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Synthesis of a new oxazoline monomer and free radical grafting of this monomer onto ABS

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Summary

In order to prepare a new reactive polymer, a new vinylbenzyloxazoline has been synthesized. The monomer has been characterized by ^{1}H, ^{13}C NMR and I.R.
A rheocord was used to graft oxazoline reactive group onto ABS by free radical initiation reaction. The grafting reaction was confirmed by using Fourier Transform Infrared Spectroscopy. This ABS based compatibiliser mixes well with ABS and is capable of reacting with the carboxylic and amine end groups of PA.

Introduction:

Several researchers explored the potential of oxazoline functionality as a compatibilizer for various polymer blends (1)-(7).Oxazoline polymers can react with a variety of reagents, such as carboxylic acids or amines(8), making them an effective functional group on polymers for blends compatibilization reaction. Difficulties arise in the blending of polymers owing to the inherent thermodynamic incompatibility in mixtures of long chain molecules. This incompatibility often results in blends having a microscopically heterogeneous structure in which the interfaces are compositionally sharp and mechanically weak. Because the properties of immiscible blends are strongly dependent on the size and distribution of the phases and on the adhesion at the interfaces, development efforts are concerned with control of theses aspects of blend structure.

Two main methods of preparing functionally compatible blends of incompatible pairs of polymers have been developed. The first is based on the modification of polymer by chemical reactions : the polymer modified have a reactive function which is used for the compatibilization(9). The second method is based on the grafting reaction by a free radical initiation reaction of a monomer containing potentially reactive groups (3)-(7),(10)-(12).

In this paper a free radical grafting of a new vinylbenzyl monomer with oxazoline group onto polymer backbones has been investigated. We have detailed the synthesis of oxazoline monomer and the functionalization onto ABS by free radical initiation reaction. Our interest in oxazoline functionality originates from the fact that this functionality helps to compatibilize polymer blends through amido-ester linkage.

Monomer was synthesized by using vinylbenzylchloride (mixture meta and para). The reactivity rates of meta and para are equal : vinylbenzylchloride is a reactive monomer and conducts to easy synthesis of monomer in one or two steps by nucleophilic substitution reactions of the chlorine atom(13).

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Experimental:

Materials

Acrylonitrile butadiene styrene (ABS) copolymer with 29% of acrylonitrile, 46% of styrene (molar proportion) was supplied by Bayer Company (M_w=137000 $g.mol^{-1}$). Polyamide 6 (M_w = 35000 $g.mol^{-1}$) was supplied by SNIA France. The mixture of meta and para vinylbenzylchloride (Dow chemical, meta/para ratio 3 :2) has been distilled under reduced pressure (1 mmHg) before use. The reagents (potassium cyanide, zinc acetate, amino ethanol) and solvents (ethanol, toluene) employed in this study were used as received (Aldrich Society).

Characterization:

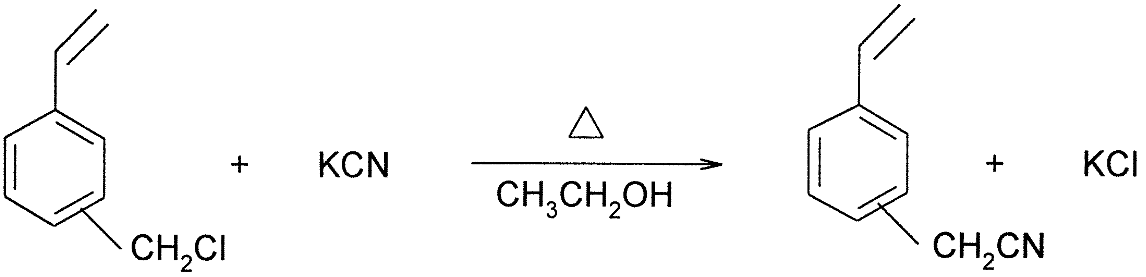
NMR spectra have been recorded with a Brucker DRX 400 apparatus at the frequency of 400 MHz for ^{1}H and 100.6 MHz for ^{13} C. Deuterated chloroform has been used as a solvent and tetramethylsilane as an internal reference. IR spectra was determinated by using FTS-7 BIORAD apparatus. Gas chromatography have been recorded by using Hewlett-Packard GCD « G 1800A »

Preparation of the monomer :

Vinylbenzyloxazoline was prepared in two steps :

In a first step, the vinylbenzylchloride reacted with sodium cyanide to give vinylbenzylcyanide. In a second step the reaction of this compound with ethanolamine gives vinylbenzyloxazoline.

