Journal of Photochemistry and Photobiology A: Chemistry 141 (2001) 85–91

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Using linear and branched polysilanes for the photoinitiated polymerization of a commercial silicone-acrylate resin. A real time FTIR study

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Received 12 March 2001; accepted 16 March 2001

Abstract

The photo-crosslinking of a silicone-based oligomer, bearing pendant acrylate groups, has been carried out using linear polysilanes (poly(methyl phenyl silane), poly(methyl-*n*-propyl silane), poly(di-*n*-hexyl silane)) and a branched one, poly(*p*-butylphenyl phenyl silane-co-phenyl silyne), as initiators. The curing rate was measured with the aid of the real time Fourier transformed infrared spectroscopy. Apart from the neat oligomer also formulations containing reactive diluents, i.e. acrylic and vinyl ether monomers were photo-cured. An excellent curing performance (final conversion of about 95%) was achieved with a 1:1 (w:w) blend of the oligomer with 2-ethyl hexyl methacrylate (EHMA). *n*-Butyl vinyl ether (BVE) was found to copolymerize with the pendant acrylate groups. Moreover, in the presence of diphenyl iodonium chloride it homopolymerized simultaneously by a cationic mechanism. In this way interpenetrating structures were formed. The iodonium ions oxidize some of the photo-generated silyl radicals thus producing initiating cations.

Keywords: Polysilanes; Macromolecular photoinitiators; FTIR; Silicone-acrylate resins

1. Introduction

UV-irradiation of polysilanes gives rise to silyl macroradicals, which are capable of initiating radical polymerizations [1–4]. The reactivity of these silyl radicals towards various unsaturated compounds in solution at room temperature was the objective of a recent investigation [5]. However, the conclusions arrived at in those studies cannot be transferred straightaway to viscous media where diffusion is restricted. This applies also to silicone acrylate systems that are applied in technical processes where curing is frequently performed in an elegant manner by UV-irradiation at room temperature. For this reason, it was the goal of our work to evaluate the initiator behaviour of polysilanes in the photo-crosslinking of a commercial oligomeric silicone resin bearing pendant acrylate groups. The present paper reports on studies regarding the initiator efficiency of several linear polysilanes (poly(methyl phenyl silane), poly(methyl n-propyl silane, poly(di-n-hexyl silane)) and a branched one, poly(*p*-butylphenyl phenyl silane-co-phenyl silyne). As can be seen from Fig. 1(b), the latter polymer possesses a broad absorption band extending from the UV to the visible wavelength range which makes it interesting for applications. Since frequently practical applications afford an adjustment regarding the viscosity of the formulation also experiments with systems containing apart from the silicon acrylate resin also a viscosity reducer were carried out. Relevant results obtained with acrylic monomers and *n*-butyl vinyl ether as reactive diluents are also reported in this paper.

The disappearance of double bonds during the photocuring of the formulations was followed by real time Fourier transformed infrared spectroscopy (FTIR) a non-destructive technique that has spread out widely in recent years [6–10]. By monitoring changes in the characteristic monomer and/or polymer IR absorption bands it allows to follow fast photopolymerization processes continuously.

In connection with the present paper former work by other authors is noticeable [11–14]. It pertains to the photochemical crosslinking of (meth)acrylate-silicones using conventional low molar mass photoinitiators and includes kinetic and mechanistic investigations.

