

New Arylidene–Siloxane Polyethers: Liquid-Crystalline and Photosensitive Properties

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ABSTRACT: By polycondensation reactions, starting from α , ω -bis(chloromethyl)polydimethylsiloxanes with different molecular weights and 2,6-bis(4-hydroxybenzylidene)cyclohexanone, new polyethers were obtained. The structure of resulting polymers was confirmed by IR and ¹H-NMR spectroscopy and their thermal properties and mesophase behavior were studied by TGA, DSC, and polarizing light microscopy. Depending on the length of the siloxane spacer, some of the obtained compounds exhibited thermotropic liquid-crystalline properties. A possible smectic texture was

investigated by X-ray diffraction measurements at room temperature. A decrease of the transition temperatures values was observed as the spacer length increased. The photochemical behavior of the siloxane polyethers was studied by ultraviolet absorption spectroscopy. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3093–3099, 2003

Key words: polyethers; siloxane–arylidene; liquid-crystalline polymers (LCP); photochemistry; thermal properties

INTRODUCTION

By chemically bonding siloxane segments with typically organic blocks or macromers, a great variety of copolymers have been obtained.^{1–4} Polysiloxanes are important because they impart attractive properties such as, for example, very low glass-transition temperature, low surface tension and surface energy, low dielectric constant, low solubility parameter, transparency to UV and visible light, stability against atomic oxygen, film-forming ability, and hydrophobic behavior.

Over the last decades, one of the most active research fields has been the study of liquid crystals (LCs) as materials with potential uses in high technologies.^{5–11} A large number of mesogens were synthesized^{12,13} and used to obtain liquid-crystalline polymers (LCPs). It is known that rigid-chain LCPs generally exhibit high transition temperatures, thus making them difficult to process. To solve this problem, polymethylene and poly(ethylene oxide) segments were used as spacers, although polysiloxanes have the advantages of low glass-transition temperature and great flexibility of the backbone. By using them as flexible spacers, important decreases in glass transition, melting, and liquid-crystalline transition temperature values were reported,^{14–17} attributed to the low rotation energy barrier of the Si–O bond.

A series of studies have been published^{18–23} on the synthesis and characterization of arylidene polyethers and polyesters containing cycloalkanone moieties. LC behavior was reported for main-chain poly(arylidene-ether)s^{21,22} and poly(arylidene-ester)s.²³ The transition temperatures of the reported polymers were rather high, and in some cases they exceeded the temperature for 10% decomposition (T_{10}).

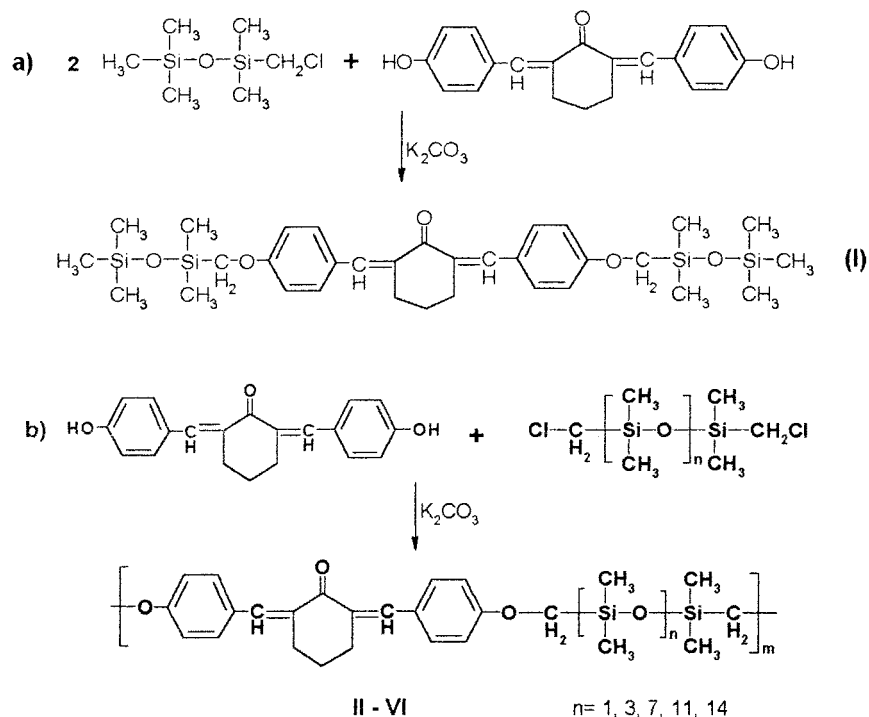
Our interest was focused on the synthesis of siloxane-containing arylidene polyethers and on their investigation for LC properties. A series of polyethers were obtained, starting from 2,6-bis(4-hydroxybenzylidene)cyclohexanone as mesogenic unit and oligosiloxanes with different average molecular weights as flexible spacers. A model compound, with siloxane tails, was also prepared to facilitate the investigation of the polymers properties. A study of photochemical behavior was also performed on some of the obtained polymers.

