New surface-coating materials: electron-beam curing of some silicon-containing acrylates

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(Received 19 March 1991; revised 16 July 1991; accepted 31 July 1991)

A series of silicon-containing mono-, di-, tri- and tetraacrylates have been synthesized. The tetraacrylates and triacrylates cure at very low doses to give hard, flexible films possessing good solvent resistance properties. The diacrylates cured rapidly to give soft films, whereas the monoacrylates polymerized to give highly viscous fluids. A quantitative evaluation of rate of cure showed that the order of reactivity was diacrylate > triacrylate > monoacrylate. The presence of silicon appears to confer many special properties. These are ascribed to the silicon atom effecting enhanced conformational mobility of the polymer chains. The high reactivity of the di- and triacrylates may be due to the silicon acting as a site for ionization, leading to the production of initiating species.

(Keywords: surface studies; coatings; curing; films; acrylates; silicon; i.r. photoacoustic spectroscopy)

INTRODUCTION

Acrylates have proved to be popular materials for the production of surface coatings using electron-beam (e.b.) technology[1]. Most acrylate prepolymers undergo polymerization at an acceptable radiation dose. They are also favoured because they produce films having a high gloss and, importantly, they are relatively low-cost materials. Rivals in the field are epoxides and vinyl ethers[2], and, although these materials may be more acceptable on toxicity grounds, they require the presence of a photoinitiator, which decomposes liberating a Bronsted acid (e.g. onium salts), to promote cure under e.b. radiation[3]. Acrylates, in contrast to epoxides and vinyl ethers, often undergo shrinkage upon curing, and this is particularly true of highly functionalized acrylates, e.g. pentaerythritol tetraacrylate (PETA)[1,4].

We now report upon the performance of some silicon-containing acrylates (*Table 1*), some of which exhibit good film-forming properties, produce hard but flexible coatings and are highly reactive.

EXPERIMENTAL

Materials

Resins and diluents. Tripropyleneglycol diacrylate (TPGDA; Cray Valley Products Ltd), trimethylolpropane (TMPTA; Cray Valley Products Ltd), 1,4-butanediol monoacrylate (4-HBA; BASF), 2-hydroxyethyl acrylate (2-HEA; Fluka AG), hexanediol diacrylate (HDDA; Cray Valley Products Ltd), hexanediol dimethacrylate (HDDMA; Cray Valley Products Ltd), trimethylolpropane trimethacrylate (TMPTMA; Cray Valley Products Ltd) and the caprolactone-based acrylate TONE-100 (Union Carbide) were all used as received.

Table 1 Silicon-containing acrylates tested for film-forming properties

Compound	Acronym
$Si(OCH_2CH_2OCOCH{=}CH_2)_4$	STEA
$C_6H_5CH_2Si(OCH_2CH_2OCOCH{=}CH_2)_3$	BSTEA
$C_{12}H_{25}Si(OCH_2CH_2OCOCH{=}CH_2)_3$	DSTEA
$CH_3Si(OCH_2CH_2OCOCH{=}CH_2)_3$	MSTEA
$C_8H_{17}Si(OCH_2CH_2OCOCH{=}CH_2)_3$	OSTEA
$C_6H_5Si(OCH_2CH_2OCOCH{=}CH_2)_3$	PSTEA
$(C_6H_5)_2Si(OCH_2CH_2OCOCH{=}CH_2)_2$	DPSDEA
$(CH_3)_2Si(OCH_2CH_2OCOCH{=}CH_2)_2$	DMSDEA
$(CH_3)_3SiOCH_2CH_2OCOCH{=}CH_2$	TMSEA
$CH_3(C_6H_5)Si(OCH_2CH_2OCOCH{=}CH_2)_2$	MPSDEA
$CH_3Si([O(CH_2)_5CO]_2OCH_2CH_2OCOCH{=}CH_2)_3$	MSTT
$C_6H_5Si([CH_2)_5CO]_2OCH_2CH_2OCOCH{=}CH_2)_3$	PSTT
$CH_3Si(OCH_2CH_2CH_2CH_2OCOCH{=}CH_2)_3$	MSTBA
$(CH_3)_2Si(OCH_2CH_2CH_2CH_2OCOCH{=}CH_2)_2$	DMSDBA
$(CH_3)_3SiOCH_2CH_2CH_2CH_2OCOCH{=}CH_2$	TMSBA

Chemicals for synthesis. Diethyl ether (BDH Chemicals Ltd) was distilled from lithium aluminium hydride and stored over molecular sieves, 4 Å.

