Radiopaque Miscible Systems Composed of Poly(Methyl Methacrylate) and Transition and Nontransition Metal Salts: Spectroscopic, Thermal, and Radiographic Characterization

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Synopsis

The preparation of miscible systems containing poly(methyl methacrylate) and cupric nitrate, manganese chloride, praseodymium chloride, and uranyl nitrate is described. The salt was dissolved in the monomer, which was subsequently polymerized. The heavy metal salts impart radiopacity to these plastics and this renders them useful for X-ray imaging in applications such as medical implants. The polymer–salt systems are characterized on the basis of their infrared spectra, thermal, and radiographic properties, and the formation of complexes between the cations and the carbonyl function of the polymer is discussed. The glass transition temperatures of the salt-containing polymers are higher than those of the salt-free polymers, the elevation being dependent on the nature and concentration of the metal salt. Miscible PMMA–uranyl nitrate systems are transparent, glassy plastics and approximately 11 wt % of uranyl nitrate hexahydrate imparts a radiopacity equivalent to that of aluminum.

INTRODUCTION

Considerable interest in the properties and applications of ion-containing polymers has been well documented in the past two decades.[1-5] Since ions with high atomic number can render radiopacifying properties to organic polymers, a systematic study on ion-chelating monomers and polymers capable of solubilizing heavy metal salts has been conducted in our laboratory with the objective of forming radiopaque or X-ray contrast materials.[6-9] Most polymer materials that do not contain heavy atoms are radiolucent, and the lack of a nondestructive imaging technique for their detection can pose a serious problem, especially when used for medical applications.[10] Earlier development of radiopaque polymers focused primarily on mixing radiopaque glasses[11,12] or heavy metal salts such as barium sulfate and bismuth halides[13-15] with the polymers. However, the incompatibility of organic polymers with most of these salts can have an adverse effect on their physical and mechanical properties. Halogenated polymers containing a high content of bromine or iodine often lack the stability required for the prolonged use of these materials under wet conditions.[16]

The current studies conducted in our laboratory have shown that some of the problems associated with the miscibility of the inorganic salt and polymer can be obviated by using monomers and polymers that can coordinate with metal salts or one of its components and thus uniformly disperse the radiopacifying moiety in the polymer at the molecular level.[6-9] Polymers incorporating carbonyl and phosphoryl groups can interact with and dissolve a variety of inorganic salts that contain a metal with high atomic number.[6] In this context, the preparation and characterization (spectroscopic, thermal, and radiographic) of homogeneous materials of poly(methyl methacrylate) with some transition and nontransition metal salts is reported. Poly(methyl methacrylate) was selected for this study because the use of this excellent material in medical applications, although widespread, is considerably hampered by its translucent properties when exposed to conventional radiographic methods.

EXPERIMENTAL

Materials and Methods

Partially hydrated cupric nitrate, cupric chloride, manganese chloride, praseodymium chloride, and methyl methacrylate (all procured from Aldrich Chemical Co.), anhydrous bismuth tribromide (Alfa Products, Morton Thiokol, Danvers, MA), and partially hydrated uranyl nitrate (Spi-Chem, West Chester, PA) were used without purification. Methyl methacrylate was distilled twice prior to use. Tetraethyleneglycol dimethacrylate (TEGDM) (Polysciences, Warrington, PA) was used as a crosslinking agent. All solvents were dried and distilled. The polymerization initiators benzoyl peroxide (BP) and 2,2-azobis-isobutyronitrile (AIBN) were purified by recrystallization.

Differential scanning calorimetry (DSC) measurements were performed at a scanning rate of $20°C$ min^{-1} using a Perkin-Elmer differential calorimeter, DSC-4, equipped with a microprocessor. The scans were conducted under a steady flow of nitrogen. Pure indium was used to calibrate the DSC. Each compound was scanned several times and the second scan was selected for the determination of the glass transition temperature, T_g, of the polymer. The T_g values were taken at the midpoint of the heat capacity change, ΔC_p, during the transition. The change in ΔC_p at T_g was calculated from the vertical distance between the two extrapolated baselines.

Infrared spectra were recorded in KBr pellets (PMMA complexes) and as neat liquids (MMA complexes) on a Nicolet 20 DX FT-IR spectrometer or a Perkin-Elmer 1820 spectrophotometer. The ^{13}C- and ^{1}H-NMR were recorded on a General Electric QE-300 MHz NMR spectrometer using CDCl$_3$ as a solvent and TMS as an internal reference.

Radiographic analysis was carried out with a Picker condenser discharge mobile X-ray diagnostic unit, Model 1010, operating at 90 kV and 6 mA. A Hitachi tungsten anode, cathode ray tube no. UG 4605, was used in the unit. The polymer samples were made into pellets of 1 mm thickness, using an infrared pellet press under 20,000 psi of pressure for ca. 60 s. In an alternative method, transparent cylindrical polymer samples were prepared in a glass tube, removed therefrom, and then carefully cut into pellets of the proper

thickness and the surfaces were subsequently polished. The specimens' radiopacity was gauged against an aluminum stepwedge bar (1 mm steps), both of which were placed about 55 cm below the tungsten anode. The images were recorded on a Kodak Ultraspeed double-sided dental X-ray film no. DF 49. The exposed film was scanned with a Joyce microdensitometer and the radiopacities of the samples measured relative to that of the aluminum stepwedge bar.