EXPERIMENTAL

Materials

Trimethylchlorosilane, chloromethyldimethylchlorosilane, octamethylcyclotetrasiloxane, and *N,N*-dimethylformamide (DMF; Fluka Chemie, Buchs, Switzerland) were used as received. 2,6-Bis(4-hydroxybenzylidene)cyclohexanone was obtained according to the method described in the literature,²³ with m.p. 284°C.

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Scheme 1 (a) Preparation of the model compound; (b) preparation of arylidene-siloxane polyethers.

General equipment

IR spectra were recorded on a Specord M80 Carl Zeiss Jena spectrophotometer (Oberkochen, Germany), using KBr pellets. $^1\text{H-NMR}$ spectra were registered on a JEOL (Peabody, MA) C60-HL spectrometer using CDCl_3 or $\text{DMSO-}d_6$ as solvent, without internal reference. Thermogravimetric analyses (TGA) were carried out by MOM derivatograph, in air, at a heating rate of $12^\circ\text{C}/\text{min}$. Differential scanning calorimetry (DSC) analyses were performed on a Mettler TA DSC 12E instrument (Nanikon, Switzerland). The mesophase behavior was observed with an Olympus BH-2 polarizing light microscope (PLM) fitted with a THMS 600/HSF9I hot stage. The textures were verified each time by a shear strain applied on the superior lamellae. The reversible change in the contour shape of the textures confirmed their homogeneity. Gel permeation chromatographic (GPC) analyses were carried out on a PL-EMD 950 evaporative mass detector instrument by using DMF as eluent after calibration with standard polystyrene samples. X-ray diffraction patterns were obtained at room temperature on a Philips (The Netherlands) PW 1830/PW 3710/PW 1050 powder diffractometer, using Cu-K_α radiation.

The electronic absorption spectra were recorded in DMSO with a Specord M42 Carl Zeiss Jena spectrophotometer. UV irradiations were carried out using a 350-W medium-pressure arc lamp at room temperature in 10-mm path length quartz cells fitted with PTFE stoppers. A suitable glass filter (365 nm) was used to obtain the irradiation light. The initial absor-

bance in the absorption band maximum was maintained between 0.9 and 1.0.

Chemical syntheses

Synthesis of chloromethylated disiloxanes

In a reaction vessel placed in an ice bath, an equimolar mixture of trimethylchlorosilane and chloromethyl-dimethylchlorosilane was poured into 250 mL distilled water within 1 h, with stirring. The reaction mass was then neutralized with sodium carbonate to pH 6. After separation and drying on anhydrous calcium chloride, the obtained mixture was vacuum distilled at 70 mm Hg; chloromethylpentamethyldisiloxane was collected at 70°C (n_D^{25} 1.4077), whereas bis(chloromethyl)tetramethyldisiloxane was distilled at $119\text{--}121^\circ\text{C}$ (n_D^{25} 1.4382). Their purity was checked by $^1\text{H-NMR}$ as well.

Synthesis of α, ω -bis(chloromethyl)-polydimethylsiloxanes

Telechelic chloromethyl siloxanes with preestablished molecular weights were obtained by equilibration reactions of cyclic siloxanes with 1,3-bis(chloromethyl)-tetramethyldisiloxane as chain transfer agent and a cation exchanger as catalyst, according to the method described in the literature.²⁵ The obtained oligomers have a polydispersity of about 1.6.

