The electron beam curing of dialkyltin diacrylates

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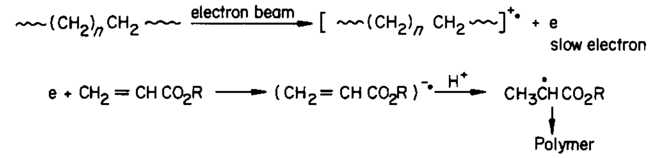
Dibutyltin diacrylate, di-2-methylpropyltin diacrylate and dioctyltin diacrylate cure to give tack-free films at much lower doses than the commonly used diluents hexanediol diacrylate, trimethylolpropane, triacrylate etc. Their reactivity is ascribed to their greater stopping power due to the presence of the tin atom and to the homolysis of the weak tin–carbon bond which leads to the production of initiating radicals. Film formation is also aided by the tin carboxylates being able to form an intermolecularly associated structure. The tin acrylates can be used in conjunction with prepolymers, e.g. an epoxidized soya bean oil (Synocure 3111) and a urethane acrylate (Synocure 3134). The tin acrylates are less effective than tripropyleneglycol diacrylate (TPGDA) in reducing the viscosity of the prepolymers. Electron beam curing of mixtures of the tin acrylates and prepolymers gave films possessing greater solvent resistance than those obtained from corresponding mixtures of TPGDA and the prepolymers.

(Keywords: electron beam; curing; dialkyltin diacrylates)

INTRODUCTION

Acrylates, because of their low cost, ready availability, variety, reactivity and final performance of the films derived from them, are the most commonly used materials in electron beam formulations[1]. Unlike epoxides and vinyl ethers, acrylates do not require the addition of initiator to trigger the polymerization process. Both fundamental work[2,3] and a more practically orientated investigation[1] have shown that acrylates usually cure at relatively low doses and this has been ascribed[2,3] to the acrylates reacting readily with the slow electrons produced on ionization of the medium:



$$\sim\sim(CH_2)_n CH_2 \sim\sim \xrightarrow{\text{electron beam}} [\sim\sim(CH_2)_n CH_2 \sim\sim]^{+\bullet} + \underset{\text{slow electron}}{e}$$

$$e + CH_2{=}CH\,CO_2R \longrightarrow (CH_2{=}CH\,CO_2R)^{-\bullet} \xrightarrow{H^+} \underset{\substack{\downarrow \\ \text{Polymer}}}{CH_3\dot{C}H\,CO_2R}$$

Substituent groups in the acrylate play an important part in determining the reactivity of the acrylate. Aromatic groups possessing electron-withdrawing properties reduce the rate of cure by scavenging the slow electrons whilst readily ionizable groups, e.g. ethers and tertiary C–H bonds, promote reactivity.

Of fundamental importance to any electron beam curing system is the efficiency of interaction of the matrix with high energy electrons and the distribution of the radicals so produced.

$$R_i = \Phi_m I[M] \qquad (1)$$

Equation (1) shows that the rate of initiation of pure monomer is directly proportional to the efficiency of radical production in the monomer, $\Phi_m[M]$ and the dose rate I, for a given energy. The distribution of the radicals in the matrix is a function of the energy of the electron beam. Low linear energy transfer (LET) radiation (<500 keV) will result in the formation of isolated concentrations of radicals whilst high LET radiation (150–200 keV) will result in a high random concentration of radicals[4,5]. High LET radiation will be promoted by minimizing the energy of the electron beam as well as using materials of high stopping value.

We now describe the electron beam curing of some dialkyltin diacrylates and compare their performance with some standard commercial diluents [hexanediol diacrylate (HDDA), tripropyleneglycol diacrylate (TPGDA) and trimethylolpropane triacrylate (TMPTA)]. It was predicted that the tin compounds would readily cure on account of: the greater stopping power of these compounds (due to the presence of tin) as calculated using Bragg's additivity rule[6]; and the ease of homolysis of tin–carbon bonds[7] leading to the production of initiating radicals. In an earlier publication[8] we showed that dibutyltin diacrylate (D-BTDA) cures (as measured by the rate of double bond consumption) at a faster rate than TMPTA, HDDA and TPGDA. We now examine the reactivity of three dialkyltin diacrylates, D-BTDA, di-2-methylpropyltin diacrylate (D-MPTDA) and dioctyltin diacrylate (D-OTDA), by determining the minimum dose of radiation required to produce a tack-free film as well as by use of standard physical tests on the films produced, such as the solvent rub test, etc. The ability of these organotin diluents to control the viscosity of formulations was also investigated and the cure responses of these systems were measured in terms of the properties of the final films.

