The Effect of Trivalent Metal Nitrates on the Properties of Dental Cements Made from Poly(acrylic acid)

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ABSTRACT: Addition of either $Al(NO_3)_3$ or $Fe(NO_3)_3$ to zinc polycarboxylate and glass polyalkenoate dental cements has been shown to cause an acceleration to their setting reactions. In the case of $Fe(NO_3)_3$, the reaction was so fast that cements could not be mixed, but $Al(NO_3)_3$ had a less severe effect, and cements containing various amounts of this additive were prepared. Their compressive strength at 24 h was lower than for the original cements, with zinc polycarboxylate being more affected than the glass polyalkenoate. Both cements are made from poly(acrylic acid), and infrared spectroscopy showed that both $Al(NO_3)_3$ and $Fe(NO_3)_3$ form adducts with this polymer, the interaction of aluminum with the polymer being significantly different from that of the iron (III) species. The binding by $Al(NO_3)_3$ was also shown to reduce the pH of a poly(acrylic acid) solution. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2353–2359, 1998

Key words: dental cements; additives; polyelectrolytes; aluminium nitrate; iron (III) nitrate

INTRODUCTION

Poly(acrylic acid) is used in 2 classes of dental cement, namely, the zinc polycarboxylate and the glass polyalkenoate (so-called "glass ionomers").¹ These cements set by neutralization involving a powdered solid base.¹ For zinc polycarboxylate, the base is a slightly nonstoichiometric zinc oxide, corresponding to $\text{ZnO}_{(1-x)}$ (x < 0.70 ppm), formed by heating²; whereas for glass polyalkenoates, the base is a special calcium fluoroaluminosilicate glass.³ The reaction of the glass is more complicated than that of ZnO and involves a process in which ion-depleted silicate and phosphate residues form an additional network.^{4–6}

The effect of ionic additives on these cements has been studied extensively.^{7–9} Monovalent salts, for example, NaCl, KCl, or KBr, have been shown to accelerate the setting of zinc polycarboxylates but to retard the setting of the glass polyalkenoates.^{9,10} The compressive strength of zinc polycarboxylates was unaffected, but glass ionomers were weakened by these additives. Divalent salts, for example, $CaCl_2$ or $ZnCl_2$, had similar effects on setting, though, in both cases, they reduced the compressive strength.¹¹ These results are related to changes in conformation and ionization of poly(acrylic acid) caused by the salts.^{10,11,12}

The present article describes the effect of 2 trivalent nitrates, $Al(NO_3)_3$ and $Fe(NO_3)_3$, in these cements. Aluminum nitrate is known to insolubilize poly(acrylic acid),^{13,14} as is the iron salt FeCl₃. Gels of FeCl₃–poly(acrylic acid) have been used in dentistry to plug dentinal tubules to prevent penetration by bacteria,¹⁵ and similar gels are known to be formed by $Fe(NO_3)_3$ with poly(acrylic acid).¹⁶

MATERIALS AND METHODS

The materials employed were a zinc polycarboxylate, PolyF Plus, and a glass polyalkenoate, Aqua-Cem (Dentsply Ltd, Konstanz, Germany). Both of these are water-activated; that is, they are supplied as a mixture of poly(acrylic acid) powder plus base, to which a controlled amount of water is added to bring about setting. The powder-toliquid ratio was as recommended by the manufacturers, 5:1 by mass for the zinc polycarboxylate and 3.3 : 1 for the glass polyalkenoate. Samples were prepared by spatulating together the appropriate amount of powder (deactivated ZnO or glass plus dried polymer) with water or aqueous solution of trivalent metal nitrate on a ceramic tile using a metal mixing spatula. The metal nitrate solutions employed were prepared from either aluminium nitrate (ACS reagent grade; Aldrich Chemical Co., Dorset, UK) or iron (III) nitrate (General Purpose Reagent grade; Hopkin and Williams, UK). Both are supplied as the hydrated salt $(M(NO_3)_3 \cdot 9H_2O)$ and were made up to give solutions of the following concentrations: $0.25, 0.50, 0.75, and 1.00 \text{ mol } dm^{-3}$.

