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LIQUID CRYSTALLINE SIDE CHAIN POLYSILOXANES WITH 4-CYANO- AND 4-ALKOXY-STILBENE MESOGENIC UNITS

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ABSTRACT

Side chain homo- and copolysiloxanes with 4-cyano- and 4-alkoxy-4'-stilbene mesogens, spaced apart from the backbone by oligomethylene segments of variable lengths, were synthesized via a hydrosilylation coupling reaction of five stilbene-containing α -olefins with four commercial poly(methylhydrosiloxane)s and poly(methyl-hydro- ω -dimethylsiloxane)s. Broad smectic phases were observed for the polysiloxanes with cyanostilbene mesogens, whereas the homologous with alkoxy-terminated stilbenes displayed only narrow mesophases in the high temperature range. Preliminary room temperature X-ray diffraction studies on mechanically oriented samples evidenced the occurrence of side chain crystallization, microphase separation and indicated the interdigitated smectic A nature of the mesophases.

INTRODUCTION

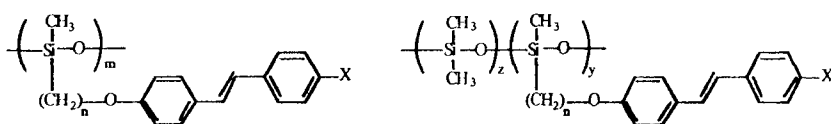
Several different applications have been devised and explored for side chain liquid crystalline polymers (LCP's), that are considered promising alternative materials to the conventional inorganics in such fields as optical switching, optoelectronics, optical data storage, photonics etc [1]. The ability of LCP's responding to external electric fields under different structural organizations of the meso-phases

prompted us to investigate the possibility of producing electroconducting materials starting from side chain polymers with pendant substituted stilbenes.

Among the LCP's reported in the literature, polymers with trans-stilbene as the side chain mesogen have not been studied as intensively as others [2]. The photochemistry and photophysics of the planar trans-stilbene and of its derivatives are well known. The reversible photoisomerization to the twisted cis isomer is followed by irreversible photocyclization to the cyclobutane derivative, this process being especially favored when electrodonating substituents are attached to the aryl groups [3]. The electronic and photochemical properties of stilbene derivatives have been the subject of several reviews suggesting their exploitation for various applications [4]. Earlier studies on non-mesomorphic polymers with trans-stilbene directly attached to the backbone have shown that photocyclization, leading to crosslinking, can be an important pathway for these materials [5]. More recently, examples have been reported concerning liquid crystalline polyacrylates [6-8], polyvinyl ethers [9], polymethacrylates [10-11], polysiloxanes [7, 12, 13], substituted polystyrenes [14] and polyphosphazenes [15] containing various 4,4'-substituted stilbene units in the side chains.

As a part of a study aimed at the exploration of new polymeric architectures for electroconducting materials, we designed the following series of side chain liquid crystalline polysiloxanes, containing 4-cyano- or 4-alkoxy-4'-stilbene mesogens connected to the backbone by oligomethylene segments of variable length.

Side chain stilbene polysiloxanes



Homopolymer	m	n	X	Copolymer	y%	n	X
12a	76	11	O-Bu	12b	35	11	O-Bu
12d	4	11	O-Bu	12c	18	11	O-Bu
13a	76	11	O-Me	14b	35	11	CN
14a	76	11	CN	14c	18	11	CN
15a	76	5	O-Me	15b	35	5	O-Me
16a	76	5	CN	16b	35	5	CN

Trans-stilbene was chosen as the mesogenic unit due to its electronic and configurational features, such as its strongly delocalized electronic structure, ease of polarizability upon introduction of electron-acceptor or electron-donor substituents, and its trans-cis isomerism leading to removal of the electronic delocalization. The polysiloxane backbone was selected assuming that its flexibility should have allowed mesomorphism to occur even with the very stiff stilbene unit as the side chain mesogen. In the present paper, the synthesis and the mesomorphic behavior of both the side chain precursors (SCP's) and the polymers will be presented.

EXPERIMENTAL

Materials and Methods

Poly(methylhydro)-siloxanes **11a** (MW=4750±50) and **11d** (MW=390±30) and poly(methylhydro-*co*-dimethyl)-siloxanes **11b** (MW=2050±50, 65-70 wt% dimethylsiloxy units) and **11c** (MW=2250±250, 82-85 wt% dimethylsiloxy units) were purchased from Petrarch Inc. 11-Chloro-1-undecene [16], 4-chloromethyl-benzonitrile (**1**) [17], 1-chloromethyl-4-methoxy-benzene [18], 4-(4-pentenyl-1-oxy)-benzaldehyde (**5b**) [12] and dichloro-(endo-dicyclopentadiene)-platinum (II) [19] were prepared according to the literature.

FTIR spectra were recorded using a Perkin Elmer 1600 spectrophotometer. ¹H- and ¹³C-NMR spectra were taken at 200 and 50.3 MHz, respectively with a Varian Gemini 200 spectrometer from CDCl₃ or hexachlorobutadiene solutions. SEC analyses were carried out using a Perkin Elmer series 10 liquid chromatograph equipped with two polystyrene gel columns (Waters Ultrastaygel packed with 10³ and 10⁴ Å pore size stationary phase) and a Perkin Elmer LC 75 spectrophotometric detector. Samples were eluted in THF at room temperature and 1 ml/min flux. Thermo-optical analyses of the phase transitions were performed on a Reichert-Jung Polyvar polarizing microscope equipped with a Mettler FP52 hot stage at scan rates of 3-10°C/min and magnification of 300x or 600x. When necessary, the polymers were annealed within the mesophase ranges for several hours to allow better development of mesomorphic textures. Differential Scanning Calorimetry (DSC) measurements were performed on a Perkin Elmer DSC 7 calorimeter at scan rates of 10°C/min, taking the peak temperatures from the second heating scans as the transition temperatures. Wide angle X-ray (WAXR) diffraction analyses were performed using a "normal" fine focusing tube with monochromatic CuK_α radiation (λ=154 nm) equipped with a flat pyrolytic graphite monochromator and a Nicolet/Siemens Xentronics X-100 two-dimensional area detector. Data were

collected at room temperature from oriented melt-drawn fibres and corrected for background scatter.