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EXPERIMENTAL

Instrumentation

All formulations were coated onto a moving web via a Dixon 164 coater unit.

Electron beam curing was carried out using an Otto Durr ESH 150/130 electron beam unit under a nitrogen blanket. The operating voltage was maintained at 150 kV and the beam current was adjusted for each applied dose.

I.r. spectra of prepared monomers were analysed using a Perkin Elmer i.r. spectrometer (model no. 599).

^{1}H n.m.r. spectra were obtained using a Jeol n.m.r. spectrometer (model no. JNM-MH-100) and referenced against tetramethylsilane.

All elemental analysis was carried out using a Carlo Erba Strumentazione elemental analyzer (model 1106).

Materials

Resins and diluents. TPGDA, TMPTA, HDDA, Synocure 3111, Synocure 3131 and Synocure 3134 were all obtained from Cray Valley Products Ltd and used as received.

Chemicals. Benzene (BDH Chemicals Ltd) was dried 24 h before use by addition of sodium wire.

Dibutyltin oxide (Schering AG), dioctyltin oxide (Schering AG), 1-iodo-2-methylpropane (Aldrich Chemicals Co.), acrylic acid (Aldrich Chemicals Co.), 2-ethoxyethanol (Aldrich Chemicals Co.), lithium bromide (BDH Chemicals Ltd) and tin (Aldrich Chemicals Co.) were all used as received.

Gateway natural tracing paper (Wiggins Teape Group Ltd) was used as a substrate for all coatings.

Synthesis

Di-2-methylpropyltin oxide[9]. Lithium bromide (1.08 g, 0.011 mol) was added to a mixture of 1-iodo-2-methyl propane (13.62 ml, 0.11 mol) and 2-ethoxyethanol (5.43 g, 0.056 mol). Granulated tin (5.93 g, 0.05 g atom) was then added and the mixture was heated under reflux for 3.5 h. The unreacted tin was removed by filtration and the filtrate stripped of excess 1-iodo-2-methylpropane. The residue was dissolved in ethanol (100 ml) and the solution was added to a stirred solution of caustic soda (25 g) in water (100 ml). The resulting precipitate of di-2-methylpropyltin oxide was collected by filtration, washed with ethanol and then with water and dried at 80°C to constant weight (13.1 g, 95%); m.p. 300°C.

Dibutyltin diacrylate. A mixture of dibutyltin oxide (24.9 g, 0.1 mol), acrylic acid (14.4 g, 0.2 mol) and two drops of concentrated sulphuric acid in dry benzene (500 ml) was refluxed until 1.8 ml of water (0.1 mol) had been removed azeotropically. The reaction mixture was dried with sodium sulphate and then filtered through kieselguhr (75 g). The solvent was removed under reduced pressure using a rotary evaporator. The clear colourless residue was D-BTDA (34.1 g, 91%).

I.r. (liquid film): 2961, 2930, 2875, 2865, 1730, 1649, 1638, 1590–1540, 1430–1405, 1383, 1365, 1262, 1184, 1047, 983, 962, 915, 880, 829 (out-of-plane bend $=CH_2$), 719, 700–670, 630 cm^{-1}.

^{1}H n.m.r. ($CDCl_3$): 0.7–1.8 (multiplet, 18H, C_4H_9–), 5.50–6.40 (multiplet, 6H, CH_2 and CH of acrylate).

Analysis for $C_{14}H_{24}O_4Sn$: calculated, C 44.83; H 6.45; found, C 44.97; H 6.45.

Di-2-methylpropyltin diacrylate. A mixture of di-2-methylpropyltin oxide (12.9 g, 0.05 mol), acrylic acid (7.2 g, 0.1 mol) and two drops of concentrated sulphuric acid in dry benzene (200 ml) was refluxed until 0.9 ml of water (0.05 mol) had been removed azeotropically. The reaction mixture was dried with sodium sulphate and then filtered through kieselguhr (75 g). The solvent was removed under reduced pressure using a rotary evaporator. The clear colourless residue was D-MPTDA (16 g, 90%).

