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Polymerization in Lyotropic Liquid Crystals. 2. Synthesis of Photo-Cross-Linkable PEO–PDMS–PEO Triblock Copolymers and Permanent Stabilization of Their Supermolecular Structures in Lyotropic Mesophases

Jianling Yang and Gerhard Wegner*

Max-Planck-Institut für Polymerforschung, Postfach 3148, D-6500 Mainz, Germany

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ABSTRACT: Photo-cross-linkable ethylene oxide–dimethylsiloxane PEO–PDMS–PEO–cinnamate triblock copolymers were prepared via Pt-catalyzed hydrosilyation of α,ω-dihydropoly(dimethylsiloxane) with bifunctional propargyl-terminated poly(ethylene oxide)-monomethyl ethers and subsequent esterification with cinnamoyl chloride. Lyotropic mesophases of the copolymer/water system were photo-cross-linked by using UV radiation. The supermolecular structures were retained after photo-cross-linking but could be destroyed by swelling with organic solvents. After the evaporation of the solvent, the films showed the original mesophases by addition of water.

Introduction

The study of the phase behavior of PEO–PDMS–PEO triblock copolymers with and without photoactive cinnamoyl moieties in water has been subject of our previous work.[1] Both systems form liquid-crystalline mesophases. This paper deals with aspects concerning the synthesis of the copolymers and the photo-cross-linking behavior of the PEO–PDMS–PEO–cinnamate/water system in the mesophase state.

Experimental Section

Materials. Chemicals and solvents used in the course of this work were purchased from commercial sources. α,ω-Dihydropoly(dimethylsiloxane) (I) was prepared following literature procedures.[2] 2,3-Epoxypropyl tetrahydropyranyl ether was prepared according to a method reported by Miyashita et al.[3] Cinnamoyl chloride was distilled to remove inhibitors prior to use. For the dialysis, cellophane dialysis tubing (diameter of pores <2 nm; Servapor, Heidelberg, Germany) was used.

Synthesis of Photo-Cross-Linkable Triblock Copolymers. General Procedure. Bifunctional Poly(ethylene oxide) (II). A total of 0.1 mol of PEO–monomethyl ether was freeze-dried and then dissolved in absolute toluene to give a 10% (wt) solution. A total of 0.2 mol of sodium was added under an argon atmosphere, and the mixture was refluxed for several hours (5 h for PEO 350, 8 h for PEO 550, 12 h for PEO 750, and 24 h for PEO 1900, the numbers indicating the average molecular weights). Excess sodium was filtered off, and 0.1 mol of 2,3-epoxypropyl tetrahydropyranyl ether was added. The reaction mixture was refluxed for a further 36 h, and then 0.15 mol of propargyl bromide was added. The mixture was stirred at 60 °C for 3 h. Sodium bromide was filtered off, and the remaining solution was concentrated. The residue was dissolved in 250 mL of methanol with addition of 2.5 g of cation-exchange resin in the acid form (Amberlyst). The mixture was stirred under argon for 8 h at 50 °C. The exchange resin was filtered off, and the remaining yellow solution was refluxed with addition of 2 g of charcoal for 1 h. After the charcoal was filtered off, the remaining solution was concentrated. The residue was poured into an excess of ether kept at −10 °C whereupon the functionalized PEO separated as a colorless precipitate. After a further freeze drying from benzene the yield was 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (t) and 2.45 (t, $C\equiv CH$, two isomers), 3.38 (s, CH_3O), 3.5–3.9 (br, m, OCH_2CH_2O and $OCHCH_2O$), 4.19 (d) and 4.30 (dd, $OCH_2C\equiv C$, two isomers). ^{13}C NMR (300 MHz, acetone-d_6): δ 57.7, 58.5, 58.7, 62.4, 62.6, 69.8–72.1, 75.4, 75.7, 79.2, 79.5, 81.2, 81.5. IR (KBr): 3240 ($\equiv CH$ stretching), 2110 cm^{-1} ($C\equiv C$ stretching).

