BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 11, pp. 2289–2296, 1995

0032-3861/95/$10.00 + 0.00

X-ray contrast polymers of *p*-styryldi(*p*-tolyl)bismuth: synthesis and properties

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(Received 10 October 1994; revised 3 November 1994)

The radiopacifying organobismuth monomer *p*-styryldi(*p*-tolyl)bismuth was synthesized in 40% yield by means of a three-step process using 4-bromotoluene, 4-bromostyrene and bismuth trichloride as starting compounds. The product is a crystalline solid of at least 95% purity, unlike the earlier reported styryldiphenylbismuth which could only be obtained in a very impure form. Radical or anionic polymerization yields a soluble homopolymer, and copolymers were made with styrene and methyl methacrylate. The products were characterized by standard techniques. Data are reported on their solubility, blending and radiopacity. The latter property, expressed in mm of aluminium per mm resin, is a linear function of the molar bismuth concentration in the polymer specimens.

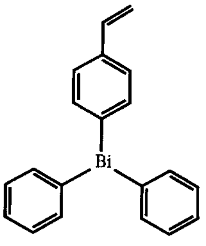
(Keywords: *p*-styryldi(*p*-tolyl)bismuth; organobismuth polymers; radiopacity; X-ray contrast polymers)

INTRODUCTION

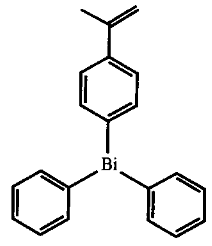
The need for X-ray contrast or radiopaque polymeric materials for use in medical devices including dental appliances has frequently been stated[1–3]. Our search for suitable radiopacifying agents has focused on compounds that are miscible with the polymers at the molecular level[4–8]. This can avoid liquid penetration or failures at phase boundaries to which heterogeneous blends are vulnerable. Triphenylbismuth has been particularly effective in this respect[9–12]. Its hydrophobic character renders it compatible with a variety of polymers. To completely eliminate the possibility that this radiopacifying agent would leach into the surroundings, we permanently anchored the triphenylbismuth on to the polymeric matrix[13,14]. This was accomplished by synthesizing styryldiphenylbismuth (**I**) which then was homopolymerized, or copolymerized with acrylates or other monomers[13].

The synthesis of **I** did not yield a pure compound[13]. The liquid-like product is contaminated with triphenylbismuth, di(*p*-styryl)phenylbismuth and a small quantity of tris(*p*-styryl)bismuth. Purification attempts by standard chromatographic procedures did not succeed. The distyryl derivative especially poses a problem since insoluble material can be detected on polymerization. A similar result was obtained in the synthesis of the α-methylstyryldiphenyl bismuth compound (**II**)[13].

For reasons that are not clear, the replacement of the two phenyl groups in **I** by *p*-tolyl moieties affords a crystalline solid devoid of di- or tristyryl impurities and containing < 5% tris(*p*-tolyl)bismuth. Polymerization of *p*-styryldi(*p*-tolylbismuth) (**III**) produces a soluble polymer. This report describes the synthesis of the monomer, the homopolymer and some copolymers, the characterization of these products, and their thermal and radiopacity characteristics.



I



II

EXPERIMENTAL

All starting materials were products from Aldrich. Bismuth trichloride, magnesium, iodine, *N*,*N*′-dimethyl-*p*-toluidine, iodomethane and *p*-bromoacetophenone were used without purification. Methyl methacrylate (MMA), styrene (St), 4-bromostyrene and 4-bromotoluene were distilled from CaH_2 prior to use. Benzoyl peroxide (BPO) and 2,2′-azobisisobutyronitrile (AIBN) were recrystallized from ethanol. Solvents were distilled prior to use.

Syntheses

Tris(p-*tolyl*)*bismuth.* Following a procedure by Barton *et al.*[15], 46.9 g (274 mmol) of 4-bromotoluene in tetrahydrofuran (THF) was converted to its magnesium derivative and the Grignard (at 0°C) was treated with a slurry of 28.7 g (91.3 mmol) of $BiCl_3$ in THF. After work-up and recrystallization from isopropanol, 31.7 g (72%) tris(*p*-tolyl)bismuth was obtained; m.p. 118–119°C, lit.[16,17] 119–120°C. The compound is now also available from Boulder Chemical Company.

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Di(p-*tolyl*)*bismuth chloride*. The synthesis of this compound was similar to that described for diphenylbismuth chloride[15]. A slurry of 18.1 g (57.4 mmol) of $BiCl_3$ in 50 ml diethyl ether was added dropwise to a solution of 27.6 g (57.4 mmol) of tris(*p*-tolyl)bismuth kept under nitrogen at 0°C. The di(*p*-tolyl)bismuth chloride was filtered off and washed repeatedly with diethyl ether. The final product was obtained in 95% yield; m.p. 180–181°C, lit.[16] 181.5°C. The purity was checked by high-performance liquid chromatography (h.p.l.c.), and infra-red (i.r.) and nuclear magnetic resonance (n.m.r.) spectra matched the reported literature data.

p-*Styryldi*(p-*tolyl*)*bismuth* (***III***). A solution of 9.2 g (50 mmol) of 4-bromostyrene in 30 ml THF was added dropwise to 10 ml THF containing 1.2 g (50 mmol) of magnesium turnings and a few drops of 1,2-dibromoethane. The temperature was kept below 40°C. After the magnesium had disappeared the mixture was cooled to 0°C, and a slurry of 21.3 g (50 mmol) of di(*p*-tolyl)bismuth chloride in THF was added slowly over a 1 h period. The reaction was continued for another 2 h at 0°C. Isolation of the product followed standard procedures for Grignard reactions as described for styryldiphenylbismuth[13]. The final product, recrystallized from isopropanol, was obtained in 60% yield (14.7 g, m.p. 81°C). The h.p.l.c. tracings showed only one sharp peak.