I.r. (liquid film): 2960, 2935, 2875, 1732, 1650, 1640, 1545–1580, 1415, 1365, 1339, 1262, 1185, 1079, 1049, 985, 965, 918, 880, 829, 700, 682, 630 cm^{-1}.

^{1}H n.m.r. ($CDCl_3$): 0.9–1.6 (multiplet, 18H, C_4H_9–), 5.7–6.5 (multiplet, 6H, CH and CH_2 of acrylate).

Analysis for $C_{14}H_{24}O_4Sn$: calculated, C 44.83; H 6.45; found, C 45.00; H 6.61.

Dioctyltin diacrylate. A mixture of dioctyltin oxide (18.1 g, 0.05 mol), acrylic acid (7.2 g, 0.1 mol) and two drops of concentrated sulphuric acid in dry benzene (200 ml) was refluxed until 0.9 ml of water (0.05 mol) had been removed azeotropically. The reaction mixture was dried with sodium sulphate, and then filtered through kieselguhr (75 g). The solvent was removed under reduced pressure using a rotary evaporator. The clear colourless residue was D-OTDA (21 g, 86%).

I.r. (liquid film): 2959, 2930, 2855, 1731, 1650, 1640, 1550–1590, 1415, 1362, 1337, 1261, 1183, 1049, 985, 965, 918, 829, 728, 699, 680, 625 cm^{-1}.

^{1}H n.m.r. ($CDCl_3$): 0.80–1.9 (multiplet, 34H, C_8H_{17}–) 5.7–6.5 (multiplet, 6H, CH and CH_2 of acrylate).

Analysis for $C_{22}H_{40}O_4Sn$: calculated, C 54.23; H 8.28; found, C 54.00; H 8.28.

Preparation of films of the acrylate esters

All formulations were coated onto aluminium foil via a Dixon 164 coater using a forward spinning smoothing roller at a setting of $\sim 221 \times 10^3$ Pa. The coatings were then passed under the electron beam. For all doses of radiation the moving web was maintained at 20 mm^{-1}.

Physical test methods

These were carried out on all films, with the exception of coatings derived from TMPTA, which produced pitted films due to reticulation. These tests are all subjective and results will vary for different coat weights of the material examined. It is therefore necessary to evaluate the film properties of coatings of similar coat weights. This was sometimes difficult to achieve due to differences in the flow properties of the materials investigated. These tests were carried out at least twice for films of similar coat weights in order that a fair comparison of film properties could be made. All coat weights were calculated from the weight of a coating over a 10×10 cm^2 surface area.

Solvent rub test. This method is based on the ASTM(D3363)27. A felt pad soaked in acetone was mechanically rubbed back and forth across the surface of the sample under test held flat under tension on a SATRA rub tester. The load on the felt pad was 0.5 kg and the pad was kept saturated with acetone. The number of 'double rubs' required before the acetone broke through the coating was recorded.

Pencil hardness. The pencil hardness of the film was assessed by drawing the coated substrate under the lead using a Rotring pencil with changeable 0.5 mm flat-ended leads. This was repeated using lead types of HB, H, 2H, 3H and 4H and the point at which the film was etched was recorded.

Brittleness. This test involved folding a coated substrate through 180° and assessing the amount of debris along the crease. An arbitrary scale from 1 (no debris, flexible) to 5 (large amount of debris, very brittle) was used to assess brittleness.

Acid/base rub test. The procedure for the measurement of acid/base rub resistance was carried out as described for the solvent rub test above, substituting the organic solvent for hydrochloric acid (1 M) and sodium hydroxide (1 M), respectively.

