Applied Organometallic Chemistry (1987) 1 311–317
© Longman Group UK Ltd 1987

0268–2605/87/01403311/$03.50

Studies of the degradation of organotin stabilizers in poly(vinyl chloride) during gamma irradiation

David W Allen*, John S Brooks†, John Unwin* and John D McGuinness‡
Departments of *Chemistry and †Applied Physics, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, UK and ‡Food Science Division, Ministry of Agriculture, Fisheries and Food, Great Westminster House, London SW1P 2AE, UK

Received 23 January 1987 Accepted 9 April 1987

Organotin stabilizers of the type Bu_2SnX_2 ($X = SCH_2CO_2C_8H_{17}$ or $O_2CCH{=}CHCO_2C_8H_{17}$) present in poly(vinyl chloride) (PVC) and subjected to varying doses of gamma irradiation in the range 1–200 kGy (0.1–20 Mrad) are shown to suffer degradation with dealkylation to form monobutyltin trichloride and tin(IV) chloride, which have been characterized by a subsequent alkylation procedure followed by gas chromatographic analysis. The extent of degradation of the stabilizers on prolonged gamma irradiation is much more severe than during thermal degradation leading to comparable blackening of the polymer.

Keywords: organotin stabilizers, dibutyltin, PVC, polymers, gamma irradiation, degradation, dealkylation

INTRODUCTION

There is considerable current interest in the possible use of ionizing radiation as a means of food preservation. Irradiation can be used to kill or reduce the numbers of pathogenic or spoilage organisms in food and to control infestation in stored products. In its recent report, the UK Advisory Committee on Irradiated and Novel Foods[1] has advised that the irradiation of food up to an overall dose of 10 kGy presents no toxicological hazard and introduces no special nutritional or microbiological problems. The UK Government is currently considering this report and comments from the public that have been made on it.

Whereas many types of irradiated food have been studied in depth,[2] there is much less information on the effects of irradiation on the many additives present in plastics used for food packaging, although it has been established that changes do occur in the migration behaviour of such additives.[3] Poly(vinyl chloride) (PVC), stabilized by organotin compounds, is widely used in the food packaging industry. Following earlier studies of the fate of organotin stabilizers present in PVC on subsequent thermal[4,5] or photochemical (artificial sunlight) degradation[6] of the polymer, using ^{119m}Sn Mössbauer spectroscopy, we have recently carried out a similar study of the fate of such stabilizers when the polymer is subjected in air to varying degrees of gamma irradiation in the range 0–200 kGy (0–20 Mrad).[7] It was shown that organotin stabilizers, e.g., dibutyltin bis(iso-octylthioglycollate) [$Bu_2Sn(IOTG)_2$] and dibutyltin bis(iso-octylmaleate) [$Bu_2Sn(IOM)_2$] undergo fairly rapid degradation with cleavage of tin–sulphur or tin–oxygen linkages and also with progressive dealkylation to form tin(IV) chloride as the ultimate degradation product. From the Mössbauer results, the extent of conversion to tin(IV) chloride appears to increase significantly after a dose of only 25 kGy (2.5 Mrad), at which point the polymer has begun to discolour markedly. Owing to the relative insensitivity of the Mössbauer technique at the low concentrations of the various possible tin-containing compounds present in the degrading polymer, we have sought additional chemical and spectroscopic evidence for the course of degradation during irradiation, and have made a comparison of the extent of degradation of the stabilizers during irradiation with that observed during extended thermal degradation. A preliminary report of some of this work has appeared.[8]

