Azo-Group Labelled Polyesters by End-Capping with 2-Oxazoline Derivatives – Photochemical Properties

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Summary: Two azobenzene containing 2-oxazolines were used for labeling of a polyester with carboxylic end groups by the end-capping method. The modification was performed under the conditions of either reactive processing or in a solution. Photochemical activity of the prepared polymers, as well as that of the modifiers was studied. The polymers prepared represent new photosensitive materials that undergo photochemical *trans-cis* isomerizations and reverse *cis-trans* reactions.

Introduction

Azobenzene containing materials represent a very interesting group of compounds with specific properties. Their photoinduced *cis-trans* isomerization reaction has been studied for many years[1,2]. Azo compounds are also known as dyes and pH indicators. More recently, liquid crystalline properties were observed for some derivatives containing azobenzene groups[3]. Furthermore, azobenzenes have been used as nonlinear optical materials or data and energy storage tools[4]. Azo compounds have also been used for photorecording[5]. Useful and special properties are obtained when the azo unit is incorporated into a polymer structure. Polyesters and polyamides containing azo units in the main chain have been prepared[3]. Poly(methacrylate)s[6,7], poly(vinylacylate)s[8] and polyisocyanates[9] containing azo units were prepared as side chain polymers as well. An overview of polymers containing azobenzene structures has recently been published[10].

The reactive modification of polymers represents a modern way for the preparation of functionalized polymers suitable for compatibilization, chain extension, crosslinking, etc11,12). The principle is based on a chemical reaction of a polymer with a modification agent in a processing machine[13].

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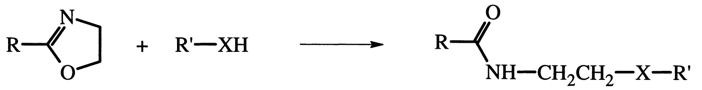
2-Oxazolines are a group of reactive compounds which can react with various functional groups[14] (Equation 1). Reactions are thermally initiated and proceed, depending on reactants and temperature, very fast.



(1)

X=COO, O, S, NH

These reactions provide new perspectives for the use of 2-oxazolines for modification of polymers containing different functional groups in the molecules. Generally, two different alternatives for the modification have to be considered. In the first case, a side chain group is the site of the reaction. In the second case, the matters of the interest are functional end-groups. One type of end-group reactions represents end-capping. This procedure is broadly used to enhance the thermal stability of polyesters. Examples of end capping include the use of epoxides[15,16], isocyanates[17], and 2-oxazolines[18]. Reactions are usually performed under the conditions of reactive processing, e.g. in processing machines at elevated temperature, during a short processing time of usually only a few minutes.

Recently we prepared polyesters labeled with azobenzene containing 2-oxazoline compounds[19]. In this paper studies on their *trans-cis* and *cis-trans* photoisomerizations are presented.

Experimental part

4'-Hydroxy-4-(2-oxazolin-2-yl)azobenzene (1)

1 was prepared from 4-aminobenzoic acid and phenol according to the procedure described elsewhere[19]. M.p. = 236-238 °C.

^{1}H NMR (DMSO-d_6): 4.00 (t, 2H, NCH_2), 4.44 (t, 2H, CH_2O), 6.96 (d, 2H, ar), 7.83 (d, 2H, ar), 7.87 (d, 2H, ar), 8.03 (d, 2H, ar), 10.38 (s, 1H, Ar-OH).

^{13}C NMR (DMSO): 54.64, 67.59, 116.10, 122.27, 125.22, 128.89, 128.92, 145.38, 153.64, 161.53, 162.51.

4'-Allyloxy-4-(2-oxazolin-2-yl)azobenzene (2)

2 was prepared from **1** according to the procedure described elsewere[19]. M.p. = 144-146 °C.

^{1}H-NMR (DMSO-d_6): 4.00 (t, 2H, NCH_2), 4.45 (t, 2H, CH_2O), 4.71 (d, 2H, OCH_2), 5.31 (d, 1H, $\underline{H_2}C=CH_2$-), 5.44 (d, 1H, $\underline{H_2}C=CH_2$-), 6.08 (m, 1H, $H_2C=\underline{CH}$-), 7.17 (d, 2H, ar), 7.90 (d, 2H, ar), 7.92 (d, 2H, ar), 8.05 (d, 2H, ar).