Synthesis of Stilbene Derivatives

(4-Cyanophenyl)methyl-diethylphosphonate (2)

The title compound was prepared according to a previous procedure [20] from chloromethyl-benzonitrile **1** and triethylphosphite. The pure product was obtained by distillation (146-150°C/0.03 mmHg) in 90% yield.

$^1\text{H NMR}$ (CDCl_3): δ = 7.54 (m, 4H, Ar-H), 4.06 (m, 4H, O-CH₂-), 3.23 (d, 2H, Ar-CH₂-), 1.26 (t, 6H, -CH₃).

1-Chloromethyl-4-butoxybenzene (3)

SOCl_2 (41 ml, 0.57 mole) was added dropwise to 1-hydroxymethyl-4-butoxy-benzene (72 g, 0.52 mole) at 0-5°C. After reacting for an additional 2 hours at 30-40°C, the mixture was then neutralized with 4g of CaCO_3 . The resulting suspension was stirred overnight at room temperature in 100 ml of diethyl ether and the salt was then filtered off. Distillation under reduced pressure (90°C/20 mmHg) in the presence of a small amount of 2,6-bis-*t*-butyl-*p*-cresol gave a colorless viscous liquid in 87% yield.

$^1\text{H NMR}$ (CDCl_3): δ = 7.07 (m, 4H, Ar-H), 4.54 (s, 2H, Ar-CH₂-), 3.94 (t, 2H, O-CH₂-), 1.75 (m, 2H, OCH₂-CH₂-), 1.48 (m, 2H, -CH₂-CH₃), 0.96 (t, 3H, -CH₃).

(4-Methoxyphenyl)methyl-diethylphosphonate (4a) [21]

A mixture of 1-chloromethyl-4-methoxybenzene (53g, 0.34 mol) and triethyl phosphite (63g, 0.38 mol) was stirred at room temperature for 2 hours. The temperature was then raised to 150°C in 2 hours, and maintained at that temperature for an additional 3 hours. Excess $\text{P}(\text{OEt})_3$ was distilled off and the fraction boiling at 123°C/0.03 mmHg was collected yielding 78g (89%) of a viscous colorless liquid.

$^1\text{H NMR}$ (CDCl_3): δ = 7.04 (m, 4H, Ar-H), 4.00 (m, 4H, O-CH₂-), 3.78 (s, 3H, O-CH₃), 3.09 (d, 2H, Ar-CH₂-), 1.24 (t, 6H, -CH₃).

(4-Butoxyphenyl)methyl-diethylphosphonate (4b)

Following the same procedure used for the synthesis of **4a**, **4b** was obtained from **3** as a viscous colorless liquid after distillation at 165°C/0.03 mmHg. Yield: 90%.

^1H NMR (CDCl_3): δ = 6.97 (m, 4H, Ar), 3.92 (m, 4H, O- CH_2 -), 3.03 (d, 2H, Ar- CH_2 -), 1.70 (m, 2H, ArO- CH_2 - CH_2), 1.42 (m, 2H, - CH_2 - CH_2 - CH_3), 1.19 (t, 3H, P-O- CH_2 - CH_3), 0.91 (t, 3H, O-(CH_2) $_3$ - CH_3).

4-(10-Undecenyl-1-oxy)benzaldehyde (5a)

Freshly prepared sodium salt of 4-hydroxybenzaldehyde (44.5g, 150 mmol) was dissolved in 100 ml of hot N-methylpyrrolidinone (NMP) and to the stirred solution was added dropwise 11-chloro-1-undecene (28.4g, 150 mmol) in 30 ml of NMP. After 5 hours at 110°C, the mixture was allowed to cool down, filtered, and the solvent removed under reduced pressure. The raw product was purified by flash chromatography (silica gel, eluent hexane/ethyl acetate 4/1) to yield 35g (86%) of a yellow oil.

^1H NMR (CDCl_3): δ = 9.87 (s, 1H, CHO), 7.40 (m, 4H, Ar-H), 5.81 (m, 1H, -CH=), 4.96 (m, 2H, = CH_2), 4.02 (t, 2H, O- CH_2 -), 2.04 (m, 2H, - CH_2 -CH=), 1.80 (m, 2H, O CH_2 - CH_2 -), 1.5-1.2 (m, 12H).

4-(10-Undecenyl-1-oxy)-4'-cyano-E-stilbene (6)

To a stirred slurry of NaH (20 mmol) in 100 ml THF containing the crown ether 15-crown-5 (11 mg, 0.5 mmol), a solution of the phosphonate **2** (20 mmol) and of the aldehyde **5a** (20 mmol) in 50 ml THF was added dropwise and the mixture stirred 15 minutes at 0°C followed by an additional 3 hours at room temperature. The obtained orange jelly mixture was then poured into 300 ml of brine and extracted with diethyl ether; the organic phase was washed with 10% sodium bisulphite, water and then dried over K_2CO_3 . After evaporation of the solvent, the raw product was crystallized from ethanol to give **6** in 83% yield. Elemental analysis: C 83.47, H 8.40, N 3.78 (calcd. C 83.60, H 8.37, N 3.75).

^1H NMR (CDCl_3): δ = 7.60-7.39 and 7.17-6.84 (m, 10H, Ar-C=C-Ar), 5.81 (m, 1H, -CH=), 4.96 (m, 2H, = CH_2), 3.98 (t, 2H, ArO- CH_2 -), 2.04 (m, 2H, - CH_2 -CH=), 1.75 (m, 2H, O CH_2 - CH_2 -), 1.5-1.2 (m, 12H).

4-(4-pentenyl-1-oxy)-4'-cyano-E-stilbene (7)

The title compound was obtained in 72% yield from the appropriate precursors, following the same procedure adopted for the synthesis of **6**. Elemental analysis: C 82.95, H 6.61, N 4.77 (calcd. C 83.01, H 6.62, N 4.84).

^{13}C NMR (CDCl_3); carbon assignments as for 1,2-disubstituted-ethylene, with underlined carbons belonging to the cyanophenyl substituent: δ = 159.79 (4), 142.38 (1'), 137.82 (R- $\underline{\text{C}}=\text{C}$), 132.52 (3',5'), 132.11 (ROAr-C=-Ar), 129.00 (1),

128.36 (2,6), 126.62 (2',6'), 110.00 (4'), 124.49 (N[C-Ar-C=Ar]), 119.22 (CN), 115.35 (C=C-R), 114.91 (3,5), 67.19 (C₁ of alkoxy chain, ArO-C-), 29.88 and 28.17 (C₂ and C₃).

