

# Photoactive Polysiloxanes. 1. Synthesis of Polydimethylsiloxane with Benzoin Terminal Groups

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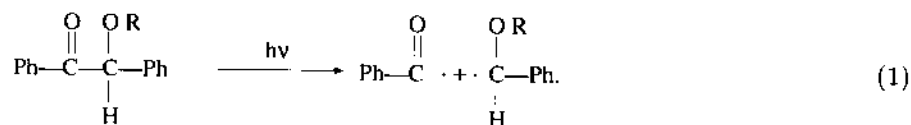
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Polydimethylsiloxanes with terminal photoactive benzoin groups were prepared by hydrosilation of benzoin acrylate in the presence of  $H_2PtCl_6$  catalyst.

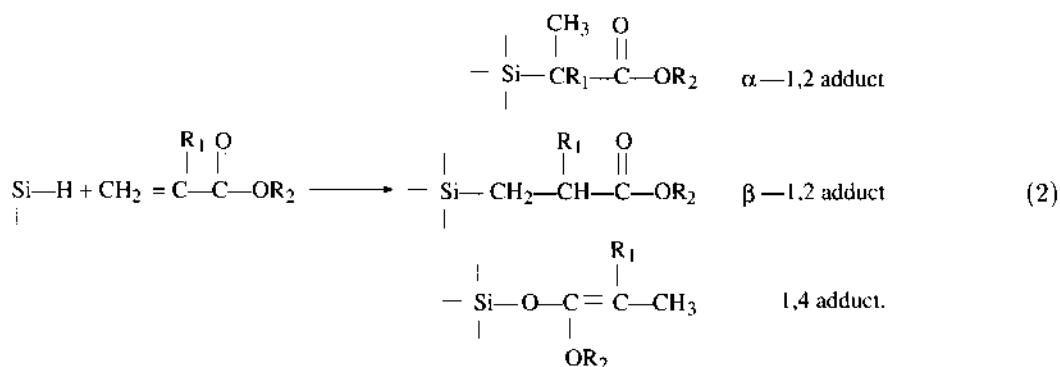
## Introduction

Benzoin and its derivatives are of prominent interest because of their utilization as photoinitiators of free radical polymerization in the surface-coating industry<sup>1</sup>. Upon irradiation, these compounds undergo dissociation to form free radicals according to the following reaction<sup>2</sup>.



Attachment of benzoin derivatives to polymer chains as terminal and side groups would afford a convenient procedure for block and graft copolymerization, respectively, by similar photoinduced dissociation<sup>3-5</sup>. Such incorporation of benzoin groups at the ends of polymer chains may be readily accomplished by utilizing azo-benzoin initiators recently developed in our laboratory<sup>6,7</sup>.

Due to its high versatility in the preparation of carbofunctional polysiloxanes, hydrosilation of unsaturated organic compounds has been used effectively in the last decade. Previously, we reported the synthesis of polysiloxanes containing hydroxypropyl or chloromethylphenethyl groups<sup>8-10</sup> which were utilized as precursors in the preparation of siloxane-containing block and graft copolymers. The hydrosilation reaction of  $\alpha, \beta$ -unsaturated esters can, in principle, occur according to the following scheme:



Generally, acrylates afford all three hydrosilation products. The choice of the reaction conditions, i.e., catalyst, solvent, structure of silicone hydride and ester, can direct the reaction<sup>11-13</sup>. However, the hydrosilation reaction in the presence of  $H_2PtCl_2$  catalyst solution in alcohols gives rise to a secondary reaction yielding Si-O-C linkages<sup>14</sup>.

In continuation of these studies we now report the synthesis of Polydimethylsiloxane with benzoin terminal groups via the hydrosilation reaction of benzoin acrylate having appropriate functionality for photoinduced cleavage.

## Experimental

### Materials

Benzoin acrylate was prepared according to the described procedure<sup>15</sup>. 1,1,3,3-Tetramethyldisiloxane (TMDSi) (Aldrich) was used as received. Hydride-terminated polysiloxanes with molecular weights of 1280, 2800 and 6400 were prepared by cationic equilibration of octamethylcyclotetrasiloxane with TMDSi using 2 % v/w conc.  $H_2SO_4$  catalyst. Tetrahydrofuran (THF) was purified by the usual drying and distillation procedure.

