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### The Synthesis and Utilization of a Polymeric Photo-Sensitizer Based on Poly(N-Tert. Butyliminoethylene)

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THE SYNTHESIS AND UTILIZATION OF A POLYMERIC PHOTO-SENSITIZER BASED ON POLY(N-TERT. BUTYLIMINOETHYLENE)

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ABSTRACT

$\alpha, \omega$ -dianthryl-terminated poly(N-tert.butylimino-ethylene) [poly(TBIE)] has been synthesized by end capping of bifunctionally living poly(TBIE) using 9(amino-methyl)anthracene (AMA) as a capping agent. It can be used as a polymeric photosensitizer for the photochemical conversion of tachysterol compounds into previtamin D<sub>2</sub> and D<sub>3</sub>. The polymeric photosensitizer can be removed from the solution by extraction with aqueous HCl or by precipitation with a polyacid such as poly(acrylic acid).

INTRODUCTION

Photosensitizers are used in the photochemical conversion of tachysterol<sub>2</sub> and tachysterol<sub>3</sub> to previtamin D<sub>2</sub> and D<sub>3</sub> respectively<sup>1-3</sup>. However, many of the photosensitizers (e.g. anthracene) have the big disadvantage that they are extremely toxic. Because of the use of the vitamin D compounds for human and veterinary administration, the final product should be absolutely free from sensitizer.

Having taken into account the solubility characteristics of high molecular weight compounds, Slemon<sup>4</sup> has proposed the attachment of the photosensitizer to polymers. Thus, the separation of the polymeric photosensitizer (PPhS) can be easily accomplished by using two different solvent systems: the reaction solvent, in which both the previtamin D reaction product and the PPhS are soluble, and another one in which the previtamin D reaction product is soluble but the PPhS is non-soluble. Although this method allows to efficiently remove the photosensitizer, it demands large quantities of at least two solvents and is therefore inconvenient from the practical point of view.

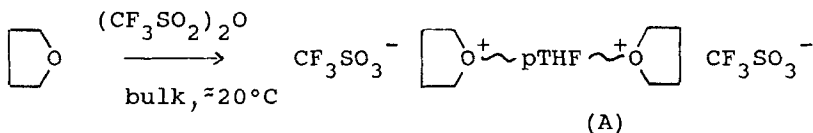
Another approach for the removal of polymer-coupled sensitizers is to use a polymeric acid or base as carrier and to achieve a complete insolubilization by transformation into the corresponding salt. This salt can then be removed either by filtration or by extraction with water.

The present communication deals with the synthesis of poly(N-tert.butyliminoethylene) end-capped with two 9-iminomethyl anthracene groups, the use of this PPhS in the photochemical conversion mentioned above, and its removal from the reaction mixture by treatment with acids.

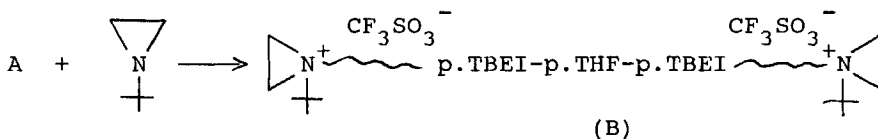
## RESULTS AND DISCUSSION

### Synthesis and characterization of the PPhS

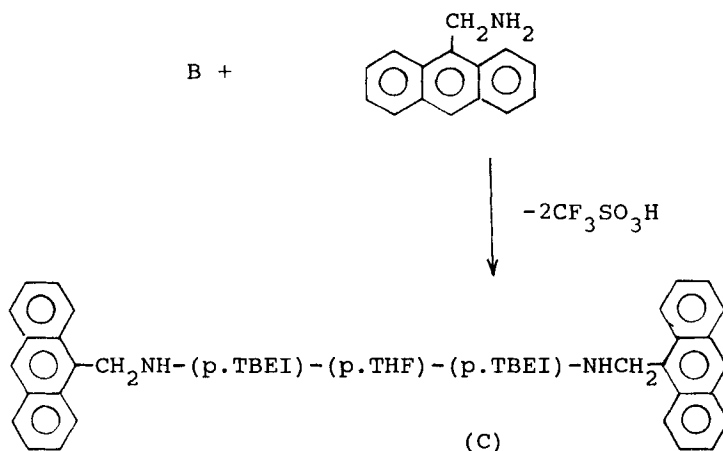
The synthesis of  $\alpha, \omega$ -dianthryl-terminated poly(N-tert.butyliminoethylene) (polyTBIE) is based on end-capping of the bifunctionally living polymerization of N-tert. butylaziridine<sup>5</sup>. The process is made up of two steps. In the first step tetrahydrofuran (THF) is polymerized cationically with triflic anhydride as initiator producing bifunctionally living poly(THF), i.e. with two cyclic oxonium ion end groups (A).