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PII: S1010-6030(01)00424-5

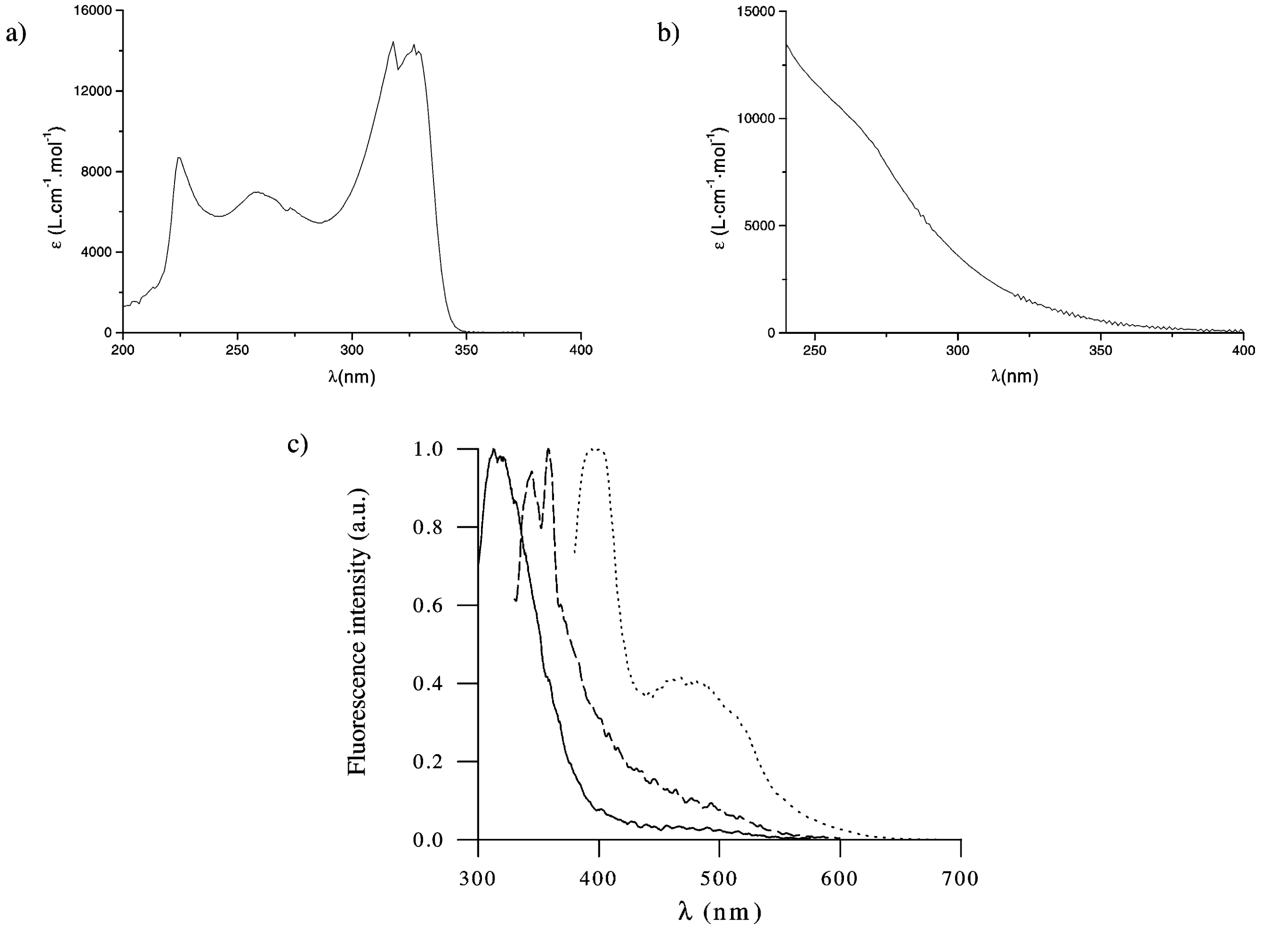


Fig. 1. Optical absorption spectra of poly(methyl phenyl silane) (a) and poly(*p*-butylphenyl phenylsilane-co-phenyl silyne) (b). (c) Emission spectra of poly(*p*-butylphenyl phenyl silane-co-phenyl silyne). Solvent: THF. (—) $\lambda_{exc} = 290\,nm$; (– – –) $\lambda_{exc} = 325\,nm$; (---) $\lambda_{exc} = 380\,nm$.

2. Experimental

2.1. Materials

Crodamer UVS-500, an oligomeric silicone bearing pendant acrylate groups (molar mass: 6000 g/mol, ester content: $1.68 \times 10^4\,mol/g$ resin, viscosity at 25°C: 20 Pa s) was obtained from Croda Resin. Crodamer UVS-500 is compatible with the reactive diluents listed in Table 1, that were distilled prior to use. Diphenyl iodonium chloride, purchased from Aldrich, was used as received. Linear polysilanes (polysilylenes) were prepared by the Wurtz coupling method with the aid of the corresponding diorgano dichlorosilanes in the presence of sodium dispersed in toluene [15]. In