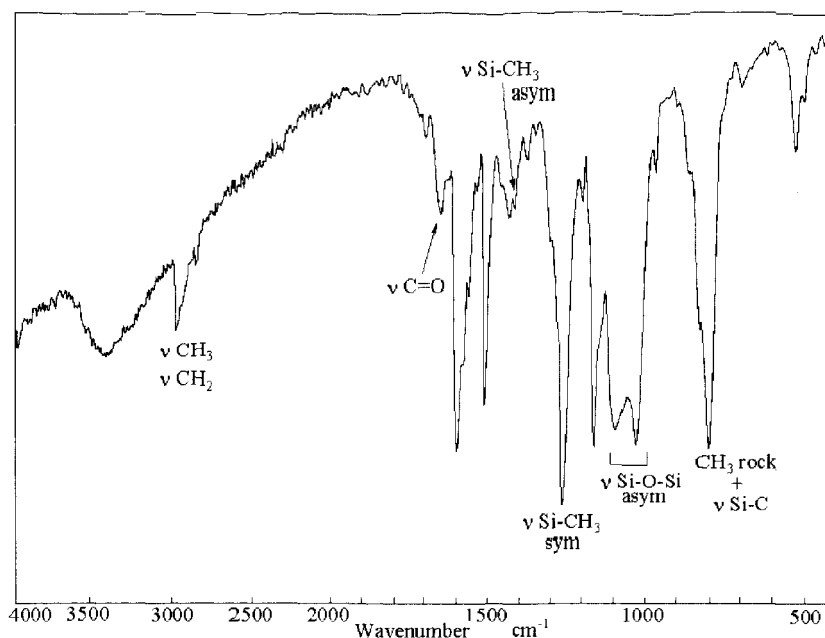


Figure 1 IR absorption spectrum of polymer IV.

Synthesis of the model compound (I) and polyethers (II-VI)

The synthesis of compounds I-VI was performed in the same manner, using either chloromethylpentamethylsiloxane or α,ω -bis(chloromethyl)oligodimethylsiloxanes of different molecular weights. An example is given below for the synthesis of polymer IV.

Siloxane oligomer 1.26 g (1.87 mmol) was placed in a reaction vessel. Then 0.573 g (1.87 mmol) of 2,6-bis(4-hydroxybenzylidene)cyclohexanone dissolved in 10 mL DMF, and 0.297 g (2.15 mmol) anhydrous K_2CO_3 were added. The reaction mixture was vigorously stirred for 8 h at 120°C. The resulting compound was precipitated into water, filtered off, and washed several times with water then with methanol. Finally, the product was washed with petroleum ether and vacuum dried.

RESULTS AND DISCUSSION

A model compound (I) was synthesized according to **Scheme 1(a)** to study the influence of the two siloxane moieties attached to the same mesogenic unit. The synthesis of arylidene polyethers was made according to **Scheme 1(b)**, using siloxane oligomers of different average molecular weights as spacers.

The IR and 1H -NMR spectra were used to confirm the obtained structures.

The main absorption bands in the IR absorption spectra of the polymers were as follows: 2980, 2860 (CH_3 , CH_2), 1660 ($C=O$), 1604 ($C=C$, aromatic), 1580 ($>C=CH-$, benzylidene), 1520 (aromatic), 1420 ($Si-CH_3$, asym.), 1268 ($\delta Si-CH_3$, sym.), 1100-1033 ($Si-O-Si$, asym.), 870, 840 (1,4-phenylene ring), 810 (CH_3 rocking asym + $Si-C$). In Figure 1 the IR spectrum of polymer IV is presented.

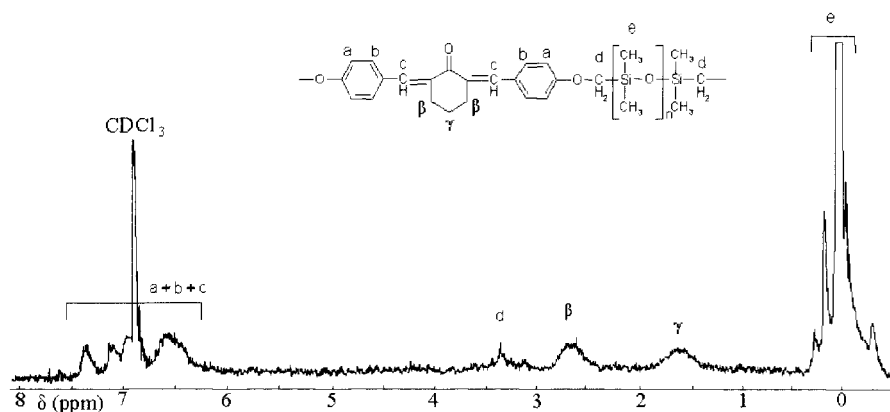


Figure 2 1H -NMR spectrum of polymer VI.