4-(10-Undecenyl-1-oxy)-4'-methoxy-E-stilbene (8)

Following the standard procedure used for **6** and **7**, but using refluxing 1,2-dimethoxyethane (DME) instead of chilled THF as the reaction medium, equimolar amounts of the aldehyde **5a** and of the phosphonate **4a** were refluxed 30 minutes, then the mixture was allowed to cool down, poured into water and purified as usual. The raw product yielded 1.8g (27%) of a yellowish powder after two crystallizations from hexane. Elemental analysis: C 80.01, H 8.80 (calcd. C 82.50, H 9.05).

¹H NMR (CDCl₃, 45°C): δ = 7.45-7.38 and 6.93-6.85 (m, 10H, Ar-C=C-Ar), 5.82 (m, 1H, -CH=), 4.98 (m, 2H, =CH₂), 3.96 (t, 2H, ArO-CH₂-), 3.79 (s, 3H, O-CH₃), 2.04 (m, 2H, -CH₂-CH=), 1.75 (m, 2H, OCH₂-CH₂-), 1.5-1.2 (m, 12H).

4-(4-Pentenyl-1-oxy)-4'-methoxy-E-stilbene (9)

The title compound was prepared by refluxing equimolar amounts (80 mmol) of 4-(4-pentenyl-1-oxy)-benzaldehyde **5b** with the phosphonate **4a** and NaH for 10 hours in 350 ml DME containing 0.35 ml of 15-crown-5. After the standard purification procedure, the obtained solid was crystallized from ethanol and from acetone to yield 13.2g (55%) of yellowish shiny leaflets. Elemental analysis: C 81.41, H 7.41 (calcd. C 81.60, H 7.54).

¹H NMR (CDCl₃, 45°C): δ = 7.45-7.38 and 6.93-6.85 (m, 10H), 5.82 (m, 1H), 4.98 (m, 2H), 3.96 (t, 2H), 3.79 (s, 3H), 2.23 (m, 2H), 1.89 (m, 2H).

4-(10-Undecenyl-1-oxy)-4'-butoxy-E-stilbene (10)

was prepared in the same way as compound **9** from **4b** and **5a** in 81% yield after crystallization from benzene and from acetone; m.p. 152°C. Elemental analysis: C 82.93, H 9.54 (calcd. C 82.82, H 9.58).

¹H NMR (CDCl₃): δ = 7.45-7.38 and 6.93-6.85 (m, 10H), 5.82 (m, 1H), 4.98 (m, 2H), 3.96 (m, 4H, ArO-CH₂-), 2.04 (m, 2H), 1.76 (m, 4H, OCH₂-CH₂-), 1.6-1.2 (m, 14H), 0.98 (t, 3H, -CH₃).

¹³C NMR (CDCl₃), carbon assignments as in **7**: δ = 159.01 (4,4'), 139.36 (-C=), 130.74 (1,1'), 127.57 (2,2',6,6'), 126.50 (Ar-C=C-Ar), 115.03 (3,3',5,5'), 114.23 (=C), 68.24 and 67.92 (ArO-C-), 33.65 (C₂), 31.33 (Et-C-), 29.27 to 28.27 (C₄ to C₉), 25.96 (C₃), 19.13 (Me-C-), 13.60 (-CH₃).

Polysiloxanes

Grafting of the vinyl-terminated SCP's **6-10** onto the poly(methylhydro)- and poly(dimethyl- ω -methylhydro)siloxanes **11a-d**, to yield the polymers from **12a-d** to **16a-b**, were performed in flame-dried flasks, equipped with reflux condenser and a side arm with a teflon stopcock and septum for injections and sampling of the reacting mixture. The chosen polysiloxane precursor was typically dissolved in 200 ml of freshly distilled toluene containing 0.75 to 2.1 g of SCP, corresponding to a 10% molar excess with respect to the calculated Si-H content of the polysiloxane. Freshly prepared catalyst (dichloro-(endo-dicyclopentadiene)-platinum (II) as a 1 g/l solution in CH₂Cl₂) was then added with a syringe (300 to 2000 ppm of Pt vs. the calculated Si-H groups); in a few cases a second addition of catalyst plus 1 ml of 1-heptene was made to ensure complete consumption of Si-H groups. Progress of the reaction was monitored via IR spectroscopy and the reaction was stopped after 16 to 80 hours, after disappearance of the Si-H absorption at 2160 cm⁻¹. The solution was then poured into methanol and the filtered precipitate was dried at 50°C in a vacuum oven. Yields were almost quantitative for the polymers with alkoxy stilbene side chains, whereas only 30 to 70% of soluble products were obtained for the polymers containing the cyano substituent, due to partial cross-linking occurred during the reaction. In most cases no residual presence of Si-H groups could be detected in the final polymer (IR spectroscopy and ¹H NMR, $\delta_{\text{Si-H}} = 4.75$ ppm) and the presence of n-heptyl side chains was always negligible, since 1-heptene additions were made when the Si-H groups had already disappeared almost completely. Most of the polymers with alkoxy-terminated side chains were only soluble in hot o-dichlorobenzene, DMF or DMSO, whereas all cyanostilbene polymers were soluble at room temperature in common organic solvents; therefore only these latter were further purified by reprecipitation from CHCl₃/methanol. Two representative syntheses are described in detail below.

Polymer 14c

1.0 g (2.67 mmol) of olefin **6**, 150 ml of toluene and 0.96 g (\approx 2.42 mmol of Si-H groups) of copolymer **11c** were introduced in the reactor and 1 ml of catalyst solution was added to the stirred solution, heated to 100°C. The reaction mixture was then refluxed for 72 hours, with a further addition of 0.5 ml of catalyst solution plus 0.5 ml of 1-heptene after the first 45 hours. The final bright yellow solution was dried under vacuum, the residue dissolved in 3 ml of CHCl₃ and precipitated twice into chilled methanol, yielding 1.0g of waxy product. SEC

analysis revealed the presence of a low molecular weight fraction, probably deriving from ungrafted SCP that could not be separated from the polymer by reprecipitation; the absence of vinyl resonances in the ^1H NMR spectrum suggests the occurrence of side reactions involving the vinyl function of the ungrafted SCP.