Table 1
Reactive diluents

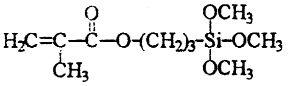
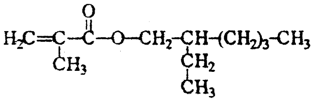
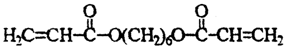
Monomer	Structure	Acronym
n-Butyl vinyl ether	$H_2C{=}CH{-}O{-}(CH_2)_3{-}CH_3$	BVE
3-(Trimethoxysilyl) propyl methacrylate	 $H_2C{=}C(CH_3){-}C({=}O){-}O{-}(CH_2)_3{-}Si(OCH_3)_3$	TMSPMA
2-Ethylhexyl methacrylate	 $H_2C{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH(CH_2CH_3){-}(CH_2)_3{-}CH_3$	EHMA
Diethylenglycol divinyl ether	$H_2C{=}CH{-}O{-}(CH_2)_2{-}O{-}(CH_2)_2{-}O{-}CH{=}CH_2$	DEDVE
1,6-Hexanediol diacrylate	 $H_2C{=}CH{-}C({=}O){-}O(CH_2)_6O{-}C({=}O){-}CH{=}CH_2$	HDDA

Table 2
Polysilanes

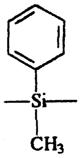
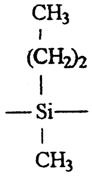
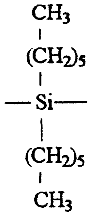
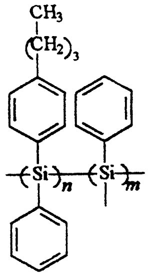
Polysilane	Structure	$\bar{M}_n$ ($\mathrm{g\,mol^{-1}}$)	$\bar{M}_w/\bar{M}_n$	λ_{max} (nm) (log ε)
Poly(methyl phenyl silane), MePhSi		5.2×10^4	1.4	339 (3.98)
Poly(methyl *n*-propyl silane), MePrSi	 $\mathrm{CH_3(CH_2)_2{-}Si(CH_3){-}}$	4.3×10^4	1.9	306 (3.72)
Poly(di-*n*-hexyl silane), DiHxSi	 $\mathrm{{-}Si[(CH_2)_5CH_3]_2{-}}$	5.9×10^5	2.0	317 (3.99)
Poly(*p*-butylphenyl phenyl silane-co-phenyl silyne), *p*-BuPhPhSi$)_m$-co-(PhSi$)_n$		2.6×10^3	2.5	–

Table 2, number average molar mass and polydispersity values are listed together with the wavelengths at the maximum absorption. A branched polysilane, poly(*p*-butylphenyl phenyl silane-co-phenyl silyne), (*p*-BuPhPhSi$)_m$-co-(PhSi$)_n$, was prepared as described in the following section.

2.1.1. Synthesis and characterization of a branched polysilane

The synthesis of (*p*-BuPhPhSi$)_m$-co-(PhSi$)_n$ was based on the copolymerization of *p*-butylphenyl phenyl dichlorosilane and phenyl trichlorosilane. The dichlorosilane was synthesized by reacting the corresponding *p*-alkylphenyl lithium reagent with phenyltrichlorosilane in toluene at room temperature for 3 h. The required lithium reagent was generated from the corresponding aryl bromide using *tert*-butyl lithium following the conventional procedure. The purified branched polysilane was obtained as a yellow powder after three precipitations in the THF/methanol solvent/non-solvent system. It was dried under vacuum to constant weight. (*p*-BuPhPhSi$)_m$-co-(PhSi$)_n$ was characterized by ^{1}H-NMR measurements as follows: ^{1}H-NMR ($\mathrm{CDCl_3}$) δ (ppm): 7.5 ($\mathrm{H_{ar}}$), 4 ($\mathrm{-CH_2-O-}$), 2.4 ($\mathrm{CH_2-Ph}$), 1.6 ($\mathrm{CH_2-}$), 1.25 ($\mathrm{CH_2}$) and 0.9 ($\mathrm{CH_3-}$). The integration of the ^{1}H-NMR signals of the benzylic and aromatic protons results in a *m*/*n* ratio equal to unity, indicating a high content of branched structures in the polymer. The signal at 4 ppm is assigned to methylenic protons of alkoxy end groups. Number average molar mass ($\bar{M}_n = 2.6 \times 10^3\ \mathrm{g\,mol^{-1}}$) and polydispersity ($\bar{M}_w/\bar{M}_n = 2.5$) were determined by GPC using linear polystyrenes of narrow molar mass distribution as standards. Notably, the real molar mass of the polysilanes could be higher because of the lower hydrodynamic volume of branched polymers in comparison to that of linear ones.

