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Azo-Group Labelled Polyesters by End-Capping with 2-Oxazoline Derivatives - Preparation

Jozef Lustoň[a*], Juraj Kronek[a], Frank Böhme[b], Hartmut Komber[b]

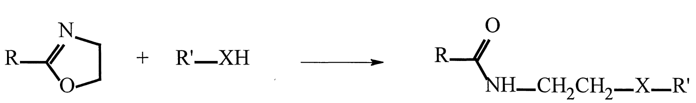
[a]Polymer Institute, Slovak Academy of Sciences, 84236 Bratislava, Slovakia,
e-mail: upollust@savba.sk
[b]Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany

SUMMARY: Two azobenzene containing 2-oxazolines were used for labelling of polyesters with carboxylic end groups by the end-capping method. The reaction proceeded under the conditions of reactive processing, and in a solution. High conversions in melt were achieved in several minutes. The coupling of the modifiers was proved by NMR spectroscopy.

Introduction

The reactive modification of polymers represents a modern way for the preparation of functionalized polymers suitable for compatibilization, chain extension, crosslinking, etc[1, 2)]. The first attempts of reactive processing led to special applications, e. g. production of degraded polypropylene, later on, the reactive processing technology was found to be a suitable method to produce novel materials based on commodity polymers. The principle is based on a chemical reaction of a polymer with a modification agent in a processing machine[3)].

2-Oxazolines are reactive compounds which can react with various functional groups[4)] (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 possibilities for the modification have to be regarded. In the first case, a side chain group is

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the site of the reaction. In the second case, the matters of interest are functional end-groups. Side chain groups have been used to convert poly(ethene-*co*-(meth)acrylic acid) to novel ethene copolymers[5-7]. The terpolymer poly(ethylene-co-butyl acrylate-co-acrylic acid) was modified by 2-(4-allyloxyphenyl)-2-oxazoline to give a polymer containing reactive unsaturated groups suitable for crosslinking or further reactions[8]. Another area of exploitation is the crosslinking of copolymers containing 2-oxazoline and carboxylic groups[9] and the compatibilization of immiscible polymers or copolymers containing 2-oxazoline and carboxylic acid groups by reactive processing[10].

One type of end-group reactions represent end-capping. This procedure was widely used to enhance thermal stability of polyesters. End-capping agents are usually monofunctional compounds. Examples of end capping include the use of epoxides [11,12], isocyanates[13], and 2-oxazolines[14]. Reactions are usually performed under the conditions of reactive processing, e.g. in processing machines at elevated temperature, during a short processing time of only a few minutes. Recently, a carboxylic end-group containing polyester[15] was modified by 2-(4-allyloxyphenyl)-2-oxazoline to give a polymer containing reactive unsaturated end-groups suitable for crosslinking or further reactions.

The reaction of functional end-groups of a polymer with bis(2-oxazoline)s has been applied for coupling or chain extension of polyesters with carboxylic end-groups[16-19]. Bis(2-oxazolines) were also used for the polymer synthesis[20-22]. Segmented polymers are available by conversion of 2-oxazoline terminated and carboxylic acid terminated polymers[23,24].

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[25]. Azo compounds are also known as dyes and pH indicators. More recently, liquid crystalline properties were observed for some derivatives containing azobenzene groups[26]. Furthermore, azobenzenes have been used as nonlinear optical materials or data and energy storage tools[27]. Azo compounds have also been used for photorecording[28]. Useful and special properties are obtained when the azo unit is incorporated into a polymer structure. Polyesters[26] and polyamides[26] containing azo units in the main chain have been prepared. Poly(methacrylate)s[29,30], poly(vinylacylate)s[31] and polyisocyanates[32] containing azo units were prepared as side chain polymers as well. An overview of polymers containing azobenzene structures has been published recently[33)].

This paper describes the modification of carboxy terminated polyesters with azobenzene compounds containing 2-oxazolines under the conditions of reactive processing and in solution.

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[34)]. M.p. = 236-238 °C.

^1H 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)

In 80 mL aqueous NaOH tetrabutylammonium bromide (0.64 g, 0.002 mol) and **1** (5.35 g, 0.02 mol) were dissolved. A solution of allyl bromide (2.2 ml, 0.025 mol) in chloroform (100 mL) was added and the reaction mixture was stirred 5 hours at ambient temperature. After separation, the organic layer was washed with aqueous NaOH, dried over Na_2SO_4, and the solvent was removed under vacuum. An orange solid was obtained and recrystallized from ethyl acetate. Orange crystals (4.9 g, 80 %) with a melting point of 144-146 °C were obtained.