Working and setting times were determined for cements set by water activation and by activation with each of the aluminium nitrate solutions. All determinations used the oscillating rheometer⁵ at ambient temperature (21–23°C), with duplicate values being recorded. The working time was taken to be the point at which the amplitude of oscillation reached 95% of the initial (maximum) value; the setting time was the point at which amplitude was 5% of this value. Attempts to prepare samples using the Fe(NO₃)₃ solutions were unsuccessful because they set so rapidly that there was not time to place them between the plates of the rheometer.

Compressive strengths at 24 h were determined for cements activated with water and with the Al(NO₃)₃ solutions. Six specimens of each cement were prepared by placing freshly mixed cement paste in cylindrical molds of dimensions 12 mm high \times 6 mm diameter. Specimens were stored in their molds for 1 h at 37°C, then in water at the same temperature for a further 23 h. After storage, samples were tested for compressive strength using a universal testing machine (Type EU500; Howden, Leamington Spa, UK) at a crosshead speed of 1.0 mm/min. Loads at failure were converted to strength values, and means and standard deviations were determined for each cement composition. Differences in compres-

Table I The Influence of Trivalent Metal
Nitrates on the Setting Characteristics
of Zinc Polycarboxylate

Liquid	Working Time (min)	Setting Time (min)
1.0 <i>M</i> Al(NO ₃) ₃ 0.75 <i>M</i> Al(NO ₃) ₃ 0.50 <i>M</i> Al(NO ₃) ₃ 0.25 <i>M</i> Al(NO ₃) ₃ We tag	0.5^{a} 0.8 1.7 2.0	$1.4^{\rm a}$ 3.0 4.4 8.5

The setting reaction with $Fe(NO_3)_3$ in the concentration range 0.25 to 1.0*M* was too fast to allow working and setting times to be determined.

^a An estimate only since the cement had reached its working time by the time it was loaded onto the rheometer.

sive strength were assessed for significance using 1-way ANOVA; values of p > 0.05 were considered insignificant.

Poly(acrylic acid)-Al(NO₃)₃ solutions were prepared by adding together equal volumes of the aqueous $Al(NO_3)_3$ solutions and 25% aqueous poly(acrylic acid) (Versicol E7; Allied Colloids, UK). The pH of these solutions was determined using a digital pH meter (Type PHA300; Whatman, UK), and the results compared with previously published values of pH for similar solutions involving other metal salts. For infrared spectroscopy, a specimen was prepared by applying a small amount of Al(NO₃)₃-poly(acrylic acid) solution by brush to calcium fluoride plates. After allowing to dry at room temperature, the spectrum was recorded in transmission using an infrared spectrophotometer [Type 983G; Perkin-Elmer, UK). To prepare a similar specimen of the Fe(NO₃)₃-poly(acrylic acid) adduct, identical volumes of solution were used, and the resulting precipitate was quickly transferred to the calcium fluoride plates, which were pressed together to obtain a thin film of material, whose infrared spectrum was then recorded.

RESULTS

The working and setting times for water and for the various solutions of $Al(NO_3)_3$ in the zinc polycarboxylate cement are shown in Table I and in the glass polyalkenoate in Table II. For both cements, all solutions containing $Fe(NO_3)_3$ reacted too quickly to allow satisfactory cements to be mixed; hence, working and setting times could not

Liquid	Working Time (min)	Setting Time (min)
$1.0M \operatorname{Al}(\mathrm{NO}_3)_3$	1.4	5.8
$0.75M \text{ Al}(\text{NO}_3)_3$	1.5	6.9
$0.50M \text{ Al}(\text{NO}_3)_3$	1.9	8.2
$0.25M \text{ Al}(\text{NO}_3)_3$	2.2	9.8
Water	4.2	12.4

Table IIThe Influence of Trivalent MetalNitrates on the Setting Characteristicsof Glass Polyalkenoate

The setting reaction with $Fe(NO_3)_3$ in the concentration range 0.25 to 1.0*M* was too fast to allow working and setting times to be determined.

be determined. In each cement, the presence of $Al(NO_3)_3$ enhanced the rate of the setting reaction, with the effect varying with concentration.