^{13}C-NMR (DMSO-d_6): 54.65, 67.62, 68.70, 115.44, 117.96, 122.42, 124.88, 128.95, 129.20, 133.21, 146.33, 153.52, 161.43, 162.47.

Polyesters

A carboxy terminated liquid crystalline poly(ethylene terephthalate-co-oxybenzoate) (LCP) was used. The preparation of the polymer, its modification under conditions of reactive processing and in a solution were described in the previous paper[19].

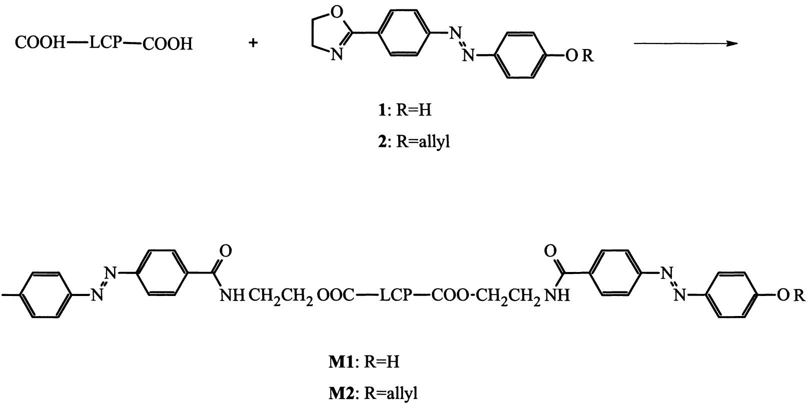
Procedures

^{1}H and ^{13}C NMR spectra were measured with a DRX-500 spectrometer (Bruker) operating at 500.13 MHz for ^{1}H and 125.75 MHz for ^{13}C. The ^{1}H and ^{13}C NMR spectra of the modifiers were measured in DMSO-d_6 at room temperature.

UV spectra were measured with a UV-VIS spectrometer Specord M40 (Carl-Zeiess Jena, Germany). Photoinitiated *trans-cis* isomerization was performed at a 8-samples merry-go-round equipped with a 125 W medium pressure Hg lamp. The light was filtered with an aqueous solution of lead (II) nitrate (1 mol/dm^3) that transmits the light with a wavelength higher than 300 nm and with an interference glass filter transmitting monochromatic light with a wavelength of 366 nm. The reverse *cis-trans* reaction was done in all cases keeping the samples in dark at room temperature. Measurements were done in chloroform and DMSO solutions at a concentration of 5×10^{-5} mol/dm^3.

Results and discussion

A liquid crystalline carboxy terminated poly(ethylene terephthalate-co-oxybenzoate) was converted with two different 2-oxazoline group containing azobenzene compounds, 4'-hydroxy-4-(2-oxazolin-2-yl)azobenzene (**1**) and 4'-allyloxy-4-(2-oxazolin-2-yl)azobenzene (**2**) as shown in Scheme 1. Details concerning this modification reaction were described elsewere[19].



1: R=H

2: R=allyl

M1: R=H

M2: R=allyl

Scheme 1

The photochemical behavior of the modifiers and the labeled polymers **M1** and **M2** was studied. It is well known that under "normal" conditions azobenzene compounds adopt preferably the more stable *trans* form[1]. The spectral characteristics of the modifiers and the polymers are given in the Table 1. The measurements were carried out at room temperature in dimethylsulphoxide or $CHCl_3$. Both, the low mass compounds and the labeled polymers exhibit a strong absorption band between 355 and 365 nm representing a π-π^* transition of the azo group and a less intensive band at 445-455 nm associated to a n-π^* transition of the azo group. Additionally, a band with a fine structure with maxima at 277 and 287 nm was found for **2**. In the UV spectra of **M1** and **M2** the absorptions of the azo groups are overlapped with absorptions of the polyester, however, the 362 nm band is clearly visible.

