Synthesis and α-substitution reactions of methoxime derivatives of alkene-carbon monoxide alternating copolymers

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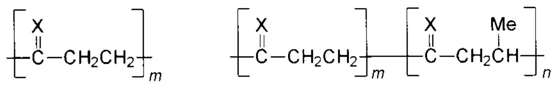
Poly(1-methoxyiminotrimethylene) 5 and poly[(1-methoxyiminotrimethylene)-*co*-(1-methoxyimino-3-methyltrimethylene)] 6, prepared by reaction of ethene/propene–carbon monoxide alternating copolymers with methoxylamine, undergo α-substitution on treatment with BuLi followed by addition of electrophiles such as MeI.

Alternating copolymers of alkenes and carbon monoxide are proving to be useful starting materials for the preparation novel functionalised polymers.[1–5] Reaction can take place at individual ketone groups or at 1,4-dione units; for example, the ketones can be converted to their 1,3-dioxolane derivatives by acid-catalysed reaction with 1,2-diols,[4] whereas with primary amines Paal–Knorr condensation of 1,4-diones affords poly(ethylenepyrroles).[2] We have previously described[5] the conversion of ethene-carbon monoxide copolymer **1** (E-CO) and ethene/propene–carbon monoxide copolymer **2** (EP-CO) to polyketoximes **3** and **4** on treatment with hydroxylamine. We now report that reaction with methoxylamine affords the corresponding methoxime polymers **5** and **6**, and that these readily undergo base-induced reactions with electrophiles at the α-methylene group.



$$\left[C(=X)-CH_2CH_2 \right]_m \qquad \left[C(=X)-CH_2CH_2 \right]_m \left[C(=X)-CH_2CH(Me) \right]_n$$

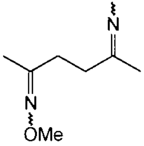
1 X = O (E-CO)
3 X = NOH
5 X = NOMe

2 X = O (EP-CO)
4 X = NOH
6 X = NOMe

Reaction of E-CO or EP-CO with methoxylamine in pyridine at room temperature resulted in slow dissolution of the polymer and complete conversion of the ketone groups to their methoxime derivatives. In a typical experiment a suspension of E-CO (M_n = 1500, 100 mg) was stirred with a four-fold excess of methoxylamine hydrochloride (595 mg) in pyridine (10 ml) at room temperature for two days. The resulting homogeneous solution was poured into water (50 ml) and the product extracted into $CHCl_3$. Washing with aq. Na_2CO_3 and water, drying, and removal of the solvent afforded poly(1-methoxyiminotrimethylene) **5** as a pale yellow gum (71%), which was purified by precipitation from $CHCl_3$ by addition of MeOH. EP-CO (m = 0.99, n = 0.01)† and EP-CO (m = 0.85, n = 0.15)‡ reacted similarly, yielding poly[(1-methoxyiminotrimethylene)-*co*-(1-methoxyimino-3-methyltrimethylene)] **6**. The products were identified from their spectroscopic properties§ by comparison with the corresponding polyketoximes **3** and **4**, and with 2,5-bis(methoxyimino)hexane **7**¶ and 3,6,9-tris(methoxyimino)undecane **8**¶ which were prepared as model compounds by methoximation of hexane-2,5-dione and undecane-3,6,9-trione respectively. For polymethoxime **5** the conversion of ketone units in the polymer to methoximes is evident from the infrared spectrum in which the carbonyl absorption at 1690 cm^{-1} is replaced by a C=N peak at 1630 cm^{-1}. Furthermore in the ^{13}C NMR spectrum the carbonyl absorptions of the starting material at 208–210 ppm are absent and there are new characteristic peaks for the imino carbons at 158.57 and 158.48 ppm, similar to those found at 161–157 ppm for the *E,E*-, *E,Z*- and *Z,Z*-isomers of model dimethoxime **7** and at 161–158 ppm for trimethoxime **8**. There are also signals for the methylene carbons at 30.63, 30.50, 30.03, 29.88, 25.35, 25.07, 24.43 and 24.13 ppm, similar to those reported[5] for polyketoxime **3**. The multiplicity of peaks in this region is attributed to the presence of *syn-anti*, *syn-syn*, *anti-anti* and *anti-syn* combinations of neighbouring oximes; those at higher frequency (29–31 ppm) are assigned to the α-*anti*-carbons by comparison with literature data for methoxyimino compounds.[6] The presence of methoxy groups is shown by signals at 3.78 (^1H) and 61.10 (^{13}C) ppm. Unlike the precursor alkene–carbon monoxide copolymers (**1**, **2**) and the polyoximes (**3**, **4**) all the new polymethoximes show good solubility in a range of organic solvents, thus giving increased scope for modification reactions.

