The photopolymerization of acrylates and methacrylates containing silicon

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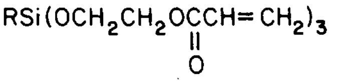
A number of di- and triacrylates and methacrylates containing silicon have been prepared. In the presence of a photoinitiator and absence of a tertiary amine, these compounds photopolymerized to give thin films, and in some cases this was not accompanied by shrinkage. The rate of polymerization, as judged by the amount of exposure to give tack-free coatings, was usually found to be much greater than standard diluents such as hexanediol diacrylate, tripropyleneglycol diacrylate and trimethylolpropane triacrylate. Monitoring the degree of cure by quantifying the extent to which the acrylate or methacrylate groups have been utilized showed that the presence of silicon affected the extent to which double-bond utilization occurs.

(Keywords: photopolymerization; coatings; films; acrylates; methacrylates; silicon)

INTRODUCTION

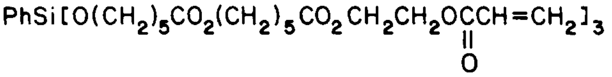
The polymerization of a wide variety of acrylates and methacrylates induced by a combination of u.v. light and photoinitiator has been well explored[1]. To produce surface coatings possessing particular properties, an appropriate oligomer functionalized with acrylate or methacrylate groups in combination with a polyfunctional acrylate/methacrylate to reduce the viscosity of the oligomer is used. An important property of the formulation is the speed of cure. This is controlled by a number of factors, such as light intensity, the absorption characteristics of the photoinitiator and medium, the concentration of the initiator, the efficiency with which the initiator gives initiating radicals, the propagating efficiency of the radicals, the presence of oxygen (which scavenges initiator radicals and radicals in the growing polymer) and the degree of functionalization of the acrylate/methacrylate[2]. Monoacrylates/methacrylates can only polymerize to give linear polymers, whereas di- and more highly functionalized acrylates/methacrylates produce crosslinked polymers, and consequently give a harder film than monofunctional compounds for a given percentage consumption of unsaturation. Use of the polyfunctionalized acrylates, however, can lead to many of the unsaturated groups being non-utilized[3] owing to the rapid gelling of the film[4] reducing the conformational mobility of the oligomers, thereby leading to occlusion of residual acrylate groups[5]. An undesirable feature associated with the use of polyfunctional acrylates is that crosslinking can produce film shrinkage, leading, ultimately, to cracks appearing in the surface coating.

We now report upon the u.v. curing of a number of silicon-containing acrylates (**1–9**) and methacrylates (**10–12**) using 2-hydroxy-2,2-dimethyl-1-phenylethan-1-one (Darocur® 1173) as a photoinitiator, in which some remarkable speeds of cure have been observed.



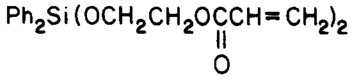
$\mathrm{RSi(OCH_2CH_2O}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{CH{=}CH_2)_3}$

(1)	R = Ph	PSTEA
(2)	R = $PhCH_2$	BSTEA
(3)	R = CH_3	MSTEA
(4)	R = $C_{12}H_{25}$	DSTEA
(5)	R = $CH_2{=}CH$	VSTEA
(6)	R = Ph_2CH	BHSTEA



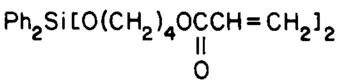
$\mathrm{PhSi[O(CH_2)_5CO_2(CH_2)_5CO_2CH_2CH_2O}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{CH{=}CH_2]_3}$

(7) PS (TONE-100)



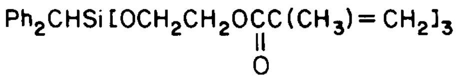
$\mathrm{Ph_2Si(OCH_2CH_2O}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{CH{=}CH_2)_2}$

(8) DPSDEA



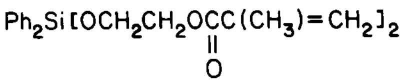
$\mathrm{Ph_2Si[O(CH_2)_4O}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{CH{=}CH_2]_2}$

