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SYNTHESIS AND PHOTOCROSSLINKING OF BENZYL (METH)ACRYLATE SUBSTITUTED POLYDIMETHYLSILOXANES: INFLUENCE OF PHOTOINITIATOR NATURE

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SYNTHESIS AND PHOTOCROSSLINKING OF BENZYL (METH)ACRYLATE SUBSTITUTED POLYDIMETHYLSILOXANES: INFLUENCE OF PHOTOINITIATOR NATURE

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ABSTRACT

The photoinduced crosslinking of silicones containing benzyl acrylate and benzyl methacrylate groups in the presence of different usual radical photoinitiators (TEPO, Darocur[®] 1173, Darocur 4265) and azo-containing polydimethylsiloxanes or mono- and bis(phenylmaleimide) functionalized disiloxanes has been investigated by photocalorimetric measurements. The influence of photoinitiator type, temperature and of the exposure time on the photocrosslinking kinetics was followed.

Key Words: Benzyl (meth)acrylate functionalized polysiloxanes; Photocrosslinking; Siloxane photoinitiators

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INTRODUCTION

Silicone polymers have received much attention as high performance and functional polymers. Polysiloxanes with excellent low temperature flexibility and high temperature stability derived from the Si-O-Si skeleton have been widely used as elastomers and plastics in various industries. Silicon containing photoreactive compounds are also expected as new functional materials for UV curable coatings.^[1,2] Polydimethylsiloxanes (PDMS) containing acrylic and methacrylic groups linked to the siloxane chains as pendant units through aliphatic ether moieties have been described in the literature.^[3–11] Our previous contributions proposed the attachment of different photoactive groups (benzyl acrylate,^[12] benzoin,^[13] glycidyl ether,^[14] and cyclohexene oxide^[15]) to the siloxane backbone by hydrosilation or chemical transformation methods. Differential scanning photocalorimetry was used to investigate their photocrosslinking initiated by appropriate radical or cationic photoinitiators.^[12,16]

The radically photocurable systems require low molecular weight photoinitiators to absorb the light and produce radicals able to initiate chain growth polymerization of appropriate monomers or functional polymers. One of the remaining frontiers in free radical photocuring is to develop rapidly polymerizing systems that respond to UV light in the absence of a common photoinitiator. This prospect is particularly attractive since photoinitiators involve several disadvantages. First, they are only partially consumed in typical photopolymerization processes since relatively high concentrations are required to ensure adequate absorption of light. A second problem for PDMSs is their low compatibility with the photoinitiators. Finally, another shortcoming with many photoinitiators is the generation of colored or harmful side products in addition to the primary radical photoproducts.

It is already known that differently substituted azo groups can be used as radical initiators in the photopolymerization of acrylates and methacrylates.^[17,18] Also, it was recently demonstrated that maleimides could be considered as “monomeric photoinitiators” since they are able, in their excited state, to generate free radicals by hydrogen abstraction.^[19–21]

This paper is aimed to discuss the efficiency of siloxane-based photoinitiators (siloxane macroinitiators containing azoester or azoamide groups (AzoE-PDMS or AzoA-PDMS) and phenylmaleimide mono- or difunctionalized disiloxanes (PhMI₁-DS or PhMI₂-DS)) in the photocrosslinking of PDMSs containing benzyl (meth)acrylate groups and to compare their behavior to those of usual radical photoinitiators.

EXPERIMENTAL

Materials

1,1,3,3-tetramethyldisiloxane (TMDS) (Aldrich), octamethylcyclotetrasiloxane (D₄) (Aldrich), hexamethyldisiloxane (HMDS) (Aldrich), 4-vinylbenzyl chloride, 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (Ap-DS), allyl alcohol (AA), 4-aminobenzoic acid (ABA), maleic anhydride, thionyl chloride (Aldrich), [(2,4,6-trimethylphenyl)-carboxy-ethoxy-phenyl] phosphorous oxide (TEPO) (BASF) and 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur[®] 1173) (Ciba Geigy), 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (TPO), 50:50 blend of Darocur[®] 1173, and TPO (Darocur 4265) were used without further purification. 4,4'-azobis(4-cyanovaleric acid) (ACVA) was dried by azeotrope evaporation of water with methanol at room temperature, under vacuum, before chlorination with PCl₅, to obtain the corresponding acid dichloride (ACVC). The sodium acrylate was prepared by reacting acrylic acid with NaOH in acetone.

All solvents were purified before use according to standard procedures.

End Substituted PDMSs

Hydro-terminated PDMSs (H_t-PDMS) of different molecular weights were obtained by a usual method, i.e., the cationic equilibration (concentrated H₂SO₄ catalyst, 2% v/w) of D₄ with TMDS.^[22] The content of active hydrogen was determined by the modified Zerewitinoff method,^[23] through dilatometric measurement of the evolved hydrogen after treating the sample with NaOH.

4-Chloromethylphenethyl-terminated PDMS prepolymers (ClPh-PDMSs) were prepared by the hydrosilation of 4-vinylbenzyl chloride with H_t-PDMSs (double bond/Si-H = 1.1 molar ratio) in the presence of H₂PtCl₆ catalyst (used as 2% solution in isopropanol) in toluene, at solvent reflux temperature. The reaction was monitored by observing the disappearance of the Si-H IR characteristic absorption at 2120–2160 cm⁻¹. The hydrosilation products were separated by vacuum distillation of the solvent and excess of the unsaturated compound, purified by dissolution in a 3/1 (v/v) mixture of petroleum ether/diethyl ether, filtered to remove the traces of poly(4-vinylbenzyl chloride) formed by thermal polymerization of the monomer, and then the solvents were removed by vacuum evaporation, yielding the desired functionalized PDMS (in amounts higher than 95%).

¹H-NMR (CDCl₃), (δ, ppm): -0.01 (6nH, CH₃Si, s), 0.64–0.82 (2H, -CH₂Si, m; β isomer), 1.20 (3H, CH₃-CH, d; α isomer), 2.05–2.20

(1H, $\text{CH}_3\text{-CH}$, q; α isomer), 2.40–2.55 (2H, $\text{CH}_2\text{-Ph}$, m; β isomer), 4.40 (2H, $\text{Ph-CH}_2\text{-Cl}$, s), 6.79–7.10 (4H, Ph, m).

The molecular weights of the synthesised chlorofunctional polysiloxanes were determined by chemical analysis of the chlorine content and/or GPC.

PDMSs contain benzyl (meth)acrylate groups (B(M)A-PDMS). Polysiloxanes possessing terminal chloromethylphenethyl substituents were reacted with sodium (meth)acrylate ($\text{Cl}/\text{COONa} = 1/2.5$ molar ratio) in chloroform (siloxane concentration, 50% by weight) in solid–liquid phase transfer conditions (Aliquat 336; $\text{Cl}/\text{Aliquat 336} = 30/1$ molar ratio) at 40°C, under stirring and nitrogen for 7 and 4 days for BA-PDMSs and BMA-PDMSs, respectively. Reaction evolution was investigated through NMR analysis. Finally, the solution was filtered, washed several times with water, dried over anhydrous Na_2SO_4 , and the solvent was removed by evaporation under vacuum at room temperature to yield over 92% of (meth)acrylate functionalized PDMSs.