Addition of tert.butylaziridine to the solution of this bifunctional living poly(THF) leads to a bifunctional living poly(TBIE) with an oligomeric polyether segment in the middle.

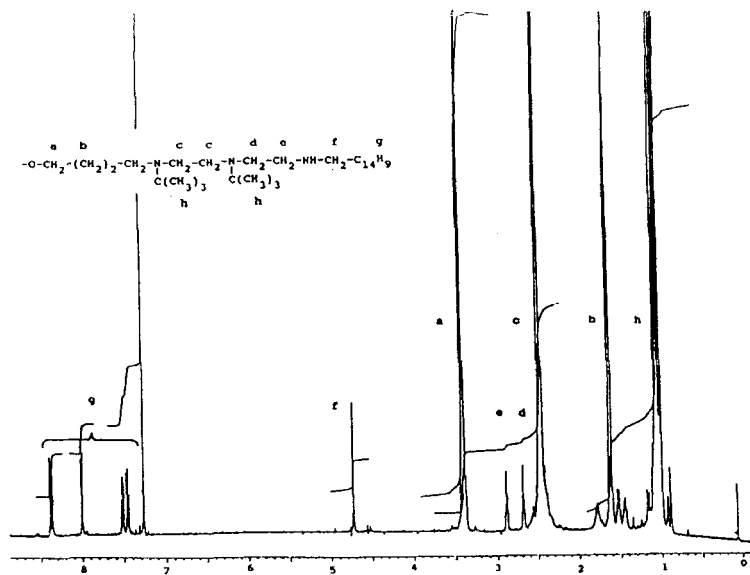


The aziridinium end groups, which are still present at the end of the polymerization due to the highly living character of the polymerization, are opened by 9(amino-methyl)-anthracene (AMA) yielding  $\alpha, \omega$ -dianthryl poly(TBIE) (C).

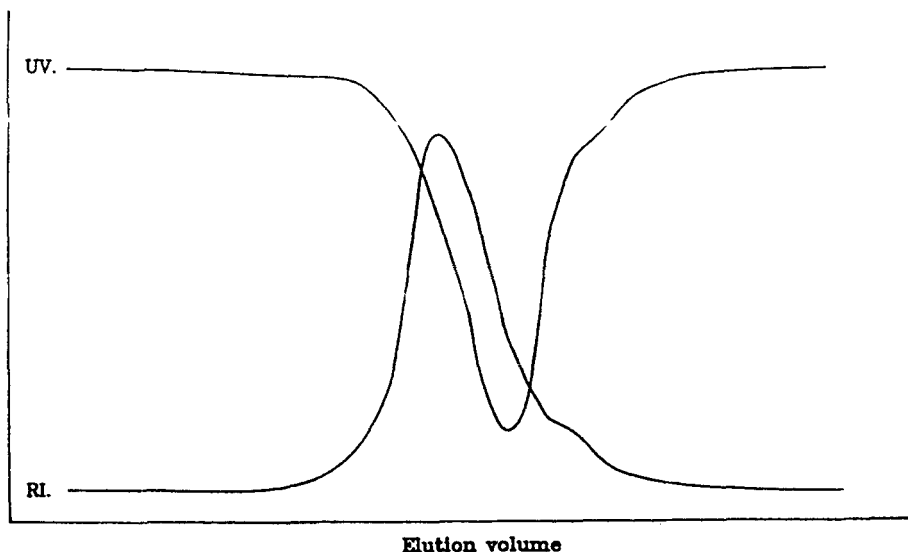


The molecular weight of the central poly(THF) segment in the polymer can be controlled by the choice of the initiator concentration and the degree of conversion of THF on addition of the aziridine. The initiation of the aziridine polymerization by oxonium ions is fast and quantitative and therefore tailor made block-copolymers can be prepared. As an example a PPHS with a total number average molecular weight  $M_n$  4000 (as measured by GPC based on PS standards) with  $M_n$  of poly(THF) central block of 900 and  $M_n$  of both poly(TBEI) blocks 1550, was prepared. The structure of the compound was confirmed by  $^1H$  NMR spectroscopy (Fig. 1). Additionally to signals corresponding to protons of poly(THF)-poly(TBEI) block-copolymer (peaks a=3.4 ppm, b=1.6 ppm, from poly(THF); peaks c=2.45 and h=1.1 ppm from poly(TBEI)) there are signals characteristic for the 9(iminomethyl)anthracene end groups. Signals g at 7.5, 8, and 8.4 ppm are assigned to the protons in anthracene moieties. The signal f at 4.7 ppm is due to the  $CH_2$  protons attached to anthracene and is shifted 0.15 ppm downfield in comparison with the starting AMA. Two triplets, d at 2.7 ppm and e at 2.9 ppm correspond to the two methylene groups of the last TBIE unit bound to the amino group of AMA. They are shifted 0.25 and 0.45 ppm respectively due to the deshielding effect of the anthracene group.

