Macromol. Symp. 137, 115–127 (1999)

Influence of the Substituent on Azobenzene Side-chain Polyester Optical Storage Materials

Marianne Pedersen, Søren Hvilsted*, Niels C.R. Holme, P.S. Ramanujam

Risø National Laboratory, DK-4000 Roskilde, Denmark

SUMMARY: A number of poly(1,3-propylenetetradecanedioates) or poly(1,3-propyleneadipates) with pendant *p*-substitued azobenzenes linked through a hexylene spacer in the 2-position are prepared. The substituents comprise: cyano, nitro, methoxy, hydrogen, methyl, n-butyl, phenyl, fluoro, trifluoromethyl, chloro, and bromo. ^{13}C NMR spectroscopic and molecular mass investigations substantiate good film forming characteristics. The optical storage performance of thin polyester films are investigated through polarization holography. The resulting diffraction efficiency is mapped and discussed as a function of irradiation power and exposure time. Polytetradecanedioates with cyano-, nitro-, methyl-, fluoro-, or trifluoromethyl-azobenzene reach more than 50% diffraction efficiency. Investigations of anisotropy induced at different temperatures reveal that the polyesters are only photosensitive in a narrow temperature range around T_g.

Introduction

Azobenzene polymers, in particular side-chain modified, have been intensively researched as potential optical storage materials and constantly provide new challenges. The number of potential azobenzene side-chain polymer systems is also on the increase. However, few systematic investigations on the influence of the azobenzene substituent in a particular polymer architecture have been undertaken. Obviously, a particular substituent directly influences the dipole strength resulting from the donor-acceptor properties of the generated azobenzene chromophore. On the other hand, do geometric factors such as substituent symmetry or steric hindrance play a role in optical storage? Recently, several groups[1-4)] observed modulated surface profiles on thin azobenzene films resulting from the interference of two laser beams. What role does the substituent play for surface relief? We present here our initial investigations on a considerable range of new azobenzene chromophores incorporated into a flexible polyester architecture[5)] for holographic storage. In addition to the most commonly investigated substituents cyano and nitro, we have inserted the following substituents: methoxy, hydrogen, methyl, n-butyl, phenyl, fluoro, trifluoromethyl, chloro, bromo.

CCC 1022-1360/98/$ 17.50

Experimental

Materials

Monomers: The substituent was introduced from the corresponding *p*-aniline, that was conventionally diazotized and coupled with phenol. The resulting azo phenols were then reacted under basic conditions with 2-methyl-2-phenyl-5-(6-bromohexyl)-1,3-dioxane6). Finally acidic alcoholysis furnished the series of 2-substituted 1,3-propanediols, which are either crystalline or liquid crystalline materials7).

Polyesters: The polyesters were prepared in a base catalyzed transesterification of equimolar amounts of either diphenyl tetradecanedioate or adipate and a diol in the melt under vacuum at elevated temperature.[5] Some copolyesters with different mixtures of diols in the feed were additionally prepared. The crude polyesters were dissolved in benzene and after centrifugation precipitated in a tenfold excess of methanol. After a further reprecipitation from benzene the polyesters were filtered off and dried under vacuum at room temperature.

Films: Polyester materials were spin coated from chloroform solutions onto glass substrates normally resulting in ~ 2-4 μm thick layers as determined by a Dektak 3030 profiler.

Analyses

^{13}C NMR spectroscopy: ^{13}C NMR experiments were performed on a Bruker Avance DPX 250 NMR spectrometer. Proton decoupled spectra of the polyesters were recorded employing 20-30 % (w/v) $CDCl_3$ solutions in 5 mm i.d. tubes at 300 K and accumulation of 2000 scans. Chemical shifts are referred to the central resonance of $C\underline{D}Cl_3$ (76.90 ppm from tetramethylsilane (TMS)).

Size exclusion chromatography (SEC): The SEC analysis (in THF) was performed by use of a viscometric detector or a low-angle laser light scattering (LALLS) detector. Calibration of the former detector was based on narrow molecular mass PS standards and employing the TriSEC™ Software.