Tetrahydrofuran (Rathburn Chemical Co.), h.p.l.c.-grade, was stabilized with hydroquinone (0.025%).

The following commercial samples obtained from Aldrich Chemical Co. were used without further purification: dichlorodimethylsilane, dichloromethylphenylsilane, 2-hydroxyethyl methacrylate, methyltrichlorosilane, octyltrichlorosilane, phenyltrichlorosilane, tetrachlorosilane, triethylamine and tri-n-propylamine.

Instrumentation

Electron-beam curing was carried out using an Otto Durr ESH 150/130 electron-beam unit under a nitrogen

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0032-3861/92/143037-07

blanket. The operating voltage was maintained at 150 kV and the beam current was adjusted for each applied dose.

Infra-red spectra of prepared monomers, as well as films cured on a KBr disc, were analysed using a Perkin–Elmer infra-red spectrometer (model 599).

Proton n.m.r. spectra were obtained using a JEOL n.m.r. spectrometer (model JNH-MH-100) and referenced against tetramethylsilane (TMS).

All elemental analyses were carried out using a Carlo Erba Strumentazione Elemental Analyzer model 1106.

Analysis of films cured on an opaque substrate was obtained using a Digilab FTS-60 Fourier transform infra-red spectrometer. The moving mirror velocity in the interferometer was 0.16 cm^{-1} and the spectra reported here were recorded at 8 cm^{-1} spectral resolution using a Digilab photoacoustic detector for 4096 scans.

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

Synthesis

The synthesis of the following compounds (see *Table 1*) has been reported previously[5]: BSTEA, DSTEA, MSTEA, PSTEA, DPSDEA and PSTT.

STEA, OSTEA, MPSDEA, MSTT, DMSDEA, TMSEA, MSTBA, DMSDBA and TMSBA were prepared according to the method described for MSTEA[5]. The yields obtained and physical data for these compounds are as follows.

Tetrakis(2-hydroxyethoxy)silane, tetraacrylate ester (STEA). Clear colourless liquid. Yield = 84%.

Infra-red (liquid film): 2960, 2890, 1640, 1620, 1410, 1300, 1275, 1200, 1130, 1105, 1065, 1040, 980, 850, 810, 670 cm^{-1}.

^1H n.m.r. ($CDCl_3$): δ 3.84 (triplet, J = 6 Hz, 8H, CH_2 at C1), 4.08 (triplet, J = 6 Hz, 8H, CH_2 at C2), 5.44–6.30 (multiplet, 12H, acrylate group).

Analysis calculated for $C_{20}H_{28}O_{12}Si$: C, 49.17; H, 5.78. Found: C, 48.89; H, 5.92.

Tris(2-hydroxyethoxy)octylsilane, triacrylate ester (OSTEA). Clear colourless liquid. Yield = 81%.

Infra-red (liquid film): 3050, 3040, 3020, 2960, 1725, 1640, 1620, 1460, 1410, 1300, 1275, 1200, 1130, 1100, 1060, 975, 801 cm^{-1}.

^1H n.m.r. ($CDCl_3$): δ 0.60–1.80 (multiplet, 17H, C_8H_{17}–), 4.00 (triplet, J = 6 Hz, 6H, CH_2 at C1), 4.30 (triplet, J = 6 Hz, 6H, CH_2 at C2), 5.70–6.50 (multiplet, 9H, acrylate group).

Analysis calculated for $C_{23}H_{38}O_9Si$: C, 56.77; H, 7.87. Found: C, 56.84; H, 8.05.

Bis(2-hydroxyethoxy)methylphenylsilane, diacrylate ester (MPSDEA). Pale yellow clear liquid. Yield = 83%.

Infra-red (liquid film): 3070, 3050, 1725, 1640, 1620, 1590, 1430, 1410, 1300, 1275, 1200, 1120, 970, 810, 740, 720, 700 cm^{-1}.

