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### Unsaturated 2-Oxazoline Modification of Polyethylene Containing Carboxylic Groups

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## UNSATURATED 2-OXAZOLINE MODIFICATION OF POLYETHYLENE CONTAINING CARBOXYLIC GROUPS

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**Key Words:** Polymer Modification, 2-Oxazoline, Poly(ethylene-co-butyl acrylate-co-acrylic acid), 2-(4-Allyloxyphenyl)-2-oxazoline, Reactive Processing, Multifunctional Crosslinker

### ABSTRACT

Chemical modification of terpolymer poly(ethylene-co-butyl acrylate-co-acrylic acid) with a bifunctional 2-oxazoline derivative 2-(4-allyloxyphenyl)-2-oxazoline has been performed in melt under the conditions of reactive processing and in a solution. The reaction in melt is very fast and, in spite of some modifier evaporation, it is completed in 15 minutes at 180°C. The product is a terpolymer containing thermally stable unsaturated groups bonded via amido-ester linkage to the main chain. The presence of unsaturation was proved by <sup>13</sup>C NMR spectroscopy. The modification does not significantly change the crystallization behavior of the terpolymer.

## INTRODUCTION

The modification of nonpolar polyolefins is still the subject of many research laboratories. The following methods have been used for the initiation of the modification of polyolefins [1]: chemical initiation, photochemical initiation, and high energy radiation induced initiation.

The chemical initiation can include direct reaction of a reactive agent with a polymer at elevated temperatures [2], the formation of polymer radicals by the decomposition of peroxides followed by their reaction with a modifier [2], or the reaction of a functional polymer with a modifier [3].

For the photochemical and high energy initiation, it is typical that polymer free radicals are directly generated (high energy initiation) or polymer free radicals are generated by a chain transfer from the molecule of a photosensitizer to a polymer [4].

Polyolefin modification has found a special application also in polymer stabilization [5] and carboxylation of polyolefins [6]. Also interesting is the modification of polypropylene containing carboxylic end group under the formation of a reactive 2-oxazoline structure [7]. In such a way, prepared 2-oxazoline terminated oligopropene was used for further modification of poly(ethylene-co-acrylic acid). In another paper, Mülhaupt *et al.* [8] referred to reactive processing of the same copolymer with aryl- and alkylsubstituted 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 minutes at 220°C, no free modifier could be found in the reaction mixture. In a model reaction of 2-phenyl-2oxazoline with benzoic acid, the reaction components were consumed even in two minutes. Another example for utilization of 2-oxazoline derivatives was presented by Inata and Matsumura [9-11], Loontjens *et al.* [12, 13] and Bohme *et al.* [14, 15] who used bis-2oxazolines as chain extenders for polyesters. Baker *et al.* [16-18] used polystyrene containing 2-oxazoline groups for reactive processing with carboxylic acid containing polymers to improve interfacial adhesion and enhance phase dispersion in multiphase polymer blends.

The aim of this contribution was the chemical functionalization of polyethylene containing carboxylic groups with an 2-oxazoline derivative containing unsaturated group, using the well known nucleophilic reaction between carboxylic group and 2-oxazoline ring [19].

## EXPERIMENTAL

### Materials

2-(4-Hydroxyphenyl)-2-oxazoline was prepared according to Saegusa [20]. Poly-(ethylene-co-butylacrylate-co-acrylic acid) (Lucalen® 3110M) with a molar content of components 0.88: 0.08: 0.04 was supplied by BASF.

2-(4-Allyloxyphenyl)-2-oxazoline was prepared under the conditions of phase transfer catalysis (PTC) [21]: 2-(4-Hydroxyphenyl)-2-oxazoline (16.32 g, 0.1 mol) and tetrabutylammonium hydrogen sulfate (3.40 g, 0.01 mol) were added under argon to a mixture of dichloromethane (200 ml) and sodium hydroxide (100 ml, 15% aqueous solution). The mixture was stirred for 5 minutes and allylbromide (13.31 g, 0.11 mol) was added at room temperature. The reaction mixture was stirred at 1000 rpm for 4 hours. The organic layer was separated, washed with water (3 times) and brine, and dried over sodium sulfate. After removing the solvent, the product (19.29 g, 95%) was recrystallized from heptane (100 ml). White crystals with m.p. = 63-65°C were obtained.