RESULTS

Synthesis. The dialkyltin diacrylates were readily prepared by reaction of the appropriate organotin oxide with acrylic acid[10].

$$R_2Sn{=}O + CH_2{=}CHCO_2H \longrightarrow R_2Sn(O\underset{\displaystyle O}{\underset{\|}{C}}CH{=}CH_2)_2 + H_2O$$

Comparison of the electron beam curing properties of the tin acrylates with conventional diluents and the performance of the films produced. The cure response of D-BTDA, D-MPTDA and D-OTDA, HDDA, TPGDA and TMPTA were initially evaluated by the process described in the previous section. The films so produced were subjected to a number of physical tests and the results are shown in *Tables 1–5*. Results are not shown for TMPTA due to this material producing pitted films. D-BTDA, D-MPTDA and D-OTDA produced tack-free films at 0.5 kGy whilst the three standard diluents all required a minimum dose of 2.5 kGy, indicating that the organotin compounds readily crosslink under electron beam radiation. The results of subjecting the films to several different physical tests confirm this deduction. It must, however, be emphasized that at best the physical tests only give an indication of relative performance since not all the films had the same coat weight (due to difficulties encountered with applying the materials to paper). It is very clear that the organotin acrylates produce hard, highly crosslinked films at low radiation doses, as shown by their superior solvent resistance and brittleness. The lower performance of D-OTDA compared with the other organotin diacrylates in the solvent rub test can be attributed to longer alkyl chains facilitating solubilization.

The results of the alkaline and acid rub tests for the films produced from D-BTDA (*Table 3*) shows that the polymer is readily hydrolysed. The films produced from D-OTDA (*Table 5*) showed a greater resistance to hydrolysis by acid and alkali and this is presumably due to the greater hydrophobicity of film due to the presence of the octyl groups.

Curing of mixtures of organotin dicarboxylates with prepolymers. The reactive monomers TPGDA and HDDA mix readily with the majority of prepolymers and reduce the viscosity of the prepolymers thereby aiding their application to a variety of substrates. The dialkyltin dicarboxylates were therefore evaluated as rheological control agents of radiation curable systems. From *Figure 1* it can be seen that the viscosity of these materials increases in the order:

$$\text{TPGDA} < \text{D-OTDA} < \text{D-BTDA}$$

The high viscosity of the dialkyltin acrylates suggests that the compounds exhibit molecular association and from i.r. spectroscopy it is concluded that this is due to the carbonyl groups interacting with the tin atom. Due to this association it was expected that the dialkyltin diacrylates would exhibit low solubility/compatibility and poor thinning action with viscous prepolymers and this was found to be the case. The study of the electron beam curing properties of dialkyltin diacrylates admixed with prepolymers was limited by the poor solvating power of these monomers. Sufficient solubility of D-OTDA in epoxidized soya bean oil (Synocure 3111) and in urethane acrylate (Synocure 3134) was attained and therefore these systems were studied in some detail.

The ability of D-OTDA compared with TPGDA to reduce the viscosity of the binder, epoxidized soya bean oil and the prepolymer, a urethane acrylate, containing 25% and 60% of the aforementioned diluents was evaluated. The results of these studies are shown in *Figures 2* and *3*. From the figures it can be seen that TPGDA is far more effective in reducing the viscosity of the prepolymers and binder than D-OTDA. The

Table 2 Physical test results for HDDA

Radiation dose (kGy)	Coat weight (g m^{-2})	Solvent rub	Pencil hardness	Brittleness
2.5	17.4	32.5	H	1
5	18.8	55	H	2
10	11.1	75	2H	2
20	20.0	500	2H	2/3
40	10.0	>500	2H	2/3
60	19.4	>500	>3H	3/4

Table 1 Physical test results for TPGDA

Radiation dose (kGy)	Coat weight (g m^{-2})	Solvent rub	Pencil hardness	Brittleness	Alkali rub	Acid rub
2.5	31.3	36	HB	1	>30	>30
5	30.7	74	2H	2	>30	>30
10	27.3	52	2H	2/3	>30	>30
20	25.7	175	>4H	2/3	>30	>30
40	24.5	437	>4H	2/3	>30	>30
60	31.4	>500	>4H	3/4	>30	>30

Table 3 Physical test results for D-BTDA

Radiation dose (kGy)	Coat weight ($g\,m^{-2}$)	Solvent rub	Pencil hardness[a]	Brittleness	Alkali rub	Acid rub
2.5	21.4	226	>2H	5	<1	<1
5	28.4	261	>2H	5	<1	<1
10	25.5	>500	>2H	5	<1	<1
20	29.2	>500	>3H	5	<1	<1
40	29.6	>500	>3H	5	<1	<1
60	26.3	>500	>3H	5	<1	<1