^1H n.m.r. ($CDCl_3$): δ 0.30 (singlet, 3H, CH_3–), 3.80 (triplet, J = 6 Hz, 4H, CH_2 at C1), 4.10 (triplet, J = 6 Hz, 4H, CH_2 at C2), 5.50–6.30 (multiplet, 6H, acrylate group), 6.95–7.50 (multiplet, 5H, C_6H_5–).

Analysis calculated for $C_{17}H_{22}O_6Si$: C, 58.27; H, 6.33. Found: C, 58.30; H, 6.49.

Methyltris(TONE-100)silane, triacrylate ester (MSTT). Clear colourless liquid. Yield = 84%.

Infra-red (liquid film): 2940, 2870, 1730, 1640, 1620, 1460, 1410, 1270, 1200–1160, 1100, 990, 850, 810 cm^{-1}.

^1H n.m.r. ($CDCl_3$): δ 0.12 (singlet, 3H, CH_3–), 1.16–1.85 (multiplet, 36H, CH_2 at C2, C3, C4, C8, C9, C10), 2.15–2.55 (multiplet, 12H, CH_2 at C5, C11), 3.50–4.40 (multiplet, 24H, CH_2 at C1, C7, C13, C14), 5.70–6.50 (multiplet, 9H, acrylate group).

Analysis calculated for $C_{52}H_{84}O_{21}Si$: C, 58.19; H, 7.88. Found: C, 58.13; H, 8.15.

Bis(2-hydroxyethoxy)dimethylsilane, diacrylate ester (DMSDEA). Clear colourless liquid. Yield = 78%.

Infra-red (liquid film): 2960, 2880, 1727, 1637, 1620, 1410, 1298, 1260, 1190, 1130, 1100, 1061, 965, 840, 806 cm^{-1}.

^1H n.m.r. ($CDCl_3$): δ 0.20 (singlet, 6H, methyl group), 3.90 (triplet, J = 6 Hz, 4H, CH_2 at C1), 4.20 (triplet, J = 6 Hz, 4H, CH_2 at C2), 5.74–6.50 (multiplet, 6H, acrylate).

Analysis calculated for $C_{12}H_{20}O_6Si$: C, 49.98; H, 6.99. Found: C, 49.92; H, 7.16.

(2-Hydroxyethoxy)trimethylsilane, acrylate ester (TMSEA). Clear colourless liquid. Yield = 86%.

Infra-red (liquid film): 2963, 2882, 1728, 1638, 1620, 1448, 1408, 1296, 1261, 1190, 1093, 1060, 985, 871, 841, 810, 740 cm^{-1}.

^1H n.m.r. ($CDCl_3$): δ 0.10 (singlet, 9H, CH_3–), 3.80 (triplet, J = 6 Hz, 2H, CH_2 at C1), 4.10 (triplet, J = 6 Hz, 2H, CH_2 at C2), 5.60–6.30 (multiplet, 3H, acrylate group).

Analysis calculated for $C_8H_{16}O_3Si$: C, 51.03; H, 8.56. Found: C, 61.33; H, 8.69.

(4-Hydroxybutoxy)trimethylsilane, acrylate ester (TMSBA). Clear colourless liquid. Yield = 84%.

Infra-red (liquid film): 2963, 2882, 1728, 1638, 1620, 1448, 1408, 1296, 1261, 1190, 1093, 1060, 985, 871, 841, 810, 740 cm^{-1}.

^1H n.m.r. ($CDCl_3$): δ 0.10 (singlet, 9H, CH_3–), 1.80 (multiplet, 4H, CH_2 at C2, C3), 3.80 (triplet, 2H, CH_2 at C4), 4.20 (triplet, 2H, CH_2 at C4), 5.60–6.30 (multiplet, 3H, acrylate group).

Analysis calculated for $C_{10}H_{20}O_3Si$: C, 55.52; H, 9.32. Found: 55.60; H, 9.39.

Bis(4-hydroxybutoxy)dimethylsilane, diacrylate ester (DMSDBA). Clear colourless liquid. Yield = 88%.

Infra-red (liquid film): 2963, 2936, 2870, 1728, 1636, 1620, 1455, 1412, 1296, 1265, 1192, 1060, 1038, 987, 899, 849, 810 cm^{-1}.