RESULTS AND DISCUSSION

In the light of the earlier Mössbauer study,[7] and other work,[9] it is reasonable to assume that the following progressive degradation sequence is involved during irradiation of the polymer:

$$R_2SnY_2 \xrightarrow[HCl]{\gamma} R_2SnClY \xrightarrow[HCl]{\gamma}$$

$$R_2SnCl_2 \xrightarrow[HCl]{\gamma} RSnCl_3 \xrightarrow[HCl]{\gamma} SnCl_4$$

$$(R = \text{butyl or octyl; } Y = SCH_2CO_2C_8H_{17}$$

or

$$O_2C.CH{=}CH.CO_2C_8H_{17}).$$

Consistent with this scheme, both dioctyltin dichloride and octyltin trichloride have been detected by mass spectrometry as degradation products arising from dioctyltin (bisiso-octylthioglycollate) present in PVC subjected to an irradiation of 100 kGy.[9]

In the case of the thioglycollate stabilizer, the formation of the monochloroester, $R_2SnCl(SCH_2CO_2C_8H_{17})$, in the early stages of irradiation is revealed by infrared spectroscopy, following earlier work by Bellenger et al.[10] and Cooray[11] on thermally degraded organotin-stabilized PVC. Whereas the parent stabilizer exhibits a carbonyl stretching band at 1720 cm^{-1}, the monochloroester gives rise to an absorption band at 1670 cm^{-1} due to intramolecular coordination of the carbonyl group to tin. After an irradiation dose of 1 kGy (0.1 Mrad), the 1670 cm^{-1} absorption is observed as a shoulder on the main carbonyl band at 1720 cm^{-1}, but intensifies steadily as irradiation proceeds until after a dose of 5 kGy (0.5 Mrad) it is observed as a well-resolved absorption band. This band is still present (though at reduced intensity) in samples which have received extended irradiation of 100 kGy (10 Mrad). However, after irradiation to 200 kGy (20 Mrad), carbonyl absorption due to the monochloroester is absent from the infrared spectrum, consistent with degradation of the stabilizers to form other chlorotin compounds, notably tin(IV) chloride.

For the chemical analysis of a potential mixture of dialkyltin compounds (unchanged stabilizer, monochloroester and dialkyltin dichloride), together with alkyltin trichloride and tin(IV) chloride, the procedure adopted initially was to subject the irradiated polymer to prolonged Soxhlet extraction using diethyl ether,[12] and then to treat the resulting extract with an excess of n-propylmagnesium chloride, thereby converting the above compounds into a mixture of dialkyldipropyl-, alkyltripropyl- and tetrapropyl-stannanes, which could be analysed by gas chromatography. This technique, however, will not differentiate between the various dialkyltin compounds, since all are converted to the related dialkyldipropylstannane. A reliable estimate of the relative amounts of the individual dialkyltin compounds will, in any event, be difficult to obtain due to ligand exchange reactions between, for example, the dialkyltin dithiolate stabilizers and the related dialkyltin dichloride, which occur rapidly in solution at room temperature.[13,14] Similar exchange reactions have also been postulated between alkyltin trichlorides and the dialkyltin dithiolate stabilizers in solution,[13,15,16] and hence various alkyl(chloro)tin thiolates, e.g. $RSnCl_{3-n}(SCH_2CO_2C_8H_{17})_n$, could also possibly occur within the polymer.[1] During the above extraction and derivatization procedure, these will be converted to the related alkyltripropylstannane.

Application of this procedure to a sample of PVC, originally stabilized with dibutyltin bis(iso-octylthioglycollate) (1.2% w/w), which had been subjected to an irradiation dose of 100 kGy (10 Mrad) revealed the presence of the mixture of stannanes derived from residual dibutyltin species, butyltin trichloride, and tin(IV) chloride, in keeping with the above degradation scheme. However, the relative proportion of tin(IV) chloride in the sample (ca. 15%) was much smaller than that suggested by the earlier Mössbauer study.[7] The Mössbauer spectrum of this sample indicated the presence of only one major component, which corresponded to tin(IV) chloride, traces of dibutyltin or monobutyltin species not being observable. In view of the major discrepancy between these results, two samples of PVC containing equal amounts of dibutyltin dichloride, butyltin trichloride and tin(IV) chloride (1.2% w/w in each case) were prepared by solvent casting from dichloromethane under nitrogen. The resulting polymer films were then subjected to Soxhlet extraction with diethyl ether, and the extracts treated with an excess of propylmagnesium chloride. Chromatographic analysis of the derivatized extracts (Table 1) indicated that tin(IV) chloride is not extracted as efficiently