$^1\text{H-NMR}$ (CDCl_3): BMA-PDMS (δ , ppm): –0.01 (6nH, CH_3Si , s), 0.70–0.79 (2H, CH_2Si , m; β isomer), 1.20–1.28 (3H, $\text{CH}_3\text{-CH}$, d; α isomer), 1.86 (3H, $\text{CH}_3\text{C}=\text{CH}_2$, s), 2.02–2.18 (1H, $\text{CH}_3\text{-CH}$, q; α isomer), 2.40–2.55 (2H, $\text{CH}_2\text{-Ph}$, m; β isomer), 5.09 (2H, $\text{Ph-CH}_2\text{-OCO}$, s), 5.46 (*cis* to COO) and 6.04 (*trans* to COO) (2H, $\text{C}(\text{CH}_3)=\text{CH}_2$, s), 6.97–7.42 (4H, Ph, m).

BA-PDMS (δ , ppm): –0.01 (6nH, CH_3Si , s), 0.64–0.82 (2H, CH_2Si , m; β isomer), 1.24–1.28 (3H, $\text{CH}_3\text{-CH}$, d; α isomer), 2.05–2.20 (1H, $\text{CH}_3\text{-CH}$, q; α isomer), 2.42–2.60 (2H, $\text{CH}_2\text{-Ph}$, m; β isomer), 5.0 (2H, $\text{Ph-CH}_2\text{-OCO}$, s), 5.70–5.75 (*cis* to COO) and 6.30–6.38 (*trans* to COO) (2H, $\text{CH}=\text{CH}_2$, dd), 6.0–6.1 (1H, $\text{CH}=\text{CH}_2$, m), 6.92–7.25 (4H, Ph, m).

The molecular weights of (meth)acrylate functional PDMSs were determined from $^1\text{H-NMR}$ spectra or by chemical analysis (titration of unsaturated groups with the bromide–bromate system).

Siloxane Macroazoinitiators

Azoester- or azoamide-containing PDMSs (AzoE-PDMS or AzoA-PDMS) were prepared by the polycondensation of hydroxypropyl- (HO-PDMS) or aminopropyl-terminated PDMSs ($\text{H}_2\text{N-PDMS}$) with 4,4'-azobis(4-cyanovaleryl chloride) (ACVC). HO-PDMSs of two molecular weights, $M_n = 1100$ and 2950, were obtained by the hydrosilation of allyl alcohol (AA) with $\text{H}_1\text{-PDMSs}$ ($\text{AA}/\text{SiH} = 1.2$ molar) in toluene, as described elsewhere.^[24,25] The reaction product was recovered (over 95% yield) after 6 hours, when toluene and AA excess were removed by vacuum distillation.

$^1\text{H-NMR}$ (CDCl_3), (δ , ppm): 0.01 (6nH, $\text{CH}_3\text{-Si}$, s), 0.45–0.55 (2H, $\text{CH}_2\text{-Si}$, m; β isomer), 0.83–0.87 (3H, $\text{CH}_3\text{-CH}$, d; α isomer), 1.15–1.23

(1H, CH₃-CH, q; α isomer), 1.52–1.56 (2H, CH₂-CH₂-CH₂, m; β isomer), 3.45–3.59 (2H, CH₂-CH₂-OH, t).

NH₂-PDMS with a molecular weight $M_n=1200$ (determined by potentiometric titration of amino end group with benzenesulfonic acid) was obtained by a procedure described by Elsbernd et al.^[26] 74 g (25 mmol) octamethylcyclotetrasiloxane were polymerized in the presence of tetramethylammonium siloxanolate initiator (0.1 mol%) and 1.2 g (6.7 mmol) 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane end blocking agent at 80°C, under nitrogen for 24 hours. The temperature was increased to 150°C for 0.5 hours to decompose the catalyst. 64.97 g (86.4% yield) of NH₂-PDMS were obtained after the distillation of cyclosiloxane oligomers at 150°C under vacuum (1 mmHg).

¹H-NMR (CDCl₃), (δ , ppm): 0.01 (6nH, CH₃-Si, s), 0.43–0.47 (2H, CH₂-Si, m; β isomer), 0.81–0.88 (3H, CH₃-CH, d; α isomer), 1.00–1.08 (1H, CH₃-CH, q; α isomer), 1.40–1.47 (2H, CH₂-CH₂-CH₂, m; β isomer), 2.73–2.85 (2H, CH₂-NH₂, m).

The NH₂-PDMS (or HO-PDMS) prepolymer (10 mmol) was dissolved in a solution of pyridine (20 mmol) in CHCl₃ (100 mL), in a pre-dried flask, under nitrogen. A solution of ACVC (10 mmol) in CHCl₃ (50 mL) was added slowly with vigorous stirring at 0°C under nitrogen. After the addition, the solution was kept at 20°C for 24 hours. The reaction mixture was then washed with water until neutral pH and dried over Na₂SO₄. AzoE- or AzoA-PDMSs were obtained after solvent evaporation, in yields higher than 90%.

¹H-NMR (CDCl₃), (δ , ppm), AzoE-PDMS: 0.02 (6nH, CH₃-Si, s), 0.43–0.49 (2H, CH₂-Si, m; β isomer), 0.81–0.87 (3H, CH₃-CH, d; α isomer), 1.12–1.20 (1H, CH₃-CH, q; α isomer), 1.18 (3H, CH₃-C(CN), s), 1.51–1.55 (2H, CH₂-CH₂-CH₂, m; β isomer and 2H, CH₂-C(CN), t), 2.26–2.31 (2H, CH₂-CO, t), 4.05–4.24 (2H, CH-CH₂-OCO, α isomer and CH₂-CH₂-CH₂-OCO, β isomer, m).

AzoA-PDMS (δ , ppm): 0.01 (6nH, CH₃-Si, s), 0.43–0.47 (2H, CH₂-Si, m; β isomer), 0.80–0.88 (3H, CH₃-CH, d; α isomer), 1.00–1.08 (1H, CH₃-CH, q; α isomer), 1.20 (3H, CH₃-C(CN), s), 1.40–1.47 (2H, CH₂-CH₂-CH₂, m; β isomer), 1.60–1.66 (2H, CH₂-C(CN), m), 2.26–2.43 (2H, CH₂-CO, m), 3.11–3.19 (2H, CH₂-NHCO, m).

The content of azo labile groups of the synthesised macroinitiators was determined by chemical analysis of the nitrogen content. The viscometric molecular weights of AzoA- or AzoE-PDMSs and of their amino and hydroxy terminated PDMSs precursors were determined in toluene, at 25°C.