Elemental analysis for  $C_{12}H_{13}NO_2$  (203.23), Calcd.: C = 70.19%, H = 6.45%, N = 6.89%; Found: C = 70.70%, H = 6.37%, N = 6.92%.  $^1H$  NMR (DMSO- $d_6$ ):  $\delta$  7.79 (d,  $J$  = 8.8 Hz, 2H, ring), 7.01 (d,  $J$  = 8.8 Hz, 2H, ring), 6.03 (m, 1H, -CH=), 5.40 (dq,  $J$  = 17.4 Hz,  $J$  = 1.6 Hz, 1H,  $CH_2=$ ), 5.27 (dq,  $J$  = 10.5 Hz,  $J$  = 1.6 Hz, 1H,  $CH_2=$ ), 4.60 (dt,  $J$  = 5.2 Hz,  $J$  = 1.5 Hz, 2H,  $CH_2O$ ), 4.36 (t,  $J$  = 9.5 Hz, 2H,  $CH_2O$ ), 3.91 (t,  $J$  = 9.5 Hz, 2H,  $CH_2N$ ).

### Procedures

$^1H$  and  $^{13}C$  NMR were measured on an AMX-300 spectrometer (Bruker) operating at 300.13 MHz for  $^1H$  and 75.47 MHz for  $^{13}C$ . The  $^1H$  NMR spectrum of the modifier was measured in DMSO- $d_6$  at room temperature and  $^{13}C$  NMR spectra of the polymers were measured in 1,2,4-trichlorobenzene/ $C_6D_6$  (9:1 v/v) at 90°C. The deuterated solvents were used as lock and internal standards (DMSO- $d_6$ :  $\delta$  ( $^1H$ ) = 2.50 ppm,  $C_6D_6$ :  $\delta$  ( $^{13}C$ ) = 128.7 ppm).

Microanalysis were done in the Microanalytical Laboratory of the Chemical Institute of the Slovak Academy of Sciences (Bratislava, Slovakia). For RP HPLC was used a column C-18 on silica gel (Tessek, Czech Republic), UV-detection at 254 nm, methanol: water = 8:2, flow 0.5 ml/min.

Thermal analysis measurements were done with Perkin Elmer DSC 7 at the heating rate of 10 K/min.

Determination of carboxylic groups was performed by titration. The polymer samples (1 g) were dissolved in xylene (50 ml) under reflux and the hot solutions were titrated with 0.1 N solution of KOH in butanol in the presence of 3–4 drops of 1% thymol blue.

### Processing

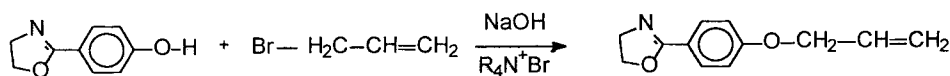
Mixing procedure was done in the chamber of a Miniature Mixing Reactor (Musashino Kikai Co., Japan) or in Brabender Plasticorder (Germany). For the modification in the Minimixing Reactor, 3 g of the polymer and the respective amount of the modifier were introduced into the preheated mixing chamber. After heating to the processing temperature (160 or 200°C), the sample was mixed (30 rpm) for the desired time and then withdrawn from the chamber. Rod-like colorless samples were obtained. During processing strong evaporation of the modifier was observed.

The modification in the Brabender Plasticorder was performed with 21.2 g of the polymer at 80 rpm at 180 or 200°C for the desired time. The amount of modifier added (4.6 g) corresponded to the amount of carboxylic groups given by the supplier. The content of the remaining carboxylic groups was determined by titration.