Preparation of Polymer Salt Mixtures. Polymer–metal salt miscible systems were obtained by dissolving a salt in methyl methacrylate and the mixture polymerized with 0.5 wt % initiator (preferably AIBN) at 65–70°C for ca. 48 h. Samples were prepared with or without a crosslinking agent. In an alternative procedure, the salt was dissolved in a solution of PMMA in methyl ethyl ketone or ethyl acetate. The solvent was slowly evaporated under a stream of nitrogen to yield a polymer film that was kept under vacuum until no residual solvent was detected by infrared spectroscopy.

The present study primarily focuses on the characterization of solid PMMA–salt systems synthesized by the first procedure. This preparation method offers an inherent advantage of complexing metal salts at the molecular level in terms of better mixing including higher entropy gain and the absence of steric constraints for interactive sites. The cupric chloride mixtures with PMMA were made by the second procedure,[2] since MMA could not be polymerized in the presence of $CuCl_2$, presumably because of the formation of CuCl, a well-known radical scavenger.

RESULTS AND DISCUSSION

Several transition and nontransition metal salts have been found to be soluble in methyl methacrylate in varied amounts, and their mixtures could be polymerized using AIBN as an initiator. Uranyl nitrate hexahydrate, for instance, is soluble in methyl methacrylate up to 45 wt % and its mixtures are easily converted to homogeneous transparent, hard (i.e., glassy) polymers. Other transition metals such as cupric nitrate, manganese chloride, and praseodymium chloride are much less soluble, i.e., 3–4 wt %. The interactions between these metal salts and MMA or PMMA have been qualitatively assessed through thermal scanning and infrared spectroscopy. DSC was particularly useful in determining the impact of salt on the glass transition temperatures and to detect the presence of free (crystalline) salt in the polymer matrix. These new materials, particularly the uranyl nitrate–PMMA mixtures, have been further evaluated as candidates for new X-ray imaging materials with potential usefulness for biomedical applications.

Infrared Spectra

To obtain information on the nature of bonding in the miscible polymer–salt systems, both dispersive and FT-IR spectra of mixtures of hydrated uranyl nitrate with MMA and PMMA were recorded. The prominent infrared bands of MMA, PMMA, and their miscible mixtures with various metal salts are summarized in Table I. Due to the relatively low concentration of the salt components and the overlap of polymer vibrations with the nitrate anion, subtle changes in the spectra are difficult to observe. There is, however, a

TABLE I
Prominent Infrared Bands (cm^{-1}) of MMA and PMMA and Their Miscible Systems
with Metal Salts[a]

Compound/ complex	Salt (wt %)	$\nu(OH)$	$\nu C=O$	$\nu(C-C-O)$ $+\nu(C-O-C)$ $+\nu(C-O)$	$\nu_{asym}UO_2$/ $\nu_{sym}UO_2$/ δUO_2	NO_3 group vibrations
$UO_2(NO_3)_2$	—	3440sb	—	—	959	1530, 1480, 1452 (ν_1)[b]
					870	1337, 1303 (ν_4)
					248–	1050, 1038 (ν_2)
					260	806 (ν_6), 746 (ν_5), 741 (ν_3)
MMA	0.0	—	1728s	1290s 1320s	—	—
$UO_2(NO_3)_2$	40.0	3420s	1696s 1728m	1300s 1325m	947s 850w	1534s
	24.0	3400m	1700s 1728m	1295s 1320m	947s —	1535s (ν_1) 1045m (ν_2)
PMMA	0.0	—	1730s	1238m 1275m	—	—
$MnCl_2$	2.5	3410m	1720mb	1240m —	—	—
$Cu(NO_3)_2$	3.5	3460m	1720sb	1250m 1275m	—	1150s 1450s
$UO_2(NO_3)_2$	3.5	3440m	1710s 1730m	1250m 1280m	947w —	1530w (ν_1) 1045m (ν_2) 800w (ν_6)
	24.0	3420m	1710s 1728m	1268s 1280m	947s 860w	1534s (ν_1) 1050w (ν_2)
	32.0	3420m	1710sb	1250m 1280m	947s	1534s (ν_1) 1052w (ν_2) 750w (ν_5)
$PrCl_3$	3.0	3420m	1710mb	1250m	—	—

[a] In this study, $UO_2(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $MnCl_2 \cdot 4H_2O$, and $PrCl_3 \cdot 6H_2O$ have been used.

[b] ν_1, ν_2, ν_3, ν_4, ν_5, and ν_6 denote NO_2 symmetric stretching, NO stretching, NO_2 symmetric bending, NO_2 asymmetric stretching, NO_2 asymmetric bending, and out-of-plane NO_2 group rocking vibrations of a bidentate nitrate group having C_{2v} point group symmetry, respectively.[21b, 22d]