Polymer 12a

Following the same procedure described for the synthesis of **14c**, olefin **10** (2.1g, 5 mmoles), homopolymer **11a** (0.28g \approx 4.7 mmoles of Si-H bonds) and Pt catalyst were stirred at reflux for 36 hours. A second addition of catalyst was made after the first 20 hours. The final mixture was poured into 1.5 l of methanol and the recovered polymer was dried in a vacuum oven without further purification, being only soluble in *o*-dichlorobenzene above 80°C and in chlorobenzene, DMF and DMSO above 140°C.

RESULTS AND DISCUSSION

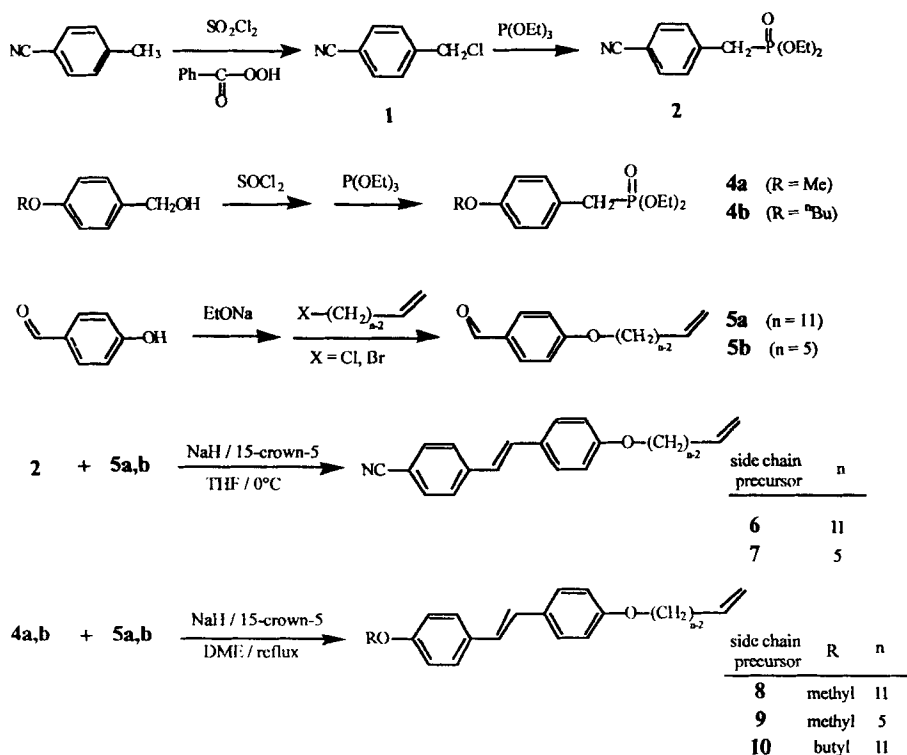
Low Molar Mass Stilbene Derivatives

Synthesis

All the 4,4'-disubstituted stilbenes were synthesized through coupling of the required 4-substituted benzaldehydes and 4-substituted benzylphosphonates, following a modification of the Wadsworth-Emmons reaction [22] that exploits the increased anion nucleophilicity provided by addition of a crown ether to obtain complete stereoselectivity toward the formation of the *trans*-stilbene isomer (Scheme 1). This method allowed reduction of reaction time and temperature, when the stabilized 4-cyano-benzylphosphonate carbanion **2** was involved, or use of otherwise unreactive alkoxy-benzylphosphonates [23] (compounds **4a,b**). In addition, higher yields were generally obtained with respect to traditional methods requiring more drastic reaction conditions [24]. To our knowledge this is the first report on the synthesis of stilbene derivatives involving non-stabilized benzylphosphonate carbanions.

Phase Behavior

The thermal properties of the olefinic side chain precursors **6-10** were studied by polarized microscopy and differential scanning calorimetry (Table 1). All the vinyl-terminated stilbene SCP's gave rise to mesophases that were either monotropic, such as for methoxystilbenes **8** and **9**, or enantiotropic, with the exception of the non-mesomorphic butoxy-stilbene **10**.



SCHEME 1

Cyanostilbene **6** presented a smectic A phase (S_A), as identified by its characteristic fan shaped. A narrow nematic mesophase could also be detected by the appearance of a nematic schlieren texture. Stilbene derivative **13** was nematic, in agreement with previous results [12]. Methoxystilbene **14** presented a monotropic ordered smectic phase (e.g. S_B). SCP **15** was also characterized by a nematic monotropic mesophase with a schlieren texture.

DSC analyses confirmed the optical microscopy observations, evidencing in a few cases the existence of narrow additional phases that could not be identified (Table 1).

Polysiloxanes

Synthesis

Side chain liquid crystalline polysiloxanes are generally obtained by grafting a-olefin mesogenic monomers onto preformed poly-(methylhydro)siloxanes in the presence of a platinum catalyst [25]. Depending on the synthetic conditions and the

TABLE 1. DSC Data for the Vinyl Side Chain Precursors^a

sample	run ^{b)}	Transition temperatures (K)		[ΔH] (kJ/mol)
		T ₁	T ₂	T ₃
6	h	343 [38.0] _{k→s}	388 [1.4] _{s→n}	391 [1.3] _{n→i}
	c	325 [34.2] _{k→s}	387 [1.4] _{k→s}	389 [1.3] _{i→n}
7	h	371 [38.0] _{k→n}	-	406 [0.6] _{n→i}
	c	353 [38.0] _{(s)→k}	354 _{n→(s)} ^{c)}	404 [0.7] _{i→n}
8	h	401 [38.0] _{k'→k}	-	408 [29.8] _{k→i}
	c	395 [38.0] _{(s)→k'}	-	404 [14.6] _{i→(s)}
9	h	435 [38.0] _{k→i}	-	-
	c	420 [38.0] _{n→k}	-	430 [1.0] _{i→n}
10	h	425 [38.0] _{k→i}	-	-
	c	420 [38.0] _{i→k}	-	-

^{a)} Peak transition temperatures: i = isotropic, n = nematic, s = smectic, k = crystalline, (s) = unidentified phase (either smectic or crystalline).

^{b)} h = 2nd heating scan, c = 1st cooling scan, scan rate 10°C/min.

