Synthesis of a Polyurethane Containing Mo–Mo Bonds in the Backbone

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A polyurethane with Mo–Mo bonds in the backbone was synthesized by reaction of the 'diol' $\{\eta^5\text{-}C_5H_4C(O)CH_2OH\}_2Mo_2(CO)_6$ with 1,6-hexamethylene di-isocyanate; irradiation of the polymer in tetrahydrofuran solution results in cleavage of the metal–metal bonds and subsequent fragmentation of the polymer.

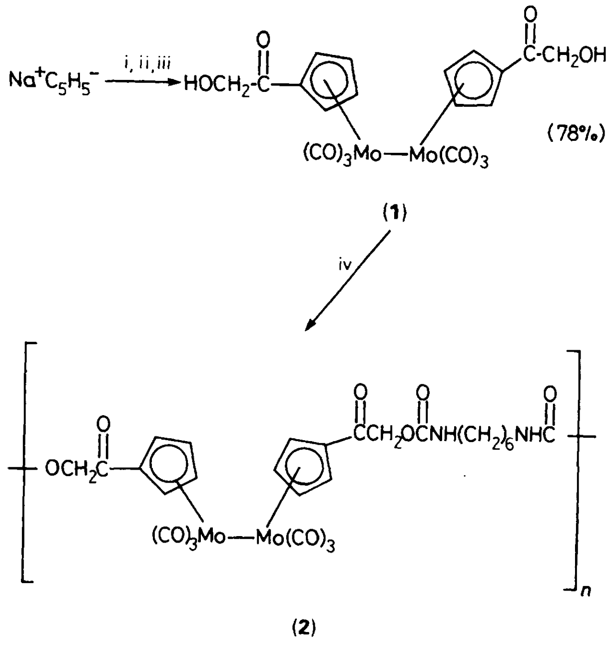
Reactive polymers have been, and continue to be, actively investigated as a category of speciality polymer.[1–8] In this communication we report the synthesis of a photochemically reactive polyurethane containing Mo–Mo bonds along the backbone.

The 'diol' used in the synthesis of the polyurethane was $\{\eta^5\text{-}C_5H_4C(O)CH_2OH\}_2Mo_2(CO)_6$ (**1**).[9] This complex was synthesized as follows. A tetrahydrofuran (THF) solution (150 ml) of $Na^+C_5H_5^-$ [generated *in situ* by reaction of Na (30 mmol) with C_5H_6 (42 mmol)] was refluxed for 12 h with the protected methyl glycolate derivative (A)[10] (48.2 mmol) shown in Scheme 1. $Mo(CO)_6$ (18.9 mmol) was then added and the mixture was refluxed for a further 12 h.[11,12] Oxidation of the resulting $\{C_5H_4C(O)CH_2OCMe_2OMe\}Mo(CO)_3^-$

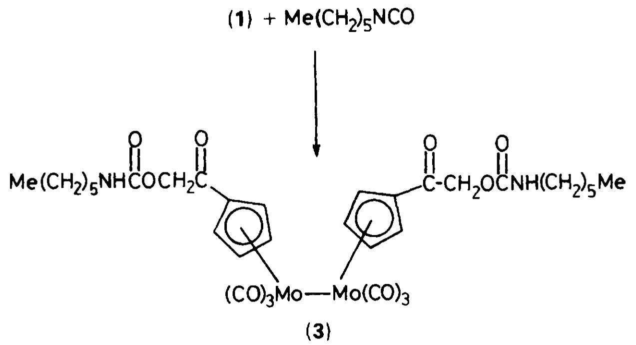
Table 1. Spectroscopic data for $(C_5H_5)_2Mo_2(CO)_6$ and (**1**)—(**3**).

Compound	I.r., ν(C≡O)/cm^{-1}	δ(^{1}H; CD_3COCD_3)[d]	λ_{max}/nm (ε)
$(C_5H_5)_2Mo_2(CO)_6$	2012sh,vw, 1954s, 1925m, 1901s, 1890s	5.60, 5.44 (each br., 5H)	509 (1730), 388 (18 600)
(**1**)	2014m, 1955s, 1928s, 1898s[a]	a: 4.59 (d, 4H, *J* 6); b: 4.17 (2H, br.); c + d: 5.59, 5.90, 6.06, 6.22 (each 2H, br.)	511 (1730), 391 (17 700)
(**2**)	2021m, 1967s, 1909s[b]	a: 1.36; b: 1.52; c: 3.14 (4H, br.); d: 4.99 (4H, s); e + f: 5.58 (1.5H, br.), 5.90 (2.7H, br.), 6.05 (1.4H, br.), 6.23 (2.3H, br.); g: 6.55 (br., 2H)	503 (1720), 389 (16 800)
(**3**)	2021m, 1984s, 1929vs, 1902vs[c]	a: 0.87 (6H, m); b: 1.29 (12H, br.); c: 1.51 (4H, quint., *J* 7); d: 3.13 (4H, quart., *J* 7); e: 4.98 (4H, s); f + g: 5.59 (1.7H, br.), 5.90 (2.7H, br.), 6.04 (1.8H, br.) 6.22 (2.5H, br.) h: 6.50 (2H, br.)	511 (1870), 389 (16 700)

[a] Additional i.r. data: ν(OH) 3482m, ν(C=O) 1682s cm^{-1}. [b] Additional i.r. data: ν(N–H) 3375m, ν(N=C=O) 2275vw, ν(C=O, urethane) 1724s, ν(C=O, keto) 1703s, δ(N–H, amide II) 1525m, ν(C–N, amide III) 1241m cm^{-1}. [c] Additional i.r. data: ν(N–H) 3381w, ν(C=O, urethane), 1728s, ν(C=O, keto) 1706s, δ(N–H, amide II), 1516m, ν(C–N, amide III) 1243m cm^{-1}. [d] *J* values in Hz.