preponderance of evidence that supports the contention that of the two possible interacting sites, i.e., the carbonyl and the methoxy oxygen atom, it is the carbonyl oxygen that coordinates with a metal[17]:
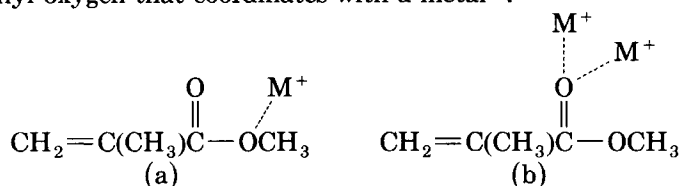
The infrared spectrum of MMA shows a strong band at ca. 1728 cm^{-1} due to $\nu(C=O)$ moiety of the ester group. A split band at ca. 1290 and 1320 cm^{-1} can be assigned to a combination of $\nu(C-O-C)$ and $\nu(C-C-O)$ with contributions from the $\nu(C-O)$ vibrations.[18] In the presence of metal salts, these two bands show negative and positive shifts, respectively. The magnitude of the shifts depends on the electronegativity of the metal ions, similar to

that observed for metal complexes of low molecular weight organic esters.[19] The dispersive infrared spectra of mixtures with low uranyl nitrate content (< 15 wt %) do not exhibit any significant perturbation of the carbonyl band. At high salt content the carbonyl band shifts to lower frequencies (maximum shift ca. 30 cm^{-1}), and in some instances a split carbonyl band is observed. The bands assigned to $\nu(C-C-O)$ vibration show a slight upward shift (Table I). These changes are consistent with the coordination of the carbonyl group with a metal atom.[17]

In order to substantiate these observations, an interactive subtraction of the FT-IR spectra of MMA and its mixture with uranyl nitrate hexahydrate (40 wt %) was carried out (MMA from its mixture with uranyl nitrate salt). It is evident from the subtracted spectrum that a residual band due to $\nu(C=O)$ group occurs at ca. 1728 cm^{-1}, while a new band is observed at 1695 cm^{-1} as a result of a metal-coordinated carbonyl group. The negative shift is probably caused by the drainage of electrons. A small upward shift in the $\nu(C-O)$ vibrations confirms the coordination of the carbonyl group to the metal atom (Table I). Interaction with the alkoxy group would reverse the shifts in the $\nu(C=O)$ and $\nu(C-C-O)$ vibrations.[19]

Polymerization of MMA or its salt mixtures causes changes in the $C=O$ bands as the conjugation with $C=C$ is removed. The bands occurring at 1310 and 1290 cm^{-1} in MMA appear at 1275 and 1238 cm^{-1} in PMMA, respectively. The carbonyl band in the dispersive infrared spectra of PMMA–uranyl nitrate systems exhibits either broadening, shifting, or splitting. The interactive subtraction of PMMA and its miscible systems with uranyl nitrate shows a conspicuous shoulder at 1695–1700 cm^{-1}, along with a strong band at 1730–1728 cm^{-1}. This shoulder appears to have its origin in the carbonyl group and a shift of approximately 30 cm^{-1} indicates that the carbonyl group remains coordinated to the uranyl atom in the polymer (Table I). Similar observations have been made for miscible systems of PMMA with other metal salts.[20]

Hydrated metal salts have been used in this study (Table I). Several infrared,[21a,b] X-ray,[21c] and neutron diffraction[21d] reports concerning uranyl salts reveal that the almost linear $[UO_2]^{2+}$ moiety in $UO_2(NO_3)_2 \cdot 6H_2O$ is surrounded by a nearly planar hexagon of four oxygen atoms $[O_4]$ from two bidentate nitrate groups $[O_2NO]$ and two oxygen atoms of two equivalent water molecules. The structural units are bound together by a host of hydrogen bonds among the water molecules, the uncoordinated oxygen of the nitrate groups and those of the uranyl group. The uranyl ion having $D_{\alpha h}$ symmetry exhibits four fundamental vibrations: a nondegenerate symmetric stretching frequency seen as a weak band in the region 700–900 cm^{-1} (normally forbidden in infrared), a nondegenerate asymmetric stretching frequency at 900–1000 cm^{-1}, and a doubly degenerate bending vibration in the region 248–260 cm^{-1}.[21b,22] In the uranyl nitrate complexes with PMMA, the presence of $[UO_2]^{2+}$ is suggested by the appearance of a strong band at 947 cm^{-1} and a weak band at ca. 850 cm^{-1} due to $\nu_{asym}(UO_2)$ and $\nu_{sym}(UO_2)$ vibrations, respectively. The doubly degenerate bending vibration has not been studied. The uranyl nitrate hexahydrate, which contains two bidentately-coordinated nitrate groups with C_{2v} symmetry, shows six infrared active modes of vibration. Four of them occur at 1530, 1337, 1050, and 805

cm^{-1} and have been assigned to symmetric ($O_2N—O$), asymmetric stretching of the two $N—O$ bonds, symmetrical stretching of two $N—O$ bonds nearest to the metal atom, and an out-of-plane rocking mode of NO_3 vibrations,[22] respectively. In the uranyl nitrate–PMMA systems, these vibrations occur at 1535, 1270, 1030, and 810 cm^{-1}, indicating that the bidentate coordination mode of the nitrate groups to the uranyl moiety is maintained in these miscible polymer–salt systems (Table I). In the PMMA–copper nitrate systems, the nitrate bands also appear at positions very similar to those of the salt itself. In these systems the bands appearing at 3420 cm^{-1} can be assigned to ν(OH) vibrations of the water molecules present in the lattice of the polymer salt