Maleimide Functionalized Disiloxanes

Mono- (PhMI₁-DS) and bis(phenylmaleimide) functionalized disiloxanes (PhMI₂-DS) were synthesized from N-(4-chlorocarbonylphenyl)maleimide

(CIPhMI) and (hydroxypropyl)pentamethyldisiloxane (HO₁-DS) or 1,3-bis(hydroxypropyl)-1,1,3,3-tetramethyldisiloxane (HO₂-DS), respectively. CIPhMI was prepared as described^[27] and the hydroxypropyl functionalized disiloxane by the hydrosilation of pentamethyldisiloxane or 1,1,3,3-tetramethyldisiloxane as described for HO-PDMSs. CIPhMI (10 mmol) was dissolved in DMSO and the solution was added dropwise to a solution of HO-DS (10 mmol OH) and triethylamine (12 mmol) in DMSO at 0°C. The reaction mixture was then stirred at room temperature for 10 h. The product was precipitated in a mixture of water and acetic acid (pH = 4), washed several times with water, and dried in vacuum at 40°C.

¹H-NMR (CDCl₃) (δ, ppm): 0.03, (6H, CH₃-Si, s), 0.46–0.61 (2H, CH₂-Si, m; β isomer), 0.79–0.85 (3H, CH₃-CH, d; α isomer), 1.09–1.16 (1H, CH₃-CH, q; α isomer), 1.68–1.72 (2H, CH₂-CH₂-CH₂, m; β isomer), 4.18–4.22 (2H, CH₂-OCO, m), 6.8 (2H, OC-CH=CH-CO, s), 7.39–7.45 (2H, aromatic ortho from -N, d), 8.04–8.18 (2H, aromatic meta from -N, d).

Analyses and Techniques

IR spectra were registered on a Nicolet 710 FT-IR apparatus. ¹H-NMR spectra were recorded on a Bruker 400 MHz. GPC data were obtained on a Waters Associated 440 instrument in THF as eluent; polystyrene standards were used for molecular weight calibration.

Differential scanning photocalorimetry (DPC). The DPC studies were performed on a DuPont 930 apparatus with a double heat differential calorimeter 912, calibrated with indium metal standard. The technique was largely described in the literature.^[28–30]

A standard high pressure mercury lamp with 4.5 mW/cm² light intensity and a spectral bandwidth of 280–600 nm was used for sample exposure to UV. The initiators were mixed with the (meth)acrylate functional siloxane prepolymers (1.9·10⁻⁴ mol photoactive groups for 1 g of B(M)A-PDMS-initiator mixture). Sample weights were 1.5 ± 0.5 mg, and the exposure was carried out using DSC DuPont standard pans. The measurements were performed in inert (nitrogen) and air atmosphere. A computer-controlled isothermal method was employed to determine the kinetic parameters. The samples were allowed to equilibrate at a preselected temperature in a first step, followed by an isothermal treatment without exposure for 1 min, then starting the isothermal exposure. The heat flow (W/G) vs. exposure time (min) for each sample was obtained and the curves were analyzed using a DPC-4-1A DuPont software to give the photoreactivity parameters (polymerization enthalpy, induction time (defined for 1% monomer conversion), time to reach peak maximum, conversion at the peak maximum). The kinetic parameters were determined according to the autocatalytic model.^[28,29]

RESULTS AND DISCUSSION

Synthesis of Functional Polysiloxanes and of Siloxane Photoinitiators

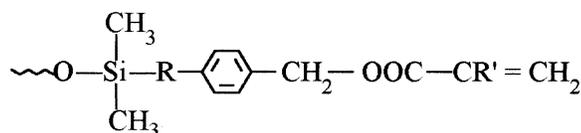
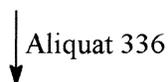
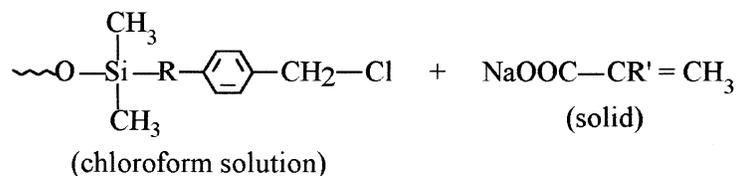
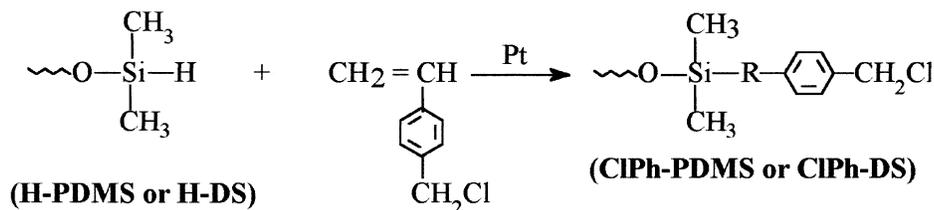
Benzyl (meth)acrylate-terminated polydimethylsiloxanes of two molecular weights and mono- and difunctional disiloxanes (Table 1) were prepared through a succession of reactions, according to Sch. 1. The hydrosilation of 4-vinyl benzyl chloride was performed according to a procedure described by Aogi et al.^[31] A better control of polymer functionality is offered by this direct method as compared to our previous results^[32] on the preparation of the same type of functional polysiloxanes through the hydrosilation of styrene, followed by the chloromethylation, in mild conditions, of the phenethyl groups linked to the siloxane backbone. The ratio of α and β addition isomers, as determined from ¹H-NMR spectra of the low molecular weight model compounds (1,3-bis(4-chloromethylphenethyl)-1,1,3,3-tetramethyldisiloxane (CIPh₂-DS) or (4-chloromethylphenethyl)-pentamethyldisiloxane (CIPh₁-DS)), was found to be about 1/2.5.

The attachment of (meth)acrylate groups to chlorine functionalized siloxanes was performed by their condensation with the sodium salts of unsaturated acids in solid-liquid phase transfer conditions (Aliquat 336) at 40°C. Chloroform was used as solvent for the siloxane prepolymers. The quite low reaction temperature was chosen to avoid a possible side reaction, i.e., the thermal polymerization of the double bond. The solid-liquid heterogeneous conditions were imposed by the sensitivity of the siloxane bond toward the hydroxyl anions at high temperature. In a water-organic system, the well known hydrolysis equilibrium $R-COO^-Na^+ + HOH \rightleftharpoons R-COOH + Na^+ + HO^-$ gives rise to hydroxyl anions. These are easily transferred by the phase transfer catalyst into the organic medium where they can interact with the siloxane chains, causing their redistribution, with negative influence on the molecular weight and polydispersity control. As reported elsewhere,^[12] polymers with quite higher molecular weights as compared to their CIPh-PDMS precursors were obtained in water-organic phase transfer conditions. In solid-liquid systems, the condensation of CIPh groups with sodium (meth)acrylate is slow (several days). As expected from the influence of a positive inductive effect of methyl group in sodium methacrylate, the reactivity of this one is higher as compared to sodium acrylate, and lower reaction duration is required (see Experimental part).

To follow the evolution of the condensation reaction and the photochemical behavior and to clearly identify the structure of (meth)acrylate functional polysiloxanes, mono- and difunctional CIPh-DS low molecular weight model compounds were reacted with sodium (meth)acrylate. At 40°C, the reaction was completed after several days. An increase in the reaction temperature yielded a high amount of (meth)acrylate polymer and the partial crosslinking of the reaction mixture for the difunctional disiloxanes.

