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# Synthesis of hydroxy-terminated polytetrahydrofuran by photoinduced process

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## Summary

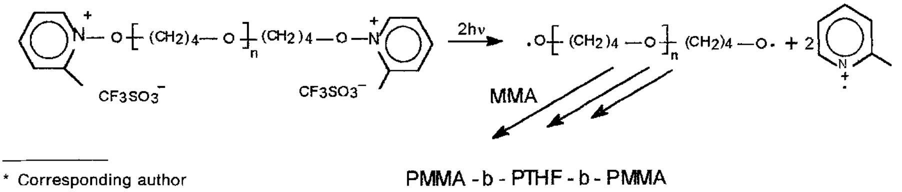
This paper describes the preparation of hydroxy-functional telechelics by photoinduced decomposition of polytetrahydrofuran possessing terminal pyridinium ions in THF solution. Hydroxyl functionality was evidenced by end capping and polycondensation with isocyanates.

## Introduction

Polymers with hydroxy, carboxyl, amine functions (telechelics) are of increasing interest due to their use as crosslinker, chain extender and precursors for block and graft copolymers [1-5]. These telechelics can be obtained by a variety of procedure. The most convenient way to prepare telechelics is the termination of living polymerization with appropriate reagents. For instance hydroxy functional polytetrahydrofuran (PTHF) was obtained by deactivation of living polymerization of tetrahydofuran with excess water [6].

Recently, we have described [7] a convenient and simple synthetic method for the preparation of amino-functional telechelics by a photoinduced process. Amino end groups were introduced effectively when polymers bearing acyloxyimino groups irradiated in the presence of benzophenone followed by hydrolysis.

More recently we have prepared [8] PTHF-pyridinium salts by pyridinium N-oxide deactivation as precursors for block copolymers. Upon direct and sensitized irradiation of these photoactive PTHFs alkoxy radicals at both chain ends capable of initiating the radical polymerization of methyl methacrylate. In this way, triblock copolymers were formed.



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The present study was primarly conducted to uncover whether photolysis of the polymers terminated by p-phenyl pyridinium ions can yield hydroxy end functional polymers.

## Experimental

### Materials

p-Phenylpyridine N-oxide, phenyl isocyanate, toluene diisocyanate and triflic anhydride (Aldrich), and dibutyltin dilaurate (Alfa) were used as receieved. Monomer tetrahydofuran (THF) and solvents were purified by conventional drying and distillation procedures.

### Synthesis of p-phenyl pyridinium ion terminated polytetrahydrofuran ($PP^+$-PTHF)

A three-necked flask equipped with an argon inlet and a rubber septum was connected to a vacuum line. The flask was dried at 130 °C under vacuum. After cooling to room temperature, THF (50 ml) was distilled into the flask. The flask was then disconnected under nitrogen and placed into a thermostatically controlled bath. The triflic anhydride (0.104 ml, 0.62 mmol) was added under stirring at 25 °C. After 35 minutes an aliquot sample was removed for g.p.c. characterization by a syringe and the polymerization was terminated by the addition of methanol. The remaining part of the living polymerization was terminated by the addition of a solution of p-phenylpyridine N-oxide (12.3 mmol) in 10 ml dichloromethane. The polymerization mixture was stirred for 15 min at 25 °C, poured into methanol and cooled to -20 °C. Finally, the precipitated polymer was filtered off and dried in vacuo.

### Photolysis

The polymer ($PP^+$-THF) (0.100 g) was dissolved in 5 ml THF and placed in a quartz tube. The tube was degassed under nitrogen prior to irradiation at 320 nm with the aid of Amco photoreactor equipped with a Xenon lamp and a monochromator. At the end of 2 h irradiation polymer was precipated as described above.

### Reaction with Isocyanates

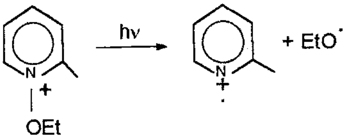
THF solution of hydroxyl terminated polymer containing dibutyltin dilaurate as catalyst was reacted with toluendiisocyanate or phenyl isocyanate under nitrogen for overnight at room temperature. At the end of reaction, polymer was precipitated into cold methanol and dried for characterization.

### Analysis

IR spectra were recorded on a Jasco FT-IR 5300 spectrometer. UV spectra were taken by using Perkin-Elmer Lambda 2 spectrophotometer. Molecular weight of polymers were determined from g.p.c. chromatograms according to polystyrene standards using Knauer M-64 type instrument and THF as the eluent at a folw rate of 1 ml min$^{-1}$.

