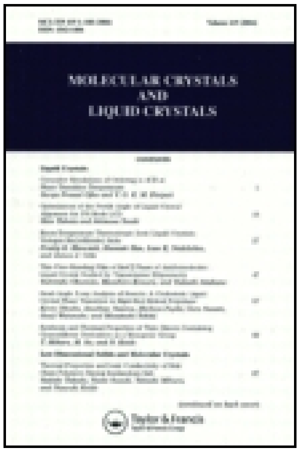


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Selectively Deuterated Liquid Crystalline Cyanoazobenzene Side-Chain Polyesters. 2. Preparation and Characterization of Polyesters

Christian Kulinna [a] , Søren Hvilsted [a] , Claudia Hendann [b] , Heinz W. Siesler [b] & Fulvio Andruzzi [c]
[a] Department of Solid State Physics, Risø National Laboratory, DK-4000, Roskilde, Denmark
[b] Department of Physical Chemistry, University of Essen, D-45117, Essen, Germany
[c] Centro Studi Processi Ionici di Polimerizzazione, CNR, Dipartimento di Ingegneria Chimica, Facoltà di Ingegneria, Via Diotisalvi 2, I-56100, Pisa, Italy

Version of record first published: 04 Oct 2006

To cite this article: Christian Kulinna, Søren Hvilsted, Claudia Hendann, Heinz W. Siesler & Fulvio Andruzzi (1998): Selectively Deuterated Liquid Crystalline Cyanoazobenzene Side-Chain Polyesters. 2. Preparation and Characterization of Polyesters, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 319:1, 231-258

To link to this article: http://dx.doi.org/10.1080/10587259808045661

Mol. Cryst. Liq. Cryst., Vol. 319, pp. 231 - 258
Reprints available directly from the publisher
Photocopying permitted by license only

Selectively Deuterated Liquid Crystalline Cyanoazobenzene Side-Chain Polyesters. 2. Preparation and Characterization of Polyesters

CHRISTIAN KULINNA[a], SØREN HVILSTED[a,*], CLAUDIA HENDANN[b], HEINZ W. SIESLER[b] and FULVIO ANDRUZZI[c]

[a] *Department of Solid State Physics, Risø National Laboratory, DK-4000 Roskilde, Denmark;*
[b] *Department of Physical Chemistry, University of Essen, D-45117 Essen, Germany;*
[c] *Centro Studi Processi Ionici di Polimerizzazione, CNR, Dipartimento di Ingegneria Chimica, Facoltà di Ingegneria, Via Diotisalvi 2, I-56100 Pisa, Italy*

(Received in final form 18 July 1996)

Two sets of specifically deuterated cyanoazobenzene side-chain polyadipates and polytetradecanedioates have been prepared by transesterification in the melt. Combinations of three different, selectively deuterium labeled 2-[6-[4-[(4-cyanophenyl)azo]phenoxy]hexyl]-1,3-propanediols or the non-deuterated analog and diphenyl adipate or tetradecanedioate in perdeuterated or non-deuterated versions were employed. The polyesters have weight average molecular masses in the range 21 000 - 183 000 as determined by SEC. The phase behaviour of the polyesters have been investigated in detail by differential scanning calorimetry. Whereas the polytetradecanedioates show a complex thermal behaviour with a number of different phases, the polyadipates are less complex and both nematic and smectic A phases have been identified by polarizing optical microscopy. Solution ^1H, ^{13}C and ^2H NMR spectroscopy have been utilized for both polyester structural assessment and determination of deuterium distribution and content. FTIR spectroscopy has revealed suitable and characteristic vibrations which unequivocally represents the absorption behaviour of individual polyester segments or molecular structures in the different selectively deuterated polyesters.

---

*Corresponding author. Tel: +45 46 77 47 84; Fax: +45 46 7 47 91;
e-mail: s.hvilsted@risoe.dk

1. INTRODUCTION

Azobenzene containing polymers possess attractive photo addressable properties [1] making them important candidates for optoelectrical or optical storage applications [2]. During the last decade various structural designs particularly focusing on differently substituted azobenzene side-chain amorphous or liquid crystalline polymers have been introduced; extensive reviews or reference compilations are provided by McArdle [2]; Xie *et al.* [3] and Hvilsted *et al.* [4]. We recently presented a novel design based on a flexible and modular cyanoazobenzene side-chain liquid crystalline architecture [4, 5]. The most prominent merits of these polytetradecanedioate based polyesters are permanent (presently almost four years) reversible optical storage, resolution of over 5000 lines/mm and diffraction efficiencies of about 40% obtained by polarization holography. However, the different structural parameters inherently possible by the modular construction significantly influence the optical storage properties. Thus the relatively short main-chain segment provided by adipate exhibits an interesting biphotonic behaviour [6, 7]. Varying the flexible alkyl side-chain spacer linking the photochromic moiety to the main chain from hexyl to decyl strongly effects the storage dynamics [8]. Other azobenzene substituents than cyano play a very crucial role [9, 10] where factors such as the substituent size, symmetry, steric hindrance and bulkiness seem to be more important than merely the resulting dipole moment generated by the effective substituted azobenzene chromophore.

Despite the numerous investigations, the origin of the laser induced permanent anisotropy in the polyester materials responsible for the long time storage is not known in detail. Indications that not only the cyanoazobenzene chromophore becomes aligned preferentially perpendicular to the laser light polarization [3, 9, 11] but also that other material parts are influenced come from atomic force and scanning near-field optical microscopic investigations [12]. However, investigations on global material properties will never reveal information on segmental alignment. The focus necessarily needs to be addressed to the molecular level. This, on the other hand, requires a unique *e.g.*, spectroscopic probe which does ideally not change the material properties. Keeping in mind that especially polarization FTIR spectroscopy has been extensively used previously [3, 9, 11] and additionally solid state NMR spectroscopy can be exploited, [13, 14] deuterium appears to be a well suited segmental probe due to the eminent spectroscopic dueterium isotope effects [15, 16] combined with absorption dichroism or orientation-dependent interactions arising from the anisotropic distribution of molecular alignment.

This present study was designed to prepare and evaluate molecular, thermal and spectroscopic characteristics of an extensive range of new cyanoazobenzene side-chain liquid crystalline (SCLC) polyesters based on the selectively deuterated diols and diphenyl adipates or tetradecanedioates detailed in the preceding account [15].

2. EXPERIMENTAL SECTION

2.1. Synthesis. Polyester Preparation

A stoichiometric ratio of the carefully purified diol [15] and diphenyl ester [15, 17] of choice, typically totaling 500–600 mg, was weighed into a glass reactor and melted under nitrogen at reduced pressure. After cooling to room temperature K_2CO_3 (1% (w/w)) was added as a basic catalyst. In a first step, the mixture was heated under nitrogen at reduced pressure (6–7 mbar) to 120–130°C until no more sublimated phenol can be detected. In a second step, the pressure is further lowered (<0.1 mbar) and the primary condensate is slowly heated to temperatures around 140–150°C until phenol evolution ceased, detected as the absence of bubble formation in the viscous melt. The first step normally lasts 1–2 h, the second unusally half an hour. The reaction mixture was dissolved in a sufficient amount of benzene, centrifuged, reprecipitated from a 10 times excess of methanol, filtered and the recovered polyester vacuum dried.

2.2. Instrumentation. Size Exclusion Chromatography (SEC)

Polyester molecular mass examinations have been performed at room temperature on a Viscotek Model 200 Differential Refractometer/Viscometer SEC system operating with a Knauer HPLC pump 64, using a Rheodyne 7125 injection valve equipped with a 200 µL loop and a 5 cm PLgel Guard. Separations have been achieved on either two 50 cm Shodex GPC A-80M columns or on a series of 50 cm Shodex GPC A805 column together with a 50 cm G4000 and a 50 cm G3000 column from TSK Toya Soda, Japan. Stabilized tetrahydrofuran (technical grade) was employed as eluent at a flow rate of 1mL/min, monitored by a syphon counter. Polyester concentrations varied between 0.20% and 0.27% (w/v). Santonox (0.02% (w/v)) was added to the polyester solutions as internal standard in order to allow corrections for possible flow rate variations during the analysis thus improving the accuracy of the calculations. The system was calibrated using polystyrene standards from Polymer Laboratories, UK, with narrow molar mass distributions. Calculations of molecular masses based on the conventional and universal calibration method were carried out utilizing TriSEC® GPC software.

Differential Scanning Calorimetry (DSC)

Calorimetric measurements of the polyesters, have been performed on a Perkin Elmer DSC 4 Differential Scanning Calorimeter equipped with a System 4 Thermal Analysis Microprocessor Controller and a Perkin Elmer 3600 Data Station. Heating and cooling cycles were carried out with a rate of 3°C/min covering a temperature range from − 10°C to + 90°C.

Polarizing Optical Microscopy (POM)

The POM investigations were carried out using a Leitz Ortholux-Pol BK polarizing microscope equipped with a Mettler FP-52 hot stage, controlled by Mettler FP50-unit.