TABLE I
Thermal and Spectral Behavior of Arylidene-Siloxane Compounds

Code	n^a	Transition temperatures by PLM ^b (°C)	λ (nm)
I	Model compound	Cr • 179 • I Cr • 90 • LC • 158 • I	362.0
II	1	Cr • 124 • LC • 160 • I	370.0
III	3	Cr • 119 • LC • 140 • I	—
IV	7	Cr • 105 • LC • 134 • I	364.5
V	11	Cr • 77 • I	—
VI	14	Cr • 70 • I	369.5

^a Number of $(\text{CH}_3)_2\text{Si-O}$ units.

^b Cr, crystalline; LC, liquid-crystal; I, isotropic.

Because redistribution of siloxane chains and fractionation processes might occur during reaction and purification, the real length of the spacer in the obtained polyethers was determined from the $^1\text{H-NMR}$ spectra. The ratio of the integrals of the peaks corresponding to the protons in $-\text{[O-Si}(\text{CH}_3)_2\text{]}_{n-1}$ groups (from 0.05 ppm) and of those attributed to methyl protons in $-\text{O-CH}_2\text{-Si}(\text{CH}_3)_2$ moieties, from 0.1 ppm,²⁶ was used for the determination of “ n ” [Scheme 1(b)].

In the $^1\text{H-NMR}$ spectra, all the expected signals of the proposed structures were present. The $^1\text{H-NMR}$ spectrum of polymer VI is shown in Figure 2.

The number-average degrees of polymerization (DP) of all the obtained polyethers were between 5 and 7, and the polydispersities were around 1.5, as determined by GPC.

The transition temperatures were determined by DSC and PLM measurements. In Table I, the thermal behavior of the obtained compounds is presented, according to PLM observations in relation with the length of the siloxane chain, as determined by $^1\text{H-NMR}$. Because the polymers had comparable DPs, their mesophase behaviors could be correlated.

By PLM observations, thermotropic LC behavior was noticed for most of the synthesized compounds. A strong melt birefringence was observed in cross-polarized light, for all the LC compounds [I–IV, Fig. 4(a)–(c)]. No isotropic distinct domains were detected within the texture as an indication of possible phase separation. Whereas siloxane end-capped model I was monotropic, the siloxane-arylidene polyethers II–IV exhibited enantiotropic mesomorphism. Polymers V and VI were isotropic in the melting state.

For model compound I, the DSC scan [Fig. 3(a), (b)] showed a single endothermic peak at 163°C in the first heating cycle, a “shoulder” at 139°C, and an exothermic peak at 86°C in the first cooling cycle. By PLM measurements, melting was observed at 179°C, in the first heating, whereas at cooling melt birefringence appeared at 158°C and crystallization occurred at 90°C. In the case of I, the bulky disiloxane tails hindered the mesophase organization of the melt at heating, but allowed it at cooling.

In DSC scans of polymers II and IV [Fig. 3(c), (d)], three main endotherms could be observed in the first heating cycle. The lowest temperature peaks could be attributable to polymorphic transitions (crystal to crystal), the second peaks were assigned to the melting processes (crystal-to-liquid crystal), and the highest temperatures corresponded to the isotropization (liquid crystal-to-isotropic melt) transitions.

These assignments were in agreement with the microscopy observations; the lowest temperature endotherms had no significance in PLM. The polymers exhibited fine-grain smectic textures (Fig. 4), and no smectic to nematic transitions could be observed by optical microscopy at 1°C/min heating rate, although the DSC scans presented small shoulders that might suggest them.

In the XRD spectrum of polymer II at room temperature (Fig. 5), some degree of crystallinity can be observed, in the same pattern as reported^{21,22} for other arylidene-containing polymers. The sharp peak at $2\theta = 4.99$ that can be seen in Figure 5 was assigned to the layer spacing ($d = 17.5 \text{ \AA}$) of a smectic mesophase.

