Organobismuth polymers as X-ray contrast materials: synthesis, characterization and properties

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Organobismuth monomers containing the Ph_3Bi moiety were synthesized and polymerized to obtain homogeneous X-ray constrast polymers. Styryldiphenylbismuth (I), α-methylstyryldiphenylbismuth (II), tris(α-methylstyryl)bismuth (III) and (p-diphenylbismuthphenyl)vinyldimethylsilane (IV) were prepared via a Grignard reaction with $BiPh_2Cl$. Monomers I and II are contaminated with significant amounts of Ph_3Bi and divinyl compounds. Monomer I can be homo- and copolymerized radically and anionically, II can only be copolymerized, while IV did not polymerize at all. In anionic polymerization the carbanion also attacks the Ph–Bi bond of I and II. Glass transition temperatures were determined as a function of bismuth comonomer content for styrene and acrylate copolymers, and the thermal decomposition was also studied. Radiopacities in millimetres of aluminium per millimetre of polymer were found to be proportional to the molar bismuth content of the transparent copolymer specimens.

(Keywords: triphenylbismuth monomers; organobismuth polymers; radiopacity)

INTRODUCTION

The extensive application of plastics in dentistry and medical devices makes radiopacity a highly desirable property for polymers. It permits the utilization of radiography as a non-destructive diagnostic tool for plastics[1,2]. To achieve this, several X-ray contrast or radiopacifying agents are presently in use, including radiopaque glasses[3,4] and metallic (e.g. barium, bismuth) salts[5,6]. However, most of these additives are incompatible with common plastics, causing them to be more sensitive to liquid penetration and to fracture as well as deterioration of mechanical and aesthetic properties.

Our efforts in this field have been concerned with polymer-compatible additives. We recently identified triphenylbismuth (Ph_3Bi)[7,8] as an effective X-ray contrast additive for plastics. It is miscible with a wide range of polymers including polyacrylates, polystyrene, poly(vinyl chloride) and poly(alkenes). Radiopacities exceeding that of aluminium by at least a factor 2 can be achieved. The organobismuth compound is colourless, heat-stable and does not significantly interfere with radical initiators or accelerators. It also is water-insoluble and has a low toxicity index. Although its leaching into water from a resin would be minimal, permanent incorporation of triphenylbismuth by covalent bonding would prevent leaching entirely even in organic solvents in which this additive is highly soluble.

In a preliminary communication[9] we briefly reported some of the results obtained with two triphenylbismuth-containing monomers and polymers. In this paper the synthesis, characterization and polymerization of four vinyl monomers containing the triphenylbismuth moiety are discussed. The thermal behaviour and radiopacities determined for a series of copolymers as a function of the bismuth content are also reported.

EXPERIMENTAL

Materials

Bismuth trichloride (Alfa), triphenylbismuth (Alfa), 4′-bromoacetophenone (Aldrich), vinyldimethylchlorosilane (Hüls) and 4′-bromochlorobenzene were used without further purification. Methyl acrylate, methyl methacrylate, styrene and 4-bromostyrene (all Aldrich products) were distilled from CaH_2 prior to use. Benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN) were recrystallized from ethanol. All solvents used in this study were distilled from $LiAlH_4$.

Synthesis

Diphenylbismuth chloride. This compound was synthesized from triphenylbismuth and $BiCl_3$ in 85% yield (m.p. 188°C) according to a reported procedure[10].

4-Bromo-α-methylstyrene. This monomer was synthesized from 4-bromoacetophenone via a Grignard reaction as outlined by Conlon *et al.*[11]. After dehydration of the hydroxy intermediate by iodine, the monomer was obtained in 90% yield.

4-Vinylphenyldiphenylbismuth (styryldiphenylbismuth, I). The published procedure[12] was modified as follows.

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A solution of 4.75 g (0.025 mol) of 4-bromostyrene in 20 ml of tetrahydrofuran (THF) was added dropwise to a mixture of 10 ml of THF containing 0.6 g (0.025 mol) of Mg turnings and a few drops of 1,2-dibromoethane. The temperature was kept below 40°C. After all the Mg had disappeared, the mixture was reacted for an additional hour, then cooled to 0°C and a slurry of 10 g (0.025 mol) of diphenylbismuth chloride in THF was slowly added. After stirring for 3 h at 0°C, saturated aqueous NH_4Cl was added, the solution was filtered through a bed of calcite, and the organic layer was separated and then dried over $MgSO_4$. Solvent removal yielded a yellow viscous oil, which was treated with petroleum ether to precipitate and remove any polymer formed during the reaction. The final product, after removal of solvent, was a clear yellow viscous oil that did not crystallize from isopropanol, contrary to earlier findings[12]. Yield was 50%. ^1H n.m.r. ($CDCl_3$): $\delta = 5.1$–6.8 ppm (3H, dd, vinyl H) and 7.2–7.7 ppm (14H, m, phenyl H). Mass spectrum: $m/z = 389$ ($M^+ - C_6H_5$), 363 ($M^+ - C_6H_5$ and $-CH{=}CH_2$), 312 ($M^+ - 2C_6H_5$), 286 ($M^+ - 2C_6H_5$ and $-CH{=}CH_2$), 209 (Bi^+) and 180 ($M^+ - C_6H_5$ and $-Bi$). Analysis: calculated for $C_{20}H_{17}Bi$, C 51.50, H 3.65; found, C 51.41, H 3.68. An h.p.l.c. tracing revealed the product to be a mixture of at least three compounds (see discussion).

