

Preparation and Characterization of Polymers with Pending UV-Absorber Groups. I. Polymers Based on Polydimethylsiloxane

JAN-H. RIEDEL and H. HÖCKER*

Lehrstuhl für Textilchemie und Makromolekulare Chemie und Deutsches Wollforschungsinstitut, Rheinisch-Westfälische Technische Hochschule Aachen, D-52062 Aachen, Germany

SYNOPSIS

The hydrosilylation reaction using dichloro(dicyclopentadiene)platinum (II) as catalyst is carried out to synthesize polymeric UV absorbers with polysiloxane backbone. An almost quantitative addition of vinyl groups of the UV absorber (benzophenone) to silane groups is observed. The IR spectra indicate the qualitative results of the reaction, whereas the $^1\text{H-NMR}$ spectra allow the following of the reaction quantitatively. Low glass transition temperatures are observed by DSC. UV spectroscopy shows that the extinction coefficient and spectra of the UV absorbers are hardly affected by the polymer analogous reaction. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

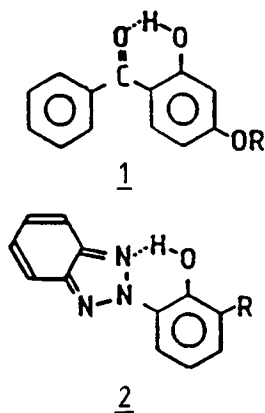
Organic fibers, such as wool or polyamide, tend to undergo a process of photodegradation when exposed to sunlight. Photochemical processes initiate reac-

tions like chain cleavage, cross-linking, and peroxidation or elimination of small molecules. These reactions lead to a reduction of physical and mechanical properties of the fibers. Therefore, organic fibers have to be treated with stabilizers.

Several types of UV stabilizers are available.^{1,2} The most common are benzophenones (**1**) and phenylbenzotriazoles (**2**). These molecules are able to absorb the damaging UV part of the sunlight. The photoexcited stabilizer molecule is transferred to the ground state by dissipating the excess energy in form of vibrational energy.^{3,4} Until now, these monomeric compounds have been used without chemical fixation.⁵

The use of polymeric UV absorbers allows immobilization of the absorber molecules at the surface. This prevents intermolecular interactions between the UV absorber and the fiber material (via hydrogen bonds) and thus increases the effectiveness of the absorber.

One way to synthesize polymeric UV absorbers is to add the absorber molecule with a functional group (e.g., a vinyl group) to a prepolymer that carries another functionality (e.g., a silane group). The choice of the prepolymer depends on the final use



* To whom correspondence should be addressed.

of the product.⁶ Polymeric UV absorbers for textile purposes should have low transition temperatures, thus providing a soft handle to the coated material.⁷ We prepared polymers with different contents of UV stabilizer units and investigated them in terms of chemical structure, light absorption, and thermal behavior.