The coordination of the carbonyl group to uranyl moiety has also been adduced from ^{1}H- and ^{13}C-NMR spectra of uranyl-nitrate-containing solutions of methyl methacrylate. In the ^{1}H-NMR spectra of Lewis acid complexes of MMA and PMMA,[17] it was observed that almost all protons shift downfield. A similar trend has also been observed in solutions of MMA and uranyl nitrate. The magnitude of the shift depends on the strength of the Lewis acid. In the ^{13}C-NMR spectra of these solutions, the signals due to α-C, β-C, C=O, and —O—C shift downfield. The carbonyl carbon in MMA shifts from 167.03 to 167.35 ppm upon adding 20 wt % uranyl nitrate, suggesting coordination of the carbonyl group to the uranyl cation. Similar observations have been reported for other metal complexes of ligands containing carbonyl groups.[17]

Thermal Analysis

Metal ions that reside in a polymer material profoundly affect the thermal properties of the polymers. The effects of salts on the T_g of neutral polymers has been extensively studied.[1-7,23,24] In this study, the T_g values of PMMA mixtures of uranyl nitrate, cupric nitrate, manganese chloride, and praseodymium trichloride were evaluated using DSC. Several scans are reproduced in Figure 1 and the respective T_g values are reported in Table II. The data reveal a significant and progressive increase in T_g as the concentration of the salt in the polymer is augmented. A plot of T_g vs. the content of uranyl nitrate hexahydrate in the polymer is depicted in Figure 2.

Hydrated uranyl nitrate, copper nitrate, manganese chloride, and praseodymium chloride melting temperatures are 60.2, 114.5, 58, and 115°C, respectively. No melt endotherm has been observed in any of the complexes of these metal salts, indicating the absence of the free salt. The elevation of T_g on adding metal salts to polymers has been widely reported, e.g., for cobalt chloride and copper chloride with PMMA,[2] and poly(propylene oxide),[3,4a] and for zinc chloride with poly(4-vinylpyridine-co-n-butyl methacrylate) copolymers.[4b]

A well-defined peak at 260°C, with the onset beginning at ca. 245°C, indicates the degradation of PMMA. Degradation of high molecular weight PMMA has also been found to occur in this temperature range.[25] A rather broad exothermic peak located at about 240°C in some of the samples also points toward degradation in these systems.[23] To confirm it further, a sample of uranyl nitrate–PMMA containing ca. 24 wt % of the salt was scanned over
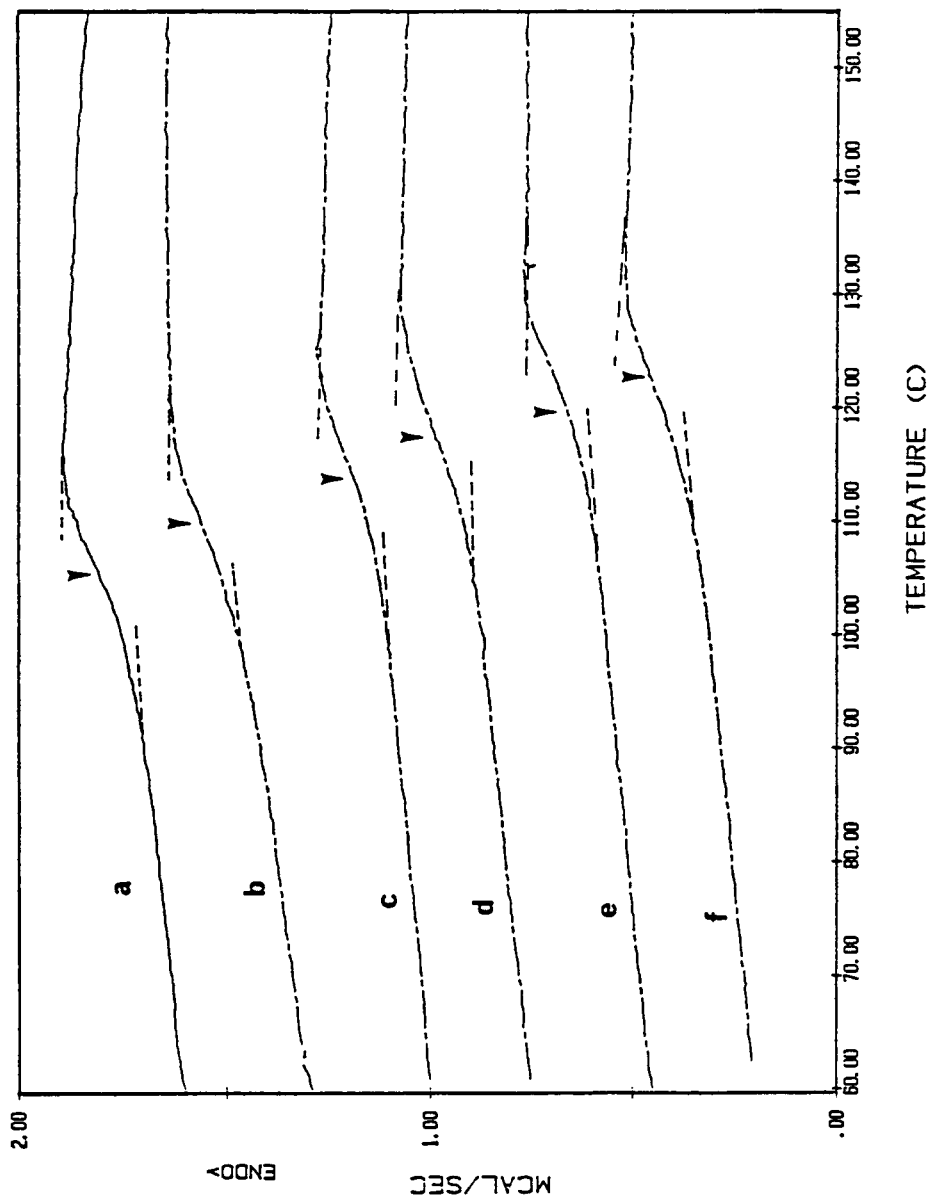
Fig. 1.   Differential scanning calorimetry thermograms of miscible PMMA–salt systems:(a) uranyl nitrate–PMMA (2.9 wt %); (b) uranyl nitrate–PMMA (3.4 wt %); (c) copper nitrate–PMMA (3.5 wt %); (d) manganese chloride–PMMA (2.5 wt %); (e) praseodymium chloride–PMMA (3.0 wt %); (f) uranyl nitrate–PMMA (15.9 wt %).