Photoinduced *trans-cis* isomerizations were done by irradiation at 366 nm, a wavelength close to the π-π^* excitation maximum of the *trans* form. In Figure 1 it is seen that during irradiation of compound **2** the absorbance of the band at 366 nm decreases whereas the band at 445 nm representing the n-π^* transition increases. Two isosbestic points at 318 and 432 nm were observed confirming the simple course of isomerization without side reactions or decomposition. In the case of compound **1**, isomerization could not be observed in DMSO and methanol. This is the reason why **1** was treated in non-polar $CHCl_3$ solution. Formation of hydrogen bonds connected with deactivation of the isomerization reaction has been observed for 2-hydroxyazobenzenes[23] in non-polar solvents. In our case we suppose that formation of intermolecular hydrogen bonds between the phenolic and the azo groups in polar solvents is responsible for this effect. In the chloroform solution, isosbestic points were observed at 313 and 421 nm.

Table 1. Spectral characteristics of 4'-hydroxy-4-(2-oxazolin-2-yl)azobenzene (**1**), 4'-allyloxy-4-(2-oxazolin-2-yl)azobenzene (**2**) and the modified LC polyesters **M1** and **M2**

Compound	λ_{max}	log ε_{max}	λ_{max}	log ε_{max}	λ_{max}	log ε_{max}	λ_{max}	log ε_{max}
	nm		nm		nm		nm	
1[a]	-	-	-	-	363	4.55	450	3.30
2[b]	277	4.23	287	4.26	366	4.36	445	3.40
M1[b]	-	-	-	-	359	4.18	450	3.41
M2[b]	-	-	-	-	362	4.40	455	3.68

[a]measured in $CHCl_3$
[b]measured in DMSO

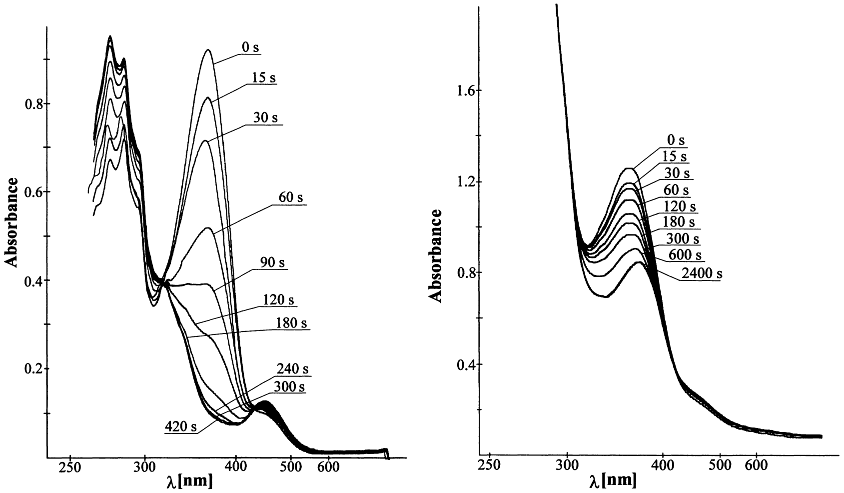


Figure 1. Spectral changes during *trans-cis* photoisomerization induced by 366 nm light for 4'-allyloxy-4-(2-oxazolin-2-yl)azobenzene **2** (left) and polyester **M2** (right) in DMSO at a concentration of 5 x 10^{-5} mol/dm^3

Spectral changes during the *trans-cis* isomerization of **M2** are partly overlapped with the spectrum of the parent polyester (Figure 1, right). However, the development of the absorption band with a maximum at 362 nm enables to evaluate this process. For the n-π* transition, a shoulder appears around 450 nm. The isosbestic point was detected at 420 nm. The decrease in the absorbance of **M1** at 359 nm is similar to that of **M2**. The isosbestic point in **M1** was detected at around 420 nm.