[a] Maximum value before film shattered

Table 4 Physical test results for D-MPTDA

Radiation dose (kGy)	Coat weight ($g\,m^{-2}$)	Solvent rub	Pencil hardness[a]	Brittleness
2.5	25.2	495	>H	5
5	30.6	>500	>2H	5
10	26.8	>500	>3H	5
20	19.3	>500	>2H	5
40	16.8	>500	>2H	5
60	27.6	>500	>3H	5

[a] Maximum value before film shattered

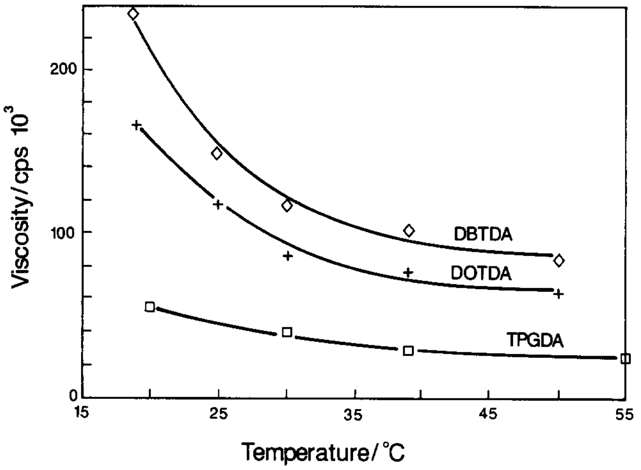


Figure 1 Viscosity *versus* temperature plots for TPGDA, D-BTDA and D-OTDA

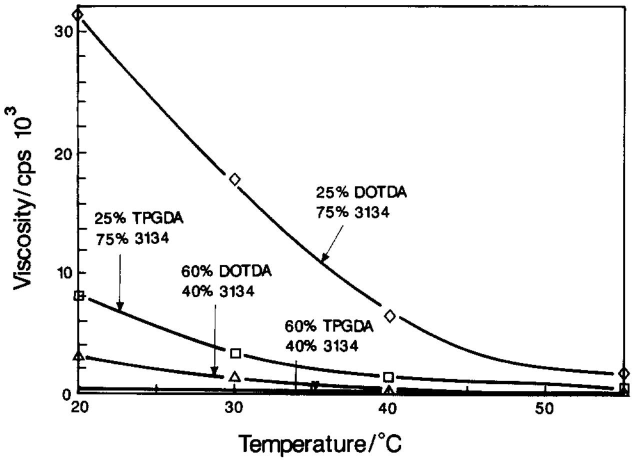


Figure 2 Viscosity *versus* temperature plots for formulations of D-OTDA in Synocure 3134 and TPGDA in Synocure 3134

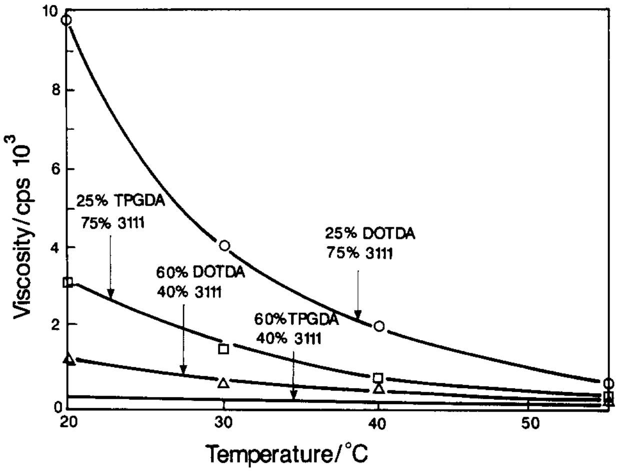


Figure 3 Viscosity *versus* temperature plots for formulations of D-OTDA in Synocure 3111 and TPGDA in Synocure 3111

formulations used in these tests and others made up with D-BTDA were subjected to electron beam curing and the films so obtained examined using a number of physical test methods. The results are shown in *Tables 6–13*. It was found that for all films where TPGDA had been substituted by the organotin acrylates, increased solvent resistance was observed. The replacement of TPGDA by dialkyltin diacrylates in the case of epoxidized soya bean oil formulations also led to an increase in the brittleness of films.

