Unsaturated 2-Oxazoline End Capping of Liquid Crystalline Polyester by Reactive Processing and in a Solution

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ABSTRACT: End capping of liquid crystalline poly(ethylene terephthalate-*co*-oxybenzoate) with a bifunctional 2-oxazoline derivative, 2-(4-allyloxyphenyl)-2-oxazoline, has been performed in melt under the condition of reactive processing and in a solution. The reaction in melt is very fast and, despite some modifier evaporation, it is completed in 2 min at 230°C. The product is a polyester containing unsaturated end groups bonded via esteramide linkage. The presence of unsaturation was proved by ¹³C-NMR spectroscopy. An increase in temperature and prolongation of the processing time gives raise to thermal-induced reactions on the unsaturated end groups, resulting in an increase of the glass transition temperature. Depending on the processing temperature decomposition, propagation and crosslinking occur in different extent and influence polymer properties. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1047–1053, 1999

Key words: polymer modification; 2-oxazoline; 2-(4-allyloxyphenyl)-2-oxazoline; liquid crystalline polyester; poly(ethylene terephthalate-*co*-oxybenzoate); reactive processing; end capping

INTRODUCTION

The reactive modification of commodity polymers represents a usual way for the preparation of functionalized polymers suitable for compatibilization, crosslinking, etc.^{1,2} In case of polyesters modification, two approaches are of interest. The first of them is the coupling of polyester chains resulting in increased molecular weights, and the second one is the endcapping reaction with a proper modifier for introducing different end groups.

Diisocyanates^{3–5} were used for coupling or chain extension of polyesters, but even better results were achieved with cyclic iminoethers, bis(2oxazolines), under the conditions of reactive processing.^{5–13} Bifunctional chain extenders have two advantages. On one hand, the molecular weight is increased by coupling of two chains, and on the other hand, the content of carboxylic end groups decreases, resulting in improved thermal stability.

Another interesting application of coupling agents is their use in compatibilization of polymer blends.^{14–19} Coupling of different thermoplastics results in phase stabilization and, subsequently, in improved mechanical properties. Reactive blending of liquid crystalline polyesters with PET has been claimed.¹⁵ Baker et al.^{16–19} used polystyrene containing 2-oxazoline groups for reactive processing with carboxylic acid containing polymers to improve interfacial adhesion and enhance

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phase dispersion in multiphase polymer blends. The modification of polypropylene containing carboxylic end groups under the formation of a reactive 2-oxazoline structure is also interesting.²⁰ In such a way prepared 2-oxazoline-terminated oligopropene was used for further modification of poly(ethylene-co-acrylic acid). In another article, Mülhaupt et al.²¹ referred to reactive processing of the same copolymer with aryl- and alkyl-substituted 2-oxazolines. These modified polymers contained amidoester linkages between the main chain and the substituent. The reactions were very fast, as required for reactive processing. After 10 min at 220°C, no free modifier could be found in the reaction mixture. In a model reaction of 2-phenyl-2-oxazoline with benzoic acid, the reaction components were consumed even in 2 min.

End-capping reaction was widely used to enhance thermal stability of polyesters. Capping agents are usually monofunctional, but polyfunctional end cappers have also been known. The examples of end capping include the use of epoxides,^{22–27} isocyanates,²⁸ and 2-oxazolines.²⁹ Reactions are usually performed under the conditions of reactive processing, for example, in processing machines at elevated temperature, during short processing time, usually only a few minutes.

Recently, we performed the modification of poly(ethylene-*co*-butyl acrylate-*co*-acrylic acid) with 2-(4-allyloxyphenyl)-2-oxazoline under the conditions of reactive processing as well as in solution.³⁰ The goal of this article is the end capping of a liquid crystalline poly(ethylene tereph-thalate-*co*-oxybenzoate) with the same modifier, and the aim to obtain a polyester containing thermally stable unsaturated end groups using the well-known nucleophilic reaction between carboxylic end groups and the 2-oxazoline ring.³¹ The allyl group is suitable for these purposes because it meets demands for temperature stability at high processing temperatures.