In contrast to the UV-absorption spectrum of linear polysilanes with the typical sharp σ–σ^* absorption band (see spectrum of MePhSi in Fig. 1(a)), the spectrum of (*p*-BuPhPhSi$)_m$-co-(PhSi$)_n$ shown in Fig. 1(b) exhibits a broad featureless band extending into the visible region. It seems that the form of this spectrum reflects the existence of branched silicon moieties. This is confirmed by the fluorescence emission spectra generated at different excitation wavelengths shown in Fig. 1(c). At $\lambda_{exc} = 290$ and 325 nm the profiles resemble those of linear polysilanes. However, at $\lambda_{exc} = 380$ nm a new broad fluorescence band appears showing a maximum at 480 nm and a tail extending to 650 nm. The latter is assigned to branched structures. Furukawa et al. [16] have proven that the photoluminescence of similar polysilane networks originates from the backbone itself and not from impurities, monomer traces or photodegradation products. The broadness of the spectrum has been suggested to originate from the size variety of the macromolecules.

The thermogravimetric analysis of (p-BuPhPhSi)$_m$-co-(PhSi)$_n$ gave rise to a high yield of non-volatile residue (44%) probably due to a Si/C ratio being more close to unity than that of linear polysilanes.

2.2. Sample preparation

Photocurable formulations were prepared by dissolving the polysilanes (1–3 wt.%) in the neat (solvent-free) acrylate-silicone oligomer. Uniform samples of controlled thickness were prepared by casting the photocurable formulation on an aluminum foil using a polyethylene spacer of 40 μm thickness. The films were covered with a polyethylene film (40-μm thick) that did not absorb IR light at the frequencies selected to follow up the photopolymerization reaction. The function of the PE film was to prevent the diffusion of oxygen from the atmosphere into the sample during the irradiation at room temperature.

2.3. Fourier-transformed infrared spectroscopy in real time, FTIR

The samples placed over a specular reflection accessory (SPECAC) in the compartment of an infrared spectrophotometer (Nicolet 520) were simultaneously exposed to a UV photolyzing and an IR analyzing light beam. The IR spectrophotometer was provided with a Fourier transformed algorithm. The photolyzing light was generated by a medium pressure mercury lamp (Sylvania, 400 W) and was conducted through a flexible fibre optic (Macam-Flexicure system) to the IR compartment. The end of the fibre optic was positioned properly to ensure that the UV-irradiation was incident onto the sample at an angle of 45°. The light intensity at 313 nm (1.5 mW/cm^2) was measured with a radiometer (International Light IL700). Infrared spectra (4 cm^{-1} resolution) were recorded at different irradiation times. The spectrophotometer was operated in the absorbance mode and the detection wave number was set either at 1637 cm^{-1} to monitor the disappearance of both the acrylate and the vinyl ether double bonds or at 1410 cm^{-1} to monitor that of the acrylate double bond [17]. The carbonyl band was used as internal standard for kinetic calculations. The decrease in the absorbance as a function of time was recorded by means of a software programme self-developed to record real time data. The limiting factor of the device is the interferometer mirror movement (acquisition time = 200 ms) which allows a correct kinetic analysis of polymerization processes occurring to an extent of 50% conversion in about 2 s. Since the IR absorbance is proportional to the monomer concentration, conversion versus time profiles were directly obtained from the curves recorded. The degree of conversion, α, can be expressed by equation [1]:

$$\alpha = \frac{A_0 - A_t}{A_0} \tag{1}$$

where A_0 is the initial absorbance at the chosen frequency and A_t the absorbance value at irradiation time t. Polymerization rates (in mol l^{-1} s^{-1}) were determined from the slope of the initial linear portion of the conversion versus time curves, according to the following equation:

$$R_\mathrm{p} = [X] \times \frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{2}$$

where $[X]$ is the initial concentration of C=C double bonds in mol l^{-1}.

