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Functional Polymers and Sequential Copolymers by Phase Transfer Catalysis.

12. Functional Polymers Containing 2-(p-phenoxy)-2-oxazoline Pendant Groups

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SUMMARY

Two new synthetic methods for the preparation of functional polymers containing 2-oxazoline pendant groups are presented. The first one consists on the phase transfer catalyzed etherification of 2-(p-hydroxyphenyl)-2-oxazoline with a mixture of m- and p-chloromethylstyrene to provide, after separation, m- and p-vinylbenzyl ethers of 2-(p-hydroxyphenyl)-2-oxazoline. Both monomers can be polymerized by a radical mechanism to provide polystyrene containing 2-oxazoline pendant groups. The second method represents a phase transfer catalyzed etherification of a poly(2,6-dimethyl-1,4-phenylene oxide) containing pendant bromomethyl groups with 2-(p-hydroxyphenyl)-2-oxazoline. Incomplete etherification of the bromobenzyl groups in this case, leads to the first example of a functional polymer containing not only cationically polymerizable heterocycles, but also their own cationic initiator as pendant groups.

INTRODUCTION

In a previous paper from this series we presented two synthetic avenues for the preparation of α,ω-di 2-(p-phenoxy)-2-oxazoline oligomers (1). The first one, entails the phase transfer catalyzed etherification of an α,ω-di(electrophilic) oligomer with 2-(p-hydroxyphenyl)-2-oxazoline. The second consists of either the phase transfer catalyzed chain extension of an α,ω-di (phenol) oligomer with CH_2Cl_2, or the polyetherification of a bisphenol with CH_2Cl_2 both in the presence of 2-(p-hydroxyphenyl)-2-oxazoline.

Functional polymers containing pendant 2-oxazoline groups have been previously obtained by the radical polymerization of 2-isopropenyl-2-oxazoline (2) and 2-vinyl-2-oxazoline (3).

The goal of this paper is to present two new avenues for the synthesis of functional polymers containing pendant 2-oxazoline groups. The first, concerns the synthesis of m- and p-vinylbenzyl ethers of 2-(p-hydroxyphenyl)-2-oxazoline, followed by their radical polymerization. The second, utilizes the phase transfer catalyzed etherification of chloromethylated or bromomethylated polyaromatics with 2-(p-hydroxyphenyl)-2-oxazoline. The example presented in this paper refers to the etherification of a radical brominated poly(2,6-dimethyl-1,4-phenylene oxide).

EXPERIMENTAL

A. Materials

A commercial sample of a mixture of m- and p-chloromethylstyrene (ClMSt, 60% m, 40% p) kindly provided by Dow Chemical Co., was distilled under vacuum in the presence of hydroquinone. A sample of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (Aldrich) was purified by precipitation with methanol from chloroform solution. $\bar{M}n$=19,000, $\bar{M}w$=49,000. All the other reagents (Aldrich) were used as received.

B. Techniques

200 MHz ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer. All spectra were obtained in $CDCl_3$, CCl_4 , or DMSO-d_6 solutions with TMS as internal standard.

C. Synthesis of 2-(p-hydroxyphenyl)-2-oxazoline

This monomer was prepared by a method reported in the literature for the synthesis of 2-(o-hydroxyphenyl)-2-oxazoline (4), and several particularities of its synthesis were presented previously (1). After two recrystallizations from acetone it showed a mp=194-195°C (lit. 4, 194-195°C). ^{1}H-NMR (DMSO-d_6): 4.2ppm (m, 4H, $-C\underline{H}_2-C\underline{H}_2-$), 6.9ppm (d, 2 aromatic H, meta to -OH), 7.8 ppm (d, 2 aromatic protons, ortho to -OH).