4-Isopropenylphenyldiphenylbismuth (*α-methylstyryldiphenylbismuth, II*). This monomer was prepared by a procedure similar to that for the styryl derivative, starting from 4.92 g (0.025 mol) of 4-bromo-α-methylstyrene. The final product, obtained in 60% yield, was obtained as a yellow viscous oil. ^1H n.m.r. ($CDCl_3$): $\delta = 2.1$ ppm (3H, s, CH_3), 4.9–5.4 ppm (2H, d, vinyl H) and 7.2–7.7 ppm (14H, m, aromatic). Mass spectrum: $m/z = 403$ ($M^+ - C_6H_5$), 363 ($M^+ - C_6H_5$ and $-C(CH_3){=}CH_2$), 326 ($M^+ - 2C_6H_5$), 286 ($M^+ - 2C_6H_5$ and $-C(CH_3){=}CH_2$), 209 (Bi^+) and 194 ($M^+ - C_6H_5$ and $-Bi^+$). Analysis: calculated for $C_{21}H_{19}Bi$, C 52.50, H 3.95; found, C 52.63, H 3.76. H.p.l.c. tracings showed the product to be a mixture of three compounds (see discussion).

Tris(4-isopropenylphenyl)bismuth (*tris(α-methylstyryl) bismuth, III*). The Grignard reagent obtained from 4.92 g (0.025 mol) of 4-bromo-α-methylstyrene and 0.6 g (0.025 mol) of Mg in 20 ml of THF was reacted for 3 h at 0°C with 2.62 g (0.0083 mol) of $BiCl_3$ in THF. After work-up a yellow solid was obtained, which on recrystallization from ethanol gave a product in 50% yield and a sharp m.p. at 124°C. ^1H n.m.r. ($CDCl_3$): $\delta = 2.1$ ppm (9H, s, CH_3), 4.9–5.4 ppm (6H, d, vinyl H) and 7.2–7.7 ppm (12H, m, aromatic). An h.p.l.c. tracing only showed one peak.

p-*Bromophenylvinyldimethylsilane*. A 50% THF solution of 6 g (0.05 mol) of vinyldimethylchlorosilane was added dropwise over a 1 h period to a Grignard solution of 1.2 g (0.05 mol) of Mg and 11.8 g (0.05 mol) of *p*-dibromobenzene in 25 ml of THF. The exothermic reaction was allowed to continue for an additional hour, and the mixture was then cooled to 0°C and treated with 20% aqueous NH_4Cl. A black precipitate was removed by filtration over calcite. After work-up the residual yellow crude product was fractionally distilled giving a colourless liquid at 78°C/1 mmHg in 50% yield. ^1H n.m.r. ($CDCl_3$): $\delta = 0.26$–0.34 ppm (6H, d, methyl H), 5.59–6.44 ppm (3H, m, vinyl H) and 7.26–7.54 ppm (4H, m, phenyl H). Mass spectrum: $m/z = 161$ ($M^+ - Br$), 146 ($M^+ - Br$ and $-CH_3$), 85 ($M^+ - C_6H_4Br$) and 59 ($M^+ - CH{=}CH_2$ and $-C_6H_4Br$). Peaks at 231 and 219 suggest the presence of 1,4-bis(dimethylvinylsilyl) benzene.