UV-Visible Absorption Spectroscopy

A Varian Cary 1E UV-Visible Spectrophotometer was employed to record UV-visible spectra of the diols as approx. 0.01 mg/mL tetrahydrofuran solutions.

Nuclear Magnetic Resonance (NMR) Spectroscopy

^{13}C, ^{1}H and ^{2}H NMR experiments were performed on a Bruker Avance DPX 250 NMR-spectrometer. Acquisition parameters (pulse width, acquisition time and relaxation delay) applied to observe the resonance signals of the different nuclei, comply with the values already reported for the NMR experiments performed on the corresponding precursors and monomers [15].

^{13}C and ^{1}H NMR spectra of the polyesters were recorded as 3% to 4% (w/v) and 1% (w/v) solutions in $CDCl_3$, respectively. The chemical shifts are referenced to the central resonance of $CDCl_3$ for ^{13}C NMR experiments (77.90 ppm from tetramethysilane (TMS)) and residual $CHCl_3$ in case of proton NMR (7.24 ppm from TMS). ^{2}H NMR spectra of the selectively labeled polyesters are recorded on $CHCl_3$ solutions after exchanging $CDCl_3$ from the samples used for the previous ^{13}C NMR experiments. Chemical shifts are referenced to the signal of residual $CDCl_3$ which has been correspondingly defined as 7.24 ppm.

Fourier Transform Infrared (FTIR) Spectroscopy

Samples for infrared spectroscopic investigations were obtained by casting films of the polyesters from chloroform solution (1 mg polyester/100 μL solvent) onto KBr pellets. The films were subsequently dried at room temperature for about 30 min. This preparation procedure results in a film thickness less than 5 μm. FTIR spectra were recorded on a Perkin-Elmer 1760X spectrometer with a resolution of 4 cm^{-1}, co-adding 32 scans.

3. RESULTS AND DISCUSSION

Polyester Preparation

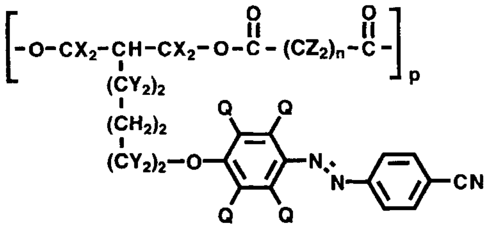
A great variety of selectively deuterated polyesters have been prepared by polytransesterification in the two step process previously developed for combshaped aliphatic side-chain polyesters [18] and the corresponding non-dueterated cyanoazobenzene analogues [4]. The target polyesters were obtained by the proper combinations of deuterated [15] or non-deuterated [17] 2-[6-[4-[(4-cyanophenyl)azo]phenoxy]hexyl]-1,3-propanediol and diphenyl adipate or diphenyl tetradecanediote.

Table I provides both a complete list of the prepared polyesters and a structural survey of these together with the short notation used throughout this paper. In the notation the number refers to adipate (4) or tetradecanedioate (12) and X, Y, Z and Q designate the deuterated positions in the particular polyester.

Determination of the Molecular Mass

The molecular mass distribution of the polyesters have been determined employing size exclusion chromatography (SEC). Table II presents number (M_n) and weight (M_w) average molecular mass for the different selectively deuterated polyesters, together with the non-deuterated analogues (P4 and P12).

TABLE I Molecular structure, position of selective deuteration and notation of the prepared cyanoazobenzene SCLC polyesters



Polyester	*n*	*X*	*Y*	*Z*	*Q*
P4	4	H	H	H	H
P4X	4	D	H	H	H
P4Y	4	H	D	H	H
P4Z	4	H	H	D	H
P4XZ	4	D	H	D	H
P4Q	4	H	H	H	D
P12	12	H	H	H	H
P12X	12	D	H	H	H
P12Y	12	H	D	H	H
P12Z	12	H	H	D	H
P12XZ	12	D	H	D	H
P12Q	12	H	H	H	D
P12ZQ	12	H	H	D	D

TABLE II Molecular masses of selectively deuterated cyanoazobenzene SCLC polyesters

Polyester	M_n	M_w	$R(M_w/M_n)$
P4	38 000	66 000	1.7
P4Z	34 000	73 000	2.1
P4Y	45 000	112 000	2.5
P4X	50 000	183 000	3.7
P4Q-I	12 000	21 000	1.8
P4Q-II	35 000	65 000	1.9
P4XZ	40 000	98 000	2.5
P12-I	32 000	84 000	2.6
P12-II	35 000	78 000	2.2
P12Z-I	14 000	46 000	3.3
P12Z-II	27 000	83 000	3.0
P12Y	41 000	78 000	1.9
P12X	66 000	132 000	2.0
P12Q-I	21 000	46 000	2.2
P12Q-II	59 000	148 000	2.5
P12XZ	26 000	59 000	2.3
P12ZQ	41 000	95 000	2.3

Reducing the reaction time and temperature during the first and second polymerization step results in a decrease of the molecular weight of the polycondensate. The indices I and II in Table II indicate polyesters of identical molecular structure, processing different molecular masses, due to variations in the polymerization parameters. It is shown that the polyester recovery and precipitation procedure removes oligomeric linear as well as cyclic fractions. The polydispersity ratio, *R*, is in most cases closed to 2 and describes the width of the mass distribution curve for a molecular mass distribution typical of polycondensation reactions at high conversions [19]. The average molecular masses have been calculated using a conventional calibration method employing narrow polystyrene standards. However, it has been shown that the polyester recovery and precipitation procedure removes oligomeric linear as well as cyclic fractions. Due to the structural differences between polystyrene and the investigated side-chain polyesters, the values reported in Table II should therefore be treated as indications for approximate molecular mass regions rather than absolute quantities. One method of obtaining absolute molecular mass data from SEC would be to measure simultaneously the viscosity of the eluent and the concentration of the solute (refractive index (RI) detection), applying the universal calibration procedure. However, in case of the investigated cyanoazobenzene SCLC polyesters, this method turned out not to be feasible. Unreliably high weight average and peak molecular mass values were obtained which could not be verified by the corresponding chromatogram. A small quantity of gel-like material always present in the polyester bulk sample seems to be responsible for this uncertainty. These high molecular weight fractions can be observed in form of a small shoulder on the high molecular mass side of the distribution curve. Due to the sensitivity of the viscosimetric response in the high molecular mass region, small quantities of these constituents are able to cause an unproportionally high viscosimetric signal, thus preventing an accurate mass determination. The gel-like formation occurs during the polycondensation process to a small extent and might be due to a thermally initiated branching reaction between partly degraded side chains [4]. This hypothesis is supported by the qualitative observation that gel-like formation is less at lower reaction temperatures and shorter reaction times. On the other hand, even a slight decrease of these two parameters causes a decrease in the molecular mass of the final polyester of up to 50%.

Thermal Characterization

The thermal behaviour of the selectively deuterated cyanoazobenzene SCLC polyesters and the corresponding non-deuterated analogues has been characterized by differential scanning calorimetry (DSC). Figure 1 illustrates

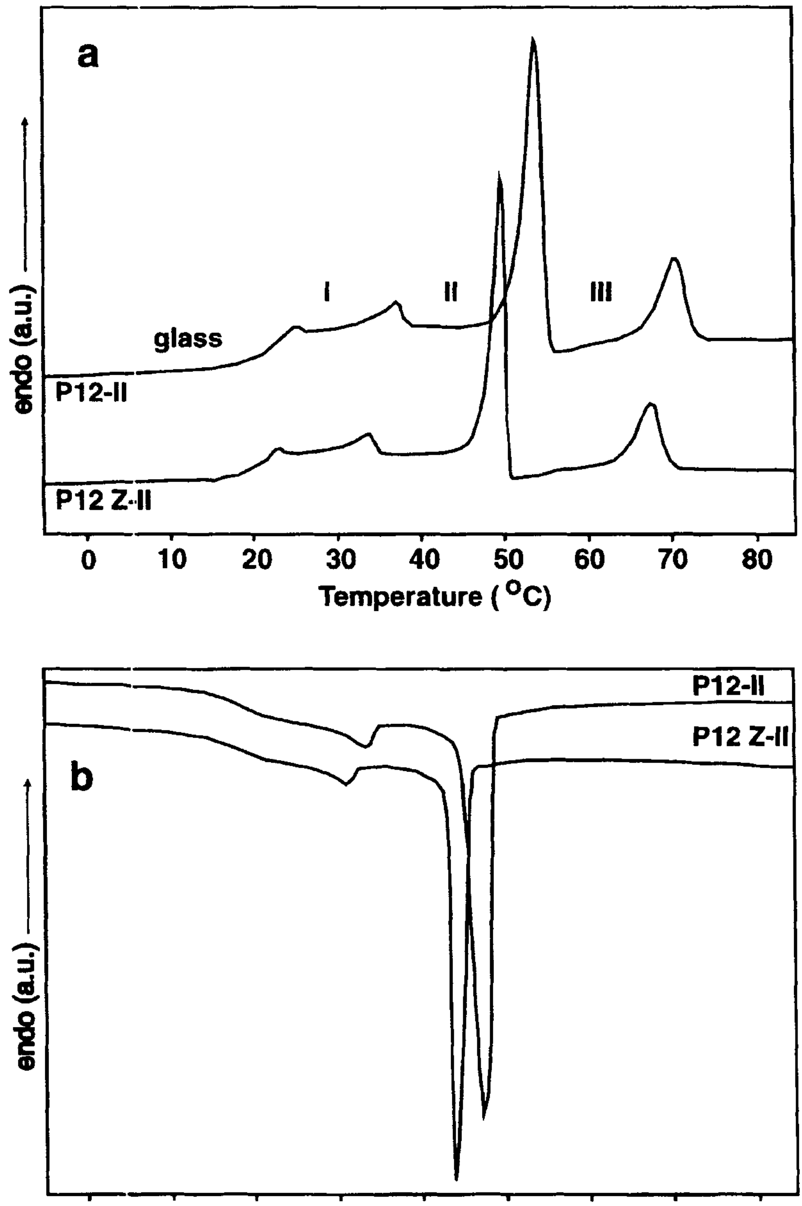


FIGURE 1 DSC second heating (a) and cooling (b) traces of polyesters P12Z-II and P12-II (heating and cooling rate: 3°C/min, y-scales equivalent).

the second heating and cooling cycles of P12Z-II and P12-II at a rate of 3°C/min as representative examples of the polytetradecanedioates.