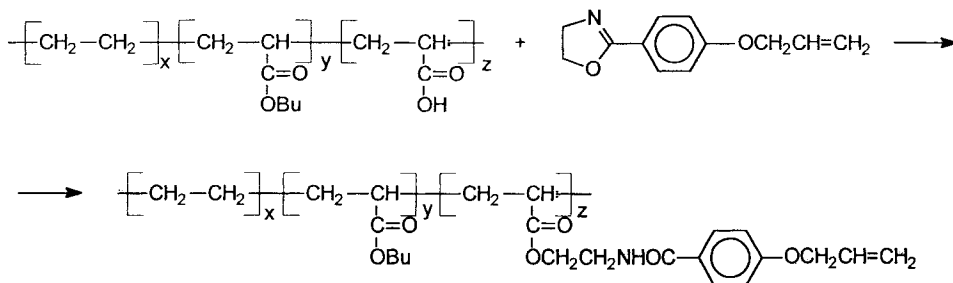
For comparison, modification experiments were carried out in a solution. In this experiment, the terpolymer (3 g) was dissolved under a slow stream of nitrogen and stirring at 190°C in 1-chloronaphthalene (10 ml). The modifier (0.646 g, 3.18 mmol, molar ratio 1:1) was added to the solution in one portion. The reaction mixture was stirred for 6 hours and then precipitated into ethanol (50 ml). Transparent elastomer was extracted with ethanol (50 ml, 3x). After drying in a vacuum oven, colorless polymer was obtained (3.38 g).

## RESULTS AND DISCUSSION

Recently, Mülhaupt *et al.* [8] performed modification of poly(ethylene-co-acrylic acid) with derivatives of 2-oxazolines bearing aliphatic hydrocarbon tail or an aromatic moiety. In another paper, the modification of the same copolymer was performed with 2-oxazoline terminated oligopropene [7]. These results, as well as results of Baker [3, 16–18], have shown that the known reaction between 2-oxazoline ring and carboxylic groups [19] provides a practical route for the modification of carboxylic groups containing polymers. The aim of our work was the synthesis of 2-oxazoline derivative having thermally stable unsaturated group in



SCHEME 1



SCHEME 2

the molecule, and its use for the modification of carboxylic group containing poly(ethylene-co-butyl acrylate-co-acrylic acid). The allyl group is suitable for these purposes because it meets these demands.

The bifunctional modifier 2-(4-allyloxyphenyl)-2-oxazoline was synthesized according to the Scheme 1.

The procedure is described in the Experimental Section. 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 proton to the carbon atom in 5-position of the oxazoline ring. The product of this attack is the ester-amide structure. A general scheme of this reaction applied to our system is shown in Scheme 2.

The modification of the terpolymer was performed in different modes. The results are shown in the Table 1.

The modification in the minimixer provided only low degree of reaction (entries 2 and 3), 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 180°C. In spite of some volatilization of the modifier, the closer chamber of the Brabender Plasticorder resulted in higher reaction degree under comparable conditions. During the first 5 minutes, the con-

TABLE 1. Processing Parameters for the Modification of Poly(ethylene-co-butyl acrylate-co-acrylic Acid) with 2-(4-Allyloxyphenyl)-2-oxazoline

no.	modification mode	temperature [°C]	reaction time [min]	polymer [g]	modifier [g]	acid no [mmol/g]	reaction degree [%]
1	virgin	-	-	-	-	0.573	-
2	A	160	15	3	0.43	0.470	19
3	A	200	5	3	0.65	0.390	33
4	B	200	15	21.2	4.60	0.056	90
5	B	180	5	21.2	4.60	0.182	68
6	B	180	10	21.2	4.60	0.219	62
7	B	180	15	21.2	4.60	0.073	87
8	B	180	20	21.2	4.60	0.117	80
9	B	180	30	21.2	4.60	0.077	87
10	C	190	360	3	0.65	0.089	84