By using the organotin acrylates in conjunction with a binder or prepolymer, films were obtained which were resistant to both acid and alkali under our standard experimental conditions. This is attributed to the hydrophobic character of the cured films which is due to the contribution made by the prepolymer/binder.

DISCUSSION

The observed rapid cure of the organotin diacrylates may be attributed to the far greater stopping power of these compounds, compared with conventional diluents, as calculated using Bragg's additivity rule[6]. *Table 14* lists the stopping power of the relevant materials. Because the organotin acrylates have greater LET values than the common diluents they will produce, under electron beam radiation, a high random concentration of initiating radicals which will account for the more rapid cure based on double bond consumption. Another feature which will contribute to the reactivity of the organotin compounds is the greater lability of the carbon–tin bond ($193\,kJ\,mol^{-1}$)[7] compared with a normal carbon–

Table 5 Physical test results for D-OTDA

Radiation dose (kGy)	Coat weight (g m^{-2})	Solvent rub	Pencil hardness	Brittleness	Alkali rub	Acid rub
2.5	17.6	10	4H	5	6.5	10
5	12.3	12	>4H	3/4	5	10
10	20.4	280	>4H	3/4	5	21
20	46.7	>500	>4H	5	2	20
40	33.9	>500	>4H	4	9	30
60	30.5	>500	>4H	3/4	7	25

Table 6 Solvent rub test results for D-BTDA/Synocure 3134

	Formulation		
Radiation (kGy)	33% 3134 67% TPGDA	33% 3134 33% TPGDA 34% D-BTDA	33% 3134 67% D-BTDA
5	5 (39.9)	–	16.5 (39.5)
10	20 (39.7)	37 (26.9)	61 (24.0)
20	26 (43.4)	–	75 (24.3)

Coat weights (g m^{-2}) in parentheses

Table 10 Solvent rub test for D-BTDA in Synocure 3111

	Formulation		
Radiation dose (kGy)	33% 3111 67% TPGDA	33% 3111 33% TPGDA 34% D-BTDA	33% 3111 67% D-BTDA
5	2.5 (18.3)	15 (17.4)	23 (35.2)
10	8.5 (23.5)	24 (21.7)	88 (29.1)
20	12.5 (18.6)	62 (22.7)	>500 (34.7)

Coat weights (g m^{-2}) in parentheses

Table 7 Pencil hardness (PH) and brittleness test results for D-BTDA/Synocure 3134

	Formulation					
	33% 3134 67% TPGDA		33% 3134 33% TPGDA 34% D-BTDA		33% 3134 67% D-BTDA	
Radiation dose (kGy)	PH	Brittleness	PH	Brittleness	PH	Brittleness
5	>4H	1		–	>4H	1
10	>4H	1	>4H	1	>4H	2
20	>4H	1		–	>4H	1

Table 8 Solvent rub test results for D-OTDA/Synocure 3134

	Formulation		
Radiation dose (kGy)	33% 3134 67% TPGDA	33% 3134 33% TPGDA 34% D-OTDA	33% 3134 67% D-OTDA
5	5 (39.9)	9 (25.2)	12.5 (46.2)
10	20 (39.7)	9 (27.6)	30 (40.4)
20	26 (43.4)	27 (34.3)	–

Coat weights (g m^{-2}) in parentheses

carbon bond (356 kJ mol^{-1})[7]. The organotin compounds will probably undergo ionization more readily than the conventional diluents and in addition the ionized species will fragment readily to either give a carbon-centred radical and a positively charged tin species or a carbocation and an organotin radical.

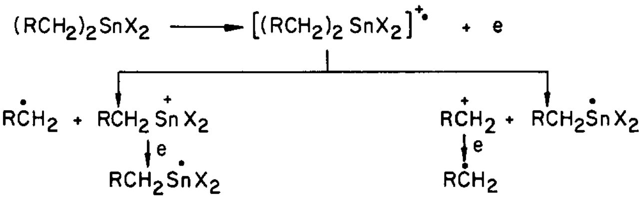


Table 9 Pencil hardness (PH) and brittleness test results for D-OTDA in Synocure 3134