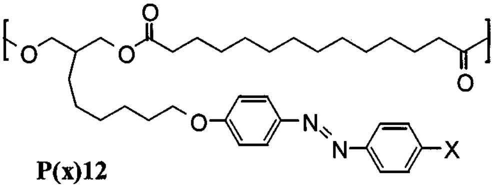
Optical investigations

Holography: Diffraction gratings were fabricated in a conventional two-beam set-up employing the 488 nm light of an Argon ion laser of different intensities (50-100 mW). Suitably arranged quarter wave plates provided orthogonally circularly polarized light made to overlap on ~ 7 mm^2 spot on the film8). A photodetector coupled to a data acquisition system recorded simultaneously the power of the first order diffracted beam of a (4.52 mW) circularly polarized HeNe laser illuminating the film from the back side. All experiments were conducted at ambient temperature.

Measurements of anisotropy: Anisotropy induced in films mounted on a Peltier element (providing sample temperature control) by linearly polarized light from an Argon ion laser at 488 nm (800 mW/cm^2) was probed by a 3 mW HeNe laser polarized 45° to that of the Argon beam$^{9)}$. The HeNe beam through the film is split into two components by a Wollaston prism with polarization perpendicular ($I_\perp$) and parallel ($I_{||}$), respectively, to the initial polarization. The relative induced phase shift, $\Delta\Phi$, is calculated from the intensities of the two beams: $I_{||}(\Delta\Phi) = I_0\cos^2(\Delta\Phi)$ and $I_\perp(\Delta\Phi) = I_0\sin^2(\Delta\Phi)$, where I_0 is the total transmitted HeNe intensity and $\Delta\Phi = \sin^{-1}((I_\perp/(I_\perp + I_{||}))^{1/2})$. Anisotropy in the films has been investigated as a function of film temperature and intensity of laser light.

Results and Discussion

The polyesters are all either poly(1,3-propylenetetradecanedioates) **(P(x)12)** or poly(1,3-propyleneadipates) **(P(x)4)** where a hexylene flexible spacer in the 2-position of the propylene moiety links the azobenzene to the main chain.



P(x)12

Here **x** indicates the substituent in the *para* position of the terminal phenylene of the azobenzene chromophore.

The recovered polyesters appear as powdered or fibrous materials and are all easily soluble in benzene, toluene, chloroform, or tetrahydrofuran. The polyester colors range from yellow to orange reflecting the absorbance behaviour of the particular substituted azophenoxy chromophore. In general, all polyester UV-VIS spectra display the azobenzene characteristic intense π–π* transition in the range between 348 nm and 377 nm with corresponding $\varepsilon_{max} \sim$ 17.000 - 24.000 l/cm mol in THF. In addition, a much weaker n-π* transition is observed between 425 and 460 nm. The peak absorbance characteristics of all polyesters are collected in Table 1. The position of this absorbance in all instances reflects the electron acceptor character of the particular substituent on the azobenzene chromophore. It is seen that the different polyester backbones have virtually no influence on the absorbance behaviour. It can also be seen that the copolyester maxima quite well mirror the weighted contribution of the different comonomers. The general behaviour is depicted in Fig. 1 for **P(CN)12** where the subsequently employed laser wavelengths are additionally indicated.

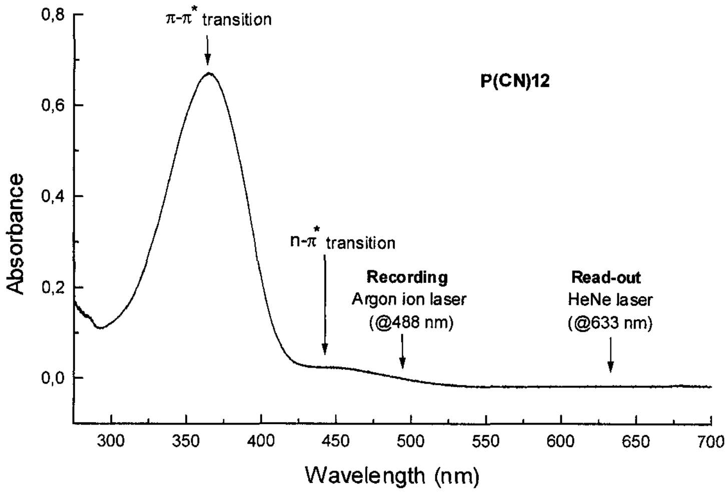


Fig. 1: UV-VIS spectrum of **P(CN)12** in THF, position of recording and probe laser wavelengths are indicated.