EXPERIMENTAL

Materials

2-(4-Allyloxyphenyl)-2-oxazoline was prepared from 2-(4-hydroxyphenyl)-2-oxazoline and allyl bromide under the conditions of phase transfer catalysis as previously described.³⁰

¹H-NMR (DMSO-d₆): δ 7.79 (d, J = 8.8 Hz, 2 H, ring), 7.01 (d, J = 8.8 Hz, 2 H, ring), 6.03 (m, 1 H, ---CH=), 5.40 (dq, J = 17.4 Hz, J = 1.6 Hz, 1 H, CH₂==), 5.27 (dq, J = 10.5 Hz, J = 1.6 Hz, 1 H, CH₂==), 4.60 (dt, J = 5.2 Hz, J = 1.6 Hz, 2 H, CH₂O), 4.36 (t, J = 9.5 Hz, 2 H, CH₂O) 3.91 (t, J = 9.5 Hz, 2 H, CH₂N).

¹³C-NMR (HFIP/CDCl₃): δ 51.55 (NCH₂), 68.71 (OCH₂), 69.51 (Ar—OCH₂), 115.21 (Ar), 117.68 (Ar), 118.84 (CH₂=), 130.68 (Ar), 132.09 (CH=), 162.49 (Ar), 168.34 (N=CR—O).

Liquid crystalline poly(ethylene terephthalateco-oxybenzoate)s with 60 mol % oxybenzoic units (PET/HBA = 40/60) were prepared in a 2-L and a 10-L stainless vessel by transesterification reaction of PET with *p*-hydroxybenzoic acid (HBA) according to Jackson and Kuhfuss.³² The molecular weight was controlled by terephthalic acid added to the reaction mixture. Independent of the reaction volume, two samples (LCP 1 and LCP 2) with almost equal properties were obtained. The ¹³C-NMR spectra correspond with spectra of earlier investigated samples.³³ Sample characteristics are summarized in Table I.

Procedures

Inherent viscosities were measured in a mixture of phenol/tetrachloroethane = 1 : 1 at 20°C, and number-average molecular weights were determined by titration with butanolic solution of KOH in a mixture *o*-cresol/CHCl₃ = 1 : 1, as described previously.⁶

¹H- and ¹³C-NMR were measured on a DRX-500 spectrometer (Bruker) operating at 500.13 MHz for ¹H and 125.75 MHz for ¹³C. The ¹H-NMR spectrum of the modifier was measured in DMSO-d₆ at room temperature, and ¹³C-NMR spectra of the modifier and of the polymers were measured in hexafluoroisopropyl alcohol/CDCl₃ (1 : 1 v/v). The deuterated solvents were used as lock and internal standards.

Thermal analysis measurements were done with a Perkin-Elmer DSC 7 at a scan rate of 10 K/min in the temperature range of -10 up to 235° C in a cycle 1. heat-cool-2. heat.

Processing

Mixing procedure was done in the chamber of a Miniature Mixing Reactor (Musashino Kikai Co., Japan) or in Brabender Plasticorder (Germany). For the modification in the Minimixing Reactor, 3 g of the polymer and the respective amount of the modifier were introduced into the preheated mixing chamber. After heating to the processing temperature 260°C, the sample was mixed (30

Polymer	Weight (g)	Modifier (g)	Mode ^a	Temperature (°C)	Time (min)	$\eta_{ m inh} \ m dL/g$	Acid Number (mmol/g)	Reaction Degree (%)
1	_					0.295	0.431	
1a	3	0.263	А	260	5	n.d.	0.332	23
1b	3	0.263	В	200	360	n.d.	0.069	84.0
2		_		_	_	0.296	0.486	
2a	38	3.80	С	230	2	0.285	0.121	75.1
2b	38	3.80	С	230	5	0.286	0.139	71.4
2c	38	3.80	С	230	10	0.278	0.136	72.0
2d	38	3.80	С	230	15	0.259	0.146	70.0
2e	38	3.80	С	230	30	0.305	0.205	57.8
2f	35	3.50	С	250	6	n.d.	0.135	72.2
$2 \mathrm{g}$	35	3.50	С	250	8	0.313	0.178	63.4
2 h	35	3.50	С	250	12	0.294	0.212	56.4
2i	35	3.50	С	250	15	0.322	0.223	54.1

Table I Modification of Liquid Crystalline Polyester with 2-(4-Allyloxyphenyl)-2-oxazoline

^a A, minimixer; B, solution in 1-chloronaphthalene; C, Brabender Plasticorder.

rpm) for the desired time and than withdrawn from the chamber. During processing, strong evaporation of the modifier was observed.