#### Hydrosilation of benzoin acrylate

The hydrosilation reaction was performed in THF at 70°C in the presence of  $H_2PtCl_6$  catalyst (2 % solution in isopropanol). A typical procedure for the hydrosilation by the model compound (TMDSi) is as follows:

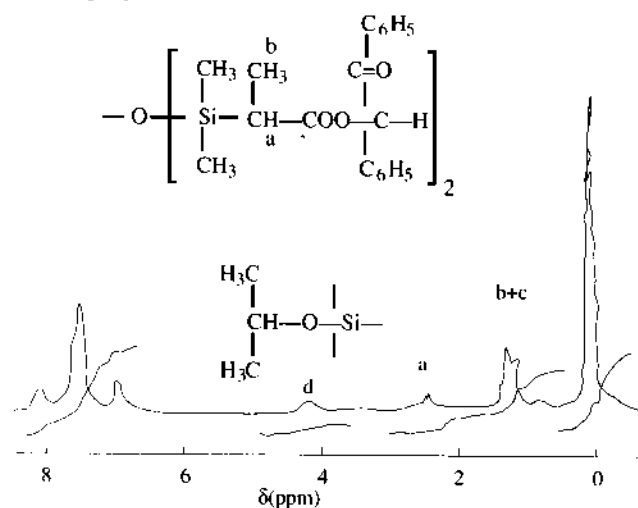
To a solution of 0.475 g. (1.79 mmol) benzoin acrylate and 0.1 ml  $H_2PtCl_6$  catalyst in 1.6 ml THF, a solution of 0.12 g. (1.79 mmol of TMDSi in 1 ml THF) was added dropwise at 70°C under nitrogen. The mixture was stirred at the same temperature for 6 hours. At the end of this period the solvent was removed by vacuum evaporation. Completion of the reaction was monitored by  $^1H$ -NMR spectroscopy. The disappearance of the signals at 5.9-6.4 ppm and 4.7 ppm indicates the total consumption of  $CH_2 = \overset{\cdot}{C}H$ - and Si-H groups, respectively.

A similar procedure was applied for the hydrosilation by hydride-terminated polysiloxanes.

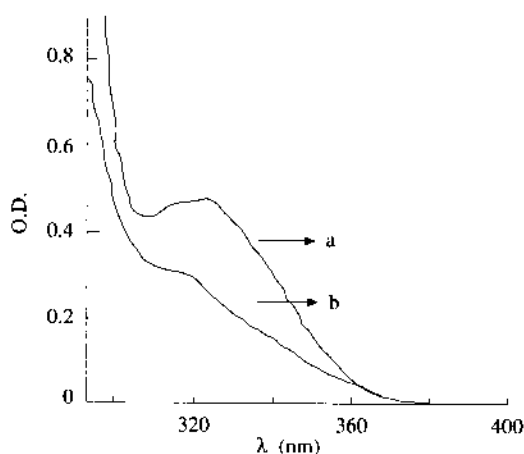
$^1H$ -NMR spectra were recorded in  $CDCl_3$  on JEOL-C60 HL spectrometer. UV spectra were recorded on a Perkin Elmer Lambda 2 UV-VIS spectrophotometer.

## Results and Discussion

Hydrosilation experiments were performed with Si-H containing polymers having three different molecular weights and also with tetramethyldisiloxane (TMDSi). The latter was used as a low molecular weight analogous of polymers in order to optimize reaction conditions. Figure 1 presents the  $^1\text{H-NMR}$  spectrum of the reaction product of benzoin acrylate with TMDSi. It appears that the hydrosilation occurs through  $\alpha$ -addition. A residual amount of ether type C-O-Si compound, formed by the reaction of isopropanol with Si-H in the presence of Pt catalyst, can be noticed. The  $^1\text{H-NMR}$  spectra of benzoin-terminated polysiloxane present the same characteristic peaks. The incorporation of benzoin groups into polysiloxanes evidenced by UV measurements. Figure 2 shows the absorption spectra of benzoin acrylate and polysiloxane obtained after the hydrosilation reaction. It can be seen that both spectra contain an absorption band characteristic of the precursor benzoin group. Expectedly, intensity of the absorption decreased as the molecular weight of the polysiloxane increased.



**Figure 1.**  $^1\text{H-NMR}$  spectrum of the hydrosilation product of benzoin acrylate with tetramethyldisiloxane



**Figure 2.** UV absorption spectra of dichloromethane solutions containing (a) benzoin acrylate ( $1.4 \times 10^{-3}$  mol/l), (b) benzoin terminated polydimethylsiloxane (initial  $M_n=1280$ ) (3.2 g/l)

Further studies on the use of these polymers as photoinitiators are now in progress and will be published elsewhere.

## Acknowledgement

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