Generation and Reactions of Polymer-bound Nitrile Sulphides

Roy M. Mortier,[b] R. Michael Paton,*[a] and Ian Stobie[a]

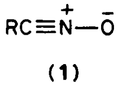
[a] *Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K.*
[b] *Imperial Chemical Industries PLC, Organics Division, P.O. Box 42, Hexagon House, Blackley, Manchester M9 3DA, U.K.*

Copolymers of 5-isopropenyl- and 5-vinyl-1,3,4-oxathiazol-2-ones with methyl methacrylate or styrene undergo thermal decarboxylation at 135—140 °C forming polymer-bound nitrile sulphides, which may be trapped as their 1,3-dipolar cycloadducts with dimethyl acetylenedicarboxylate or ethyl cyanoformate; in the absence of a dipolarophile the oxathiazolone units are converted into nitriles.

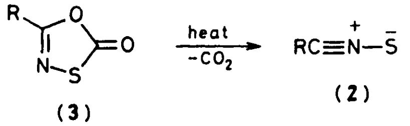
The 1,3-dipolar cycloaddition reactions of nitrile oxides (**1**) find widespread use in heterocyclic synthesis,[1] and to a more limited extent for the formation[2] and modification[3] of polymers. In contrast much less attention has been paid to the corresponding nitrile sulphides (**2**), and examination of their chemistry has so far concentrated on developing methods for their generation and exploring the scope of their reactions.[4] We now report the formation and cycloaddition reactions of some polymer-bound nitrile sulphides.

While nitrile sulphides can be generated from a variety of sources the most generally applicable route involves thermal decarboxylation of 1,3,4-oxathiazol-2-ones (**3**). The 5-isopropenyl and 5-vinyl compounds, (**3a**) and (**3b**), which are available[5] by treatment of methacrylamide and acrylamide respectively with chlorocarbonylsulphenyl chloride, have recently been shown[6] to copolymerise with methyl methacrylate (MMA) and styrene. The products (**4**) incorporate both monomers together with a trace of nitrile units, the latter arising from partial decomposition[7] of the oxathiazolones during the polymerisation process.

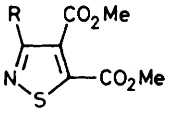
The terpolymer (**4a**) (1.0 g) comprising units of (**3a**) (x = 39%), methacrylonitrile (y = 3%), and MMA (z = 58%) was heated for 6 h at 135—140 °C with dimethyl acetylenedicarboxylate (DMAD) (2.7 g, giving a 5:1 molar ratio of DMAD to oxathiazolone units in the polymer) in xylene (25 ml). Removal of the solvent and excess of the dipolarophile by distillation under reduced pressure and purification of the residue by precipitation (×3) from chloroform into hexane afforded a pale yellow solid (0.85 g). The product was identified from its analytical and spectroscopic properties as the terpolymer (**5a**), containing units of isothiazole (x = 17%), methacrylonitrile (y = 16%), and MMA (z = 67%). The presence of isothiazole units is evident from the ^{13}C n.m.r. spectrum (Figure 1). The oxathiazolone absorptions at 176—173 (C-2) and 167—162 p.p.m. (C-5) in the starting material are replaced by peaks at 174—172, 165.6, 159.0, 157—155, and 133.5 p.p.m. These are assigned to C-3, CO$_2$Me, CO$_2$Me, C-5, and C-4 respectively of the isothiazole-4,5-dicarboxylate units by comparison with the 3-alkyl analogue (**6c**) (174.5, 164.2, 159.4, 155.4, and 131.5 p.p.m.), which was selected as a model compound. A broad peak at δ 4.0 in the ^{1}H n.m.r. spectrum provides supporting evidence. During the course of the reaction the intensity of the infrared absorption at 2220 cm^{-1} increased, suggesting that some of the oxathiazolones had been converted into nitriles.


$\overset{+}{\mathrm{RC{\equiv}N}}\!-\!\overset{-}{\mathrm{O}}$

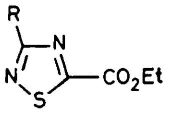
(**1**)



(**3**) (**2**)

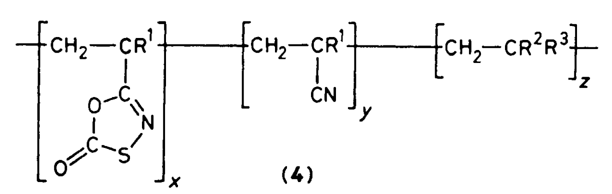


(**6**)

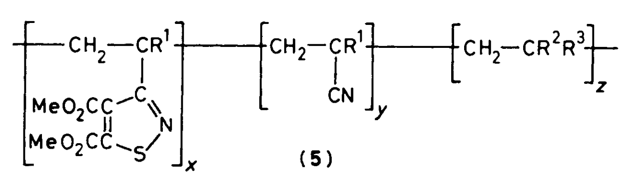


(**8**)

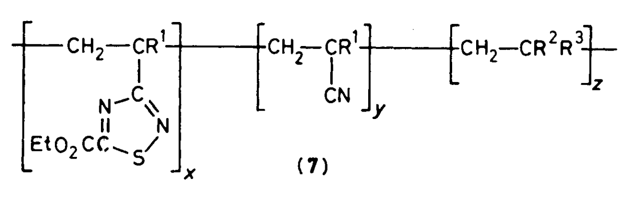
a; R = CMe=CH$_2$
b; R = CH=CH$_2$
c; R = Pr^i