In this case, a 3–4°C depression of corresponding phase transition temperatures can be observed for the selectively deuterated sample, compared to the non-deuterated analogous. However, the number of observable transitions and therefore, the number of different morphological structures present in the bulk material, is not influenced by the exchange of protons at different locations in the repeating unit. In case of the glass transition, T_g, noticeable effects are only observed when the long main-chain segments are deuterated (P12Z samples) ensuring a high deuterium content. The main-chain deuterated polytetradecanedioate (P12Z-II), exhibits a T_g around 20°C (correspondingly 21°C in P12-II), followed by three endotherm transitions at 33.8°C (P12-II = 37.3°C), 49.8°C (P12-II = 54.0°C) and 67.6°C (P12-II = 70.5°C), respectively, comprising different enthalpy values. When the deuteration only is present in other parts of the polyesters the phase transition temperatures are less effected (*cf.* Tab. III). It is noted that the differences in

TABLE III Transition temperatures and enthalpies of selectively deuterated cyanoazobenzene SCLC polyesters. Obtained by DSC of second heating at 3°C/min

Polyester	*Transitions*						
	T_g	*I → II*		*II → III*		*III → IV*	
	°*C*	°*C*	ΔH (*kJ/mol*)	°*C*	ΔH (*kJ/mol*)	°*C*	ΔH (*kJ/mol*)
P12-I	22.4	38.7	1.69	54.2	13.62	71.0	0.63
P12-II	21.4	37.3	1.24	54.0	10.94	70.5	4.09
P12Q-I	22.7	37.1	1.17	53.4	11.52	69.5	1.53
P12Q-II	21.7	37.5	1.37	53.2	12.46	69.7	1.73
P12X	22.9	38.1	1.48	55.4	13.71	71.0	0.41
P12Y	22.6	38.8	1.77	54.1	13.77	71.7	0.59
P12Z-I	20.3	35.2	1.23	49.8	9.32	67.6	5.04
P12Z-II	20.2	33.8	0.91	49.8	10.08	67.6	3.97
P12ZQ	20.9	34.4	1.29	50.6	12.64	68.9	0.37
P12XZ	20.5	34.5	1.08	50.3	12.14	68.1	1.26

	T_g °*C*	*I → II* °*C*	*II → III* °*C*	ΔH_{total} (*kJ/mol*)
P4	6.4	56.8	58.2	1.38
P4Q-I	3.7	51.1	53.2	1.39
P4Q-II	6.2	55.8	57.3	1.58
P4X	8.9	57.7	59.5	1.22
P4Y	8.5	54.8	56.7	1.19
P4Z	7.9	57.7	59.0	1.44
P4XZ	8.3	58.2	59.3	1.48

transition temperatures between polyesters with the same composition but different molecular masses in all cases are around 1°C or less.

These transitions define the stability range of three distinct morphological structures (marked I–III in Fig. 1a). The low temperature phase transition occurring in P12Z-II at 33.8°C (phase I → phase II) is associated with a relatively small heat of fusion (0.9 kJ/mol). On the other hand, the transitions occurring at higher temperatures (49.8°C (phase II → III) and 67.6°C (phase III → isotropoic)) require a larger heat supply with a total of 14.1 kJ/mol, indicating the presence of higher ordered structures. In fact, in all cases the sum of ehthalpies of the two high temperature transitions is in the range 13–14 kJ/mol. A similar behaviour was previously observed for another P12 sample [4]. Annealing at temperatures in the stability range of phase II and III favors the conversion into the high melting structure (phase III), verified by an increasing enthalpy value for the high temperature transition (67.6°C), accompanied by a decrease of transition enthalpies associated with phase I and II (Fig. 2). It should be noted, however, that the thermal behaviour of these polyesters is very sensitive to the thermal treatment. The influence of annealing of P12 polyesters was previously

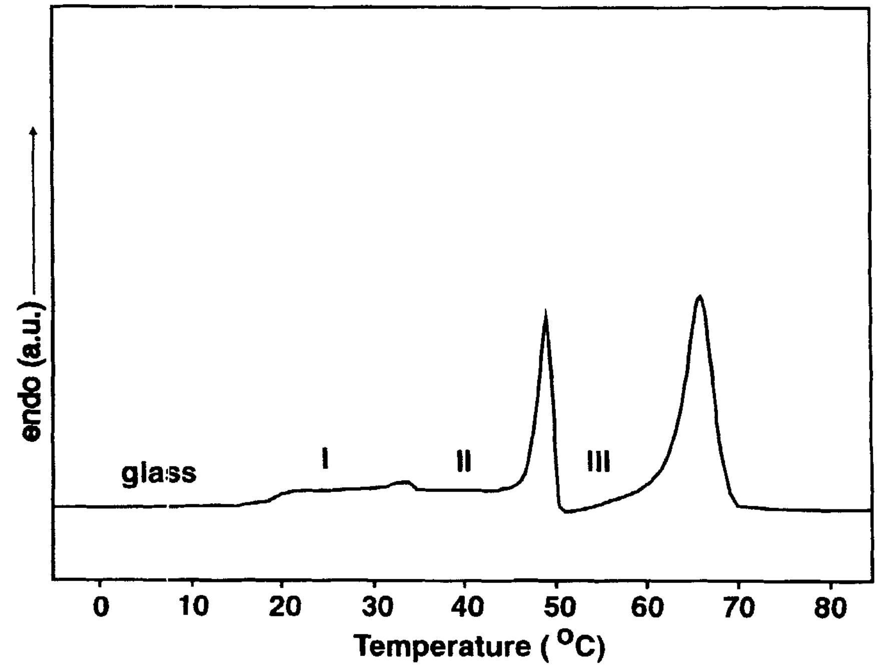


FIGURE 2 DSC heating trace (3°C/min) of polyester P12Z-II after annealing for 2 h at 41°C (*y*-scale equivalent to Fig. 1).

investigated by applying both DSC and X-ray diffraction techniques without conclusive evidence [20].

However, all morphological changes, induced by annealing procedures, as monitored by DSC, are entirely reversed upon heating the polyesters into the isotropic phase (≈80°C). Upon cooling from the isotropic state, only two transitions occur (Fig. 1b), indicating the sensitivity of particularly the high melting structure towards thermal treatment. A detailed thermal analysis and corresponding findings of a somehow similar polyester with an octamethylene spacer is available elsewhere [21].

The POM investigations carried out on films as thin as 2–3 µm cast from solutions of both deuterated and non-deuterated P12 polyesters, heated to 80°C and normally cooled in air, didn't disclose the characteristic optical texture of the liquid crystalline phase. When observed between crossed polarizers the polyester films in particular exhibit rough fine granulated textures made of randomly distributed birefringent domains, which lack the distinctive character for an unambiguous mesophase classification. Attempts to coarsen and transform the fine grain pattern into a well-defined and assignable optical texture, which were based on a careful cooling and annealing treatment within a temperature range from 38°C to 65°C, failed probably because the multiphase nature of the polyesters and/or a high viscosity of the polyester melts. It's worth pointing out that the blurred fine-grained textural patterns had already been observed for the medium high molecular mass P12 polyester, whereas the typical optical textures of true liquid crystalline phase were obtained for a P12 sample with a very low molecular mass [4] ($M_w \approx 5000$).

The differences in transition temperatures between deuterated and non-deuterated analogues become even less for cyanoazobenzene side-chain polyadipates (Fig. 3). However, it has to be considered that in case of *e.g.*, a predeuterated main-chain spacer, the relative amount of incorporated deuterium atoms compared to remaining protons, is higher for P12Z (67% of all protons substituted) than for P4Z (40% of all protons substituted). The small transition temperature differences observed are mainly due to alterations in the molecular masses of the various polyadipates. Considerable molecular mass differences however, as determined for P4Q-I and P4Q-II and listed in Table II, result in a significant difference between the transition temperatures. Thus all transitions observed in P4Q-I (relatively low molecular mass sample) are 3–4°C lower than the corresponding transitions in P4Q-II, as reported in Table III. Even larger polyester molecular mass differences, on the order of 10 times, leads to more dramatic changes in thermal behaviour [4], and in fact, totally changes the features of the respective thermograms.

