Coordinative cross-linking of pyridyl- and bipyridyl-based hydrogel polymer membranes

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The preparation of a series of hydrogel copolymer membranes of 2-hydroxyethyl methacrylate with 4-vinyl pyridine (VPy) in the range of 0.5–17 wt%, or 4′-vinyl 4-methyl 2,2′-bipyridine (VBpy) in the range 0.5–8 wt%, are described. The membranes are shown to coordinate selected transition metal ions from aqueous solution. Interactions with Cu(II) and Fe(II) were isolated for individual attention on the basis that, under certain conditions, bands appear in the visible spectra characteristic of the Cu(II) tetra(VPy) and the Fe(II) tris(VBpy) complexes. The complexation of more than one ligand group per metal ion leads to the potential anchoring of two or more previously unconnected polymer chains at a metal-centred cross-link. The effects of 'coordinative cross-linking' on the tensile properties of the hydrogel polymers were studied in elongation at 25°C and 100% humidity, until failure of the membranes occurred. The tensile strengths of both the Cu(II) and Fe(II)-coordinated polymers are found to increase in conjunction with copolymer ligand content, as a consequence of a greater degree of coordinative cross-linking. In more classical hydrogel systems, the equilibrium water content of the polymer is caused to fall with degree of cross-linking. Here, this is not the case, as the equilibrium water content remains relatively unchanged owing to the incorporation of further water-structuring groups in the guise of metal complexes. Together with the capability of a reversible cross-linking effect by metal leaching under acid conditions, these ligand-modified systems offer a novel and unique route to the enhancement of mechanical properties in hydrogel-type materials.

(Keywords: coordinative cross-linking; iron(II) tris (4′-vinyl 4-methyl 2,2′-bipyridine); copper(II) tetra(4-vinyl pyridine); hydrogel membranes)

INTRODUCTION

Hydrogels are a family of hydrophilic polymers possessing chemical functional groups that enable interaction with water, to produce a highly swollen material. The high water contents of these compounds often impart biocompatibility; this makes them suitable for use in the field of biomaterials and their application in contact lens technology is particularly extensive[1–3]. Highly swollen gel-like materials usually have poor mechanical properties, and the technique of cross-linking the polymer chains is of extreme importance in determining the overall three-dimensional characteristics of the structure, often leading to enhancement of physical traits such as strength and thermal resistance. Mechanical property characterization techniques such as tensometry and microindentation have been used successfully in the study of these systems[4]. They help in the appreciation of the effects of hydrogel copolymer composition on the physical integrity of the polymers, a *sine qua non* for their efficient utilization.

We have described separately the preparation of a series of hydrogel membranes based on copolymers of 2-hydroxyethyl methacrylate (HEMA) with 4-vinyl pyridine (VPy) or 4-vinyl 4′-methyl 2,2′-bipyridine (VBpy), which are capable of coordinating selected transition metal ions from aqueous solution[5]. Analysis of the visible absorption spectra of appropriately treated complexed membranes demonstrates the presence of polymer-bound Cu(II) tetra(VPy) and Fe(II) tris(VBpy) complexes (*Figure 1*).

As a consequence of the formation of more than one metal–ligand interaction per metal ion, complex formation acts as an unusual method of cross-linking the hydrogel matrix. There have been infrequent reports in the literature concerning the use of transition metal ions in the modification of polymers such as polyethers[6] and more specific purpose-synthesized systems containing ligand residues such as salicylic acid[7], resulting in coordinatively cross-linked networks. Kopeikin[8] has reported the synthesis of a number of chelating polymers containing the acetylacetone (acac) group, and Yeh *et al.*[9] have developed a number of spectroscopic means for studying the Cu(II), Fe(III) and Cr(II) bis and tris complexes of these polymers. They have extended their

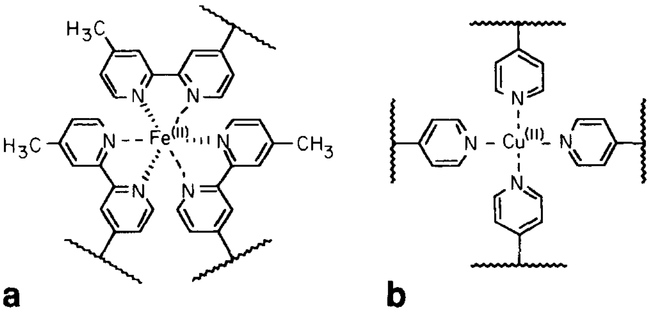

Figure 1 (a) The bolymer-bound Fe(II) tris(VBpy) complex; (b) the Cu(II) tetra(VPy) complex

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work to include a novel approach to the investigation of the effects of coordinative cross-linking by studying mechanical properties of the polymers[10]. In an analogous fashion we have been able to employ the tensometric methods developed for hydrogels, to determine the effects of coordinative cross-linking on the physical properties of our ligand-based copolymer membranes.