(**4**)



(**5**)



(**7**)

a; R^1 = R^2 = Me, R^3 = CO$_2$Me
b; R^1 = H, R^2 = Me, R^3 = CO$_2$Me
c; R^1 = Me, R^2 = H, R^3 = Ph
d; R^1 = R^2 = H, R^3 = Ph

Treatment of (**4a**) with ethyl cyanoformate (ECF) afforded the 1,2,4-thiadiazole copolymer (**7a**; x = 20, y = 16, z = 64%), the structure of the product being established by ^{13}C and ^{1}H n.m.r. spectroscopy by comparison with (**8c**). Similar results were obtained for the vinyl analogue (**4b**; x = 11, y = 5, z =

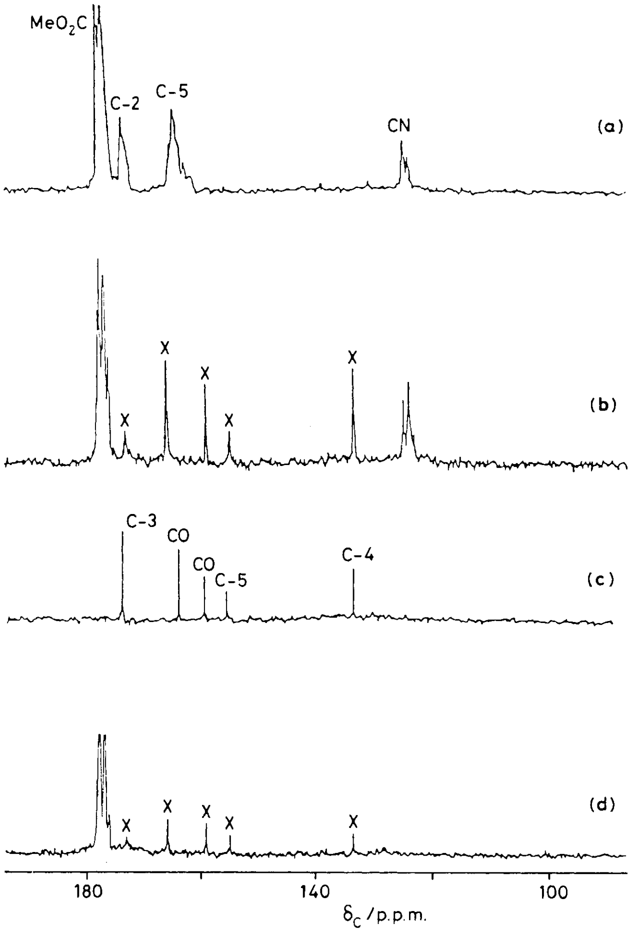


Figure 1. ^{13}C N.m.r. spectra in the range 100—190 p.p.m. of (a) oxathiazolone–methacrylonitrile–MMA terpolymer (**4a**), (b) isothiazole–methacrylonitrile–MMA terpolymer (**5a**) formed by reaction of (**4a**) with DMAD, (c) isopropyl isothiazole (**6c**), (d) isothiazole–MMA copolymer formed by copolymerisation of (**6a**) with MMA. The peaks marked X in (b) and (d) are assigned to isothiazole units by comparison with (**6c**) (see text).

84%), when (**5b**; $x = 10, y = 3, z = 87\%$) and (**7b**; $x = 5, y = 13, z = 82\%$) were formed with DMAD and ECF respectively. Likewise the styrene copolymers (**4c**; $x = 35, y = 5, z = 60\%$) and (**4d**; $x = 33, y = 3, z = 64\%$) afforded (**5c**; $x = 22, y = 17, z = 61\%$) and (**5d**; $x = 17, y = 17, z = 66\%$) with DMAD, and (**7c**; $x = 23, y = 21, z = 56\%$) and (**7d**; $x = 13, y = 21, z = 66\%$) with ECF.

In the absence of a dipolarophile the oxathiazolones are converted into nitriles (δ_C 126—123 p.p.m.; ν_{max} 2220 cm^{-1}); *e.g.* (**4a**; $x = 39, y = 3, z = 58\%$) yielded (**4a**; $x = 8, y = 27, z = 65\%$). These results are consistent with decarboxylation of the oxathiazolone to afford a polymer-bound nitrile sulphide, which either fragments to nitrile and sulphur or undergoes 1,3-dipolar cycloaddition with the dipolarophile.

A complementary approach to isothiazole- and 1,2,4-thiadiazole-containing polymers involves 1,3-dipolar cycloaddition of α-alkenylnitrile sulphides, generated from the corresponding oxathiazolones,[5] and subsequent copolymerisation of the resulting cycloadducts with MMA or styrene. For example, a mixture of (**6a**) (1.0 mmol), MMA, (10 mmol), and azoisobutyronitrile (25 mg) was heated in refluxing methyl ethyl ketone for 5 h. Evaporation of the solvent and purification of the product by precipitation (×3) from chloroform into methanol afforded a white solid (30% yield). ^{13}C N.m.r. spectroscopy (Figure 1d) and elemental analysis demonstrated the presence of isothiazole (12%) and MMA (88%) units. In these cases nitriles are not produced, as shown by the absence of the characteristic peaks at δ_C 126—123 p.p.m. and ν_{max} 2220 cm^{-1}.

The reactions of the polymeric oxathiazolones closely parallel those of their monomeric analogues, suggesting that a variety of polymer-bound heterocycles incorporating the C=N–S fragment may be accessible by this means.

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