EXPERIMENTAL

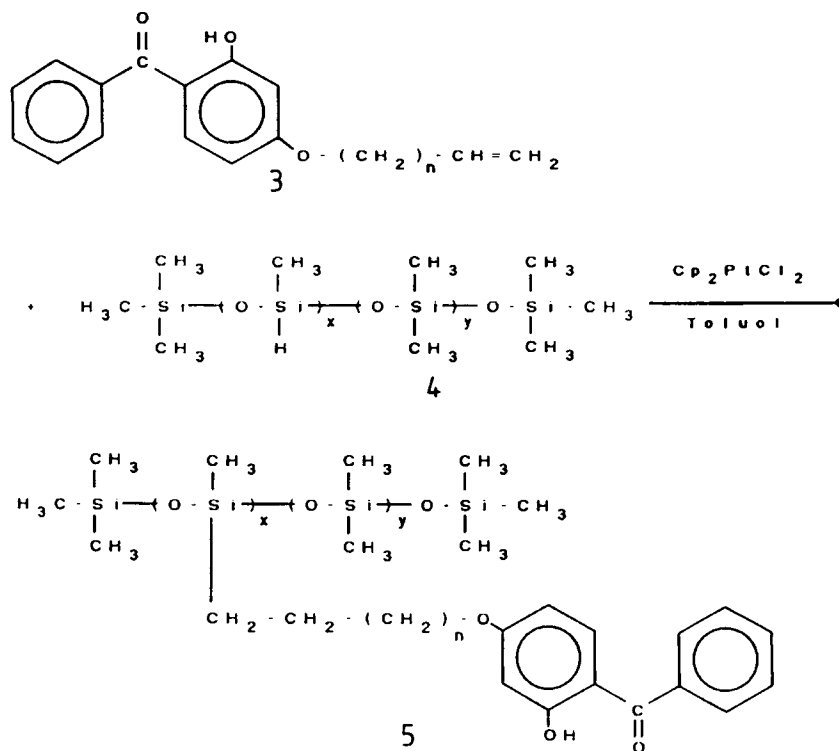
Materials

Toluene and THF were refluxed 3 days over sodium and then in a distilled N₂ atmosphere. Hexane, heptane, and acetone were analytical grade and distilled before use. Oligo(hydromethyl-*co*-dimethyl/silox-

anes) (**4a**, $M_n = 2600$; **4b**, $M_n = 3600$) (Wacker-Chemie), UV absorbers (Riedel-DeHaen), and dichloro(dicyclopentadiene)platinum (II) catalyst (Consortium für Elektrochemische Industrie) were used as received.

Preparation of Polymeric UV Absorbers

A mixture of polysiloxane and the UV absorber in toluene was heated to 50°C in a reaction flask equipped with a condenser and magnetic stirrer in an inert gas atmosphere. Then, the catalyst was added. After stirring overnight, the mixture was cooled down to room temperature and the toluene was removed. Afterward, the oily product was diluted in THF and the polymer precipitated in an excess of CO₂-cooled hexane (polymers **5a–c**), heptane (polymer **5d**), or acetone (polymers **5e–h**). The



n	3	4	8	12
UV-Abs.	3a	3b	3c	3d
Polysiloxane	4a 4b	4a 4b	4a 4b	4a 4b
Polymer	5a 5e	5b 5f	5c 5g	5d 5h

procedure was carried out twice. The polymers were dried under reduced pressure for 1 day.⁸

Characterization of Polymers

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker CXP 200 spectrometer in CDCl₃ using CHCl₃ as an internal standard. A Nicolet 20 DXB FTIR spectrometer was used to record the infrared spectra from the KBr pellets.

The molecular weights of the polymers were determined using vapor-pressure osmometry with a Knauer vapor-pressure osmometer at 50°C and THF as a solvent. A calibration curve was determined by measuring three concentrations of the corresponding monomeric UV absorber.

Differential scanning calorimetry (DSC) data were obtained with a Perkin-Elmer DSC-7 differential scanning calorimeter between -130 to 0°C at a scan rate of 10°C/min. The glass transition temperature data were taken from the second heating curves. The instrument was calibrated with indium.

The GPC measurements to determine the residual low-molecular UV-absorber content were carried out on a Waters high-performance gel permeation chromatograph ALC 200, equipped with an RI and UV (280 nm) detector. Two Ultrastaygel columns (Showa Denko K.K., Shodex GPC KF-804 and -8025) of 30 cm length were used. Flow rate was 0.5 mL/min. Calibration was based on monodisperse polystyrene samples.

The absorption spectra were recorded on a Shimadzu UV-200 spectrophotometer using THF as a solvent. Concentration of the monomeric UV-absorber solution was 1×10^{-4} mol/L. To investigate the influence of the coupling reaction on the UV

spectra, solutions of polymeric UV absorber were prepared with an equivalent UV-absorber content.

RESULTS AND DISCUSSION

The polymeric UV absorbers **5a-d** (Table I) were prepared by a hydrosilylation reaction of oligo(hydromethyl-*co*-dimethyl/siloxane) (**4**) with the terminal double bond of the alkenyl side chain of the benzophenone derivatives **3a-d**.⁸

Dichloro(dicyclopentadiene)platinum (II) (systematic name: dichloro[(2,3,5,6- η)-3a,4,7,7a-tetrahydro-4,7-methano-1H-indene]platinum) was used as catalyst for the hydrosilylation reaction.^{9,10} Besides its solubility in toluene, its high activity is favorable (10^{-4} mol/mol SiH; cf. Table I). The resulting polymers exert a high degree of substitution as given in Table I.¹¹ The reaction of silane groups is almost quantitative.