(9) DPSDBA



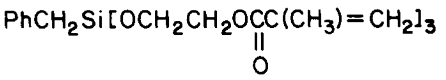
$\mathrm{Ph_2CHSi[OCH_2CH_2O}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{C(CH_3){=}CH_2]_3}$

(10) BHSTEMA



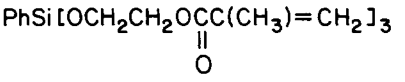
$\mathrm{Ph_2Si[OCH_2CH_2O}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{C(CH_3){=}CH_2]_2}$

(11) DPSDEMA



$\mathrm{PhCH_2Si[OCH_2CH_2O}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{C(CH_3){=}CH_2]_3}$

(12) BSTEMA



$\mathrm{PhSi[OCH_2CH_2O}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\mathrm{C(CH_3){=}CH_2]_3}$

(13) PSTEMA

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EXPERIMENTAL

Materials

Methylsilicon trichloride (Aldrich Ltd), dodecylsilicon trichloride (Fluka AG), phenylsilicon trichloride (Aldrich Ltd), benzylsilicon trichloride (Aldrich Ltd), silicon tetrachloride (Aldrich Ltd), diphenylsilicon dichloride (Aldrich Ltd), trichlorosilane (Aldrich) and vinyl trichlorosilane (Fluka AG) were all used as received. The photoinitiators, 2-hydroxy-2,2-dimethyl-1-phenylethan-1-one (Darocur® 1173, E. Merck), hexane-1,6-diol diacrylate (Cray Valley Products), trimethylolpropane triacrylate (Cray Valley Products), 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate (Fluka AG) and 4-hydroxybutyl acrylate (BASF), were used as received.

Spectra

Infra-red spectra were recorded on a Perkin–Elmer 983 spectrophotometer as thin films. ^{1}H n.m.r. spectra (in deuteriochloroform, with tetramethylsilane as internal standard) were recorded on a JEOL JNH-MH-100 instrument. Microanalyses were carried out on a Carlo Erba 1106 analyser by Mr P. E. Hemming at City University.

Syntheses

Representative acrylate, PSTEA (**1**). Trichlorophenylsilane (5.92 g, 0.028 mol) was slowly added to an ice-cooled mixture of 2-hydroxyethyl acrylate (9.75 g, 0.084 mol), triethylamine (8.50 g, 0.084 mol) and dry diethyl ether (100 ml). The mixture was heated under reflux for 2 h and then cooled. The precipitate of triethylamine hydrochloride was filtered off and the solution decolourized by the addition of activated charcoal. The ethereal solution was dried over anhydrous sodium sulphate and the solvent removed by evaporation under reduced pressure to give a clear colourless liquid. The material was not subjected to vacuum distillation owing to its tendency to polymerize upon heating.

Analysis calculated for $C_{21}H_{26}O_9Si$: C, 55.99; H, 5.82. Found: C, 55.74; H, 5.82.

Infra-red (liquid film): 3080, 3040, 2950, 2890, 1725, 1640, 1620, 1410, 1300, 1270, 1190, 1130, 1100, 1060, 970, 810, 740 and 700 cm^{-1}.

^{1}H n.m.r. (CDCl$_3$): 4.0 (t, $J = 6$ Hz, 6H), 4.2 (t, $J = 6$ Hz, 6H), 5.6–6.4 (m, 9H), 7.0–7.25 (m, 5H).

Other materials prepared in a similar way showed similar spectral properties (*Table 1*) and these together with the analytical figures confirmed their structural assignment, e.g. in the i.r. all exhibited absorptions associated with the acryloyl group at 1725, 1640, 1620 and 810 cm^{-1}.

Diphenylmethylsilicon trichloride[6]. To a mixture of benzophenone (12.6 g) and tri-n-propylamine contained in a dry three-necked flask equipped with a reflux condenser, trichlorosilane (21.05 ml) was added over a 40 min period, keeping the temperature of the reaction mixture around 0°C by means of an ice–salt bath. Following the addition of the silane, the mixture was heated under reflux for 1 h. After cooling excess n-pentane was added to the reaction mixture and the precipitate so produced removed by filtration. Excess solvent was removed under vacuum and the residue subjected to vacuum distillation, b.p. 109°C (0.5 mmHg). Yield: 10 g, 64%. The product was usually contaminated with a small amount of benzophenone (detected by i.r. spectroscopy) but the material was of sufficient purity for use in the preparation of the acrylated and methacrylated derivatives.

