

## LOW-TEMPERATURE EQUILIBRATION REACTION AND PROPERTIES OF TELECHELIC SILOXANE OLIGOMERS

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**Abstract:** Siloxane equilibration reaction in the presence of appropriate functional disiloxanes is a common method for the synthesis of telechelic siloxane oligomers. Due to the high reaction temperature, the synthesis of hydroxy-terminated polysiloxane is accompanied by several side reactions. In this paper, the synthesis of hydroxy-terminated siloxane oligomers at relatively low temperatures was optimized. The oligomers of the controlled molecular weight were synthesized in the presence of a heterogeneous catalyst and characterized by spectroscopic and thermal methods, as well as thermogravimetric analysis – infrared spectroscopy (TG-FTIR) and dilute solution viscometry.

**Keywords:** hydroxy-terminated PDMS, siloxane equilibration reaction, <sup>1</sup>H NMR spectroscopy.

### 1. INTRODUCTION

$\alpha,\omega$ -Functionalized, telechelic poly(dimethylsiloxane), PDMS, oligomers of relatively low molecular weights are versatile starting materials for the preparation of a wide variety of linear siloxane-containing copolymers including thermoplastic siloxane-urethane, siloxane-urea, siloxane-urethane-urea, and siloxane-ester elastomers [1,2]. PDMS is an extremely flexible molecule with almost complete rotation along the macromolecular chain. Mobility of the PDMS molecule, through rotation and segmental cooperative chain motion, makes the inter-molecular distance larger, and intermolecular interactions significantly lower than for the corresponding carbon polymers, which causes many of the unusual properties of these materials. PDMS polymers have one of the lowest values of the glass transition temperature ( $T_g = -123$  °C), and a large value of the molar volume ( $75.5$  cm<sup>3</sup> mol<sup>-1</sup>) [3]. Flexibility and weak

intermolecular forces also lead to low surface tension, low value of solubility parameter, and low dielectric constant. PDMSs are transparent to visible and UV light, ozone resistant, and very stable to the atomic oxygen. Permeability to various gases, hydrophobicity, ability to build films, surface activity, as well as excellent chemical and physiological inertness are other interesting properties of PDMS polymers.

Telechelic PDMS oligomers are usually synthesized by siloxane equilibration reaction at relatively high temperatures. Previous studies showed that hydroxypropyl and hydroxybutyl terminated polydimethylsiloxane oligomers showed degradation upon heating, through the loss of functional end groups [4]. Instability of the end groups is due to the backbiting of the terminal silicon in the PDMS by the primary hydroxyl oxygen, leading to the formation of 5 and 6-membered, stable, heterocyclic compounds [5]. Loss of end groups also resulted in a dramatic

increase in the molecular weights of the oligomers produced.

In the present paper, a series of  $\alpha,\omega$ -dihydroxybutyl-poly(dimethylsiloxane)s (PDMS) was synthesized in the presence of a cation-exchange resin as the heterogeneous catalyst. The influence of the reaction temperature on the molecular weight of the PDMS oligomers was investigated by  $^1\text{H}$  NMR spectroscopy, thermogravimetric analysis – infrared spectroscopy (TG-FTIR), and dilute solution viscometry.

## 2. EXPERIMENTAL

### 2.1. Materials

The PDMS oligomers with the predetermined number-average molecular weight of  $2000 \text{ g mol}^{-1}$  were prepared by the siloxane equilibrium reaction under different experimental conditions. Octamethylcyclotetrasiloxane (D4) and 1,3-bis (4-hydroxybutyl) tetramethyldisiloxane (DS-OH) were purchased from ABCR, Germany. The chemical structure of D4 and DS-OH was previously confirmed by  $^1\text{H}$  NMR spectroscopy.

As a catalyst, the commercial-grade macroporous cation-exchange resin Lewatit® Mono-Plus SP 12  $\text{Na}^+$  form, from Fluka (Germany), was used, which was previously activated by eluting the hydro-chloric acid solution and overnight drying at  $50 \text{ }^\circ\text{C}$  in a vacuum dryer.