2.4. Instrumentation

Average molar masses were measured using a gel permeation chromatography (GPC) set-up. It consisted of a Waters high-pressure pump (model M-45), a U6K injector and four Ultrastyragel columns arranged in series (pore size: 500, 10^3, 10^4 and 10^5 Å). The calibration was carried out with a series of poly(styrene) standards having narrow molar mass distribution. *Spectroscopic measurement*: UV spectra were recorded by means of a Perkin-Elmer UV-spectrophotometer (model 250) and fluorescence spectra were recorded on a Perkin-Elmer spectrofluorimeter (model LS-50B). *^{1}H-NMR spectra* were recorded in $CDCl_3$ solution on a Bruker instrument (model AM-200) operated at 200 MHz. *Thermogravimetric analysis* was carried out with a Perkin-Elmer thermobalance (model TGA7).

3. Results

3.1. Photocuring of undiluted formulations

In Fig. 2(a)–(c) kinetic profiles referring to the polymerization of Crodamer UVS-500 under polychromatic light irradiation are shown. Polysilanes with different substituents served as photoinitiators. The curves were obtained by monitoring the absorption decrease of the band at 1637 cm^{-1} corresponding to the frequency of the stretching vibration of the double bonds. The shape of the curves indicates the existence of two stages. A rapid first stage which is followed up by a slow stage. The polymerization rate obtained from the slope of the initial linear portion of the curves and the final conversion are given in Table 3. Notably, the silicone-acrylate resin was photo-cured under air. Therefore, the presence of molecular oxygen is very likely to be responsible for the fact that the limiting conversion is lower than 100%. From similar studies with conventional photoinitiators it is known [9] that O_2 prevents the photo-crosslinking of silicon acrylate oligomers and that at low oxygen concentrations the rate of polymerization

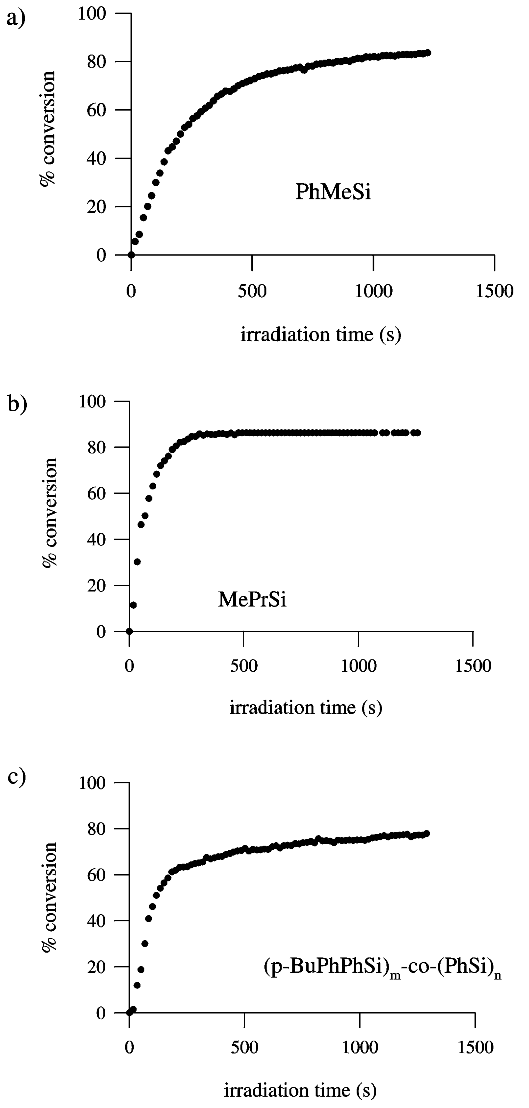


Fig. 2. Kinetic profiles demonstrating the photocuring of neat Crodamer UVS-500 containing different polysilanes with polychromatic light. Photoinitiator: (a) MePhSi, (b) MePrSi and (c) (p-BuPhPhSi)$_m$-co-(PhSi)$_n$. Film thickness: 40 μm.

is retarded and the limiting conversion is reduced. Such a situation very likely pertains to the present experiments. Although diffusion of oxygen from the outside was strongly retarded by the polyethylene sheet coated onto the resin it was not completely prevented. Therefore, oxygen played still a role during the photocuring of the silicon acrylate.