^1H 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

The carboxy terminated liquid crystalline polyester (LCP) (copolyester PET/PHB=40/60) was prepared by transesterification reaction of PET with p-acetoxybenzoic acid according to

Jackson and Kuhfuss[35)]. The inherent viscosity of the LCP measured in a mixture of phenol/tetrachloroethan = 1:1 at 20 °C was 0.296 what corresponds to M_n= 4000. The number average molecular weight of the polymer determined by titration with a butanolic solution of KOH in a mixture o-cresol / $CHCl_3$ = 1:1 was 4110. It also means that the LCP was carboxy terminated on both sides. The content of carboxylic end groups was 4.86×10^{-4} mol/g.

The poly(ethylene terephthalate) (PET) used was also carboxy terminated on both chain ends. Its number average molecular weight was M_n = 3600 Da. The content of carboxylic end groups was 5.08×10^{-4} mol/g.

Processing

Mixing was carried out in double-screw microcompounder (Daca Instruments). For the modification, 4 g of the polymer were charged into the preheated mixing head. After heating to the processing temperature of 240 °C, the respective amount of the modifier was added and the mixture was processed at 60 rpm for the desired time. For the investigation of the the temperature dependence of the modification reaction, the procedures were done also at 180 °C, 195 °C and 220 °C. The content of the remaining carboxylic groups was determined by titration.

For the solution modifications, the polymer (1.5 g) was dissolved under stirring at 200 °C in 1-chloronaphthalene (5 ml) under argon atmosphere. The modifier (0.65 mmol, molar ratio 1:1) was added to the solution in one portion. The reaction mixture was stirred for 6 hours and then precipitated in ethanol (50 ml). The modified polymer was extracted with ethanol (50 ml, 3x) and dried in a vacuum oven at 90 °C for 8 hours. The content of the remaining carboxylic groups was determined by titration.

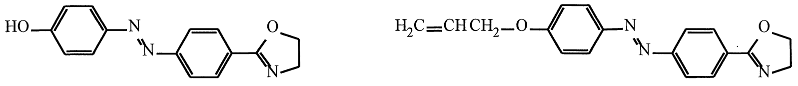
Procedures

^{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. The ^{1}H and ^{13}C NMR spectra of the modifier and the modified polymer were measured in a mixture of hexafluoroisopropanol/$CDCl_3$ (1:1 v/v). The deuterated solvents were used as lock and internal standards.

The determination of carboxylic groups was performed by titration. The polymer samples (0.7 g) were dissolved in a mixture o-cresol/$CHCl_3$ = 7:3 at 60 °C and the hot solutions were titrated with 0.1 N solution of KOH in butanol with a potentiometrical detection of the equivalence point.

Results and discussion

Two different 2-oxazoline group containing azobenzene compounds were used for modification of liquid crystalline polyester. 4'-Hydroxy-4-(2-oxazolin-2-yl) azobenzene (**1**) was prepared from 4-aminobenzoic acid by coupling reaction with phenol[34]. 4'-Allyloxy-4-(2-oxazolin-2-yl)azobenzene (**2**) was prepared by the reaction of **1** with allyl bromide under the conditions of phase transfer catalysis (PTC). The structures of **1** and **2** are shown in the Figure 1.



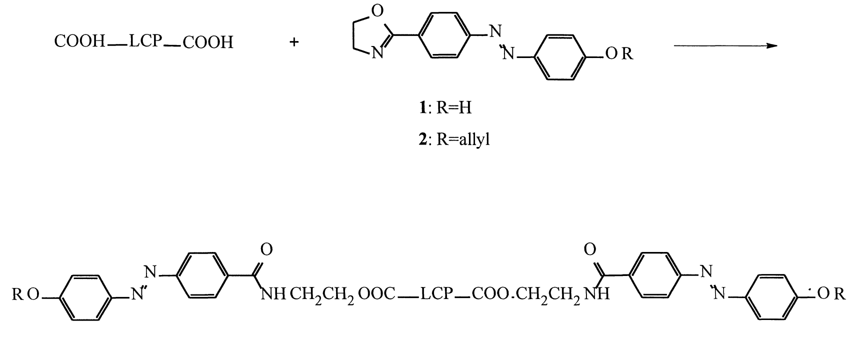
1 **2**

Figure 1

It is seen that both modifiers are in fact three functional compounds. They contain a reactive 2-oxazoline ring for bonding to the polymer chain ends, an azobenzene dye part for labelling of a polymer, and a free phenolic group in the compound **1** and a thermally stable unsaturated allyl group in the compound **2**. Both functional groups are available for further use.