(p-*Diphenylbismuthphenyl*)*vinyldimethylsilane* (*IV*). A total of 10 g (0.025 mol) of diphenylbismuth chloride was added in small amounts to a Grignard solution at 0°C made from 0.6 g (0.025 mol) of Mg in THF and a 30% THF solution containing 6.0 g (0.025 mol) of *p*-bromophenylvinyldimethylsilane. The solution was then stirred for 1 h, after which 20% aqueous NH_4Cl was added. A black precipitate was removed by filtration over calcite, the organic layer was separated and dried over $MgSO_4$, the solvent was removed and the residue was dissolved in petroleum ether. Any polymer formed during the monomer synthesis is insoluble and can be removed by filtration. After evaporation of the solvent, the monomer was obtained in 60% yield as a yellow viscous liquid. ^1H n.m.r. ($CDCl_3$): $\delta = 0.26$–0.34 ppm (6H, d, methyl H), 5.56–6.44 ppm (3H, m, vinyl H) and 7.10–7.78 ppm (14H, m, phenyl H). Mass spectrum: $m/z = 447$ ($M^+ - Ph$), 370 ($M^+ - Ph_2$), 329 ($M^+ - Ph_2$, $-CH_3$ and $-CH{=}CH_2$), 286 ($M^+ - Ph_2$, $-Si(CH_3)_2$ and $-CH{=}CH_2$), 209 (Bi^+), 161 ($M^+ - Bi$ and $-Ph_2$) and 145 ($M^+ - Bi$, $-Ph_2$ and $-CH_3$). Analysis: calculated for $C_{22}H_{23}SiBi$, C 50.93, H 4.04; found, C 50.41, H 4.38.

Polymer synthesis

A sealed ampoule containing a de-aerated mixture of monomer(s), initiator (0.5 wt% BPO or AIBN calculated on monomer(s)) and solvent (benzene or toluene) was heated for 24 h at 65°C. The polymer was precipitated from methanol, filtered, washed and dried in vacuum. For copolymers the composition was checked by ^1H n.m.r. For bulk polymerization known amounts of the bismuth-containing monomers were dissolved in methyl methacrylate (MMA) or styrene with BPO as initiator. The de-aerated mixtures were polymerized in sealed cylindrical tubes at 65°C. Specimens of 1 and 2 mm thickness were cut and polished from the transparent polymers for radiopacity measurements. Anionic polymerizations were carried out under high vacuum in a sealed all-glass apparatus using break-seals. The monomers were dried under high vacuum and by repeated azeotropic distillation with benzene. Cumylpotassium or the dipotassium salt of the α-methylstyrene dianion in THF was used as the initiator.

Measurements

^1H n.m.r. spectra were recorded on a GE-QE 300 with tetramethylsilane (TMS) as standard, and mass spectra on a Finnegan 4500 GC/MS/DS. Glass transition temperatures (T_g) were measured under a N_2 atmosphere on a Perkin–Elmer DSC-4 differential scanning calorimeter at a heating rate of 20°C min^{-1}. T_g values were taken at the inflection point of the d.s.c. tracings. The thermal decomposition of some of the polymers was recorded on a Perkin–Elmer TGA2 in the temperature range 25–500°C under a helium atmosphere and at a heating rate of 20°C min^{-1}. Radiopacities were measured with a Picker X-ray unit operating at 90 kV and 6 mA.

The transparent polymer samples were placed next to an aluminium step wedge (1 mm steps) on a Kodak ultraspeed double-sided X-ray film no. DF49. The film was placed 20 inch (~51 cm) below the tungsten anode. The developed film was scanned with a Joyce microdensitometer and the radiopacities of the specimens measured relative to that of the aluminium step wedge. Radiopacities, expressed in millimetres of aluminium, were determined as a function of the molar concentration of the bismuth-containing monomer unit.

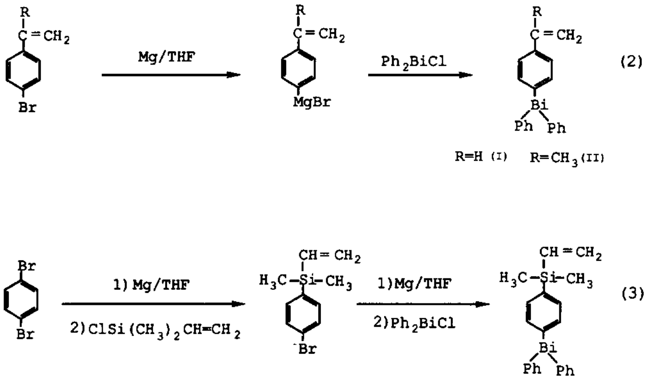
RESULTS AND DISCUSSION

Bismuth trimethacrylate and other bismuth acrylates were synthesized as early as 1968[13]. Minute quantities of these monomers copolymerized with other monomers can impart certain beneficial properties to polymers. For example, bismuth-containing polymers are used as bactericidal paints and coatings in hospitals[13]. However, the application of bismuth acrylates as compatible X-ray contrast comonomers is severely limited by their low solubility in most solvents and monomers. Even the monomer diphenylbismuth methacrylate, which we recently synthesized[13,14], has a solubility in MMA of less than 5%. Considerably more is needed to impart a radiopacity equivalent to that of aluminium[15], a standard frequently used for X-ray contrast plastics in medical applications[16]. Also, once incorporated into polymers, bismuth acrylates would significantly increase the moisture sensitivity of such resins. For this reason it was decided to investigate the more hydrophobic styryldiphenylbismuth monomers, which are expected to have solubilities comparable to that of triphenylbismuth itself.