	Formulation					
	33% 3134 67% TPGDA		33% 3134 33% TPGDA 34% D-OTDA		33% 3134 67% D-OTDA	
Radiation dose (kGy)	PH	Brittleness	PH	Brittleness	PH	Brittleness
5	>4H	1	>4H	1	>4H	1
10	>4H	1	>4H	2/3	>4H	2
20	>4H	1	>4H	1	–	

Table 11 Pencil hardness (PH) and brittleness test results for D-BTDA in Synocure 3111

	Formulation					
	33% 3111 67% TPGDA		33% 3111 33% TPGDA 34% D-BTDA		33% 3111 67% D-BTDA	
Radiation dose (kGy)	PH	Brittleness	PH	Brittleness	PH	Brittleness
5	>4H	2/3	>4H	2	>4H	5
10	>4H	2	>4H	2/3	>4H	4
20	>4H	3	>4H	3	>4H	5

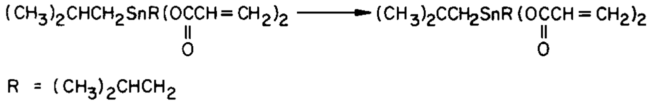
Table 12 Solvent rub test results for D-OTDA/Synocure 3111

	Formulation		
Radiation dose (kGy)	33% 3111 67% TPGDA	33% 3111 33% TPGDA 34% D-OTDA	33% 3111 67% D-OTDA
5	2.5 (18.3)	–	15.0 (23.7)
10	8.5 (23.6)	25 (18.5)	–
20	12.5 (18.6)	31 (20.4)	19.5 (17.8)

Coat weights ($g\,m^{-2}$) in parentheses

Both the carbon- and tin-centred[11] radicals will act as effective initiating species by adding to the acrylate group. Our proposals are consistent with the findings of Lloyd and Rodgers[12] who showed that the rupture of carbon–tin bonds by ^{60}Co radiation is a facile process for small molecules of the type $(CH_3)_nSnCl_{4-n}$ where $n = 1, 2, 3$ and 4. Labadie *et al.*[13] have also shown that the polymers derived from trimethylstannyl styrene are excellent negative electron beam resists due to ease of breaking the weak carbon–tin bonds and thereby creating radical sites which lead to crosslinking.

The data presented in *Tables 3* and *4* suggest that D-MPTDA may be slightly more reactive than D-BTDA. This may be due to the presence of two tertiary C–H bonds in D-MPDTA which will aid the fragmentation of the ionized D-MPTDA to produce a β-stannylalkyl radical and a proton.



$$(CH_3)_2CHCH_2SnR(O\underset{\underset{O}{\|}}{C}CH=CH_2)_2 \longrightarrow (CH_3)_2\dot{C}CH_2SnR(O\underset{\underset{O}{\|}}{C}CH=CH_2)_2$$

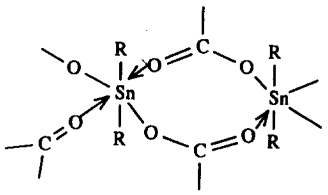
$R = (CH_3)_2CHCH_2$

The reactivity of these tertiary C–H bonds will also be enhanced by homoconjugation between the incipient radical and the 5d orbital on the tin atom (pπ–dπ homoconjugation) as well as hyperconjugation between the carbon–tin bond and the incipient radical[11,14]. The β-stannylalkyl radicals may have a further part to play by forming crosslinks.

The crosslink density of the films from the dialkyltin diacrylates and the commercial diluents, as evaluated by solvent resistance, pencil hardness and brittleness (*Tables 1–5*) was shown to increase in the order:

$$\text{TPGDA} < \text{HDDA} < \text{D-OTDA} < \text{D-BTDA} < \text{D-MPTDA}$$

The solvent resistance of the films from D-OTDA was significantly lower than those produced from D-BTDA and D-MPTDA. The former coatings also exhibited greater flexibility compared with the D-BTDA and D-MPTDA as indicated by their lower brittleness ratings. The D-OTDA derived films were of comparable flexibility to those derived from TPGDA and HDDA. The lower crosslink density and resulting increased flexibility of the D-OTDA derived films compared with those from the other tin acrylates may be accounted for on the basis of the slightly lower stopping power of the D-OTDA as well as the considerably greater alkyl content of these films. The high crosslink density and hardness of the films obtained from the organotin acrylates may also be in part due to these compounds forming a polymeric structure in which there is bonding between the carbonyl groups and the tin atoms.