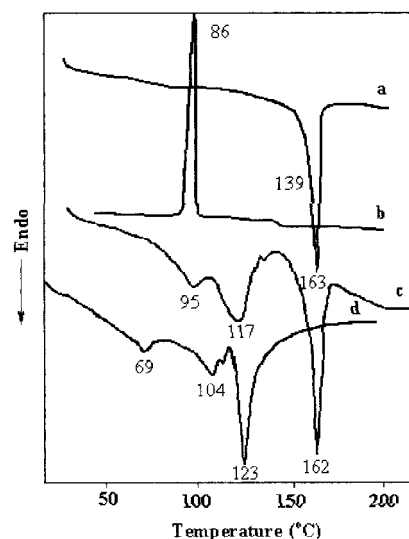


Figure 3 DSC curves: (a) model compound I, first heating scan; (b) model compound I, first cooling scan; (c) polymer II, first heating scan; (d) polymer IV, first heating scan.

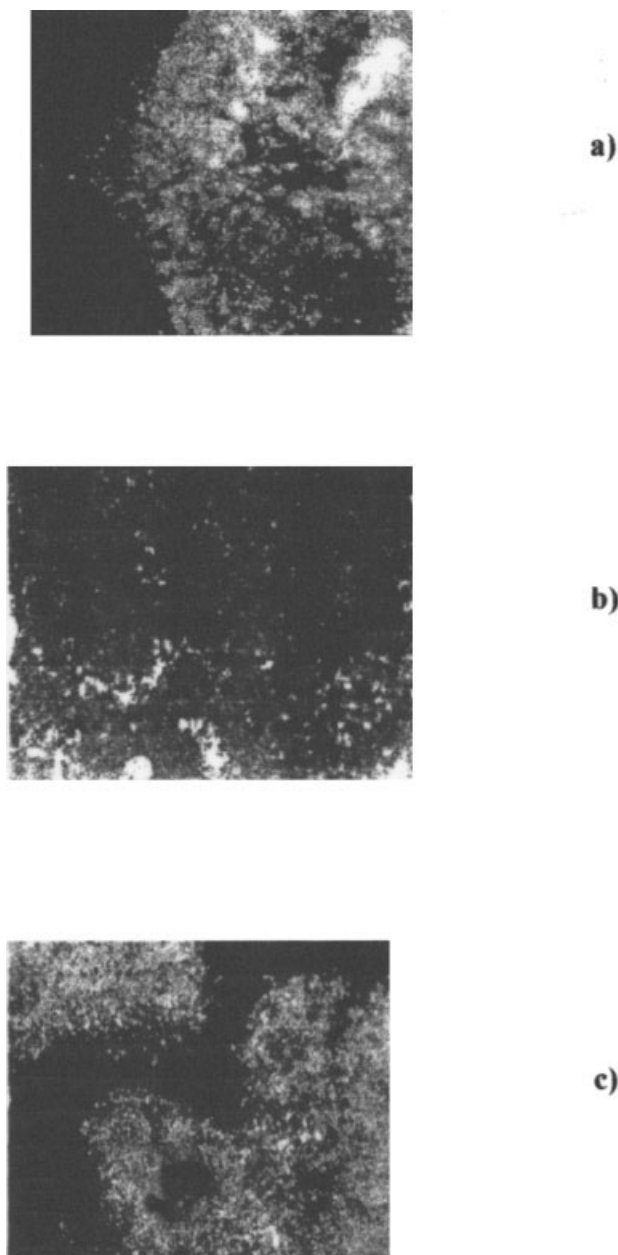


Figure 4 Polarized light photomicrographs, magnification $\times 200$: (a) model compound I, 126°C (cooling); (b) polymer II, 128°C; (c) polymer IV, 120°C.

Only nematic textures were reported^{21–23} for poly(arylidene-ether)s containing polymethylene and poly(ethylene oxide) spacers. It seems that the presence of siloxane moieties determined the occurrence of a more organized mesophase, which can be attributed to the nanophase separation of the chemically distinct components, siloxane and hydrocarbon.²⁷

As can be seen from Table I, both the melting (T_m) and the isotropization (T_i) temperature values decreased as the siloxane segment length increased. This fact confirms the efficiency of the siloxane spacers in decreasing the transition temperatures, comparatively with similar polyethers bearing polymethylene spac-