PEO–PDMS–PEO Triblock Copolymer with Free Hydroxy Groups (III). A total of 0.1 mol of α,ω-dihdyropoly(dimethylsiloxane) (I) and 0.25 mol of bifunctional PEO (II) were dissolved in dry toluene to give a 30% (wt) solution. The mixture was saturated with argon under vigorous stirring. Hexachloroplatinic acid (10^{-4} mol) was added as a 1% solution in isopropyl alcohol. The reaction mixture was stirred for at least 10 h at 90 °C. Solvent was then removed in vacuum, and the slightly yellow residue was dissolved in water. The micellar solution was subjected to dialysis for at least 4 days, sufficient to remove the excess PEO. The aqueous solution was concentrated, and the residue was purified by freeze drying from benzene. Yield: 80–85%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.10–0.30 (m, $OSi(CH_3)_2$), 3.38 (s, CH_3O), 3.50–3.90 (br, m, OCH_2CH_2O and $OCHCH_2O$), and 4.10–4.30 (m, $OCH_2C=$ and $OCH_2CC=$, two isomers), 5.50 (m) and 5.75 (m, $C=CH_2$, two isomers), 5.85 (d) and 6.15 (dt, $CH=CH$, two isomers). ^{13}C NMR (300 MHz, acetone-d_6): δ −0.8–2.9, 58.7, 62.5, 62.6, 69.8–75.3, 80.1, 81.0, 129.7, 130.1, 145.1, 145.7.

Table I
Characterization of α,ω-Dihydropoly(dimethylsiloxane)

sample	^{1}H NMR[a]	$\bar{M}_n$ VPO[b]	$\bar{M}_n$ GPC	$\bar{M}_w$[c]	$\bar{M}_w/\bar{M}_n$[c]
1	670	750	780	1070	1.37
2	1170	1090	1440	2120	1.44
3	1520	1500	1810	2980	1.64
4	2460	2300	2970	4950	1.67
5	4390	3900	4890	8710	1.78

[a] Determined by end-group analysis. [b] Vapor pressure osmometry. [c] Determined by GPC.

PEO–PDMS–PEO–Cinnamate Triblock Copolymer (IV). A total of 10 mmol of functional triblock copolymer (III), 40 mmol of cinnamoyl chloride, 40 mmol of pyridine, and 4 mmol of 4-(dimethylamino)pyridine were dissolved in 250 mL of dry dichloromethane. The mixture was refluxed under argon for 20 h. The precipitate was filtered off, and the solvent was removed. The residue was chromatographed on a silica gel column with a chloroform/methanol gradient. After a freeze drying from benzene the yield was about 85%. ^{1}H NMR (300 MHz, acetone-d_6): δ 0.05–0.30 (m, $OSi(CH_3)_2$), 3.38 (s, CH_3O), 3.50–3.90 (m, OCH_2CH_2O and $OCHCH_2O$, two isomers), 4.10–4.40 (m, $OCH_2C=$ and $OCH_2CC=$, two isomers), 5.40–6.30 (m, $C=CH_2$ and $CH=CH$, two isomers), 6.75 (d, J = 17 Hz) and 7.70 (d, J = 17 Hz, $PhCH=CHCO$), 7.45–7.65 (m, aromatic protons). ^{13}C NMR (300 MHz, acetone-d_6): δ 0.4–2.9, 58.8, 64.6, 69.7–75.2, 77.1, 118.9, 125.8–129.4, 129.8, 131.2, 135.4, 145.4, 166.8. IR (KBr): 1717 (ester $C=O$ stretching), 1637 cm^{-1} ($C=CH$ stretching).

Methods. Infrared spectra were recorded by a Perkin-Elmer Model 1430 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained by a Bruker 300-MHz FT instrument. Deuteriochloroform and