This type of bonding appears to be present in the unpolymerized diluents since they exhibit absorptions at ~1560 and 1415 cm^{-1} which is consistent with this proposal[15,16]. This bonding in the organotin diluents is no doubt responsible for the high viscosity of these compounds and their poor solubility in a range of prepolymers.

In the curing of the organotin diacrylates compounded with epoxidized soya bean oil and acrylated polyurethane it was found that the organotin compounds imparted increased solvent resistance to the cured films. With the epoxidized soya bean oil, incorporation of the organotin compounds increased brittleness whereas this was not observed with the acrylated polyurethane. This observation may be explained by there being little crosslinking between the organotin compounds and the epoxidized soya bean oil leading to a coating in which there are islands of oligomers and islands of highly crosslinked organotin diacrylate. Increasing the content of the latter will increase the brittleness until eventually the brittleness of the film produced from pure organotin diacrylate is attained. By way of contrast the acrylated polyurethane will readily crosslink with the dialkyltin diacrylate thereby decreasing the occurrence of highly crosslinked islands or diorganotin acrylates and also decreasing the probability of intermolecular co-ordinative bonding between the organotin species.

Table 13 Physical test results for D-OTDA/Synocure 3111

	Formulation					
	33% 3111 67% TPGDA		33% 3111 33% TPGDA 34% D-OTDA		33% 3111 67% D-OTDA	
Radiation dose (kGy)	PH	Brittleness	PH	Brittleness	PH	Brittleness
5	>4H	2/3		–	>4H	2
10	>4H	2	>4H	2/3		–
20	>4H	3	>4H	3	>4H	3

Table 14 Stopping power of D-BTDA, D-OTDA, TPGDA, HDDA and TMPTA for a high energy electron beam (1 MeV)

Compound	Stopping power (MeV cm^2 g^{-1})
DBTDA	0.0425
DOTDA	0.0352
TPGDA	0.0149
HDDA	0.0147
TMPTA	0.0150

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REFERENCES

1 Roffey, C. G. 'Photopolymerisation of Surface Coatings', Wiley-Interscience, New York, 1982

2 Schafer, O., Allan, M., Haselbach, E. and Davidson, R. S. *Photochem. Photobiol.* 1989, **50**, 717

3 Batten, R. J., Davidson, R. S. and Wilkinson, S. A. *Polym. Paint Col. J.* 1989, **179**, 176

4 Farhataziz and Rodgers, M. A. J. (Eds) 'Radiation Chemistry—Principles and Applications', VCH Publishers, New York, 1987, Ch. 20

5 Tabata, Y. Conf. Proc. Radcure, Basel, Switzerland, 1985

6 Meisels, G. G. *J. Chem. Phys.* 1964, **41**, 51

7 'Handbook of Chemistry and Physics' (Ed. R. C. Weast), 47th Edn, Chemical Rubber Co., Boca Raton, 1967

8 Davidson, R. S., Ellis, R., Wilkinson, S. A. and Summersgill, C. A. *Eur. Polym. J.* 1987, **23**, 105

9 Oakes, V. and Hutton, R. E. *J. Organometal. Chem.* 1965, **3**, 472

10 Davies, A. G. and Smith, P. J. 'Comprehensive Organometallic Chemistry' (Eds G. Wilkinson, F. G. A. Stone and E. W. Abel), Pergamon Press, New York, 1982, p. 519

11 Davies, A. G. *Adv. Chem. Ser.* 1976, **157**, 26

12 Lloyd, R. V. and Rodgers, M. T. *J. Am. Chem. Soc.* 1978, **95**, 2459

13 Labadie, J. W., MacDonald, S. A. and Wilson, C. G. *J. Imaging Sci.* 1986, **30**, 169

14 Davies, A. G., Roberts, B. P. and Tse, M. W. *J. Chem. Soc. Perkin Trans.* 1978, 145

15 Okawara, R. and Wada, M. 'Organotin Compounds' (Ed. A. K. Sawyer), Dekker, New York, 1971

16 Maeda, Y. and Okawara, R. *J. Organomet. Chem.* 1967, **10**, 247