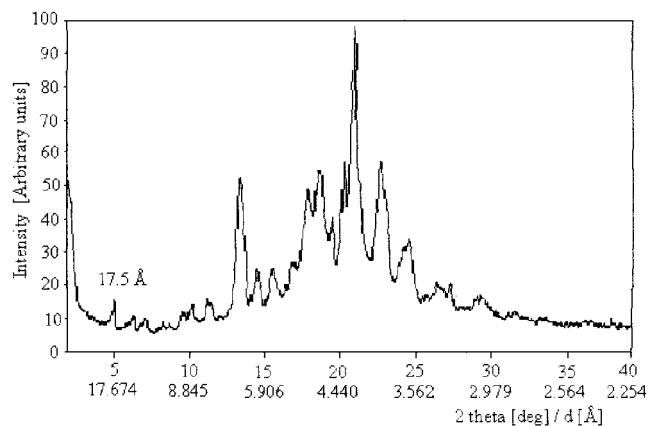


Figure 5 XRD spectrum of polymer II.

ers.^{21,22} The mesophase ranges are relatively narrow, of about 30°C, but comparable with most of the other similar reported polymers.

The thermal stability of polyethers II and IV was evaluated by TGA in air, and the results are shown in Table II. It can be noted that the thermal decomposition began at temperatures higher than isotropization temperatures. In the study by Aly and Hamman,²¹ poly(arylidene-ether)s containing cyclopentanone moieties and polymethylene spacers were reported to have T_{10} in the mesophase domain or very close to it, so that the mesophase could not be thermally stable. For the polyethers reported in the present study, T_m and T_i were much lower than T_{10} , so that the mesophase is not affected by decomposition phenomena, and the obtained polyethers might be processed in the LC state. This is a consequence of the influence of the siloxane spacers on the transition temperatures of the polyethers. From Figure 6 it can be seen that the LC domains are situated under the limit of 1% weight losses. On the other hand, the selected polyethers (especially IV, having a polysiloxane spacer) had good thermal stability.

The photobehavior of model compound I and polyethers was studied by ultraviolet absorption spectra. The change in the UV spectral pattern during photolysis of model compound I at different intervals of time is shown in Figure 7. The absorption band at 362 nm can be assigned to the bis(benzylidene)cyclohexanone moiety.²⁸ During the successive irradiation of model

TABLE II
Thermal Stability of Polyethers II and IV

Weight loss	Temperature (°C) for different weight losses (%)						
	Sample	10	20	30	40	50	60
II		210	240	300	370	430	510
IV		317	355	378	406	500	570

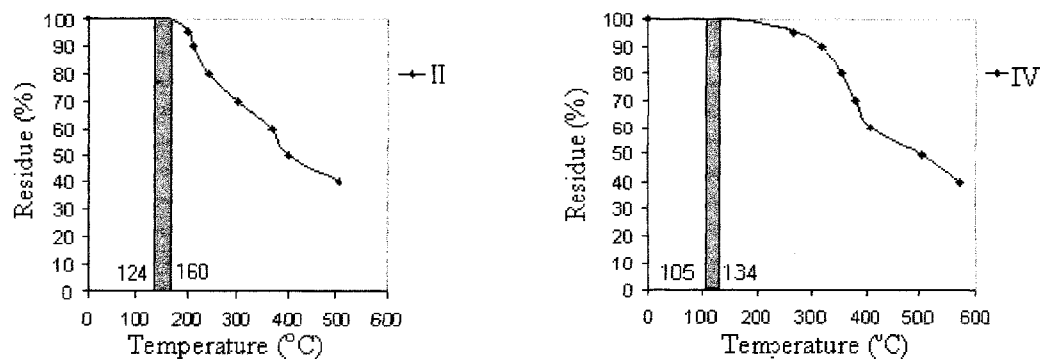


Figure 6 Mesophase stability evaluated by TGA, in air, for polymers II and IV.

compound I, a decrease in the intensity at 362 nm took place, as seen in Figure 7.

In the first 5 min of 365-nm irradiation two isosbestic points appeared at 326 and 420 nm, respectively, and a blue shift for the 362-nm absorption band was observed. In the first stages of the photoreaction, the decrease in intensity of the 362-nm band and the presence of the isosbestic points indicate that a photoisomerization process of the bis(benzylidene)cyclohexanone chromophores occurs in solution. Upon further photolysis a new absorption band at about 287 nm appeared (after 95 min of irradiation), which can be attributed to the photodimerization reactions involving bis(benzylidene)cyclohexanone moiety.²³

A rather close similarity between the electronic absorption spectra of model compound I and the polyethers during photolysis was confirmed. The relative photoreactivity $(A_0 - A_t)/A_0$ was plotted against the irradiation time (Fig. 8), where A_0 is the absorbance before irradiation and A_t is the absorbance at time t . Model compound I was found to be more reactive than the siloxane-arylidene polyethers.