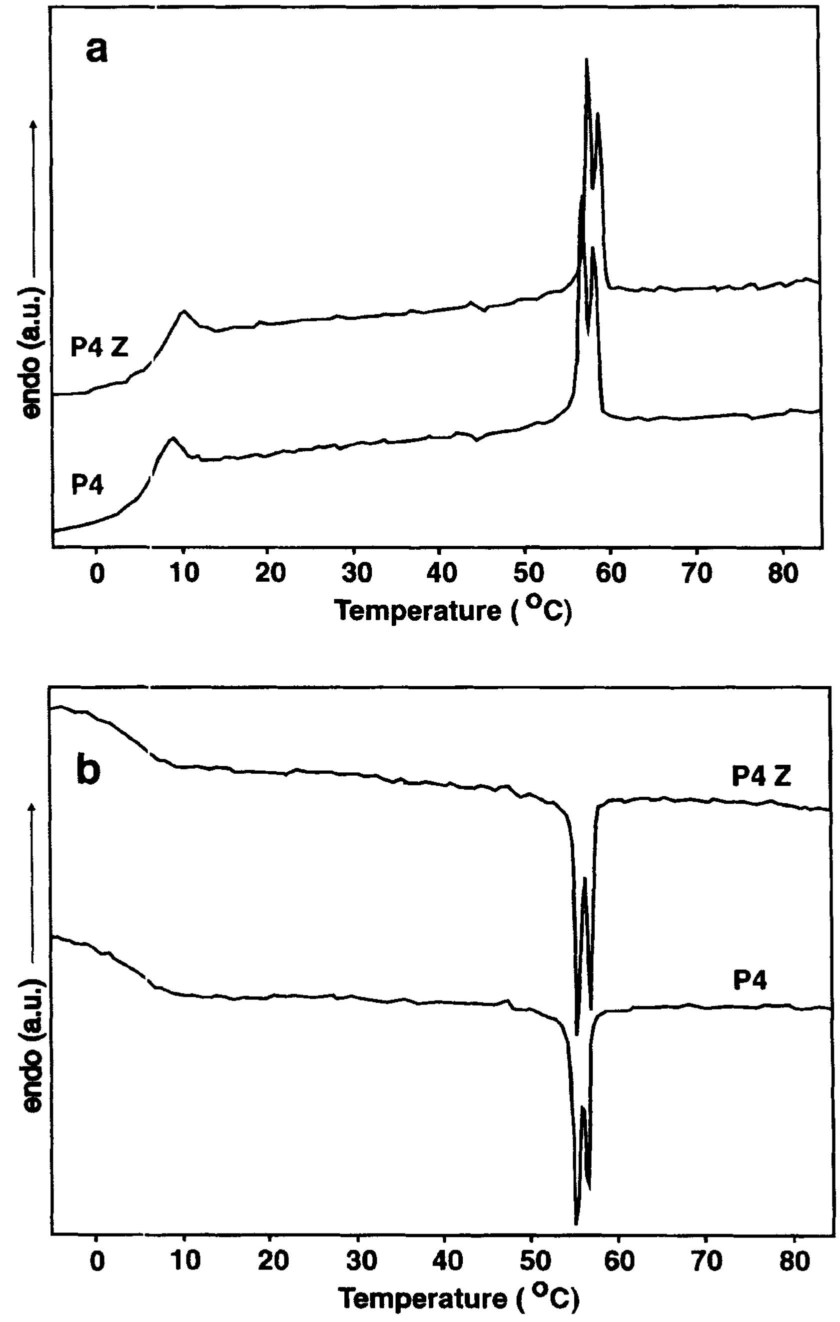


FIGURE 3 DSC second heating (a) and cooling (b) traces of polyesters P4 and P4Z (heating and cooling rate: 3°C/min, y-scales equivalent).

The DSC traces of polyadipates exhibit in addition to a glass transition in the region 6–9°C, two endotherm peaks in the temperature range between 56°C and 59°C, associated with a total enthalpy of 1.3–1.6 kJ/mol undergoing only limited supercooling (1–3°C, Fig. 3). The observable transition temperatures and the corresponding low enthalpy values remain almost unaffected by cooling and re-heating as well as annealing procedures thus indicating an enantiotropic phase behaviour. The complex temperature dependent multiphase behaviour, as revealed for the polytetradecanedioates is not present in the polyadipates. This observable thermal behaviour strongly implies the formation of a liquid crystalline mesophase in the polyadipates. Clear evidence of an inherent mesomorphic phase behaviour for these polyester systems – in terms of different mesophases – can be observed by POM analysis. The optical investigations have been carried out on polyester films, cast from chloroform solution (5 mg/mL) onto glass slides. This preparation procedure results in a film thickness of approximately 2–3 μm. Upon annealing at 59°C for 20 h, a schlieren texture with two and four brushes develops, indication the formation of a nematic phase (Fig. 4a). Subsequent heating (1°C/min) leads to the corresponding nematic to isotropic phase transition at 61–62°C.

Performing the annealing process at 49°C for 20 h results in the appearance of a smectic A phase, which can be identified by its characteristic fan shaped texture (Fig. 4b). Upon heating (1°C/min), the smectic structure disappears at 51–53°C, undergoing a direct conversion into the isotropic phase. However, as mentioned above, the two endothermic peaks observable in the calorimetric characterization of bulk samples, exhibit both the thermal characteristics of mesomorphic transitions. Table III summarizes the transition temperatures together with the corresponding transition enthalpies as revealed from the DSC heating trace for selectively deuterated and non-deuterated polytetradecanedioates (P12 series) and polyadipates (P4 series).

UV-Visible Absorption Spectroscopy

The UV-VIS spectra of the investigated azobenzene SCLC polyesters resemble the absorptional behaviour of the employed 2-[6-[4-[(4-cyanophenyl)azo]phenoxy]hexyl]-1,3-propanediols [15]. The spectra comprise two absorption bands, where the strongest absorption with maximum in the near UV-region occurs at 365 nm and can be assigned to the intense $\pi-\pi^*$ transition of the $(N = N)$ bond. The orange color of these cyanoazoben-

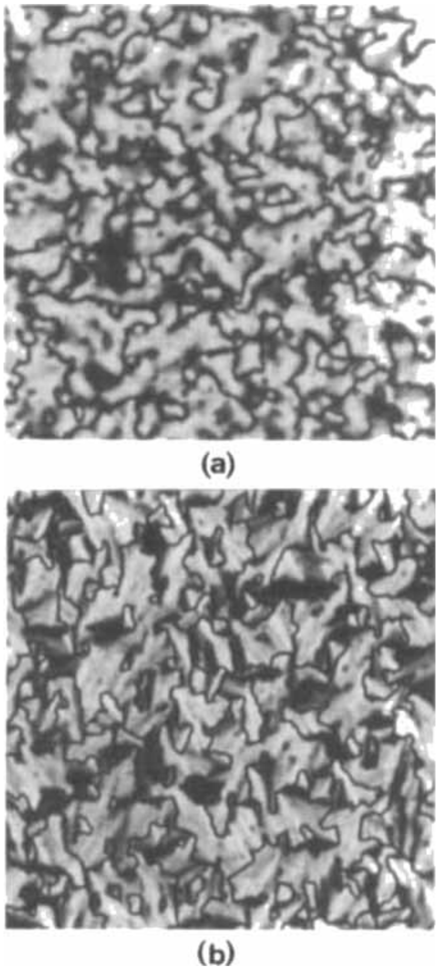


FIGURE 4 Photomicrographs showing optical textures of P4: (a) schlieren texture with two and four brushes obtained after annealing at 59°C for 20 h.; (b) fan shape texture obtained after annealing at 49°C for 20 h. Crossed polarizers; magnification x 640.

zene SCLC polyesters, however, originates from a weak and broad band around 445 nm which is attributed to the corresponding $n-\pi^*$ transition. In case of the present systems, the $\pi-\pi^*$ and the broad $n-\pi^*$ transitions overlap and cover a relatively wide absorption region, with an extended shoulder on the long wavelength side (Fig. 5).