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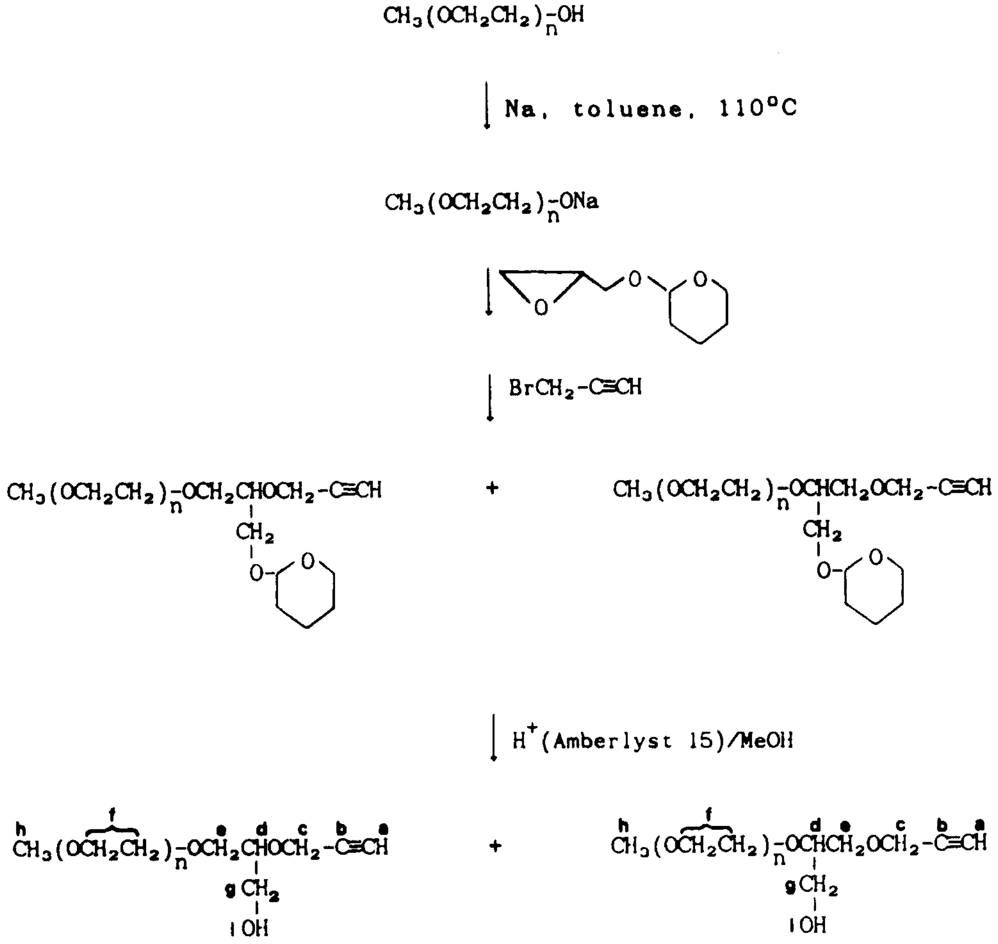
Scheme I



(IIa) (II) (IIb)

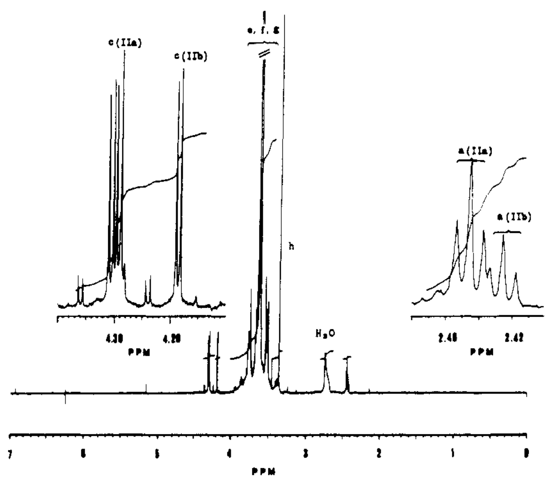


Figure 1. Typical ^{1}H NMR (300-MHz) spectrum of functionalized PEO (II) (mixture of two isomers IIa and IIb) in $CDCl_3$.

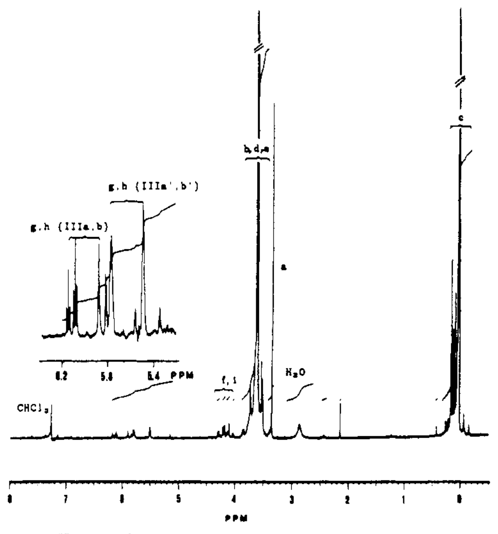


Figure 2. Typical ^{1}H NMR (300-MHz) spectrum of PEO–PDMS–PEO triblock copolymer (III) in $CDCl_3$ (composition: $\overline{DP_n}$ of PEO = 19, $\overline{DP_n}$ of PDMS = 16).