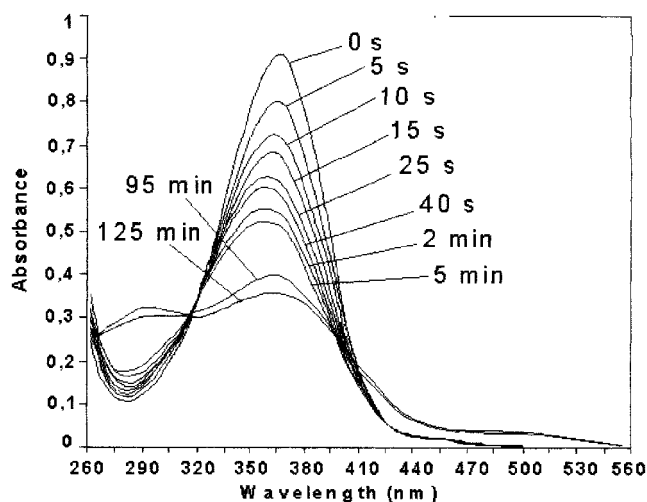


Figure 7 Change of electronic absorption spectra during photolysis of model compound I.

At the initial stages of the photoreaction the following order of photosensitivity was established: I > VI > IV > II. This order is determined by the siloxane spacer length and the different flexibilities of the polymer chain. This might suggest that the local environment for the bis(benzylidene)cyclohexanone chromophore is different in polyethers II and IV compared to that in model compound I and polyether VI where the movement of chromophores is much less restricted.

The UV absorption spectra of the irradiated polyethers and model compound were practically unchanged by maintaining them at 80°C for different durations, suggesting that a photodegradation process can occur.

The polyether solutions in DMSO were heated to 135°C and the thermal effect was monitored by the modifications of the absorption band at about 370 nm as a function of temperature. On heating, a gradual decrease in the absorbance was observed until the temperature reached 95°C. Above this temperature, the absorbance at about 370 nm exhibited a small increase up to 135°C for all samples, except for polyether III, where the intensity of the 370-nm band remained constant between 100 and 135°C. The recovery took place at room temperature with the restora-

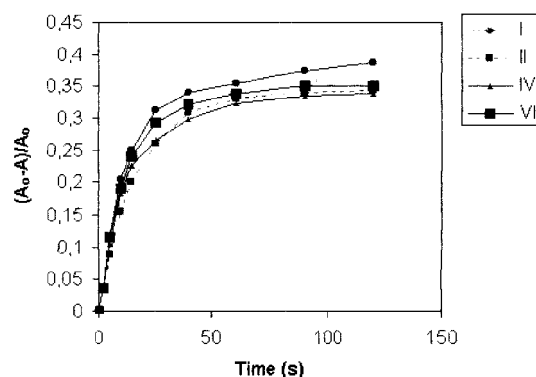


Figure 8 Dependency of relative photoreactivity on irradiation time of samples I, II, IV, and VI.

tion of the initial absorption band. However, these changes in the intensity of the absorption band were rather small because a conversion about 15% was achieved for samples **I**, **II**, and **IV**, whereas the conversion for sample **VI** was about 10%.

It seems that the presence of a siloxane environment reduced the photochemical reactivity of the bis(benzylidene)cyclohexanone polyethers, given that both the time and temperature dependencies were smaller compared with those of the poly(ethylene oxide)-containing homologs.²³

CONCLUSIONS

New siloxane-containing arylidene polyethers and a siloxane end-capped model compound were synthesized. The investigation of their LC properties and thermal behavior revealed that siloxane segments used as spacers are responsible for lowering of the transition temperatures of the obtained polyethers, while maintaining reasonable thermal stability. This effect was more pronounced than that of polymethylene spacers. The consequence of such behavior could be an increased processability. The photobehavior of the siloxane-arylidene polyethers is influenced by the siloxane spacer length, with polyether **VI** having a higher relative photochemical reactivity. A higher photostability was obtained in the case of siloxane-arylidene compounds, compared with that of poly(ethylene oxide) homologs reported in the literature.

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