Tab. 1. Absorbance data of all polyesters in THF

Substituent (**x**)	**P(x)12**		**P(x)4**	
	λ_{max} (nm)	$\varepsilon_{max}{}^{a}$ (l/cm mol)	λ_{max} (nm)	$\varepsilon_{max}{}^{a}$ (l/cm mol)
CN	365	20,000	365	19,000
NO_2	377	24,000	375	22,000
OCH_3	358	22,000	357	24,000
H	349	21,000	348	18,000
CH_3	351	20,000	351	21,000
C_4H_9	351	21,000	352	20,000
C_6H_5	364	24,000	363	23,000
F	349	22,000	348	23,000
CF_3	351	18,000	355	19,000
Cl	355	18,000	354	18,000
Br	355	20,000	356	19,000
CN/NO_2,3/1	368	18,000		
CN/NO_2,1/1	370	20,000		
CN/NO_2,1/3	373	22,000		
CN/F,1/1	353	19,000		
NO_2/F,1/1	360	17,000		

[a] ε_{max} is calculated per polyester repeat unit; in case of copolyesters the comonomers are weighted

Tab. 2. Polytetradecanedioate, **P(x)12**, and polyadipate **P(x)4**, molecular masses, degrees of polymerization and intrinsic viscosities obtained by SEC

Polyester	Viscometry					LALLS
	M_n	DP	**M_w**	**M_w/M_n**	$[\eta]_n$	**M_w**
P(CN)12	12,000	20	76,000	6.3	0.28	
P(NO_2)12	13,000	21	46,000	3.6	0.27	
P(OCH_3)12	27,000	44	228,000	8.4	0.67	
P(H)12	14,000	24	40,000	2.9	0.41	
P(CH_3)12	16,000	27	74,000	4.6	0.42	
P(C_4H_9)12	18,000	28	28,000	1.6	0.22	
P(C_6H_5)12	48,000	73	80,000	1.7	0.52	
P(F)12	37,000	62	112,000	3.0	0.48	118,000
P(CF_3)12	33,000	51	83,000	2.5	0.47	88,000
P(Cl)12	7,000	11	12,000	1.7	0.16	
P(Br)12	15,000	23	25,000	1.7	0.20	
P(^{a}CN/NO_2)12	22,000	36	52,000	2.4	0.34	
P(^{b}CN/NO_2)12	38,000	62	95,000	2.5	0.37	
P(^{c}CN/NO_2)12	11,000	18	80,000	7.3	0.21	
P(^{b}CN/F)12	35,000	58	114,000	3.3	0.39	
P(^{b}NO_2/F)12	31,000	31	81,000	2.6	0.31	
P(CN)4	11,000	22	17,000	1.5	0.13	
P(NO_2)4	4,000	8	7,000	1.8	0.09	
P(OCH_3)4	10,000	20	16,000	1.6	0.11	
P(H)4	44,000	92	71,000	1,6	0.31	
P(CH_3)4	34,000	69	55,000	1.6	0.24	
P(C_4H_9)4	41,000	77	117,000	2.9	0.30	
P(C_6H_5)	7,000	13	17,000	2.0	0.11	
P(F)4	47,000	95	73,000	1.6	0.27	
P(CF_3)4	27,000	50	42,000	1.6	0.19	
P(Cl)4	31,000	61	61,000	2.0	0.20	
P(Br)4	35,000	63	62,000	1.8	0.25	

$^{a\text{-}b}$Compositions (molar ratios): ^{a}3:1, ^{b}1:1, ^{c}1:3

The SEC analyses reveal high degrees of polymerization (DP) up to ~ 90 and molecular masses easily around or exceeding 100,000, as seen from Table 2. It is noted that all polyesters are produced as the result of high conversions. Attempts to increase the molecular masses tend to slightly broaden the molecular weight distributions. In fact, the limited thermal stability of the azobenzene side chain should be considered and the final heating of the polyester melt furnishing the high molecular mass materials should be