^{1}H n.m.r. ($CHCl_3$): δ (ppm) 7.62–7.52 (6 H, dd, $J = 12.0$, 7.8 Hz), 7.31 (2 H, dd, $J = 7.8$, 2.7 Hz), 7.14–7.08 (4 H, dd, $J = 7.6$, 2.3 Hz), 6.63–6.54 (1 H, dd, $J = 17.6$, 10.8 Hz), 5.65 (1 H, dt, $J = 17.6$, 1.0 Hz), 5.13 (1 H, dt, $J = 10.8$, 1.0 Hz), 2.23 (6 H, s). ^{13}C n.m.r. ($CDCl_3$): δ (ppm) 151.0, 137.8, 137.5, 137.3, 136.9, 131.3, 131.2, 128.1, 128.0, 113.9, 113.7, 21.5. Mass spectrometry (MS) (chemical ionization, reagent gas CH_4): 535 ($M^{+\cdot} + 41$), 523 ($M^{+\cdot} + 29$), 495 ($M^{+\cdot} + 1$), 403 ($M^+ -$ tolyl), 391 ($M^+ -$ styryl), 312 ($M^+ -$ tolyl), 300 ($M^+ -$ tolyl $-$ styryl), 209 (Bi^+). Calc. for $C_{22}H_{21}Bi$: C, 53.44; H, 4.25. Found: C, 53.57; H, 4.33.

p-(α-*Methylstyryl*)*di*(p-*tolyl*)*bismuth* (***IV***). This compound was synthesized in the same way as the styryl analogue starting with *p*-bromo-α-methylstyrene. The latter was obtained in 90% yield from *p*-bromoacetophenone and iodomethane[18]. After work-up of the Grignard an oily product was obtained in 50% yield which resisted crystallization from isopropanol. H.p.l.c. analysis showed the presence of four compounds, very similar to what was obtained for styryldiphenylbismuth[13]. No further characterization was done on this product.

Polymerization. Free radical homo- or copolymerizations were carried out in sealed ampoules containing a de-aerated mixture of monomer(s), initiator (0.5 wt% BPO or AIBN) and toluene. The solutions were heated for 24 to 72 h at 65–80°C, and the polymers precipitated from methanol, then filtered, washed and dried *in vacuo*. The composition of the copolymers was checked by ^{1}H n.m.r. Anionic polymerizations were performed in THF at −80°C in high vacuum using an all-glass apparatus provided with breakseals. The bismuth monomer was dried prior to use by repeated azeotropic distillation with benzene. Cumyl potassium or the dipotassium salt of the α-methylstyrene dianion in THF was used as initiator. The living polymers were terminated by adding a drop of methanol.

Measurements

^{1}H and ^{13}C n.m.r. spectra were obtained on a Bruker 300 MHz spectrometer, and mass spectra on a Finnegan 4500 GC/MS/DS. Glass transition temperatures and other thermal data were obtained under nitrogen on a Perkin–Elmer DSC4 differential scanning calorimeter at a heating rate of 5–20°C min^{-1}. H.p.l.c. tracings were recorded using a reverse phase Phenomenex C-18 column hooked to a Waters 401 differential refractometer, with acetonitrile as the solvent at a typical flow rate of 0.5 ml min^{-1}. Gel permeation chromatography (g.p.c.) was carried out using Waters Ultrastyragel columns (three columns of 10^4, 10^3 and 500 Å in series) connected to a Waters 410 differential refractometer, with THF as the solvent at a flow rate of 0.7 ml min^{-1}. Polystyrene standards were used in the calibration of the g.p.c. trace. Radiopacities were measured with a Picker X-ray unit operating at 65 kV and 6 mA. The monomer *p*-styryldi(*p*-tolyl)bismuth was copolymerized with MMA in bulk (AIBN as initiator) at 65°C to obtain a hard transparent material. This was cut into 2 mm discs which were placed next to an aluminium step wedge on a Kodak ultraspeed double-sided X-ray film no. DF49. The film was placed 55 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.

RESULTS AND DISCUSSION

Polymeric materials can acquire certain beneficial properties with the incorporation of bismuth-containing monomers. For example, small quantities of bismuth acrylates have been used in the manufacture of bactericidal coatings and paints[19]. Because of their low toxicity and the high atomic number of bismuth, derivatives of this metal should be attractive radiopacifying agents. However, bismuth acrylates are poorly soluble in media of low polarity, and the relatively large quantity needed to obtain polymers of high radiopacity would make it difficult to acquire a homogeneous material. Moreover, in an aqueous environment the metal acrylates are sensitive to hydrolysis. For these reasons we have explored monomers which on polymerization yield macromolecules with a triphenylbismuth moiety, notably 4-vinylphenyldiphenylbismuth or styryldiphenylbismuth (**I**) and 4-isopropenyldiphenylbismuth or α-methylstyryldiphenylbismuth (**II**)[13]. Their solubility in polymers is similar to that of triphenylbismuth, and their polymers are stable in an aqueous environment.