Table 1 Chromatographic analysis of PVC samples (solvent-cast from dichloromethane) containing a mixture of dibutyltin dichloride, butyltin trichloride and tin(IV) chloride (at 1.2% w/w for each compound) after Soxhlet extraction with diethyl ether

	Relative proportion of tin compound extracted		
Sample	Bu_2SnCl_2	$BuSnCl_3$	$SnCl_4$
1	1.00	1.02	0.40
2	1.00	1.04	0.53

Table 2 Chromatographic analysis of irradiated PVC samples containing dibutyltin bis(iso-octylthioglycollate) [$Bu_2Sn(IOTG)_2$]

	Relative proportion of degradation products[a] (%)		
Exposure (kGy)	Bu_2SnX_2	$BuSnX_3$	$SnCl_4$
(a) Milled sheet [1.2% w/w $Bu_2Sn(IOTG)_2$]			
0	92	6	2
5	87	10	3
10	88	7	5
15	75	15	10
20	72	17	11
25	70	16	14
50	52	14	34
100	35	18	47
200	15	17	68
(b) Solvent-cast film [1.2% w/w $Bu_2Sn(IOTG)_2$]			
0	100	<1	<1
10	86	10	4
50	59	25	16
100	31	29	40
200	36	17	47
(c) Milled sheet [4% w/w $Bu_2Sn(IOTG)_2$]			
0	99	1	<1
10	86	9	5
50	70	18	12
100	57	25	18
200	35	18	47

[a] $X=SCH_2CO_2C_8H_{17}$ or Cl.

as the organotin chlorides. This may be due to the formation within the polymer of ether-insoluble ionic complexes, e.g. H_2SnCl_6, and/or the relatively low solubility of the tin(IV) chloride dietherate complex.[17] Consequently, in order to overcome this problem, it was decided that, before derivatization, the degradation products of the tin stabilizers should be liberated from the PVC by total dissolution of the polymer in tetrahydrofuran, an approach developed by Rocket et al.[18] in studies of the hydrogen chloride-induced degradation of organotin stabilizers.

This modified procedure was then applied to samples of progressively irradiated PVC which originally contained $Bu_2Sn(IOTG)_2$ and $Bu_2Sn(IOM)_2$, respectively, the stabilizers having been initially incorporated into the polymer at various concentrations either by conventional hot-milling or solvent-casting from dichloromethane or tetrahydrofuran.

From the results of the chromatographic analysis of samples derived from PVC stabilized with $Bu_2Sn(IOTG)_2$ (Table 2), it is clear that the fate of the organotin compound is very much dependent both on the processing history of the sample and the original level of stabilizer incorporated into the polymer. The results for the milled sheet originally containing the stabilizer at 1.2% w/w show that, prior to irradiation, the polymer already contains a mixture of organotin compounds resulting from the thermomechanical degradation which occurs in the hot-milling process, and some conversion to monobutyltin species (ca. 6%) and tin(IV) chloride (2%) is observed. The results for the related solvent-cast film reveal a much smaller degree of initial degradation of the stabilizers, as would be expected. Progressive irradiation of the milled sheet reveals a steady increase in the proportion of tin(IV) chloride present, the proportion of monobutyltin species reaching a steady state at ca. 17% of the total, even up to an exposure of 200 kGy (see Fig. 1). For the solvent cast film, it is clear that the extent of degradation on irradiation is generally smaller than for the milled material, indicating the importance in the latter of the formation of mechanochemically-induced initiation sites from which subsequent degradation proceeds. A similar reduction in the degree of degradation of the stabilizer is also observed on increasing its initial level to 4% w/w. Consistent with this, a greater stabilization effect is conferred on the polymer, since after an exposure of 100 kGy the sample remains transparent, whereas the related 1.2% w/w milled sample has blackened at the same stage of irradiation.