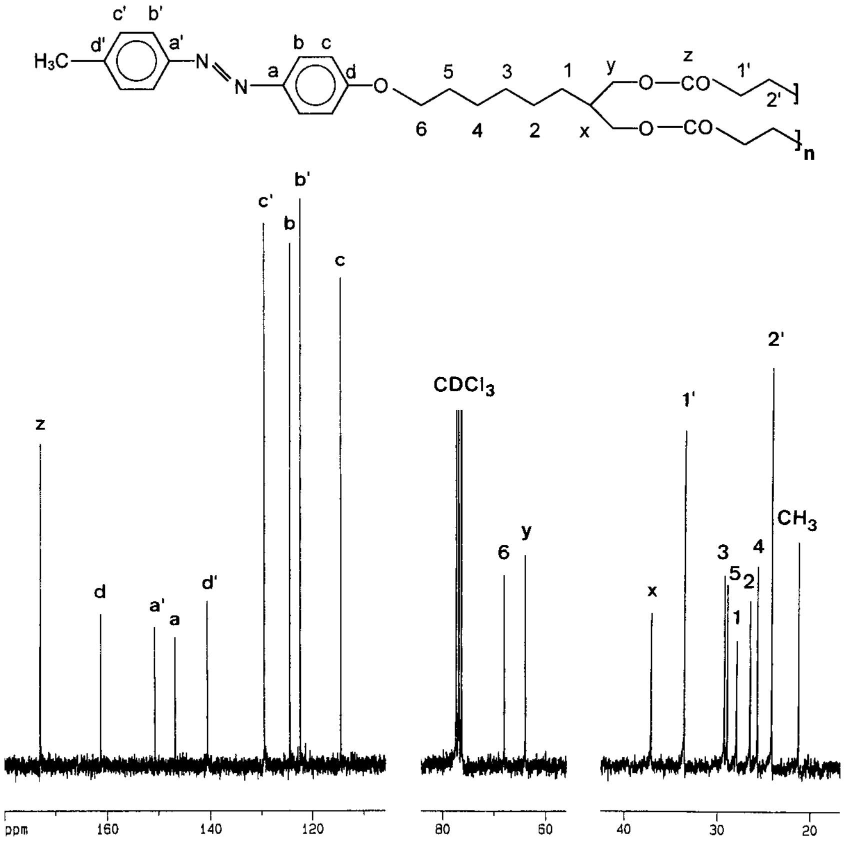
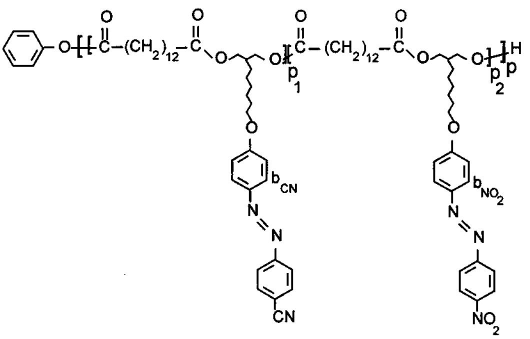


Fig. 2: ^{13}C NMR spectrum of **P(CH$_3$)4** in CDCl$_3$

carefully controlled. Otherwise a cross-linked and insoluble material will emerge. The calculated weight average molecular masses were verified in a couple of instances, (**P(F)12** and **P(CF$_3$)12**), by use of LALLS resulting in a good agreement.

All polyesters were additionally characterized by ^{13}C NMR spectroscopy. The spectra reveal an abundant number of peaks grouped in two broad spectral regions. A low field part contains the ester carbonyl and the aromatic azobenzene carbons and a high field part displays all main- and side-chain carbons in addition to the carbons from several (azobenzene) substituents. The spectrum of **P(CH$_3$)4** is shown in Figure 2 as a representative example of a polyadipate. The eight non-equivalent aromatic carbons were generally assigned by a combination of calculated shift values, published information on some 4'-substituted 4-hydroxyazobenzene precursors and the intensity differences of the tertiary and quaternary