Time dependencies of the absorption maxima are shown in the Figure 2. It is seen that the decrease of the absorbance has hyperbolic shape. For **2**, we can expect nearly quantitative conversion from the *trans* to the *cis* form. This is in accordance with results of Ichimura[7] who obtained a ratio of *cis/trans* izomers equal 0.99 in THF solution and 0.98 in a spin coated film of polymethacrylates functionalized with alkoxy-substituted azobenzene groups. Comparison of the starting absorbance of **1** with the final value after leveling off allows to approximate the final value of the *cis/trans* ratio tó be 0.5. This is the evidence that the isomerization of hydroxy-containing azobenzenes is restricted even in non-polar solvents. Because of overlapping with the spectrum of the parent polymer it is impossible to determine the degree of isomerization for the modified polyesters **M1** and **M2**. However, we can conclude that, also in this case, transformation of the phenolic group containing **M1** is much lower than that of the allyloxy derivative **M2**.

In first order coordinates (Figure 3), the time dependencies of intensities of the absorption maxima of **1** and **2** are straight lines . However, deviations from straight lines were observed for the labeled polyesters **M1** and **M2**. For these samples the rate constants were calculated from the slopes at the beginning of the irradiation. The calculated values are given in the Table 2.

The rate constants show that the allylated modifier **2** is much more sensitive for isomerization in comparison with **1**. This conclusion is also valid for the modified polymers **M1** and **M2**. Again, it might be the consequence of the presence of hydrogen bonds between the phenolic and azo groups. Deviations from the straight line have not been observed in solution[7,24] for side chain azobenzene containing polymethacrylates. On the other hand, also some effect related to the presence of polymer may lead to deviations from the straight line for spin coated films. In the solid phase also the rate of transformation was slower[7].

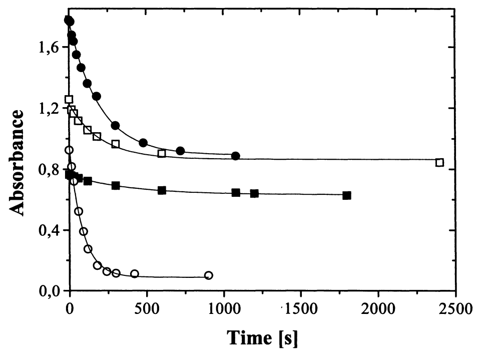


Figure 2. Time dependence of the absorbances of the π-π^* transition during *trans-cis* photoisomerization induced by 366 nm light for 4'-hydroxy-4-(2-oxazolin-2-yl)azobenzene 1 (●), 4'-allyloxy-4-(2-oxazolin-2-yl)azobenzene 2 (○), labelled polyester M1 (■) and labelled polyester M2 (□) in DMSO at a concentration of $5x10^{-5}$ mol/dm^3

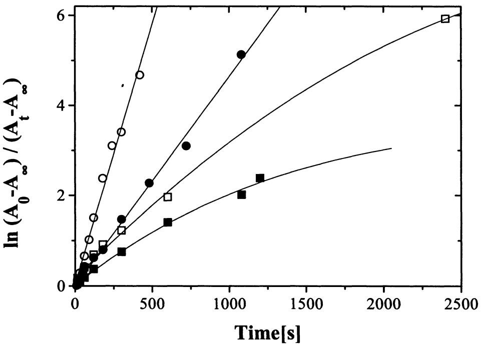


Figure 3. The dependence of the absorbance on irradiation time during *trans-cis* photoisomerization induced by 366 nm light for 4'-hydroxy-4-(2-oxazolin-2-yl)azobenzene **1** (●), 4'-allyloxy-4-(2-oxazolin-2-yl)azobenzene 2 (○), labelled polyester **M1** (■) and labelled polyester **M2** (□) in DMSO at a concentration of 5 x 10^{-5} mol/dm^3 in first order coordinates

When the polarity and the chain flexibility of polymethacrylates is compared with these of the polyesters it seems to be reasonable to assume that the deviations from the straight lines for **M1** and **M2** are based on a polymer effect. This includes polarity and rigidity of the respective polymers. Additionally, absorbance of the polymer (see Figure 2) could also be taken into consideration.