Scheme 1. *Reagents and conditions:* i, MeOC(:O)CH_2OCMe_2OMe (A), THF, reflux, 12 h; ii, $Mo(CO)_6$, THF, reflux, 12 h; iii, $Fe(NO_3)\cdot 9H_2O$, AcOH, 1 h; iv, $OCN(CH_2)_6NCO$ (HMDI), $Bu_2Sn(OAc)_2$ (DBTDA), 3 h.

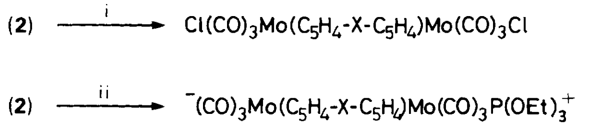


Scheme 2

with iron(III) nitrate (30 mmol) in aqueous acetic acid (1.3 M)[13] yielded the complex (**1**). To obtain the polymer, complex (**1**) (3.21 mmol) was treated with 1,6-hexamethylene di-isocyanate (HMDI) (3.2 mmol) in refluxing THF (200 ml) using dibutyltin diacetate (DBTDA; 0.3 mmol) as a catalyst.

The polymer was precipitated by concentrating the solution to 100 ml and then adding the solution to pentane (250 ml). Following filtration, washing with diethyl ether and pentane, and drying *in vacuo*, the polymer was obtained as a bright red–purple powder in 65% yield. Other di-isocyanates (*e.g.* tolylene 2,4-di-isocyanate) formed polymers under similar conditions.

Spectral data for the polymer are summarized in Table 1. The electronic absorption spectrum shows that the Mo–Mo bond is intact because the spectra of the polymer, $(C_5H_5)_2Mo_2(CO)_6$, and (**1**) are all essentially identical. In all three complexes, the band at approximately 390 nm is assigned to the $\sigma \rightarrow \sigma^*$ transition and the band at 504 nm is assigned to a $d\pi \rightarrow \sigma^*$ transition.[14] The i.r. spectrum (Table 1) is also consistent with the proposed structure. Note that the C≡O stretching frequencies of the polymer are similar to those in the dimers $(C_5H_5)_2Mo_2(CO)_6$ and (**1**). In addition, the C=O stretch at 1724 cm^{-1} is evidence for the urethane linkage in the polyurethane.[15] To confirm the assignment of the n.m.r. spectrum of the polymer in Table 1, the model complex (**3**)



$$(\mathbf{2}) \xrightarrow{\text{i}} \mathrm{Cl(CO)_3Mo(C_5H_4\text{-}X\text{-}C_5H_4)Mo(CO)_3Cl}$$

$$(\mathbf{2}) \xrightarrow{\text{ii}} \mathrm{^{-}(CO)_3Mo(C_5H_4\text{-}X\text{-}C_5H_4)Mo(CO)_3P(OEt)_3^{+}}$$

$X = \text{-C(:O)CH}_2\text{OC(:O)NH(CH}_2)_6\text{NHC(:O)CH}_2\text{C(:O)-}$

Scheme 3. *Reagents and conditions:* i, *hv*, CCl_4; ii, hv, $P(OEt)_3$.

was synthesized as shown in Scheme 2. The n.m.r. spectrum of (**3**) (Table 1) is similar to that of the polymer.

Elemental analyses were also consistent with the proposed polymer formula: $C_{28}H_{26}Mo_2N_2O_{12}\cdot 0.19C_5H_{12}\cdot 0.24(C_2H_5)_2O\cdot 0.11C_4H_8O$; calc. C, 44.8; H, 3.9; N, 3.4. Found: C, 44.6; H, 4.0; N, 3.8%. [The amounts of pentane, diethyl ether, and THF trapped in the polymer lattice (as given in the elemental analyses) were determined by ^1H n.m.r. spectroscopy.]

The number-average molecular weight ($\bar{M}_n$) of the polymer, measured by vapour pressure osmometry (in acetone), was 4.0×10^3.[16] The molecule is thus best described as an oligomer.

The oligomer forms a bright red film when cast from a THF solution. After exposure to air the film becomes less soluble in acetone and in THF. The decrease in solubility probably results from chain extension.

The oligomer undergoes typical photochemical metal–metal bond cleavage reactions in THF solution. For example, it reacted with CCl_4 (Scheme 3).[17] The product has $\nu(C{\equiv}O)$ bands at 2059 and 1974 cm^{-1} in THF. For comparison, $(C_5H_5)Mo(CO)_3Cl$ also has bands at 2059 and 1974 cm^{-1} in THF. Fragmentation of the oligomer is confirmed by the disappearance of the $\sigma{\rightarrow}\sigma^*$ and $d\pi{\rightarrow}\sigma^*$ absorption bands in the electronic spectrum of the reaction solution. In another photochemical reaction, the Mo–Mo unit disproportionated when the oligomer was irradiated in the presence of ligands, *e.g.* $P(OEt)_3$, Scheme 3. The product has i.r. bands at 1999w, 1926s, 1911vs, and 1805vs. For comparison, $[\{\eta^5\text{-}C_5H_4C(O)CH_2OH\}Mo(CO)_3]^-$ has bands at 1910 and 1805 cm^{-1}, and $\{\eta^5\text{-}C_5H_4C(O)CH_2OH\}Mo(CO)_2\{P(OEt)_3\}_2]^+$ has bands at 1999 and 1926 cm^{-1}. This reactivity is also typical of metal–metal bonded dimers.[18] Work is continuing to synthesize other polymers with metal–metal bonds along the backbone and to investigate their photochemical properties.

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