The results for the related maleate stabilizer, $Bu_2Sn(IOM)_2$ (Table 3) are similar. Some initial degradation of the stabilizer is again observed as a result of the hot-milling process. Similarly, on

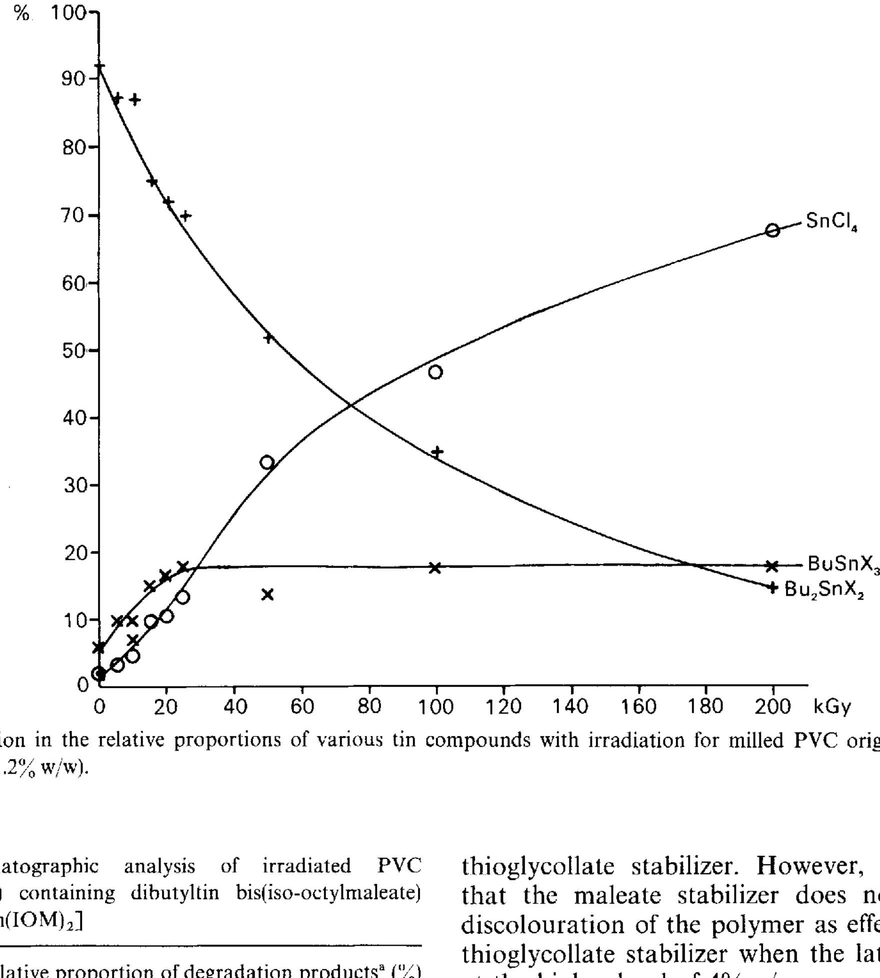

Figure 1 Variation in the relative proportions of various tin compounds with irradiation for milled PVC originally containing $Bu_2Sn(IOTG)_2$ (1.2% w/w).

Table 3 Chromatographic analysis of irradiated PVC samples (milled) containing dibutyltin bis(iso-octylmaleate) (2% w/w) [$Bu_2Sn(IOM)_2$]

Exposure (kGy)	Relative proportion of degradation products[a] (%)		
	Bu_2SnX_2	$BuSnX_3$	$SnCl_4$
0	97	3	<1
5	91	5	4
10	90	7	3
15	92	4	4
20	92	4	4
25	89	6	5
50	68	16	16
100	59	22	19
200	41	17	42

[a] $X = O_2CCH{=}CHCO_2C_8H_{17}$ or Cl.

progressive irradiation, the proportion of tin(IV) chloride increases, the proportion of monobutyltin species again appearing to reach a plateau (see Fig. 2). In general, the extent of degradation of the maleate stabilizer as irradiation progresses is smaller than that of the thioglycollate stabilizer. However, it was noted that the maleate stabilizer does not retard the discolouration of the polymer as effectively as the thioglycollate stabilizer when the latter is present at the higher level of 4% w/w.

