

NOTE

**Determination of silanol end groups in polysiloxanes obtained from dimethyldichlorosilane hydrolysate (DDSH)**

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*Abstract:* Dimethyldichlorosilane hydrolysate, DDSH, the linear part of which contains SiOH end groups, can be used in the preparation of difunctionally terminated (any end groups other than SiOH) polysiloxanes *via* equilibration polymerisations. In such a case, the problem arises: as to whether the obtained functionalised polymers also contain silanol end groups. To the best of our knowledge, the only direct and the most precise analytical procedure to clarify this question is the Karl Fischer titration/determination of SiOH groups. This determination was performed on a model system consisting of trimethylsilyl terminated polysiloxanes, and it was shown that the obtained polymers contained no SiOH groups.

*Keywords:* silanol terminated polysiloxanes, trimethylsilyl terminated polysiloxanes, Karl Fischer titration/determination of silanol groups.

INTRODUCTION

In a recently published article, the preparation of dicarboxypropyl terminated polysiloxanes *via* equilibration polymerisation was reported.<sup>1</sup> The specific point in that investigation was the use of DDSH, the linear part of which was silanol, SiOH, terminated. The main uncertainty was whether the obtained polymers contained silanol end groups. Silanol groups could appear as end groups, but also they could be absent, because they were consumed in a condensation reaction occurring under conditions comparable to those normally present in redistribution/equilibration reactions.<sup>2</sup> On the basis of the determinations carried out on the polymer products, *i.e.*, infrared spectroscopy, IR, vapour pressure osmometry, VPO, gel permeation chromatography, GPC, proton nuclear magnetic resonance spectroscopy, <sup>1</sup>H-NMR, and end group analysis (acid number determination), EGA, it was concluded that silanol groups were not present in the obtained polymers, in other words, that only dicarboxypropyl groups appeared as end groups. However, all the applied methods

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were not methods of the highest precision, and/or they were not suitable to directly confirm either the presence or absence of SiOH groups. To the best of our knowledge, the only method which can be used for the direct and very precise determination of SiOH groups is the Karl Fischer (KF) titration method, especially because a detailed description of the KF titration procedure for the determination of the hydroxyl content of silanol terminated polysiloxanes exists.<sup>3</sup> Unfortunately, it was not possible to apply this simple method in the present case, because several functional groups, including carboxyl, COOH, groups, can react with the components of the KF solutions, causing a quantitative interference to the SiOH determination. To overcome this problem and in order to definitely clarify and remove any doubt, it was decided to make an additional series of experiments on such a model system, which should to a very high level, as high as possible, correspond to the originally investigated one. Such a model system was formed in such a way that the dicarboxypropyl tetramethyl disiloxane used in the original reaction mixtures as the end-capping agent was replaced by hexamethyldisiloxane, MM, all the other reaction parameters remaining unchanged. The use of hexamethyldisiloxane as the end-capping agent should eliminate the interference problem appearing in the KF titrations, since now only unreactive non-interfering methyl groups are present.

## EXPERIMENTAL

### *Materials*

D<sub>4</sub> and MM, obtained from ABCR GmbH & Co. KG, were used as received.

DDSH, a Bayer product, was kindly supplied by the "Prva Iskra" – Barič Chemical Works. Its main characteristics were as follows: the composition, linear polymer/cyclics, was 42/58 by weight, and the molecular weight,  $\overline{M}_n$ , of the linear, silanol terminated part was 4112, as determined by vapour pressure osmometry, VPO.

A commercial grade macroporous cation exchange resin, strong acid type, Duolite C 26, from Diamond Shamrock Co., having a total ion exchange capacity of 1.85 eq/l, was used as the equilibration catalyst after preliminary overnight drying at 50 °C.

Toluene p.a., used as the solvent in the VPO measurements, obtained from Zorka Pharma, Šabac, was distilled and dried over molecular sieves before use.

In the Karl Fischer titrations, a single component reagent, "Karl Fischer-Reagenz 5", obtained from Merck, Darmstadt, was used.

### *Equilibrations*

In the equilibrations performed in this study, all the reaction parameters – reaction temperature and duration (95 °C and 24 h, respectively), catalyst concentration (22 meq/100 g of reactants) and post-preparative work-up procedure – were identical to those applied in a previous investigation.<sup>1</sup>

### *Measurements*

KF titrations were used to determine the silanol groups in the obtained polymers. The procedure was the same as that described in detail for the determination of the hydroxyl content of silanol terminated polysiloxanes.<sup>3</sup> This procedure, differed from standard KF titrations in that approximately 20 min elapsed between transfer of the sample to the titration holder and the titration itself, and the temperature was elevated and held constant at 50 °C.

Vapour pressure osmometry was performed on a Knauer osmometer which was calibrated with poly(dibutyl itaconate). Toluene was used as the solvent and the temperature was 60 °C.