The compressive strengths of cements made from solutions of Al(NO₃)₃ are shown in Tables III and IV. For the zinc polycarboxylate (Table IV), all cements containing Al(NO₃)₃ were significantly weaker than the cement with no additive (p < 0.001). Cements formulated from 0.25, 0.5, and 0.75 mol dm⁻³ showed no significant variation in compressive strength, but the cement made from 1.0 mol dm⁻³ Al(NO₃)₃ was significantly weaker than these (p < 0.001) and also weaker than the additive-free cement (p < 0.001).

For the glass polyalkenoate (Table IV), all cements containing Al(NO₃)₃ were weaker than the one with no additive, but this was not significant for 0.25 mol dm⁻³ Al(NO₃)₃. For the others, it was significant to at least p < 0.01. The difference between 0.5 and 0.75 mol dm⁻³ was not significant; the difference between 0.75 and 1.0 mol dm⁻³ was significant to only p < 0.05; and the difference between 0.5 and 1.0 mol dm⁻³ was also not significant.

Table IIICompressive Strength at 24 h of ZincPolycarboxylate Cements with AluminiumNitrate

Liquid	Compressive Strength ^a (MPa)
1.0 <i>M</i> Al(NO ₃) ₃ 0.75 <i>M</i> Al(NO ₃) ₃ 0.50 <i>M</i> Al(NO ₃) ₃ 0.25 <i>M</i> Al(NO ₃) ₃ Water	19.1 (6.6) 42.1 (12.3) 37.2 (6.6) 39.1 (8.2) 86.0 (13.8)

Table IVCompressive Strength at 24 hof Glass Polyalkenoate Cementswith Aluminium Nitrate

Liquid	Compressive Strength ^a (MPa)
$1.0M \operatorname{Al(NO_3)_3}$	58.0 (10.8)
$0.75M \text{ Al}(\text{NO}_3)_3$	73.6 (9.1)
$0.50M \text{ Al}(\text{NO}_3)_3$	68.3 (6.3)
$0.25M \text{ Al}(\text{NO}_3)_3$	88.9 (10.1)
Water	94.3 (8.3)

^a Standard deviations are in parentheses.

The values of net weight gain are shown in Tables V and VI. This was found to vary with the concentration of $Al(NO_3)_3$. For the zinc polycarboxylate, the maximum weight loss occurred with 0.75 mol dm⁻³ $Al(NO_3)_3$ and was significantly different from the modest weight gain with no additive to p < 0.001. At the lowest concentration of $Al(NO_3)_3$, there was a gain in mass that was significantly greater than for the pure cement at p < 0.01. The glass polyalkenoate showed a clearer trend, from a gain of 1.77% for the pure cement to a loss of 1.84% for 1.0 mol dm⁻³ $Al(NO_3)_3$. This overall difference was significant to p < 0.001.

Results for pH measurement are shown in Table VII. At all concentrations, mixtures of $Al(NO_3)_3$ with poly(acrylic acid) showed a lower pH than the acid alone. Results for the infrared spectroscopic examination of poly(acrylic acid) with both $Al(NO_3)_3$ and Fe(NO₃)₃ appear in Table VIII. The main region of interest is 1525–1640 cm⁻¹, and this was different for poly(acrylic acid) and for samples containing either of nitrates, indicating the occurrence of metal–carbonyl chelation, which varied, depending on the nature of the metal.

Table V	Net Wei	ght Gair	1 at 24	h for	Zinc
Polycarb	oxylate (Cements	with .	Alumi	nium
Nitrate					

-	Liquid	Weight Gain ^a (%)
	1.0 <i>M</i> Al(NO ₃) ₃ 0.75 <i>M</i> Al(NO ₃) ₃ 0.50 <i>M</i> Al(NO ₃) ₃	$\begin{array}{c} 0.61(0.32)\\ -0.10(0.03)\\ -0.95(0.15)\\ 0.12(0.47)\end{array}$
	0.25 <i>M</i> Al(NO ₃) ₃ Water	-0.10(0.47) 0.08(0.11)

^a Standard Deviations are in parentheses.