The modification in the Brabender Plasticorder was performed at 80 rpm and 230 or 250°C for the desired time. The amount of modifier added corresponded to the concentration of carboxylic groups as determined by titration. The content of remaining carboxylic groups was determined by titration.

Modification experiments were also carried out in a solution. In this experiment, the polymer (3 g)was dissolved under a slow stream of nitrogen and stirred at 200°C in 1-chloronaphthalene (10 mL). The modifier (0.263 g, 1.293 mmol, molar ratio 1 : 1) was added to the solution in one portion. The reaction mixture was stirred for 6 h and then precipitated into ethanol (50 mL). The modified LCP was extracted with ethanol (50 mL, $3\times$) and dried in a vacuum oven at 90°C for 8 h.

RESULTS AND DISCUSSION

Two poly(ethylene terephthalate-*co*-oxybenzoate)s, LCP **1** and LCP **2**, were used for modification. Their inherent viscosities shown in Table **1** are nearly equal, and correspond to number-aver-



age molecular weights of $M_n = 4060$ and 4000 Dalton, respectively.³⁴ From the content of carboxylic end groups and the assumption that the polyesters are carboxy terminated on both sides, M_n of 4110 and 4650 Dalton were calculated for LCP **1** and **2**, respectively, which are in a good agreement with the M_n determined by viscometry.

The bifunctional modifier 2-(4-allyloxyphenyl)-2-oxazoline was synthesized according to Scheme 1. The procedure was described in a previous article.³⁰ The desired product was obtained in excellent yield (95%) and sufficient purity and, after recrystallization, was used for modification experiments.

The reaction between carboxylic acid groups and the 2-oxazoline ring proceeds by the attack of the carboxylic oxygen to the carbon atom in the 5-position of the oxazoline ring. The product of this attack is the esteramide structure. A general scheme of this reaction applied to our system is shown in Scheme 2.

The modification of the LCP **1** was performed in a minimixer at 260°C and in solution at 200°C. LCP **2** was converted in a Brabender Plasticorder at 230 and 250°C. The extent of reaction was





Figure 1 Dependence of the degree of reaction on the processing time for modification of liquid crystalline polyester with 2-(4-allyloxyphenyl)-2-oxazoline in a Brabender Plasticorder at 230°C.

estimated by means of acid numbers. From the ratio of acid numbers of the modified and unmodified sample the reaction degree was calculated. The results are shown in the Table I.

The modification in the minimizer at 260°C provided only a low degree of reaction (23% 1a), which was obviously caused by strong volatilization of the modifier from the system. Much better results were obtained during the modification in the Brabender Plasticorder at 230°C (2a-e) and 250°C (**2f-i**). Despite some volatilization of the modifier, the closer chamber of the Brabender Plasticorder resulted in a higher reaction degree under comparable conditions. Surprisingly, the highest conversions were achieved at the shortest reaction times (75.1% for 2a within 2-min processing at 230°C, and 72.2% for 2f within 6-min processing at 250°C). This means that the endcapping reaction of the 2-(4-allyloxyphenyl)-2-oxazoline with carboxylic end groups of the LCP is extremely fast.

With the extension of processing time the reaction degree steadily decreased (Fig. 1). This is in strong contradiction with the previous results from the modification of a carboxy groups containing polyolefine,³⁰ where increase of conversion with reaction time was observed. Probably, the higher reaction temperature applied for modification of the polyesters caused side reactions, resulting in increase of carboxylic groups content. Beside thermal decomposition of the polymer the reversibility of the oxazoline reaction has to be regarded. Recently, Loontjens et al.³⁵ pointed out that at temperatures above 250°C the reaction of oxazolines with carboxylic acid groups is reversible. That means if volatile oxazolines are used for modification, evaporation at elevated temperature becomes more and more likely.