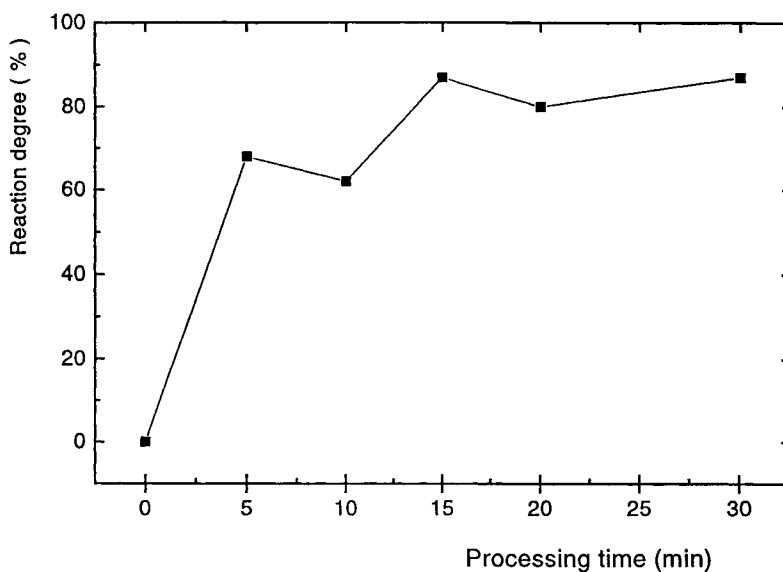
A minimixer

B Brabender Plasticorder

C modification in 1-chloronaphthalene

version was more than 60%, leveled off at approximately 15 minutes, and approached 90% (entries 5-9, Figure 1). It is reasonable to assume that non-volatile additives or reactions in well sealed systems can provide higher conversions, as previously reported by Mülhaupt [8]. The highest conversion was observed after 15 minutes processing at 200°C (entry 4). Also, modification in relatively highly diluted solution of 1-chloronaphthalene at 190°C resulted in high yields. The obtained conversion after 6 hours was 84 %.

The structure of the modified polymers was investigated by <sup>13</sup>C NMR spectroscopy. The <sup>13</sup>C NMR spectrum of the sample modified in the Brabender



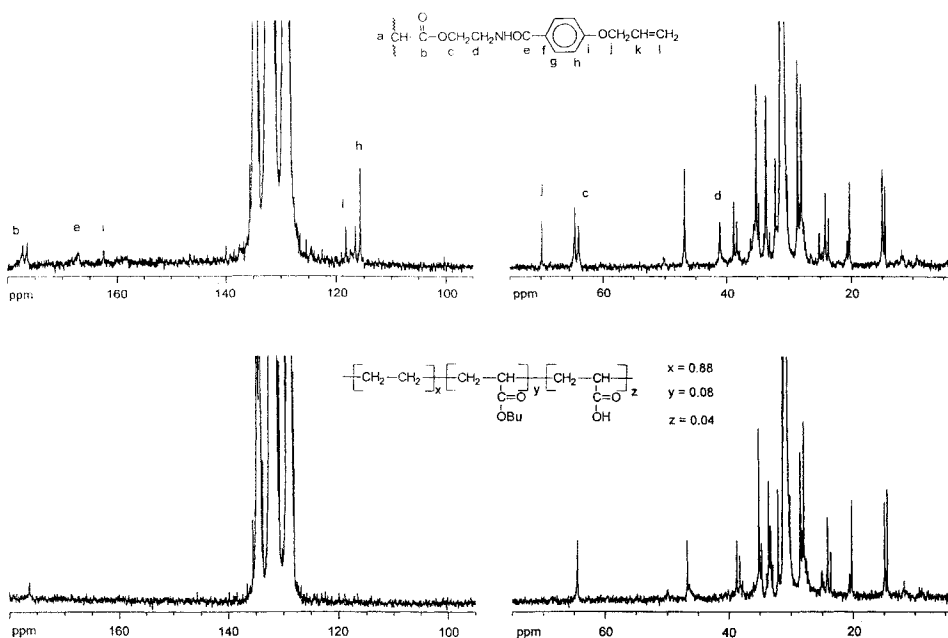
**Figure 1.** The dependence of the degree of reaction on the processing time for modification of poly(ethylene-co-butyl acrylate-co-acrylic acid) with 2-(4-allyloxyphenyl)-2-oxazoline in Brabender Plasticorder at 180°C.