It is significant that the above chromatographic studies of irradiated PVC containing $Bu_2Sn(IOTG)_2$ and $Bu_2Sn(IOM)_2$, respectively, indicate significantly less conversion of the stabilizers to tin(IV) chloride than was originally estimated from the Mössbauer spectra of these samples.[7] Thus, for example, whereas the Mössbauer spectrum of a milled sample of PVC originally containing $Bu_2Sn(IOTG)_2$ (1.2% w/w) which had received a dose of 100 kGy, indicated that complete conversion to tin(IV) chloride had occurred, chromatographic analysis reveals that the sample contains significantly less tin(IV) chloride (ca. 47%), together with appreciable quantities of residual dibutyltin species (35%), and monobutyltin species (18%). Since earlier problems of extraction of tin(IV) chloride have been overcome in the modified chromatographic procedure, it would seem, therefore, that the ability of the Mössbauer tech-

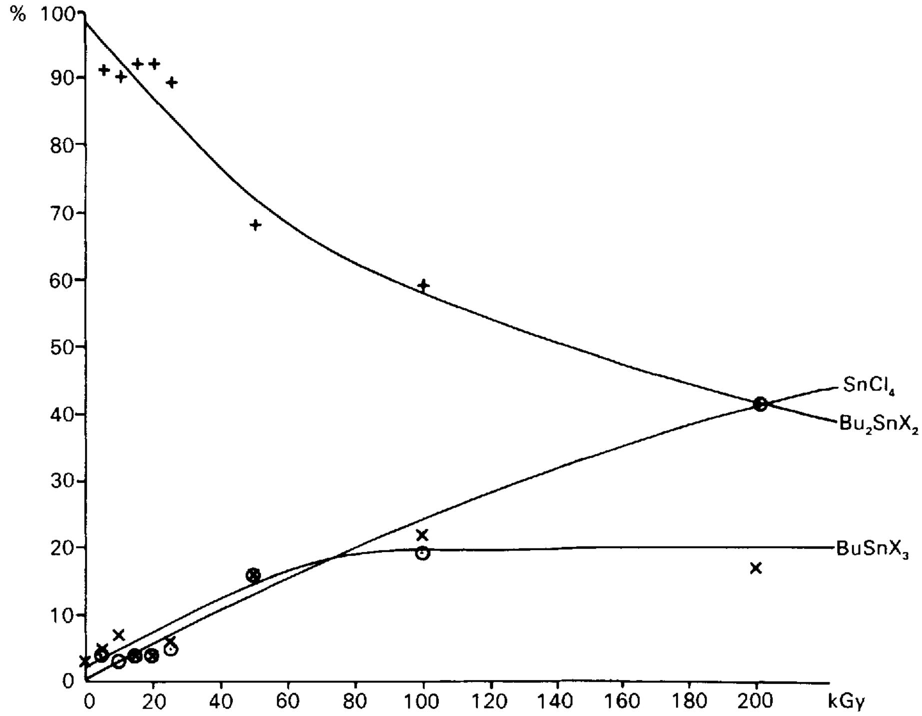

Figure 2 Variation in the relative proportions of various tin compounds with irradiation for milled PVC originally containing $Bu_2Sn(IOM)_2$ (2% w/w).