The liquid crystalline poly(ethylene terephthalate-*co*-oxybenzoate) prepared according to Jackson and Kuhfuss[35] was used for end capping with functional azobenzene labels. The polymer contains carboxylic end groups on both sides of the chain. The same polymer was also converted with 2-(4-allyloxyphenyl)-2-oxazoline[15]. For the modification in solution also PET with M_n corresponding to that of the LCP was used for comparison.

The used method of polymer labelling is based on the known reaction of the 2-oxazoline ring with carboxylic acids (Eq. 1) which proceeds by a nucleophilic attack of a carboxylate upon the 2-oxazoline ring in 5 position[36] with the formation of an esteramide structure. The reaction has found applications for reactive blending of polymers bearing 2-oxazoline and carboxylic acid groups[10]. The reaction scheme for this particular case is shown in Scheme 1.



1: R=H
2: R=allyl

M1: R=H
M2: R=allyl

Scheme 1

To ensure easier melting of the modifier **1** and for better homogenization of the reaction mixture, the processing temperature was slightly increased over the melting point of **1,** to 240 °C. The results are summarized in Table 1. As one can see, 14 % conversion was reached after 2 min processing (Entry 1). The relatively small conversion at the beginning can be explained by the effect of poor distribution of the modifier **1**. Otherwise, the reaction was fast enough for reactive processing, and a maximal conversion was achieved within five to ten minutes (Entries 2,3,8,9). In a model reaction of 2-phenyl-2-oxazoline with benzoic acid, the reaction components were consumed even in 2 min[7]. Then, some degradation processes appeared. The end-capping reaction with **2** proceeds smoothly, and even within 2 minutes a relatively high reaction degree was achieved (Entry 8). Then, after further increase in conversion, some degradation reactions appeared. The degradation process could also be recognized visually, since the colour of the polymer changed from orange to brown. The same course was observed for both modifiers (Figure 2). At first, a rapid start of the reaction was observed and after reaching the maximum the conversion slowed down due to degradation processes. The influence of temperature is not significant (Table 1, entries 2, 6, 7). Only small differences in conversion were observed in the temperature range 195-240 °C. The temperature of 180 °C was too low to obtain well-mixed and processable materials (Entry 5).

Table 1 Modification of the LCP with 4’-hydroxy-4-(2-oxazolin-2-yl)azobenzene (**1**) and 4’-allyloxy-4-(2-oxazolin-2-yl)azobenzene (**2**) at a molar ratio of polymer end groups to the modifier of 1:1 by reactive processing.

Entry	Modifier	Weight [g]	Weight of polymer [g]	Temperature [°C]	Time [min]	Conversion [%]
1	**1**	0.588	4.5	240	2	14
2	**1**	0.588	4.5	240	5	60
3	**1**	0.588	4.5	240	10	74
4	**1**	0.588	4.5	240	20	56
5	**1**	0.588	4.5	180	5	-
6	**1**	0.588	4.5	195	5	65
7	**1**	0.588	4.5	220	5	64
8	**2**	0.676	4.5	240	2	71
9	**2**	0.676	4.5	240	5	82
10	**2**	0.676	4.5	240	10	73
11	**2**	0.676	4.5	240	20	60