The spectrum of P12Z-II (Fig. 5) has λ_{max} $(\pi - \pi^*)$ at 365 nm with an ε_{max} of 25,000 L mol^{-1} cm^{-1} and $n - \pi^*$ at 445 nm with ε_{445} of 1,800 L mol^{-1} cm^{-1}

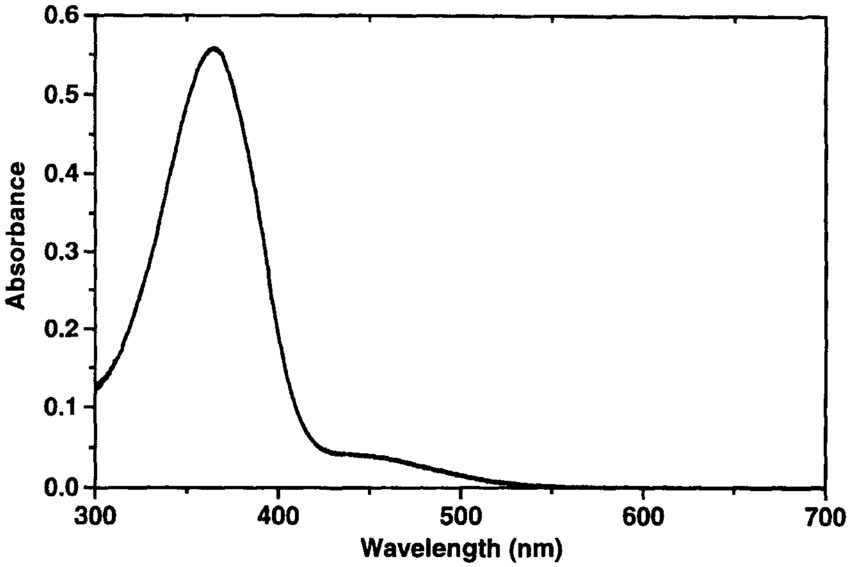


FIGURE 5 UV-Visible absorption spectrum of polyester P12Z-II.

and is representative of all samples. No differences in optical absorption properties can be detected between any of the investigated deuterated and the corresponding non-deuterated polyesters. The absorption behaviour can be directly related to the unique optical properties of these systems. It has been shown for azo-compounds [1] that irradiation of wavelengths close to the $\pi-\pi^*$ transition causes a *trans-cis* isomerization of the azo group, whereas irradiation in the spectral region of the $n-\pi^*$ transition induces preferably the *cis-trans* isomerization [22].

NMR Analysis

High resolution ^{1}H, ^{2}H and ^{13}C NMR investigations have been carried out in order to characterize the molecular structure of the prepared selectively deuterated P4 and P12 SCLC polyesters with respect to location and degree of deuteration. In accordance with the NMR characterization of diphenyl predeuterated dicarboxylates [15] ^{1}H NMR has been applied to determine quantitatively the amount of deuterium incorporation, whereas additionally ^{2}H and ^{13}C NMR experiments yield further information concerning the distribution of deuterium along the labeled aliphatic sequences. Since no significant spectral differences have been observed between samples of the same structural composition with different molecular mass the distinction is abandoned in the following discussion. The ^{1}H NMR spectrum of P12Z in Figure 6 shows the proton resonance characteristics of a partly main-chain deuterated polyester. Selective deuteration also turns out to become a valuable tool in the assignment of the various resonances originating from other methylene units in the main-chain and the side-chain spacer, respectively. Table IV summarizes the chemical shifts of the proton resonances for the P4 and P12 SCLC polyesters, mainly based on the information obtained from the selectively deuterated diphenyl esters and monomers [15]. The shift value reported in Table IV refer to the central resonance of corresponding complex multiplets or to the maximum of broad unstructured signals.

Generally, the ^{1}H NMR spectra of these polyesters consist of three absorption regions. Within 7 to 8 ppm the signals of the deshielded aromatic protons (**c**, **d**, **g**, **h**) can be observed. These protons from an EE′FF′ (**c**, **d**) and a AA′GG′ (**h**, **g**) spin system [23] which are not well resolved in the presented 250 MHz ^{1}H NMR spectrum leading to three resonance groups each governed

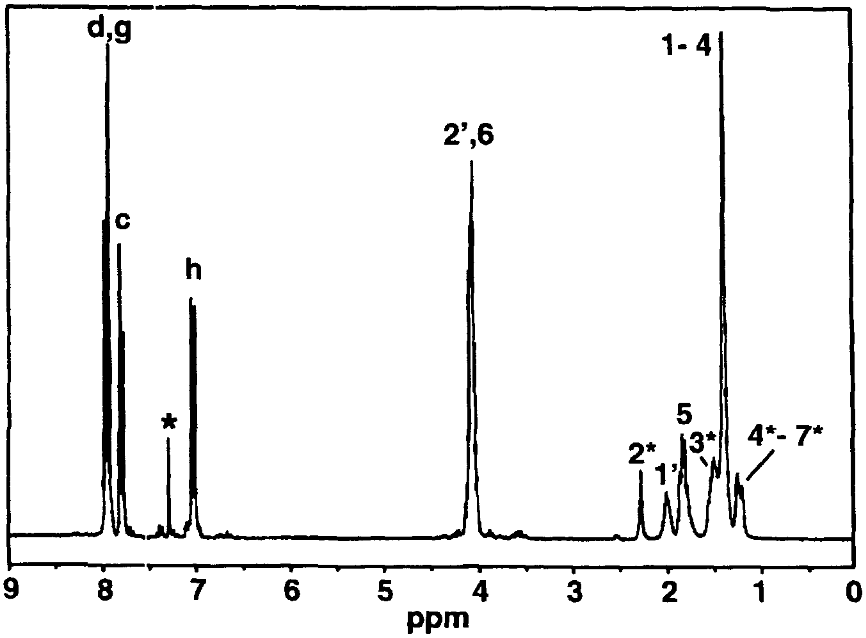
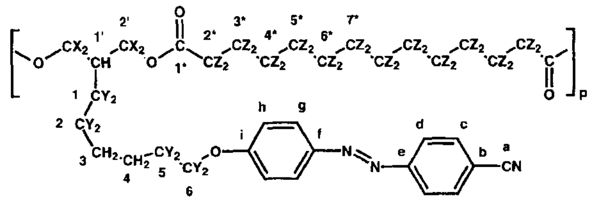


FIGURE 6 250.13 MHz ^{1}H NMR spectrum of polyester P12Z in $CDCl_3$ (* residual $CHCl_3$, for assignment refer to Tab. IV).

TABLE IV 250.13 MHz ^1H NMR chemical shifts in cyanoazobenzene SCLC polyesters (ppm in $CDCl_3$)



Polyester	**1'**	**2'**	**2***	**3***	**4*−7***	**1−4**	**5**	**6**	***c***	***d***	***g***	***h***
P4-series	1.95	4.02	2.30	1.62		1.34[a]	1.78	4.01	7.73[a]	7.89[a]	7.89[a]	6.97[a]
P12-series	1.96	4.03	2.27	1.58	1.22[a]	1.36[a]	1.80	4.02	7.75[a]	7.91[a]	7.91[a]	6.98[a]

[a] Central resonance of respective protons.

by two broad and unstructured signals. Utilizing the polyesters, labeled in the aromatic azobenzene core (P12Q, P12ZQ, P4Q), it has been possible to assign the aromatic resonance groups to the corresponding spin systems. Hereby, it became apparent that the signals attributable to the FF′ (**d**) and GG′ (**g**) parts are superimposed (Tab. IV). The other labeling patterns assist in the identification of other structural units and sequences. Thus the complex multiplet around 4 ppm is due to a superimposition of resonances originating from methylene protons directly attached to an oxygen atom, namely the glycol methylene units in the main-chain (**2′**) and the oxymethylene group in the aliphatic side-chain spacer (**6**) attached to the azobenzene unit. Various resonances and multiplets of unresolved structure appear in the region between 1 and 2.5 ppm originating from the methylene protons in the aliphatic main-chain (**2*** – **7***) and side-chain spacer (**1** – **5**) as well as the methine proton located at the side-chain junction (**1′**). The degree of deuteration in a repeating unit might be derived from the integral of this entire region, by relating this value to the integrals obtained from the 8 aromatic protons or the 6 oxymethylene protons, respectively. Applying this method, an average of 89% deuteration of the main-chain spacer repeating unit is calculated from the integrals of the spectrum depicted in Figure 6. Compared to 93% determined for the precursor [15], diphenyl perdeuterated tetradecanedioate, 89% incorporated deuterium conveys a loss of 4% during the polymerization procedure. Probably, the long duration at higher temperature under the applied basic conditions is responsible for the observable back exchange. However, a more detailed analysis reveals a deuterium content of 86% in the α-positions next to the carbonyl group, whereas a total of 91% can be calculated for the methylenes in β-position and the 8 corresponding central methylene units. This illustrates the pronounced acidic character of protons located in α-carbonyl positions, capable of exchange reactions under relatively moderate conditions. Table V reports the deuterium content of the different labeled side-chain polyesters, determined by ^{1}H NMR.