Table 2. *Trans-cis* and reverse *cis-trans* isomerization of 4'-hydroxy-4-(2-oxazolin-2-yl)azobenzene (**1**), 4'-allyloxy-4-(2-oxazolin-2-yl)azobenzene (**2**) and the modified polyesters **M1** and **M2**

Compound	Solvent	$k_{trans\text{-}cis} \cdot 10^3$	$k_{cis\text{-}trans} \cdot 10^5$
		s^{-1}	s^{-1}
1	chloroform	4.7	-
2	DMSO	16	10.6
M1	DMSO	3.2	-
M2	DMSO	5.1	1.22

The reverse *cis-trans* isomerization is also a well-known reaction which can be initiated either in dark as a thermal reaction or by visible light[1,2]. We studied this dark reaction with compounds **2** and **M2** (Figure 4). The reaction is very slow at room temperature in comparison with the reverse photochemical reaction. The equilibrium is reached in about 10 hours for **2** and 30 hours for polymer **M2**. For both samples the final values of absorbance are the same as for unirradiated samples. It means that the process of isomerization is completely reversible. In first order coordinates (Figure 5) the low mass sample **2** provides a straight line from which the rate constant of *cis-trans* isomerization was calculated. Also in this case the polymer sample does not provide linear relationship. After a slow start the reaction is accelerated. The rate constant for **M2** was calculated from the slope at the beginning of the reaction. Data are collected in Table 2.

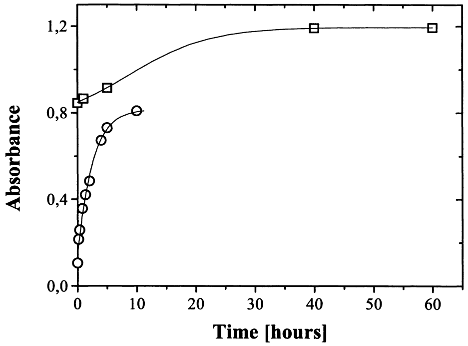


Figure 4. Time dependence of the absorbances during *cis-trans* thermal isomerization in dark at room temperature for 4'-allyloxy-4-(2-oxazolin-2-yl)azobenzene **2** (○) and the labelled polyester **M2** (□) in DMSO at a concentration of 5×10^{-5} mol/dm^3

The data in Table 2 indicate that the spontaneous *cis-trans* isomerization of **2** and **M2** in dark is about two orders slower than the *trans-cis* reaction initiated by UV light. Also in this case, the rate of isomerization of the low mass compound **2** is about nine times faster than that of the labelled polymer **M2**.

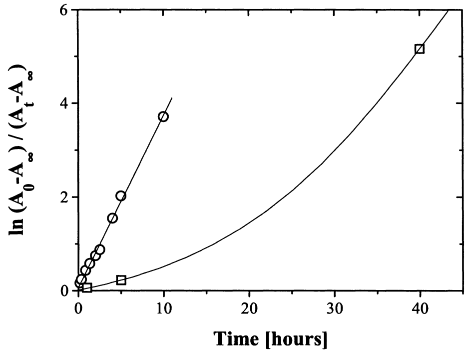


Figure 5. The dependence of the absorbance on time during *cis-trans* thermal isomerization in dark at room temperature for 4'-allyloxy-4-(2-oxazolin-2-yl)azobenzene **2** (○) and the labeled polyester **M2** (☐) in DMSO at a concentration of 5 x 10^{-5} mol/dm^3 in first order coordinates

Conclusions

End-capping of a carboxy group terminated LCP with azo group containing 2-oxazoline derivatives provides a new route for labeling of polymers. The polymers obtained by a modification reaction represent new photosensitive materials that undergo photochemical *trans-cis* isomerizations and reverse *cis-trans* reactions. *Trans-cis* isomerization of the low mass labels proceeds according to a first order reaction. The isomerization of labeled polyesters was influenced by a polymer effect. The reaction is completely reversible thus acting as a ”switch effect” between the *cis-trans* and *trans-cis* isomeric forms. This “switch effect” might be of interest for some industrial applications and for studying chain end mobility in bulk.

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