GPC analysis (Fig. 2) shows that the polymer gives a strong response to UV detection. According to UV analysis using the extinction coefficient of anthracene (8000 at 370 nm) this  $\alpha,\omega$ -dianthryl-terminated polymer contains about 80 mg of



**Fig. 1.** 360 MHz  $^1\text{H}$  NMR of  $\alpha,\omega$ -dianthryl-terminated poly(THF)-poly(TBIE) block-copolymer with  $M_n$  of poly(THF) segments 900 and two poly(TBIE) segments each of 1550.



**Fig. 2.** GPC analysis of  $\alpha,\omega$ -dianthryl-terminated poly(THF)-poly(TBIE) block-copolymer (UV detection at 254 nm).

TABLE I

Photochemical transformation of tachysterol in the presence of PPhS<sup>(a)</sup>

irradiation time (min) <sup>(b)</sup>	% previtamin D	% tachysterol
0	0	100
5	26	74
10	50	50
20	92	8
40	98	2

(a) 2.5 g.l<sup>-1</sup> corresponding to 0.2 g.l<sup>-1</sup> of anthracene.  
 (b) solvent MTBE, t : 4°C.

anthracene per gram of PPhS what is consistent with the calculated value (88).

The photochemical reaction in the presence of the new PPhS.

The new PPhS is soluble in tetrahydrofuran, methyl tert.butyl ether, chloroform, benzene and 0.1 N aqueous hydrochloric acid. Irradiation of tachysterol in methyl tert.butyl ether (MTBE) in the presence of PPhS converted the starting material almost completely into previtamin D (Table I).

For comparison, the same reaction was carried out with AMA as photosensitizer. It appeared that with the low molecular weight compound the reaction was approx. four times faster than with the polymeric compound: 93% conversion was reached in 5 min (compared with 20 min for the polymer). Apparently, the energy transfer from the anthracene group to the substrate is hampered by the presence of the bulky polymer substituent.

Removal of the PPhS from organic solution.

After the reaction the PPhS can be removed from the solution by washing with diluted aqueous HCl or by adding a solution of polymeric acid, e.g. poly(acrylic acid) (PAA), in water or in dioxane. PAA forms a poly-electrolyte complex with the amine-containing PPhS which instantaneously precipitates. This is especially convenient when the PAA is dissolved in the same (or a miscible) solvent as the one used for carrying out the reaction so that the introduction of water can be avoi-

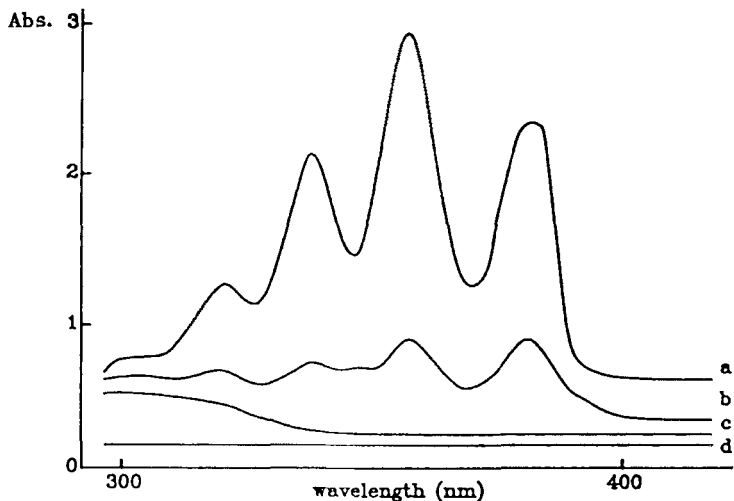


Fig. 3. UV spectra of PPhS in methyl tert.butyl ether (a): before extraction (conc. of polymer 1 g/l), (b) and (c): after the first and the second extraction by 1 wt. % aqueous solution of PAA, (d): after extraction by 0.1N HCl aq.

