Communications

Photo-Cross-Linkable Liquid-Crystalline Side-Chain Polysiloxanes

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Liquid-crystalline elastomers prepared from side-chain, main-chain or combined liquid-crystalline polymers have been intensively studied recently.[1-8] These new materials are interesting for fundamental studies as well as potential technological applications.

Liquid-crystalline elastomers have been synthesized by two different ways: a one-pot procedure and a two-step procedure. The one-pot procedure consists of the simultaneous formation of the principal linear polymer chain and of the cross-links by mixing, *in a solvent*, for example,[2a] a mesogenic acrylate monomer with a bifunctional cross-linking agent (diacrylate) and then submitting them to a radical polymerization (for the one-pot synthesis of a polysiloxane elastomer see ref 1a). In the two-step procedure, the linear liquid-crystalline polymer is prepared first, which possesses in its chemical structure a reactive function (carbon–carbon double bond,[4a,c,e] hydroxyl[4a,d]). In the second step, the linear liquid-crystalline polymer reacts *in solution* with an appropriate difunctional reagent to give the liquid-crystalline elastomer.

In this communication, we present a new two-step procedure for the synthesis of liquid-crystalline side-chain polysiloxane elastomers in which the cross-linking reaction is performed by ultraviolet irradiation of the linear side-chain polysiloxane *in the glassy state* (i.e., *without solvent*). This procedure might give the opportunity of preparing organic thin films with controlled, polar orientation of functional groups relative to a substrate, which are of interest for microelectronic and optoelectronic applications.[13] Indeed, the mesomorphic side-chain polymer precursors would be able, due to their liquid-crystalline properties, to be first oriented by various ways (e.g., surface effects, application of electric or magnetic fields) and then, either in the mesomorphic state or after cooling down to the glassy state, submitted to UV irradiation to give, eventually, macroscopically oriented liquid-crystalline side-chain elastomers.

Table I. Transition Temperatures for Polysiloxanes 2

polym	*n*	*m*	phase transitions[a]
2a	5	1	g 35 $\mathrm{S_C}$ 112 I
2b	6	1	g 36 $\mathrm{S_C}$ 117 I
2c	8	1	g 40 $\mathrm{S_C}$ 129 I
2d	8	6	K 95 $\mathrm{S_C}$ 133 I
2e	8	7	K 85 $\mathrm{S_C}$ 128 I
2f	10	6	K 80 $\mathrm{S_C}$ 138 I
2g	10	7	K 80 $\mathrm{S_C}$ 130 I

[a] *T* in °C; g = glass; K = crystal; $\mathrm{S_C}$ = smectic C; I = isotropic.

The linear side-chain liquid-crystalline polysiloxanes (2) have been prepared by hydrosilation of poly(methylsiloxane) with low molar mass mesogens (1) containing a terminal vinyl group in the presence of a platinum catalyst[9] (Scheme I).

Liquid-crystalline polysiloxanes produced to date possessed in their structure various types of chemical groups as the mesogenic part such as Schiff base, azobenzene, or phenyl benzoate.[9] Instead, we have used a phenyl cinnamate based mesogenic group that, besides its very well-known ability to give liquid-crystalline phases,[10] has been extensively used as photo-cross-linkable group for photoresist applications and related studies.[11]

Starting with bromoalkenes and methyl 4-hydroxycinnamate, 4-(alkenyloxy)cinnamic acids were obtained by classical synthetic methods.[12a] These acids were esterified[12b] in a second step with 4-alkyloxyphenols to give the desired functional mesogens (1). With these substrates, liquid-crystalline polysiloxanes (2) were obtained by an already reported method,[9c,d] the mesomorphic properties of which are listed in Table I. (The phase behavior was established by polarization microscopy and DSC measurements.)

All the polysiloxanes (2) exhibit only a smectic C phase, regardless of the lengths of both the spacer and the terminal tail: the phenyl cinnamate group enhances the

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(1) (a) Finkelmann, H.; Kock, H. J.; Rehage, G. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 317. (b) Oppermann, W.; Braatz, K.; Finkelmann, H.; Gleim, W.; Kock, H. J.; Rehage, G. *Rheol. Acta* **1982**, *21*, 423. (c) Finkelmann, H.; Kock, H. J.; Gleim, W.; Rehage, G. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 287. (d) Gleim, W.; Finkelmann, H. *Makromol. Chem.* **1987**, *188*, 1489. (e) Schätzle, J.; Finkelmann, H. *Mol. Cryst. Liq. Cryst.* **1987**, *142*, 85.