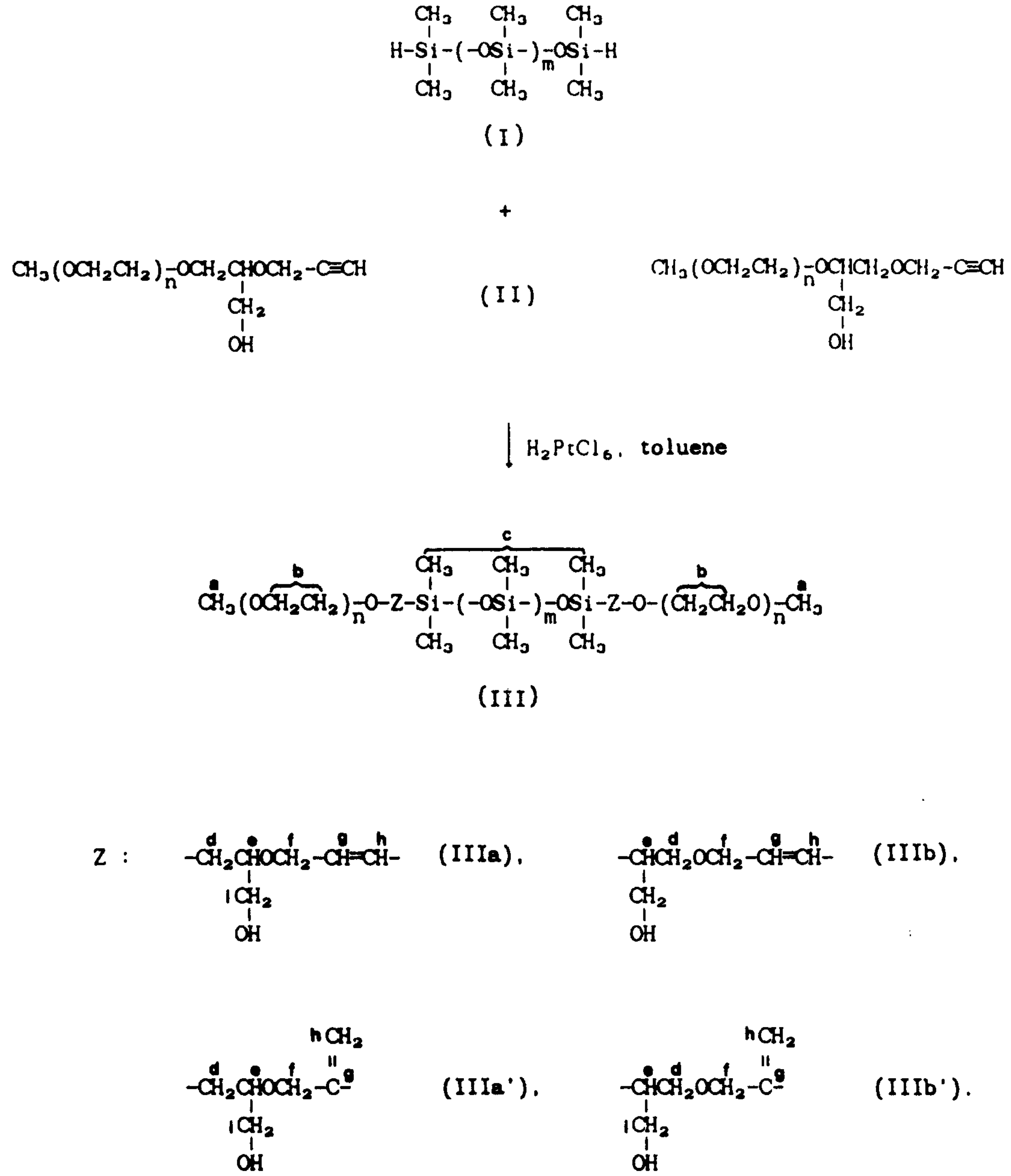
hexadeuterioacetone were used as solvents. UV spectra were recorded by a Perkin-Elmer Lambda 3 UV/vis spectrometer. GPC was performed with a Waters and Erma Optical Works Associates model equipped with three PL gel columns (50, 500, and 10^4), using toluene (for PDMS) or *o*-dichlorobenzene (for block copolymers) as eluent. VPO measurements were performed with a Wescan 232A instrument (toluene, 50 °C). The textures of samples were observed with a Zeiss photomicroscope III equipped with crossed polarizers.