The methacrylates (**10–12**) were prepared in a similar way to the acrylate analogues, using 2-hydroxyethyl methacrylate in place of 2-hydroxyethyl acrylate. These compounds were characterized by i.r. and ^{1}H n.m.r. but were not redistilled for C and H analysis owing to their proneness to polymerize upon heating.

U.v. curing

Curing in paper. The photoinitiator was dissolved in the acrylate to give the appropriate concentration. The solutions were coated onto Gateway natural tracing paper (GNT; Wiggins Teape Group Ltd) (70–75 g m^{-2}) using a K Bar (R. K. Print Coat Instruments Ltd, Royston, Herts) to give coatweights of approximately 12 g m^{-2}. The samples were u.v. cured using a Colordry (Colordry Ltd, Chessington, Surrey) u.v. curing unit fitted with one u.v. lamp (9 inch) rated at 200 W per linear inch situated 15 cm above the belt. The extent of exposure was controlled by the belt speed (calibrated in m min^{-1}) and the number of passes.

Curing on potassium bromide discs[7]. Potassium bromide discs (13 mm diameter) were prepared using a Pye Unicam disc press. The initiator–monomer formulation was applied to the disc using a Meyer Bar coater (R. K. Print Coat Instruments Ltd, Royston, Herts) so as to give films approximately 6 μm thick. The materials were cured by passing through a Colordry twin lamp u.v. curing unit at 8.3 m min^{-1} and utilizing both lamps (9 inch, 200 W per linear inch rating).

Test methods

Speed of cure. The relative cure speeds of the samples were assessed by recording the number of passes under the lamp that were required to give a touch-dry coating for a given belt speed and initiator level.

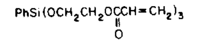
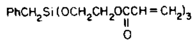
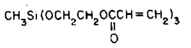
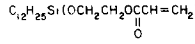
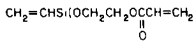
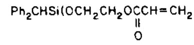
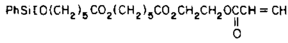
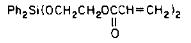
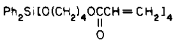
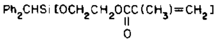
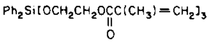
Degree of cure[8,9]. Infra-red spectra of samples cured on potassium bromide discs were used to measure the degree of cure, i.e. the percentage of double bonds consumed in the curing process. Absorptions due to the acrylate group appear at 1730, 1640, 1620 and 810 cm^{-1}. In order to overcome inaccuracies due to variation in film thickness, a reference peak (700 cm^{-1}, associated with aromatic group) was used. Thus the ratio of the acrylate peak (at 810 cm^{-1}) to that at 1730 cm^{-1} was determined for films prior to irradiation and after irradiation for known durations.

Solvent resistance. The cured samples were clamped onto a SATRA rub tester and subjected to an acetone-soaked felt pad rubbing back and forth. The number of double bonds required to break the cured film was recorded.

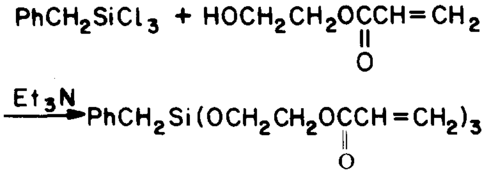
RESULTS

The new silicon-containing acrylates and methacrylates were prepared by reaction of either 2-hydroxyethyl acrylate or 2-hydroxyethyl methacrylate with the