Figure 1 shows the ¹H-NMR spectrum of polymer **5a**. A comparison of the integration of the aromatic protons (1-5/13) and of the methylprotons of the polysiloxane backbone (Si—Me) allows one to calculate a 93% conversion of Si—H groups for polymer **5a**. In all cases, vinylic and hydrosilyl functions are absent. The ¹³C-NMR spectrum (Fig. 2) is typical of all respective polymers.

The reaction of the hydrosilyl group of the polysiloxane with the allyl group of the UV absorber can be detected by following the disappearance of the Si—H infrared absorption band at 2158 cm^{-1} .¹² In Figure 3, the infrared spectra of prepolymer **4a** (a) and **5b** (b) are given as an example.

In Figure 4, the time-conversion curve for the reaction of **3a** with **4a** is given. The conversion cor-

Table I Synthesis of Polymeric UV Absorbers

Polymer	UV Absorber (mol)	Siloxane (mol)	Mol Pt/Mol SiH	SD ^a (NMR)
5a	3a/ 8.4×10^{-3}	4a/0.03	1×10^{-4}	93
5b	3b/ 8.4×10^{-3}	4a/0.03	1×10^{-4}	98
5c	3c/ 8.4×10^{-3}	4a/0.03	1×10^{-4}	93
5d	3d/ 8.4×10^{-3}	4a/0.03	1×10^{-4}	94
5e	3a/ 3.33×10^{-3}	4b/0.03	3×10^{-4}	96
5f	3b/ 3.33×10^{-3}	4b/0.03	3×10^{-4}	97
5g	3c/ 3.33×10^{-3}	4b/0.03	3×10^{-4}	94
5h	3d/ 3.33×10^{-3}	4b/0.03	3×10^{-4}	93

^a Degree of substitution in %.