Styrylbismuth monomers

The synthesis of styryldiphenylbismuth (I) is shown in *Scheme A*. It essentially follows the procedure outlined by Braun *et al.*[12], who determined copolymerization reactivity ratios for styrene with a series of styryldiphenyl monomers containing fifth main group elements (P, As, Sb, Bi). The sharp-melting diphenylbismuth chloride (Ph_2BiCl) precursor can be obtained in high purity free from triphenylbismuth and phenylbismuth dichloride (h.p.l.c.).

$$2\,Ph_3Bi + BiCl_3 \longrightarrow 3\,Ph_2BiCl \qquad (1)$$



In the second step the reaction of Ph_2BiCl with the Grignard reagent of *p*-bromostyrene yielded a yellow oil, which resisted recrystallization from isopropanol as described[12]. Purification by chromatography also did not produce monomer I in solid form. The compound is claimed to have a m.p. of 43°C[12]. Elemental analysis, ^1H n.m.r. and mass spectrometry suggested I to be reasonably pure[9], but radical polymerization of the oily product produced a significant amount of insoluble material, implying the presence of distyryl or tristyrylbismuth impurities. This was later confirmed by reverse-phase h.p.l.c. (C18-bonded silica with acetonitrile as eluent). The chromatogram (*Figure 1a*) reveals that I is a mixture of 31% triphenylbismuth, 42% I, 20% distyrylphenylbismuth and 3% tristyrylbismuth. A few per cent *p*-bromostyrene is also present, but no Ph_2BiCl.

The monomer α-methylstyryldiphenylbismuth (II) made by the same procedure as I exhibits a similar h.p.l.c. chromatogram (*Figure 1b*). In addition to 45% II it contains 32% Ph_3Bi, 20% bis(α-methylstyryl)phenylbismuth and 2.7% tris(α-methylstyryl)bismuth (III). Several modifications were attempted to improve the purity of II: using chloro- instead of bromo-α-methylstyrene, using excess Ph_2BiCl, or reversing the addition of the reagents; but none led to a significant change in the distribution of the three main products. Samples withdrawn at different intervals of the Grignard reaction revealed that product distribution did not change much with the extent of the reaction. Although a preparative reverse-phase h.p.l.c. column probably can yield pure I and II, no attempt was made to resolve these mixtures. In a separate synthesis the tris compound III was recovered as a pure solid melting at 124°C and showing only one peak in the h.p.l.c. (*Figure 1c*).

Organobismuth compounds are prone to redistribution reactions and this may be the chief cause of the impurities. For example, Ph_3Bi is detected after 24 h when Ph_2BiCl is dissolved in THF. Also, white, solid Ph_2BiCl slowly turns yellow due to formation of $PhBiCl_2$. Mixed triarylbismuth compounds are reported[10] to equilibrate to the symmetrical products:

$$Ar'_2Ar''Bi + Ar'Ar''_2Bi \rightleftharpoons Ar'_3Bi + Ar''_3Bi$$

This process may be faster with the styryl monomers as the C–Bi bond appears to be weaker than in Ph_3Bi itself (see 'Anionic polymerization'). However, on mixing III with Ph_3Bi in THF we did not find any formation of asymmetric products after 24 h. It is not surprising that our ^1H n.m.r., mass spectrometry and C–H analysis data led us to believe that monomer I was a relatively pure product[9]. It can be shown that the actual mixture of triphenylbismuth, monomer I and the divinyl derivative should give ^1H n.m.r. and mass spectra very similar to that of pure I, and the C–H data are also close. Moreover, the earlier h.p.l.c. tracings with a silica gel column only showed one peak.

Radical polymerization

Polymerization of I in toluene is reported to be about 10 times faster than for styrene itself[12]. In our case, a considerable amount of insoluble product is formed, especially at high conversion. This is to be expected considering the significant amount of divinyl compound present in I. The soluble part can be recovered from methanol as a white, powdery solid. The presence of triphenylbismuth in the starting monomer does not interfere with the polymerization, and the compound remains dissolved when the polymer is precipitated from methanol. The α-methylstyryl derivative II, as expected, does not homopolymerize at 60–70°C, but can be