^a Standard deviations are in parentheses.

Liquid	Weight Gain ^a (%)
1.0 <i>M</i> Al(NO ₃) ₃ 0.75 <i>M</i> Al(NO ₃) ₃ 0.50 <i>M</i> Al(NO ₃)	$-1.84 (0.51) \\ -0.85 (0.50) \\ 0.57 (0.34)$
0.25M Al(NO ₃) ₃ Water	$\begin{array}{c} 0.57 \ (0.54) \\ 0.72 \ (0.41) \\ 1.77 \ (0.34) \end{array}$

Table VINet Weight Gain at 24 h for GlassPolyalkenoate Cements with Aluminium Nitrate

^a Standard deviations in parentheses.

DISCUSSION

For both cements, the presence of $Al(NO_3)_3$ was found to speed up the setting reaction at all concentrations. The effect was less than that of $Fe(NO_3)_3$, where the reaction was so fast that it was impossible to mix satisfactory cements. This acceleration of setting has been found previously for a variety of metal salts, for example, NaCl, KBr, CaCl₂, and ZnCl₂, in zinc polycarboxylates and relates to the increased stability of the polyanion in the presence of such compounds, which leads, in turn, to a lowering of pH of the polyacid.⁹⁻¹¹ This was modelled by experiments in which solutions of metal salt were added to equal volumes of 25% aqueous poly(acrylic acid). The mixture with 1.0 mol dm⁻³ Al(NO₃)₃ had the lowest value of pH recorded, 0.2, compared with pH 0.8 for CaCl₂, pH 1.0 for ZnCl₂, and pH 1.1 for NaCl at identical concentrations.

In the case of zinc polycarboxylate, the setting reaction is relatively straightforward. It involves attack of the base by protons from the acid, which results in swift liberation of Zn^{2+} into the matrix, where they react to form ionic crosslinks with the carboxylate groups of the polymer.¹⁷ Decomposition of the base by acid leads directly to formation of the stiff matrix. Consequently, the enhanced

Table VII $\,$ pH of 1 : 1 Mixtures of Aluminium Nitrate Solutions and 25% Poly(acrylic acid) at 25°C

Salt Solution	pH
$\begin{array}{c} 1.0M \ {\rm Al}({\rm NO}_3)_3 \\ 0.75M \ {\rm Al}({\rm NO}_3)_3 \\ 0.50M \ {\rm Al}({\rm NO}_3)_3 \\ 0.25M \ {\rm Al}({\rm NO}_3)_3 \\ {\rm None} \end{array}$	$0.2 \\ 0.4 \\ 0.5 \\ 0.8 \\ 1.5$

Table VIII Selected Infrared Bands of 1:1Mixtures of 1 mol dm⁻³ Metal Nitrate Solutions and 25% Poly(acrylic acid)

Salt Solution	$\frac{\nu \mathrm{CO}_2 \ \mathrm{Asym}}{(\mathrm{cm}^{-1})}$	$\substack{\nu \text{CO}_2 \text{ Sym} \\ (\text{cm}^{-1})}$	$\Delta \nu \ ({ m cm^{-1}})$
None		1450	
$Al(NO_3)_3$	1616	1449	167
Fe(NO ₃) ₃	1632, 1526	1450	182, 76

acidity caused by Al(NO₃)₃ speeds up the overall reaction, shortening both working and setting times relative to the pure zinc polycarboxylate cement. For glass polyalkenoates, on the other hand, setting is more complex.^{5,6} Initial attack of the base liberates Ca^{2+} ions; but when this ion reacts with the polymer, the product is fairly soft. Full setting to give a mechanically strong and stiff cement requires the additional reaction of the ion-depleted glass. Premature formation of calcium polyacrylate probably interferes with the latter reaction since it impedes diffusion of the relatively bulky reactants. This explanation has been advanced to account for the observation that the initial part of the setting process, as measured by the working time, is reduced, for example, with ZnCl₂; but the later stage, as measured by the setting time, is extended.⁹