Table 3
Photocuring of neat Crodamer UVS-500 containing different polysilanes

Polysilane	x_∞ (%)[a]	$R_p \times 10^2$ (mol l^{-1} s^{-1})
PhMeSi	84	2.3
MePrSi	86	6.3
(p-BuPhPh)$_m$-co-(PhSi)$_n$	79	3.6

[a] Limiting conversion.

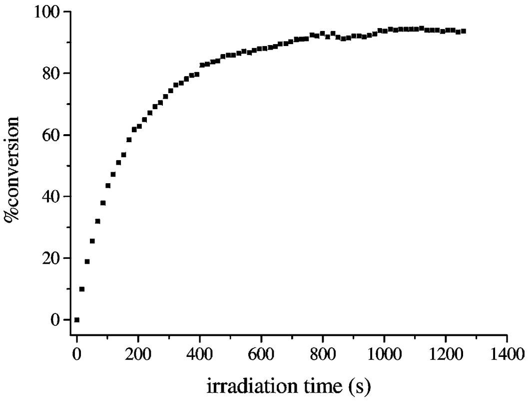


Fig. 3. Kinetic profile demonstrating the photocuring of the system Crodamer UVS-500/EHMA (1:1, w:w) with polychromatic light. Photoinitiator: poly(di-n-hexyl silane). Film thickness: 40 μm.

3.2. Photocuring of formulations containing reactive diluents

3.2.1. Radical polymerization

Formulations containing a reactive diluent and Crodamer UVS-500 in a 1:1 (w:w) ratio were studied. The photoinitiator was the polysilane DiHxSi. A typical conversion time profile obtained with 2-ethyl hexyl methacrylate (EHMA) is shown in Fig. 3. In this case the final conversion was about 95%. Other monomers (see Table 1) such as 1,6-hexanediol diacrylate (HDDA) and 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) were also examined. However, the final conversion was lower for reasons that have not yet been elucidated.

3.2.2. Simultaneous radical and radical promoted cationic polymerization

Vinyl ethers are known [18] to homopolymerize by a cationic mechanism only, although copolymerizations with acrylates and other monomers via a free radical mechanism are possible [19]. In the present work formulations containing n-butyl vinyl ether (BVE) and Crodamer UVS-500 in a 1:1 (w:w) ratio and poly(di-n-hexyl silane) as photoinitiator were tested and found to be curable upon irradiation with polychromatic light. The initial ratio of vinyl ether to acrylate unsaturations was about 60, and, since the ratio of the extinction coefficients $\varepsilon_{\mathrm{BVE}}/\varepsilon_{\mathrm{acryl}}$ at 1637 cm^{-1} is about 4, the initial absorption at this wavelength corresponded to 99.4% to vinyl ether unsaturations. Therefore, by neglecting the small contribution of acrylate groups at 1637 cm^{-1} the conversion of the two unsaturated components could be monitored conveniently at 1637 cm^{-1} (BVE) and at 1410 cm^{-1} (acrylate). Typical results concerning the curing of formulations in the absence and presence of diphenyl iodonium chloride are presented in Fig. 4. In the absence of the onium salt the final conversion of BVE was about 60% and that of acrylate about 30% (see Fig. 4(b)). Interestingly, the addition of diphenyl iodonium chloride to the formulation