- Vinylbenzylcyanide : This monomer have been synthesized by using the described procedure by M.Tahan et al (14). A solution of meta and para mixture of vinyl benzyl chloride (42.6 g ; 0.28 mol) in ethanol (66 mL) was added with stirring to potassium cyanide (37 g ; 0.57 mol) in water (32 mL). The reaction mixture was stirred and heated at 80°C for 6h. The mixture was filtered from potassium chloride and washed with ethanol. Ethanol was evaporated in vacuum and the residue was extracted with ether, dried over magnesium sulfate and distilled in vacuum. The mixture (meta and para)-vinylbenzylcyanide was collected at 100-102°C (3 mm Hg) yield (80%).



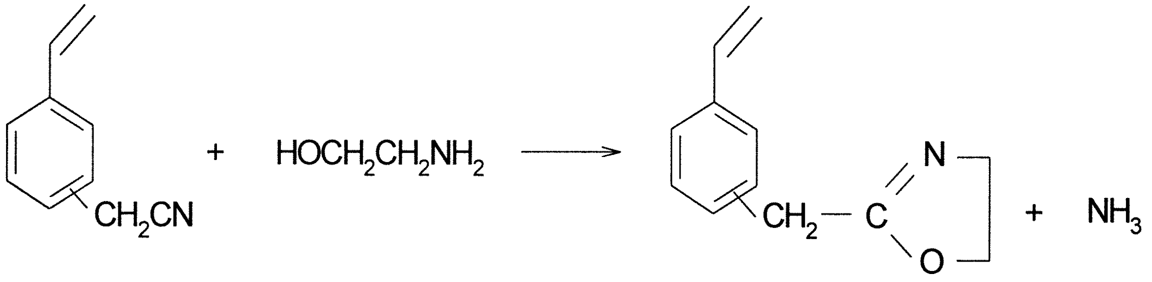
The monomer structure was confirmed by FT-IR showing C≡N stretching band, and by gas chromatography (purity : 96%)

I.R. : 2247 cm^{-1}(C≡N), 1630 cm^{-1}(C≡C), 1600 cm^{-1}(aromatic).

- Vinylbenzyloxazoline : This new monomer was prepared by using a similar procedure described by B.M. Culbertson et al (15).

Vinylbenzylcyanide (5 g ; 0.035 mol) was combined with ethanolamine (3.4 g ; 0.055 mol), zinc acetate (0.2 g) catalyst and 40 mL of toluene in a 500 mL three necked round bottomed flask (fitted with a magnetic stirrer reflux condenser, thermometer, N_2 gas inlet tube, and NH_3 trap). The mixture was heated, in presence of 1‰ of hydroquinone, with moderate stirring at the reflux temperature of toluene, under a slow nitrogen stream until no more ammoniac gas was detected (22h). The excess of ethanolamine was removed by using a separatory funnel, and toluene was distilled off.

The product was purified by distillation twice under vacuum, to give the vinylbenzyl oxazoline with bp = 100°C/0.5mm. Hg and a yield of 65%.



The monomer structure was confirmed by FT IR showing strong C=N stretching band, ^{13}C and ^{1}H NMR spectra having the expected CH_2 protons at 3.5-4.3 ppm.