Monomer synthesis

The synthesis of **I** was first reported by Braun *et al.*[20]. Following their procedure, i.e. the reaction of diphenylbismuth chloride with the Grignard of *p*-bromostyrene, we obtained monomer **I** but not in the crystalline form reported by these authors. Both **I** and **II** were liquid-like products, and h.p.l.c. tracings showed them to be a mixture of ~40–45% of the monostyryl compound, 30–35% triphenylbismuth, ~20% of the distyryl derivative and a few percent of the tristyryl compound (*Figure 1*). Attempts to purify **I** or **II** by chromatography or

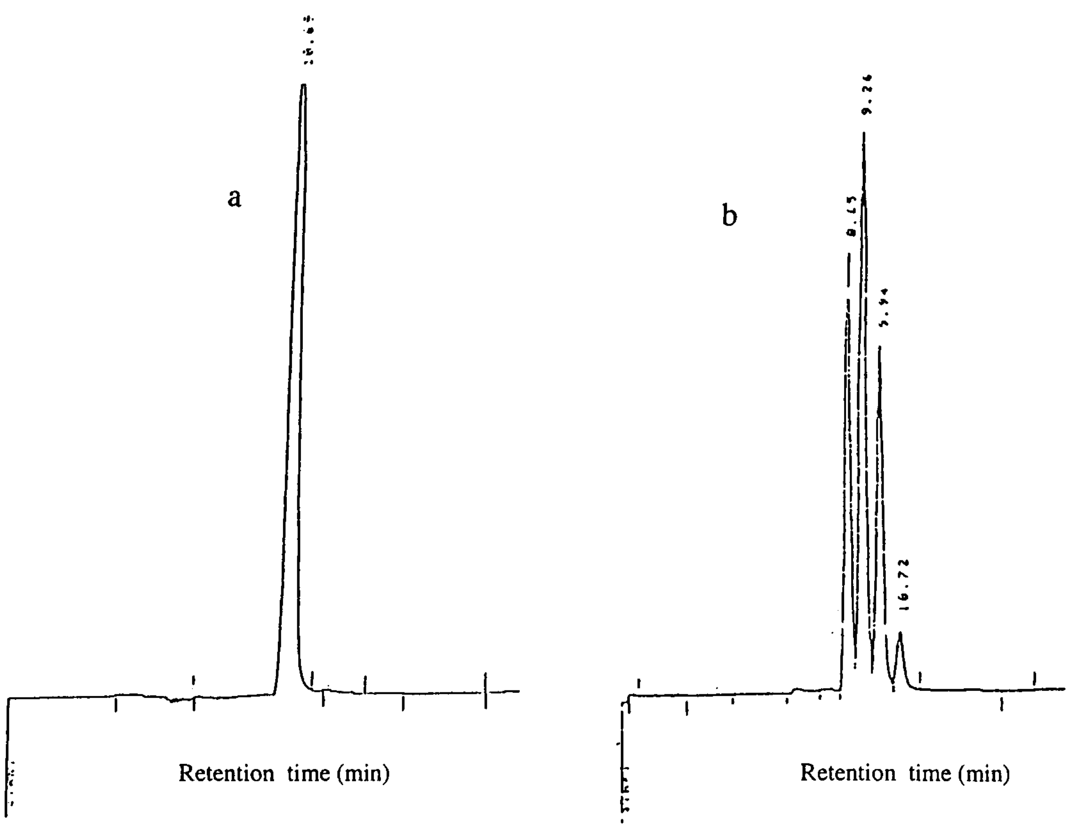
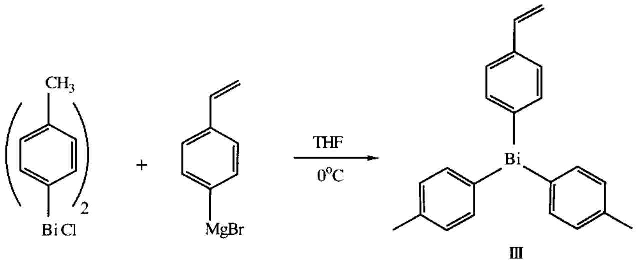


Figure 1 H.p.l.c. tracings of: (a) *p*-styryldi(tolyl)bismuth and (b) *p*-styryldiphenylbismuth (column, reverse phase C-18; solvent, acetonitrile; flow rate, 0.5 ml min^{-1}; chart speed, 1 cm min^{-1})



Scheme 1

repeated crystallization were not successful. Changing the reaction conditions also failed to improve their yield significantly. After polymerizing the mixture by radical initiators, the triphenylbismuth could easily be removed when the polymer was precipitated. However, the presence of the distyryl compound caused crosslinking, and insoluble material could be detected above ~30% conversion.

The presence of impurities was attributed to the sensitivity of organobismuth compounds to redistribution reactions[13,15]. For example, pure Ph_2BiCl in solid form slowly turns from white to yellow due to formation of $PhBiCl_2$, while in THF solution Ph_3Bi can be detected after 24 h[13]. It is also known that the relative weakness of the Bi–C bond causes mixed triarylbismuth compounds to equilibrate to the more stable symmetrical products[15], a process that may occur even faster for the styryl monomers since their C–Bi bond appears to be weaker than in Ph_3Bi itself[13].