D. Synthesis of m- and p-vinylbenzyl ethers of 2-(p-hydroxyphenyl)-2-oxazoline

To a stirring solution of 5g (30.68 mmole) of 2-(p-hydroxyphenyl)-2-oxazoline in 100ml THF, 50ml of 50% aqueous NaOH solution were added. The sodium salt of 2-(p-hydroxyphenyl)-2-oxazoline precipitated from the organic phase and did not dissolve in the aqueous phase due to the high concentration of NaOH (salting out effect). Tetrabutyl ammonium hydrogen sulfate (TBAH) (2.08g, 6.14mmole) and 30ml of water were added to the reaction mixture, and it returned to a two phase system. A mixture of m- and p-chloromethylstyrene (60% m, 40% p) was then added to the reaction mixture which was stirred for 10hr at room temperature. The organic layer was separated from the aqueous NaOH solution and dried over Na_2SO_4. After filtration, the THF was evaporated on a rotovapor at room temperature and the resulting solid was stirred with 30ml of methanol. The p-vinylbenzyl ether of 2-(p-hydroxyphenyl)-2-oxazoline (insoluble in this amount of methanol) was separated by filtration. The methanolic solution was allowed to stand at 10°C overnight and another quantity of the p-isomer crystallized. These two fractions of the p-isomer were recrystallized from methanol giving 2.2g (65%) of white crystals with mp=137-138°C. Its 200 MHz ^{1}H-NMR spectrum is presented in Fig.1. Part of the methanol solution containing the m-isomer was evaporated, and the m-vinylbenzyl ether of 2-(p-hydroxyphenyl)-2-oxazoline (still containing some p-isomer) crystallized as white crystals. Yield, 5.9g (123%), mp=95-96°C. The overal yield of both m- and p-vinylbenzyl ethers of 2-(p-hydroxyphenyl) -2-oxazoline was 8.1g (93%). The 200 MHz ^{1}H-NMR spectrum of the m-isomer is shown in Fig. 2.

E. Radical polymerization of p-vinylbenzyl ether of 2-(p-hydroxyphenyl)-2-oxazoline

The p-vinylbenzyl ether of 2-(p-hydroxyphenyl)-2-oxazoline (0.4g), AIBN (0.004g) and 4ml dioxane (dried over sodium and distilled under argon) were sealed under argon in a polymerization tube. After 12hr heating at 60°C, the reaction mixture was precipitated into methanol. The product was filtered and reprecipitated with methanol from THF solution. Conversion, 89%. Fig. 3 presents the H-NMR spectrum of the obtained polymer.

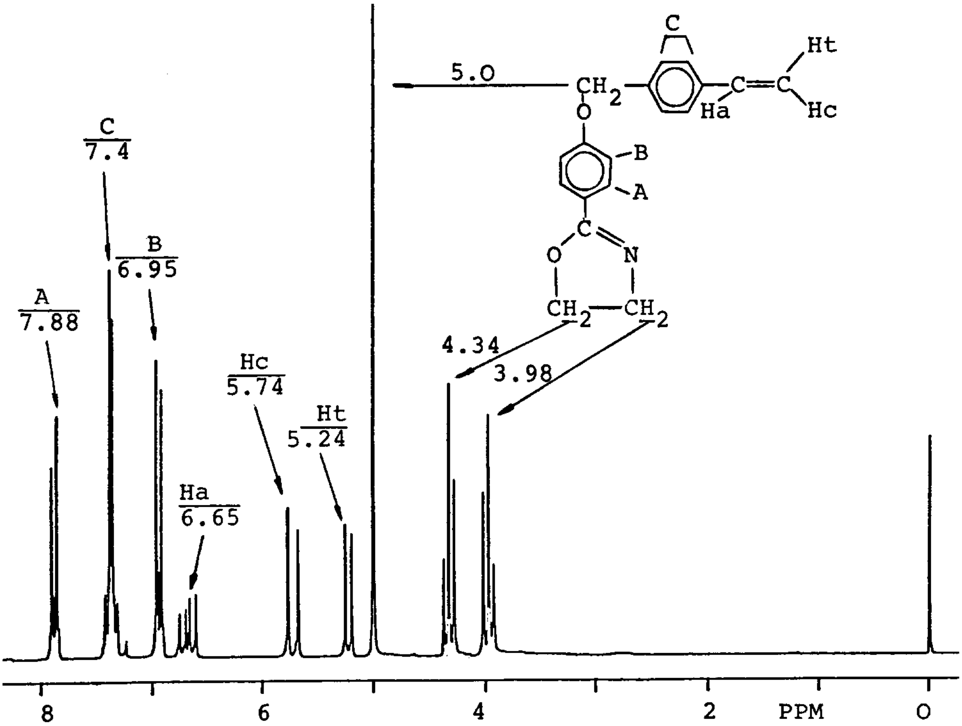


Figure 1: ^{1}H-NMR spectrum ($CDCl_3$) of the p-vinylbenzyl ether of 2-(p-hydroxyphenyl)-2-oxazoline

F. Radical bromination of poly(2,6-dimethyl-1,4-phenylene oxide)

A solution of bromine (1.3ml, 25mmole) in 1,1,2,2-tetrachloroethane (TCE) (250ml) was added dropwise to a boiling solution of poly(2,6-dimethyl-1,4-phenylene oxide) (24g, 0.2mole in 1000ml TCE) and refluxed for 1.5hr. The resulting polymer was precipitated with methanol (1.200ml) and purified by reprecipitation from chloroform solution with methanol. The degree of bromination determined by comparing the area of the signal at 4.3ppm ($-CH_2Br$) with the area of the signal at 2.1ppm ($-CH_3$) was 0.14 bromomethyl groups per PPO structural unit (Fig.4).