Table 1. Synthesis and Characterization of Functional Polysiloxanes

Chloromethylphenethyl Functional Precursors			Benzyl (Meth)Acrylate Functional Polysiloxanes					
Sample Code	Chlorine Content (mol/kg)	Mn (NMR)	Mn (GPC)	Mw/Mn (GPC)	Sample Code	Acrylate Content (mol/kg) Calc. Found	Mn (GPC)	Mw/Mn (GPC)
CIPh ₁ -DS	3.33	—	—	—	BA ₁ -DS	2.97 2.97	—	—
CIPh ₂ -DS	4.55	—	—	—	BA ₂ -DS	3.90 3.90	—	—
CIPh ₁ -DS	3.33	—	—	—	BMA ₁ -DS	2.84 2.84	—	—
CIPh ₂ -DS	4.55	—	—	—	BMA ₂ -DS	3.92 3.92	—	—
CIPh-PDMS ₁	0.84	2400	2600	1.52	BMA-PDMS ₁	0.82 0.79	2650	1.71
CIPh-PDMS ₂	0.58	3450	3850	1.75	BA-PDMS ₂	0.57 0.49	3850	1.62



(B(M)A-PDMS or B(M)A-DS)

R is $\begin{array}{c} -\text{CH}- \\ | \\ \text{CH}_3 \end{array}$ (α -isomer) and $-\text{CH}_2-\text{CH}_2-$ (β -isomer); $\beta/\alpha = 2.5$

R' is H (BA-PDMS and BA-DS) or CH_3 (BMA-PDMS and BMA-DS)

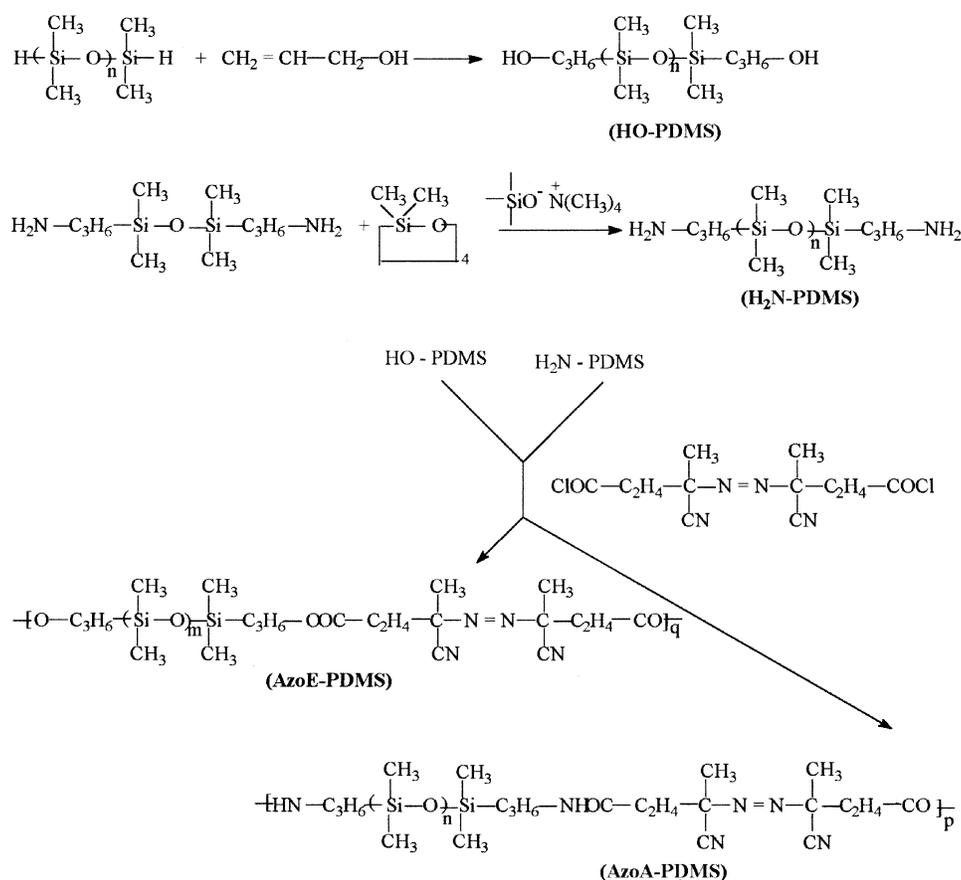
Scheme 1.

The transformation of the chloromethylphenethyl groups was monitored by $^1\text{H-NMR}$ spectroscopy. The appearance of specific signals for the $-\text{Ph-CH}_2\text{-OCO-}$ protons at 5.0 and at 5.09 for acrylate and methacrylate functionalized disiloxane, respectively, and the disappearance of the $\text{Ph-CH}_2\text{-Cl}$ peak at 4.4 ppm was observed. The yields of ClPh-PDMSs conversion into B(M)A-PDMSs homologues were higher than 84%. The molecular weights of (meth)acrylate functionalized PDMSs as determined by $^1\text{H-NMR}$ spectroscopy or chemical analysis (titration of unsaturated groups with

bromide–bromate system) are in good agreement with those of their chlorine-functionalized precursors, denoting the absence of important siloxane chain reequilibration side reactions.

To verify the efficiency of siloxane-containing initiators on the photocrosslinking of meth(acrylate)-terminated polysiloxanes, azoester, azoamide, and maleimide groups were linked to the siloxane chains. Siloxane macroinitiators were prepared by the polycondensation of hydroxypropyl-^[24, 25] or aminopropyl-terminated PDMSs^[33] with ACVC (Sch. 2). Starting from different molecular weight siloxane precursors, macroinitiators with various photocrosslinkable unit contents were obtained (Table 2).

Mono- and difunctional disiloxanes containing phenylmaleimide groups were prepared (Table 2) by the condensation of ClPhMI with mono- (HO₁-DS) or bis(hydroxypropyl) functionalized disiloxanes (HO₂-DS) in the presence of triethylamine as acid acceptor (Sch. 3), through a procedure applied



Scheme 2.

Table 2. Synthesis and Characterisation of Siloxane Initiators

Sample Code	Amionopropyl or Hydroxypropyl Functionalised Precursor				Siloxane Initiator				
	M_n (chem. an. ^a)	M_n (GPC)	M_v	M_w/M_n (GPC)	Sample Code	Photoactive Groups Content (mol/kg) Calculated	Photoactive Groups Content (mol/kg) Found ^b	M_v ^c	q (p) ^d
H ₂ N-PDMS	1200	—	2200	—	AzoA-PDMS	0.693	0.614	33 000	15
HO-PDMS ₁	1100	1400	2050	1.52	AzoE-PDMS ₁	0.744	0.685	28 700	14
HO-PDMS ₂	2950	3100	4700	1.83	AzoE-PDMS ₂	0.313	0.298	47 000	10
HO ₁ -DS	200	—	—	—	PhMI ₁ -DS	2.463	2.462	—	—
HO ₂ -DS	250	—	—	—	PhMI ₂ -DS	3.077	3.070	—	—