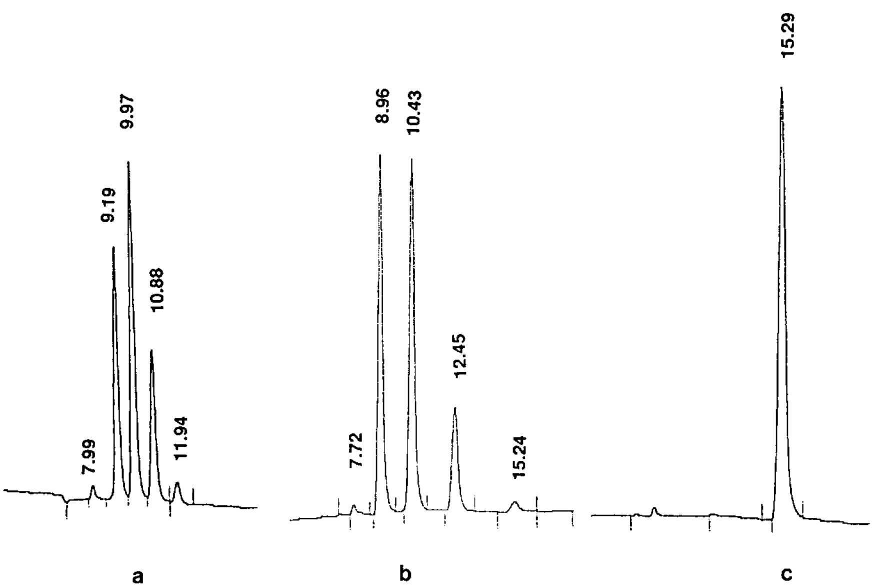


Figure 1 H.p.l.c. tracings of (a) styryldiphenylbismuth, (b) α-methylstyryldiphenylbismuth and (c) tris(α-methylstyryl)bismuth. The five peaks in (a) and (b) are the starting *p*-bromo- compound, Ph_3Bi and mono-, di- and trivinyl (or isopropenyl) substituted Ph_3Bi, respectively

copolymerized with methyl acrylate in benzene. If stopped at low conversion, soluble polymers are obtained. From the ^1H n.m.r. spectrum the percentage incorporation of bismuth monomer can be computed. This spectrum clearly shows a small fraction of vinyl protons resulting from the incorporation of some of the bis(α-methylstyryl)bismuth derivative present in monomer II in a very significant amount. The vinylsilane monomer IV resisted radical polymerization, consistent with reports that $p\pi$–$d\pi$ interactions with the neighbouring Si atoms in vinylsilanes hinder their polymerization[17].

Anionic polymerization

Ionic polymerization of monomers I or II with other monomers such as styrene could lead to block copolymers in which one of the blocks would consist of a radiopaque chain of bismuth-containing monomer units. This could be of interest in morphological studies utilizing electron microscopy since the presence of phase-separated domains could then easily be detected without the use of staining agents normally required in such investigations. The ionic polymerization of the styrylbismuth monomer I was attempted earlier by Braun *et al.*[12]. Both the cationic (BF_3) and anionic route (BuLi in benzene at −20°C) were reported to yield insoluble materials. Before attempting the anionic polymerization of our styrylbismuth monomers, it was ascertained that triphenylbismuth itself did not decolorize a THF solution of poly(styrylpotassium) or cumyl-potassium at room temperature. Under these conditions the Bi–Ph bond appears to be stable in the presence of benzyl-type carbanions. However, when a benzene solution of poly(styryllithium) was added to an equivalent amount of Ph_3Bi the colour immediately disappeared. This may not be surprising in view of the reported exchange reaction between Ph_3Bi and alkyllithium compounds yielding PhLi and trialkylbismuth[18]. For this reason, the Li^+ counterion was avoided and potassium salts of the carbanion initiators were used.

When a 30 times excess of I was added to a solution of potassium α-methylstyrene dianion initiator in THF at −78°C, rapid polymerization ensued. The dark red colour persisted even when the mixture was allowed to warm up to room temperature. After termination with a drop of methanol, the solution was filtered to remove some insoluble material. Precipitation from methanol then produced a white powdery material. Its ^1H n.m.r. spectrum was consistent with that of the homopolymer of monomer I and did not show any significant amount of pendant vinyl groups expected from incorporation of the distyryl compound present in I. The g.p.c. trace of a THF solution of this polymer exhibits a broad bimodal molecular-weight distribution (*MWD*). It indicates that, in addition to branching caused by the presence of the distyryl derivative, significant termination or other side reactions occur before all the monomer is polymerized. It was suggested earlier that residual Ph_2BiCl used in the synthesis of I may have caused premature termination of active ends[9], but subsequent h.p.l.c. tracings of the monomer (*vide supra*) ruled out this possibility. An attempt to free the monomer from carbanion-terminating impurities by treating a THF solution of I with a network containing bound fluorenyl carbanions (made from styrene, divinylbenzene and 2-vinylfluorene, and reacted in THF with cumyl-potassium) did not improve the *MWD*. Therefore, it was suspected that either the styrylbismuth monomer itself, or the distyryl and tristyryl impurities, could be susceptible to side reactions.