EXPERIMENTAL

Monomers

Optical grade HEMA was used as supplied by Ubichem Ltd. Ethylene glycol dimethacrylate (EGDM) cross-linking agent and α-azobisisobutyronitrile initiator were obtained from BDH and Aldrich respectively and used without further purification. VPy was obtained from Aldrich and purified by reduced-pressure distillation (62–64°C at 15 mmHg), and the pure clear liquid stored under nitrogen at 5°C until needed. VBpy was prepared by a previously described method[5] and satisfactory elemental and n.m.r. analyses were obtained.

Membrane preparation

Two series of copolymer membranes were made, with VPy weight loadings ranging from 0.5 to 17% (HEMA:VPy mole ratios of 150:1–4:1), and VBpy weight loadings of 1–8% (HEMA:VBpy mole ratios of 149:1–17:1). Previous studies on the reactivity ratios of these monomers indicated that the resulting copolymers should be random and homogeneous[11]. Copolymerization of the desired monomers, with 1% EGDM to cross-link for intrinsic strengthening, was achieved *in situ* within a glass membrane mould by a procedure outlined fully elsewhere[12]. Membranes were subsequently leached for 1 week with frequent changes of deionized water, and then stored in deionized water in a sealed container until required.

Transition metal salt solutions

Analytical grade $FeSO_4.7H_2O$ and $CuCl_2.6H_2O$ (BDH) were used as supplied and salt solutions were prepared using deionized water of conductivity $1.5 \pm 0.5\ \mu S\ cm^{-1}$. Only freshly made Fe(II) solutions were used as, over time, these undergo atmospheric oxidation to Fe(III), with a resultant precipitation of $Fe(OH)_3$. It is essential that iron(II) sulfate is used as opposed to other Fe(II) salts, as other studies have shown the complexation process to be kinetically complicated; the total ligand utilization is dependent both on concentration, and more importantly, on the nature of the anion[13].

Transition metal coordination procedure

Iron(II) complexation. VBpy copolymer membranes were placed in a sealed vessel containing 0.25 M $FeSO_4$ for a number of days, to allow complete complexation to occur. The membranes take on a deep-red coloration due to the formation of the Fe(II) tris(VBpy) coordination centre within the membrane. The visible spectrum of these membranes is extremely intense, and the characteristic metal-to-ligand charge-transfer band, with λ_{max} at 534 nm, can only be measured on membranes containing less than 0.5% ligand loading. Fully coordinated membranes were stored in distilled water until required.

Copper(II) complexation. VPy membranes were placed in 0.25 M $CuCl_2$ for several days, after which the visible absorption spectrum showed a broad band with λ_{max} varying from 810 to 740 nm for the ligand loadings from 0.5 to 8% respectively. After leaching the excess Cu^{2+} from the membrane in distilled water for an additional 2 days, the absorption intensity was reduced and λ_{max} shifted to around 620 nm for all ligand loadings. This has previously been attributed to the effect of an enhanced ligand field resulting from the conversion from predominantly mono to tetra (VPy)–Cu^{2+} complexes within the membrane[5]. These membranes were also stored in distilled water prior to the testing of their mechanical properties.

Mechanical property measurements

Stress–strain measurements were carried out in elongation on the hydrated membranes at 21°C. Tensile testing was performed on a 20KM Hounsfield tensometer with 10 N load cell, interfaced to an IBM 55SX computer and operated by customized software. The dumb-bell sample shape was adopted (the wider portions fitting within the jaws of the tensometer) with a gauge length of 8 mm. A micrometer was used to measure sample thickness. The strain rate has a critical effect on the tensile properties, and was fixed at 200% min^{-1} extension for this study. It was important that the membranes remained in their fully hydrated state for the tensile readings to be consistent and, therefore, the sample was periodically sprayed with a fine mist of water during testing in order to maintain the water content balance, producing essentially 100% humidity.