### 2.2. Synthesis of PDMS oligomers

The hydroxybutyl-terminated PDMS oligomers were synthesized by siloxane equilibration reaction from the cyclic D4 monomer and the DS-OH in the presence of cation-exchange resin as a catalyst. The reaction was carried out in a two-necked round bottom flask equipped with a magnetic stirrer, dry nitrogen inlet, and a reflux condenser during 24-48 h at a temperature range of  $30\text{-}95^\circ \text{C}$  in a silicone oil bath. The composition of the reaction mixture for the synthesis of PDMS prepolymer is shown in Table 1. To remove residual cyclic siloxanes, the synthesized hydroxy-terminated PDMS oligomers were distilled at  $200 \text{ }^\circ\text{C}$  in a vacuum. The chemical structure and number-average molecular weight of PDMS oligomers were confirmed by  $^1\text{H}$  NMR spectroscopy.

**Table 1.** The composition of the reaction mixture for the synthesis of PDMS oligomers

Sample	Mass of D <sub>4</sub> , g	Mass of DS-OH, g	Mass of catalyst, g
PDMS-30	10.36	1,56	0.53
PDMS-65	5.16	0,76	0.26
PDMS-95	10.37	1,51	0.54

### 2.3. Measurements

$^1\text{H}$  NMR spectra of synthesized PDMS samples were obtained on a Varian Gemini-200 instrument in  $\text{CDCl}_3$  solutions and with tetramethylsilane (TMS) as the internal standard.

Thermogravimetric analyses (TGA) were performed on a Perkin Elmer TGA 4000 thermal analysis instrument. For the evaluation of results, the Pyris software, Version 10.02.0468, was used. The first analyses were carried out in a nitrogen atmosphere from  $40$  to  $700 \text{ }^\circ\text{C}$  with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  using an  $\text{Al}_2\text{O}_3$  crucible without a lid. The second analysis was carried out in an oxygen atmosphere from  $40$  to  $700 \text{ }^\circ\text{C}$  with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  using an  $\text{Al}_2\text{O}_3$  crucible without a lid. All measurements were done with

coupled FT-IR. Spectra were recorded on a Perkin Elmer Spectrum 65 FT-IR spectrometer with a spectral resolution of  $4 \text{ cm}^{-1}$  and a measuring range from  $450 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$ . For the evaluation of the results, the Spectrum software, Version 10.03.09.0139, was used.