To pursue this problem further the α-methylstyryldiphenylbismuth monomer was synthesized. The final product, as shown above, also contains a substantial amount of the bis(α-methylstyryl)derivative and a small amount of the tris(α-methylstyryl)bismuth compound. Anionic polymerization of α-methylstyrene in THF is much slower than for styrene, and only proceeds to completion at low temperature[19]. When the α-methylstyrylbismuth monomer was added to a THF solution of cumyl-potassium at −80°C, very little if any polymer was recovered after several hours of reaction. Instead, the red colour of the cumyl carbanion slowly changed to bluish black, and the solution eventually decolourized. Addition of more initiator resulted in its deactivation. When cumyl-potassium was added dropwise to a 10^{-3} M solution of the pure compound tris(α-methylstyryl)bismuth in THF at −80°C, a bluish black colour was produced instantaneously. No polymer could be recovered.

The results suggest that when a *p*-vinyl substituent is present in one of the phenyl groups of Ph_3Bi, it renders the phenyl–Bi bond more susceptible to carbanion attack (or electron transfer could occur), and any such side reaction is more rapid when two or all three phenyl groups are *p*-vinyl-substituted. The styrylbismuth monomer, like styrene itself, probably polymerizes at −80°C in a matter of seconds, and side reactions, while causing a bimodal and broad *MWD*, do not prevent polymer formation. On the other hand, α-methylstyrylbismuth, if at all polymerizable, propagates much slower. Therefore, for this monomer side reactions prevail, especially those with the di- and tri-substituted impurities. It is debatable whether a polymer of II exists at all. The high T_g values obtained for copolymers of II with methyl acrylate suggest that steric hindrance may prevent its homopolymerization even at −80°C. We have not yet attempted to remove the di- and tristyryl impurities from the two monomers. Preparative h.p.l.c. is a possible way to accomplish this. Absence of these impurities, which we believe to be more susceptible to side reactions with carbanions than I itself, is likely to improve the *MWD* of the homopolymer of I when made by anionic polymerization.

POLYMER PROPERTIES

Glass transition temperatures

Addition of the radiopacifying agent triphenylbismuth to polystyrene, poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) was found[8] to lower the T_g of these polymers by 1.3 ± 0.1°C for each 1 wt% Ph_3Bi. For example, 26 wt% of Ph_3Bi dissolved in atactic PMMA decreased its T_g from 117 to 86°C[8]. It was anticipated that the plasticizing effect of Ph_3Bi might be reduced by anchoring the bismuth compound to the polymer backbone using monomers such as I or II. The bulky *p*-$BiPh_2$ substituent on the styrene unit could either enhance T_g by reducing chain flexibility or decrease T_g by hindering chain packing and increase the free volume.

T_g measurements were carried out on copolymers prepared by radical polymerization of I or II with styrene, methyl acrylate or methyl methacrylate. The polymers were precipitated from methanol, redissolved in chloroform, any insoluble material filtered off, and the polymer reprecipitated from methanol. Some insoluble product is formed as a result of the presence of significant quantities of distyryl compounds in monomers I and II. G.p.c. tracings of the soluble fraction reveal a wide molecular-weight distribution, suggesting significant branching. The M_n, based on polystyrene standards, was found to be 30 000–40 000. The presence of a small amount of the distyryl derivatives in the polymers can also be deduced from the detection of residual vinyl protons in the ^1H n.m.r. spectra of these macromolecules. Copolymer compositions were determined by comparing the area of aromatic protons *versus* aliphatic protons.

T_g values for the respective polymers are collected in *Table 1*. The styryldiphenylbismuth homopolymer appears to have a T_g of 100°C, but in some samples it was difficult to detect any T_g. Some crosslinking may occur on heating the polymer, although the d.s.c. scans for the acrylate copolymers with both monomer I and II were reproducible on repeating the heating/cooling cycle.

Table 1 Glass transition temperatures of polymers containing styryldiphenylbismuth (I) and α-methylstyryldiphenylbismuth (II)

Monomer I			Monomer II		
Comonomer[a]	Composition (mol%, I)	T_g (°C)	Comonomer[a]	Composition (mol%, II)	T_g (°C)
MA	25	89	MA	16	90
MA	21	87	MA	20	100
MMA	6.9	122	MA	23	102
St	8.5	97	MA	26	112
St	11	103	MA	40	125