^1H n.m.r. ($CDCl_3$): δ 0.20 (singlet, 6H, CH_3–), 1.80 (multiplet, 8H, CH_2 at C2, C3), 3.80 (triplet, 4H, CH_2 at C1), 4.20 (triplet, 4H, CH_2 at C4), 5.60–6.30 (multiplet, 6H, acrylate group).

Analysis calculated for $C_{16}H_{28}O_6Si$: C, 55.79; H, 8.19. Found: C, 55.90; H, 8.25.

Tris(4-hydroxybutoxy)methylsilane, triacrylate ester (MSTBA). Clear colourless liquid. Yield = 84%.

Infra-red (liquid film): 2955, 2874, 1728, 1635, 1620, 1455, 1411, 1300, 1269, 1190, 1065, 987, 899, 849, 810 cm^{-1}.

^1H n.m.r. ($CDCl_3$): δ 0.20 (singlet, 3H, CH_3–), 1.80 (multiplet, 12H, CH_2 at C2, C3), 3.80 (triplet, 6H, CH_2 at C1), 4.20 (triplet, 6H, CH_2 at C4), 5.65–6.40 (multiplet, 9H, acrylate).

Analysis calculated for $C_{22}H_{36}O_9Si$: C, 55.91; H, 7.68. Found: C, 55.98; H, 7.71.

Physical test methods

Solvent rub resistance test. This test has been described previously[5].

The pencil hardness test. 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.

Determination of gel content of diluents irradiated at 20 kGy. Solvent extraction of cured films of 4-HBA, 2-HEA, TPGDA, TMPTA, TMSEA, DMSDEA, MSTEA, TMSBA, DMSDBA and MSTBA on GNT paper as well as a blank of uncoated paper was carried out as follows.

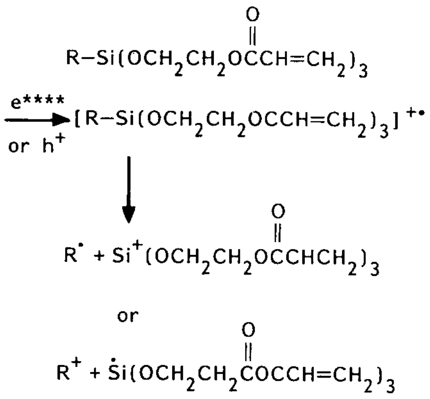
Four 10 × 10 cm^2 templates of a cured coating on GNT of known coatweights were extracted using tetrahydrofuran (50 ml) for 24 h. The solvent was removed over a rotary evaporator and the amount of extract was recorded and calculated as the percentage extract.

RESULTS

A number of silicon-containing acrylates were synthesized by reacting the appropriate chlorosilane with either 2-hydroxyethyl acrylate or 4-hydroxybutyl acrylate in the presence of a base. The compounds tested are shown in *Table 1*. These materials were coated onto paper and then exposed to e.b. radiation. The films so formed were submitted to physical testing, namely the 'solvent rub test', 'pencil hardness' and 'brittleness'. Their performance was compared with that of three standard prepolymers: tripropyleneglycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA) and 2-hydroxyethyl acrylate (2-HEA). In the event, curing of TMPTA led to so much shrinkage that the films exhibited severe reticulation and as a consequence it proved impossible to submit them to the standard physical testing procedure. The results obtained are shown in *Table 2*. From this table, it will be seen that difficulty was experienced in obtaining uniform coatweights and this was due to the method of application. The results shown in *Table 2* are therefore only a guide to the properties of the films. Nevertheless, it can be seen that the silicon-containing acrylates give coatings at low doses of radiation and in all cases it was found that these compounds gave tack-free coatings at lower doses than TPGDA, HDDA, TMPTA and 2-HEA. In order to quantify cure rate of thin films in terms of double-bond consumption, the films were examined by Fourier transform infra-red photoacoustic spectroscopy (*FT*i.r.-p.a.s.) after discrete doses of e.b. radiation had been administered[6]. The results are shown in *Figures 1* and *2*. Several acrylates were subjected to 20 kGy radiation and the films so produced subjected to solvent extraction in order to determine gel content (*Table 3*). For the silicon-containing acrylates it can be seen that the reactivity in terms of double-bond consumption is related to the degree of functionality, i.e. the reactivity was seen to decrease in the order diacrylate, triacrylate, monoacrylate. The degree of crosslinking as measured by gel content is triacrylate > diacrylate > monoacrylate.