Figure 7 shows the expanded ^{13}C NMR spectra (40 to 22 ppm) of P12Z and P12. The rest of the spectra is not shown but represented by the chemical shifts listed in Table VI, in addition spectra of analogs to P12 have previously been presented [4]. The depicted resonance region contains most of the ^{13}C resonances originating from the methylene groups in the main-chain and side-chain spacer, respectively. Comparison of the spectra clearly reveals the expected reduction of ^{13}C resonance intensity due to the main-chain deuteration. Only five sharp and intensive ^{13}C resonances are observed between 30 and 26 ppm (**1**–**5**), which can be attributed to the remaining CH_2 units in the aliphatic side-chain spacer (for peak assignment see Tab. VI). Due to spin–spin coupling betwen adjacent ^{13}C and ^{2}H nuclei, a replacement of protons by deuterons results in a splitting of the corresponding ^{13}C NMR signal into a multiplet structure. Hence for a CD_2 unit, a quintet exhibiting a 1:2:3:2:1 intensity distribution is predicted. An enlargement of the resonance region around 24 ppm (Fig. 7) shows that such a pattern can be observed for the methylene units in the β-position relative to the carbonyl group (**3***), indicating a fairly complete exchange at this location. The multiplet structure assigned to the α-methylene units (**2***, 34 ppm) exhibits an asymmetric shape. This deviation from the expected intensity distribution can be ascribed to additional CHD units located in the α-position. For this structure, a triplet pattern with equal signal intensities is to be expected. The possibility to resolve the complex multiplet pattern

TABLE V Deuterium content of labeled cyanoazobenzene SCLC polyesters determined by ^{1}H NMR spectroscopy

Polyester	*Deuterium content %*
P4X	100
P4Y	89
P4Z	88
P4Q	95
P4XZ	88(Z) and 100(X)
P12X	100
P12Y	89
P12Q	95
P12Z	89
P12XZ	100(X) and 88(Z)
P12ZQ	88 (Z) and 94 (Q)

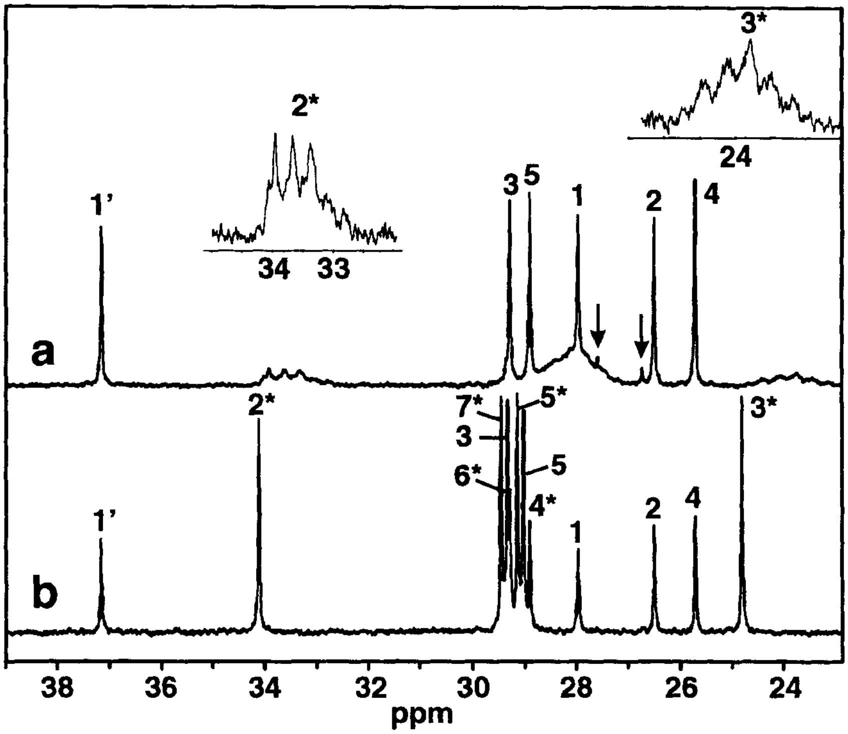


FIGURE 7 Partial 62.9 MHz ^{13}C NMR spectra of polyesters P12Z (a) and P12 (b) in $CDCl_3$ (for assignment refer to Tab. IV, ↓ diol end-groups [4]).

centered at 34 ppm into a triplet superimposed on a quintet indicates the presence of protons in the α-position. As no singlet resonance at lower field as expected from unlabeled CH_2 is observed such units in the α-position (2*) of P12Z can be excluded. The remaining CD_2 units of the aliphatic main-chain spacer give rise to a broad, unstructured signal between 30 and 29 ppm. However, no evidence for CH_2 structures in the central part of the aliphatic chain can be found.

A complete list of all the ^{13}C NMR chemical shifts of partly deuterated and unlabeled polytetradecanedioates are presented in Table VI. The individual assignments are based on a combination of information gained from selective deuteration as well as detailed NMR information already existing on comparable systems [4]. It is noted that all the deuterium isotope effects previously discussed in detail [15] in the corresponding analysis on partly deuterated diols are observed in the polyester ^{13}C spectra as well. All the cyanoazobenzene SCLC polyadipates have been examined in similar manner with a compilation of the data in Table VII.

TABLE VI 62.9 MHz ^{13}C NMR chemical shifts[a] of selectively deuterated cyanoazobenzene SCLC Polytetradecanedioaes (ppm in $CDCl_3$)

Polyester	**7***	**6***	**5***	**4***	**3***	**2***	**1***	**2′**	**1′**	**6**	**5**	**4**	**3**	**2**	**1**
P12	29.49	29.37	29.18	29.06	24.85	34.15	173.66	63.86	37.20	68.22	28.94	25.74	29.32	26.53	27.99
P12X	29.48	29.37	29.18	29.06	24.84	34.15	173.67	63.19	36.84	68.21	28.94	25.74	29.31	26.52	27.89
P12Y	29.47	29.36	29.16	29.05	24.83	34.14	173.64	63.83	36.99	67.40	28.32	25.47	29.10[c]	26.20	27.20
P12Q	29.48	29.37	29.17	29.06	24.84	34.15	173.65	63.85	37.19	68.21	28.93	25.74	29.32	26.52	27.99
P12Z	28.7 – 27.2[b]	28.7 – 27.2[b]	28.7 – 27.2[b]	28.7 – 27.2[b]	23.79	33.67	173.74	63.83	37.20	68.22	28.95	25.75	29.33	26.53	28.00
P12ZQ	28.7 – 27.2[b]	28.7 – 27.2[b]	28.7 – 27.2[b]	28.7 – 27.2[b]	23.76	33.64	173.72	63.82	37.19	68.27	28.93	25.74	29.31	26.52	27.99
P12XZ	28.7 – 27.2[b]	28.7 – 27.2[b]	28.7 – 27.2[b]	28.7 – 27.2[b]	23.83	33.64	173.75	63.18	36.85	68.22	28.95	25.75	29.33	26.53	27.90

polyester	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*
P12	118.49	113.02	133.01	122.93	154.65	146.59	125.33	114.73	162.55
P12X	118.49	113.02	133.00	122.93	154.64	146.57	125.33	114.73	162.55
P12Y	118.47	113.00	132.99	122.91	154.63	146.56	125.33	114.71	162.56
P12Q	118.49	113.01	133.00	122.92	154.65	146.47	124.93	114.36	162.49
P12Z	118.50	113.03	133.02	122.94	154.65	146.59	125.34	114.74	162.56
P12ZQ	118.48	113.01	133.00	122.92	154.65	146.47	124.94	114.34	162.49
P12XZ	118.50	113.04	133.02	122.94	154.64	146.59	125.35	114.74	162.58

[a] The carbon numbers refer to polyester structure in Table IV;

[b] Broad resonance region;

[c] Superimposed by 4* and 5*.

TABLE VII 62.9 MHz ^{13}C NMR chemical shifts[a] of selectively deuterated cyanoazobenzene SCLS polyadipates (ppm in $CDCl_3$)

Polyester	**3***	**2***	**1***	**2′**	**1′**	**6**	**5**	**4**	**3**	**2**	**1**
P4	24.20	33.64	173.06	63.94	37.20	68.21	28.95	25.76	29.33	26.55	28.00
P4X	24.18	33.63	173.06	63.34	36.84	68.19	28.93	25.74	29.31	26.53	27.89
P4Y	24.20	33.64	173.06	63.93	37.00	67.38	28.37	25.45	29.03	25.87	26.23
P4Q	24.20	33.64	173.05	63.95	37.20	68.21	28.95	25.76	29.33	26.55	28.00
P4Z	23.15	33.12	173.10	63.91	37.10	68.20	28.94	25.75	29.32	26.54	27.99
P4XZ	23.17	33.12	173.12	63.23	36.86	68.22	28.96	25.77	29.34	26.56	27.92

Polyester	***a***	***b***	***c***	***d***	***e***	***f***	***g***	***h***	***i***
P4	118.48	113.04	133.02	122.93	154.61	146.58	125.33	114.73	162.53
P4X	118.46	113.02	132.09	122.91	154.60	146.56	125.31	114.72	162.52
P4Y	118.48	113.04	133.01	122.93	154.62	146.57	125.33	114.72	162.55
P4Q	118.48	113.04	133.01	122.93	154.63	146.47	124.93	114.35	162.47
PZ	118.47	113.03	133.00	122.92	154.61	146.57	125.32	114.72	162.52
P4XZ	118.49	113.06	133.03	122.94	154.64	146.60	125.34	114.74	162.54

[a] The carbon numbers refer to polyester structure in Table IV.

^{2}H NMR experiments carried out on P12Z (Fig. 8) supports the results obtained by ^{13}C NMR.