This assumption is supported by thermogravimetric investigations. The modified samples **2a** and **2f** showed a more pronounced mass loss (ML) at temperatures around 250°C. ML (1%) was found at 315°C for sample **2**, at 257°C for samples **2a**, and at 281°C for sample **2f**. The determined temperatures for 10% ML of **2**, **2a**, and **2f** were 410, 390, and 383°C, respectively.

However, it is reasonable to assume that nonvolatile additives or reactions in well-sealed systems (for instance, in the extruder) can provide higher conversions, as previously reported by Mülhaupt.²¹ Also, modification in a relatively highly diluted solution of 1-chloronaphthalene at 200°C resulted in high yields (**1b**). The obtained conversion after 6 h was 84% (Table I).

The structure of the modified polymers was investigated by ¹³C-NMR spectroscopy. An interpretation of spectra of unmodified poly(ethylene terephthalate-*co*-oxybenzoate)s was given in a previous publication.³³ Additional signals appearing in the spectrum of the sample **2a** modified in the Brabender Plasticorder at 230°C for 2 min could be assigned to the resulting end-group structure shown in Table II. The absence of characteristic oxazoline group signals at 51.55 ppm

$ \begin{array}{c} O & H & O \\ \blacksquare & H & O \\ \blacksquare & -O - CH_2 - CH_2 - CH_2 - H_2 \\ a & b & c & d \\ e & f \end{array} \begin{array}{c} O - CH_2 - CH_2 - CH_2 \\ O - CH_2 \\$										
Signal	а	b	с	d	е	f	g	h	i	k
δ in ppm	64.30	39.65	170.38	125.22	128.84	115.25	162.13	69.39	132.14	118.67

Table II Assignment of ¹³C-NMR End Group Signals of Modified Polyesters



Figure 2 DSC curves (second heating) of the virgin and the modified liquid crystalline polyesters.

 (NCH_2) and 68.71 ppm (OCH_2) showed that the reaction proceeded completely. From the spectrum, especially from the signals of the olefinic CH₂= carbon at 118.67 ppm (k) and of the CH= carbon at 132.14 ppm (i), it was concluded that the double bond is preserved during modification. Increase in temperature and prolongation of reaction time, however, resulted in a destruction of the end groups. The spectrum of sample 2i modified at 250°C for 15 min did not contain any of the signals mentioned in Table II. Instead, several other signals appeared whose assignation has not yet been possible. It is assumed that rearrangements such as transesterification and transamidification reactions and progressive crosslinking of the allyl groups are responsible for the new signals. It has to be mentioned that signals for unsaturated groups are still in the spectra, however, to a lesser extent.

Cleavage of the terminal groups as mentioned above cannot be excluded, but, from the low acid numbers of all modified samples one can conclude that this process is less significant. The course of inherent viscosities (Table I) rather point to the fact that degradation and propagation or crosslinking occurred simultaneously. A steady decrease of inherent viscosities (**2a–2d**) could be observed at 230°C within the first 15 min, followed by a significant increase (**2e**) after prolongation to 30 min. At higher temperatures (250°C) a drop of η_{inh} could not be observed. Apparently, the propagation reactions compensate degradation.

Figure 2 shows the DSC curves (second heating), and Table III an overall view of the thermal data of the virgin sample 2 and the modified samples **2a** and **2i**. In each curve there appears two glass transitions between 60 and 80°C. The two glass transitions are caused by the multiphase structure of poly(ethylene terephthalate-co-oxybenzoate)s. It is known that in this copolymer two phases that differ in oxybenzoate content exist.^{36–38} According to Chen and Zachmann,³⁸ the low-temperature transition belongs to a frozen liquid crystalline phase that is rich in oxybenzoate, and the higher glass transition to an amorphous-phase rich in PET. Comparing the glass transition temperatures of the virgin sample 2 and the sample **2a** modified at 230°C for 2 min, one can conclude that the modification resulted in softening. Especially, the T_g at higher temperatures decreased significantly. Longer reaction time and higher modification temperature cause an increase in both T_g , as shown for the sample 2imodified at 250°C for 15 min. This is in accordance with the above assumption that propaga-