RESULTS AND DISCUSSION

Uncoordinated copolymer membrane characterization

PolyHEMA membranes cross-linked with 1% EGDM have relatively poor mechanical properties and are essentially soft materials capable of moderate elongation before fracture. Typically, the tensile strength (σ) is reported to be in the region of 0.5 MPa, with an elongation to break (ε_b) of around 200%. Copolymerization with hydrophobic monomers such as styrene and methyl methacrylate results in an increased σ with a concomitant reduction in ε_b as the polymer undergoes a transition from flexible to more rigid behaviour. This occurs because the bulk 'freezing' water content, and thus the plasticizing effect on the polymer chains, is reduced in these copolymers (*Table 1*). Similarly, increasing the density of cross-links within the structure makes the gel network more tightly bound and there is an obvious drop in the equilibrium water content (EWC) of the material. This again, will result in an enhanced σ and reduced ε_b.

Data from *Table 2* show that the incorporation of the hydrophobic ligand components used here also lowers the EWC of the membranes to some extent. However, VPy and VBpy are by no means as hydrophobic as the corresponding styrene and vinyl biphenyl analogues, because the nitrogen atoms within the heterocyclic rings of the ligands are able to participate in weak hydrogen bonding to water molecules[14].

Table 3 summarizes data that compare the tensile properties of polyHEMA-only membranes with those of the ligand-based analogues, and *Figures 2* and *3* are the corresponding load–extension curves observed for these systems. The general observation is that a notable increase in both σ and ε_b results from an increase in the

Table 1 Equilibrium water content data for various HEMA copolymer membrane types. (All compositions shown are expressed as percentage by weight, and all membranes were cross-linked by 1% EGDM unless stated otherwise)

Styrene (%)	EWC (%)	MMA (%)	EWC (%)	EGDM (%)	EWC (%)
0	37.5	0	37.5	0	44.0
5	29.3	5	34.9	1	37.5
10	25.4	10	32.5	2.5	33.3
15	20.2	20	27.8	5	30.5
20	12.3	30	24.8	10	25.7
50	4.8	50	13.9	20	20.0

Table 2 Equilibrium water content data for ligand-modified HEMA membranes: uncomplexed and complexed. (All compositions shown are expressed as percentage by weight, and all membranes were cross-linked by 1% EGDM unless stated otherwise)

VPy (%)	EWC (%)	VBpy (%)	EWC (%)	VPy/Cu (%)	EWC (%)[a]	VBpy/Fe (%)	EWC (%)[a]
0	37.5	0	37.5	0	34.1	0	32.1
0.5	39.2	0.25	39.5	0.5	36.0	0.25	37.5
1	37.3	0.5	39.2	1	36.1	0.5	38.1
2	35.9	1	39.0	2	38.0	1	38.8
4	35.7	2	38.1	4	39.9	2	39.3
8	34.2	4	38.0	8	42.7	4	40.3

[a] Complexed membranes measured after hydration in 0.25 M metal salt solution

Table 3 Collection of mechanical property data for ligand-modified membranes: uncomplexed and complexed

Membrane polymer type	Modulus, E_{25} (%)	Modulus, E_{50} (%)	Tensile strength, σ (MPa)	Elongation to break, ε_b (%)
PHEMA	–	0.5 ± 0.06	0.52 ± 0.02	125 ± 24
1% VBpy	0.71 ± 0.02	0.63 ± 0.01	0.67 ± 0.11	130 ± 22
2% VBpy	0.7 ± 0.02	0.65 ± 0.04	0.75 ± 0.12	143 ± 21
4% VBpy	0.67 ± 0.12	0.66 ± 0.06	0.85 ± 0.11	155 ± 22
8% VBpy	–	0.68 ± 0.04	0.93 ± 0.13	170 ± 23
1% VBpy: [Fe^{2+}]	0.92 ± 0.04	0.83 ± 0.03	0.64 ± 0.04	85 ± 4
2% VBpy: [Fe^{2+}]	1.42 ± 0.1	1.25 ± 0.06	1.04 ± 0.2	85 ± 7
4% VBpy: [Fe^{2+}]	1.63 ± 0.09	1.69 ± 0.09	1.52 ± 0.39	83 ± 15
8% VBpy: [Fe^{2+}]	–	4.24 ± 0.23	2.88 ± 0.57	64 ± 8
2% VPy	–	0.32 ± 0.07	0.68 ± 0.13	110 ± 17
4% VPy	–	0.63 ± 0.02	0.68 ± 0.06	133 ± 13
8% VPy	0.47 ± 0.06	0.5 ± 0.02	0.99 ± 0.09	241 ± 18
16% VPy	0.33 ± 0.13	0.44 ± 0.04	2.24 ± 0.33	323 ± 27
2% VPy: [Cu^{2+}]	–	0.28 ± 0.02	0.52 ± 0.04	135 ± 18
4% VPy: [Cu^{2+}]	–	0.6 ± 0.02	0.69 ± 0.06	142 ± 9
8% VPy: [Cu^{2+}]	3.98 ± 0.24	2.7 ± 0.12	3.62 ± 0.54	264 ± 36
16% VPy: [Cu^{2+}]	4.25 ± 0.2	4.08 ± 0.11	4.58 ± 0.25	110 ± 22