However, the ^{2}H resonances are relatively broad and the resonance from the β-(CD_2) (**3***) and the central (CD_2) units (**4*** to **7***) are not well resolved. This prevents a direct quantitative evaluation of the deuterium distribution. On the other hand, a qualitative comparison of all three deuterium signal intensities reveal a deviation from the 1 : 1 : 4 ratio expected for equal distribution. The observed area of the resonance from **2*** appears to be less than 20% of the sum of the areas from the resonances **3*** to **7*** and thus confirms the loss of deuterium in the α-position during the polymerization procedure. All the chemical shifts of the ^{2}H resonances from the different selectively deuterated cyanoazobenzene SCLC polyesters are listed in Table VIII.

Fourier Transform Infrared Spectroscopy

Due to structural similarities, the selectively deuterated SCLC polyesters exhibit analogously light absorption behaviour. Therefore, the effect of

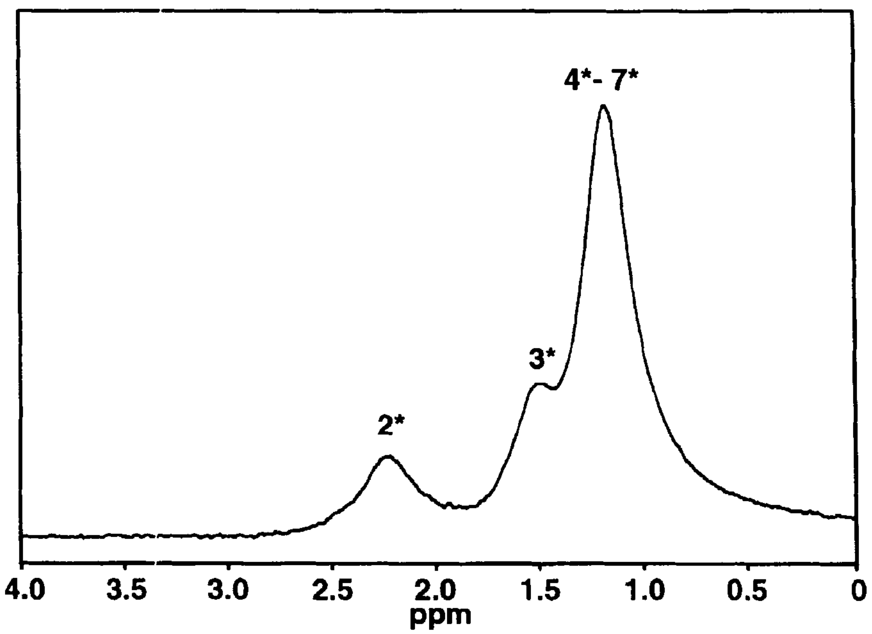


FIGURE 8 38.4 MHz ^{2}H NMR spectrum of polyester P12Z in $CHCl_3$ (for assignment refer to Tab. IV).

TABLE VIII 38.4 MHz ^2H NMR chemical shifts [a] of selectively deuterated cyanoazobenzene SCLC polyesters (ppm in $CHCl_3$)

Polyester	**2′**	**2***	**3***	**4*–7***	**1 + 2**	**5**	**6**	***g***	***h***
P4X	4.02								
P4Y					1.33	1.72	4.00		
P4Z		2.28	1.61						
P4XZ	4.05	2.28	1.58						
P4Q								7.95	7.00
P12X	4.05								
P12Y					1.35	1.76	4.02		
P12Z		2.22	1.49	1.18					
P12XZ	4.05	2.25	1.52	1.19					
P12ZQ		2.23	1.52	1.18				7.95	7.02
P12Q								7.95	7.02

[a] The numbers refer to polyester structure in Table IV.

deuterium exchange on the FTIR-spectrum will only be discussed in detail for two specific systems, namely P12Z and P12Q. Since a (CD) absorption occurs at a comparatively lower frequency than the equivalent (CH) mode [15] deuterium – located in the aliphatic sequences of the polyester repeating unit – should give rise to distinct absorptions in the frequency range between 2200 and 2000 cm^{-1}. An illustration of this effect is provided in Figure 9 which simultaneously presents the FTIR spectra of P12 and the corresponding main-chain deuterated polyester, P12Z.

For both polyesters in Figure 9, separate absorption bands can be assigned to group vibrations arising from the azobenzene chromophore and the ester functionalities located in the polymer main chain [4, 11, 24]. Two additional bands become apparent in the spectrum of P12Z occurring at 2195 and 2091 cm^{-1}, respectively. These spectral positions are in accordance with the mass dependent frequency shift of asymmetric and symmetric (CD_2) stretching vibrations, observed for the corresponding diphenyl perdeuterated tetradecanedioate [15] which was employed as polyester precursor. If one considers that CD_2 units are solely located in the aliphatic main-chain spacer, any orientational or conformational information obtained from their absorptional behaviour can hence exclusively be associated with this particular aliphatic segment. Therefore, each labeled cyanoazobenzene SCLC polyester provides a set of group vibrations which probes the absorptional behaviour of the corresponding structural segments (cyanoazobenzene chromophore, aliphatic main-chain, diol part of main-chain or aliphatic side-chain sequence) or particular segmental polyester links (ester bond, ether bond). Table IX summarizes the most important group vibrational assignments with absorption modes and frequencies of all

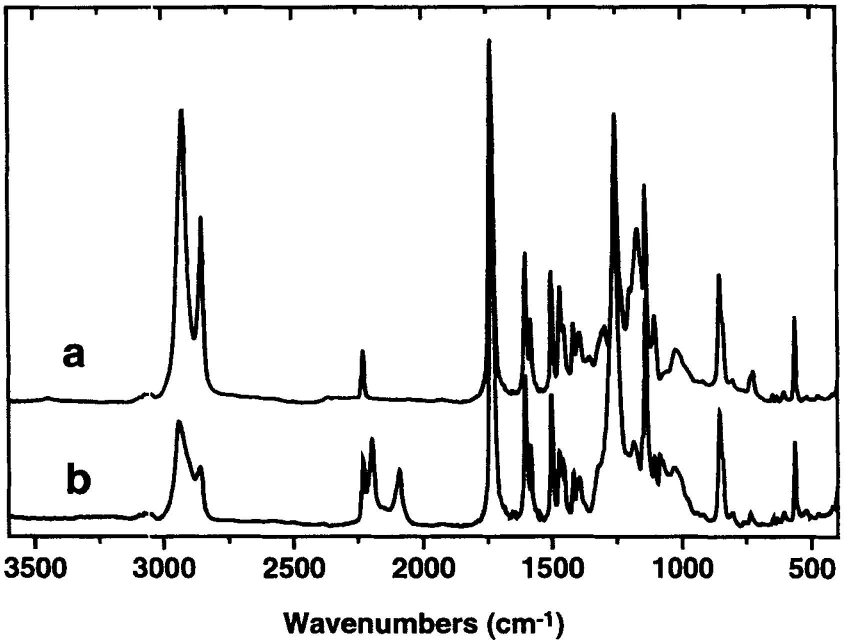


FIGURE 9 FTIR spectra of polyesters P12 (a) and P12Z (b) (film on KBr).

the cyanoazobenzene polyesters with selective deuteration in the aliphatic moieties. The aim of Table IX is not to provide a complete list of all polyester vibrations but rather to present a guide to the particular vibrations which will be used to monitor the absorptional behaviour of a particular segment or molecular structure in the repeating unit of a polyester. Obviously both P12XZ and P4XZ have an abundance of CD_2 vibrations, however, it is the remaining CH_2 vibrations originating entirely from the aliphatic side-chain segment which in these cases will be the valuable tool.

In contrast to the deuteration of aliphatic structures, where the attention is mainly focused on the shifted (CD_2) and the remaining (CH_2) group vibrations, respectively, deuteration can also be very essential with respect to the separation of superimposed absorption bands. This ability is illustrated by the enlarged FTIR spectra of P12Q and P12 presented in Figure 10. Since the asymmetric and symmetric aromatic (C – D) stretching vibrations occur as very weak absorptions [25] around 2180 and 2080 cm^{-1}, interference with the intensive $\nu(C \equiv N)$ vibration (2228 cm^{-1}) prevents an accurate evaluation.

TABLE IX Assignment and absorption modes of characterstic sequential vibrational modes[a] of selectively deuterated cyanoazobenzene SCLC polyesters

Polyester	*aliphatic main-chain spacer*		*diol unit*		*aliphatic side-chain spacer*				*azobenzene chromophore*		*ester*	*ether*
	$\nu_{as}(CD)_2$	$\nu_s(CD)_2$	$\nu_{as}(CD)_2$	$\nu_s(CD)_2$	$\nu_{as}(CD)_2$	$\nu_s(CD)_2$	$\nu_{as}(CH)_2$	$\nu_s(CH)_2$	$\nu(\mathrm{C}\equiv\mathrm{N})$	$\nu(\mathrm{C}=\mathrm{C})$	$\nu(\mathrm{C}=\mathrm{O})$	$\nu_{as}(\mathrm{C}-\mathrm{O}-\mathrm{Ar})$
P12Z	2195	2091							2228	1601	1733	1255
P12XZ							2938	2861	2228	1601	1732	1255
P12X			2176	2120					2228	1601	1731	1255
P12Y					2200	2098			2228	1601	1734	1265
P4Z	2175	2115							2228	1601	1733	1255
P4XZ							2935	2861	2228	1601	1732	1256
P4X			2175	2121					2228	1601	1734	1256
P4Y					2195	2091			2228	1601	1735	1264

[a] Vibration frequencies in cm^{-1}.