The present results appear to indicate that replacing the two phenyl groups in **I** by two *p*-tolyl moieties yields a much purer product. *p*-Styryldi(*p*-tolyl)bismuth (**III**), formed as shown in *Scheme 1* from the reaction of di(*p*-tolyl)bismuth chloride and the Grignard of *p*-bromostyrene, was obtained as needles with a m.p. of 81°C. The h.p.l.c. tracing (*Figure 1a*) showed one sharp peak. However, this does not exclude the presence of tris(*p*-tolyl)bismuth since its retention time was found to be identical with that of **III**. The ^{13}C n.m.r. spectrum displays all the expected peaks, and so does the ^{1}H n.m.r. spectrum (*Figure 2*). Integration of the latter was very close to the expected structure (see below). Chemical analysis also was within experimental errors. However, our experience with compounds **I** and **II** is that n.m.r. spectra and chemical analysis are poor indicators of the purity of these monomers. The structures and relative amounts of the impurities were such that mixtures containing **I** or **II** have spectra which are very similar to those of the pure compounds. The difficulty in using n.m.r. or i.r. spectroscopy to distinguish between the various redistribution products in the synthesis of unsymmetrical triarylbismuth compounds was pointed out earlier by Barton *et al.*[15].

The best indication that the *p*-tolyl derivative **III** is a pure product comes from mass spectrometry, a technique recommended by Barton *et al.*[15] to check the purity of arylbismuth compounds. *Table 1* shows the fragmentation patterns which are possible for each of the four triarylbismuthines that could be formed when the Grignard of *p*-bromostyrene is reacted with di(*p*-tolyl)bismuth chloride. Careful examination leads to the conclusion

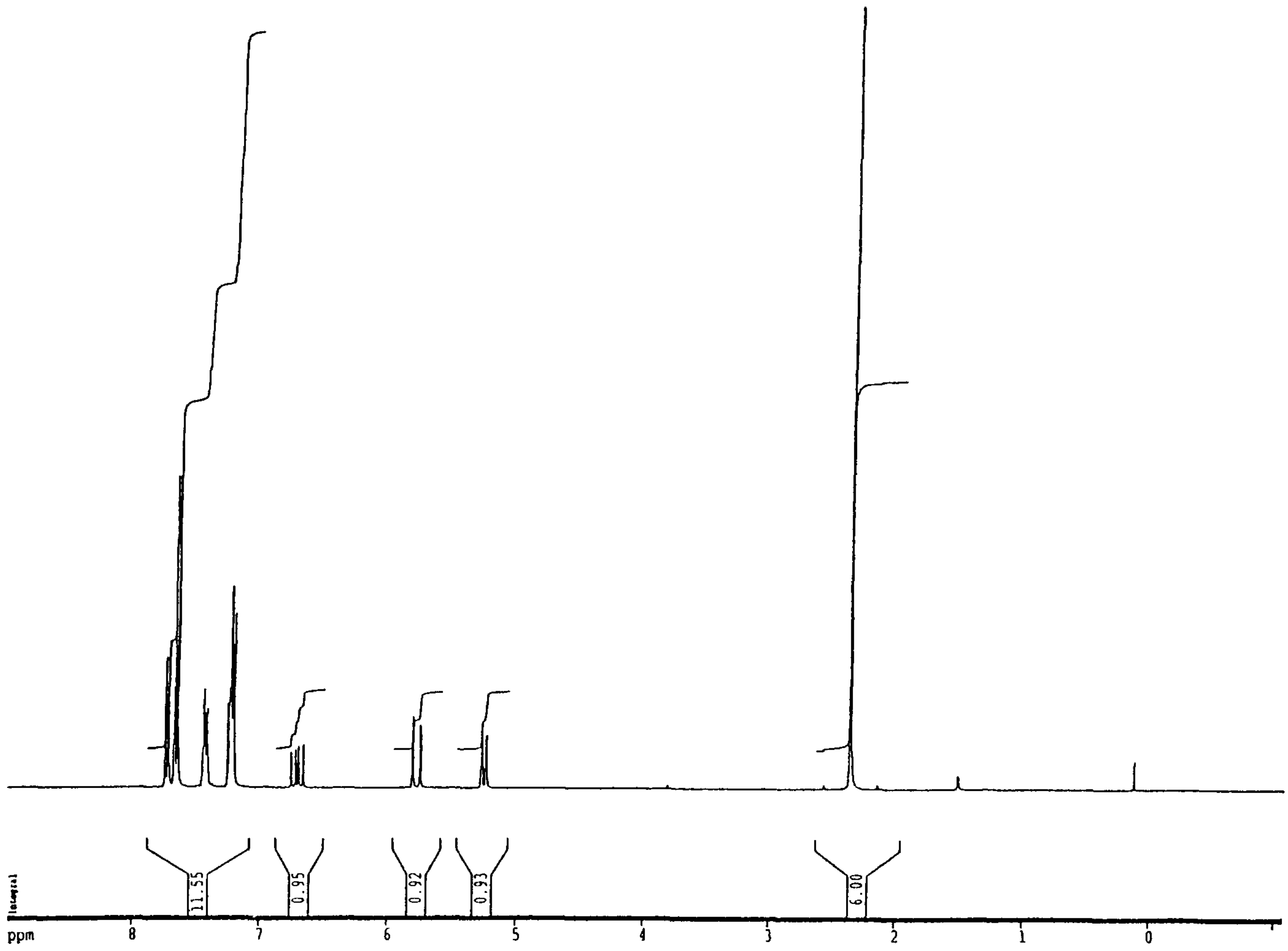
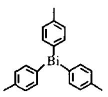
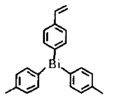
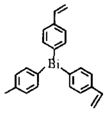
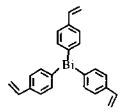