I.R : 1670 cm^{-1}(C=N) ; 1630 cm^{-1}(C=C) 1600 cm^{-1} (aromatic);

^{1}H NMR (Figure 1 a)

^{1}H NMR	CH_2-C	CH_2O	CH_2N	$\underline{C}H_2$=CH	$\underline{C}H$=	aromatic
	3.6 ppm(s)	3.8ppm(m)	4.2ppm(m)	5.2;5.7ppm(m)	6.7ppm(m)	7.1-7.5ppm(m)

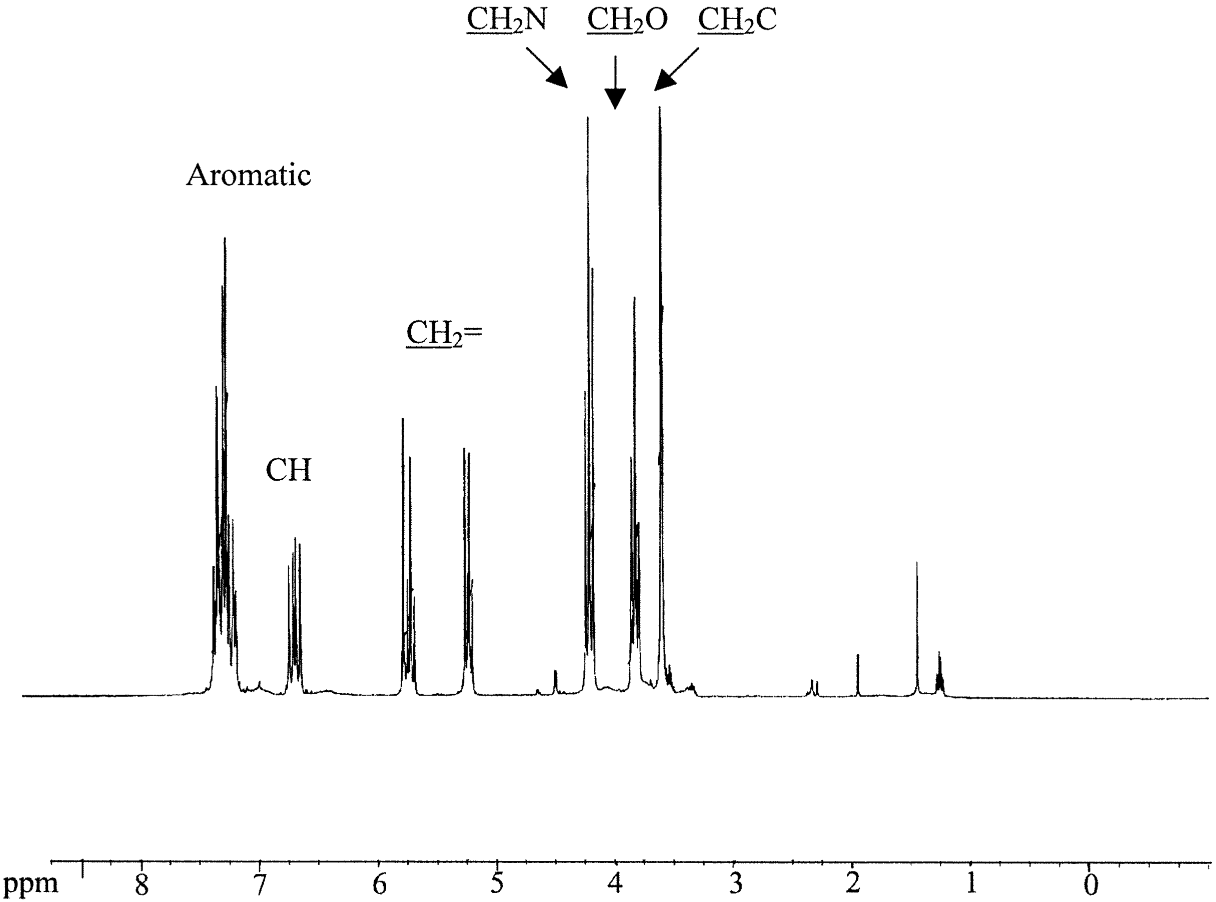
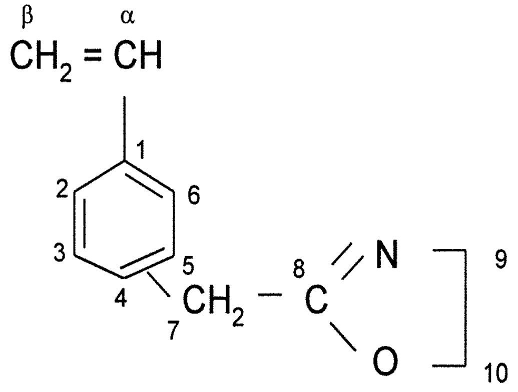