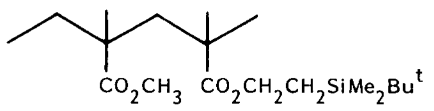
DISCUSSION

All the silicon-containing acrylates shown in *Table 1* displayed enhanced reactivity, in terms of minimum dose to give tack-free films, compared with HDDA, TPGDA and TMPTA. We originally argued that incorporating elements into acrylates of higher atomic number than carbon would lead to more efficient interaction with the highly energized primary electrons[7]. However, another factor to be borne in mind is ease of ionization of tetrasubstituted silanes and derivatives. The radical cations of a number of alkysilanes have been generated by γ radiation[8]. It is known that arylsilanes will undergo photoinduced electron transfer with good electron acceptors such as 9,10-dicyanoanthracene[9]. It is therefore proposed that ionization of silicon acrylates occurs either as a primary event or as a result of hole hopping with consequent homolysis occurring to give initiating radicals. For example:



$$\mathrm{R{-}Si(OCH_2CH_2O\overset{O}{\overset{\|}{C}}CH{=}CH_2)_3}$$
$$\xrightarrow[\text{or } h^+]{e^{****}} \mathrm{[R{-}Si(OCH_2CH_2OCCH{=}CH_2)_3]^{+\bullet}}$$
$$\downarrow$$
$$\mathrm{R^\bullet + Si^+(OCH_2CH_2O\overset{O}{\overset{\|}{C}}CHCH_2)_3}$$
$$\text{or}$$
$$\mathrm{R^+ + \dot{S}i(OCH_2CH_2CO\overset{O}{\overset{\|}{C}}CH{=}CH_2)_3}$$

Given that the Si–O bond is considerably stronger than the Si–C bond (444 and 318 kJ mol^{-1} respectively)[10], the cation radical is likely to fragment as shown, the preferred fragmentation of the radical cation being determined by the stability of the carbocation. Silicon radicals, e.g. $(CH_3CH_2)_3Si$, have been shown to be highly reactive towards methyl methacrylate, and these are therefore likely to be good initating species[11]. That fragmentation of silicon-containing derivatives can occur under e.b. radiation is substantiated by the finding that polymers such as [A] behave as negative e.b. resists[12]:



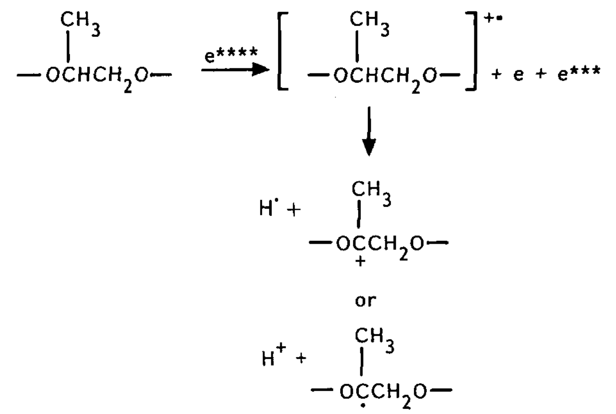
[A]

In an earlier study it has also been shown that e.b. radiation of polysiloxanes, e.g. polydimethylsiloxane, polydiphenylsiloxane and polymethylphenylsiloxanes, does not cause main-chain scission[13], but crosslinks of