nique to detect tin(IV) chloride in the polymer matrix is significantly greater than that for the precursor organotin compounds. This implies that tin(IV) chloride (or its complexes) within the polymer matrix may have an enhanced recoil-free fraction compared with those of dibutyl and monobutyl tin compounds. We have recently explored this aspect in detail,[19] and find that the recoil-free fraction of tin(IV) chloride is approximately three times that of dibutyltin dichloride when present in PVC at comparable concentrations. Since the Mössbauer spectrum of tin(IV) chloride in PVC appears as a broad absorption with an isomer shift of ca. 0.3–0.4 mm s^{-1} (relative to $BaSnO_3$), whereas dibutyl and monobutyl tin compounds give rise to quadrupole-split spectra having low-velocity components which overlap with the tin(IV) chloride absorption, the resulting relative insensitivity of the technique for the detection of minor amounts (< 5%) of the organotin compounds is compounded by the significant difference in recoil-free fractions.

Application of the above chromatographic procedure to similar milled samples of PVC, which had been subjected to prolonged thermal degradation so as to cause the material to blacken, indicated that the extent of degradation of the organotin stabilizer under these conditions is much less severe than that observed on prolonged gamma irradiation (e.g. 100 kGy) which also results in blackening of the sample (Table 4).

Table 4 Chromatographic analyses of thermally degraded PVC containing dibutyltin bis(iso-octylthioglycollate) $[Bu_2Sn(IOTG)_2]$ and dibutyltin bis(iso-octylmaleate) $[Bu_2Sn(IOM)_2]$, thermally degraded for 120 min at 180°C

Sample	Relative proportion of tin compound[a] (%)		
	Bu_2SnX_2	$BuSnX_3$	$SnCl_4$
4% (w/w) $Bu_2Sn(IOTG)_2$ (milled)	94	6	<1
4% (w/w) $Bu_2Sn(IOTG)_2$ (solvent-cast)	93	7	<1
4% (w/w) $Bu_2Sn(IOM)_2$ (milled)	92	6	2

[a] $X = SCH_2CO_2C_8H_{17}$ or $O_2CCH{=}CHCO_2C_8H_{17}$ or Cl.

Thus, whereas analysis of a thermally-degraded milled sample of PVC, stabilized originally with $Bu_2Sn(IOTG)_2$ (4% w/w), reveals that approximately 94% of the tin remains in the dibutyl state, that of the comparable 100 kGy irradiated material (Table 2) reveals a much greater degree of dealkylation. A similar situation applies to the maleate-stabilized systems. However, in the context of the possible application of gamma irradiation to organotin-stabilized PVC food-packaging materials, up to the likely maximum permitted dose of 10 kGy, it is reassuring to note that the extent of degradation of the stabilizer is not far advanced, and that there is comparatively little physical change in the appearance of the polymer. This finding is of some significance given the greater propensity of the degradation products of organotin stabilizers to migrate from the polymer into food than the original stabilizers themselves.[9, 20]

EXPERIMENTAL

The stabilizers were incorporated into the PVC, either by conventional hot-milling techniques or solvent-casting. Solvent casting was carried out by dissolving the PVC in the minimum amount of solvent (dichloromethane for PVC containing the thioglycollate stabilizer and tetrahydrofuran for PVC containing the maleate stabilizer) and allowing slow evaporation of the solvent under nitrogen.

The PVC samples containing the organotin stabilizers were irradiated in air by ^{60}Co gamma irradiation. The source consisted of ^{60}Co tubes mounted in a circular array at the bottom of a water pond 20 ft deep. The sample was loaded into watertight containers and lowered to the centre of the array, where it received a dose rate of $5\,kGy\,h^{-1}$ at ambient temperature. Doses in the range 1–200 kGy were used during the course of this investigation.

Preparation of chromatographic standards

The appropriate organotin chloride or tin(IV) chloride (2 g) was dissolved in diethyl ether (25 ml) and treated with n-propylmagnesium chloride solution (25 ml), prepared from n-propyl chloride (39.3 g, 0.50 mol) and magnesium (12.2 g, 0.5 mol) in ether (250 ml). After 30 min at room temperature, the excess n-propylmagnesium chloride was decomposed by the addition of methanol. The filtered solution was reduced in volume and vacuum-distilled to obtain the pure stannane. The purity of the stannanes was ensured by chromatographic analysis.