G. Synthesis of PPO containing pendant 2-(p-phenoxy)-2-oxazoline groups

To a stirring solution of 2-(p-hydroxyphenyl)-2-oxazoline (0.2575g, 1.58mmole) in 30ml THF, 5ml of 50% aqueous NaOH were added. The sodium salt of the 2-(p-hydroxyphenyl)-2-oxazoline precipitated. After the addition of 0.53g (1.58mmole) TBAH and 5ml of water, the reaction mixture returned to a two phase system. The brominated PPO (0.3g, 0.316mmole) was added to the reaction mixture which was then stirred for 12hr at room temperature. The organic layer was separated, and the polymer precipitated with methanol. Two more purifications were performed by precipitating the modified PPO with methanol from chloroform solution. The 200 MHz ^{1}H-NMR spectrum of the PPO containing 2-oxazoline pendant groups is presented in Fig. 5.

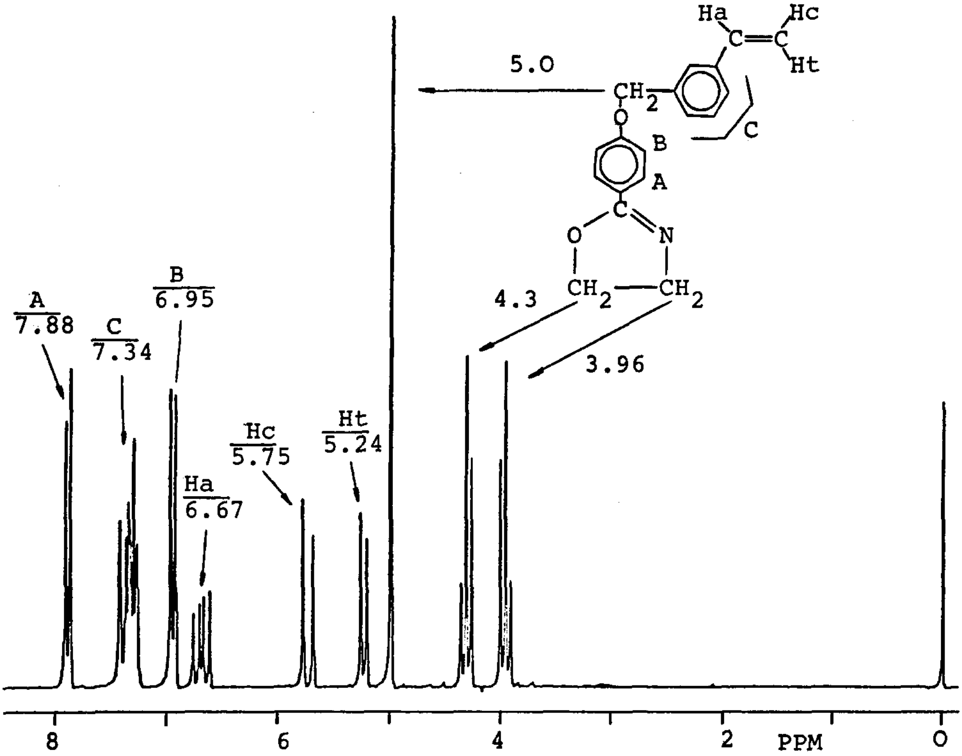


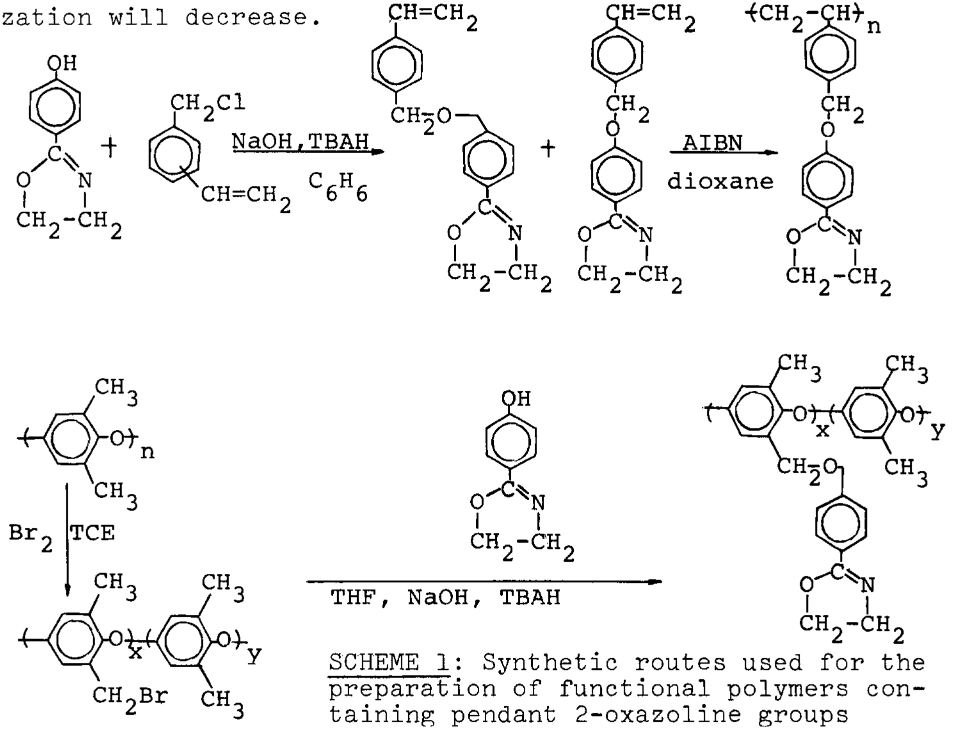
Figure 2: 200 MHz ^{1}H-NMR spectrum ($CDCl_3$) of the m-vinylbenzyl ether of 2-(p-hydroxyphenyl)-2-oxazoline

RESULTS AND DISCUSSION

Functional polymers containing 2-oxazoline groups are interesting starting materials for further functionalization (2), and for the preparation of polymer networks (1). The only available method for the preparation of polymers containing pendant 2-oxazoline groups was through the radical polymerization of 2-vinyl-2-oxazoline and 2-isopropenyl-2-oxazoline (2,3).

Two novel avenues for the preparation of the functional polymers containing pendant 2-(p-phenoxy)-2-oxazoline groups are presented in this paper. These two synthetic routes are outlined in Scheme 1.