All previous modifications have involved manipulation of the carbonyl groups, either singly or as 1,4-dione or 1,4,7-trione units. Functionalisation of the backbone methylene groups has not been achieved so far, largely due to the very low solubility of these polymers in common organic solvents. The availability of the new polymethoxime derivatives described above provided the opportunity to examine the feasibility of base-induced α-substitution reactions with electrophiles, as illustrated in Scheme 1.

Preliminary experiments were carried out using the model methoximes **7** and **8** in order to establish suitable reaction conditions and also to facilitate spectroscopic identification of the polymer products. Treatment of dimethoxime **7** (1.16 mmol) in THF at −78 °C with BuLi (3.52 mmol), followed by addition of MeI (3.55 mmol) afforded, on work-up, a mixture of compounds **9** and **10** (96% combined yield). Trimethoxime **8** reacted similarly yielding a mixture of α-methylated products (62%), of which compounds **11** and **12** are representative examples. The corresponding reactions of methoximes **7** and **8** with BnBr afforded α-benzylated products **13**/**14** (24%) and *e.g.* **15**/**16** (58%) respectively. The *syn* selectivity of the lithiation process[6,7] was established by reacting dimethoxime **7** with BuLi in THF at −78 °C and quenching the resulting solution with [*O*-^2H]methanol. The isolated product was shown by NMR spectroscopy to be predominantly a mixture of mono- and dideuterio compounds **17** and **18**, together with some unreacted



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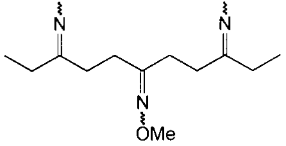

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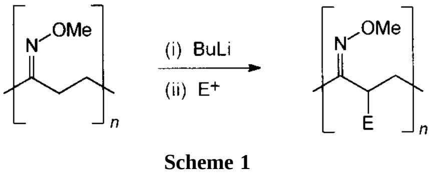
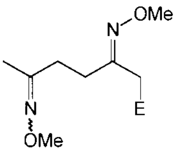
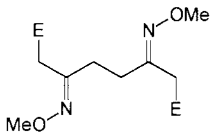


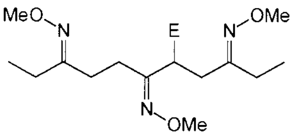
Scheme 1



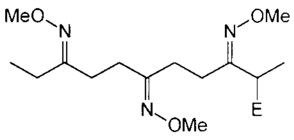
9 E = Me
13 E = Bn
17 E = D



10 E = Me
14 E = Bn
18 E = D



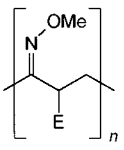
11 E = Me
15 E = Bn
19 E = D



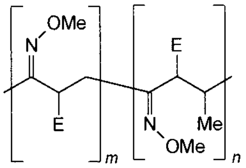
12 E = Me
16 E = Bn
20 E = D

starting material. α-Deuteration at the *syn* methyl is confirmed by the presence of a peak at 1.79 ppm in the ^{2}H NMR spectrum; there is also a corresponding reduction of *ca.* 30% in the intensity of the signal for the protons of this group in the ^{1}H spectrum, with part of the singlet at 1.79 ppm in the starting material being replaced by a 1:1:1 triplet at 1.75 ppm. The analogous reaction of trimethoxime **8** resulted in 8% deuterium incorporation, representing an average of one hydrogen atom being replaced per molecule. Deuterium NMR peaks at 2.16, 2.27 and 2.44 ppm indicate isotopic substitution at several of the syn α-methylene positions, *e.g.* **19**/**20**.