Table 2 Physical test data for films produced from compounds shown in *Table 1*

Compound	Dose of radiation (kGy)	Coatweights ($g\ m^{-2}$)	Solvent rubs	Pencil hardness	Brittleness
PSTEA	2.5	25.7	95	4H	1
	5	29.0	100	4H	1
	10	21.0	180	4H	1
	20	20.8	333	4H	1
	40	24.5	500	4H	1
	60	15.0	500	4H	2
BSTEA	2.5	49.3	465	4H	1
	5	54.2	500	4H	2
	10	25.4	500	4H	2
	20	44.4	500	4H	2
	40	56.3	500	4H	2
	60	45.3	500	4H	2
MSTEA	2.5	36.0	500	H	2
	5	41.6	500	2H	1
	10	22.1	500	2H	2
	20	22.4	500	3H	2
	40	18.8	500	3H	2
	60	17.9	500	3H	1
OSTEA	2.5	47.4	142.5	H	1
	5	41.4	111	2H	1
	10	43.0	500	2H	2
	20	44.4	500	3H	1
	40	40.3	500	3H	2
	60	40.1	500	4H	2
DSTEA	2.5	29.0	500	H	2
	5	38.8	500	2H	1
	10	29.3	500	2H	2
	20	20.0	500	3H	1
	40	22.2	500	3H	2
	60	42.9	500	3H	3
DPSDEA	2.5	25.6	14.5	–	1
	5	30.4	–	–	–
	10	29.2	31.0	–	1
	20	22.3	95.0	–	–
	40	25.1	97.5	–	–
	60	36.2	126.0	–	–
MPSDEA	2.5	53.9	18	–	1
	5	47.2	25	–	2
	10	53.9	89	–	2
	20	56.0	47	–	–
	40	68.4	500	–	–
	60	49.1	373	–	–
MSTT	2.5	38.6	2.5	2H	2
	5	62.6	13.5	4H	2
	10	50.3	40.5	4H	2
	20	53.3	29.0	4H	3
PSTT	2.5	21.8	4.0	3H	1
	5	32.0	22.0	4H	2
	10	18.5	32.0	4H	3
	20	30.3	50	4H	3
STEA	2.5	47.8	>500	H	2
	5	49.7	>500	3H	1
	10	39.6	>500	3H	2
	20	33.2	>500	3H	1
	40	29.2	>500	3H	1
	60	41.0	>500	>3H	1

would indicate that it readily ionizes, generating slow electrons that initiate polymerization:



In the case of TMPTA, high doses of radiation failed to induce total double-bond consumption (*Figure 1*), and this is no doubt in part due to the trifunctional character of the material, which leads to rapid crosslinking and hence gelation[6]. Given that the early stages of double-bond consumption reflect the rate of propagation and initiation, it would seem that TMPTA does not ionize as easily as TPGDA. The presence of the ether links in TPGDA will aid ionization by stabilizing the incipient radical and radical cation. In previous work[14] we have shown that cyclic ethers (epoxides) ionize far more readily than materials such as linear ethers and propylene carbonate.

Table 2 shows how groups attached to silicon can alter film performance in terms of solvent resistance and hardness. Not surprisingly, STEA cures at low doses to give hard films (5 kGy) showing a good solvent resistance and remarkable degree of flexibility. For this compound, film formation is probably entirely due to polymerization via the acrylate group. Replacement of one of the hydroxyethyl acrylates by a methyl group to give MSTEA also leads to a material that cures rapidly to give hard, flexible films possessing good solvent resistance. BSTEA and DSTEA behave in a similar way to MSTEA. PSTEA and OSTEA also cured at low doses to give hard, flexible films but their solvent resistance was not quite as good as MSTEA. This result may be due to a variation in applied coatweights rather than a reflection of any effect of true chemical origin. However, with the acrylates having a polyester substituent (MSTT and PSTT), the effect of the substituent group at silicon is most marked since the films possess very low solvent resistance. We attribute this finding to the solubility of the polyester group in the acetone, which renders the coating overall more soluble than that based on silicon having a simple alkyl or aryl group attached. Both diacrylates tested (DPSDEA and MPSDEA) formed soft films having very poor solvent resistance. It is unlikely in both cases that the substituents at silicon are accounting for this. From the results shown in *Figures 1* and *2*, the diacrylates clearly polymerize efficiently, and therefore the formation of soft films with poor solvent resistance is most probably due to the polymer having a very open structure, aiding solvent permeation. These compounds may prove useful as reactive plasticizers.