Copolyester	Charged Molar Ratio	b_{CN}		b_{NO2}		Calculated Molar Ratio
	(p_1:p_2)	δ (ppm)	h_{CN} (mm)	δ (ppm)	h_{NO2} (mm)	h_{CN}: h_{NO2}
P(CN/NO$_2$)12	1:3	125.32	35	125.47	102	35:102 ≈ 1:2.9
P(CN/NO$_2$)12	1:1	125.32	72	125.48	73	72:73 ≈ 1:1
P(CN/NO$_2$)12	3:1	125.33	105	125.49	36	105:36 ≈ 2.9:1

Fig. 3: Determination of comonomer content in **P(CN/NO$_2$)** copolyesters

aromatic carbons$^{10)}$. The rather complex aliphatic region were assigned by use of a number of different selectively deuterium labeled diols and **P(CN)4** polyesters^{11,12}. Especially the crowded methylene (C-$\underline{C}H_2$-C) region, 24-29 ppm, and the methoxy (-$\underline{C}H_2$-O) region, 64-68 ppm, greatly benefited from the use of deuterated analogues. It can be seen that both the individual hexamethylene spacer carbons and the non-equivalent main-chain carbons from oxypropylene and adipate segments are identified. Thus every non-equivalent carbon of the **P(CH$_3$)4** repeat unit is unequivocally assigned.

The polytetradecanedioate ^{13}C NMR spectra contained more peaks from the longer methylene main-chain sequence although the central six carbons were normally not resolved^5. Generally, in almost all cases the thorough spectral inspection allowed assignment of the observed resonances to the expected particular polyester repeat unit. This points to polyesters with a regular structure; at least possible structural defects are below the ^{13}C NMR detection limit. In a few (low molecular mass) instances even resonances assignable to end groups could be identified as previously reported$^{5)}$.

^{13}C NMR also proved valuable in the confirmation of the comonomer content of the copolytetradecanedioates. As expected small spectral differences could only be observed either at the side-chain methoxy carbon or some of the aromatic carbons as a result of the

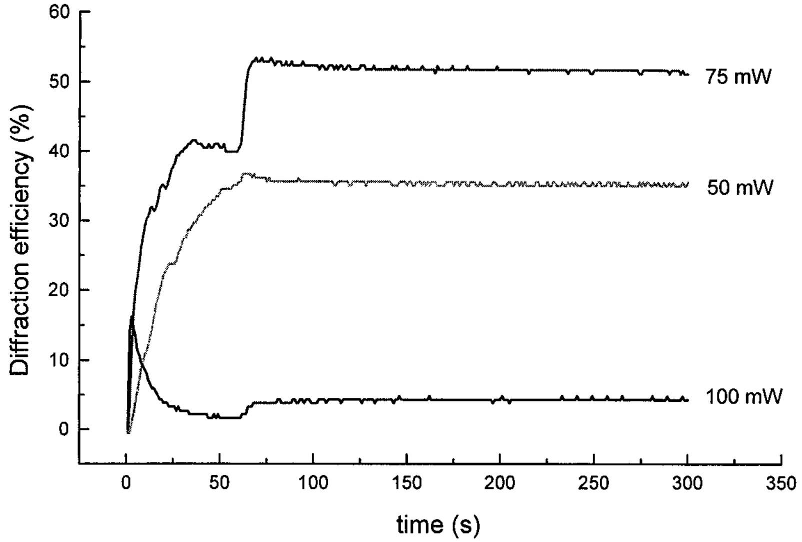


Fig. 4: Diffraction efficiency of a 2.7 µm film of **P(CN/NO$_2$)12** (1:3) exposed 60 s to 50, 75, and 100 mW (@ 488 nm)

different coexisting substituents$^{10)}$. This is demonstrated in Figure 3 that elaborates on the calculation of the comonomer content in the **P(CN/NO$_2$)** copolyesters. The heights, h_{CN} and h_{NO2}, of the carbon resonances are defined as a measure of the amount of each monomer. It should be stressed that the very near identical environment justifies the quantitative use of ^{13}C NMR spectroscopy without the normal carbon relaxation analysis.

In combination, all the observations and referred analytical investigations point to materials consisting of long linear main-chain polyesters with pendant, regularly spaced azobenzene side chains. In addition, all polyesters were investigated by polarizing optical microscopy (POM, crossed polarizers) and DSC. Normally, only a fine grain structure of some randomly distributed birefringent domains were observed by POM. The DSC traces, on the other hand, were complex, revealing one or more, often partly overlapping endothermic peaks$^{10)}$ during the second heating in addition to a T_g that is listed in Table 4. On cooling, normally only one peak was observed corresponding to the transition from the isotropic melt to some aggregated (crystalline) structures.