	T_g (°C) (Δc_p in J/gK)			$\Delta H_{f}^{\mathrm{a}} (\mathrm{J/g})$	
Sample	First Step	Second Step	$\Sigma \Delta H_i \; (J/g)$	$\Delta H_c^{~\rm a}~({\rm J/g})$		
2	59 (0, 106)	78 (0, 05)	4.56 (110–220°C)	-0.44 (110-145°C)	5.0 (145–220°C)	
2a	(0, 122)	69 (0, 07)	2.6 (95–210°C)	-1.5 (95–220°C)	4.1 (140–210°C)	
2i	65 (0, 12)	83 (0, 14)	0.1 (110–180°C)	-0.7 (110-145°C)	0.8 (145–180°C)	

Table IIIThermal Characteristics of the Virgin and the Modified Liquid Crystalline PolyestersDetermined by DSC (Second Heating)

^a The heat of exothermic cold crystallization ΔH_c and the heat of endothermic melting ΔH_f were determined by partial integration within the given temperature range.



Figure 3 Correlation between step heights of the glass transitions Δcp and the enthalpy balance $\Sigma \Delta H_i$ used as a measure of crystallinity at room temperature.

tion and crosslinking occurs at higher temperatures. The fact that the higher T_g is affected more strongly than the lower one leads to the assumption that end capping takes place preferably in the PET-rich phase.

Above the glass transition range an exothermic cold crystallization can be observed followed by an endothermic melting at about 140°C. The balance $(\Sigma \Delta H_i)$ of the heat of exothermic cold crystallization ΔH_c and the heat of endothermic melting ΔH_f (Table III) is a measure of the crystallinity formed during the cooling scan after the first heating. This value decreases with modification. This means that modification reduces the ability of the polymer to crystallize, and consequently, the amorphous part is increased.

In Figure 3 the correlation between the step heights of the glass transition Δcp and the balance of the transition heats $\Sigma \Delta H_i$ is plotted. Δc_{n1} and Δc_{n2} correspond to the glass transitions of the oxybenzoate-rich phase at lower temperatures, and the PET-rich phase at higher temperatures, respectively, and $\Sigma \Delta c_{pi}$ is the sum of Δc_{p1} and Δc_{p2} . Δc_{p1} is almost independent from $\Sigma \Delta H_i$, whereas Δc_{p2} strongly correlates. This confirms that both the glass transition at higher temperatures and the crystallizable phase can be assigned to the PET-rich phase in the polymer. The decrease of $\Sigma \Delta H_i$ and the decrease of the melting heat after modification shows that the occurring reactions restrict more and more crystallization and reduce the crystallizable part of the PET-rich phase.

Although phase behavior and crystallinity is significantly influenced by modification, no disturbance in liquid crystalline properties could be observed. Above 200°C a nematic phase was observed as for the unmodified samples.

CONCLUSIONS

We can conclude that the reaction of unsaturated 2-oxazoline derivative with polymer carboxylic groups provides a versatile method for introduction of different functional groups into polyester chains. In the present case, an end-capped liquid crystalline polyesters having unsaturation in end groups was obtained. Due to the high rate of reaction, this modification is suitable to be carried out on an extruder. The unsaturated groups reacted after prolongation of reaction time resulting in an increase of glass transition temperature and decrease of crystallinity. It could be shown by DSC measurements that the modification reactions mainly effect the properties of the PET-rich phase of the liquid crystalline polyester. From this it was concluded that the modification reaction proceeds preferably in the PET-rich phase. Different carboxylic group concentrations or differences in solubility of the modifier in the two phases of the polymer may be responsible for this behavior.