## Results and Discussion

During our investigation on photoinitiated cationic polymerization using pyridinium salts [9] it soon became evident that ethanol is formed upon photolysis of pyridinium salt in hydrogen donor solvents such as THF according to the following sequence of reactions.



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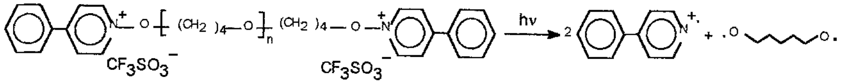
(3)

It seemed therefore appropriate to use alkoxy pyridinium terminated polymers as precursors for hydroxy-functional polymers. For this purpose PP$^+$-PTHF was prepared by living polymerization of THF initiated by triflic anhydride as bifunctional initiator as described in the experimental section. Irradiation of this polymer in THF at 320 nm resulted in the shift of the characteristic pyridinium ion absorbtion band ( max = 300nm) to shorter wavelength (Figure 1 a and b) and in the formation of hydroxyl end groups. The observed blue-shift is due to the absorbance of p-phenylpyridine formed according to the reactions 4-6. Indeed, this new band dissapeared when the polymer was reprecipated into methanol (Figure 1c).



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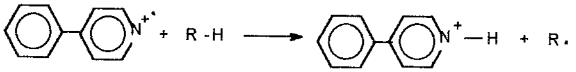

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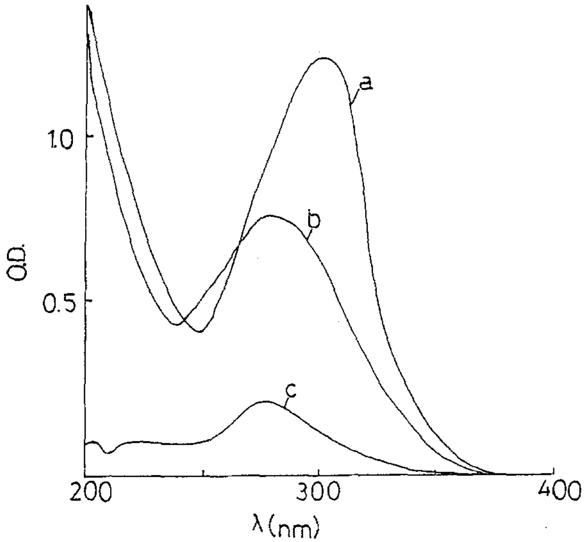


Figure 1. UV spectra of PP+-PTHF (a) before (b) after irradiation at 320 nm in THF and (c) after precipitation into methanol.

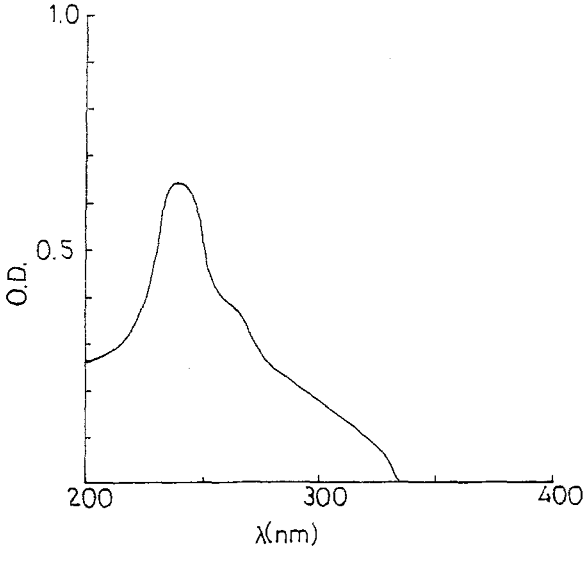
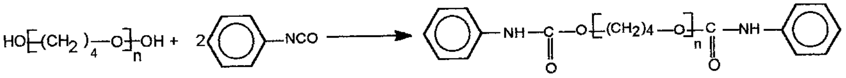