The results shown in *Figures 1* and *2* show that the diacrylates are more reactive than the triacrylates, although in both cases 40 kGy of radiation induced a high percentage of double-bond consumption. Presumably the triacrylates increase in viscosity as a function of dose more rapidly than the diacrylates, and hence the extra availability of acrylate grouping in the triacrylates is offset by the lower degree of mobility of the growing polymer chains[15]. This is particularly true for MSTEA but is far less marked for MSTBA. With the latter compound, the greater distance between the silicon and the acrylate group will confer greater conformational freedom and will result in lower crosslink density of the polymer matrix. These factors will probably lead to the viscosity increase as a function of dose being less for MSTBA compared with MSTEA. The silicon-containing monoacrylates TMSEA and TMSBA proved to be relatively unreactive and did not exhibit film formation. With these compounds, only linear polymer formation is possible unless the e.b. radiation induces crosslinking via the backbone. From the evidence, this appears to be unlikely, particularly in view of the zero gel content after 20 kGy radiation (*Table 3*).

The rapid curing of 2-HEA and high gel content after 20 kGy radiation deserve comment. Good film formation will undoubtedly be aided by hydrogen bonding but this cannot account for the high degree of crosslinking. If the latter is not due to polyfunctional impurities, it must be due to backbone radical formation, probably via ionization of the C–H bond adjacent to the hydroxy group[16].

CONCLUSIONS

The silicon-containing tetraacrylate (STEA) and triacrylates (BSTEA, DSTEA, MSTEA, OSTEA and PSTEA) are remarkable materials in that they cure at low dose to give hard, flexible films, and furthermore film formation is not accompanied by noticeable shrinkage. These properties are rationalized as being due to the silicon atom.

ACKNOWLEDGEMENTS

We thank the SERC for a Co-operative Award (R. J. Batten and S. A. Wilkinson), the industrial partner being Wiggins Teape Research and Development Ltd. This company also provided substantial funds to support personnel (R.J.E.) and the project. Their support in terms of expertise and enthusiasm is gratefully acknowledged, and in particular we should like to thank M. R. Chamberlain, R. Wallis, A. K. Webb and not least Miss C. Summersgill.

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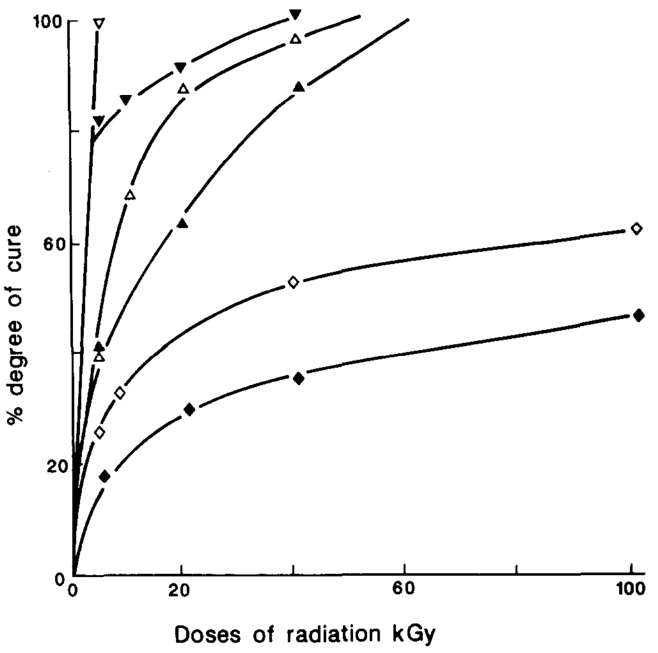


Figure 1 Percentage degree of cure of 2-HEA (▽), TMSEA (◆), DMSDEA (▼), MSTEA (▲), TPGDA (△) and TMPTA (◇) cured at various doses of radiation