Recently, 2-(p-hydroxyphenyl)-2-oxazoline became of interest,both for Kobayashi and Saegusa (5,6) and for our research group (1). 2-(p-Hydroxyphenyl)-2-oxazoline reacts with NaOH on heating to provide N-(2-hydroxyethyl)-p-hydroxybenzamide, and with weak electrophilic compounds like benzyl bromide or chloride to provide poly N-(p-hydroxybenzoyl)ethylenimine . Consequently, the etherification of benzyl chloride with the sodium salt of 2-(p-hydroxyphenyl)-2-oxazoline in an aprotic dipolar solvent like DMSO (i.e., conventional reaction conditions) would be accompanied by these two side reactions, even though the nucleophilicity of the phenolate is higher than that of the oxazoline ring. A phase transfer catalyzed etherification of 2-(p-hydroxyphenyl)-2-oxazoline with benzyl bromide or chloride derivatives performed under the reaction conditions presented in the experimental part, avoids these side reactions for the following reasons. First, the etherification is performed at room temperature, and consequently NaOH will not hydrolize the cyclic imino ether ring during the time it is present in the aqueous phase. Secondly, the ammonium phenolate is dissolved in a nonpolar aprotic solvent, and consequently is not solvated and very reactive. Because the etherification is carried out in a nonpolar aprotic solvent, the rate of etherification will increase while the rate of initiation of the oxazoline polymerization will decrease.