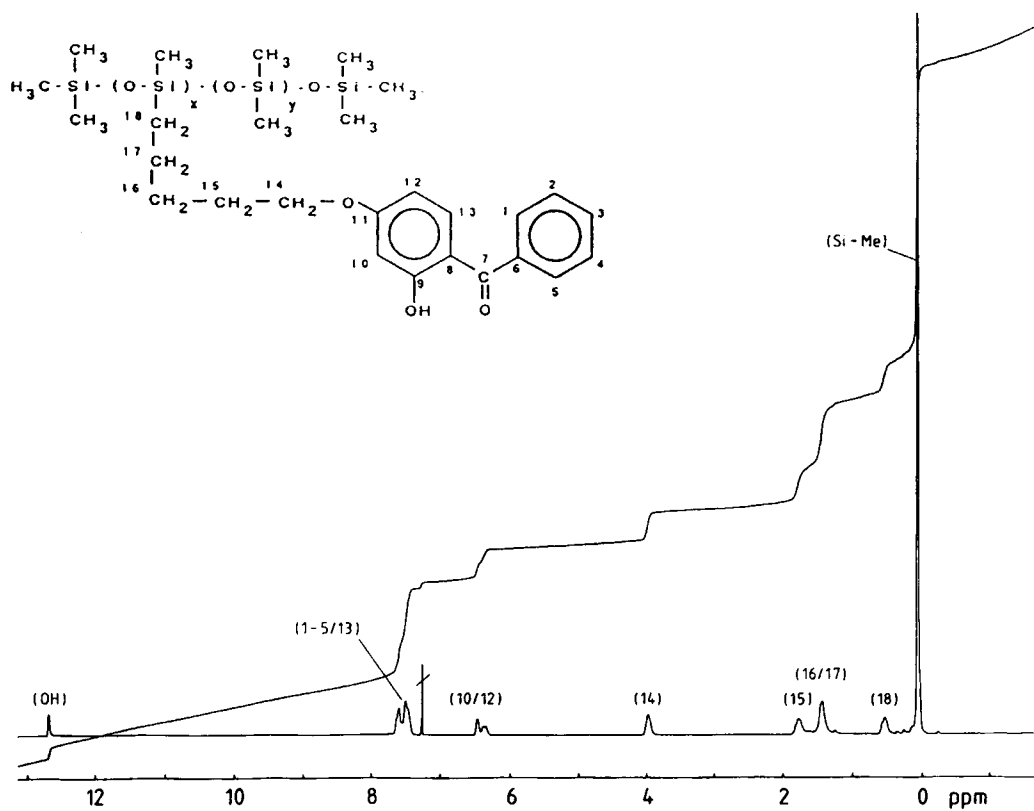


Figure 1 200 MHz ^1H -NMR spectrum of polymer **5a** in CDCl_3 (internal standard CHCl_3).

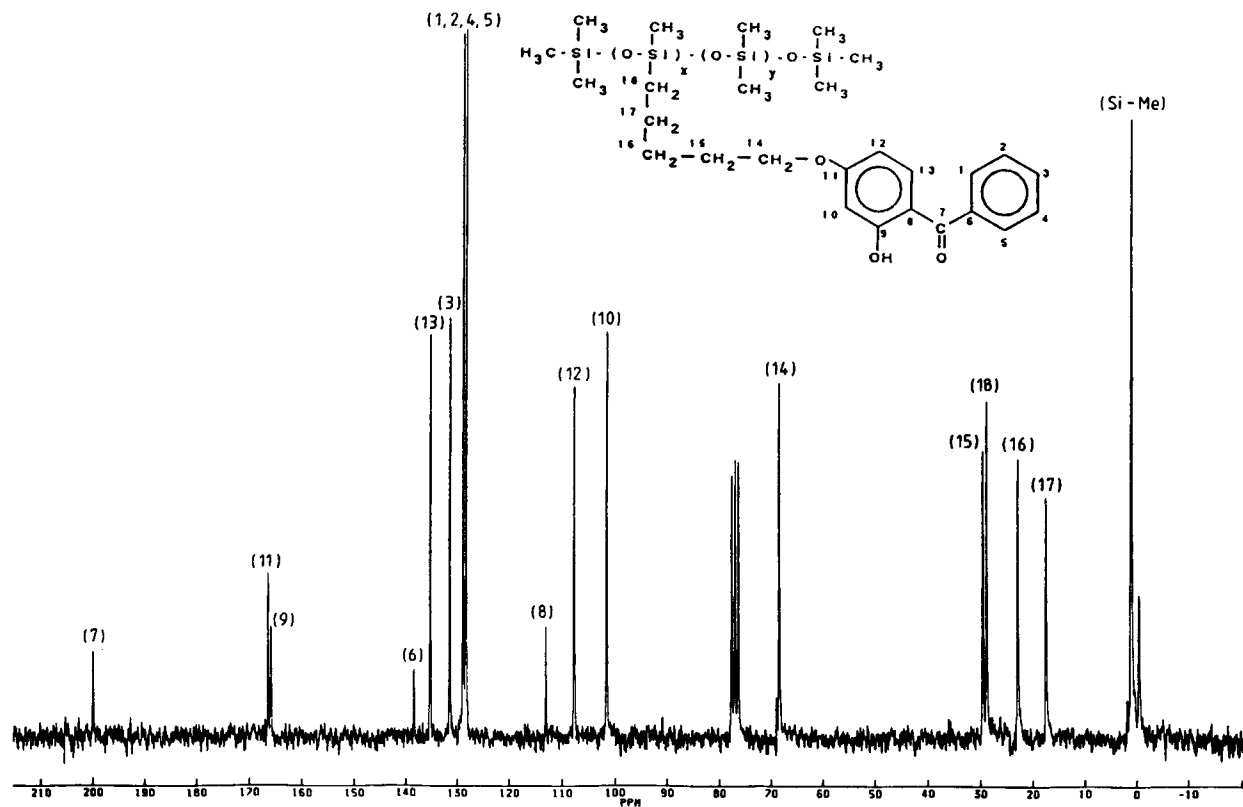


Figure 2 ^{13}C -NMR spectrum of **5a** (50 MHz, CDCl_3 with internal CHCl_3).