Plasticorder at 180°C for 30 minutes is shown in Figure 2 (entry 9), together with the spectrum of the unmodified sample. The additional signals appearing in the spectrum of the modified sample can be assigned to the resulting structure (Scheme 2). From the spectrum, especially from the signal of the olefinic CH<sub>2</sub> carbon at 118.23 ppm, we can conclude that the double bond is preserved during the modification. The signal of the second olefinic carbon at about 133 ppm is overlapped by the solvent signals.

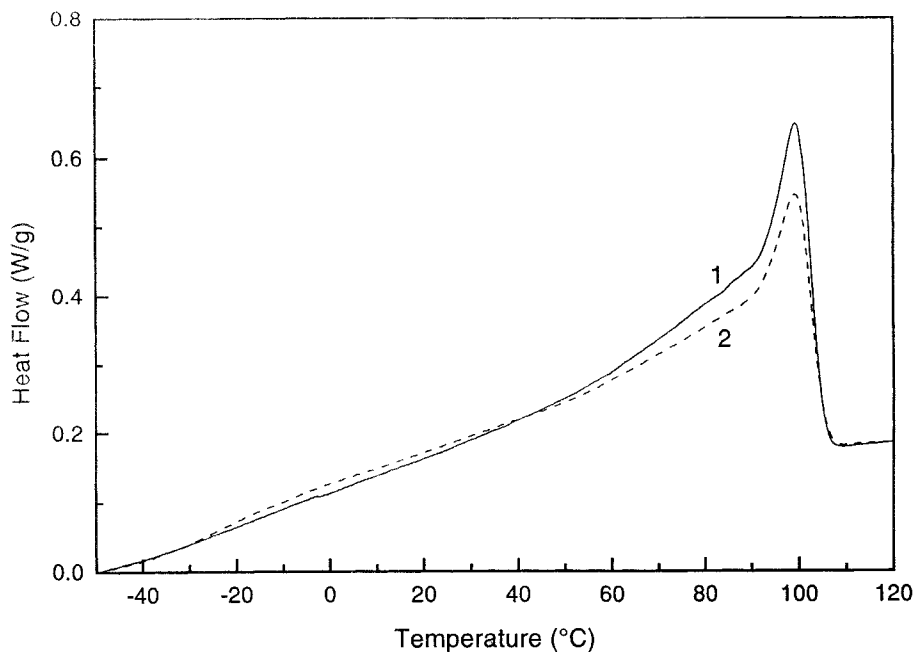
Figure 3 shows the DSC curves (2nd heating) of the virgin and the modified terpolymer. The glass transition temperature at -20°C and the maximum of the melting transition at 99°C remain almost the same. It is remarkable that the crystallization behavior, that is a sensitive indicator for structural changes, does not differ significantly. The degree of crystallinity, however, is slightly reduced which resulted also in a slight reduction of the step height of T<sub>g</sub>. From this we can conclude that the modification reaction does not strongly influence phase behavior of the polymer.

Based on these results, we can say that reaction of unsaturated 2-oxazoline derivative with polymer carboxylic groups provides a versatile method for intro-





**Figure 2.**  $^{13}\text{C}$  NMR spectra of the virgin and the modified terpolymer in 1,2,4 trichlorobenzene/ $\text{C}_6\text{D}_6$  (9:1 v/v) at  $90^\circ\text{C}$ .



**Figure 3.** DSC curves (2nd heating) of the virgin (full line) and the modified (dotted line) terpolymer.

duction of different functional groups into carboxylated polyolefins. In this case, the prepared modified copolymers having unsaturation in pendant part can be used as multifunctional crosslinking agents or as compatibilizers for polymer blends.

## CONCLUSIONS

The reaction of unsaturated 2-oxazoline derivative, 2-(4-allyloxyphenyl)-2-oxazoline with commercial terpolymer poly(ethylene-co-butyl acrylate-co-acrylic acid) during thermal treatment provides a polymer with thermally stable unsaturated groups. Due to the high rate of the reaction, this modification can be performed conveniently in processing machines.

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