Having established that directed α-substitutions could be accomplished on the model compounds the reactions of the polymethoximes were studied under similar conditions. To test the extent of anion formation a sample of EP-CO-derived polymethoxime **6** (m = 0.99, n = 0.01) was treated with BuLi (5 equiv.), excess [O-^{2}H]methanol added to the resulting solution, and the recovered polymer examined by NMR spectroscopy. α-Substitution in the product **21** is confirmed by the presence of a peak at 2.45 ppm in the ^{2}H NMR spectrum very similar to that observed for the model compounds **19**/**20**; there is also a *ca.* 15% reduction in the intensity of the signal for the methylene protons in the ^{1}H spectrum, indicating that on average there are ~0.6 deuterium atoms per methoxime unit.



22 E = Me or H
23 E = Bn or H



21 E = D or H
24 E = Me or H
25 E = Bn or H

These results suggested that multiple electrophilic substitutions on the polymer backbone should be possible, and to test the feasibility of introducing alkyl substituents by this means the polymethoxime polyanions were reacted with MeI and BnBr. E-CO-derived polymethoxime **5** (100 mg) in dry THF was treated with BuLi (1.0 equiv.) at −78 °C and MeI (1.0 equiv) added to the resulting solution. After stirring for 2 h at −78 °C and warming to 0 °C the mixture was quenched with water and the product extracted into Et$_2$O. Drying, removal of the solvent *in vacuo* and precipitation from CHCl$_3$ solution by addition of MeOH afforded a pale yellow gum (60 mg). The NMR spectra of the product **22** were broadly similar to those observed for the polymethoxime **6** (m = 0.85, n = 0.15) previously prepared by methoximation of the alternating copolymer of carbon monoxide and 85% ethene/15% propene. The introduction of the methyl substituents was confirmed by the appearance of a new proton doublet signal at 1.00 ppm with a 6.7 Hz coupling to the adjacent backbone CH; by comparison with the oximino methyl signal the extent of reaction was estimated as 29%. In the ^{13}C NMR spectrum there are additional peaks for the ethylidene group at 16.28, 16.67 (CH$_3$) and 29.27, 36.00 ppm (CH). The reaction of E-CO polymethoxime **5** with BnBr proceeded similarly, yielding a yellow gum (**23**) which was purified by precipitation from CHCl$_3$ by addition of MeOH. The NMR spectra of the product showed characteristic peaks for the benzylidene group [7.1–7.3 ppm (Ph*H*); 37.52 (*C*HPh), 126.13, 128.18, 128.69 (Ph*C*H), 139.34 ppm (Ph*C*)] similar to those observed for model compounds **13**–**16**. From the proton spectrum it was estimated that there were on ~0.3 benzyl groups per methoxime unit. The corresponding reactions of BuLi / MeI and BuLi / BnBr with EP-CO-derived polymethoximes **6** (m = 0.99, n = 0.01) and **6** (m = 0.85, n = 0.15) proceeded in a similar manner to afford modified polymers **24** and **25**. On the basis of the deuterium exchange experiments it is presumed that for all the alkylated polymers the substituents are introduced *syn* to the methoximino group.

In conclusion, the conversion of the ketone groups in alkene–carbon monoxide copolymers to methoximes allows directed α-substitution reactions to be carried out on the polymer backbone. Previous modification reactions have all involved functionalisation at the carbonyl groups; the results described above therefore represent the first examples involving reaction at the alkene units. It is anticipated that a range of novel polymers will be accessible by reaction with appropriate electrophiles.

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Notes and references

† Alternating copolymer of CO and 99% ethene/1% propene.

‡ Alternating copolymer of CO and 85% ethene/15% propene.

§ NMR spectra were acquired on either a Bruker WH360 (^{1}H, ^{2}H, ^{13}C) or Bruker AC250 (^{13}C) spectrometer.

¶ Compounds **7** and **8** were mixtures of *E*- and *Z*-isomers.

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