Table 1 Selected physical properties of synthesized acrylates

Compound	Structure	Yield of crude product (%)	Abbreviation	Analysis Calculated (%) C	H	Found (%) C	H	^{1}H n.m.r. ($CDCl_3$) (ppm)
(1)	 $\mathrm{PhSi(OCH_2CH_2O\underset{\overset{\|}{O}}{C}CH{=}CH_2)_3}$	83	PSTEA	55.99	5.82	55.74	5.82	4.0 (t, J = 6 Hz, 6H), 4.2 (t, J = 6 Hz, 6H), 5.6–6.4 (m, 9H), 7.0–7.25 (m, 5H)
(2)	 $\mathrm{PhCH_2Si(OCH_2CH_2O\underset{\overset{\|}{O}}{C}CH{=}CH_2)_3}$	79	BSTEA	60.54	6.47	60.49	6.57	2.19 (s, 2H), 3.8 (t, J = 6 Hz, 6H), 4.1 (t, J = 6 Hz, 6H), 5.6–6.4 (m, 9H), 7.0–7.25 (m, 5H)
(3)	 $\mathrm{CH_3Si(OCH_2CH_2O\underset{\overset{\|}{O}}{C}CH{=}CH_2)_3}$	86	MSTEA	49.47	6.23	49.40	6.20	0.2 (s, 3H), 4.0 (t, J = 6 Hz, 6H), 4.3 (t, J = 6 Hz, 6H), 5.7–6.5 (m, 9H)
(4)	 $\mathrm{C_{12}H_{25}Si(OCH_2CH_2O\underset{\overset{\|}{O}}{C}CH{=}CH_2)_3}$	82	DSTEA	59.75	8.54	59.62	8.73	0.5–1.4 (m, 25H), 3.9 (t, J = 6 Hz, 6H), 4.18 (t, J = 6 Hz, 6H), 5.6–6.3 (m, 9H)
(5)	 $\mathrm{CH_2{=}CHSi(OCH_2CH_2O\underset{\overset{\|}{O}}{C}CH{=}CH_2)_3}$	83	VSTEA	50.98	6.04	50.87	6.28	3.8 (t, J = 6 Hz, 6H), 4.1 (t, J = 6 Hz, 6H), 5.4–6.3 (m, 12H)
(6)	 $\mathrm{Ph_2CHSi(OCH_2CH_2O\underset{\overset{\|}{O}}{C}CH{=}CH_2)_3}$	72	BHSTEA	62.21	5.97	60.32	5.99	3.8 (t, J = 6 Hz, 6H), 4.1 (t, J = 6 Hz, 6H), 4.34 (s, 1H), 5.60–6.50 (m, 9H), 6.90–7.20 (m, 10H)
(7)	 $\mathrm{PhSi[O(CH_2)_5CO_2(CH_2)_5CO_2CH_2CH_2O\underset{\overset{\|}{O}}{C}CH{=}CH_2]_3}$	74	PS (TONE-100)	60.29	7.63	60.08	7.73	1.10–1.90 (m, 36H), 2.10–2.60 (m, 12H), 3.74–4.60 (m, 24H), 5.60–6.50 (m, 9H), 7.0–7.3 (m, 5H)
(8)	 $\mathrm{Ph_2Si(OCH_2CH_2O\underset{\overset{\|}{O}}{C}CH{=}CH_2)_2}$	83	DPSDEA	64.06	5.86	64.08	6.04	3.8 (t, J = 6 Hz, 4H), 4.1 (t, J = 6 Hz, 4H), 5.4–6.3 (m, 6H), 6.8–7.5 (m, 10H)
(9)	 $\mathrm{Ph_2Si[O(CH_2)_4O\underset{\overset{\|}{O}}{C}CH{=}CH_2]_4}$	–	DPSDBA	66.64	6.88	65.82	7.03	1.8 (m, J = 6 Hz, 8H), 3.8 (t, J = 6 Hz, 4H), 4.20 (t, J = 6 Hz, 4H), 5.6–6.30 (m, 6H)
(10)	 $\mathrm{Ph_2CHSi[OCH_2CH_2O\underset{\overset{\|}{O}}{C}C(CH_3){=}CH_2]_3}$	–	BHSTEMA	–	–	–	–	1.9 (s, 9H), 3.8 (t, 6H), 4.13 (t, 6H), 6.13 (s, 6H), 7.2 (m, 10H)
(11)	 $\mathrm{Ph_2Si[OCH_2CH_2O\underset{\overset{\|}{O}}{C}C(CH_3){=}CH_2]_3}$	–	DPSDEMA	–	–	–	–	1.9 (s, 6H), 4.15 (m, 8H), 5.5 (s, 2H), 6.1 (s, 2H), 7.4 (m, 10H)
(12)	$\mathrm{PhCH_2Si[OCH_2OCC(CH_3){=}CH_2]_3}$	–	BSTEMA	–	–	–	–	1.9 (s, 9H), 2.19 (s, 2H), 3.8 (t, 6H), 4.15 (t, 6H), 5.5 (s, 3H), 6.1 (s, 3H), 7.15 (m, 5H)