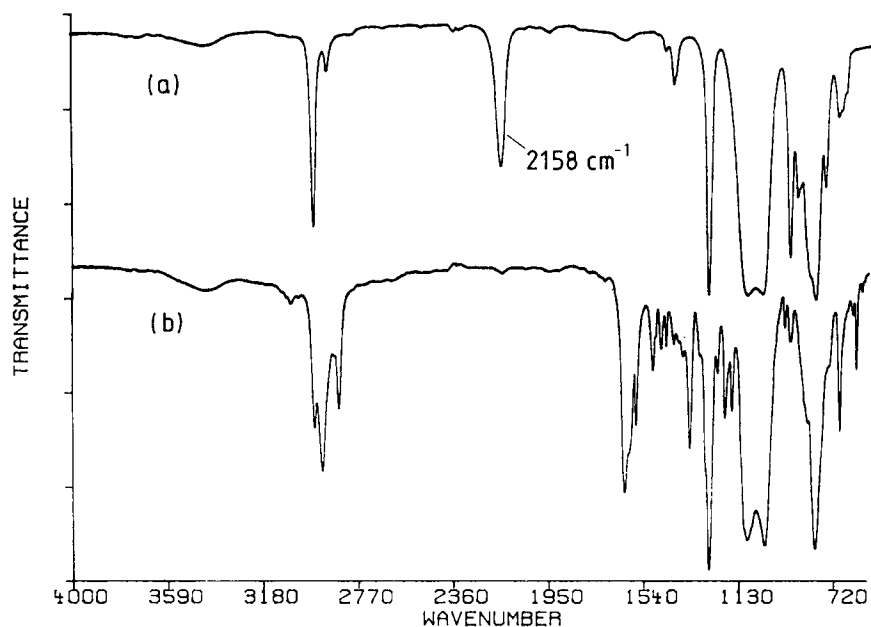


Figure 3 Infrared spectrum of (a) **4a** and (b) **5b** on KBr (transmission).

responds to the ratio of Si—CH₂ protons emerging from the reaction related to the O—CH₂ protons of an amount of UV absorber corresponding to a full conversion of Si—H groups of the prepolymer. The conversion after 12 min is 91% for the reaction of **3a** with **4a** in toluene-*d*₈. After 30 min, the reaction is almost complete.

Table II shows the molecular weights of the polymeric UV absorbers as determined using vapor-pressure osmometry. They are in good agreement with those calculated from molecular weights of the prepolymer and conversion rate found by ¹H-NMR.

Further, it can be seen in Table II that glass transition temperatures (*T*_g) of the substituted polysi-