Figure 2 ^{1}H n.m.r. spectrum of *p*-styryldi(*p*-tolyl)bismuth

Table 1 Mass spectral fragmentation pattern of styryltolylbismuthines

Fragment				
$M^{+\cdot}$	482	494	506	518
−(*p*-tolyl)	391	403	415	–
−(*p*-styryl)	–	391	403	415
−2(*p*-tolyl)	300	312	–	–
−(*p*-tolyl) −(*p*-styryl)	–	300	312	–
−2(*p*-styryl)	–	–	300	312
$Bi^{+\cdot}$	209	209	209	209

that the only fragment exclusively associated with the di- or tristyryl compound is the one at $m/e = 415$. Neither the electron impact nor the chemical ionization mass spectrum (*Figure 3*) showed a peak at 415. All other peaks were easily detected in the spectra. In contrast, the peak at 415 was clearly seen in the mass spectrum of **I**, which from h.p.l.c. tracings (*Figure 1b*) was known to contain the di- and tristyryl impurities. There was a small amount of tris(*p*-tolyl)bismuth present in **III** as confirmed by the $(M+1)/e$ peak at 483 in the chemical ionization mass spectrum (*Figure 3*). Integration of the ^{1}H n.m.r. spectrum of **III** (*Figure 2*) indicated that the presence of tris(*p*-tolyl)bismuth in **III** was $<5\%$. The ^{13}C n.m.r. spectrum and the elemental analysis data were also consistent with

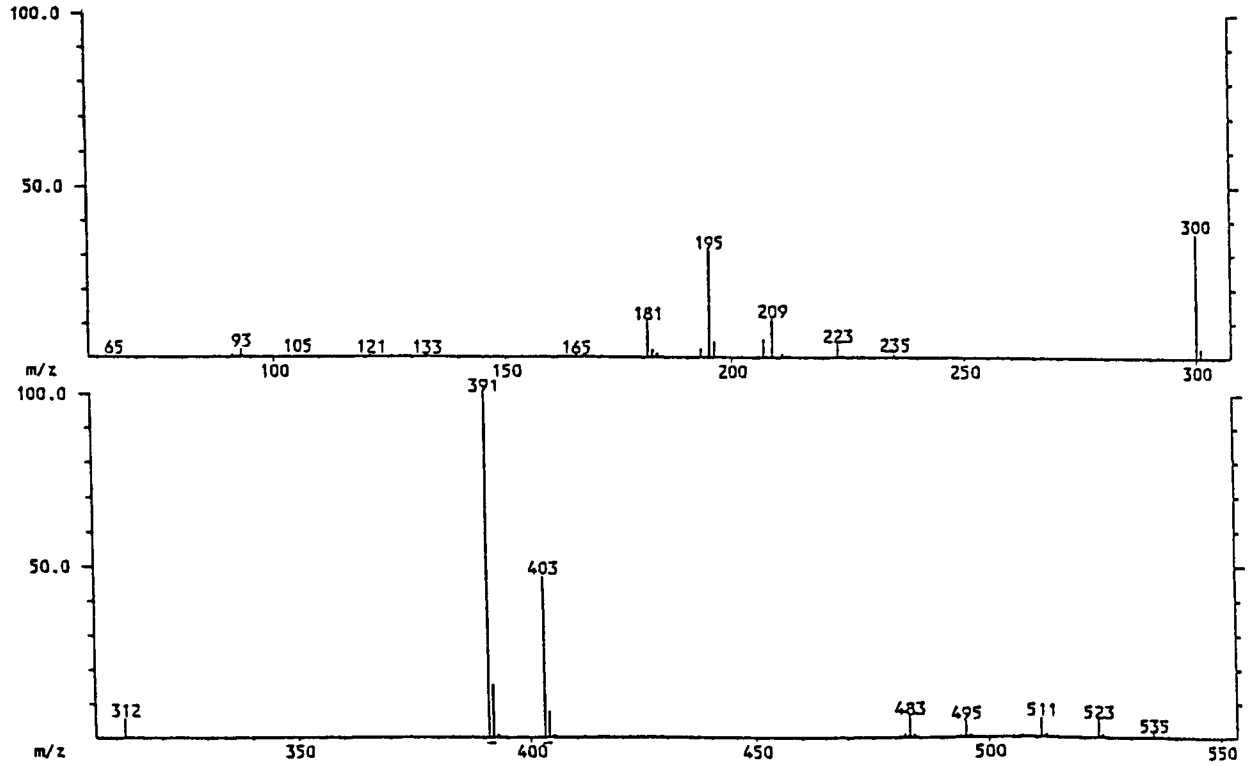


Figure 3 Chemical ionization mass spectrum of *p*-styryldi(*p*-tolyl)bismuth ($m/e = 494$; carrier gas, methane)

