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PHOTOACTIVE POLYTETRAHYDROFURAN MACROINIMER

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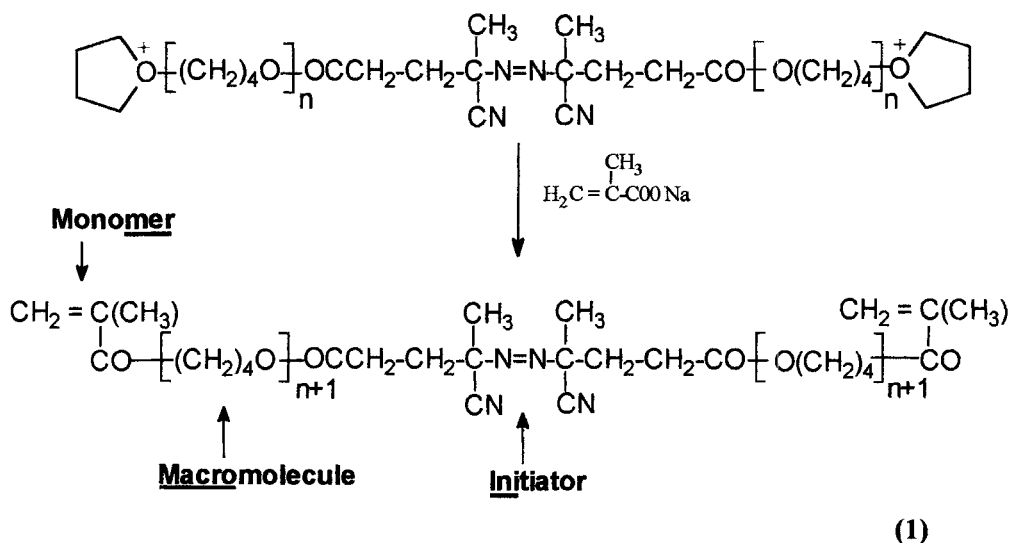
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ABSTRACT

Photoactive polytetrahydrofuran macroinimers were prepared by the polymerization of tetrahydrofuran initiated by unsaturated oxocarbenium salt and subsequent termination by N-oxides. These polymers underwent self-crosslinking upon direct and anthracene sensitized irradiation in dichloromethane solutions.

INTRODUCTION

Macroinimers are polymer molecules carrying both initiator and polymerizable unsaturated end functionalities¹. We have recently synthesized a polytetrahydrofuran macroinimer by terminating living polytetrahydrofuran, initiated by azo-oxocarbenium initiators, with the sodium derivative of methacrylic acid².



These macroinimers were used for thermal curing of formulations containing acrylate monomers without requirement of low-molar mass free radical initiators. Moreover, the use of macroinimers offers better final properties of the cured products since the soft polytetrahydrofuran (PTHF) segment is chemically incorporated in to the polymer network.

Polymeric photoinitiators capable of initiating a polymerization are of interest in various UV curing applications³. The potential advantages of these initiators include low volatility, low migration, good compatibility and reduced yellowing properties of the cured products⁴. Polymerizable photoinitiators are also highly reactive photoinitiators and copolymerize during the process⁵.

Hizal et al⁶ recently prepared triblock copolymers by the photolysis of pyridinium ion terminated polytetrahydrofuran in the presence of methyl methacrylate. The photoactive N-alkoxy pyridinium end groups were quantitatively introduced to polymers upon deactivation of living polymerization of THF by pyridine N-oxides. In the present work, we have described the synthesis of photoactive macroinimer possessing polymerizable methacrylate and pyridinium salt moieties separated by a PTHF spacer by using the similar approach i.e. termination of living polymerization of THF by N-oxides. As shown below, synthetic procedure enabled us to adjust the absorption characteristic of the initiator site of the macroinimer.

EXPERIMENTAL

Materials: THF was dried over potassium hydroxide, distilled over sodium wire and finally distilled over sodium/benzophenone ketyl prior to use.