## RESULTS AND DISCUSSION

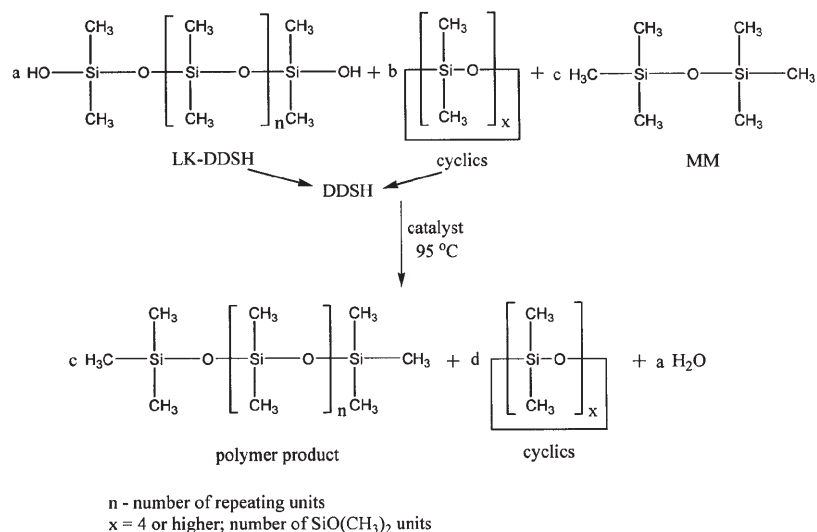
The polymer samples obtained in equilibrations of DDSH with MM were analysed by KF titration and their number average molecular weights,  $\overline{M}_n$ , were determined by vapour pressure osmometry, VPO. The obtained values were compared with those calculated from the composition of the reaction mixtures,  $M_{nCalc1}$  and  $M_{nCalc2}$ .  $M_{nCalc1}$  is the molecular weight if only trimethylsilyl groups would appear as end groups, and  $M_{nCalc2}$  is the molecular weight if all the initially present groups, both trimethylsilyl and silanol, would terminate the polymer chains.

The following KF titrations were performed. A blank determination was done first. A polymer sample obtained by equilibrating octamethylcyclotetrasiloxane, D<sub>4</sub>, and MM, which could not contain any silanol end groups, was titrated. The obtained result of 128 mg H<sub>2</sub>O/100 g polymer (sample 1, Table I) was taken into account in all subsequent calculations. Then the content of OH groups in DDSH was determined. For this purpose, determinations were made on both DDSH and its linear part, LK-DDSH, whereby values of 457 and 974 mg H<sub>2</sub>O/100 g were obtained, respectively (samples 2 and 3 in Table I). These results were then used to calculate content of OH groups in DDSH. The KF titration of pure DDSH (457 mg/100 g of DDSH) gave 18.4 mmol OH groups/100 g of DDSH. The titration result for the linear part of DDSH (974 mg H<sub>2</sub>O/100 g of LK-DDSH), combined with the experimentally determined composition of DDSH, obtained by fractional distillation (linear polymer/cyclics = 42/58 by weight), gave 19.4 mmol OH groups/100 g of DDSH. As can be seen, the results of both determinations were in excellent accordance, and were thereafter used to calculate  $M_{nCalc2}$  molecular weight values.

TABLE I. The results of KF titration and VPO molecular weight determinations

Sample	Composition/g	Molecular weight			KF titration mg H <sub>2</sub> O/100 g of polymer
		$M_{nCalc1}$	$M_{nCalc2}$	$M_{nVPO}$	
1	27.8 D4 2.2 MM	1961	–	1895	128
2	DDSH	–	–	–	457
3	LK-DDSH	–	4330	4112	974
4	27.8 DDSH 2.2 MM	1950 1961	1659 1667	2175 1885	122 122
		1955	1664	1838	122
5	28.8 DDSH 1.2 MM	3638	2699	3450	113
6	29.19 DDSH 0.81 MM	5391	3531	5100	122
7	27.8 LK-DDSH 2.2 MM	1953	1378	1808	122

Then, four samples were prepared, the initial mixture compositions of which, as well as the results obtained from KF titration and VPO molecular weights determination, are given in Table I (sample 4–7). The initial mixture compositions were selected to target polymer molecular weights in the range of approximately 2000–5500. For sample 4, the results were obtained from three repeated, *i.e.*, independent, experiments – with respect to both synthesis and measurements. In sample 7, DDSH was replaced by its linear component, LK-DDSH. It can be seen that the results of the KF titration for all the samples corresponded exactly to the result obtained in the blank determination. This finding is an obvious proof that the samples did not contain SiOH groups. Additional evidence, although less precise, was the fact that the VPO molecular weights were very close to the  $M_{nCalc1}$  values, *i.e.*, these calculated for the case that only trimethylsilyl groups appeared as end groups.



Scheme 1.

On the basis of these results, the reaction between DDSH and MM can now be represented in the following generalized way, as shown in Scheme 1.

#### CONCLUSION

The results of this investigation – the Karl Fischer titration being the crucial argument – led to the conclusion that equilibration polymerisations with DDSH as reactant, if performed under the above described conditions, give polymer products which definitely do not contain silanol end groups. This conclusion confirms our former statements, namely that the obtained dicarboxypropyl terminated polysiloxanes were free of silanol end groups.

## ИЗВОД

ОДРЕЂИВАЊЕ СИЛАНОЛНИХ КРАЈЊИХ ГРУПА У ПОЛИСИЛОКСАНИМА  
ДОБИЈЕНИМ ИЗ ДИМЕТИЛДИХЛОРСИЛАН ХИДРОЛИЗАТА (DDSH)

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Диметилдихлорсилан хидролизат, DDSH, чији линеарни део садржи крајње SiOH групе, може да се употреби за добијање дифункционално терминираних (било којим крајњим групама, осим SiOH) полисилоксана у реакцији еквилибрационе полимеризације. У том случају се јавља следећи проблем: да ли добијени функционализовани полимери садрже и силанолне крајње групе или не. Колико знамо, једини директан а и најпрецизнији метод одређивања силанолних група је Карл Фишера титрација. Ово одређивање је извршено на модел систему који се састојао од полисилоксана са завршним триметилсилнил групама, и показано је да добијени полимери уопште не садрже SiOH групе.

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