SCHEME 1: Synthetic routes used for the preparation of functional polymers containing pendant 2-oxazoline groups

The phase transfer catalyzed etherification of 2-(p-hydroxyphenyl)-2-oxazoline with chloromethylstyrene takes place quantitatively at room temperature. The m- and p-vinylbenzyl ethers of 2-(p-hydroxyphenyl)-2-oxazoline can be separated by selective crystallization from methanol. The p-isomer can be obtained in a pure form by recrystallization. The aromatic region of the NMR spectrum of the p-vinylbenzyl residue (signal C at 7.4ppm) shows an AA'BB' pattern which confirms the purity of the p-isomer (Fig. 1). The NMR spectrum of the m-isomer is presented in Fig. 2. The signal C at 7.34ppm presents a supperposition of an AA'BB' (due to the p-isomer) with a complex pattern for the m-compound. No further attempts were made to remove completely the p-isomer from the m-one. The radical polymerization of the p- or m-vinylbenzyl ethers of the 2-(p-hydroxyphenyl)-2-oxazoline occurs quantitatively at 60°C. After the polymerization, the pendant 2-oxazoline ring is preserved as we had expected (Fig. 3).

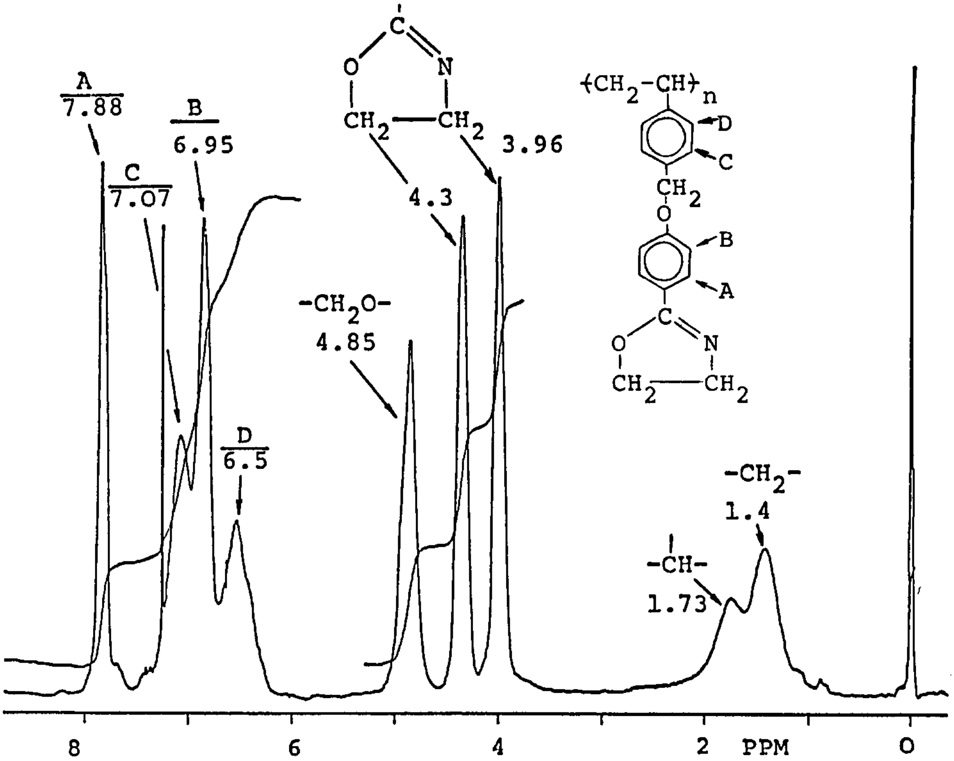


Figure 3: 200 MHz ^{1}H-NMR spectrum ($CDCl_3$) of the polymer prepared by radical polymerization of the p-vinylbenzyl ether of 2-(p-hydroxyphenyl)-2-oxazoline

As an example for the etherification of a chloromethylated or bromomethylated polymer with 2-(p-hydroxyphenyl)-2-oxazoline we have selected the PPO backbone. The bromination of PPO at room temperature occurs through an electrophilic mechanism, incorporating bromine groups into the aromatic ring. On the other hand, the same reaction at high temperature occurs through a radical mechanism, providing bromomethyl groups (7-10). A PPO containing 0.14 $-CH_2Br$ groups per structural unit was prepared and its NMR spectrum is presented in Fig. 4.

The ^{1}H-NMR spectrum of the PPO etherified with 2-(p-hydroxyphenyl)-2-oxazoline is shown in Fig. 5. The first important remark is that the parent signal from 4.3ppm ($-CH_2Br$, Fig. 4) was shifted to 5.0ppm ($-CH_2O-$, Fig.5) due to the etherification. The resonances specific to the 2-oxazoline ring are present in this figure. It is interesting to observe that the triplet at 4.34ppm is not symmetric in contrast to the triplet at 3.98ppm. This is because some unreacted $-CH_2Br$ groups are still left in the etherified PPO. No further attempts were made to consume all the $-CH_2Br$ groups through etherification.