TABLE II
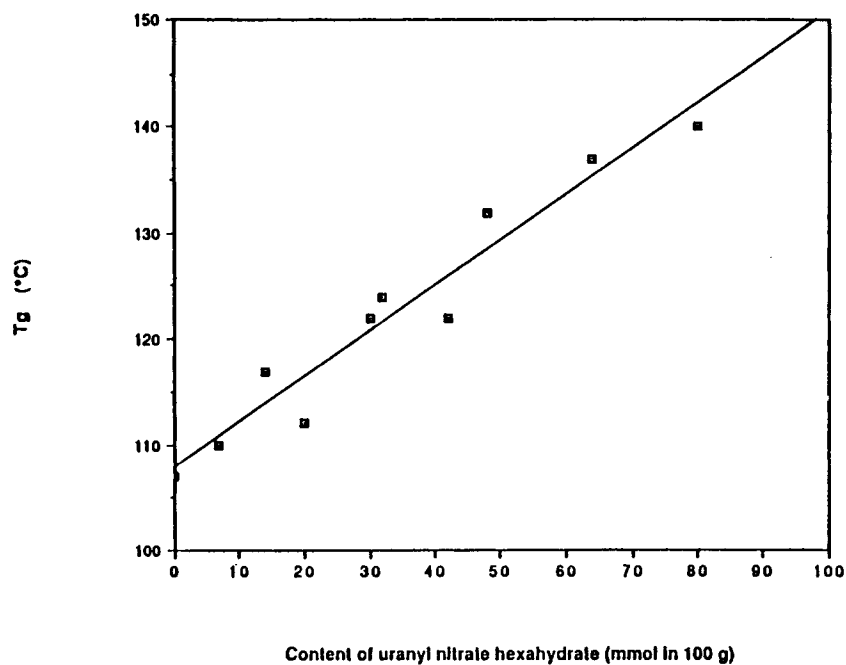Glass Transition Temperatures of PMMA and Its Miscible Systems with Metal Salts[a]

Metal salt	Salt content (wt %)	Salt Content (mmol in 100 g)	T_g
(PMMA)	—	—	107
$UO_2(NO_3)_2$	3.4	6.8	110
	7.0	14.0	117
	9.8	20.0	112
	15.0	30.0	122
	16.0	32.0	124
	21.0	42.0	122
	24.0	48.0	132
	32.0	64.0	137
	40.0	80.0	140
$Cu(NO_3)_2$	2.5	10.0	116
	3.5	14.0	117
$MnCl_2$	2.5	12.0	120
$PrCl_3$	3.0	8.4	125

[a] In this study, $UO_2(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $MnCl_2 \cdot 4H_2O$, and $PrCl_3 \cdot 6H_2O$ have been used.
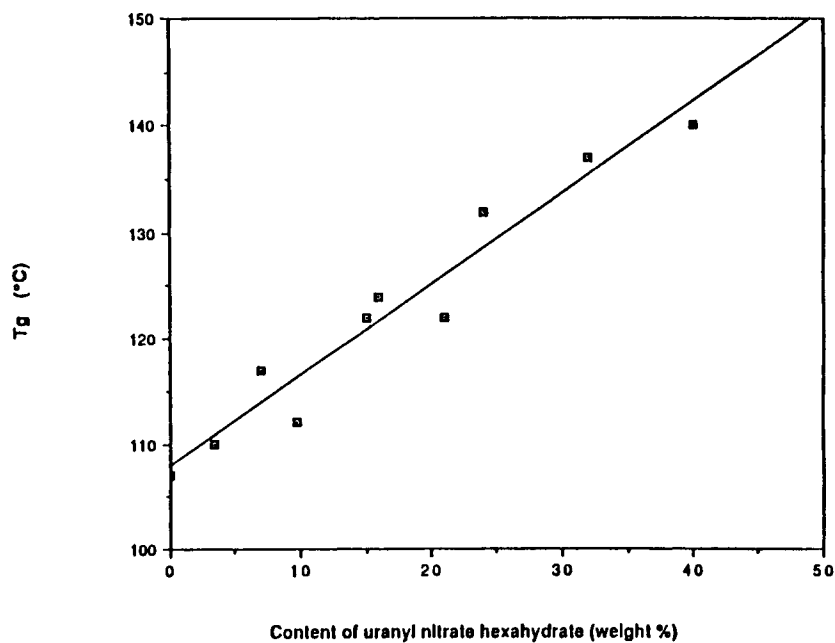
different temperature ranges and the peak at ca. 240°C was consistently found in all the scans.