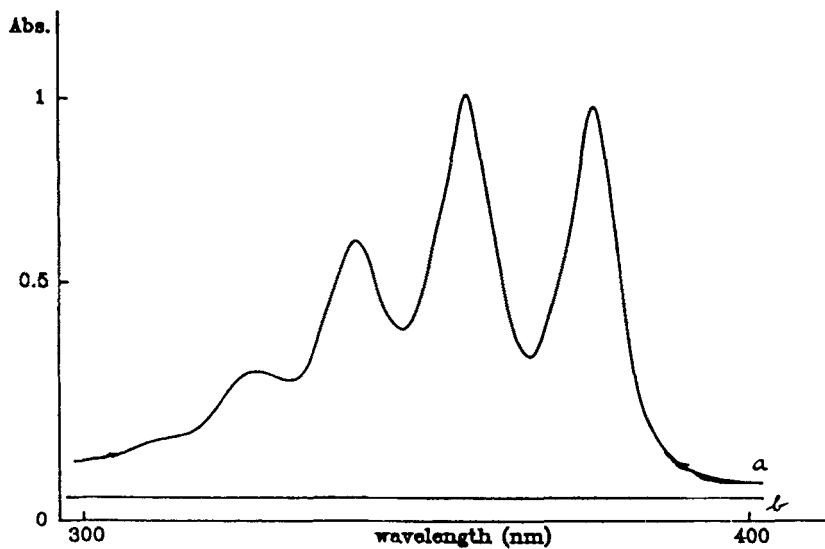


Fig. 4. UV spectra of PPhS in dioxane (a): original solution (conc. of polymer 0.2 g/l), (b): after precipitation by 0.2 wt.-% dioxane solution of PAA.

ded. During the washing with diluted aqueous HCl an emulsion is formed and the separation procedure is more complex thereby. So, although both acids efficiently remove the PPhS from the solution, the use of PAA is more favourable. The removal of the PPhS was monitored by UV spectroscopy. The results are shown in Figs. 3 and 4. These figures demonstrate (horizontal lines c and d in Fig. 3 and line b in Fig. 4) that the last traces of the PPhS have been removed from the solution after treatment with acid.

#### EXPERIMENTAL PART

##### Reagents.

THF (Merck) was dried over calcium hydride for one night and then refluxed and distilled over sodium wire just before use. Triflic anhydride (Aldrich) was dried and distilled over phosphorous pentoxide. N-tert.butylaziridine was dried and distilled over  $\text{CaH}_2$ . 9(amino-methyl)anthracene was prepared by reduction of 9-cyanoanthracene according to refs. 6 and 7.

##### Polymerization.

144  $\mu\text{l}$  of triflic anhydride was added to 70 ml of dry THF at 20°C. After 2 min. 2.33 ml of N-tert.butylaziridine was injected to the gently stirred solution and the reaction was continued for 10 min. at 20°C. Then, 0.593 g of AMA was added and after 10 min. the reaction mixture was poured to 700 ml of cold (0°C) methanol. The precipitate was filtered off and after drying 1.2 g of white material was collected. The polymer was purified by threefold dissolution in THF and precipitation in methanol.

##### Irradiation experiments.

In a typical irradiation experiment 250 mg of PPhS (or 25 mg of AMA) are dissolved in 15 ml of methyl tert.butyl ether (MTBE). To this mixture is added a solution of approx. 200 mg tachysterol in 10 ml of hexane. Tachysterol is freshly prepared from its 3,5-dinitro-4-methyl-benzoate ester by saponification under nitrogen. Then the total volume is made up to 100 ml by MTBE. Irradiation is performed in a nitrogen atmosphere at 4°C in a merry-go-round apparatus. The light-source is a high-pressure mercury lamp (Philips HPK-125). The wavelengths below 300 nm are filtered off by means of a filter solution consisting of NaBr,  $\text{Ag}_2\text{SO}_4$  and  $\text{HgSO}_4$  in water<sup>8</sup>. The reaction is monitored by means of HPLC-analysis.

##### Extraction of the PPhS from solution.

5 ml of a MTBE solution of PPhS (conc. 1 g/l) was placed to a test tube followed by 1 ml of an extracting



agent: 0.1 N HCl aq. or 1 wt.-% water solution of PAA (M.W. 90.000). After vigorous shaking a sample was placed in a centrifuge so that the water phase could be separated from MTBE by centrifugation. Then, 3 ml of MTBE phase was transferred to a cuvette and the UV spectrum was taken. In case of PAA, after the first extraction, the second one was carried out according to the same procedure.

Extraction of the PPHS from both MTBE and dioxane solution (conc. of polymer 2 g/l) by 0.2 wt.-% dioxane solution of PAA was carried out in the same way.

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