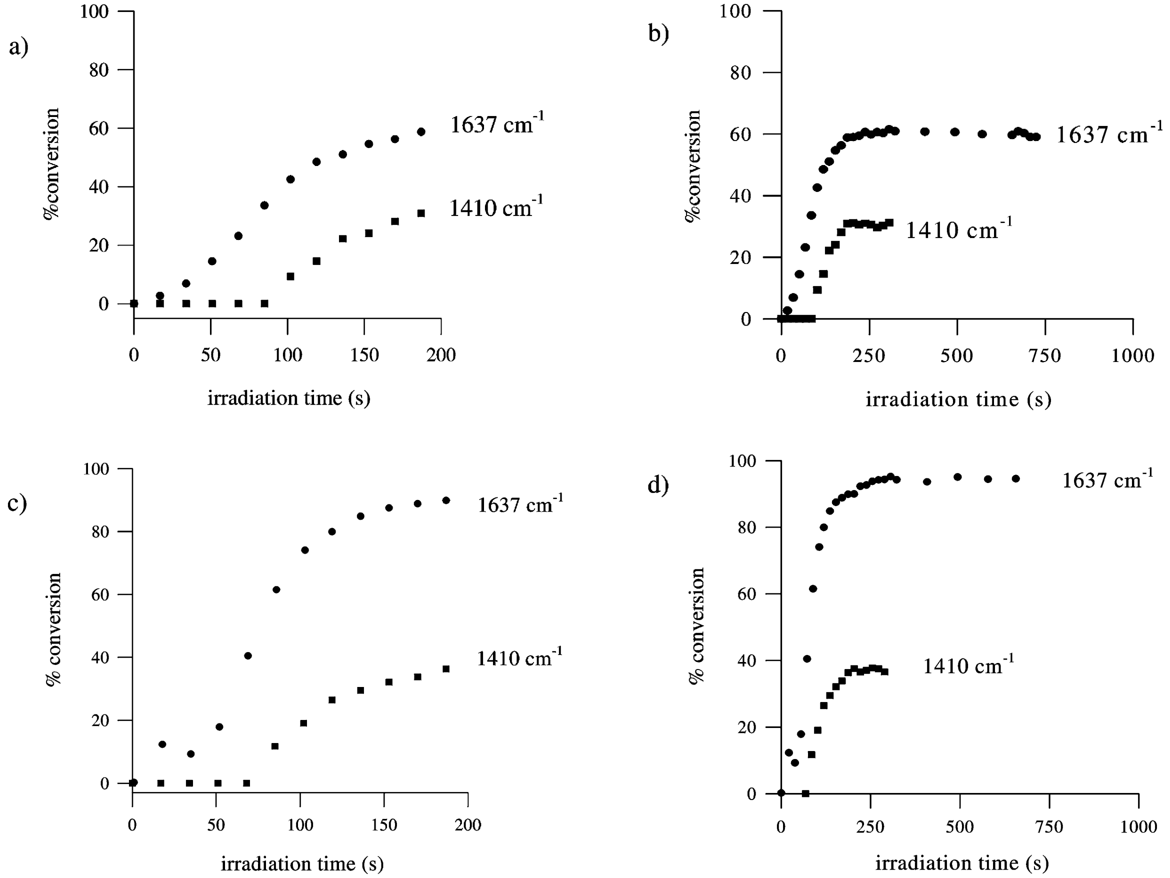


Fig. 4. Kinetic profiles demonstrating the photocuring of the system Crodamer UVS-500/BVE (1:1, w:w) by irradiation with polychromatic light in the absence (a and b) and presence (c and d) of diphenyl iodonium chloride. Photonitiator: DiHxSi. Concentration of diphenyl iodonium chloride: 3.2×10^{-5} mol l^{-1}. Film thickness: 40 μm.

resulted in final conversions of about 95% (BVE) and about 35% (acrylate) as can be seen from Fig. 4(d). The increase in the final conversion of butyl vinyl ether upon the addition of the onium salt is taken as evidence for cationic polymerization of the monomer occurring in the formulation. Noticeably, BVE is also converted in the absence of the onium salt indicating that acrylate groups copolymerize with BVE via a free radical mechanism. It is seen from Fig. 4(a) and (c) that the conversion-time profiles recorded both in the absence and presence of the onium salt exhibit induction periods. In the case of free radical polymerizations induction periods are indicative of the presence of small amounts of molecular oxygen and in the case of cationic polymerizations induction periods can be caused by small amounts of water or other impurities being reactive towards cationic species.

The idea for this experiment arose on the basis that polysilanes in conjunction with appropriate diphenyl iodonium and pyridinium ions are capable of acting as photoinitiators for the free radical promoted cationic polymerization of vinyl ethers [20,21]. The onium ions oxidize photogenerated macrosilyl radicals thus producing cationic species capable of initiating cationic polymerizations [22]. Actually, it is quite noticeable, that the counter ion of the onium salt used here is not a non-nucleophilic complex anion such as hexafluoro phosphonate or arsenate but the chloride ion, which is highly nucleophilic and, therefore, highly reactive towards initiating or propagating cations. In accordance with this fact is the observation, that BVE did not polymerize in a silicone-acrylate-free system containing diphenyl iodonium chloride and poly(di-*n*-hexyl silane) only. The phenomenon of the unreactivity of the Cl^- ion in silicone-acrylate formulations is explainable on the basis that the chloride ion cannot be solvated in unpolar silicone-based formulations to an extent that allows independent movements in the system. Therefore, the Cl^- ion is forced to stay permanently in the close neighbourhood of the positive partner ion and thus its reactivity is strongly reduced.