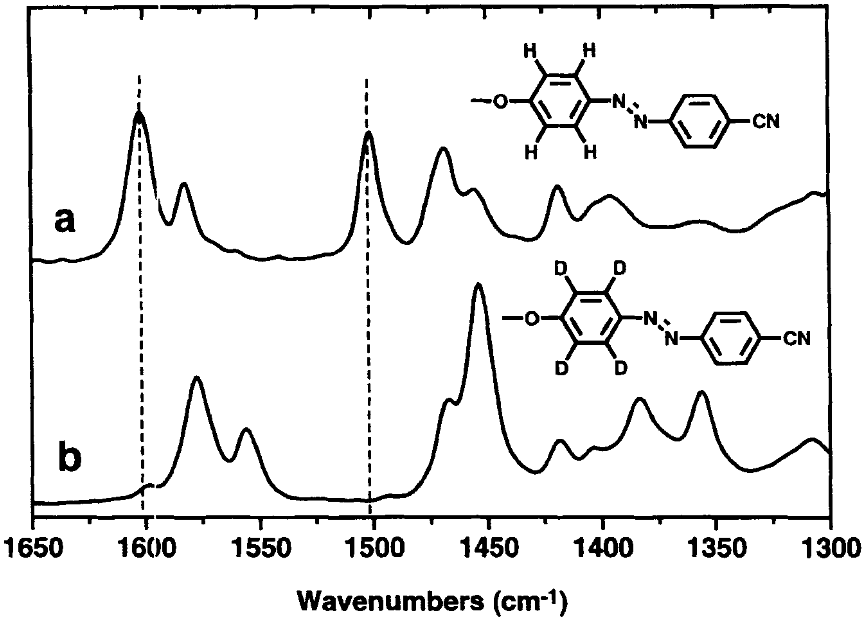


FIGURE 10 Partial FTIR spectra of polyesters P12 (a) and P12Q (b) (film on KBr).

However, as indicated in Figure 10 (---), deuterium exchange in the aromatic ring next to the hexyl spacer causes a shift of the the conjugated aromatic ring vibrations ($1601 + 1582\,\mathrm{cm}^{-1}$, $1501\,\mathrm{cm}^{-1}$) towards lower wavenumbers ($1577 + 1557\,\mathrm{cm}^{-1}$, $1453\,\mathrm{cm}^{-1}$). Thus, the absorption regions, previously covered by the ring stretching modes are now accessible. Infrared investigations of unsubstituted azobenzene [26] have shown that the $\nu(\mathrm{N=N})$ absorption of the azo group in the *cis* state gives rise to a weak absorption around $1511\,\mathrm{cm}^{-1}$. Nevertheless, deuteration of the aromatic ring can be considered as an indirect way to gain detailed information about the population and the lifetime of the *cis* state in azobenzene chromophores.

4. CONCLUSIONS

The applied transesterification procedure enables the preparation of selectively deuterated cyanoazobenzene SCLC polyesters with both short and long main-chain methylene segments in a large molecular mass range. Detailed NMR spectroscopic investigations have shown that the procedure normally preserves the deuterium content from the proper precursor or diol with the only exception of minor deuterium loss in the labile α-positions next to carbonyl. The thorough thermal characterizations have demonstrated that even a large deuterium exchange only has a relatively small influence on phase transition temperatures of a particular polyester structure. On the other hand, the general form of the thermograms and the transition enthalpies, seem to be vertically insensitive to position and degree of deuterium exchange in comparison to non-deuterated analogues. In contrast, strong indications are provided that in modeling work molecular masses should preferably be comparble in order to avoid significantly different thermal behaviour. Low molecular mass samples should be avoided.

Large infrared spectroscopic deuterium isotope effects have been observed and assessed. These can be exploited as addressable and unequivocal molecular probes. If fact, the correct combination of selective deuteration allows in-depth and time or temperature dependent infrared dichroic analysis of all the significant segments of these polyester architectures. The present deuterium labeling also appears attractive for solid state NMR and small-angle neutron scattering studies of aligned segments.

Investigations of the segmental orientation in thin films of these deuterated SCLC polyesters induced by laser light irradiation have been performed with polarized FTIR spectroscopy [27].

Acknowledgement

C. K. and S. H. (Risø National Laboratory) gratefully acknowledge the financial support for this research from The Danish Polymer Centre supported by the Danish Materials Technology Development Programme (MUP 2). C.H., H.W.S. (University of Essen) and F.A. (CNR) extend their thanks to the Brite/EuRam Programme under contract BRE2.CT93.0449.

References

[1] H. Rau, Photochemistry and Photophysics (CRC Press, Inc., Boca Raton, Florida, 1990), Vol. II, Chap. 4, p. 119.

[2] C. B. McArdle, Side Chain Liquid Crystal Polymers (Blackie and Son Ltd., Glasgow, U.K., 1989), Chap. 13, pp. 357–394, and cited literature.

[3] S. Xie, A. Natansohn and P. Rochon, *Chem. Mat.*, **5**, 403 (1993).

[4] S. Hvilsted, F. Andruzzi, C. Kulinna, H. W. Siesler and P. S. Ramanujam, *Macromolecules*, **28**, 2172 (1995).

[5] S. Hvilsted, F. Andruzzi and P. S. Ramanujam, *Opt. Lett.*, **17**, 1234 (1992).

[6] P. S. Ramanujam, S. Hvilsted and F. Andruzzi, *Appl. Phys. Lett.*, **62**, 1041 (1993).

[7] P. S. Ramanujam, S. Hvilsted, F. Andruzzi, C. Kulinna and H. W. Siesler, *Organic Thin Films for Photonic Applications* (Technical Digest Series Vol. 17, Optical Society of America: Washington D.C., 1993), p. 244.

[8] P. S. Ramanujam, S. Hvilsted and F. Andruzzi, *Optical Review*, **1**, 30 (1994).

[9] I. Zebger, C. Kulinna, H. W. Siesler, F. Andruzzi, M. Pedersen, P. S. Ramanujam and S. Hvilsted, *Macromol. Symp.*, **94**, 159 (1995).

[10] S. Hvilsted, M. Pedersen, N. C. R. Holme and P. S. Ramanujam, *Polymer Preprints*, **39**(2), (1998) in press.

[11] C. Kulinna, I. Zebger, S. Hvilsted, P. S. Ramanujam and H. W. Siesler, *Macromol. Symp.*, **83**, 169 (1994).

[12] P. S. Ramanujam, N. C. R. Holme and S. Hvilsted, *Appl. Phys. Lett.*, **68**, 1329 (1996).

[13] H. W. Spiess, *J. Chem. Phys.*, **72**, 6755 (1980).

[14] H. W. Spiess, *Pure and Appl. Chem.*, **57**, 1617 (1985).

[15] C. Hendann, H. W. Siesler, F. Andruzzi, C. Kulinna and S. Hvilsted, *Mol. Cryst. Liq. Cryst.*, submitted.

[16] P. E. Hansen, *Annu. Rep. NMR Spectrosc.*, **15**, 105 (1983).

[17] S. Hvilsted, F. Andruzzi, P. Cerrai and M. Tricoli, *Polymer*, **32**, 127 (1991).

[18] F. Andruzzi and S. Hvilsted, *Polymer*, **32**, 2294 (1991).

[19] A. R. Cooper, Determination of Molecular Weight (John Wiley & Sons, Inc., New York, 1989), p. 1.

[20] P. S. Ramanujam, C. Holme, S. Hvilsted, M. Pedersen, F. Andruzzi, M. Paci, E. L. Tassi, P. L. Magagnini, U. Hoffman, I. Zebger and H. W. Siesler, *Polym. Adv. Techn.*, **7**, 768 (1996).

[21] E. L. Tassi, M. Paci and P. Magagnini, *Mol. Cryst. Liq. Cryst.*, **266**, 135 (1995).

[22] H. Menzel, *Nach. Chem. Tech. Lab.*, **39**, 636 (1991).

[23] H. Günther, NMR Spectroscopy (John Wiley & Sons, New York, 1980), p. 171.

[24] C. Kulinna, Characterization of the Orientational Behaviour of Liquid-Crystalline Side-Chain Polymers by Fourier-Transform Infrared Spectroscopy (Dr. Jörgen Ebert Verlag, Leverkusen, Germany, 1994).

[25] D. O. Hummel and F. Scholl, Atlas der Polymer- und Kunststoffanalyse (Carl Hanser Verlag, München, 1988), Vol. 2, Part b/I Text, p. 401.

[26] R. Kübler, W. Lüttke and S. Weckherlin, *Z. Elektrochem.*, **54**, 650 (1960).

[27] C. Kulinna, S. Hvilsted, C. Hendann, H. W. Siesler and P. S. Ramanujam, *Macromolecules*, **31**, 2141 (1998).