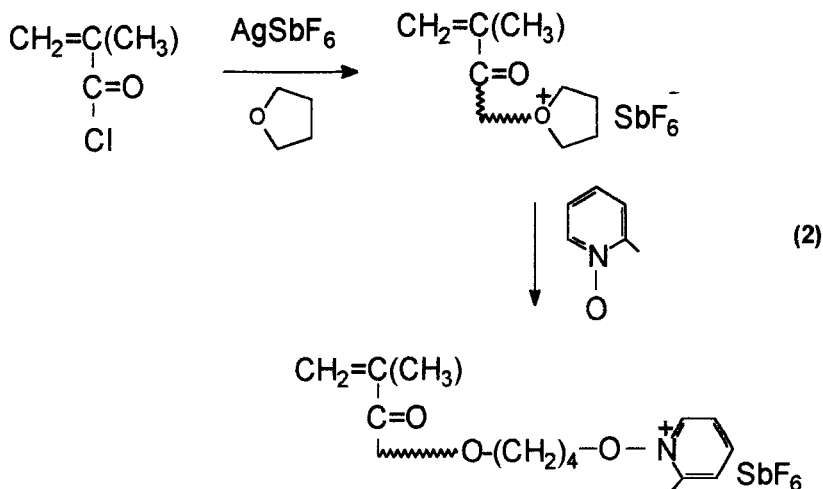
Methacryloyl chloride was distilled over phosphorous pentoxide. Silver hexafluoro antimonate (Aldrich) was used as received. The N-oxides (2-picoline), isoquinoline and 4-phenyl pyridine) (Aldrich) were used as received. Dichloromethane was distilled over CaH_2 .

Preparation of Polytetrahydrofuran Macroinimers: A schlenk tube equipped with a two-way stopcock and a stir bar was heated in vacuo with a heat gun and flushed with dry nitrogen. Freshly distilled THF was put into the tube and then disconnected under nitrogen and placed into a thermostatically controlled oven at a given temperature. The initiation of polymerization was induced by successive addition of known amount of stock solutions of methacryloyl chloride and silver salt in THF so as to adjust the final initiator concentration. After a given time the living PTHF was terminated by the addition of a solution of an N-oxide (two mol equivalent of the initiator concentration) in dichloromethane. The polymerization mixture was stirred for 15 min and poured into methanol cooled to -20°C finally, the precipitated polymer was filtered off and dried in vacuo.

Photocrosslinking: Dichloromethane solutions containing polytetrahydrofuran macroinimers were irradiated in pyrex tubes in a photoreactor equipped with a monochromator.

RESULTS AND DISCUSSION

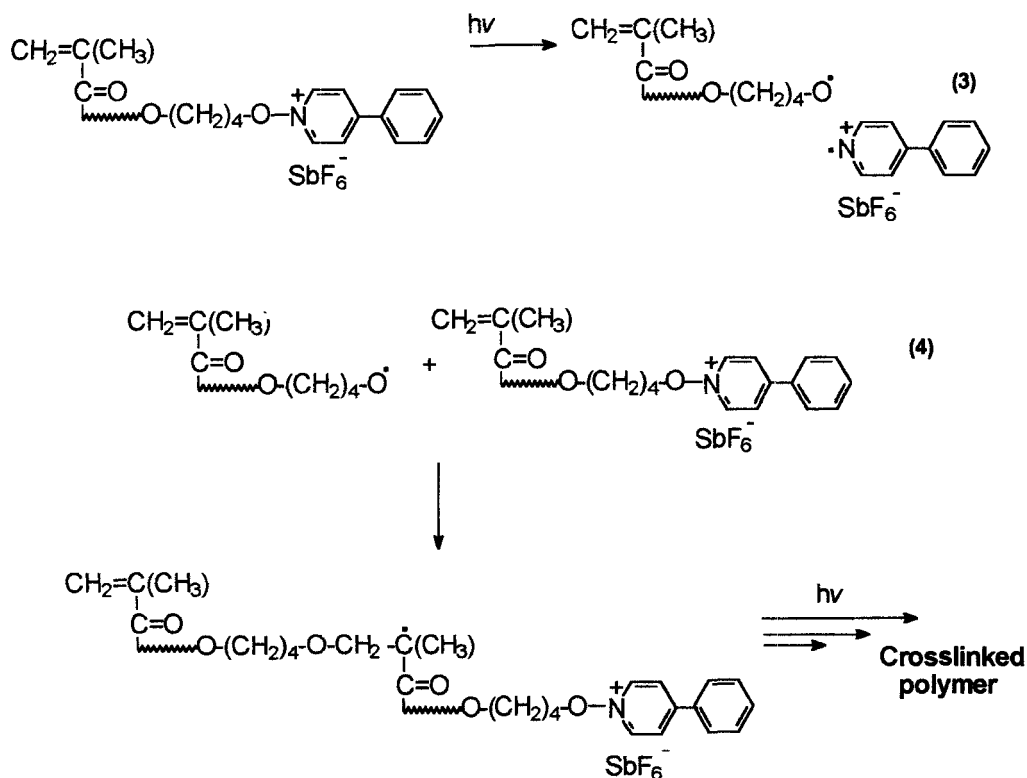
The macroinimers were synthesized essentially by regulating the initiation and termination steps of the cationic polymerization of THF. The overall reaction paths are represented below,