appropriate silyl chloride in the presence of base. For example,



$$\mathrm{PhCH_2SiCl_3 + HOCH_2CH_2O\underset{\overset{\|}{O}}{C}CH{=}CH_2 \xrightarrow{Et_3N} PhCH_2Si(OCH_2CH_2O\underset{\overset{\|}{O}}{C}CH{=}CH_2)_3}$$

The performance of the new materials was compared with that of hexane-1,6-diol diacrylate (HDDA), trimethylolpropane triacrylate (TMPTA) and tripropyleneglycol diacrylate (TPGDA) for the acrylates, and, for the methacrylates, hexane-1,6-diol dimethacrylate. The samples were coated onto sheets of 70–75 g m^{-2} GNT paper by hand and cured by passing under a Colordry 200 W per linear inch medium-pressure mercury lamp on a conveyor belt. The speed of the belt could be varied and, therefore, for a particular concentration of the photoinitiator (2-hydroxy-2,2-dimethyl-1-phenylethan-1-one, Darocur® 1173), the number of passes under the lamp to achieve a dry coating was determined. In some cases a slightly tacky coating was obtained and further passes were required before a hard film was obtained. The results are shown in *Tables 2* and *3*. Further testing of the films was carried out by

Table 2 Number of passes required of the coated paper under the lamp to give a hard coating using TPGDA and TMPTA^a

	Belt speed (m min^{-1})	Initiator (%) 1	2	4	6
TPGDA	5	*	*	15 (12.5)	8 (12.5)
	10	*	*	*	17 (11.6)
	20	*	*	*	30 (12.5)
	40	*	*	*	*
TMPTA	5	*	*	11 (12.0)	4 (13.2)
	10	*	*	19 (11.6)	7
	20	*	*	*	11 (12.8)
	40	*	*	*	15 (12.0)
HDDA	5	*	*	19 (11.5)	11 (11.8)
	10	*	*	*	30 (11.9)
	20	*	*	*	*
	40	*	*	*	*

^{a}Coatweight given in parentheses (g m^{-2}); * indicates does not give a touch-dry coating after 30 passes

Table 3 Number of passes required of the paper coated with silicon acrylates under the lamp in order to produce a hard coating[a]