^a M_n of amino terminated PDMS was determined by potentiometric titration of end groups with p-toluene sulphonic acid; M_n of hydroxy terminated PDMSs was calculated from end groups content as determined through the reaction with acetic anhydride followed by the titration of acetic anhydride excess with sodium hydroxide

^bfrom elemental analysis of nitrogen content

^ccalculated with the relation $[\eta] = 8.28 \times 10^{-3} M_v^{0.72}$ valid for pure PDMS [34], considering that the relation is not substantially modified by the presence of small amounts of azo-ester groups in the main chain

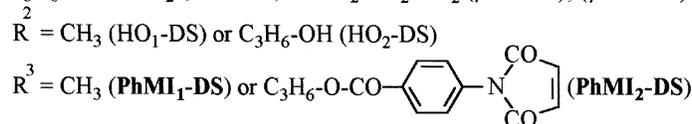
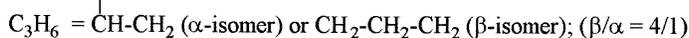
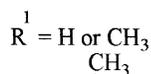
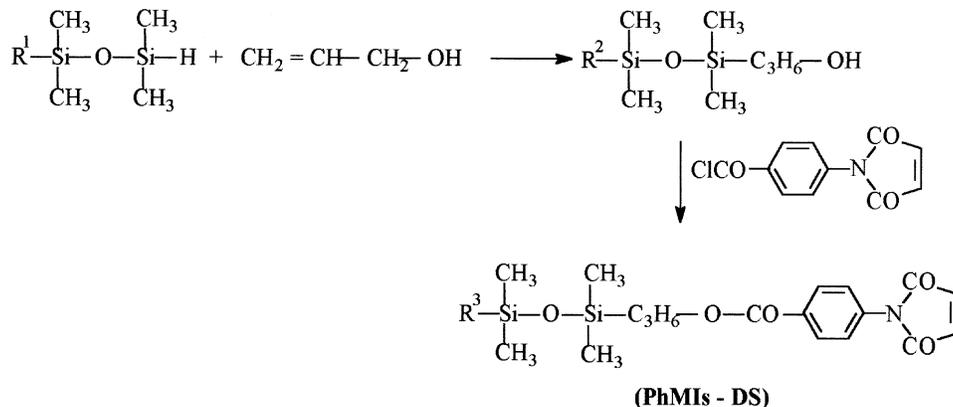
^d q and p represent the polycondensation degrees of AzoA-PDMS and AzoE-PDMSs, respectively, calculated from the ratio M_v , $AzoA(E)-PDMS/M_v$, $H_2N(HO)-PDMS$

earlier for PDMS prepolymers^[35] and were further used as initiators in the photocrosslinking of acrylated siloxanes.

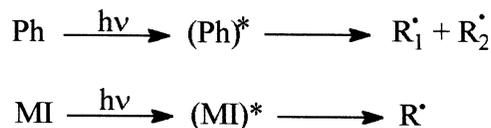
Photocrosslinking of Benzyl (Meth)Acrylate Functionalized PDMSs (B(M)A-PDMSs)

The photocrosslinking of silicone (meth)acrylates in bulk starts with photochemical radical formation. On irradiation, both usual photoinitiators and siloxane macroazoinitiators undergo α -cleavage and generation of two radical species able to initiate the polymerization of (meth)acrylate double bond (Sch. 4).

Recent studies^[19,20,36] demonstrated that different N-substituted malimides act as efficient "monomeric copolymerisable photoinitiators" in the polymerization of (meth)acrylate groups upon UV irradiation when the abstraction of hydrogen atoms is possible. Moreover, the photopolymerization rate is increased by the presence of extractable hydrogen atoms on either one of the two monomers or by addition of small amounts of H-donor molecules. To confirm this mechanism for the phenylmaleimide functionalized disiloxanes, an oxygen saturated solution of PhMI₁-DS in toluene was irradiated with a Hg lamp for 10 min. ¹H-NMR spectra of PhMI₁-DS before and

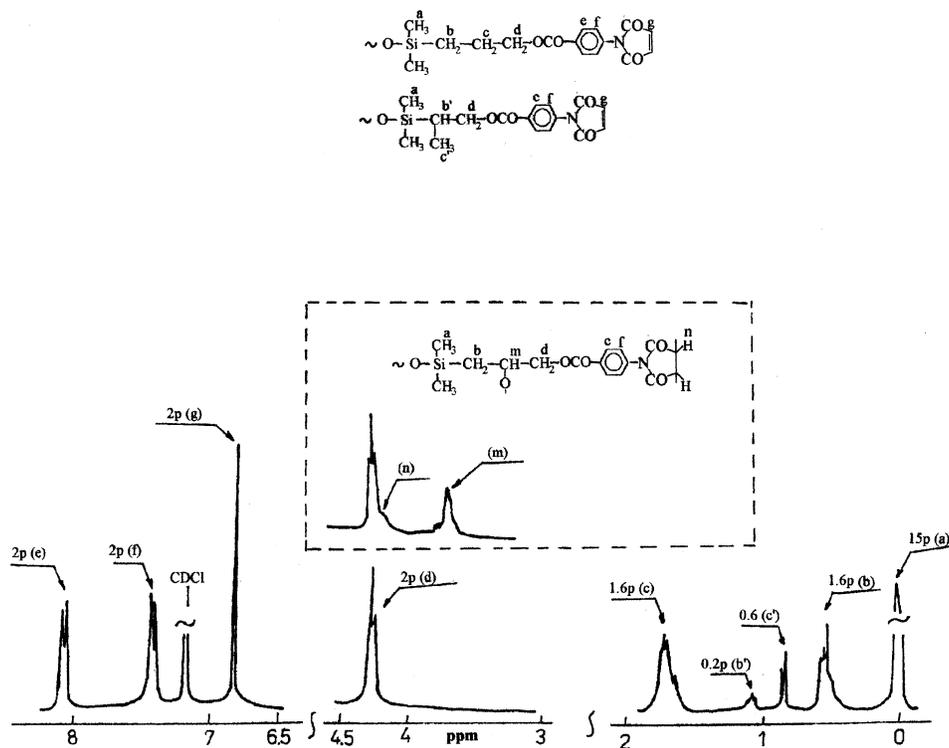


Scheme 3.



Scheme 4.