In a previous article, a correlation was observed between pH of the additive-polyacid mixture and the compressive strength of the glass polyalkenoate cements, with lower pH values, leading to reduced strengths.⁹ These observations were based on results from various metal chlorides, all used at concentrations of 1.0 mol dm^{-3} . In the current work, however, this attractively simple correlation breaks down. The 1.0 mol dm^{-3} concentration of Al(NO₃)₃ gave a pH of 0.2 with 25% poly(acrylic acid); yet this liquid yielded a cement of strength 58.0 \pm 10.8 MPa. Within experimental error, this is the same as the cement formed from NaCl (59.8 \pm 4.4 MPa); yet this gave a solution with poly(acrylic acid) with a pH of 1.1. Conversely, the pH of poly(acrylic acid) with 0.25 mol dm⁻³ Al(NO₃)₃ was 0.8, identical to that of 1.0 mol dm⁻³ CaCl₂; yet the respective strengths of the cements were 88.9 \pm 10.1 and 50.4 ± 6.7 MPa. These results demonstrate that pH cannot be the sole cause of the observed variations in strength.

In previous studies, the zinc polycarboxylate cement has been found to be less affected by the

presence of additives than the glass polyalkenoate. In the extreme case of monovalent salts, for example, NaCl, NaNO₃ and KI, the compressive strength of the zinc polycarboxylate was unaffected, while that of the glass polyalkenoate was significantly reduced.⁷ In the presence of divalent salts, there was a reduction in strength for the zinc polycarboxylate, but it was less than for the glass polyalkenoate. For example, with CaCl₂, the zinc polycarboxylate had 66.6% of its original strength, whereas glass polyalkenoate had only 53.4%; with $ZnCl_2$, strengths were 74.7 and 61.5%, respectively.8 However, in the current study, it was the zinc polycarboxylate that was weaker; for example, with 1.0 mol dm⁻³ Al(NO₃)₃, the zinc polycarboxylate had 22.2% of its original strength, compared with 61.5% for the glass polyalkenoate.

This may arise because the reductions in strength occur for different reasons. In the zinc polycarboxylate, binding of the additive to the polymer inhibits crosslink formation, and this may result in lower resistance to failure and, hence, lower strength. In the glass polyalkenoate, on the other hand, the additive not only reduces the crosslink density, it also alters the balance between neutralization and network formation. It may be that, provided the network can still form, a cement of reasonable strength will still develop, regardless of the reduced crosslink density.

The presence of $Al(NO_3)_3$ was shown to alter the change in mass on storage in water for 24 h for each cement. For zinc polycarboxylate, the insignificant gain in mass of the original cement became a more substantial gain with 1.0 mol $dm^{-3} Al(NO_3)_3$, though there was a significant loss with 0.5 mol $dm^{-3} Al(NO_3)_3$. For the glass polyalkenoate, the significant gain in mass in the original cement became a significant loss with 1.0 mol $dm^{-3} Al(NO_3)_3$. Quite how these changes occur is not clear, but they do show that this additive, like many of the others studied previously, not only changes the strength, but also alters the water content of the set cements.

The infrared spectra of poly(acrylic acid) in the presence of the 2 metal nitrates show that there are clear interactions between the additives and the carbonyl groups of the polymer and that these are different with aluminum and iron (III). Table VIII shows the assignments of the bands. As before,⁹ there is ambiguity about the band at 1450 cm⁻¹, since it appears in the spectrum of pure poly(acrylic acid), so its earlier assignment to symmetric stretches of the CO₂ group is in doubt.



Figure 1 Possible interactions of metal ions with carboxylate functional groups.

On the other hand, assignment of the bands in the region of $1525-1640 \text{ cm}^{-1}$ to the asymmetric stretch seems more reliable, as there are no corresponding bands in the spectrum of pure poly-(acrylic acid).