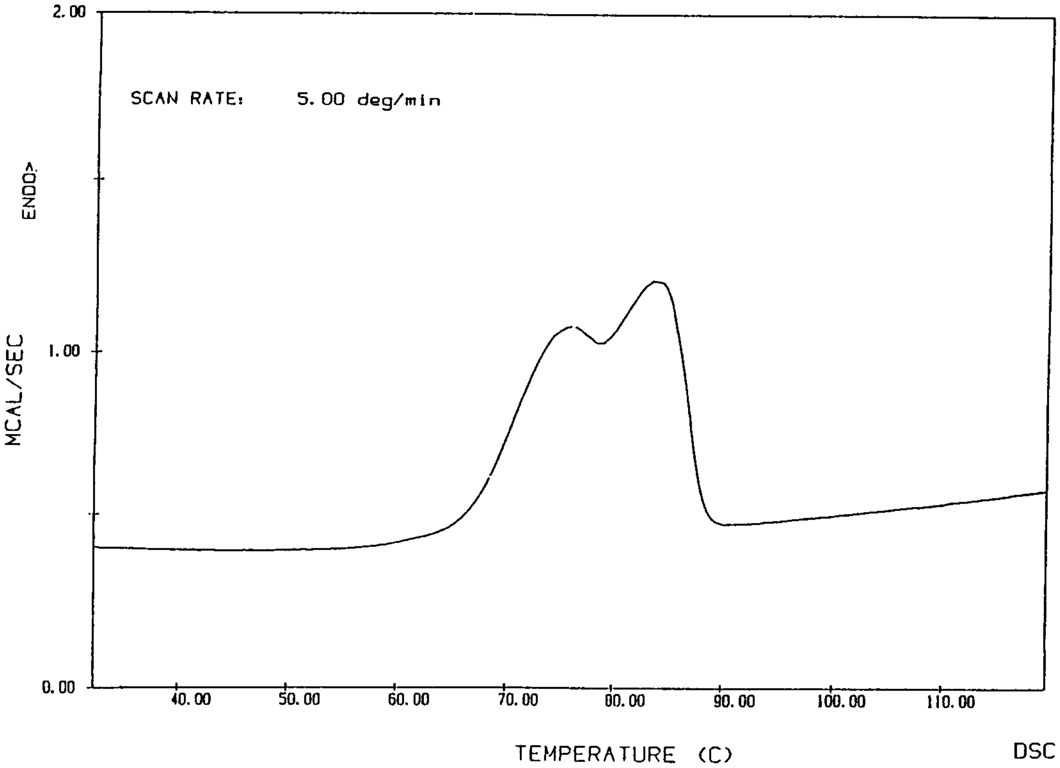


Figure 4 D.s.c. tracing of *p*-styryldi(*p*-tolyl)bismuth (heating rate, 5°C min^{-1})

the structure of compound **III**. Interestingly, the differential scanning calorimetry (d.s.c.) scan of *p*-styryldi(*p*-tolyl)bismuth showed two melting (T_m) peaks at around 79 and 83°C (*Figure 4*). Tris(*p*-tolyl)bismuth, which was present as a trace impurity, has a T_m of 120°C. The two peaks may arise from a liquid crystalline compound-like phase transition behaviour before the final transition into the isotropic phase at 83°C. Two different crystal forms are also a possibility.

The reason why a much purer product was obtained when the two phenyl groups in monomer **I** were replaced by two tolyl groups is not immediately clear. Unsym-

Table 2 Glass transition temperatures of copolymers of MMA and St with monomer **III**

Polymer	Monomer **III** content[a] (wt%)	T_g(°C)
Poly(MMA-*co*-III)	0	105
	4	104
	10	103
	12.5	102
	21	100
	24.5	99
Poly(St-*co*-III)	0	100
	5	99
	11	98
	15	97
	20	96
	24	95

[a] Determined from the n.m.r. spectra of the copolymers

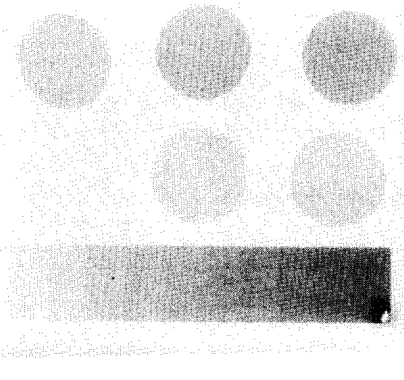


Figure 5 Positive radiographs of transparent 2 mm thick discs of poly(MMA-*co*-III). Monomer **III** content (wt%), from left to right, bottom, then top: 0, 3.3, 6.7, 13.3, 20.0 and 26.7

metrical triarylbismuthines are prone to redistribution reactions[15] and convert in part to the more stable symmetrical triaryl compounds. It could be argued that adding a methyl group at the *p*-position of the two phenyl moieties makes **III** a more symmetrical triarylbismuthine than monomer **I**. It is interesting to note that the less symmetrical α-methylstyryldi(*p*-tolyl)bismuth compound **IV** is again an oily product with an h.p.l.c. tracing that resembles that of compounds **I** and **II**. Preliminary h.p.l.c. data on *p*-styryldi(*p*-anisyl)bismuth again show four products but the monostyryl compound in the mixture amounts to about 85%.