Figure 1 a : ^{1}H NMR spectrum of vinylbenzyloxazoline

^{13} C NMR



C_1-C_6 and C_α	C_β	C_7	C_8	C_9	C_{10}
127-138 ppm	114 ppm	35 ppm	167 ppm	55 ppm	68 ppm

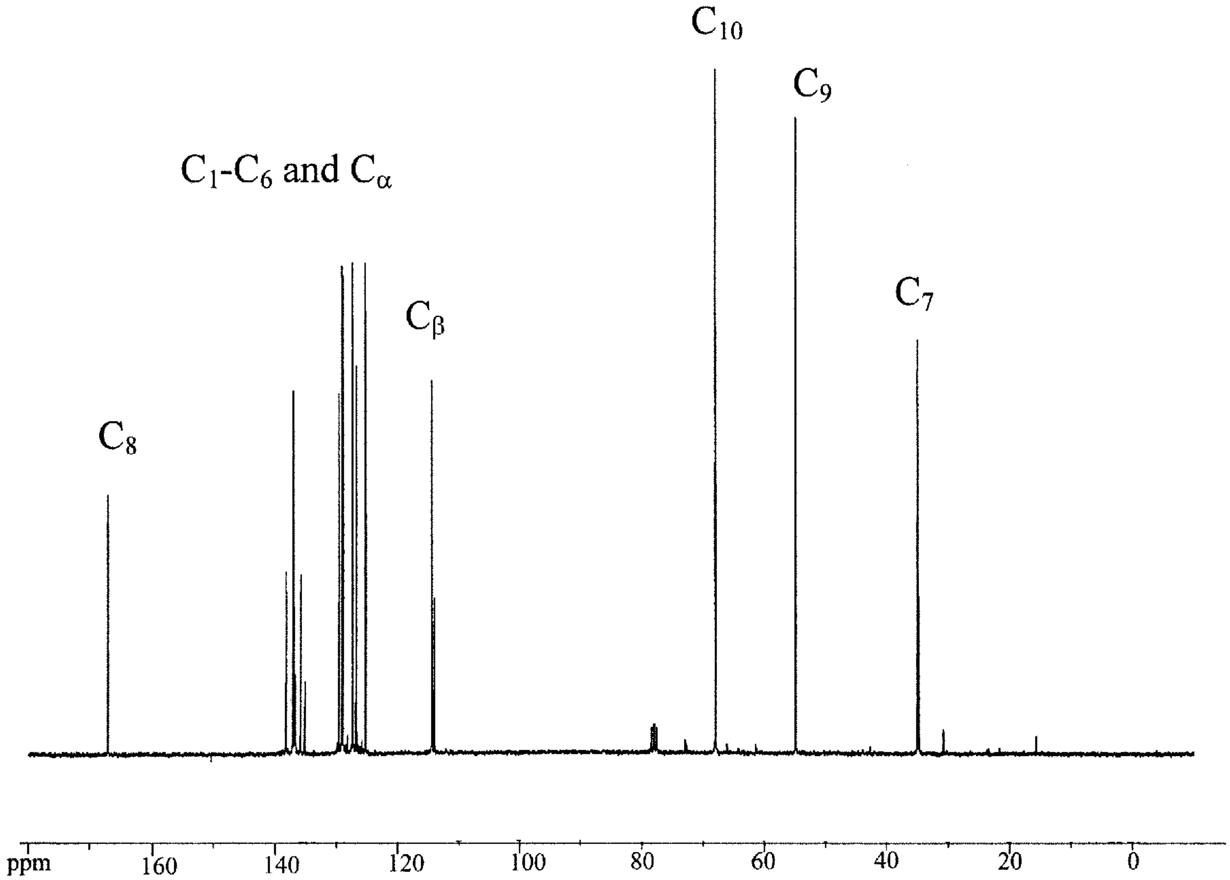


Figure 1 b : ^{13}C NMR spectrum of vinylbenzyloxazoline

Monomer structure was also confirmed by gas chromatography.