The precise position of the asymmetric carbonyl band is known to vary according to the details of the local structure formed. In polyacrylate salts, bands in this region have been distinguished as arising from purely ionic or partially covalent interactions, with the latter divided into unidentate, bridging bidentate, and chelating bidentate (Fig. 1).¹ The spectrum of the poly(acrylic acid)-Al(NO3)3 adduct shows a single band at 1616 cm^{-1} , a position that is generally assigned to a bridging bidentate structure. As such, it is similar to the structure formed by ZnCl₂ with poly-(acrylic acid), but different from the structures that occur with calcium, magnesium, or strontium chlorides. In a previous study,¹⁸ the product of reaction between aluminum chloride and poly-(acrylic acid) was found to give an absorption band at 1620 cm^{-1} , that is, very similar to the position of the band in the $Al(NO_3)_3$ -poly(acrylic acid) adduct. This implies that they have similar structures. Reaction of aluminum chloride with monomeric carboxylic acids does not yield simple aluminum carboxylates, but rather complex species containing bridging chlorines,¹⁹ and these kind of units have been assumed to occur in the AlCl₃-poly(acrylic acid) adduct. The infrared results imply that a similar complexation occurs with $Al(NO_3)_3$.

The interaction of aluminum with poly(acrylic acid) as glass polyalkenoate cements set has been studied with Fourier Transform infrared spectroscopy²⁰ and is shown to give a band at 1599 cm⁻¹. This is reasonably close to the absorption at 1616 cm⁻¹ of the Al(NO₃)₃-poly(acrylic acid) adduct. In glass polyalkenoates, this band has been

assumed to arise from interaction of the polymer with aluminum complexes such as AlF_2^+ or other species, which also incorporate bound water molecules.²⁰ Thus, the addition of $Al(NO_3)_3$ can be seen to create structures of the type that occur anyway as these cements form. This may be why the presence of Al(NO₃)₃ has relatively little effect on the strength of glass polyalkenoates compared with the metal salts studied previously. In the zinc polycarboxylate, by contrast, the addition of species such as Al(NO₃)₃ or ZnCl₂ introduces new types of metal-carboxylate interaction, as evidenced by bands in the region of $1615-1620 \text{ cm}^{-1}$. No such bands appear in the infrared spectrum of zinc polycarboxylate cement at any stage of its setting.21

The reaction of Fe(NO₃)₃ with poly(acrylic acid) was found to lead to the rapid formation of an insoluble gel. This is similar to the effect of FeCl₃ on poly(acrylic acid).^{15,22} Analysis of the product showed the metal ions to distribute unevenly between the macromolecules, forming an iron-rich fraction that precipitated and an iron-free fraction that stayed in solution. The crosslinking species has been shown to be FeCl²⁺ using infrared spectroscopy¹⁵; similarly, therefore, in the Fe(NO₃)₃-poly(acrylic acid) adduct, the crosslinkers are likely to be $Fe(NO_3)^{2+}$ ions, rather that Fe^{3+} ions. The reason for the excessively fast setting reaction of either type of cement in the presence of $Fe(NO_3)_3$ is that it rapidly forms a similar precipitate with the poly(acrylic acid). Infrared spectroscopy reveals the presence of 2 types of interaction between Fe(NO₃)₃ and poly-(acrylic acid). One gives rise to a band at 1526 cm^{-1} , the characteristic position for chelating bidentate carboxylate groups; the other gives rise to a band at 1632 cm^{-1} , which is unusually high, and in the region that has been assigned to the rare case of unidentate binding.^{8,23} Both are well removed from the bands in the spectrum of the Al(NO₃)₃-poly(acrylic acid) adduct, confirming that the interactions of these 2 metal nitrates with poly(acrylic acid) are distinctly different.