Detection and analysis of organotin compounds and tin(IV) chloride in PVC

The PVC samples (2 g) were dissolved in tetrahydrofuran (50 ml) at room temperature. The solution was treated with n-propylmagnesium chloride solution (40 ml) and after 1 h the excess n-propylmagnesium chloride was decomposed by the addition of methanol. The polymer was precipitated by the further addition of methanol and the filtered solution was reduced in volume to 2 ml. The degradation products were separated by gas–liquid chromatography on a 10 ft glass column packed with 10% SE30 on Celite, using a Pye Series GCV Chromatograph at a temperature of 200°C.

Acknowledgements The authors are indebted to Dr M T J Mellor, Lankro Chemicals Ltd, for the supply of materials. This work was supported by funds provided by the UK Ministry of Agriculture, Fisheries and Food, to whom our thanks are also due. The results of this work are the property of the Ministry of Agriculture, Fisheries and Food and are Crown Copyright.

ENDNOTE

[1] These compounds also exhibit a carbonyl infrared absorption band at approximately $1670\,cm^{-1}$,[13] and therefore may also contribute to the infrared absorption of the irradiated polymers as discussed on p. 312.

REFERENCES

1. Advisory Committee on Irradiated and Novel Foods *Report on the Safety and Wholesomeness of Irradiated Foods*, HMSO, London, April 1986
2. See for example Josephson, E S, Thomas, M H and Calhoun, W K *J. Food Proc. Preserv.*, 1978, 2: 299
3. Figge, K and Freytag, W *Deutsche Lebensmittel-Rundschau*, 1977, 73: 205
4. Allen, D W, Brooks, J S, Clarkson, R W, Mellor, M T J and Williamson, A G *Chem. Ind. (London)*, 1979, 663
5. *Idem*, *J. Organomet. Chem.*, 1980, 199: 299
6. Brooks, J S, Clarkson, R W, Allen, D W, Mellor, M T J and Williamson, A G *Polym. Deg. Stab.*, 1982, 4: 359
7. Brooks, J S, Allen, D W and Unwin, J *ibid.*, 1985, 10: 79
8. Allen, D W, Brooks, J S, Unwin, J and McGuinness, J D *Chem. Ind. (London)*, 1985, 524
9. Haesen, G, Depaus, R, van Tilbeurgh, H, Le Goff, B and Lox, F *J. Ind. Irrad. Technol.*, 1983, 1: 259
10. Bellenger, V, Verdu, J, Carette, L B, Vymalalova, Z and Vymazal, Z *Polym. Deg. Stab.*, 1982, 4: 303

11. Cooray, B B *ibid.*, 1984, 7: 1

12. Krause, A and Lange, A. In: *Introduction to the Chemical Analysis of Plastics*, Haslam, J (ed), Iliffe Books, London, 1965, p 163

13. Blunden, S J, Hobbs, L A, Smith, P J, Davies, A G and Beng Teo, S *J. Organomet. Chem.*, 1985, 282: 9

14. Parker, R G and Carman, C J *Am. Chem. Soc., Adv. Chem. Series*, 1978, 169: 363

15. Bellenger, V, Verdu, J and Carette, L B *Polym. Deg. Stab.*, 1981, 3: 3

16. Burley, J W and Hutton, R E *Polym. Deg. Stab.*, 1981, 3: 285

17. Beattie, I R and Rule, L *J. Chem. Soc.*, 1964, 3267

18. Rocket, B W, Hadlington, M and Poyner, W R *J. Appl. Polym. Sci.*, 1974, 18: 745

19. Brooks, J S, Allen, D W and Unwin, J *Appl. Organomet. Chem.*, 1987, 1: 319

20. Figge, K and Zeeman, A *Kunststoffe*, 1973, 63: 543