Photo-Cross-Linking. The samples were prepared as described for obtaining the phase diagram.[1] The photo-cross-linking of samples was performed with a thin film between sealed quartz plates. UV irradiation was by a 100-W high-pressure mercury lamp (Photon Technology). The degree of photo-cross-linking was followed by UV spectroscopy. To remove the exothermic heat caused by irradiation, cold air was flown around the sample.

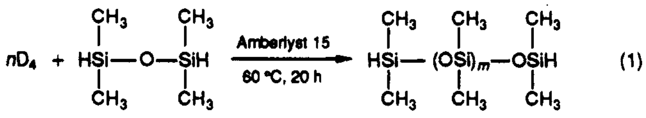
Results and Discussion

Synthesis and Characterization of Triblock Copolymers. Equation 1 shows the general reaction used to prepare an α,ω-dihydropoly(dimethylsiloxane) (I). A study of the literature revealed that the cationic ring-

Scheme II



opening polymerization of octamethylcyclotetrasiloxane (D_4) using tetramethyldisiloxane as the chain-transfer reagent was an equilibrium reaction.[4] The equilibrated



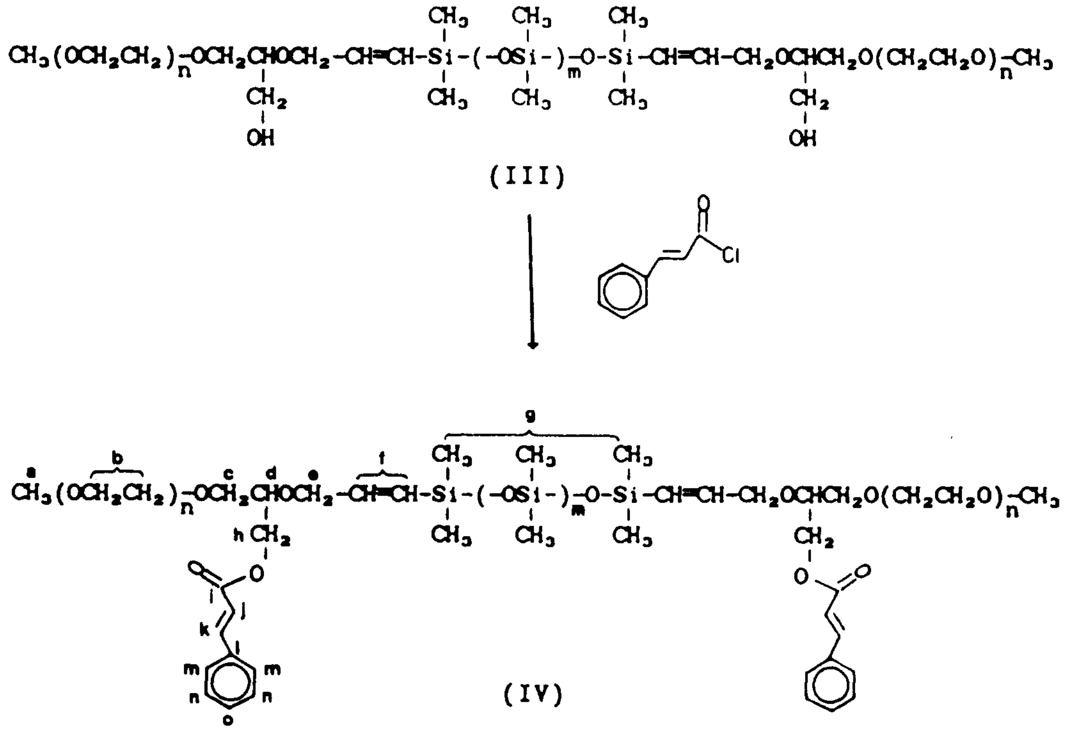
$$nD_4 + \mathrm{HSi(CH_3)_2{-}O{-}Si(CH_3)_2H} \xrightarrow[60\ ^\circ\mathrm{C},\ 20\ \mathrm{h}]{\text{Amberlyst 15}} \mathrm{HSi(CH_3)_2{-}(OSi(CH_3)_2)_{\mathit{m}}{-}OSi(CH_3)_2H} \quad (1)$$

reaction mixture was stripped of starting materials and other volatiles at 100 °C and approximately 10^{-2} mbar for several hours. The chain length was controlled by the molar ratio of the reactants in the reaction mixture; however, the molecular weight was determined by end-group analysis using a ^{1}H NMR technique and vapor-pressure osmometry (VPO). GPC was used to check the molecular weight distributions.[5] Table I lists the data.