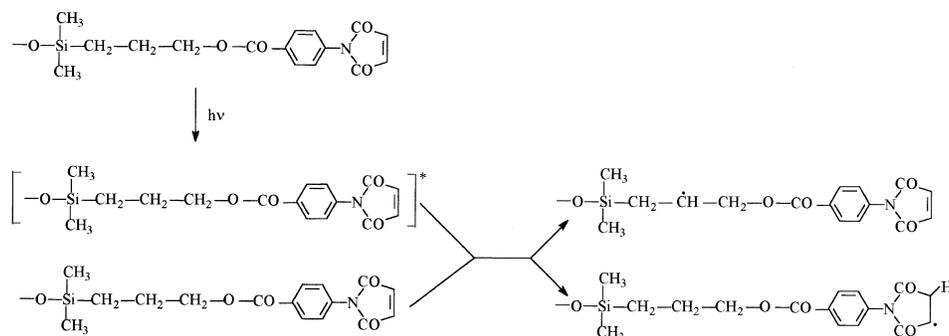
after irradiation were recorded (Fig. 1). From a multitude of aliphatic protons existing in the spacer between siloxane and maleimide units, the protons in β position from the silicon atom (protons (c) in β isomer) seem to be more sensitive to homolytic scission as the integral corresponding to their peak is diminished following irradiation and a new peak, attributed to a $>\text{CH}-\text{O}-$ unit resulting from the reaction between the formed radical and oxygen, appears around 3.70 ppm (Fig. 1 in dashed frame). The decreasing of the maleimide double bond and the formation of a large peak partially masked by the peak corresponding to $-\text{CH}_2-\text{OCO}$ group at 4.18–4.22 ppm were also observed (peak (n) in dashed frame). This peak was attributed to polymerized (dimerized) maleimide units ($-\text{CO}-\text{CH}-\text{CH}-\text{CO}-$).^[37] For $\text{PhMI}_{1(2)}\text{-DS}$, the

Figure 1. ^1H -RMN spectra of $\text{PhMI}_{2}\text{-DS}$.

mechanism given in Sch. 5 is proposed for the formation of the initiating radicals. In excited state, the maleimide group is able to extract a hydrogen atom from another PhMI-DS molecule forming alkyl and maleimide radicals. Both radical species are able to initiate the polymerization of (meth)acrylate groups. After irradiation, the (meth)acrylate bonds content in the PhMI-DS/B(M)A-PDMS mixture is diminishing. Figure 2 gives the IR spectra of the initial BA₂-DS/PhMI₂-DS mixture and of the product resulting after 10 min of photoirradiation. The diminishing of -CH=CH₂ specific absorption band at 1630 cm⁻¹ confirms the photocrosslinking reaction.

The kinetics of photocrosslinking of benzyl (meth)acrylate functionalized polysiloxanes was investigated by differential scanning photocalorimetry. The B(M)A-PDMS/photoinitiator mixtures were irradiated with a Hg lamp at 4.5 mW/cm² light intensity. The reaction was carried out in inert (N₂) atmosphere and air. The photocrosslinking behavior in the presence of usual photoinitiators (Sch. 6), azoester or azoamide siloxane macroazoinitiators and phenylmaleimide functionalized disiloxanes was investigated. To compare the efficiency of azo and maleimide groups linked to the siloxane moieties, the same concentrations of initiating groups was used in all experiments, i.e., 0.99·10⁻⁴ mol/g (meth)acrylated siloxane/photoinitiator mixture.

As already demonstrated for BA-PDMS/usual photoinitiator systems, the faster photoinitiator is TEPO.^[12] The same TEPO > Darocur 4265 > Darocur[®] 1173 activity series was obtained for the photocrosslinking of BMA-PDMSs. Figure 3 shows typical conversion–time curves for the photocrosslinking of BMA₂-DS. The reaction rates in the presence of both macroazoinitiators and PhMI_{1(2)}}-DS are much lower as compared to those registered for the usual photoinitiators. However, the final conversion for TEPO and AzoA-PDMS initiators reached almost the same value, while the polymerization in the presence of other initiators reached only smaller final



Scheme 5.

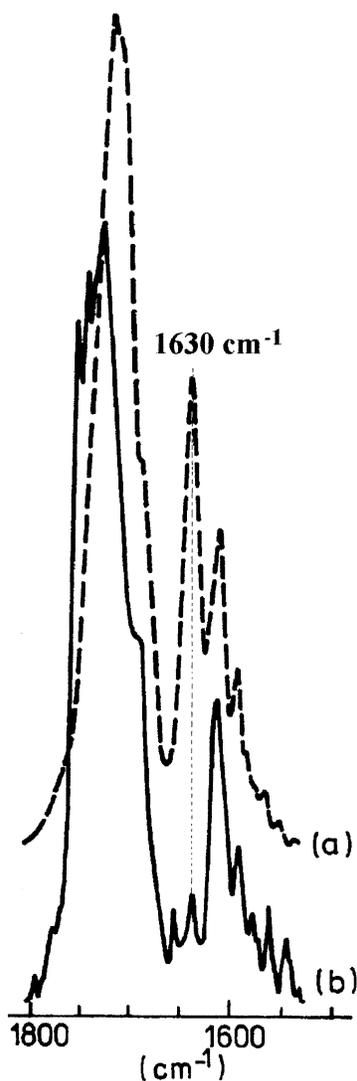
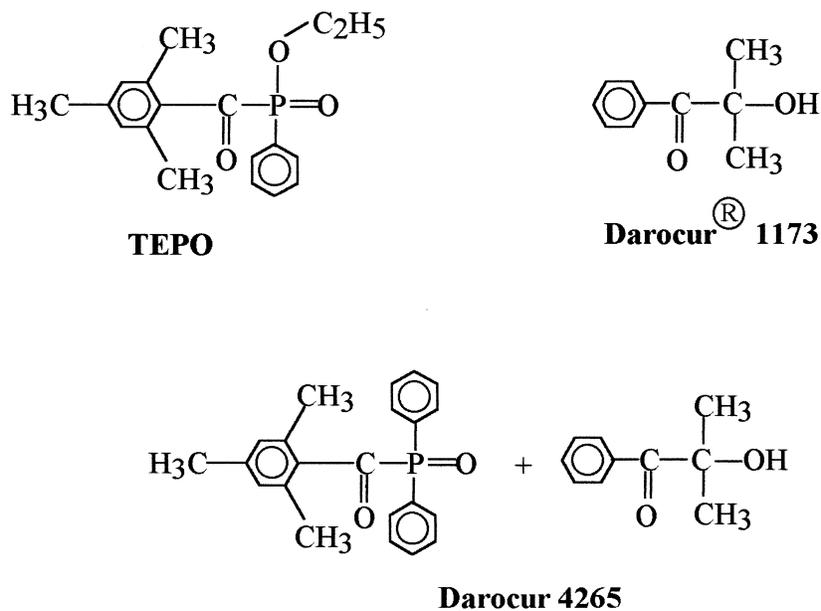


Figure 2. IR-spectra of BA₂-DS – (a) before irradiation, (b) after irradiation.

conversions ranged according to the series AzoA-PDMS > AzoE-PDMS₁ > AzoE-PDMS₂ ≈ PhMI₁-DS > PhMI₂-DS.

As expected from the less known efficient propagation of methacrylate double bond, the photocrosslinking of BMA-PDMSs is slower than that of BA functionalized homologues and lower final conversions are reached (Fig. 4).

The photocrosslinking of (meth)acrylates is strongly influenced by the presence of oxygen. The reaction rates and the final conversions attained very low values for processes carried out in air as compared to those performed in inert atmosphere. For the photocrosslinking of B(M)A-PDMSs in the



Scheme 6.