^{c)} additional transition, only detectable upon slow cooling at 3°C/min.

type of catalyst, several possible side reactions have been reported, leading to partially substituted, structurally disordered and/or crosslinked polymers [26-28]. In order to minimize these effects, (dicyclopentadienyl-dichloro)platinum(II) was chosen as the catalyst. However this catalyst did not allow to completely offset all undesired side reactions (as is the case of other Pt catalysts requiring milder reaction conditions [27]). In fact some crosslinking was observed during the hydrosilylation with CN-containing SCP's, probably as a consequence of side reactions involving addition to the nitrile function [26] and/or the stilbene double bond; in these cases longer reaction times were needed to fully react the residual Si-H groups and the obtained polymers had to be purified by repeated reprecipitations in order to exclude the presence of crosslinked material. SEC analyses on those polymers that were soluble also at room temperature (i.e. **12c**, **14a-c** and **16a-b**) showed the presence of some contamination by low MW products; this was generally negligible except for polymers **14a** and **14c**, containing more than 10 wt% of low MW stilbene derivatives (as estimated by the relative integrated absorptions of the UV detector). Attempts to further purify these latter polymers by repeated reprecipitations were unsuccessful, due to the very similar solubilities of low MW and polymeric products.

Phase Behavior

Optical polarization microscopy and DSC analyses did not always allow straightforward characterization of the mesophases, due to the sometimes unclear texture of the birefringent mesophase and/or to the overlap of phase transitions. For a few polymers the isotropization, occurring over a very broad temperature range, was barely detectable by DSC; however it could always be observed at the microscope, which allowed to distinguish the liquid crystalline and isotropic melts. On the other hand all polymers displayed quite sharp first order melting transitions, indicating that side chain crystallization was always present irrespective of the flexible spacer length and the nature of the stilbene substituent. The transition temperatures with the relevant thermodynamic data are summarized in Table 2.

The isotropization enthalpies (ΔH_i) and entropies (ΔS_i) for all homopolymers are consistent with a smectic to isotropic transition. The larger ΔS_i of **14a** with respect to that of **16a** must be related to a greater degree of order of the smectic mesophase as favored by the longer spacer. Lower melting temperatures (T_m) were always induced by longer flexible spacers, whereas the influence of the spacer length on the isotropization temperature (T_i) varied, depending also on the polarizability of the mesogen (i.e. 4-alkoxy-4'-cyanostilbene vs 4,4'-dialkoxy-stilbene). Reduction of

TABLE 2. Thermal Properties of Side Chain Substituted Polysiloxanes^a

polymer	T_m	T_1	ΔH_1	ΔS_1	T_2	ΔH_2	ΔS_2	T_i	ΔH_i	ΔS_i
12a	451		/			/		469	2.4	5.1
12b	432	446 ^{b)}			458	2.3	5.1	468 ^{e)}		
12c	429		/			/			/	
12d	458		/			/		478 ^{e)}		
13a	435		/			/		470 ^{e)}		
14a	332	489 ^{b)}				/		494	3.6	7.3
14b	324	333	0.5	1.5	405	1.5	3.7	495 ^{e)}		
14c	326		/			/		394	4.0	10.1
15a	483	507 ^{b)}				/		513	4.9	9.6
15b	431	461 ^{b)}			481	2.3	4.8	510 ^{e)}		
16a	405	450 ^{e)}				/		489	2.1	4.3
16b	360	380	1.1	2.8	394	0.9	2.2	480 ^{e)}		

^{a)} Thermodynamic data from DSC heating scans (unless otherwise specified); melting (T_m), mesophase to mesophase (T_1 and T_2) and isotropization (T_i) temperatures are given in degree Kelvin, transition enthalpies ΔH in kJ/mole and entropies ΔS in J/K·mole (mole of repeating units with a side chain).

^{b)} Monotropic transition temperatures from DSC cooling scan; thermodynamic data not given due to poor peak resolution.

^{c)} From optically polarized microscopy observations.

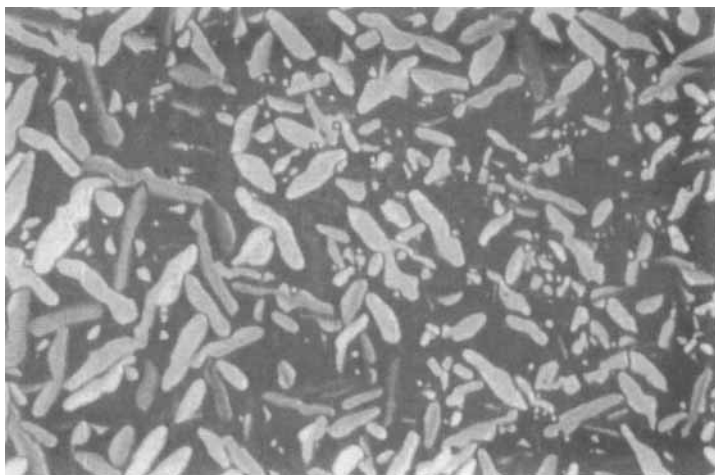


Figure 1. Optical polarization micrograph of polymer **12a** (600x, blue color due to mercury lamp light): bâtonnets at 190°C developed on cooling from the isotropic melt.

the mesogen volume fraction, e.g. by insertion of side chain mesogenic units onto a copolymeric precursor, always determined a depression of both T_m and T_i . Broader mesophases were observed for the polysiloxanes with cyanostilbene mesogens, whereas the mesophases of those with alkoxystilbene units generally occurred within a narrower temperature range due to the higher melting points of their side chains.

All polymers with the butoxy-stilbene mesogen displayed at least one mesophase, as observed at the optical microscope under cross polarizers, with the only exception of copolymer **12c** that was not mesomorphic. The mesophase developing from the isotropic melt was generally identified as smectic from its incipient birefringence in the form of bâtonnets (Figure 1), evolving to fine fan-shaped texture after long annealing or upon further cooling. Well defined focal conic textures of the mesophase of homopolymer **12a** (170-215°C) and oligomer **12d** (180°-205°C) could only be observed after annealing at temperatures close to the clearing point. Copolymer **12b** presented an additional mesophase to mesophase transition at about 180°C, as detected from the onset of striations perpendicular to the long axes of the focal conics of the high temperature mesophase. A single mesophase was observed by optical microscopy for the homopolymers with