Polymerization

Polymerization of 10 wt% solutions of **III** in benzene or toluene with BPO or AIBN as initiator proceeded smoothly when carried out at 70°C over 24 to 48 h; 70–93% polymer was recovered after precipitation from methanol. From a total of six experiments with 0.5 wt% initiator, the number-average molecular weight of the polymers as determined by g.p.c. was found to be $M_n = (4.9 \pm 0.3) \times 10^4$. There was no evidence of a bimodal distribution as seen earlier in the g.p.c. of poly(styryldiphenylbismuth)[13]. A small amount of tris(*p*-tolyl)bismuth was recovered on evaporating the methanol from which the polymer was precipitated. No gel formation occurred during polymerization, and the precipitated polymer, after drying, was completely soluble in THF or $CDCl_3$. Its ^1H n.m.r. spectrum did not reveal any residual vinyl protons from pendant vinyl moieties. The latter should have been present if a significant quantity of the distyryl derivative was present in **III**. They were found in the n.m.r. spectrum of the homopolymer of **I**[13]. Anionic polymerizations of **III** carried out in THF at −80°C with cumyl potassium or with the dipotassium salt of the α-methylstyrene dianion also resulted in soluble polymers. A more detailed account of the anionic polymerization of **III**, which produces a narrow molecular weight homopolymer, will be published later. Radical copolymerization of **III** with methyl methacrylate yielded THF-soluble copolymers having molecular weights (g.p.c.) in the range of 30 000 to 45 000.

An attempt was made to blend the homopolymer of **III** with polystyrene (PSt) and poly(methyl methacrylate) (PMMA). The polymers were dissolved in a common solvent (THF or toluene), and the solvent evaporated. The homopolymer of **III** did not blend with PSt but a nearly homogeneous material was obtained with PMMA with $\leqslant 25$ wt% poly(**III**).

The glass transition temperature (T_g) of poly(**III**) was difficult to observe from the d.s.c. tracings. A similar observation was reported for poly(styryldiphenylbismuth)[13]. The first scan of several samples showed a T_g near 80°C, but the second and third scans failed to repeat that result. The plasticizing effect of Ph_3Bi when added to polymers such as PMMA[9] is diminished when this bismuth moiety is anchored to the polymer backbone using monomers like **I** and **II**[13]. Similar results were observed for copolymers of **III** with MMA (*Table 2*). Assuming that the T_g of the copolymers is given by the expression $T_g = T_{g1}W_1 + T_{g2}W_2$ (W_1 and W_2 being the weight fractions of the two monomers in the copolymer), it can be calculated from the data of *Table 2* that the T_g of homopolymer **III** should be close to 80°C.

Radiopacities

Bulk copolymerization of MMA with **III** at 65°C in the presence of 2.5 wt% AIBN produced solid materials which were transparent up to 25 wt% of **III**. The same material could be obtained at room temperature using BPO as initiator and *N,N'*-dimethyl-*p*-toluidine as accelerator. Positive radiographs of 2 mm discs of these copolymers with increasing content of **III** are shown in *Figure 5*. By comparison with an aluminium step wedge, their radiopacity can be determined in terms of mm aluminium per mm resin. The various data are given in *Table 3*.

It was shown earlier[4,7,9,11,13] that the radiopacity, *R*, of a homogeneous blend of a polymer and radiopacifier is proportional to the molar concentration, M_a, of the additive:

$$R = R_0 + (R_a - R_0)\bar{V}_a M_a \qquad (1)$$

where R_0 is the radiopacity of the additive-free polymer while R_a and $\bar{V}_a$ are the radiopacity and molar volume of the pure radiopacifier. The linear correlation between *R* and M_a holds for PMMA blends with $BiCl_3$ and $BiBr_3$ (ref. 4), as well as for blends of several types of polymer with triphenylbismuth[7,9,11] and for copolymers of styryldiphenylbismuth with MMA or styrene[13]. It apparently also holds for copolymers of MMA and *p*-styryldi(*p*-

Table 3 Correlation between radiopacity and bismuth monomer (**III**) content in copolymers

Copolymer	Polymerization conditions	Monomer **III** content[a] (wt%)	Radiopacity, *R* (mm Al/mm polymer)
Poly(**III**)-*co*-PMMA	65°C, bulk/N_2	0.0 (0.00)	0.14
	2.5 wt% AIBN	3.3 (0.08)	0.31
		6.7 (0.16)	0.42
		13.3 (0.31)	0.74
		16.7 (0.39)	0.95
		20.0 (0.47)	1.06
		26.7 (0.62)	1.36
Poly(**III**)-*co*-PMMA	25°C, bulk/N_2	0.0 (0.00)	0.13
	2.5 wt% BPO	3.2 (0.07)	0.29
	1.5 wt% amine	6.4 (0.15)	0.41
		9.7 (0.22)	0.55
		12.9 (0.30)	0.74
		16.1 (0.37)	0.88
		19.4 (0.45)	1.01
Poly(**III**)-*co*-PSt	65°C, bulk/N_2	0.0 (0.00)	0.14
	2.5 wt% AIBN	3.3 (0.07)	0.28
		6.7 (0.15)	0.46
		10.1 (0.22)	0.56
		13.4 (0.30)	0.68
		16.8 (0.37)	0.87
		20.1 (0.45)	1.01
		23.5 (0.52)	1.15

[a] Values in parentheses are mol l^{-1}

tolyl)bismuth as shown in *Figure 6*, and for the same bismuth monomer with styrene. From the data it can be calculated* that 18.7 wt% (0.44 M) of monomer **III** must be copolymerized with MMA to obtain a material that in its radiopacity is equivalent to aluminium. For triphenylbismuth[11] this amount is 16.2 wt% or 0.44 M. Because of the slightly higher molecular weight of **III** compared with Ph_3Bi, a greater wt% of **III** for attaining aluminium equivalency is to be expected. The radiopacity results for the copolymer of MMA and **III** made with the amine accelerator, or for poly(St-*co*-**III**), were nearly identical to those of poly(MMA-*co*-**III**) synthesized with AIBN at 65°C.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of this project by the Department of Health and Human Services through the National Institute of Dental Research, Grant No. 5R01DEO617909, and of the Polymers Program of the National Science Foundation, Grant No. DMR8722245.