Figure 2. UV spectrum PTHF with a phenylcarbamate end groups

Confirmation of the presence hydroxyl groups was obtained from the characterization of PTHF end-capped with phenylcarbamate groups. Hydroxyl chain ends were converted into phenylcarbamate by treatment with phenylisocynate in the presence of catalytic amount of dibutyltin dilaurate.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The phenylcarbamate end-groups exhibit a strong absorption at 235 nm (Figure 2). Knowing the extinction coefficient ($\varepsilon_{235}$ = 15600) [10] and assuming that each polymer chain contains two phenylcarbamate groups, the value of Mn can be calculated. The data obtained on chracterization of PTHF with phenylurethane end groups are collected in Table 1. As can be seen, there is a remarkable agreement between the number-average molecular weights obtained by both methods. This clearly indicates that polymer chains carry two hydroxyl functions after the photolysis. Even more convincing evidence for the presence of the hydroxyl functionality was obtained from the <u>in situ</u> polyurethane formation upon photolysis of $PP^+$-PTHF at 320 nm in THF containing toluen diisocyanate and catalyst. As the irradiation proceeds an insoluble product is formed. The IR spectrum of the insoluble polyurethane formed possesses urethane carbonyl bands at 1730 and 1540 $cm^{-1}$ in addition to characteristic band of PTHF at 1100 $cm^{-1}$. The cross-linking behavior may be due to the formation of allophanate and of biuret linkages [11] from an isocyanate function and already existing urethane link since hydroxyl functions are available only when the pyridinium ions are decomposed by light.

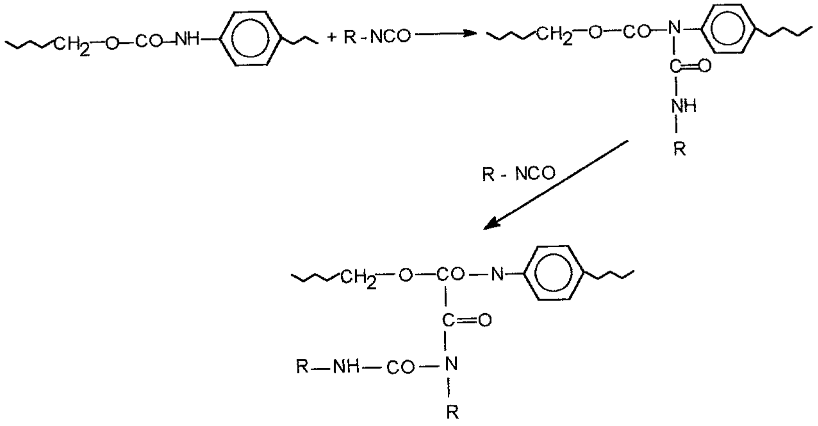
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Table 1
Number average molecular weights of polytetrahydofuran

| Method of Determination | Mn |
|---|---|
| GPC | 12600 |
| UV(phenyl carbamate) | 12000 |

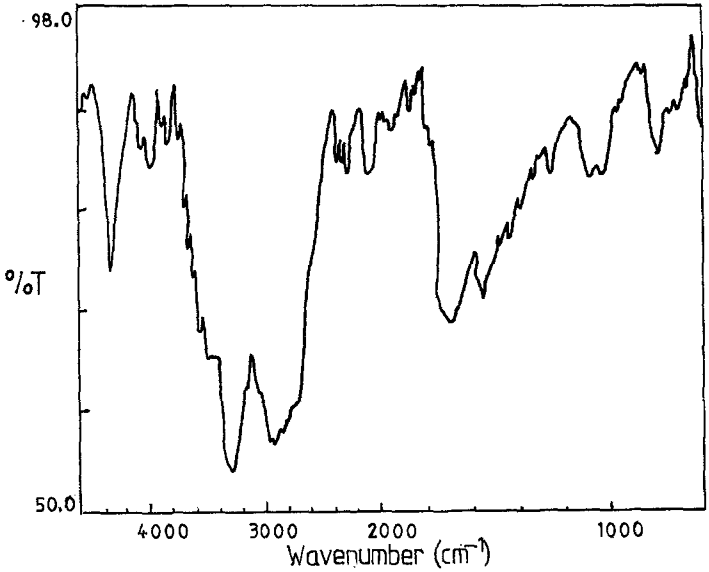

Figure 3. IR spectrum of the cross-linked polyurethane, produced by the photolysis of PP$^+$-PTHF and toluene diisocyanate in THF at 320 nm, on KBr disc.

In conclusion it has been shown that alkoxy pyridinium terminated polymers are suitable to produce hydroxy-functional telechelics via photoinduced process. This process is particularly atractive in applications where hydroxyl groups are needed to be protected. Further works on the application of resulting polymers in other reactions as well as the preparation of side chain alkoxy pyridinium salts as precursors for vinyl polymers with pendant hydroxyl groups are now in progress.

## Acknowledgement

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