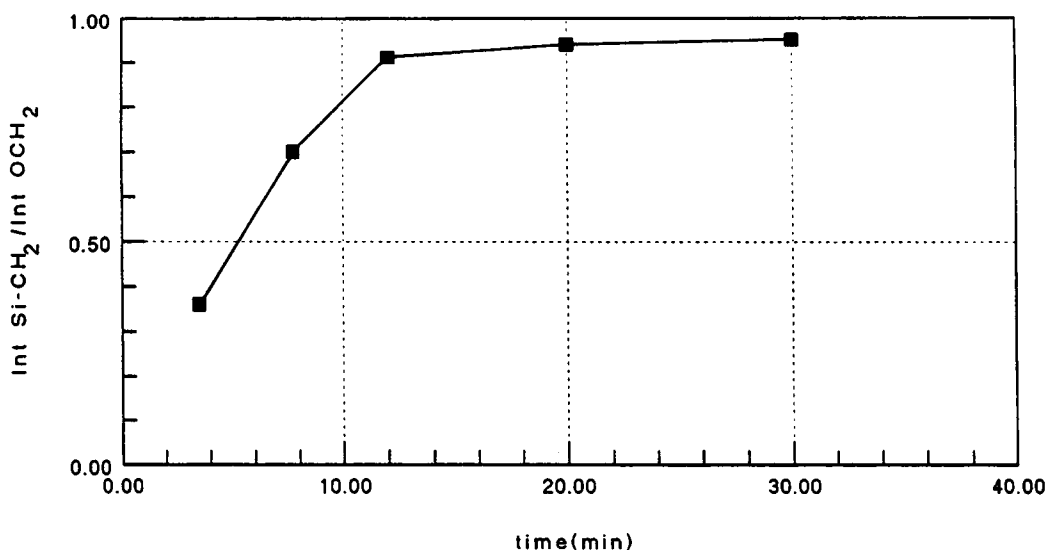


Figure 4 Conversion of **3a** with **4a** (polymer **5a**) in toluene determined by comparison of integration of Si—CH₂ and O—CH₂ signals (¹H-NMR spectrum) of the UV-absorber side chain depending on time.

Table II Characterization of Polymeric UV Absorbers

Polymer	M_{VPO}	M_{calc}	$T_g/^\circ C$ (DSC)	Residual Low Molecular Weight UV Absorber Content ^a in mol % (GPC/UV Detector)
5a	6900	4300	-48	1.1
5b	6700	4900	-45	1.7
5c	6700	4900	-42	1.3
5d	6900	5400	-28	2.0
5e	7000	4600	^b	2.3
5f	6900	4900	^b	0.6
5g	6900	4900	-67	1.8
5h	6800	5200	-49	3.8

^a In resulting polymer.^b No glass transition temperature observed.

loxanes increase with increasing spacer length from $-48^\circ C$ for **5a** to $-28^\circ C$ for **5d**. T_g also increases with increasing UV-absorber content of the polymer. Thus, polymer **5h** shows a T_g of $-49^\circ C$, and **5d**, of $-28^\circ C$ (Table II).

The content of residual low molecular weight UV absorber is determined by GPC. It is between 0.6 and 3.8 mol % (with respect to base units of the respective polymer).

An important indication for the efficiency of the UV absorber is its UV spectroscopic behavior.^{13,14} The UV spectra of **5a** and **3a** are given in Figure 5. The absorption peaks of the monomeric and polymeric UV absorber appear at equal wavelengths. The extinction coefficient ($1.35 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ for **5a**; $1.55 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ for **3a**), determined at 290 nm, is little affected by coupling to the polysiloxane.

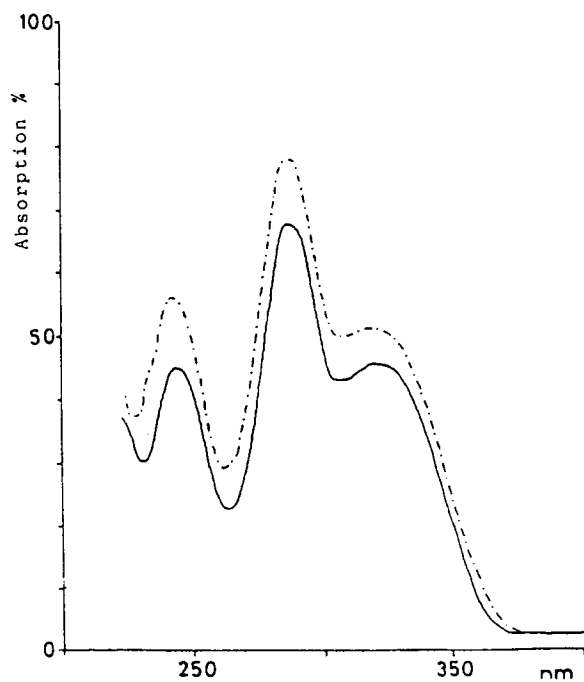


Figure 5 UV spectra of (—) **5a** and (- · - ·) **3a** in THF (for concentrations, see Experimental section).

CONCLUSIONS

The present study shows the high capability of the hydrosilylation reaction using dichloro(dicyclopentadiene)platinum as catalyst to prepare polymeric UV absorbers with polysiloxane backbone. The low glass transition temperatures, on the one hand, and the high UV-absorption capacity (extinction coefficient and wavelength) as compared with the monomeric UV absorbers, on the other, make the polymer valuable for textile applications.

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