[a] MA = methyl acrylate; MMA = methyl methacrylate; St = styrene

The T_g of poly(methyl acrylate) is 10°C[20]. Incorporating 25% monomer I into this polymer increases its T_g to 89°C, and 40% of monomer II raises the T_g to 125°C. Although the homopolymer of II could not be prepared, the much higher T_g of poly(α-methylstyrene) (T_g = 168°C) relative to that of polystyrene (T_g = 100°C) makes it likely that the T_g of homopolymer II, if it did exist, would be much higher than that of the styryldiphenylbismuth homopolymer. The T_g values for the copolymers, therefore, seem reasonable, although those for the methyl acrylate – I copolymers appear rather high if the value of T_g = 100°C for the polymer of I is correct. In homogeneous mixtures of polyacrylates and bismuth trihalides n.m.r. and i.r. spectra reveal the existence of strong carbonyl–Bi interactions[21]. No spectral evidence was found for adduct formation when Ph_3Bi was solubilized in polyacrylates[8]. Nevertheless, weak complexation between carbonyl and the polymer-bound Bi cannot be entirely excluded. If present, they would raise the T_g, similar to what was reported for copolymers of 3-tris(n-butyl)stannylstyrene with acrylic monomers[22]. At any rate, anchoring Ph_3Bi to the polymer backbone appears to minimize its plasticizing effect when used as an additive.

Thermal stability

The thermal degradation of the organobismuth polymers was investigated in the temperature range 25–500°C. Two representative scans are shown in *Figure 2*. The styryldiphenylbismuth homopolymer shows a small weight loss of less than 5% in the region 160–260°C. This is followed by a steep degradation in the region 260–380°C with a weight loss of 38%. The final degradation with a 17% weight loss occurs between 380–490°C, leaving a black residue of 40%, close to the calculated amount of 42% bismuth present in the homopolymer. The initial loss of about 5% may be a volatile impurity, but could also result from the presence of pendant Bi–styryl moieties coming from the incorporation of the distyryl compound. As observed earlier, in reactions with carbanions the bismuth–styryl bond appears weaker than the bismuth–phenyl bond. The degradation ensuing around 260°C most likely involves the Bi–phenyl bond. Triphenylbismuth has a bond dissociation energy[23] of only 46.2 kcal mol^{-1}. The decomposition recorded between 380 and 490°C coincides with the reported single-stage catastrophic decomposition of polystyrene in a nitrogen atmosphere[24]

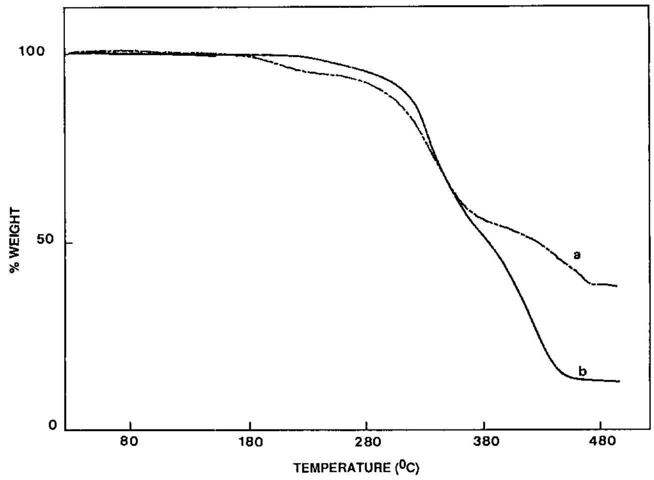


Figure 2 T.g.a. tracings of (a) the anionically prepared homopolymer of styryldiphenylbismuth and (b) the copolymer of methyl acrylate and α-methylstyryldiphenylbismuth (10 mol%)

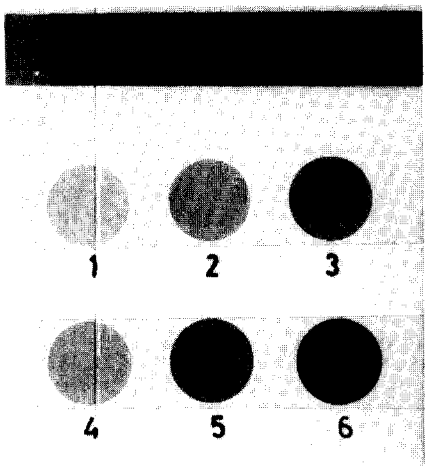


Figure 3 Positive radiographs of transparent specimens of poly(styrene-*co*-styryldiphenylbismuth). Specimen number/weight per cent bismuth monomer/specimen thickness: 1/12.0/1.14; 2/21.8/1.12; 3/35.2/1.2; 4/12.0/1.77; 5/21.8/2.03; 6/35.2/1.93

and has been attributed to the depolymerization of the polystyrene backbone resulting in low-molecular-weight products including styrene. The starting temperature for this step is known to be lower for a radically made polystyrene as compared to one made anionically[25]. In our system the temperature for the first major degradation step (260°C) is the same for radical and anionic homopolymer I, suggesting that this step involves cleavage within the triphenylbismuth moiety.