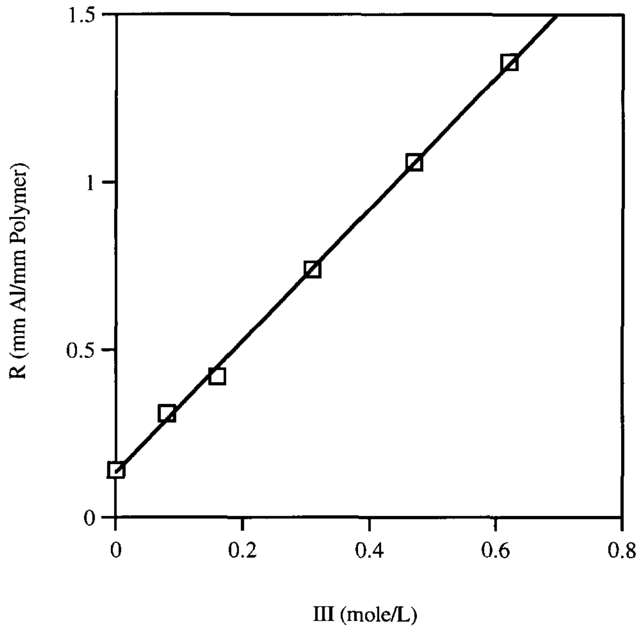


Figure 6 Plot of radiopacity (in mm aluminium per mm polymer) *versus* molar concentration of *p*-styryldi(*p*-tolyl)bismuth in poly(MMA-*co*-III)

REFERENCES

1 Brauer, G. M. *J. Am. Dent. Assoc.* 1981, **101**, 347
2 Chandler, H. H., Bowen, R. L. and Paffenbarger, G. C. *J. Biomed. Mater. Res.* 1971, **5**, 253, 335, 359
3 Adelman, H. C. *J. Forensic Sci.* 1988, **33**, 389

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* Until recently we used an aluminium step wedge that, on re-inspection, was found to contain heavy metal impurities. The step wedge used in our present work is a high grade aluminium with a radiopacity that is about 15% less than the earlier step wedge. As a result, our previously reported radiopacities of polymer blends are too low. We have recently taken our original radiopacity data for various polymer/radiopacifier blends and replotted them using corrected radiopacities. Some systems such as PMMA/Ph_3Bi were remeasured. These data are given in ref. 11

4 Delaviz, Y., Cabasso, I. and Smid, J. *Polymer* 1990, **31**, 2083

5 Cabasso, I., Smid, J. and Sahni, S. K. *J. Appl. Polym. Sci.* 1990, **41**, 3025

6 Rawls, H. R., Starr, J., Kasten, F. H., Murray, M., Smid, J. and Cabasso, I. *Dent. Mater.* 1990, **6**, 250

7 Cabasso, I. and Smid, J. *Bull. Bismuth Inst.* 1990, **60**, 1

8 Sahni, S. K., Smid, J. and Cabasso, I. *J. Appl. Polym. Sci.* 1989, **38**, 1653

9 Delaviz, Y., Zhang, Z. X., Cabasso, I. and Smid, J. *J. Appl. Polym. Sci.* 1990, **40**, 835

10 Ignatious, F., Delaviz, Y., Cabasso, I. and Smid, J. in 'Integration in Polymer Science and Technology' (Eds L. J. Kleintjens and P. J. Lemstra), Elsevier Applied Science, London, 1991, Vol. V, p. 400

11 Chatterjee, G., Cabasso, J. and Smid, J. *J. Appl. Polym. Sci.* 1995, **55**, 851

12 Smid, J., Delaviz, Y. and Smid, J. *U.S. Patent 5 246 334*, 26 October 1993

13 Ignatious, F., Sein, A., Delaviz, Y., Cabasso, I. and Smid, J. *Polymer* 1992, **33**, 1724

14 Ignatious, F., Delaviz, I., Cabasso, I. and Smid, J. *Makromol. Chem., Macromol. Symp.* 1992, **60**, 247

15 Barton, D. H. R., Bhatnagar, N. Y., Finet, J. P. and Motherwell, W. B. *Tetrahedron* 1986, **42**, 3111

16 Harrison, P. G. *Organomet. Chem. Rev. A.* 1970, **5**, 182

17 Gilman, H. and Yablunky, H. L. *J. Am. Chem. Soc.* 1941, **63**, 207

18 Conlon, D. A., Crivello, J. V., Lee, J. L. and O'Brien, M. J. *Macromolecules* 1989, **22**, 509

19 M&T Chemicals, Inc. *Neth. Pat. Appl. 6405309*, 1964; *Chem. Abstr.* 1965, **62**, 16300

20 Braun, B., Diamon, H. and Becker, G. *Makromol. Chem.* 1963, **62**, 183