(2) (a) Davies, F. J.; Gilbert, A.; Mann, J.; Mitchell, G. R. *J. Chem. Soc., Chem. Commun.* **1986**, 1333. (b) Mitchell, G. R.; Davis, F. J.; Ashman, A. *Polymer* **1987**, *28*, 639.

(3) Schwarz, J. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 21.

(4) (a) Zentel, R.; Reckert, G. *Makromol. Chem.* **1986**, *187*, 1915. (b) Zentel, R. *Liq. Cryst.* **1986**, *1*, 589. (c) Zentel, R.; Schmidt, G. F.; Meyer, J.; Benalia, M. *Liq. Cryst.* **1987**, *2*, 651. (d) Zentel, R.; Benalia, M. *Makromol. Chem.* **1987**, *188*, 665. (e) Buakek, S.; Zentel, R. *Makromol. Chem.* **1988**, *189*, 791.

(5) Creed, D.; Griffin, A. C.; Grass, G. R. D.; Hoyle, C. E.; Venkataram, K. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 57.

(6) Loth, H.; Euschem, A. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 35.

(7) Warner, M.; Gelling, K. P.; Vilgis, T. A. *J. Chem. Phys.* **1988**, *88*, 4008.

(8) Brand, H. R. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 57.

(9) (a) Finkelmann, H.; Rehage, G. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 31. (b) Apfel, H. A.; Finkelmann, H.; Janini, G. M.; Laub, R. J.; Lühman, B. H.; Price, A.; Roberts, W. L.; Show, T. J.; Smith, C. A. *Anal. Chem.* **1985**, *57*, 651. (c) Keller, P. *Ferroelectrics* **1988**, *85*, 425, and references therein. (d) Determination of the substitution ratio of the vinyl derivative to the main chain was performed by ^{1}H NMR ($CDCl_3$, SiH = 4.75ppm). For all the polymers, this ratio exceeds 95%.

(10) (a) Demus, D.; Demus, H.; Zaschke, H. *Flüssige Kristalle in* Tabellen; Deutscher Verlag für Grundstoffindustrie: Leipzig, 1972; (b) *Ibid. Flüssige Kristalle in Tabellen II*; Deutscher Verlag für Grundstoffindustrie: Leipzig, 1984.

(11) (a) Egerton, P. L.; Pitts, E.; Reiser, A. *Macromolecules* **1981**, *14*, 95, and references therein. (b) Egerton, P. L.; Trigg, J.; Hyde, E. M.; Reiser, A. *Macromolecules* **1981**, *14*, 100. (c) Lemaitre, E.; Coqueret, X.; Mercier, R.; Lablache-Combier, A.; Loucheux, C. *J. Appl. Polym. Sci.* **1987**, *33*, 2189. (d) Mercier, R.; Coqueret, X.; Lablache-Combier, A.; Loucheux, C. *Eur. Polym. J.* **1988**, *24*, 639. (e) Hajaiej, A.; Coqueret, X.; Lablache-Combier, A.; Loucheux, C. *Makromol. Chem.* **1989**, *190*, 327, and references therein. (f) Strzelecki, L.; Liebert, L.; Keller, P. *Bull. Soc. Chim. Fr.* **1975**, 2750.

(12) (a) Keller, P.; Liebert, L. *Liquid Crystals*; Solid State Physics Supplement 14; Academic Press: New York, 1978; p 19. (b) Hassner, A.; Alexanian, V. *Tetrahedron Lett.* **1978**, 4475.