Reaction of vinyl benzyloxazoline with ABS.

The reaction of ABS with vinylbenzyloxazoline (molar content oxazoline in ABS was 5mol %) was initiated with dicumylperoxide (5‰). The reaction was carried out in a melt mixer (Haake Rheomix 600) equiped with a mixing chamber of 50 cm^3 and a two counterrotating sigma rotors. The rotor speed was 16 rpm and the set temperature 160°C (because of to viscous dissipation the real melt temperature ranged from 165°C to 170°C), the grafting time is 10 min and 20 min in a second experiment. The ABS macroradicals can be formed in the reaction of butadiene with the radical initiator. Then, vinylbenzyloxazoline is added to ABS macroradicals.

The grafting mechanism is not well defined. It's more probable that the radicals obtained from the decomposition of dicumylperoxide react with hydrogen from the allylic position, and in this position the monomer vinylbenzyloxazoline will react.

The homopolymer of vinylbenzyloxazoline was removed by extraction with ethanol.

Then the sample was dried to constant mass.

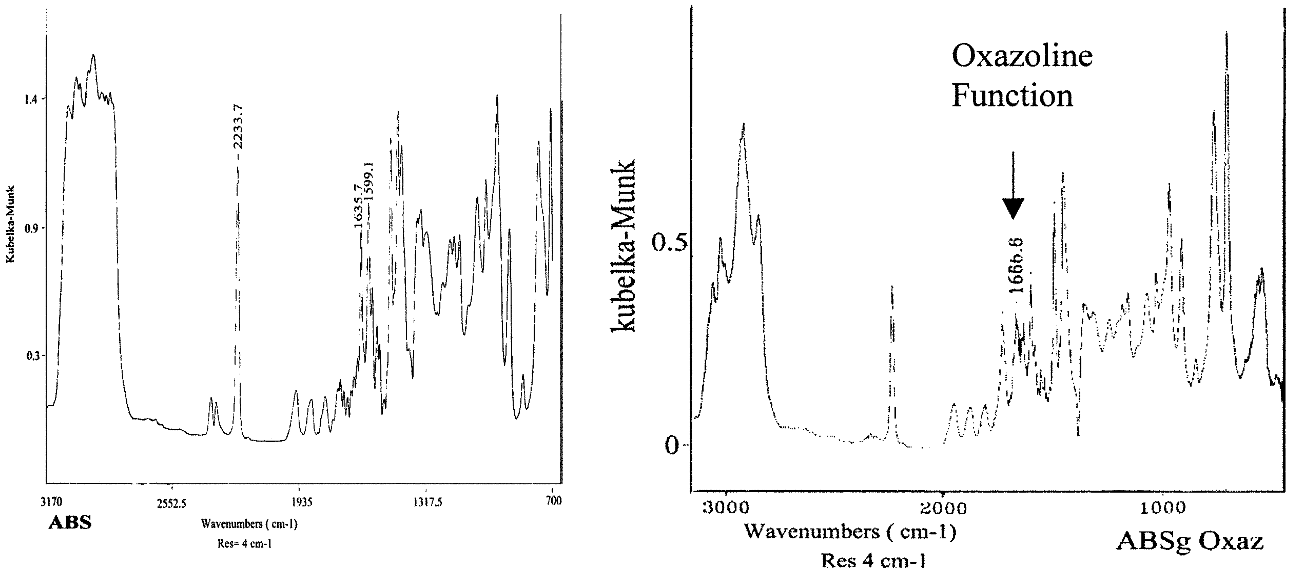
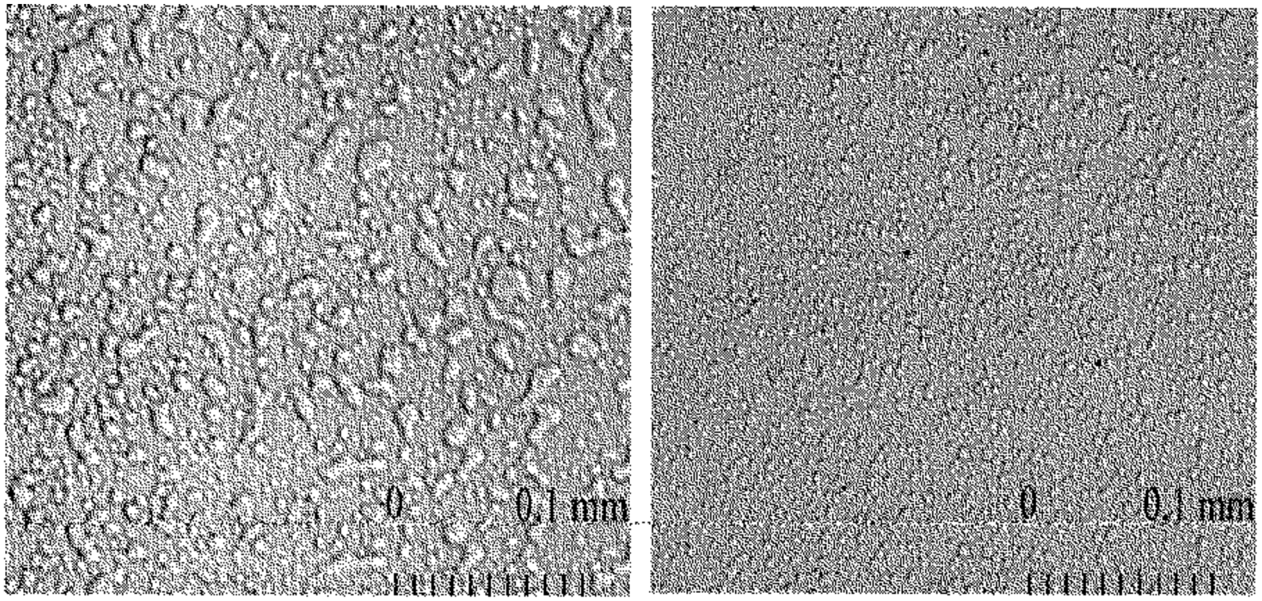