ligand content of the copolymer. The weak hydrogen-bonding ability of the nitrogen functions helps to improve elongation and contribute to an increased strength by forming transient 'cross-links' between the polymer chains, whilst allowing the structure to maintain its elasticity.

Coordinative cross-linking

Cross-linking of the polymers by coordination with transition metal ions has a dramatic effect on the mechanical properties of the membranes. *Table 3* contains the relevant tensile data for these membranes, and *Figures 4* and *5* are the load–extension curves observed. However, as *Table 2* shows, this is not at the expense of the overall EWC of the membrane. Indeed, each metal complex incorporated within the polymer possesses its own hydration sphere which contributes to the overall water content of the gel. Therefore, unlike conventional cross-linking in these materials, high EWC values are maintained whilst vastly improved mechanical properties are achieved.

As the VBpy content of the copolymer increases, and hence effectively the degree of cross-linking after complexation, the value of σ significantly improves. However, the effect on ε_b is severe: the material becomes extremely brittle and typical of a highly

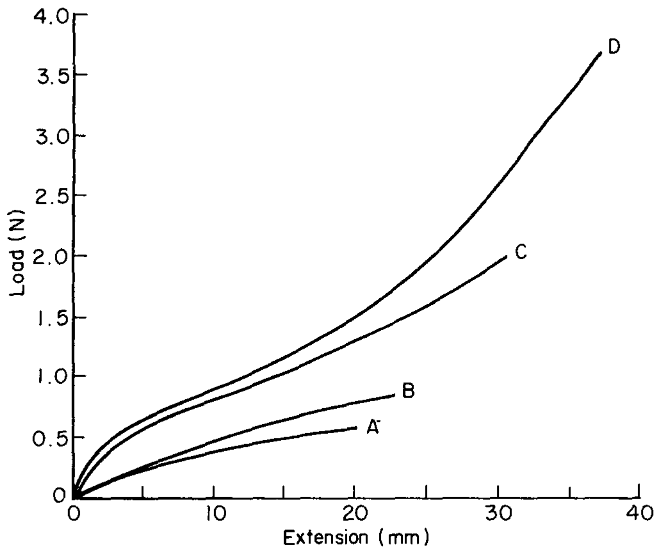

Figure 2 Load *versus* extension curves for a series of VPy copolymer membranes. VPy content (%): A, 2; B, 4; C, 8; D, 17

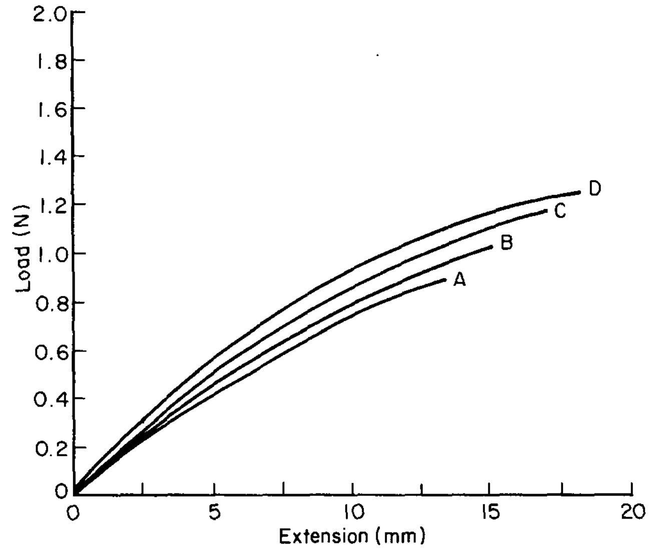

Figure 3 Load *versus* extension curves for a series of VBpy copolymer membranes. VBpy content (%): A, 1; B, 2; C, 4; D, 8