The terminal methacrylic group was introduced in the initiation step. The methacryloyl chloride-silver salt initiating system is known to be fast, quantitative and proceeds via an addition mechanism⁷. Moreover, the methacryloyl group is unaffected by cationic initiators which ensures successful incorporation of the monomer functionality. Typical results are represented in Table 1. Macroinimers have absorption maxima at the same wavelengths of the corresponding low molecular weight pyridinium ion analogues. The structure of the macroinimers was deduced by ¹H-NMR measurements.

In a typical ¹H-NMR spectrum of a PTHF macroinimer (isoquinolinium terminated) (PTHF-2) in addition to the characteristic CH protons of the aromatic ring (7.6-8.5 ppm), vinyl protons (5.7-6.1 ppm) are detected, indicating incorporation of methacrylic and isoquinolinium functionalities.

Due to the bifunctional nature of the macroinimers, they are expected to undergo self-crosslinking upon irradiation. As a crude demonstration, *p*-phenylpyridinium ion terminated PTHF macroinimer (PTHF-1) (100g/l) in dichloromethane was irradiated by monochromatic light at 337nm. Complete gelation occurred after 4h irradiation according to the following reaction.



As has been shown⁸ previously by us, the spectral sensitivity of pyridinium salts may be extended to longer wavelengths with the aid of certain sensitizers.

TABLE 1.
Preparation^a of Photoactive Polytetrahydrofuran Macroinimers

Polym. Time (min)	N-Oxide (mol l ⁻¹)	Conversion (%)	λ (max)	Mn ^b	Code
10	4-phenyl-pyridine N-oxide(2.10 ⁻²)	5.06	310	11000	PTHF-1
20	Isoquinolinium N-oxide(2.10 ⁻²)	7.01	337	16000	PTHF-2
30	2-picoline (2.10 ⁻²)	8.71	270	31000	PTHF-3

^a) Polymerization conditions; Methacryloyl chloride=10⁻² mol l⁻¹, AgSbF₆=10⁻² mol l⁻¹, Temp=20°C

^b) Determined by UV measurements using the value of extinction coefficient of the low molecular weight pyridinium ions.

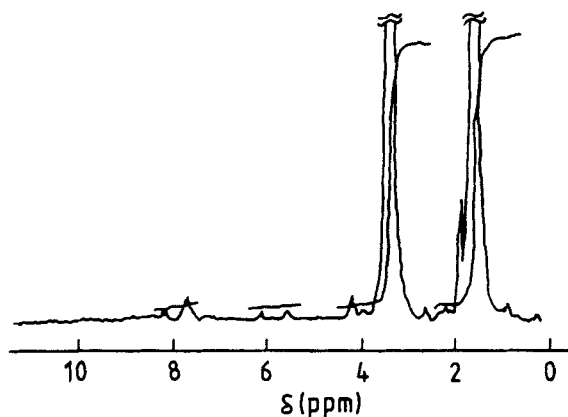
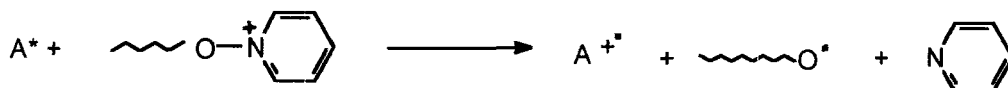


Figure 1. ¹H-NMR spectrum of p-phenyl-pyridinium terminated polytetrahydrofuran macroinimer (PTHF-2) in CDCl₃

Indeed, upon irradiation of a solution containing 2-methyl-pyridinium macroinimer (PTHF-3) and anthracene (A) at 350 nm resulted in crosslinking. In this case macroradicals are formed via electron transfer from the electronically excited sensitizer (anthracene) to terminated pyridinium ion and due to the presence of methacryloyl end groups in the same polymer chain, crosslinking would occur as in the case of direct irradiation.



In addition to their selfcrosslinking ability, photoactive macroinimers may be used as precursors for graft copolymers possessing soft and hard segments in the side chains. In this case, macroinimers should be copolymerized with vinyl monomers thermally by using free radical initiators. Subsequent photolysis in the presence of another monomer would result in the formation of desired graft copolymers. Further studies in this line are in progress and will be published elsewhere.

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