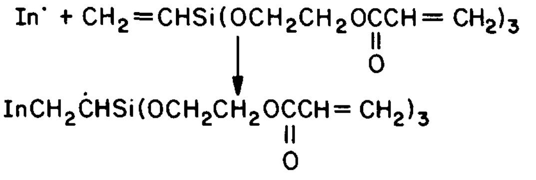
	Belt speed (m min^{-1})	Initiator (%)			
		1	2	4	6
DSTEA	5	*	*	20 (11.8)	6 (12.5)
	10	*	*	*	17 (12.1)
	20	*	*	*	25 (11.8)
	40	*	*	*	*
PSTEA	5	21 (13.2)	14 (13.2)	4 (12.3)	1 (12.8)
	10	*	30 (12.8)	10 (12.4)	3 (12.9)
	20	*	*	21 (12.5)	5 (12.7)
	40	*	*	30 (12.7)	6 (12.3)
PS (TONE-100)	5	*	15 (10.8)	16 (10.8)	8 (11.6)
	10	*	*	27 (11.2)	17 (11.2)
	20	*	*	9[b] (10.8)	25 (11.6)
	40	*	*	30 (11.2)	30 (10.2)
DPSDEA	5	*	*	21 (48.8)	5 (59.2)
	10	*	*	30 (54.4)	6 (53.2)
	20	*	*	*	14 (56.8)
	40	*	*	*	15 (57.2)
VSTEA	5	*	*	19 (11.2)	5 (10.8)
	10	*	*	*	12 (10.8)
	20	*	*	*	28 (10.4)
	40	*	*	*	*
BSTEA	5	20 (11.7)	14 (13.1)	6 (13.0)	1 (13.1)
	10	*	*	18 (12.8)	3 (13.0)
	20	*	*	26 (12.6)	6 (13.0)
	40	*	*	*	8 (12.2)
BHSTEA	5	4 (13.2)	3 (14.4)	2 (14.4)	2 (14.0)
	10	9 (13.2)	6 (12.4)	4 (13.6)	2 (12.8)
	20	15 (14.4)	8 (13.2)	5 (13.2)	3 (12.8)
	40	19 (14.0)	11 (12.0)	7 (12.8)	3 (14.8)

[a] See footnote to *Table 2*

[b] Tacky

examining the solvent resistance of selected films (*Table 4*).

Solvent resistance is partly a measure of the extent of crosslinking in the film, but is also affected by the solubility of the polymer backbone and pendant groups. Thus, the films produced by TPGDA, which contain ether groups in the backbone, have a poor solvent resistance. The low solvent resistance of the DSTEA no doubt reflects the more open structure of the film owing to the presence of the dodecyl group and the solubilizing effect that the latter group will have. Similarly the slow cure and poor solvent resistance of films produced from the PS(TONE-100) is probably due to both the more open structure of the film and the solubilizing contribution of the ester groups. The one result that does not accord with the above rationale is the relatively low reactivity of the vinylsilicon triacrylate. With this compound there is the possibility that the vinyl group traps some of the initiating radicals to give a radical that for steric reasons is inefficient at propagating polymerization.



$$\mathrm{In^{\bullet} + CH_2{=}CHSi(OCH_2CH_2O\overset{\displaystyle O}{\overset{\|}{C}}CH{=}CH_2)_3} \longrightarrow \mathrm{InCH_2\dot{C}HSi(OCH_2CH_2O\overset{\displaystyle O}{\overset{\|}{C}}CH{=}CH_2)_3}$$

Since the silicon acrylates are often more reactive than materials such as TPGDA, an investigation was therefore carried out to determine whether silicon-containing methacrylates would cure at acceptable speeds (*Table 5*). In order to compare the reactivity of the methacrylates

Table 4 Solvent rub test results for u.v.-cured films

Monomer	Initiator (%)	Belt speed (m min^{-1})	No. of passes	No. of passes to cause failure in rub test
TPGDA	4	5	15	40
	6	10	17	15
HDDA	4	5	19	>500
	6	10	30	>500
DSTEA	4	5	20	90
	6	10	17	85
PSTEA	1	5	21	>500
	2	10	30	>500
	4	20	21	>500
	6	40	6	>500
BHSTEA	1	5	20	>500
	2	5	14	>500
	4	20	26	>500
	6	40	8	>500

Table 5 Number of passes required under the lamp to produce a tack-free coating of methacrylates[a]

	Belt speed (m min^{-1})	Initiator (%)			
		1	2	4	6
PSTEMA	5	*	*	14 (64)	6 (50.8)
	10	*	*	20 (62.4)	13 (50.8)
	20	*	*	23 (79.2)	17 (63.6)
	40	*	*	26 (57.2)	19 (58.6)
BSTEMA	5	*	*	*	16 (12)
	10	*	*	*	30 (12)
	20	*	*	*	*
	40	*	*	*	*

[a] HDDMA and TMPTMA did not cure under any of the conditions

Table 6 Percentage degree of cure (measured by i.r.) of various silicon acrylates upon u.v. irradiation[a] as a function of number of passes under the lamps