cross-linked network. Previous work on the Fe(II) ion-binding capacity of the copolymer membranes has shown that the polymer chains in these systems are extremely mobile and capable of coordination to Fe(II). Over 80% utilization of available ligand groups can be achieved[5,13]. Coordinative three-centre cross-linking potentially anchors three independent or widely separated polymer chains at a single point, and with 80% of ligands cooperating in this manner, great improvements in the tensile strength of the material are gained.

Similar effects are seen when the VPy copolymer composition is increased in favour of the ligand. Coordination produces an increase in the cross-link density and a subsequent improvement in σ. The effect on the value of ε_b is not as simple as for the VBpy system. Between 2 and 8% VPy, the material behaves as an elastomer, ε_b being enhanced from 135 to 264%. This is a consequence of the structure of the material moving from that of essentially unconnected chains linked by weak van der Waals' forces, to chains bonded by few but strong coordinative cross-links, at which stage the polymer can be thought of as a quasi-single molecule. However, when the VPy content has risen to 17% the structure becomes highly cross-linked, which continues to strengthen the polymer, but the elongation properties are outweighed by the material's inability to deform to any extent. The load–extension curve for 17% VPy (*Figure 4*) displays a characteristic hump, indicative of the onset of 'necking' in the specimen, which continues until eventual failure of the membrane.

The formation of the Cu(II) tetra(VPy) complex could anchor up to four separate polymer chains, as opposed to the VBpy system where the maximum is three. Such high degrees of cross-linking in the VPy copolymer would confer mechanical properties analogous to, if not more extensive than, those of the highly cross-linked and brittle VBpy materials. This is found to be the case, and as the spectroscopic evidence is of a high proportion of

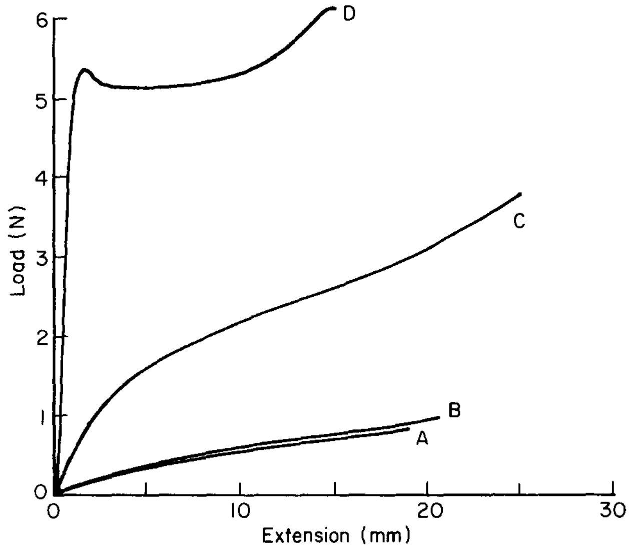

Figure 4 Load *versus* extension curves for a series of Cu(II)-complexed VPy copolymer membranes. VPy/Cu(II) content (%): A, 2; B, 4; C, 8; D, 17

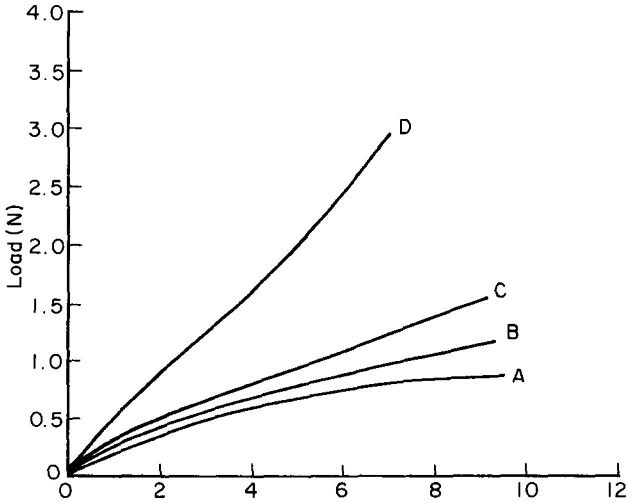

Figure 5 Load *versus* extension curves for a series of Fe(II)-complexed VBpy copolymer membranes. VBpy/Fe(II) content (%): A, 1; B, 2; C, 4; D, 8