The bifunctional PEO (II) was synthesized by the route shown in Scheme I. The alcoholysis of the epoxide ring was not regiospecific; two isomers (IIa and IIb) were obtained. The ratio of IIa to IIb was 70 to 30% which was determined by ^{2}H NMR spectroscopy. A 300-MHz proton spectrum together with appropriate assignments is given in Figure 1.

PEO–PDMS–PEO triblock copolymers (III) were prepared by hydrosilylation of α,ω-dihydropoly(dimethylsiloxane) (I) with propargyl-terminated PEO (II) using hexachloroplatinic acid as the catalyst (Scheme II). Usually the synthesis of PEO–PDMS block copolymers with hydrolytically stable Si–C linkages between blocks is carried out by hydrosilylation of the terminal functional PDMS with vinyl-terminated PEO.[6,7] However, the reaction is not quantitative because of the isomerization of the allylic double bonds occurring as a side reaction. Further, a large excess of PEO is necessary for a quantitative conversion of ≡SiH end groups into Si–C bonds. The use of propargyl-terminated PEO has the advantage that the conversion is quantitative under the reaction conditions. However, an excess of PEO was used to ensure a quantitative yield of the desired triblock copolymers. The extent of the reaction was followed by IR spectroscopy. The infrared spectrum at the end of the reaction proved the complete disappearance of the Si–H vibrations (2120 and 910 cm^{-1}). The excess PEO homopolymer was separated from the copolymer by dialysis of the aqueous copolymer solution versus pure water. GPC measurements showed no trace of PEO in the block copolymer.

Scheme III


(III)

(IV)

The Pt-catalyzed hydrosilylation of terminal acetylenes is known to occur both in a Markovnikov and an anti-Markovnikov (Si addition to the terminal carbon) manner.[8] This was also found in the block copolymers produced by the hydrosilylation. The ratio of isomeric adducts was 1:1. A representative ^{1}H NMR spectrum with signal assignments is presented in Figure 2 (compare with Scheme II).

The photo-cross-linkable PEO–PDMS–PEO–cinnamate triblock copolymers (IV) were obtained by esterification of the hydroxy groups in the triblock copolymers (III; Scheme III, for a better survey, only one isomer of copolymer III is shown). An excess of cinnamoyl chloride which helped to ensure quantitative esterification was easily removed via column chromatography on silica gel with a chloroform/methanol gradient. It should be noted that, after the column chromatography, the distribution of molecular weight of the triblock copolymers changed remarkably. In general, a decrease of the average PEO chain lengths was observed, due to the remains of some stronger hydrophilic copolymers in the column.

NMR and IR analyses showed the good functionality of the block copolymer with respect to the photosensitive groups. A representative ^{1}H NMR spectrum is shown in Figure 3. The assignment of the signals is suggested according to Scheme III.

Photo-Cross-Linking Behavior in the Mesophases. The mesophases are unstable with respect to temperature and mechanical stress. For that reason the photochemical method was suitable for the stabilization of the mesophases especially.

The location of photosensitive cinnamoyl moieties near the linkages between the hydrophilic PEO and the hydrophobic PDMS parts of the blocks has the advantage that, above the critical micelle concentration (cmc), the cinnamoyl moieties will accumulate at the hydrophilic–hydrophobic interface, providing for a very high local concentration of the photoactive centers. The photopolymerization and photo-cross-linking of cinnamate ester derivatives have been extensively investigated and are well documented.[9,10] In the solid state, the photoreaction produces α- or β-truxillic esters according to the crystal structures. However, the stereocontrol of the structure found in the crystalline state for photodimerization is not preserved in solution or in mesophases. Moreover, it seems that the photo-cross-linking in the mesophases proceeds with participation of a radical mechanism.