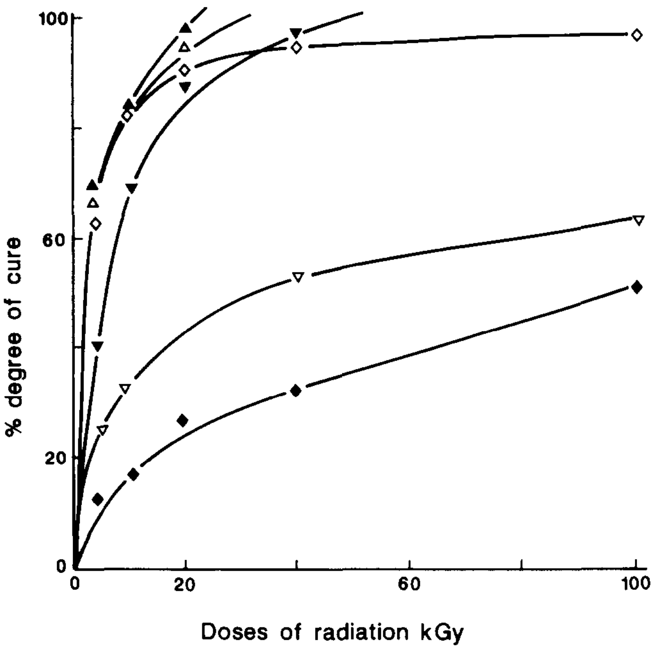


Figure 2 Percentage degree of cure of 4-HBA (▲), DMSDBA (△), MSTBA (◇), TPGDA (▼), TMPTA (▽) and TMSBA (◆) cured at various doses of radiation

Table 3 Gel content of 10 diluents irradiated at 20 kGy

Compound	Percentage gel	Functionality
MSTEA	84	3
DMSDEA	63	2
TMSEA	0	1
2-HEA	76	1
MSTBA	82	3
DMSDBA	52	2
TMSBA	0	1
4-HBA	66	1
TPGDA	79	2
TMPTA	85	3

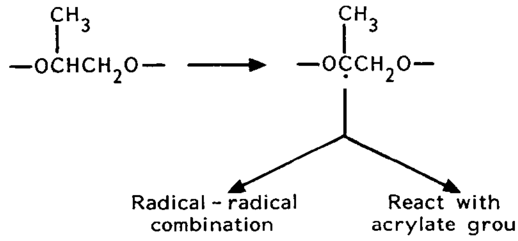
the type

$\equiv Si-Si \equiv$ $\equiv SiCH_2Si \equiv$ and $\equiv SiCH_2CH_2Si \equiv$

are produced, thereby showing that Si–C bond fission is preferred over Si–O bond fission. The reactivity of the silicon-containing acrylates may therefore reflect the stopping power of silicon and the susceptibility of these materials to fragment to give effective initiating radicals.

A further remarkable feature of these marterials, which may have a bearing on their reactivity, is that a high percentage of the double bonds in the triacrylates and diacrylates are utilized; for example, from *Figures 1* and *2* it can be seen that a dose of 40 kGy has led to 80% double bonds utilized whereas for TMPTA the level is 50%. These results would indicate that the silicon-containing acrylates require higher doses than TMPTA to gel, but in contradistinction to this the silicon-containing di- and triacrylates form tack-free films at lower doses than TMPTA! It would appear that, within the structure of the polymerizing silicon-containing acrylates, there is greater conformational mobility, thereby allowing the radical on the growing chains to explore a greater volume than is the case for TMPTA. Consequently, a larger proportion of acrylate groups is used up. That the polymers derived from the silicon-containing acrylates may have a more open structure is indicated by the results of the extent of gel formation (*Table 3*). The diacrylates show a lower percentage of gel formation compared with their non-silicon-containing counterparts; rather than reflecting fewer crosslinks (which is unlikely in view of the efficiency of consumption of double bonds), this is a reflection of the more open structure of the film, which aids solvent permeation. A further indication of conformational mobility for the films formed from the silicon-containing triacrylates and the one tetraacrylate examined comes from the finding that these highly crosslinked films (as evidenced by their hardness and solvent resistance) are flexible.

Some interesting features concerning the cure of TMPTA and TPGDA can be gleaned from *Figure 1* and *Table 2*. For TPGDA it can be seen (*Figure 1*) that double-bond consumption is 85% complete after a dose of 20 kGy, with further consumption occurring more slowly when further irradiation is applied. Inspection of *Table 2* shows that the films of TPGDA only become hard (pencil hardness) and achieve solvent resistance (solvent rubs) at 20 kGy, i.e. the films are undergoing significant change at doses much higher than are required to polymerize the acrylate groups. Thus, with TPGDA, we judge that an essential part of obtaining good film performance is due to crosslinking via the backbone[6]. For example:



This fact is not so surprising when one considers the sensitivity of TPGDA towards e.b. radiation, which

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