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Scheme I

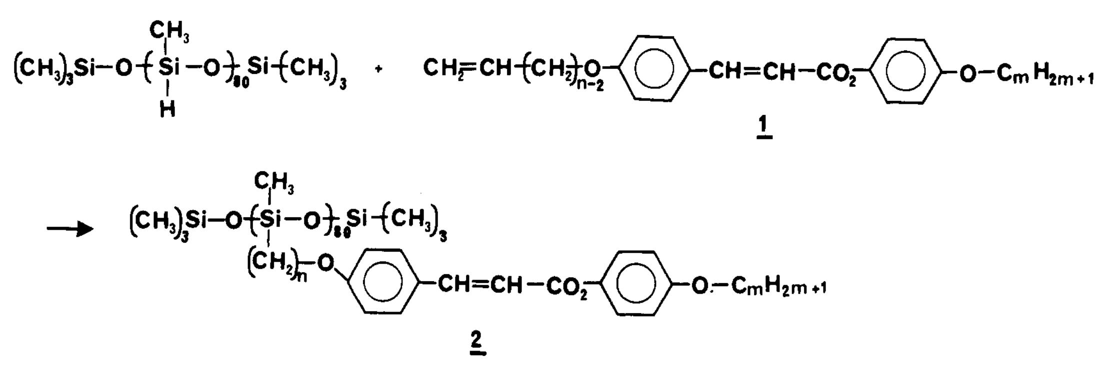

Figure 1. Changes in the UV spectra of polysiloxane **2d** upon irradiation for (a) 0, (b) 5, (c) 15, (d) 30, and (e) 45 min and (f) photo-cross-linked film after washing with dichloromethane.

well-known tendency of side-chain polysiloxanes to give smectic C phases.[9]

For photo-cross-linking procedures, the polymers (**2**) were cast as thin films on the outside of a 1-mm quartz cell by coating from dichloromethane solutions. The resulting films were annealed for several minutes in the liquid-crystalline phase and then cooled to the glassy state. UV light irradiation (Hanovia low-pressure mercury lamp) of the thin films of **2** resulted in modifications of their UV spectra (Figure 1), IR spectra (decrease of the IR absorbance at 1650 cm^{-1} due to the conjugated carbon-carbon double bonds), and phase-transition temperatures (for compound **2d** changes in the S_C to isotropic transition temperatures upon irradiation are the following: (a) 0 min, T = 133 °C; (b) 5 min, T = 122-125 °C; (c) 15 min, T = 115-120 °C; (d) 30 min, T = 109-116 °C; (e) 60 min, T = 104-113 °C). The cross-linking was tested by washing the films after irradiation by immersing the quartz cell for a few minutes in dichloromethane, drying, and then recording the UV spectra (Figure 1, curve f). The photochemical process leading to the cross-link formation might be postulated to be similar to the one put forward in chemically related photoresist materials: photochemical 2 + 2 dimerization of the photosensitive cinnamate groups.[11a,b,d] Work is in progress to confirm the postulated mechanism.

In conclusion, a new procedure has been described for the synthesis of liquid-crystalline side-chain polysiloxane elastomers that consists of the photo-cross-linking of thin films made with mesomorphic side-chain polysiloxanes possessing a phenyl cinnamate group as mesogenic part. Utilization of this procedure to the creation of insoluble and eventually macroscopically oriented organic thin films made with ferroelectric liquid-crystalline side-chain polysiloxanes[9c,13d,14] of interest for various applications is now in progress, and results will be published shortly.

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(13) (a) Popovitz-Biro, R.; Hill, K.; Landau, E. M.; Lahav, M.; Lieserowitz, L.; Sagev, J. *J. Am. Chem. Soc.* **1988,** *110,* 2672, and references therein. (b) Hubbard, M. A.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1989,** *1,* 167, and references therein. (c) Tillman, N.; Ulman, A.; Shildkraut, J. S.; Penner, T. L. *J. Am. Chem. Soc.* **1988,** *110,* 6136. (d) Walba, D.; Keller, P.; Parmar, D. S.; Clark, N. A.; Wand, M. D. *J. Am. Chem. Soc.* **1989,** *111,* 8273.

(14) Okawa, T.; Ohnuma, T.; Sakon, Y. *Makromol. Chem., Rapid Commun.* **1988,** *9,* 755.

Squarylium Dye-Doped Polymer Systems as Quadratic Electrooptic Materials

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Large bulk third-order nonlinear optical susceptibilities, $\chi^{(3)}$, have been reported in conjugated polymers such as polydiacetylene,[1] polythiophene,[2] polyacetylene,[3] and polybisbenzthiazoles.[4] Conjugated polymers have been the main focus of organic $\chi^{(3)}$ research because of the potential

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(1) Kajzar, F.; Messier, J. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987; Vol. 2, pp 51-83.

(2) Prasad, P. N. In Nonlinear Optical Properties of Polymers. *Mater. Res. Soc. Symp. Proc.* **1988,** *109,* 271-282.

(3) Sinclair, M.; Moses, D.; Akagi, K.; Heeger, A. J. *Mater. Res. Soc. Symp. Proc.* **1988,** *109,* 205-215.

(4) Prasad, P. N. In Molecular and Polymeric Optoelectronic Materials: Fundamentals and Applications. *Proc. SPIE—Int. Soc. Opt. Eng.* **1986,** *682,* 120-124.

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