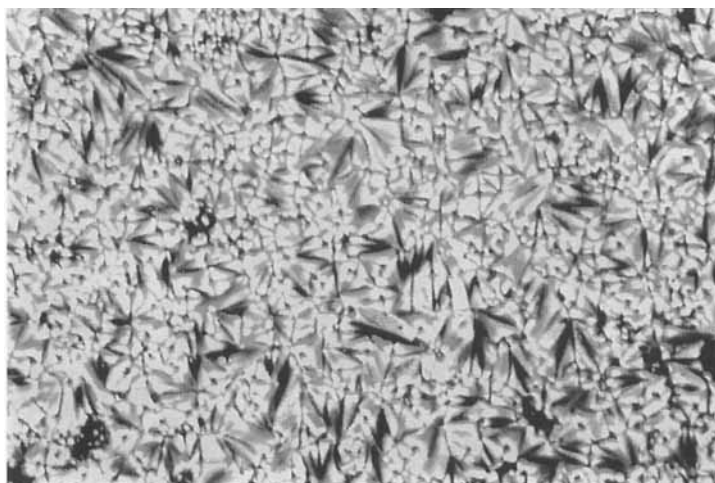


Figure 2. Optical polarization micrograph of the smectic phase of polymer **14a** (600x): focal conic fans at 170°C obtained upon slow cooling (1°C/min) from the isotropic melt.

methoxy-stilbene mesogen **13a** (between 160 and 200°C) and **15a** (between 200 and 245°C), whereas at least two mesophases were observed in copolymer **15b** ($T_m \approx 160^\circ\text{C}$, isotropization between 220 and 240°C), in which a transition to a second mesophase below 185°C could be recognized from the onset of a broken fan texture and the sharp increase of the viscosity of the melt.

Some of the polymers bearing the cyano group displayed a rather complex phase behavior. Melting to an ordered smectic phase took place in **16a** at 130°C, a temperature slightly higher than the one previously reported for a polymer sample prepared according to a different synthetic route and characterized by a lower degree of polymerization [12]. Above 170°C the melt fluidity increased and new domains of total extinction appeared, possibly because of the occurrence of a biphasic region with homeotropic alignment of the higher temperature mesophase; the actual occurrence of a smectic mesophase above 170°C was recognized from the appearance of bâtonnets at 220°C on cooling from the isotropic melt. Homopolymer **14a** presented a single quite viscous smectic phase between 60 and 225°C (Figure 2), while the liquid liquid crystalline polymorphism of copolymers **14b** and **16b** could not be investigated in detail because of the occurrence of some decomposition well below their isotropization temperature (220°C in both cases). Well defined focal

conic textures similar to those of homopolymer **14a** were also observed for copolymer **14c** in the temperature range from 55–135°C, with progressive development of isotropic zones above 90°C. For all these polymers the appearance of bâtonnets on cooling from the isotropic melt was the main evidence for the smectic nature of the mesophases. It is worth recalling that the two latter polymers contained some ungrafted mesogens that could have caused broadening and lowering of the transition temperature ranges. However examples have also been reported of a negligible influence of up to 10 wt% SCP contamination on the mesomorphic behavior of side chain stilbene polysiloxanes [13]; in addition, the occurrence of zones of total extinction has been ascribed to enhanced homeotropic alignment in the presence of “free” low MW mesomorphic molecules rather than (or in addition to) partial isotropization [29].

The DSC curves of representative homo- and copolymers are reported in Figure 3. A single mesophase could be detected in the heating scan of all homopolymers; among them, those with longer alkoxy terminated side chains, i.e. **12a**, **12d** and **13a**, presented additional transitions before and overlapped with the relatively sharp melting to the mesophase, followed by a broad isotropization. On the contrary homopolymers **14a**, **15a** and **16a** gave well resolved melting and isotropization transitions. The presence of an additional narrow monotropic mesophase, that had not been observed at the polarizing microscope, could be detected in **14a** and **15a** on cooling from the isotropic melt.

The copolymers with greater contents of mesogenic side chains (i.e. 35 mol% of substituted repeat units) showed rather complex polymorphism with at least two mesophases before isotropization (Figure 3), the latter always occurring well above 190°C as confirmed by polarizing microscope observations. The highest mesophase stability was observed for copolymer **15b** with methoxy stilbene side chains, its isotropization occurring at around 240°C. It was noted that the lower temperature mesophase of copolymers **14b** and **16b** formed on cooling with supercooling of about 15°C. Such an effect is most probably related to the onset of a highly ordered, viscous smectic phase. In addition, one or more transitions, strongly influenced by the thermal history of the sample, were observed in the semicrystalline state.

Polymers **13a** and **14a-b**, containing a long undecamethylene spacer, have lower T_m than homologous **15a** and **16a-b** with a shorter pentamethylene spacer. However, T_i decreased with increasing length of the spacer in polymers with apolar alkoxy stilbenes (**13a** vs. **15a**), whereas it slightly increased in homologues containing polar cyanostilbenes (**14a-b** vs. **16a-b**). Thus, introduction of longer spacers resulted in a broadened mesophase range, when strongly polar mesogens were used.

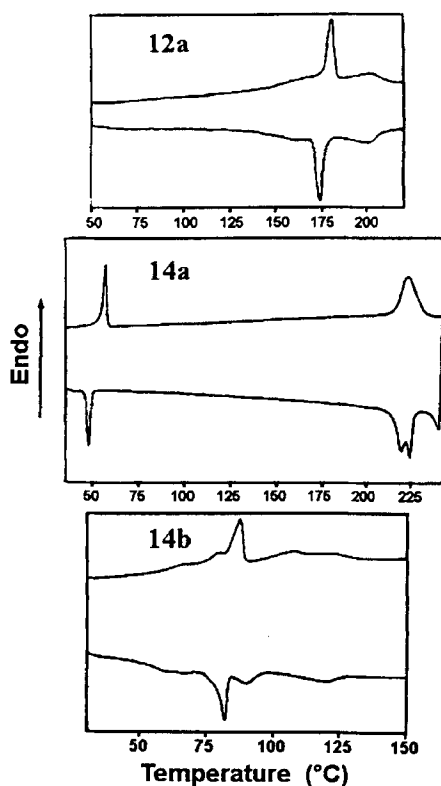


Figure 3. Typical DSC traces of homopolymers with alkoxystilbene (**12a**) and cyanostilbene (**14a**) mesogenic side chains and of a copolymer (**14b**). Scan rate 10°C/min; 2nd heating and cooling cycle. The broad isotropization transition at around 200°C of the polymorphic **14b**, barely detectable by DSC, is not shown.