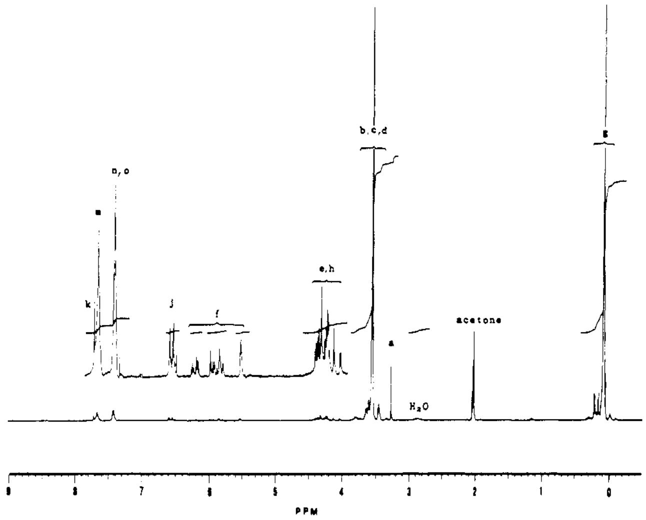


Figure 3. Typical ^{1}H NMR (300-MHz) spectrum of PEO–PDMS–PEO–cinnamate triblock copolymer (IV) in $CDCl_3$ (composition: $\overline{DP}_n$ of PEO = 16, $\overline{DP}_n$ of PDMS = 16).

A PEO–PDMS–PEO–cinnamate triblock copolymer (IV) ($\overline{DP}_n$ of PEO = 16, $\overline{DP}_n$ of PDMS = 16) was used to study the photo-cross-linking behavior in the lyotropic mesophases. The phase behavior of this copolymer/water system was documented in the previous paper.[1] Two samples were prepared in the hexagonal phase (50 wt % copolymer) and lamellar phase (73 wt % copolymer). The irradiation was performed with films of a thickness of about 10 μm. The UV spectra showed that the cinnamic chromophore with an absorption maximum at 275 nm had practically disappeared after 1 h of irradiation time. Figure 4 describes the variation of the UV spectra with irradiation time for the two samples.

The reticulated films were then studied by a polarizing microscope. The typical textures of the mesophases were

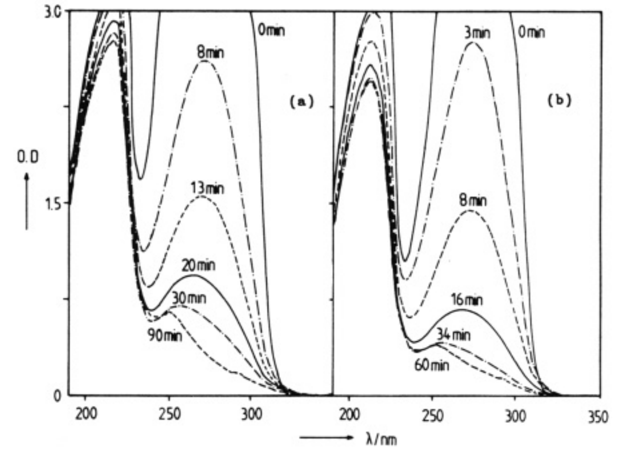


Figure 4. Evolution of the UV spectra of a copolymer (IV) ($\overline{DP}_n$ of PEO = 16, $\overline{DP}_n$ of PDMS = 16)/water system in mesophases with irradiation time: (a) 50 wt % copolymer, H_1 phase, thickness approximately 15 μm; (b) 73 wt % copolymer, L_α phase, thickness approximately 5 μm.

Table II
Bragg Spacing Values d and Structural Parameters (Hexagonal Structure $D = (2/\sqrt{3})d$, Lamellar Structure $D = d$) of the Photo-Cross-Linkable Copolymer (IV)/Water Systems

		d_{Bragg}, Å		D, Å	
sample	mesophase	*a*	*b*	*a*	*b*
50 wt % copolymer	H_1	94.8	88.1	109.5	101.7
73 wt % copolymer	L_α	83.4	80.3		

[a] Before UV irradiation. [b] After UV irradiation.

not changed after the irradiation. Even after several days in high vacuum for evaporation of water, the textures of the films were retained (Figure 5a). The films were insoluble in water and common solvents. The insolubility can probably be attributed to intermicellar cross-linking in the continuous phase between the micelles which arrange to hexagonal or lamellar superstructures. The mesophase structures were consequently fixed by photo-cross-linking. The films lose the anisotropic structures during the swelling with organic solvents; however, after evaporation of the organic solvents, isotropic films were obtained (Figure 5b). The isotropic films showed the very interesting property that if water was added, the typical texture of the original mesophase was reconstituted (Figure 5c). The procedure was reversible. In addition, the reticulated films were investigated by small-angle X-ray scattering (SAXS). Table II lists the SAXS data of the films before and after UV irradiation. A contraction of the distance D between cylinders in the hexagonal structure as well as the layer thickness D in the lamellar structure of the mesophases was observed after irradiation.