Figure 2 : Comparison of IR spectra of ABS and ABSg oxazoline (ABSg Oxaz) polymers

The principal peaks at 2233.7 cm^{-1} (CN) and 1599 cm^{-1} (aromatic) representing the skeleton of ABS were identified. The peak at 1666 cm^{-1} was attributed to CN stretching band of oxazoline (Figure 2).

The morphological structures of the blends (weight percent :15% ABS, 5% ABSg Oxaz, 80% PA6) were studied by using a LEICA DM LSP transmission microscope. The morphology was revealed by examining sample after heating on Mettler thermosystem FP 900 at 250°C (speed 20°C/min). The addition of the oxazoline functionality to the ABS polymer causes significant changes in the morphology of ABS/PA blends, as illustrated by micrographs shown in figure 3. Quantitative image analysis indicates that the average size of the dispersed particles in the ABS/ABS-ox/PA blend is smaller than the average size of the dispersed particles in the unreactive ABS/PA blend. This represents a proof that chemical reactions have occurred between oxazoline groups in the ABS matrix with the carboxylic acid or amine functions of PA. More extensive investigation are required by mechanical properties study to draw a definitive conclusion on the effectiveness of oxazoline grafted polymers in reactive compatibilization of polymer blends.
The studies of mechanical properties are in progress.



a) b)

Figure 3:Morphology of a) ABS/PA blend and b) ABS/ ABS-ox /PA blend

Conclusion:

The main objective of this paper is to show that vinylbenzyl oxazoline monomer plays an important role in compatibilization of immiscible polymer blends.
Monomer with oxazoline groups has been synthesized in two steps by nucleophilic substitution reaction of chlorine atom of vinylbenzylchloride. The monomer has been characterized by ^{1}H, ^{13}C NMR and IR. Incorporation of vinylbenzyloxazoline into ABS chains facilitated the in situ formation of ABS- ox/ PA copolymers by reaction between oxazoline and PA end groups resulting in desirable modifications to blend properties.
The addition of vinylbenzyl oxazoline by grafting onto ABS polymer by free radical initiation reaction causes significant changes in the morphology of ABS/PA blends.

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