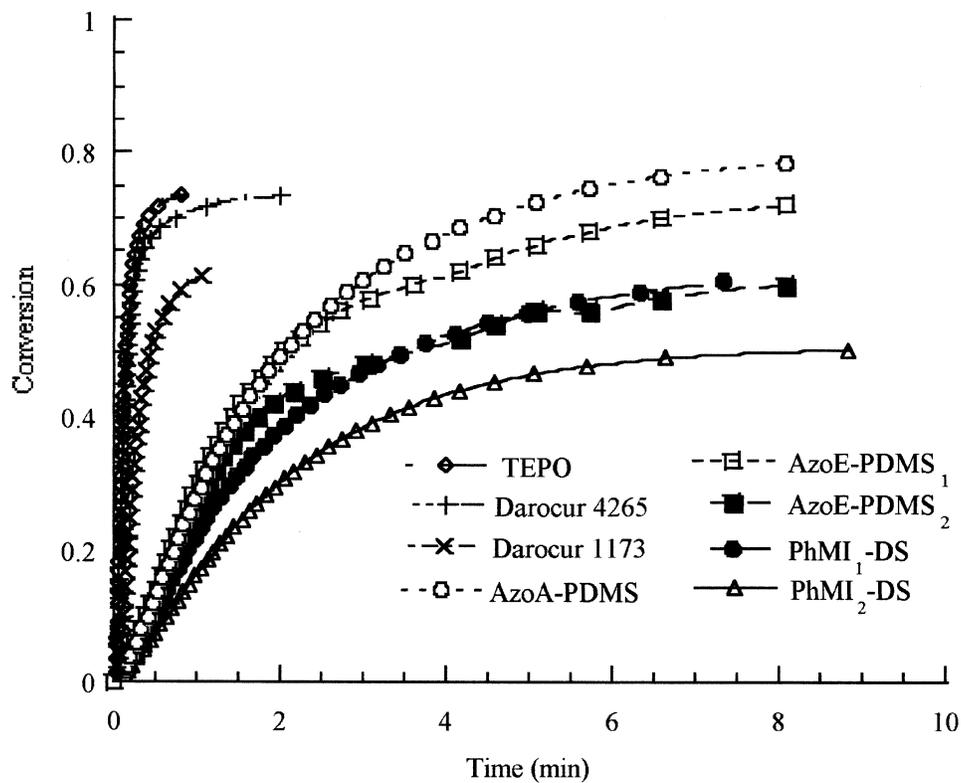


Figure 3. Photocrosslinking of BMA₂-DS in the presence of different photoinitiators in nitrogen at 30°C.

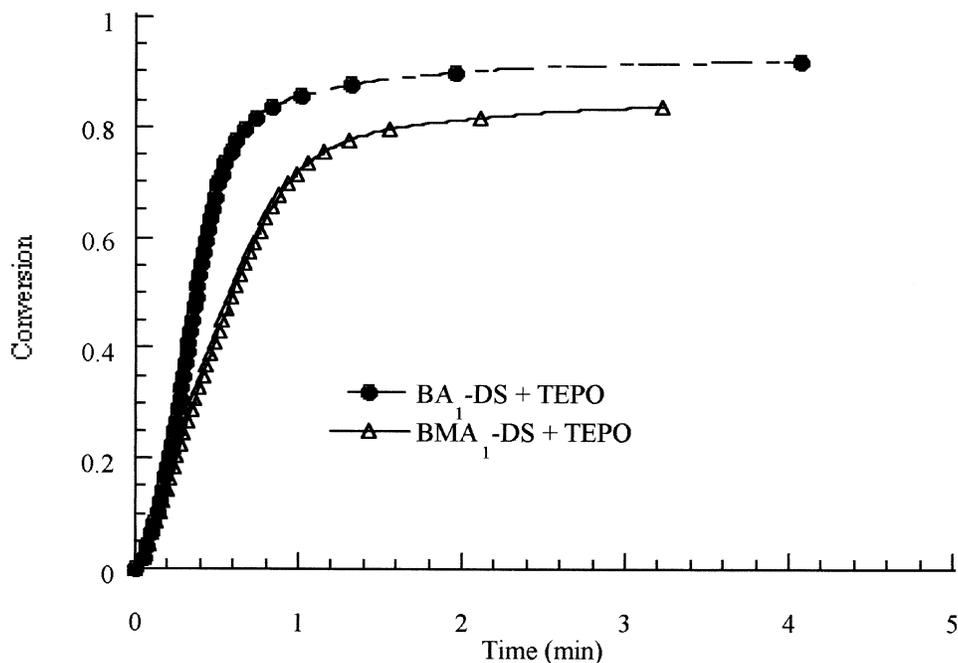


Figure 4. Photocrosslinking of BA₁-DS and BMA₂-DS in the presence of TEPO in nitrogen at 30°C.

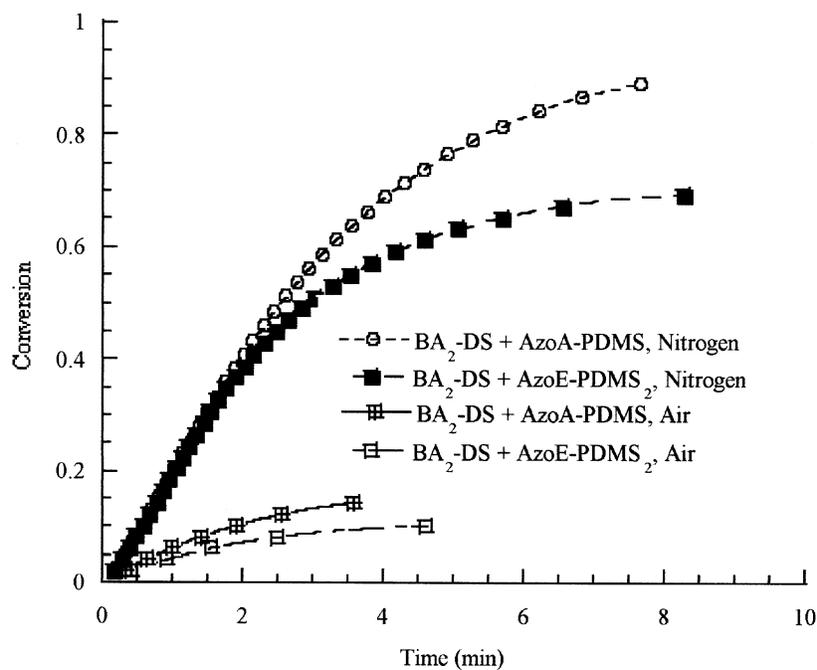


Figure 5. Photocrosslinking of BA₂-DS in the presence of siloxane macroinitiators in nitrogen and air at 30°C.