X-ray diffraction patterns were recorded at room temperature on oriented melt-drawn fibers of four homopolymers (**12a**, **13a**, **14a** and **15a**) and of four copolymers (**14b** and **16b**, with higher content of mesogenic units, and **12c** and **14c**, with only 18% of mesogenic side chains). In general, the presence of one to three sharp equatorial reflections at small angles with Bragg distances in the ratio 1:2:3 indicated the existence of a layered structure with long range correlation and layers aligned parallel to the stretching direction [30], as is generally the case for mechanically oriented side chain polymers [31]. The calculated layer spacings d , ranging from 34.3 to 54.5 Å, resulted strongly dependent on the macromolecular structure, being higher for the copolymers with respect to the parent homopolymers.

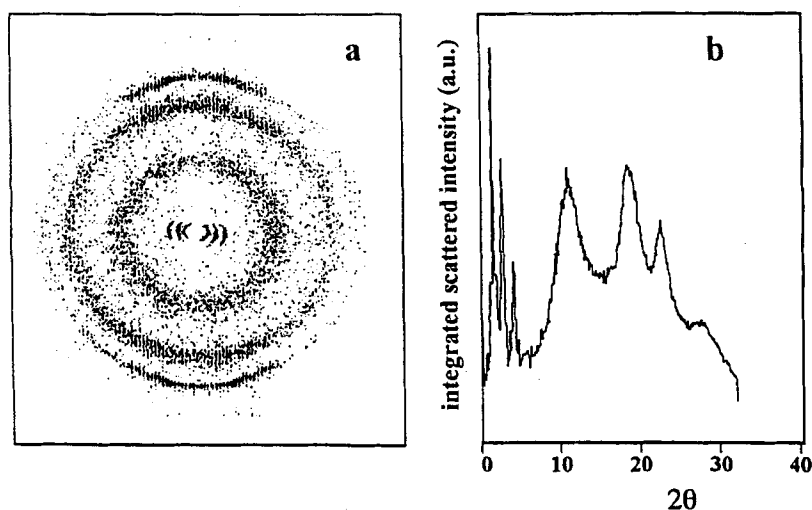


Figure 4. (a) X-ray diffraction pattern and (b) integrated azimuthal $2q$ scan for copolymer **14c**. Mechanically oriented fiber.

At wide angles the occurrence of diffuse reflections with meridional crescents, as shown in Figure 4a, suggests that the side chains within the layers are oriented with their mesogen director perpendicular to the fibre axis, i.e. normal to the layer. In most cases the wide angle reflections were split in two relatively sharp rings at $2\theta \approx 22.4^\circ$ and 20.2° , suggesting either a high degree of crystallinity or the occurrence, during the quenching process, of transitions to an ordered smectic phase with dense lateral packing of the side chains.

The layer spacing, d , as calculated from the small angle reflections of the “frozen” smectic lamellae, was compared to the relevant side chain length, l , as estimated for the fully extended *all-trans* conformation of the methylene spacers. In any case, except for **14c**, it was found that $l < d < 2l$; this indicates the occurrence, in the mesophase, of either an interdigitated smectic A organization (S_{ad}) or a tilted arrangement of the side chains in the smectic lamellae. As a typical example, Figure 5 illustrates the X-ray pattern of homopolymer **12a**. For this sample $d = 31.3 \text{ \AA}$ and $l = 36.5 \text{ \AA}$, indicating the probable formation of a double layer smectic A phase with strongly interdigitated side chains. The copolymers exhibited one further diffuse reflection at intermediate scattering angle ($2\theta \approx 11^\circ$) corresponding to a periodicity of $\sim 8 \text{ \AA}$, with intensity increasing with decreasing content of stilbene side chains in the copolymers (compare copolymer **14c** in Figure 4 with homo-

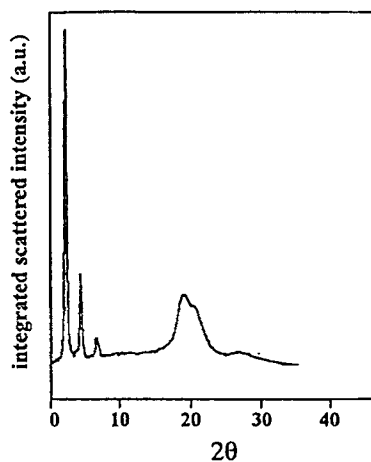


Figure 5. Integrated azimuthal intensity profile of the X-ray diffraction pattern of homopolymer **12a**; mechanically oriented fibre.

polymer **12a** in Figure 5). This reflection is normally assigned to the polysiloxane backbone [32] and suggests that intramolecular microphase separation takes place between the mesogenic side chains and the amorphous siloxane backbone [33]. This process was evidently more favoured in the copolymers with lower proportions of side chains substituted repeat units. Consistently, the smectic layer spacing d lengthened and reached the greatest value of 54.5 Å in copolymer **14c**, that incorporates the lowest mole fraction of stilbene side chains. In the latter case, where $l = 27.5 \text{ \AA} \approx 1/2 d$, the contrast with the anticipated interdigitated structural organization of the side chains is only apparent, since for this sample the expansion of the polysiloxane separated microphase actually offsets the shortening of the smectic layer spacing due to interdigitation of the mesogens. Details of the structural organization of the side chains within the smectic lamellae have been presented elsewhere [34].

It is worth noting that in these polysiloxanes the formation of smectic phases was favored with respect to the formation of the nematics usually observed in side chain stilbene acrylates and methacrylates [6-8, 13]; this is probably a consequence of a more efficient decoupling of the side chain mesogens allowed by the flexible polysiloxane backbone. At the same time the occurrence of side chain crystallization, due to the strong tendency of the planar stilbene moiety to crystallize into stacked assemblies, determined the narrowing of mesophase ranges as compared to glassy polymers with more flexible, not crystallizing mesogens and/or less flexible backbones.

It is also well documented that copolymers with a not mesogenic comonomer generally present lower T_m (or T_g) and T_i and narrower liquid crystalline range than those of their parent homopolymers [11, 13]. In contrast, in the present work copolysiloxanes with intermediate contents of non-mesogenic units (i.e. 65 mol-%) displayed broader mesophases than their respective homopolymers. Dilution of the stilbene mesogenic side chains did not significantly alter the stability of the high temperature mesophase but reduced the tendency toward crystallization of the side chains and permitted the occurrence of smectic polymorphism.