Tab. 3. First order diffraction efficiency (%) of polyester films

Polyester	Film thickness (μm)	Intensity (mW/cm^2)				
		700	1050			1400
		Irradiation time (s)				
		60	10	30	60	60
P(CN)12	1.8	55	60	61	61	9
P(NO$_2$)12	2.6	5	5	18	35	50
P(OCH$_3$)12	2.9	10	28	49	37	69
P(H)12	3.5	44	28	28	51	46
P(CH$_3$)12	2.7	42	52	45	49	12
P(C$_4$H$_9$)12	4.0	<1	1	2	5	12
P(C$_6$H$_5$)12	3.8	<1	<1	<1	<1	<1
P(F)12	3.3	41	64	67	32	18
P(CF$_3$)12	2.2	48	49	56	62	47
P(Cl)12	2.7	2	1	6	19	18
P(Br)12	2.5	<1	<1	<1	2	4
P(CN/NO$_2$,)12 (3:1)	2.9	52	45	54	56	52
P(CN/NO$_2$,)12 (1:1)	3.3	67	50	54	70	72
P(CN/NO$_2$,)12 (1:3)	2.7	35	39	52	52	5
P(CN/F) (1:1)	2.9	43	52	56	60	5
P(NO$_2$/F) (1:1)	3.3	4	38	40	57	62
P(CN)4	1.2	<1	<1	<1	<1	<1
P(NO$_2$)4	1.6	3	1	7	9	<1
P(OCH$_3$)4	3.1	31	16	16	27	20
P(H)12	3.2	0	0	0	0	0
P(CH$_3$)4	1.9	44	42	45	46	16
P(C$_4$H$_9$)4	2.3	0	0	0	0	0
P(C$_6$H$_5$)4	2.2	<1	<1	<1	<1	<1
P(F)4	3.9	0	0	0	0	0
P(CF$_3$)4	2.4	<1	1	1	1	2
P(Cl)4	3.9	41	26	26	23	1
P(Br)4	2.3	0	0	0	0	0

Polarization holographic investigations on thin unoriented films of the different polyesters were conducted in order to study the optical storage properties. Figure 4 shows the development of the first order diffraction efficiencies (diff. eff.) in a typical experiment with variation of the irradiation power for one of the thin film materials. Table 3 lists the diff. eff. achieved with varying laser irradiation power and exposure times for the polyesters with different substituent on the azobenzene side chain. The small variations in film thickness are not taken into account, in a similar manner the variations in molecular mass and mass distributions are disregarded. It can be seen that several substituents furnish materials with good optical storage properties whereas others appear to be almost ineffective (**P(C_6H_5)12** and **P(Br)12**). Among the well performing materials there also seem to be a nonlinear response. Thus, for some materials, **P(CN)12**, **P(CH_3)12** and **P(F)12**, irradiation with the highest power, 1400 mW/cm^2 for 60 s, clearly has a detrimental effect resulting in lower diff. eff. than either lower power or shorter irradiation time at lower power (Table 3). On the other hand, the opposite effect is observed for **P(NO_2)12** and **P(OCH_3)12** which need the highest power in order to develop the highest diff. eff. Other materials again, perform best at the medium power (1050 mW/cm^2) but after only 10 s irradiation time as in **P(CH_3)12**, or after 30 s as seen in **P(F)12**. Finally, one system, **P(CF_3)12**, appears to behave well almost unaffected by either irradiation power or time. These investigations, however, do not provide any conclusive answers to the questions on the azobenzene dipole strength or the substituent geometry.