It should be mentioned at this point that the modified PPO

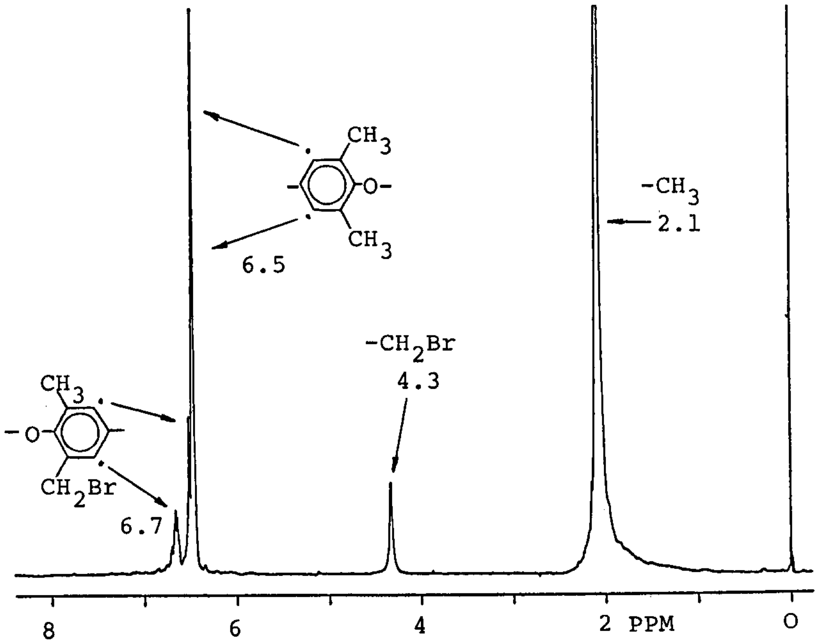


Figure 4: 200 MHz ^{1}H-NMR spectrum (CCl_4) of the brominated poly(2,6-dimethyl-1,4-phenylene oxide)

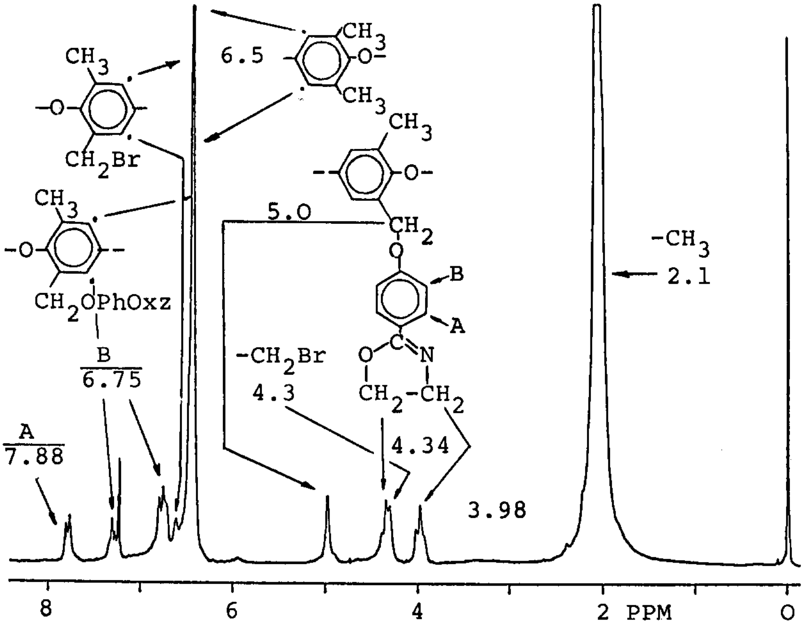


Figure 5: 200 MHz ^{1}H-NMR spectrum ($CDCl_3$) of the PPO containing 2-oxazoline pendant groups

prepared in this paper could be thermally reactive above its Tg, because the unetherified $-CH_2Br$ groups can initiate the ring opening polymerization of the 2-oxazoline groups. Thus, this seems to be the first example in which a cationically polymerizable heterocyclic monomer and its cationic initiator are attached to the same polymer backbone. Further research on this new class of thermally stable functional polymers containing cyclic imino ethers is in progress, and will be reported soon.

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