CONCLUSIONS

A new class of polymers with side chain stilbene mesogenic units was synthesized within a study aimed at the exploration of new polymeric structures for electroresponsive materials [34].

Liquid crystalline polymers were generally obtained upon grafting of stilbene derivatives onto polysiloxane precursors. Both homo- and copolymers present a pronounced tendency to form stable and persistent smectic mesophases, even in polymorphic sequences.

A suitable choice of length and structure of the flexible spacer, fraction of side chain substituted repeat units and nature of stilbene mesogen can allow tailoring of macromolecular properties such as film-forming ability and phase morphology, which might be useful for optimization of the physical properties in view of possible utilization as electrically and/or electrooptically active materials.

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REFERENCES

- [1] P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York, 1991.
- [2] C. Fouquey, J.-M. Lehn, and J. Malthête, *J. Chem. Soc. Chem. Comm.*, 1424 (1987).

- [3] H. Ulrich, D. V. Rao, F. A. Stuber, and R. Sayigh, *J. Org. Chem.*, **35**, 1121 (1970).
- [4] H. Meier, *Angew. Chem.*, **31**, 1399 (1992).
- [5] F. Ciardelli, C. Carlini, R. Solaro, A. Altomare, O. Pieroni, J. L. Houben, and A. Fissi, *Pure Appl. Chem.*, **56**, 329 (1984).
- [6] M. Zhao, M. Bautista and W. T. Ford, *Macromolecules*, **24**, 844 (1991).
- [7] G. Kossmehl and C. Pithart, *Acta Polym.*, **42**, 438 (1991).
- [8] D. R. Robello, *J. Polym. Sci. Polym., Chem. Ed.*, **28**, 1 (1990).
- [9] C. Hellermark, U.W. Gedde, and A. Hult, *Polym. Bull.*, **28**, 267 (1992).
- [10] G. S'heeren, A. Persoons, P. Rondou, J. Wiersma, M. van Beylen, and C. Samyn, *Makromol. Chem.*, **194**, 1733 (1993).
- [11] (a) Y. H. Mariam, K. P. W. Pemawansa, F. Okoh, and K. B. Bota, *Mol. Cryst. Liq. Cryst.*, **141**, 77 (1986); (b) P. L. Carr, G. R. Davies, and I. M. Ward, *Polymer*, **34**, 5 (1993).
- [12] G. Subramaniam and R. K. Gilpin, *Macromolecules*, **23**, 693 (1990).
- [13] M. O. Bautista, R. S. Duran, and W. T. Ford, *Macromolecules*, **26**, 659 (1993)
- [14] (a) D. R. Robello, R. J. Perry, and E. J. Urankar, *Macromolecules*, **26**, 6940 (1993); (b) P. Hesemann, J. M. Oberski, and A. Greiner, *Macromol. Symp.*, **77**, 315 (1994).
- [15] H. R. Allcock, A. A. Dembek, C. Kim, R. L. S. Devine, Y. Shi, W. H. Steier, and C. W. Spangler, *Macromolecules*, **24**, 1000 (1991).
- [16] C. S. Hsu and V. Percec, *J. Polym. Sci. Polym. Chem. Ed.*, **25**, 2909 (1987).
- [17] M.S. Kharasch and H.C. Brown, *J. Am. Chem. Soc.*, **61**, 2142 (1939).
- [18] F. Gialdi, R. Ponci, and A. Baruttini, *Farmaco Ed. Sci.*, **15**, 856 (1960); *Chem. Abstr.* **55**, 21040i .
- [19] M. A. Apfel, H. Finkelmann, G. M. Janini, R. J. Laub, B.-H. Lühmann, A. Price, W. L. Roberts, T. J. Shaw, and C. A. Smith, *Anal. Chem.*, **57**, 651 (1985).
- [20] F. Kagan, R. D. Birkenmeyer, and R. E. Strube, *J. Am. Chem. Soc.*, **81**, 3026 (1959).
- [21] (a) A.K. Bhattacharya and G. Thyagarajan, *Chem. Rev.*, **81**, 415 (1981); (b) C. Bellucci, F. Gualtieri, and A. Chiarini, *Eur. J. Med. Chem.*, **22**, 473 (1987).
- [22] R. Baker and R. J. Sims, *Synthesis Comm.*, 117 (1981).
- [23] W. S. Wadsworth, *Org. React.*, **25**, 73 (1977).

- [24] O. H. Weeler and H. N. Batlle de Pabon, *J. Org. Chem.*, **30**, 1473 (1965).
- [25] (a) H. Finkelmann and G. Rehage, *Mol. Cryst. Liq. Cryst.*, **1**, 31 (1980);
(b) H. Ringsdorf and A. Schneller, *Makromol. Chem. Rapid Commun.*, **3**, 557 (1982).
- [26] G. W. Gray, D. Lacey, G. Nestor, and M. S. White, *Makromol. Chem. Rapid Commun.*, **7**, 71 (1986).
- [27] M. S. K. Lee, G. W. Gray, D. Lacey, and K. J. Toyne, *Makromol. Chem. Rapid Commun.*, **10**, 325 (1989).
- [28] (a) V. Percec and J. Heck, *Polym. Bull.*, **24**, 255 (1990); (b) E. Lukevics, *Russ. Chem. Rev.*, **46**, 507 (1977).
- [29] J. M. Gilli, C. Fulcheri, P. Sixou, P. Robert, J. J. Villenave, and M. Fontanille, *Mol. Cryst. Liq. Cryst.*, **167**, 73 (1989).
- [30] G. Decobert, J. C. Dubois, S. Esselin, and C. Noël, *Liq. Cryst.*, **1**, 307 (1987).
- [31] P. Davidson, P. Keller, and A. M. Levelut, *J. de Phys.*, **46**, 939 (1985).
- [32] S. Diele, S. Ölsner, F. Kuschel, B. Hisgen, H. Ringsdorf, and R. Zentel, *Makromol. Chem.*, **188**, 1993 (1987).
- [33] (a) V. Percec and C. Pugh, in: *Side Chain Liquid Crystal Polymers*, C. B. MacArdle, Ed., Blackie, Glasgow, 1989, p. 43; (b) C. Tsitsilianis, *Macromolecules*, **26**, 2977 (1993).
- [34] V. Castelvetro, F. Ciardelli, H. Fischer, and F. E. Karasz, *Polym. Int.*, **39**, 37 (1996).

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