The qualitative picture emerging from the DSC study suggests that the dissolved salt impedes free motion in the polymer. The uranyl salt that usually forms 1:2 (metal:ligand) complexes with several types of ligands, such as phosphonates and β-diketones,[21] can interact with two carbonyl groups of PMMA, thus hindering segmental motion in the polymer and significantly raising the T_g. The crosslinking caused by metal salts can also be responsible for elevation in T_g values of salt complexes. The exact role of water molecules is not clear. Water tends to plasticize the matrix and depresses the T_g, but also participates in hydrogen bonding with the carbonyl groups of PMMA. In uranyl nitrate–PMMA complexes, water molecules can also form hydrogen bonds with the oxygen atoms of the uranyl moiety $[UO_2]^{2+}$.[22d]

The thermal history of the samples has to be considered when assessing the T_g of the polymer–salt mixtures as well as any other glassy polymer. For example, the sample that contains ca. 24 wt % of uranyl nitrate hexahydrate (Table II) when scanned in the DSC in four consecutive runs (to an upper temperature of 150°C followed by fast quenching of ca. 60°C/s), yielded progressively higher T_g. The first scan conducted on the "as prepared" sample exhibited two transitions at the temperature range of 70–90 and 105–110°C. The first scan may indicate the removal of dissolved water and the existence of pure PMMA domains in the yet unequilibrated material. The three other runs yielded singlets at 112, 119, and 122°C, respectively. The T_g can be augmented significantly by exposing the samples briefly to elevated temperatures; thus, for example, the value of the former can be increased from 112 to 132°C in a single step, scanning the "as prepared" samples to a higher temperature (300°C) with the same fast quenching rate. The sample was not

Content of uranyl nitrate hexahydrate (mmol in 100 g)

(a)

Content of uranyl nitrate hexahydrate (weight %)

(b)

Fig. 2.   A plot of T_g vs. uranyl nitrate concentration in PMMA–uranyl nitrate systems: (a) T_g vs. content of uranyl nitrate hexahydrate (mmol in 100 g); (b) T_g vs. content of uranyl nitrate hexahydrate (in wt %).

allowed to degrade due to short residence time at the high temperature. Thus, the values quoted in Table II show a definite trend for the T_g with regard to salt loading. Nevertheless, each sample listed may have its own response to the thermal treatment and, therefore, any extrapolation should be taken cautiously.

The data listed in Table II reveal that even a small amount (≈ 3 wt %) of dissolved salt can significantly elevate the T_g of the polymer. The nature of the bond between metal and the polymer ligand is important in this respect. Transition metals with unfilled d-orbitals are known to form strong coordinate bonds with electron donor-containing oxygen atoms such as those present in a phosphoryl group. Metal salts of the lanthanide and actinide series having unfilled f-orbitals mainly form complexes through electrostatic bonding. The way these factors influence the T_g is the subject of further studies in this laboratory.

Radiographic Evaluations

Since poly(methyl methacrylate) is radiolucent, its detection by radiography when used for implants is difficult. In many reported instances when these materials are impacted *in vitro*, inhaled or swallowed, it imposed a severe threat to the patient and, therefore, it is desirable to employ radiopaque polymers for most biomedical applications. The absorption of X-rays is related directly to the atomic number. The relationship is approximated by[26]

$$\mu = k\lambda^3 Z^4 + 0.2$$

where μ is the absorption coefficient, k a constant, λ is the wavelength of the X-rays, Z is the atomic number, and 0.2 is the average coefficient of scattering.

The strong dependency on the atomic number prompted attempts to impart radiopacity to acrylic polymers through physical mixing with nonsoluble heavy metal salts such as barium sulfate.[11] In the present method, salts are solubilized in acrylic monomers and the mixture is subsequently polymerized.[6-9] Homogeneous dispersion of the salt in the polymer prevails through the specific interactions between the metal atoms and the carbonyl moiety of the polymer.

Radiographs of some of the uranyl nitrate–PMMA transparent homogeneous materials are shown in Figure 3. Specimens containing a low content (3–4 wt %) of metal salts such as cupric chloride, praseodymium chloride, and uranyl nitrate could also be easily detected. Uranium is an effective radiopacifying agent. Radiographs of the miscible hydrated uranyl nitrate–PMMA systems crosslinked with a small amount of tetraethyleneglycol dimethacrylate look similar. The complete dispersion of the salts in the polymer contrasts sharply with the radiographs of PMMA composites with finely ground barium sulfate shown in Figure 4.