four-coordinate complexes, the mechanical properties suggest that the majority of cross-linking sites in the VPy system arise from the combination of two or more ligands immobilized on the same chain, i.e. effectively two-centred in nature. This is not an unreasonable deduction, as the polymer could easily behave as a super-chelate, in which the complexation of one ligand to a metal ion is sufficient to hold the ion in the vicinity of, and at the correct orientation for, a nearest neighbour along the chain to therefore preferentially coordinate.

CONCLUDING REMARKS

A range of VBpy copolymer membranes are described, which are capable of coordinating Fe(II) ions from solution to produce immobilized iron(II) tris(VBpy) complexes within the polymer. Similarly, a series of VPy membranes are shown to take up and coordinate Cu(II) from solution, with the potential to form membrane-bound Cu(II) tetra(VPy) complexes. In both cases the complexation process leads to cross-linked materials with vastly different mechanical properties to those of the uncoordinated precursors.

Previous methods for improving the mechanical characteristics of hydrogel-type polymers include the introduction of hydrophobic components to improve rigidity, or increased levels of cross-link density. Conventional cross-linking sites are not as mobile as the rest of the backbone, and they will tend to stiffen and strengthen the polymer but reduce the hydrophilicity by tightening the three-dimensionally bonded matrix. Therefore, attempts to improve the mechanical strength of hydrogels usually result in an unacceptable drop in the EWC. The complex-bound hydrogels described here offer a novel method for improving tensile capabilities by cross-linking, without the accompanying loss in water content that is usually observed. The incorporation of immobilized transition metal ion complexes produces a very strong coordinative cross-link, but additionally introduces the hydration shell of the ion into the matrix, which helps to maintain the water content balance.

Although not fully investigated in this work, these materials also possess the potential for reversible cross-linking. The Cu(II)-coordinated VPy polymers can certainly be dissociated in 0.1 M HCl, the Cu^{2+} being displaced from the VPy donor N-atoms by H^+, resulting in a disappearance of the blue coloration within the membrane. The Fe(II) tris(VBpy) complex has a much greater stability constant, but solution studies show that this too can be dissociated in the presence of strong acid.

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REFERENCES

1 Pedley, D. G., Skelly, P. J. and Tighe, B. J. *Br. Polym. J.* 1980, **12**, 99

2 Larke, J. R. and Tighe, B. J. (to national Research Development Corporation), British Patent 1 395 501, 1975

3 Larke, J. R., Pedley, D. G. and Tighe, B. J. (to national Research Development Corporation), British Patent 1 500 692, 1978

4 Corkhill, P.H. PhD Thesis, University of Aston in Birmingham, 1988

5 Lewis, A. L. and Miller, J. D. *J. Mat. Chem.* in press

6 Wetton, R. E., Jones, D. B. and Whiting, W. *J. Polym. Sci., Polym. Chem. Edn* 1976, **14**, 571

7 Braun, D. and Bouderstan, H. *Eur. Polym. J.* 1976, **12**, 525

8 Kopeikin, V. V. *Acta Polym.* 1983, **34**, 307

9 Yeh, H. C., Eichinger, B. E. and Andersen, N. H. *J. Polym. Sci., Polym. Chem. Edn* 1982, **20**, 2575

10 Ning, Y.-P., Mark, J. E., Iwamoto, N. and Eichinger, B. E. *Macromolecules* 1985, **18**, 55

11 Mikes, F., Strop, P., Seycek, O., Roda, J. and Kálal, J. *Eur. Polym. J.* 1974, **10**, 1029

12 Pedley, D. G. and Tighe, B. J. *Br. Polym. J.* 1979, **11**, 130

13 Lewis, A. L. and Miller, J. D. *J. Mat. Chem.* in press

14 Miller, J. D. and McWhinnie, W. R. *Adv. Inorg. Chem. Rad. Chem.* 1969, **12**, 135