	Number of passes					
Compound	0	1	3	5	7	10
TMPTA[b]	0	65.9	67.0	68.1	69.8	72.0
DPSDEA	0	86.2	88.6	91.0	92.0	93.5
DPSDBA	0	84.9	85.4	85.8	86.4	86.9
BSTEA	0	70.9	75.9	76.9	77.9	79.4
MSTEA	0	64.0	68.0	68.0	68.2	68.4

[a] 3.3% photoinitiator, two lamps, line speed 8.3 m min^{-1}
[b] Used as reference compound

Table 7 Percentage degree of cure (measured by i.r.) of various silicon methacrylates upon u.v. irradiation[a] as a function of number of passes under the lamps

	Number of passes					
Compound	0	1	3	5	7	10
TMPTMA[b]	0	0.9	2.7	2.7	5.5	5.5
DPSDEMA	0	36.3	58.0	59.0	61.5	62.4
BHSTEMA	0	19.7	49.8	53.7	58.1	60.9
BSTEMA	0	13.9	23.8	30.7	38.2	40.5

[a] 3.3% photoinitiator, two lamps, line speed 8.3 m min^{-1}
[b] Used as reference compound

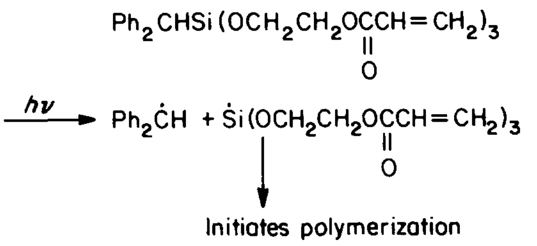
with that of the acrylates, films of the materials were applied to potassium bromide discs and then subjected to u.v. curing. The degree of cure was assessed by i.r. transmission spectroscopy. The results are presented in *Tables 6* and *7*.

The fact that some silicon-containing acrylates cure faster than TMPTA leads to a comparison being made of the rate of cure (as measured by the number of passes under the lamp to give a tack-free coating) of a pigmented (titanium dioxide–rutile) acrylate with that of a pigmented sample of the silicon-containing acrylate. The results are summarized in *Table 8*.

DISCUSSION

Examination of *Tables 2* and *3* shows that the PSTEA, BSTEA and BHSTEA triacrylates and the PS(TONE-100) cure to give tack-free films faster than either TPGDA, HDDA and TMPTA. The VSTEA and DPSDEA cured at comparable rates to TPGDA and TMPTA. The increase in reactivity, where observed, may be attributable to the compounds being trifunctional acrylates, whereas two of the reference materials are difunctional. Certainly, the greater degree of functionality will lead to more rapid crosslinking and hence should lead to a more rapid attainment of a tack-free coating[3,8]. The finding that the diphenylsilicon diacrylate cures more slowly than the phenylsilicon triacrylate supports this line of thinking. However, it should be noted that TMPTA, a trifunctional acrylate, shows similar reactivity to TPGDA and HDDA, and therefore the extent of acrylate functionality can at best be considered as only partly responsible for the greater reactivity of the silicone triacrylates.

The most reactive material as far as giving a tack-free coating is concerned was shown to be the diphenylmethylsilicon triacrylate (*Table 3*). This compound was found to cure in the absence of a photoinitiator, albeit far more slowly than when a photoinitiator was present. This would indicate that reactions of the following type may occur:



Whether or not the stabilized diphenylmethyl radical can initiate polymerization is a moot point[2]. The reactivity of the benzylsilicon triacrylate may also be in part due to photoinduced homolysis of the benzylsilicon bond. The reactivity of this compound is similar to that of the phenylsilicon triacrylate, in which homolysis of a silicon–carbon bond is, however, much less likely to occur. One factor that must affect film-forming characteristics is the size of the groups attached to the silicon atom. Presumably, increasing the size of the attached groups will lead to a decrease in the density of the polymer formed and hence require a larger number of crosslinks to be formed before the T_g value becomes sufficiently high to facilitate film formation. This rationale is borne out in the solvent rub test data (*Table 4*), where it can be seen that the dodecylsilicon triacrylate gives films with a very poor solvent resistance.

