Functionalisation of Alkene–Carbon Monoxide Alternating Copolymers *via* Transketalisation Reactions

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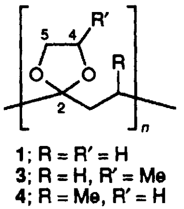
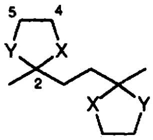
Alkene–dioxolane alternating copolymers 1 and 4, formed from ethane-1,2-diol and the corresponding alkene–carbon monoxide copolymers, undergo transketalisation reactions with ethane-1,2-dithiol, propane-1,3-dithiol and sulfanylethanol to yield novel dithiolane-, dithiane- and oxathiolane-containing polymers 6, 8, 9, 11 and 12.

Copolymers of alkenes and carbon monoxide provide a reactive and inexpensive starting material for the preparation of functionalised polymers.[1] Reaction can take place at the carbonyl group, at the adjacent α-methylene position and, for alternating copolymers, at the 1,4-dione unit.[2] For alternating ethene–carbon monoxide (E–CO) and ethene/propene–carbon monoxide (EP–CO) copolymers we have examined the conversion of the carbonyl groups to ketals by reaction with 1,2-diols, and now report that the products are of interest, both in their own right and as useful precursors for derivatives not directly accessible from the original alkene–CO copolymers.

Acid-catalysed condensation of E–CO and EP–CO copolymers with 1,2-diols in toluene results in complete dissolution of the polymer and smooth conversion of the carbonyl groups to their 1,3-dioxolane derivatives.[3] For example, heating under reflux for 24 h, using a Dean and Stark trap a suspension of E–CO (M_n = 1500, 5.0 g) in a toluene solution of ethane-1,2-diol (30 ml) and toluene-*p*-sulfonic acid (50 mg) afforded 7.8 g of ethene–dioxolane copolymer **1** as a white powder. The structure of the product was established by spectroscopic methods. In the ^{13}C NMR spectrum ($CDCl_3$) there are characteristic absorptions for the heterocyclic ring at δ 110.83 (C-2) and 64.56 (C-4,5), and at δ 30.74 for the methylene carbons of the polymer backbone, similar to those observed (Table 1) for model compound **2** derived from ethane-1,2-diol and hexane-2,5-dione. The complete conversion of the carbonyl groups is evident from the absence of peaks at δ_C 208 and in the IR at ν_{max} 1690 cm^{-1}. Propane-1,2-diol reacted similarly affording copolymer **3** which incorporates 4-methyl-1,3-dioxolane units. The corresponding reactions of EP–CO terpolymer (23% ethene, 27% propene, 50% CO, M_n 6000) with ethane- and propane-1,2-diols also yielded the expected dioxolane derivatives **4** and **5**.



1; R = R′ = H
3; R = H, R′ = Me
4; R = Me, R′ = H
5; R = R′ = Me



2; X = Y = O
7; X = Y = S
13; X = O, Y = S

Table 1 Selected NMR data[a] for polymers and model compounds

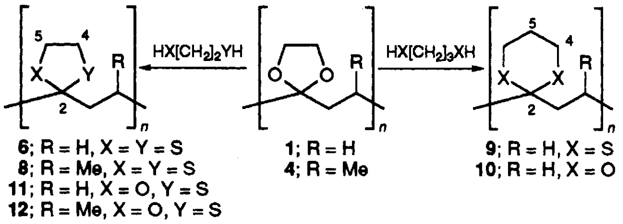
			δ_C			
Compound	X	Y	C(2)	C(4)	C(5)	C(α)
1	O	O	110.83	64.56	64.56	30.74
2	O	O	109.43	64.32	64.32	33.07
3[b]	O	O	111.36	72.02	71.16	31.67 31.26
10	O	O	99.45 98.94[c]	58.67	24.71	29.95
6	S	S	70.35	39.33	39.33	39.77
7	S	S	66.17	39.70	39.70	42.40
9	S	S	52.78	25.87	24.96	32.80
12	O	S	97.29	70.02	33.26	35.34
13	O	S	94.59	70.05	33.85	38.34

[a] Recorded at 50 MHz in $CDCl_3$. [b] Additional peak at δ 18.09 (4-Me). [c] Attributed to presence of unreacted dioxolane units in the polymer.

Having established that the alkene–carbon monoxide copolymers condense readily with vicinal diols, the analogous reactions with 1,2- and 1,3-dithiols were examined. Direct condensation of E–CO and EP–CO proved to be unsatisfactory. Although an increase in mass of the polymeric solid and the formation of water indicated that some reaction had taken place, the polymers did not dissolve, an effect attributed to crosslinking under the reaction conditions.[4] An alternative approach was therefore adopted which involved acid-catalysed ketal to dithioketal conversion using the new ethene–dioxolane copolymers **1** and **4** as the starting materials (Scheme 1). For example, a solution of **1** (1.0 g), ethane-1,2-dithiol (5.6 g) and toluene-*p*-sulfonic acid (10 mg) in toluene (150 ml) was heated under reflux for 72 h and the displaced ethane-1,2-diol removed by azeotropic distillation. Washing the resulting solution with 0.2% NaOH (aq) and with brine, drying ($MgSO_4$), and removal of the solvent afforded a pale-yellow solid (0.87 g) which was purified by precipitation from chloroform solution by adding methanol. The polymeric product was identified from its analytical and spectroscopic properties as ethene–dithiolane copolymer **6**. The ^{13}C NMR chemical shifts for the carbons of the heterocyclic ring closely resemble those of model compound **7** (Table 1). The absence of peaks at δ_C 110.83 and 64.56 and appearance of new peaks at δ 70.35 and 39.33 indicated complete conversion of dioxolane to dithiolane. The analogous dioxolane derivative **4** derived from EP–CO also proved to be a good starting material, affording dithiolane derivative **8**. Propane-1,3-dithiol reacted similarly with dioxolane polymer **1** to yield alkene–dithiane copolymer **9**.

Transketalisation was also used for the interconversion of dioxolane units thus providing a useful method for the preparation of ketals for which direct condensation between diol and alkene–carbon monoxide copolymers was impracticable. For example, displacement of ethane-1,2-diol from copolymer **1** with propane-1,3-diol afforded a product with a high proportion of 1,3-dioxane units **10**, whereas the corresponding reaction of the 1,3-diol with E–CO itself resulted in extensive crosslinking.

Polymers comprising alternating ethene and 1,3-oxathiolane units were prepared by both methods. Direct condensation of 2-sulfanylethanol with E–CO and EP–CO resulted in clean conversion of the carbonyl groups to 1,3-oxathiolane-containing polymers **11** and **12**, which were identified from their NMR spectra (Table 1) by comparison with model



6; R = H, X = Y = S
8; R = Me, X = Y = S
11; R = H, X = O, Y = S
12; R = Me, X = O, Y = S

1; R = H
4; R = Me

9; R = H, X = S
10; R = H, X = O

Scheme 1

compound **13**. The same units were also formed when copolymer **1** was used as starting material for transketalisation.

These results demonstrate that the alkene–dioxolane copolymers such as **1** and **4** provide a convenient source of new heterocyclic polymers. Furthermore, unlike the precursor alkene–carbon monoxide copolymers, all the new ketal, thioketal and dithioketal derivatives show good solubility in a range of organic solvents.

Received, 21st June 1994; Com. 4/03759F

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