CONCLUSIONS

Both zinc polycarboxylate and glass polyalkenoate cements can be made with the addition of $Al(NO_3)_3$. By contrast, it was not possible to make cements containing $Fe(NO_3)_3$ because it makes the setting reaction too fast. The presence of $Al(NO_3)_3$ also caused an acceleration, but it was less marked than for $Fe(NO_3)_3$. Cements prepared from $Al(NO_3)_3$ solutions were weaker than those made from pure water, though in contrast to results for mono- and divalent metal salts, the zinc polycarboxylate was more affected than the glass polyalkenoate. There are subtle changes in mass when either zinc polycarboxylate or glass polyalkenoate are stored in water, and these were found to vary when $Al(NO_3)_3$ was present.

Infrared spectroscopy demonstrated that Al- $(NO_3)_3$ chelates with carbonyl groups of the poly-(acrylic acid), forming units that are probably bridging bidentate in structure, an interaction that is similar to that of $ZnCl_2$ with poly(acrylic acid). This is different from the interaction of Fe(NO_3)₃, which seems to involve a mixture of chelating bidentate and unidentate interactions. The overall effect of these interactions is to enhance the acidity of the polymer, leading to the observed increase in reaction rate. However, no simple relationship was apparent between this acidity and the properties of the resulting cements.

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REFERENCES

- A. D. Wilson and J. W. Nicholson, Acid Base Cements, The University Press, Cambridge, UK, 1993.
- N. N. Greenwood and A. Earnshaw, *The Chemistry* of the Elements, Pergamon Press, Oxford, UK, 1984.
- A. D. Wilson and R. G. Hill, *Glass Technol.*, **29**, 150 (1988).
- E. A. Wasson and J. W. Nicholson, J. Dent. Res., 72, 481 (1993).
- 5. S. Matsuya, T. Maeda, and M. Ohta, J. Dent. Res., **75**, 1920 (1996).
- K. A. Milne, N. J. Calos, J. H. O'Donnell, C. H. L. Kennard, S. Vega, and D. Marks, J. Mater. Sci.; Mater. Med., 8, 349 (1997).
- J. W. Nicholson, J. Mater. Sci.: Mater. Med., 6, 404 (1995).
- J. W. Nicholson and F. Abiden, J. Mater. Sci.: Mater. Med., 9, 269, (1998).
- J. W. Nicholson, J. Mater. Sci.; Mater. in Med., 9, 273, (1998).
- T. Kitano, A. Taguchi, and M. Nagasaw, *Macromolecules*, 13, 57 (1980).

- G. Staikos and G. Bokias, *Polym. Int.*, **31**, 385 (1993).
- W. Zhang and S. Nilssen, *Macromolecules*, 26, 2866 (1993).
- A. C. Habert, R. Y. M. Huang, and C. M. Burns, J. Appl. Polym. Sci., 24, 489 (1979).
- A. C. Habert, R. Y. M. Huang, and C. M. Burns, J. Appl. Polym. Sci., 24, 801 (1979).
- L.-A. Linden and J. F. Rabek, J. Appl. Polym. Sci., 50, 1331 (1993).
- 16. H. Yokoi and N. Nishi, Chem. Lett., 1765 (1989).
- H. M. Anstice, N. L. Bubb, and J. W. Nicholson, J. Mater. Sci.; Mater. in Med., 5, 176 (1994).

- J. W. Nicholson and A. D. Wilson, *Br. Polym. J.*, **19**, 67 (1987).
- 19. R. C. Mehrotra and R. Bohra, *Metal Carboxylates*, Academic Press, New York, 1983.
- J. W. Nicholson, P. J. Brookman, O. M. Lacy, and A. D. Wilson, J. Dent. Res., 67, 1451 (1988).
- J. W. Nicholson, P. J. Brookman, O. M. Lacy, G. S. Sayers, and A. D. Wilson, *J. Biomed. Mater. Res.*, **22**, 623 (1988).
- Y. G. Tropsha, A. S. Polinskii, A. A. Yaroslavov, V. S. Pshezhetskii, and V. A. Kabanov, *Polym. Sci.* U.S.S.R., 28, 1527 (1986).
- 23. M. A. Mesubi, J. Mol. Struct., 81, 61 (1982).