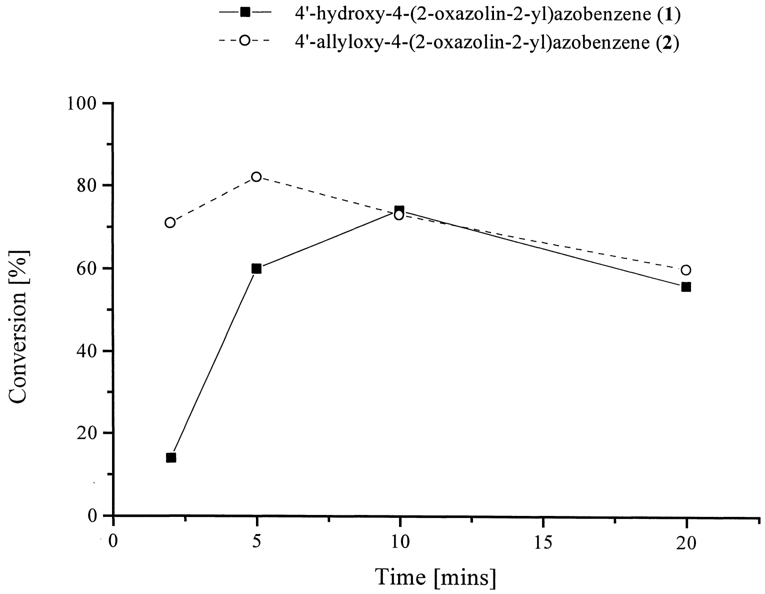


Figure 2 Conversion of the LCP with azobenzene containing 2-oxazolines

The presence of the end-capped modifier in the polymers was proved by ^{13}C NMR spectroscopy. In Figure 3 the spectrum of PET modified with 4′-hydroxy-4-(2-oxazolin-2-yl)azobenzene is given together with the assignment of the particular carbons.

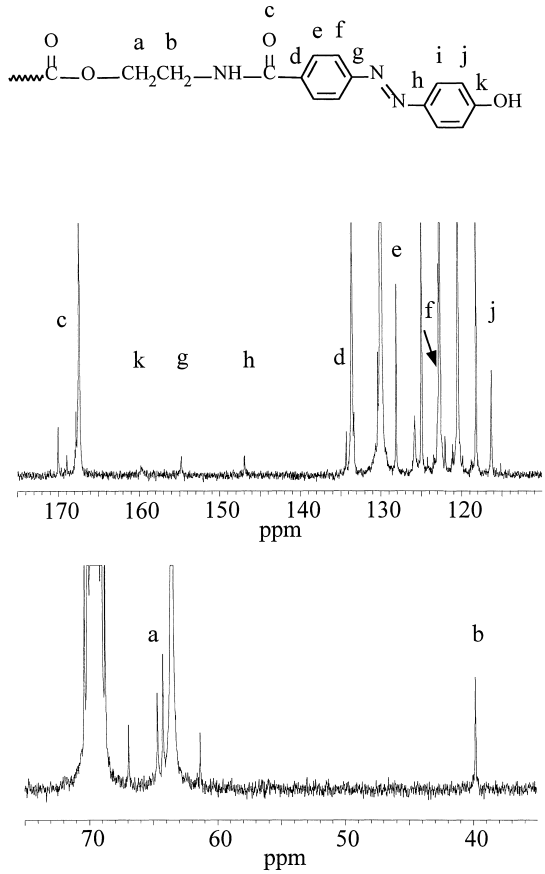


Figure 3 ^{13}C NMR spectrum of PET modified with 4′-hydroxy-4-(2-oxazolin-2-yl)azobenzene measured in $CDCl_3$/HFIP

Interesting results were achieved for the reaction in solution (Table 2) where conversions of **1** and **2** between 90 and 100 % were obtained in 6 hours at 200 °C for the LCP and for the PET as well. These values are higher than those achieved during reactive processing. This fact is evidently the result of better homogeneity of the reaction mixture and easier accessibility of the reactants in solution. However, it also shows that higher conversions are possible and that the reaction also proceeds at lower temperatures. This could be advantageous from the technological point of view and reduces degradation.

Table 2 Modification of the LCP and PET with 4'-hydroxy-4-(2-oxazolin-2-yl)azobenzene (**1**) and 4'-allyloxy-4-(2-oxazolin-2-yl)azobenzene (**2**) in a solution of 1-chloronaphthalene[a]

Entry	**Modifier**	**Weight [g]**	**Polymer**	**Temperature [°C]**	**Time [hours]**	**Yield**
1	**1**	0.173	LC	200	6	90
2	**1**	0.204	PET	200	6	95
3	**2**	0.199	LC	200	6	100
4	**2**	0.2343	PET	200	6	88

[a]For the reaction 1.5 g polymer and 5 ml 1-chloronaphthalene were used; the molar ratio of the carboxylic end groups to the modifier was 1:1

The prepared polymers exhibit photochemical activity. The azobenzene structure is able to undergo *trans-cis* isomerization during irradiation with UV light and backwards *cis-trans* reaction in the dark. This will be subject of further investigations.

Conclusions

End-capping of carboxy group terminated polyesters with azo group containing 2-oxazoline derivatives provides a new route for labelling polymers. The reaction is very fast and the modification is proper for reactive processing. However, extension of the processing time led to some degradation reactions. This could be prevented completely when the reaction was carried out in solution. The polymers prepared represent new photosensitive materials that undergo photochemical *trans-cis* isomerizations and backward *cis-trans* reactions. This "switch effect" might be of interest for some industrial applications and for studying chain end mobility in bulk.

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