Similar results with bismuth bromide–PMMA[6,9] and barium bromide dihydrate–poly[methoxypoly(ethyleneglycol)monomethacrylates] containing a $CH_3O(CH_2CH_2O)_n$ moiety[7] have also been recently reported from this laboratory. The results with radiographic measurements of uranyl nitrate–PMMA resins are graphically depicted in Figure 5, where the radiopacities of the polymer–salt complexes expressed in mm of aluminum are

Thickness (in mm) of aluminum stepwedge

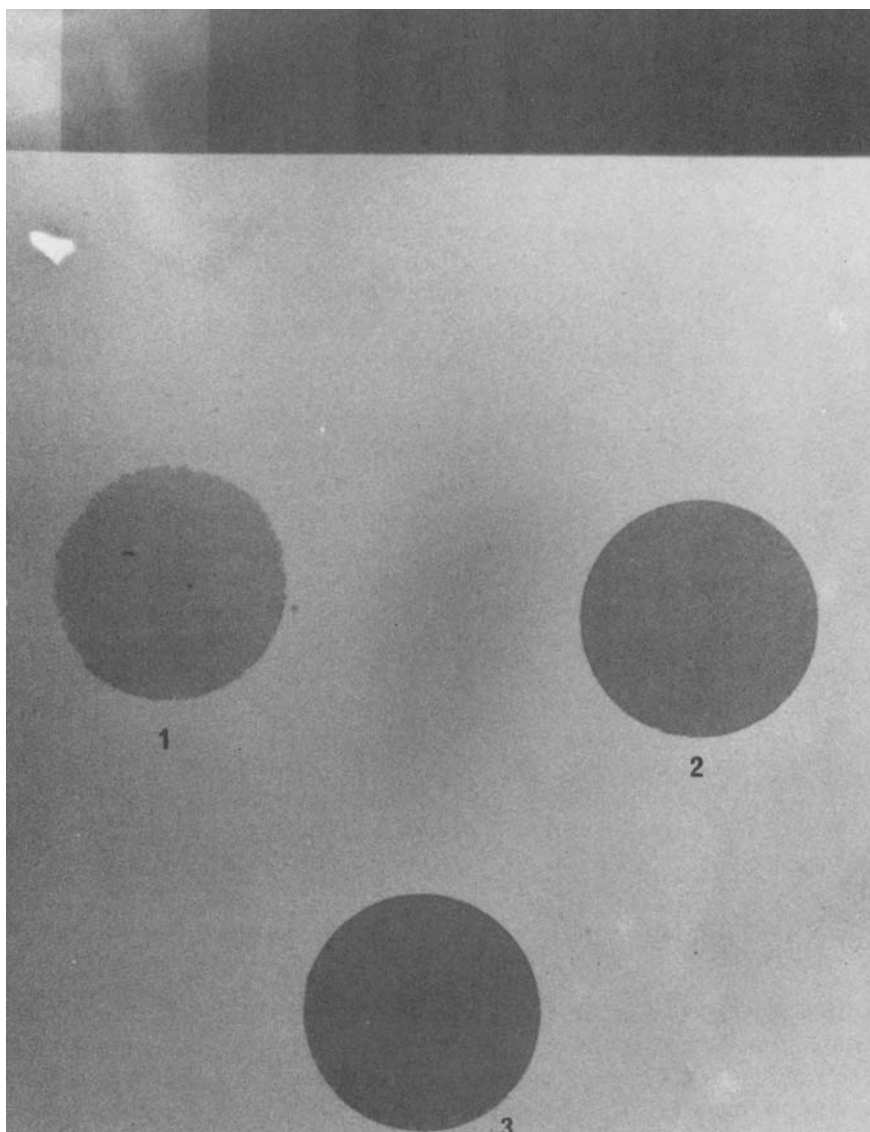1   2   3   4   5   6   7

Fig. 3. Positive radiographs of homogeneous miscible PMMA–uranyl nitrate systems relative to an aluminum stepwedge. Pellet number/wt % uranyl nitrate/thickness of pellet in mm: 1/16/0.98; 2/24/1.05; 3/32/1.00.

plotted as a function of the content of uranyl nitrate hexahydrate; an almost linear relationship is found. Similar results have also been obtained for homogeneous systems of bismuth bromide–PMMA[9] and barium bromide dihydrate–MG22 [where MG22 is a glyme methacrylate of the general formula $CH_2 = C(CH_3)COO(CH_2CH_2O)_nCH_3$, with $n = 22$].[7] Approximately 19.5 wt % of barium bromide hydrate and 13–14 wt % of bismuth bromide are