Conclusions

PEO–PDMS–PEO triblock copolymers with free hydroxy groups at the linkages between blocks were prepared by hydrosilylation of α,ω-dihydropoly(dimethylsiloxane) with bifunctional propargyl-terminated PEO–monomethyl ethers. The corresponding photo-cross-linkable PEO–PDMS–PEO–cinnamate triblock copolymers were obtained by reaction of the hydroxy groups with cinnamoyl chloride. The mesophases of the PEO–PDMS–PEO–cinnamate/water systems were fixed by UV irradiation of the samples. The anisotropic structures of the reticulated films were retained after removal of water but could be destroyed by swelling with an organic solvent. The swelled films were isotropic, even when the solvent was evaporated.

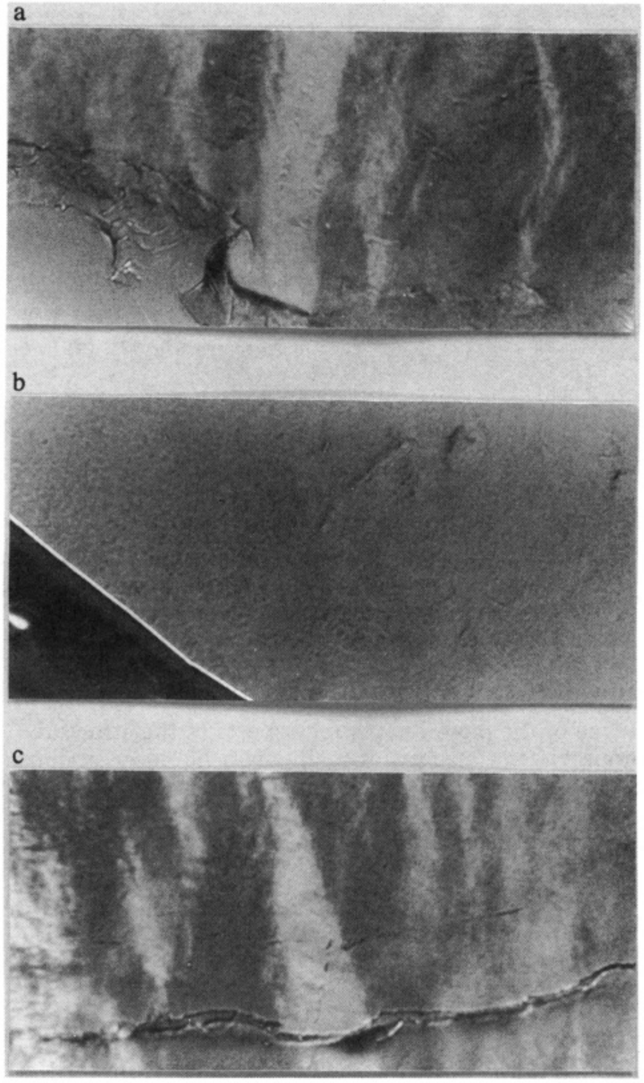


Figure 5. Optical microscopy textures in polarized light of the hexagonal (H_2) mesophase: (a) UV-cross-linked film after evaporation of water; (b) isotropic film after swelling with chloroform; (c) addition of water to the isotropic film after evaporation of chloroform.

By addition of water, the original mesophase was reproduced. Thus, the reticulated films have a memory of their initial state.

References and Notes

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Registry No. IIa, 138955-83-6; IIa tetrahydropyranyl, 138955-81-4; IIb, 138955-84-7; IIb tetrahydropyranyl, 138955-82-5; Me(OCH_2CH_2)$_n$OH, 9004-74-4; $BrCH_2C{\equiv}CH$, 106-96-7; epoxypropyl tetrahydropyranyl ether, 64244-53-7.