An interesting and important feature of the films formed from the trifunctional silicon acrylates is the lack of visible shrinkage upon curing. The control compounds such as TMPTA display this effect in a very marked manner, often leading to cracked films[1,10].

Incorporation of titanium dioxide into the films led to there being little differences in the rate of cure to give tack-free coatings between TMPTA and PSTEA (*Table 8*). Comparing these results with those in *Table 2*, it appears that the presence of titanium dioxide has increased the rate of cure of TMPTA but has hardly affected that of PSTEA. It is difficult to say precisely how the presence of titanium dioxide will affect film-forming

Table 8 Number of passes under the lamp required to produce a tack-free coating of titanium dioxide (rutile, 12%) pigmented acrylates

	Belt speed (m min^{-1})	Initiator (%)			
		1	2	4	6
TMPTA	5	*	*	7 (13.6)	3 (16.4)
	10	*	*	23 (11.3)	6 (12.8)
	20	*	*	*	10 (14.0)
	40	*	*	*	15 (16.4)
PSTEA	5	*	*	6 (15.2)	2 (14.0)
	10	*	*	13 (15.2)	5 (14.0)
	20	*	*	15 (14.8)	6 (14.0)
	40	*	*	20 (14.8)	8 (14.0)

properties. However, its presence should reduce the number of photoinitiator molecules being excited, which in turn could reduce the rate of cure. Perhaps the high light intensities used for the curing and internal reflection offset this effect.

Not surprisingly, curing of the methacrylates to give tack-free films (*Table 5*) was a much slower process than for the corresponding acrylates. Even the silicon-containing materials were retarded to a considerable degree and the only satisfactory results were obtained with PSTEMA.

Following the rate of double-bond consumption of the acrylates and methacrylates upon exposure to u.v. radiation, the presence of a photoinitiator proved to be very informative (*Tables 6* and *7*). For all the acrylates, one pass leads to a very high percentage of the double bonds available for consumption being utilized. If one takes 10 passes as leading to almost complete cure, it can be seen that the number of residual double bonds is dependent upon the structure of the acrylate. The latter will determine the rate of increase in viscosity as the double bonds are consumed. Clearly, a material that undergoes a large viscosity increase for consumption of relatively few double bonds will give rise to a film in which little movement is possible, thereby decreasing the probability of radical–double bond interaction. Consequently, such systems give tack-free films, which often contain a high percentage of unreacted double bonds. The order of reactivity of the silicon acrylate and TMPTA based on double-bond consumption is different to that of rate of cure to give tack-free films (*Table 2*). Some variations are to be expected because of the difficulty in obtaining consistent coatweights. (From *Table 2* it can be seen that the coatweights for DBDEA were much higher than for the other compounds shown in the table, and this could account for the apparent slowness of cure of this material.) In accord with previous work, the diacrylates led to greater double-bond consumption upon cure (e.g. at 10 passes) compared with the triacrylates[8]. The curing of BSTEA led to more double-bond consumption than either MSTEA or TMPTA. This may account for the good performance of this material as shown in *Table 2*, although one has to recognize that double-bond consumption is not the only factor that controls film-forming properties. It will be noted that DPSDBA showed a slightly lower rate of double-bond consumption than DPSDEA. Further work using more carefully controlled conditions is required before any firm conclusions can be drawn concerning the relative reactivity of these two closely related compounds. U.v. irradiation of the methacrylates led to very slow double-bond consumption, thereby explaining why such materials require long exposure periods in order to give tack-free films. The results show the greater reactivity of the silicon compounds, with DPSDEMA leading the field.

The described results show that the silicon di- and triacrylates give tack-free films more rapidly than many of the conventionally used di- and triacrylates. This may, in part, be due to them acting as sources of radicals owing to light-induced carbon–silicon bond cleavage, but, more importantly, the silicon atoms appear to allow more molecular conformations, which are required to give a high crosslink density. An unusual, unexplained benefit of incorporation of silicon is the ability of the latter to ameliorate reticulation.

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