The copolyester materials are also interesting, first of all because very high diff. eff. (up to 72%) can be obtained here. Secondly, because to a certain degree some kind of cooperative motion seem to happen especially in the three **P(CN/NO_2)12** materials, where the materials generally respond more efficiently than the **P(NO_2)12** and almost as efficient as the **P(CN)12**. However, the resulting cooperative motion is much smaller than effects recently discussed by Natansohn *et al.*13) in copolymethacrylic materials prepared from azobenzene and polar non-azobenzene comonomers. In this comparison it should nevertheless be stressed that the distances between the side groups in the polyesters are much longer than in copolymethacrylates. On the other hand, very thorough recent investigations by Kulinna *et al.*14) of the laser-induced segmental mobility of this particular polyester architecture have shown that in addition to the cyanoazophenoxy chromophore also the main-chain segments and to a smaller extent the side-chain methylenes are aligned perpendicular to the laser polarization. In other words, a matrix-assisted reorganization is taking place in these materials. It should also be remarked that the observed diff. eff. is due to the sum of the induced optical anisotropy and surface relief. The influence of the different substituents for the surface relief is under investigation.

The polyadipates, on the other hand, appear to be less photosensitive in as much as only a few, **P(OCH_3)4**, **P(CH_3)4**, and **P(Cl)4**, furnish appreciable diff. eff. at these experimental conditions. However, at either lower irradiation power or shorter exposure times most of the polyadipates will also attain considerable diff. eff. In fact, the employed conditions cause melting of many of the adipate films. **P(CN)4** has previously been investigated15) and in particular the biphotonic nature was studied16). Kulinna *et al.*14) also investigated the segmental

Tab. 4. Maximum phase shift of polytetradecanedioates at different film temperatures. The highest value of each polyester is indicated in bold

		Film	Film temperature (°C)						
Polyester	T_g[a]	thickn.	10	20	25	30	35	40	45
	(°C)	(μm)	Maximum phase shift ΔΦ (Rad)						
P(CN)12	24		0.04	0.30	-	**0.50**	0	0	0
P(NO_2)12	41		0	0	0	0	0.04	**0.14**	0
P(OCH_3)12	43		0	0	0	0.06	0.23	**0.37**	0
P(H)12	35		0	0.025	0.05	**0.14**	0	0	0
P(CH_3)12	45		0	0	0.02	0.12	**0.25**	0	0
P(C_6H_5)12	50		0	0	0	0	0	0	0
P(F)12	30		0	0.01	0.08	**0.24**	0.07	0	0
P(CF_3)12	35		0	0	0	0.05	**0.09**	0	0
P(C_4H_9)12	10	3.2	**0.62**	0.32	0	0	0	0	0
P(Cl)12	32	3.5	0	0	0.32	0.57	**0.66**	0	0
P(Br)12	44	3.3	-	0	0	0.28	0.74	**0.80**	0
P([b]CN/NO_2)12	22	4.0	-	0.05	0.14	**0.28**	**0.28**	0	0
P([c]CN/NO_2)12	24	2.5	-	0	0.11	0.22	**0.35**	0.11	0
P([d]CN/NO_2)12	30	3.3	-	0	0.08	0.23	**0.33**	0.05	0
P([c]CN/F)12	24	3.4	-	0.44	1.38	**1.57**	0	0	0
P([c]NO_2/F)12	25	2.6	-	0	0.42	1.03	**1.2**	0	0

[a] From DSC second heating trace.

[b-d]Compositions (molar ratios): [b]3:1, [c]1:1, [d]1:3

motion of **P(CN)4** and found that only the cyanoazophenoxy chromophore and to a smaller extent the side-chain methylenes became aligned but not the main-chain segments. The inclusion of the polyadipates in Table 3 clearly illustrates the difference between the performance of materials with short (polyadipates) and long (polytetradecanedioates) main-chain methylene sequences. At the same time, it stresses the need to search the proper experimental conditions for particular materials.

All the above investigations were performed at ambient temperature. Furthermore, the materials differ in both molecular mass characteristics and thermal behaviour. Consequently, an investigation of the influence of temperature when the anisotropy was induced was undertaken. Table 4 reports the maximum phase shifts obtained on a number of materials at temperatures typically ranging from 10-15 °C below to 0-5 °C above the T_g. In some cases the operational range is very narrow and terminates below T_g. One of the holographic insensitive materials, **P(C_6H_5)12,** is seen to have a relatively high T_g on the order of 50 °C. The other poorly responding materials, **P(Cl)12** and **P(Br)12** have T_g at 32 and 44 °C, respectively. Unfortunately, an absolute comparison of the anisotropy induced between the different substituents is not possible, because the thicknesses of the first eight films have been estimated to lie between 1 and 2 μm. The temperature influence is quite obvious although the lack of sensitivity at a certain temperature at least in the holographic experiment can be somehow compensated by higher laser power or longer irradiation time.