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REFERENCES

- 1. Xanthos, M., Ed.; Reactive Extrusion, Principles and Practice; Hanser Publishers: Munich; 1992.
- Platé, N. A.; Litmanovich, A. D.; Noah, O. V. Macromolecular Reactions, Pecularities, Theory and Experimental Approaches; Wiley: Chichester, 1995.
- Gebauer, F.; Kaeuufer, W.; Klingenberg, H. Belg. Pat. 868186 (1978); C. A. 90,72645 (1979).
- 4. Kolouch, R. J.; Michael, R. H. EP 0056293 (1982).
- Leistner, D.; Stephan, M.; Häußler, L.; Vogel, R.; Rätzsch, M. Angew Makromol Chem 1993, 206, 141.
- Böhme, F.; Leistner, D.; Baier, A. Angew Makromol Chem 1995, 224, 167.
- Inata, H.; Matsumura, S. J Appl Polym Sci 1985, 30, 3325.

- Inata, H.; Matsumura, S. J Appl Polym Sci 1986, 32, 4581.
- Inata, H.; Matsumura, S. J Appl Polym Sci 1986, 32, 5193.
- Inata, H.; Matsumura, S. J Appl Polym Sci 1987, 33, 3069.
- Loontjens, T.; Belt, W.; Stanssens, D.; Weerts, P. Polym Bull 1993, 30, 13.
- Loontjens, T.; Belt, W.; Stanssens, D.; Weerts, P. Makromol Chem Macromol Symp 1993, 75, 211.
- Baier, A.; Böhme, F.; Vogel, R.; Martin, H.; Leistner, D. Angew Makromol Chem 1995, 228, 117.
- Parsy, R.; Rivas, N. EP 331554 (1989), CA 112, 159723 (1990).
- Suenaga, J. EP 438128 (1991), CA 115, 281313 (1991).
- 16. Baker, A.; Saleem, M. Polymer 1987, 27, 1634.
- 17. Baker, W. E.; Saleem, M. Polymer 1987, 28, 2057.
- Fowler, M. W.; Baker, W. E. Polym Eng Sci 1988, 28, 1427.
- Saleem, M.; Baker, W. E. J Appl Polym Sci 1990, 39, 655.
- Wörner, C.; Rösch, J.; Hähn, A.; Mülhaupt, R. Polym Bull 1996, 36, 303.
- Müller, P.; Wörner, C.; Mülhaupt, R. Macromol Chem Phys 1995, 196, 1917.
- 22. Schwarz, E. C. A. U.S. Pat. 3,627,867 (1971).
- 23. Titzmann, R.; Thaler, H.; Walter, J. U.S. Pat. 3,657,191 (1972).

- 24. Korver, G. L. U.S. Pat. 4,071,504 (1978).
- Inata, H.; Ogasawara, M.; Morinaga, T.; Norike, A. U.S. Pat. 4,196,066 (1980).
- Inata, H.; Ogasawara, M.; Morinaga, T.; Norike, A. U.S. Pat. 4,269,947 (1981).
- Rothwell, R. E.; Rowan, H. H.; Dunbar, J. J. U.S. Pat. 4,374,960 (1983).
- Gilliam, K. D.; Paschke, E. E. U.S. Pat. 4,166,873 (1979).
- Matsumura, S.; Inata, H.; Morinaga, T. U.S. Pat. 4,351,936 (1982).
- Lustoň, J.; Böhme, F.; Komber, H.; Pompe, G. J Macromol Sci Chem, 1998, A35, 1045.
- 31. Frump, J. A. Chem Rev 1971, 71, 483.
- Jackson, W. J.; Kuhfuss, H. F. J Polym Sci Polym Chem Ed 1976, 14, 2043.
- Böhme, F.; Komber, H.; Leistner, D.; Rätzsch, M. Macromol Chem Phys 1994, 195, 3233.
- Rafler, G.; Tesch, F.; Böhme, F. Acta Polym 1987, 38, 585.
- Loontjens, T.; Pauwels, K.; Derks, M.; Neilen, M.; Sham, C. K.; Serne, M. J Appl Polym Sci 1997, 65, 1813.
- Scheller, D.; Kressler, J.; Kammer, H. W.; Böhme, F.; Voigt, C.; Leistner, L.; Rätzsch, M. Polym Bull (Berlin) 1989, 21, 585.
- Benson, R. S.; Lewis, D. Polym Commun 1987, 28, 289.
- 38. Chen, D.; Zachmann, H. G. Polymer 1991, 32, 1612.