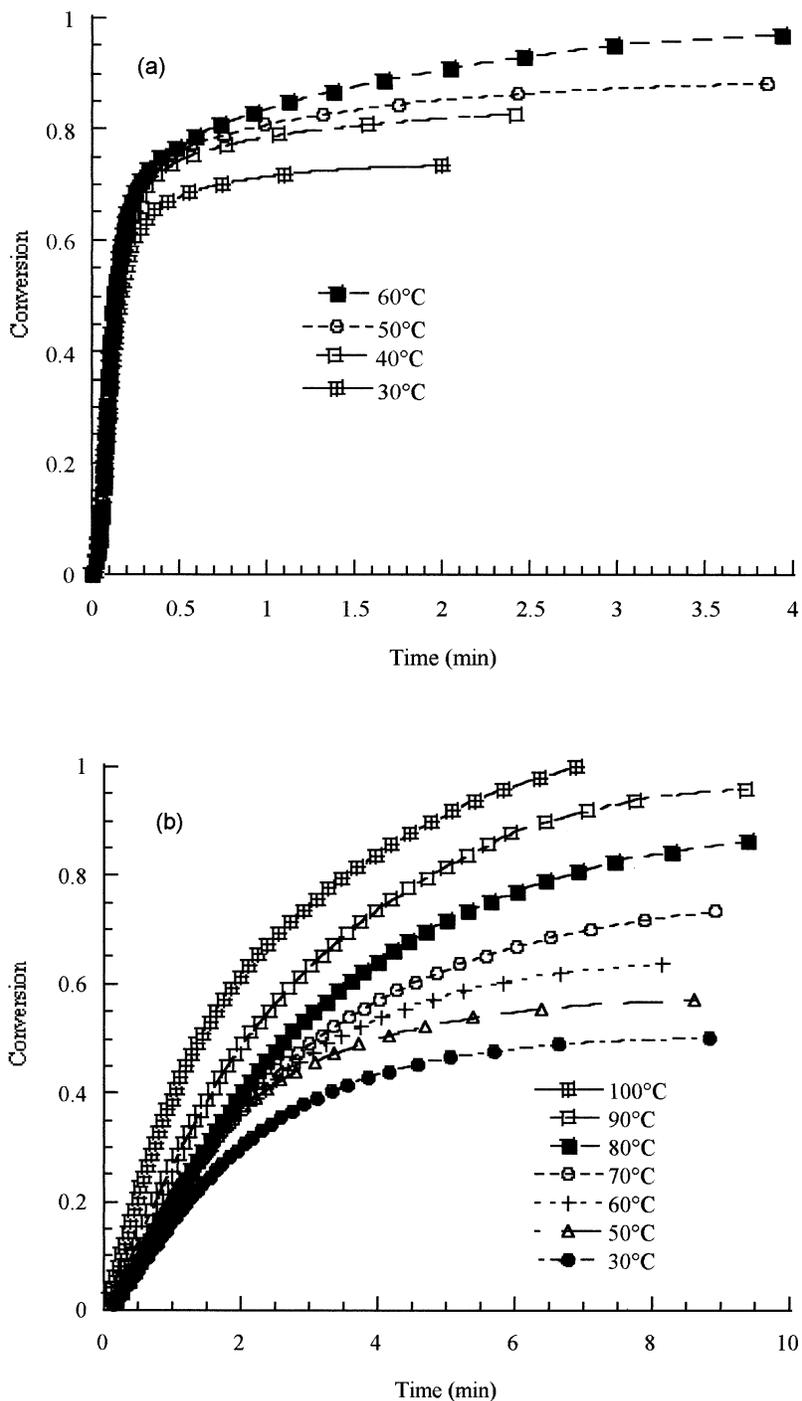


Figure 6. Photocrosslinking of BMA₂-DS in nitrogen atmosphere, (a) in the presence of TEPO, (b) in the presence of PhMI₁-DS, at different temperatures.

presence of azoester and azoamide containing polysiloxanes both the reaction rate and the final conversion are greatly diminished by oxygen (Fig. 5), while the process is completely shut down for the mixtures initiated by the less efficient PhMI-DSs.

The reaction temperature also influences the photocrosslinking of acrylated siloxanes. Using a usual photoinitiator (Fig. 6a), the increase of temperature from 30 to 60°C does not affect the polymerization rate but the final conversion is increased from 63% to 100%, while for siloxane initiators both the rate and the final conversion are strongly dependent on temperature (Fig. 6b). Moreover, to reach a total conversion of BMA groups, a much lower temperature is required by TEPO initiator (60°C) as compared to PhMI₁-DS (100°C). The B(M)A-PDMS/TEPO (or other usual initiators) and B(M)A-PDMS/PhMI-DS systems were also investigated by DSC (heating rate, 10°C/min) and no thermal polymerization was observed up to 140 and 120°C, respectively.

With increasing polymer molecular weight, the photocrosslinking efficiency of B(M)A-PDMS/usual photoinitiator systems decreases (Fig. 7). It should be mentioned that with increasing polymer molecular weight, the solubility of the usual photoinitiator in the reaction mixture diminishes and the final conversion and photocrosslinking rate are slightly lower for the

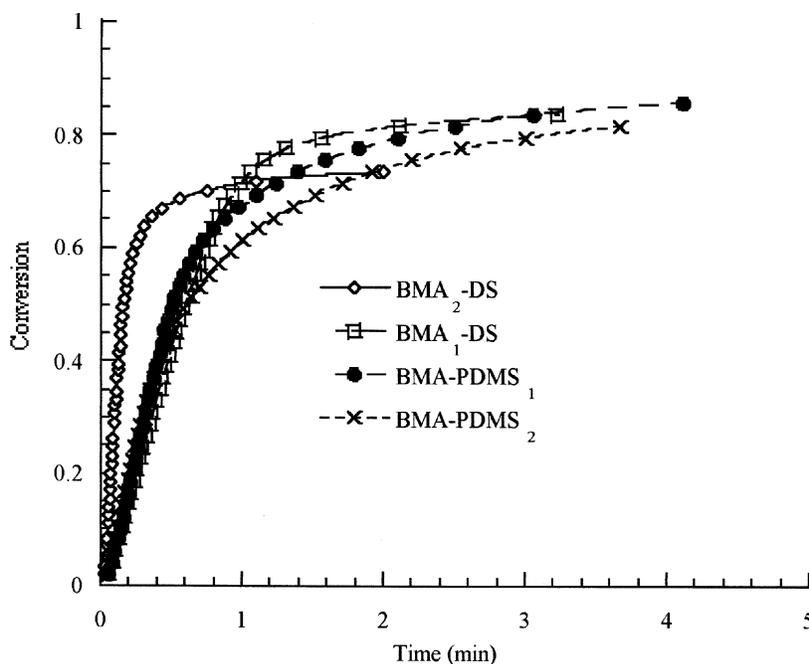


Figure 7. Conversion vs. time curves as a function of the molecular weight of end methacrylated PDMSs.

longer chains. The BMA₂-DS attains only a maximum conversion of about 70%, probably due to the pronounced increase of medium viscosity through crosslinking, while the photopolymerization of BMA₁-DS proceeds with a slower rate and reaches almost 90% conversion.

CONCLUSION

The photoreactivity of benzyl (meth)acrylate-terminated polysiloxanes depends on both the nature of the polymerizable group (the acrylic group is more active as compared to the methacrylate unit) and the nature of the initiator. Siloxane containing photoinitiators were proved to possess lower reactivity than the usual photoinitiators, but the final conversions for macroazoinitiators having relatively low siloxane lengths between two azo groups are very close to those registered for usual photoinitiators. This behavior is a consequence of the balance between the initiating ability of the active group and the compatibility of the photoinitiator with the siloxane photocrosslinking prepolymer.

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