Conclusions

A number of new materials, where differently substituted azobenzene linked through a hexylene spacer to poly(1,3-propylenetetradecanedioate) or poly(1,3-propyleneadipate), has been prepared and investigated for their use as candidates for optical information storage. Due to excellent molecular mass characteristics the materials have very attractive film forming properties. More importantly, in the case of the poly(1,3-propylenetetradecanedioates) many new substituents, such as methyl, hydrogen, methoxy, fluoro, and trifluoromethyl, provide film materials with excellent first order diffraction properties (resulting from polarization holographic experiments) in the experimental range investigated. In some cases, combinations of different substituents both provide the highest achievable diffraction efficiency (> 70 %) and seem to complement the behaviour of a corresponding material based on the single substituent. On the other hand, the initially raised questions on azobenzene dipole strength or substituent shape can not be enlightened by the conducted experiments. The azobenzene substituent seems to strongly influence the particular poly(1,3-propylenetetradecanedioate) material morphology. That is crucial and the temperature range open for inducing the anisotropy (corresponding to the writing process) is quite narrow. Creation of anisotropy is only possible in a narrow temperature range around T_g and seems to be performed most efficiently at T_g or slightly above. In the evaluation of new materials it is therefore important to disclose the material optimum temperature response and not restrict the experiments to room temperature.

Acknowledgements

The Danish Research Academy and Danish Materials Technology Development Program (MUP 2) are thanked for financial support.

References

1) P. Rochon, E. Batalla, A. Natansohn, *Appl. Phys. Lett.* **66**,136 (1995)

2) D.Y. Kim, S.K. Tripathy, L. Li, J. Kumar, *Appl. Phys. Lett.* **66**, 1166 (1995)

3) P.S. Ramanujam, N.C.R. Holme, S. Hvilsted, *Appl. Phys. Lett.* **68**, 1329 (1996)

4) N.C.R. Holme, L. Nikolova, P.S. Ramanujam, S. Hvilsted, *Appl. Phys. Lett.* **70**, 1518 (1997)

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

6) S. Hvilsted, P.S. Ramanujam, *Current Trends Polym. Sci.* **1**, 53 (1996)

7) M. Pedersen, S. Hvilsted, F. Andruzzi, to be published.

8) P.S. Ramanujam, C. Holme, S. Hvilsted, M. Pedersen, F. Andruzzi, M. Paci, E. Tassi, P Magagnini, U. Hoffman, I. Zebger, H.W. Siesler, *Polym. Adv. Technol.* **7**, 768 (1996)

9) N.C.R. Holme, P.S. Ramanujam, S. Hvilsted, *Appl. Opt.* **35**, 4622 (1996)

10) M. Pedersen, *New Azobenzene Side-Chain Polyesters for Optical Information Storage*, Ph.D. Thesis, Technical University of Denmark (1997)

11) C. Hendann, H.W. Siesler, F. Andruzzi, C. Kulinna, S. Hvilsted, *Mol. Cryst. Liq. Cryst* **319**, 207 (1998)

12) C. Kulinna, S. Hvilsted, C. Hendann, H.W. Siesler, F. Andruzzi, *Mol. Cryst. Liq. Cryst.* **319**, 231(1998)

13) A. Natansohn, P. Rochon, X. Meng, C. Barrett, T. Buffeteau, S. Bonenfant, M. Pézolet, *Macromolecules* **31**, 1155 (1998)

14 C. Kulinna, S. Hvilsted, C. Hendann, H.W. Siesler, P.S. Ramanujam, *Macromolecules* **31**, 2141 (1998)

15) P.S. Ramaujam, S. Hvilsted, F. Andruzzi, *Appl. Phys. Lett.* **62**, 1041 (1993)

16) P.S. Ramaujam, S. Hvilsted, I. Zebger, H.W. Siesler, *Macromol.Rapid Commun.* **16**, 455 (1995)