Thickness (in mm) of aluminum stepwedge

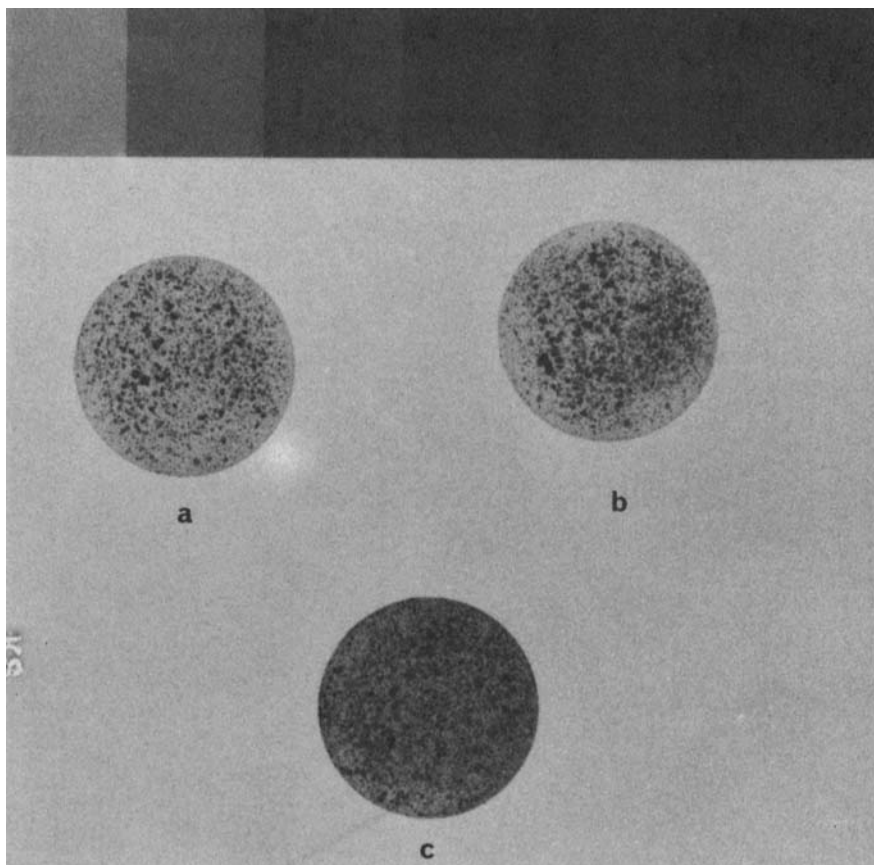1   2   3   4   5   6   7

Fig. 4. Positive radiographs of heterogeneous poly(methyl methacrylate) composites with barium sulfate [(a) 30 wt %; (b) 35 wt %; 40 wt %] relative to an aluminum stepwedge bar.

required to achieve a radiopacity equivalent to that of aluminum, a standard adopted for dental and other medical applications.[27] In comparison to bismuth bromide and barium bromide dihydrate, only 11 wt % of uranyl nitrate hexahydrate is needed to meet this requirement. Thus, the radiopacifying capacity of the salts follows the order of increasing atomic weight of the metal, and the amount of salt required to render PMMA radiopaque equivalent to aluminum increases in the order: uranyl nitrate < bismuth bromide < barium bromide. For the last two salts the bromide anion also contributes to their radiopacifying capacity.

CONCLUSIONS

A number of transition-metal salts (cupric nitrate and manganese chloride), actinides (uranyl nitrate) and lanthanides (praseodymium chloride), are miscible with methyl methacrylate. The monomer–salt solutions can be polymer-
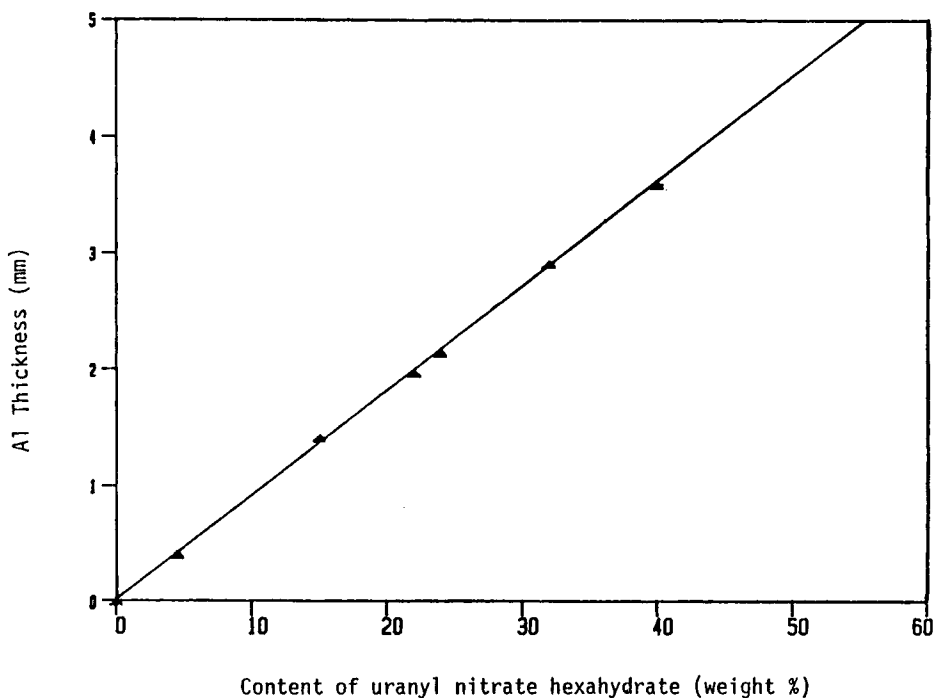
Fig. 5. Comparison of radiopacities of an aluminum stepwedge bar with that of 1 mm pellets of transparent PMMA resins containing different wt % of uranyl nitrate hexahydrate.

ized to yield clear hard plastics. Results from infrared spectroscopy indicate that interactions between the metal and the carbonyl group of PMMA are responsible for the homogeneous dispersion of salt in the polymer. However, a quantitative study that will assess the ratio between free ions, salt molecules, and water of hydration in the material is still required.

In many instances the presence of a metal salt raises the T_g of PMMA, a phenomenon reported before and caused by the loss of free volume in the polymer matrix as the specific interactions between salt and the polymer stiffens the chains. The incorporation of these salts produces homogeneous radiopaque materials with radiopacities comparable to that of aluminum.

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