), 3.25 (t, 4 H, COOCH₂CH₂, $^3J=4.7$ Hz), 3.20 (t, 4 H, COOCH₂CH₂, $^3J=4.9$ Hz), 3.06 (s, 6 H, OMe), 3.03 (s, 6 H, OMe), 2.61 (m, 4 H, NCHCH₂CO), 2.08 (dt, 2 H, NH, $^3J=7.2$ Hz, $^3J=6.2$ Hz). ^{13}C -NMR (C_6D_6 , RT, 100 MHz, δ [ppm]): 171.8, 169.4 (COOCH₃), 75.8 (t, CCCH₂N, $^2J=8.6$ Hz), 69.3, 69.2 (t, COOCH₂CH₂, $^1J=142$ Hz), 67.7 (t, CCCH₂N, $^3J=4.3$ Hz), 63.2, 62.7 (t, COOCH₂CH₂, $^1J=147$ Hz), 57.3 (q, OCH₃, $^1J=140$ Hz), 55.8 (d, NCHCH₂, $^1J=140$ Hz), 37.0 (dt, NCHCH₂CO, $^1J=130$ Hz, $^2J=4.3$ Hz), 36.6 (dt, CCCH₂NH, $^1J=141$ Hz, $^2J=4.3$ Hz). HRMS (ESI⁺) calcd. for C₁₃H₂₂NO₆Na 595.2479; found 595.2482.
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