4. Conclusions

This paper demonstrates that linear polysilanes can be employed as efficient photoinitiators for the photocuring of commercial silicone-based formulations at wavelengths of incident light ranging up to about 350 nm. This range can be extended to wavelengths up to about 400 nm if branched polysilanes are used. The test material used in this investigation was Crodamer UVS-500, an oligomeric silicone bearing pendant acrylate groups. With respect to practical applications also formulations containing reactive diluents were employed. Of interest, in this connection, is butyl vinyl ether that was found to copolymerize with the silicone-based acrylate groups by a free radical mechanism and, moreover, to homopolymerize by a cationic mechanism provided the formulation contained, apart from the polysilane, also diphenyl iodonium chloride, an electron acceptor capable of oxidizing silyl macroradicals generated by the photolysis of the polysilane. Noticeably, the possibility of inducing the simultaneous free radical crosslinking of the silicon acrylate and the cationic polymerization of a vinyl ether opens up a new way of generating interpenetrating structures with the prospect of improving material properties.

Acknowledgements

The authors thank the Comisión Interministerial de Ciencia y Tecnología (CICYT) for financial support (MAT2000-1671) as well as the Spanish Ministerio de Educación y Cultura and the International Bureau Karlsruhe for the travel grants provided within the frame of Acción Integrada Spain–Germany.

References

[1] R. West, A.R. Wolff, D.J. Peterson, J. Radiat. Curing 13 (1986) 35.
[2] A.R. Wolff, R. West, Appl. Organomet. Chem. 1 (1987) 7.
[3] I. Kminek, Y. Yagci, W. Schnabel, Polym. Bull. 29 (1992) 277.
[4] T.C. Chang, Y.S. Chiu, H.B. Chen, S.Y. Ho, J. Chin. Chem. Soc. 41 (1994) 843.
[5] A. Alonso, C. Peinado, A.E. Lozano, F. Catalina, C. Zimmermann, W. Schnabel, J. Macromol. Sci. A 36 (1999) 605.
[6] C. Decker, K. Moussa, Makromol. Chem. 189 (1988) 2381.
[7] C. Decker, K. Moussa, Macromolecules 22 (1989) 4455.
[8] C. Decker, K. Moussa, Makromol. Chem. 191 (1990) 963.
[9] U. Müller, J. Macromol. Sci. A 31 (1994) 1905.
[10] F. Catalina, M. Shah, M. Edge, N.S. Allen, Rev. Plast. Mod. 624 (1996) 480.
[11] U. Müller, H.J. Timpe, J. Neuenfeld, Makromol. Chem., Rapid Commun. 10 (1989) 539.
[12] U. Müller, C. Vallejos, Angew. Makromol. Chem. 206 (1993) 171.
[13] U. Müller, J. Macromol. Sci. A 33 (1996) 33.
[14] U. Müller, J. Photochem. Photobiol. A 102 (1997) 237.
[15] R.D. Miller, J. Michl, Chem. Rev. 89 (1989) 1359.
[16] K. Furukawa, M. Fujino, N. Matsumoto, Macromolecules 23 (1990) 3423.
[17] C. Decker, K. Moussa, J. Appl. Polym. Sci. 34 (1987) 1603.
[18] H.G. Elias, Makromoleküle, Hüthig & Wepf, Basel, 1971.
[19] G. Odian, Principles of Polymerization, 3rd Edition, Wiley, New York, 1991.
[20] W. Schnabel, in: N.S. Allen, I.R. Bellobono, E. Selli (Eds.), Current Trends in Polymer Photochemistry, Ellis Horwood, Chichester, UK, 1995.
[21] W. Schnabel, Macromol. Rapid Commun. 21 (2000) 628.
[22] Y. Yagci, I. Kminek, W. Schnabel, Eur. Polym. J. 28 (1986) 35.