A similar pattern of decomposition was observed in a copolymer of methyl acrylate with 10 mol% (36 wt%) of the α-methylstyrylbismuth monomer (*Figure 2*). The amount of non-volatile material is slightly higher than the calculated amount of bismuth. The initial decomposition is less, probably because fewer bismuth–styryl moieties are present in the polymer.

RADIOPACITY STUDIES

The prime objective of this study is the permanent incorporation of the biocompatible radiopacifying agent triphenylbismuth into a polymeric matrix. Bulk polymerization of styryldiphenylbismuth with either styrene or MMA at 65°C and AIBN as initiator yielded perfectly transparent, hard materials. The polymerization is much faster than for a MMA/Ph_3Bi mixture of similar bismuth content. This is consistent with the reported high reactivity of the styryldiphenylbismuth monomer when copolymerized with other vinyl monomers[12]. Residual vinyl groups could not be detected in the i.r. spectrum of the polymer, which probably was considerably crosslinked as a result of the presence of distyrylphenylbismuth and which also contained the triphenylbismuth present in the starting bismuth monomer. The copolymerization with MMA was also accomplished at ambient temperatures with a mixture of BPO and an amine accelerator. This confirms an earlier observation that Ph_3Bi does not interfere with amine accelerators, unlike the bismuth halides, which complex with amines[8].

Positive radiographs of transparent specimens of some of the bismuth-containing polymers as a function of copolymer composition and specimen thickness are depicted in *Figure 3*. We established previously that the radiopacity R of a material expressed in millimetres of aluminium per millimetre of polymer, and the molar concentration M_a of the radiopacifier are related by the expression:

$$R = R_0 + (R_a - R_0)\bar{V}_a M_a$$

where R_0 and R_a are the respective radiopacities of the pure polymer and the additive, and $\bar{V}_a$ is the molar volume of the additive[26]. This relationship was experimentally confirmed for bismuth trihalides in PMMA and for Ph_3Bi solubilized in various polymers[15].

Plots of R *versus* the molar bismuth content of the polymers with MMA or with styrene as comonomer are also linear (*Figure 4*). The fact that the starting bismuth monomer also contains Ph_3Bi and the divinyl compound does not alter the bismuth content of the polymer since all three compounds remain in the polymer. From the plots the molar concentration M_a (or the weight per cent) of bismuth monomer at which the radiopacity of the material equals that of aluminium can be determined. The M_a values are 0.67 M (26 wt%) and 0.68 M (27 wt%) for the copolymers of I with MMA and styrene, respectively. This is identical to the value of 0.67 M

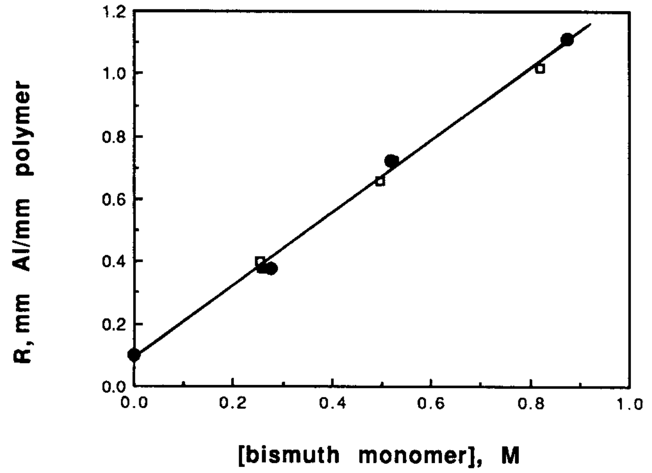


Figure 4 Plots of radiopacity R in millimetres of aluminium per millimetre of polymer *versus* the molar concentration of bismuth monomer: (□) PMMA/Bi/1 mm; (■) PMMA/Bi/2 mm; (●) PSt/Bi/1 mm

(24 wt%) found for Ph_3Bi in polystyrene and PMMA[15]. M_a is expected to be essentially independent of polymer structure as long as the intrinsic radiopacity of the polymer itself is very low. Poly(vinyl chloride), for example, has a substantial radiopacity, and the M_a for a Ph_3Bi/PVC mixture at aluminium equivalence is only 0.47 M[15].

CONCLUSIONS

Triphenylbismuth, an X-ray contrast additive highly soluble in many polymers, can be permanently incorporated in the polymer matrix by replacing one of the phenyl groups with a styryl or α-methylstyryl moiety. This prevents leaching of bismuth, and the plasticizing effect of free Ph_3Bi is largely eliminated. Transparent materials with radiopacities exceeding that of aluminium can easily be obtained. The two bismuth monomers contain considerable amounts of Ph_3Bi and distyryl compounds, and further purification as well as alternative syntheses are being pursued to obtain pure compounds. This is especially important when the bismuth-containing polymers are made by anionic polymerization.

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