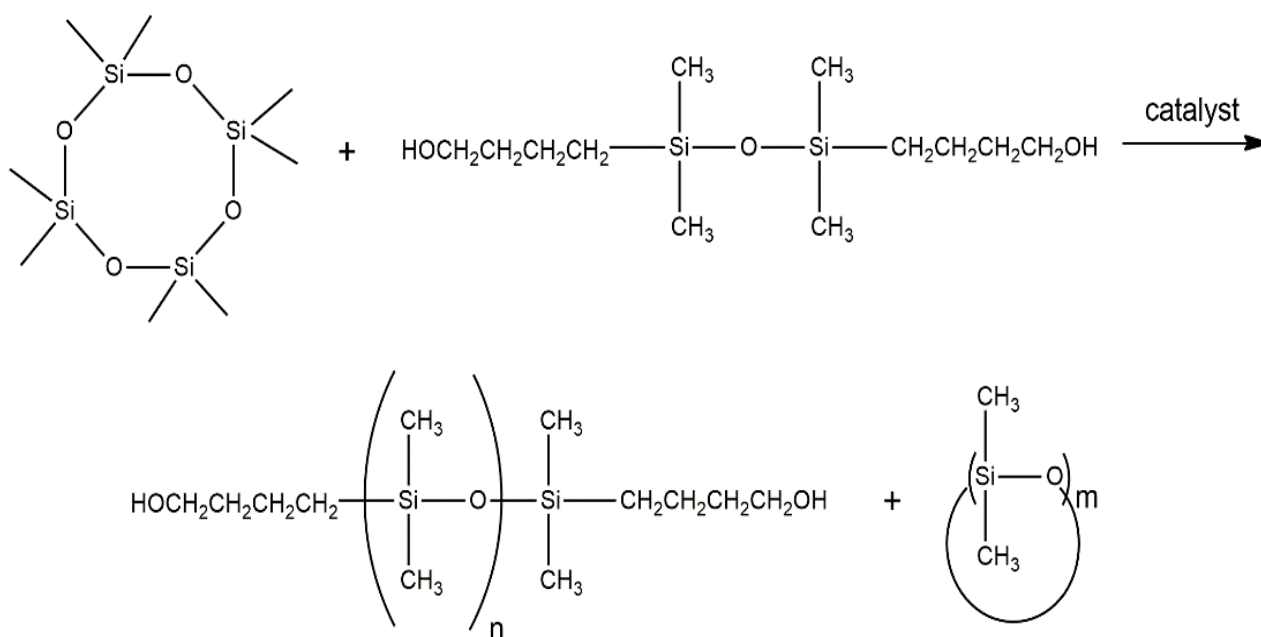
The intrinsic viscosities,  $[\eta]$ , of the PDMS oligomer samples were calculated based on the flow time,  $t$ , in toluene at  $25 \text{ }^\circ\text{C}$ , determined by an Ubbelohde viscometer. The three different concentrations of the samples were in the range of  $0.2\text{-}2.0 \text{ g dL}^{-1}$ . The mean value of at least four measurements of  $t$  was taken to calculate the relative viscosity,  $\eta_r = t/t_0$ , where  $t_0$  is the flow time of the pure solvent. The specific viscosity ( $\eta_{sp}$ ) was calculated based on the  $\eta_r$  values as  $\eta_{sp} = \eta_r - 1$ . The reduced,  $\eta_{red}$ , and inherent,  $\eta_{inh}$ , viscosities were

calculated as  $\eta_{red} = \eta_{sp}/c$  and  $\eta_{inh} = \ln \eta_r/c$ , where  $c$  is concentration, expressed in  $\text{g dL}^{-1}$ . The values were obtained by extrapolation of the straight lines of  $\eta_{red}$  and  $\eta_{inh}$ , as functions of solution concentration to zero concentration given.

### 3. RESULTS AND DISCUSSION

The general synthesis route of the hydroxybutyl-terminated PDMS oligomers from the

cyclic D4 monomer and the DS-OH disiloxane, in the presence of cation-exchange resin, is shown in Figure 1. The ratio of reactants was chosen to achieve a degree of polymerization of  $\sim 23$  in all syntheses, i.e., to obtain prepolymers with a molecular weight of  $2000 \text{ g mol}^{-1}$  (Table 1). The masses of the required reactants were obtained on the assumption that, at equilibrium, the proportion of siloxane cycles in the equilibrates is about 10% and that 90% of the siloxane units derived from D4 are incorporated into the linear polymer [1,6].



**Figure 1.** Synthesis of the hydroxybutyl-terminated PDMS oligomers by siloxane equilibration reaction

The chemical structure of the synthesized oligomers was confirmed by  $^1\text{H}$  NMR spectroscopy. The  $^1\text{H}$  spectra of the PDMS-30 sample are shown in Figure 2. In the  $^1\text{H}$  NMR spectrum the following characteristic signals were observed: intensive signal at  $\delta = 0.04$  of Si-CH<sub>3</sub> protons; signal of CH<sub>2</sub> protons from the terminal PDMS

butylene groups residue bonded to Si atom at  $\delta = 0.54$ ; signals of protons from two internal CH<sub>2</sub> groups at 1.35 and 1.55 ppm; signal of protons from terminal CH<sub>2</sub> group bonded to oxygen atom at 3.64 ppm; and weak signal of hydroxyl OH protons appeared at  $\delta = 1.25$  ppm.

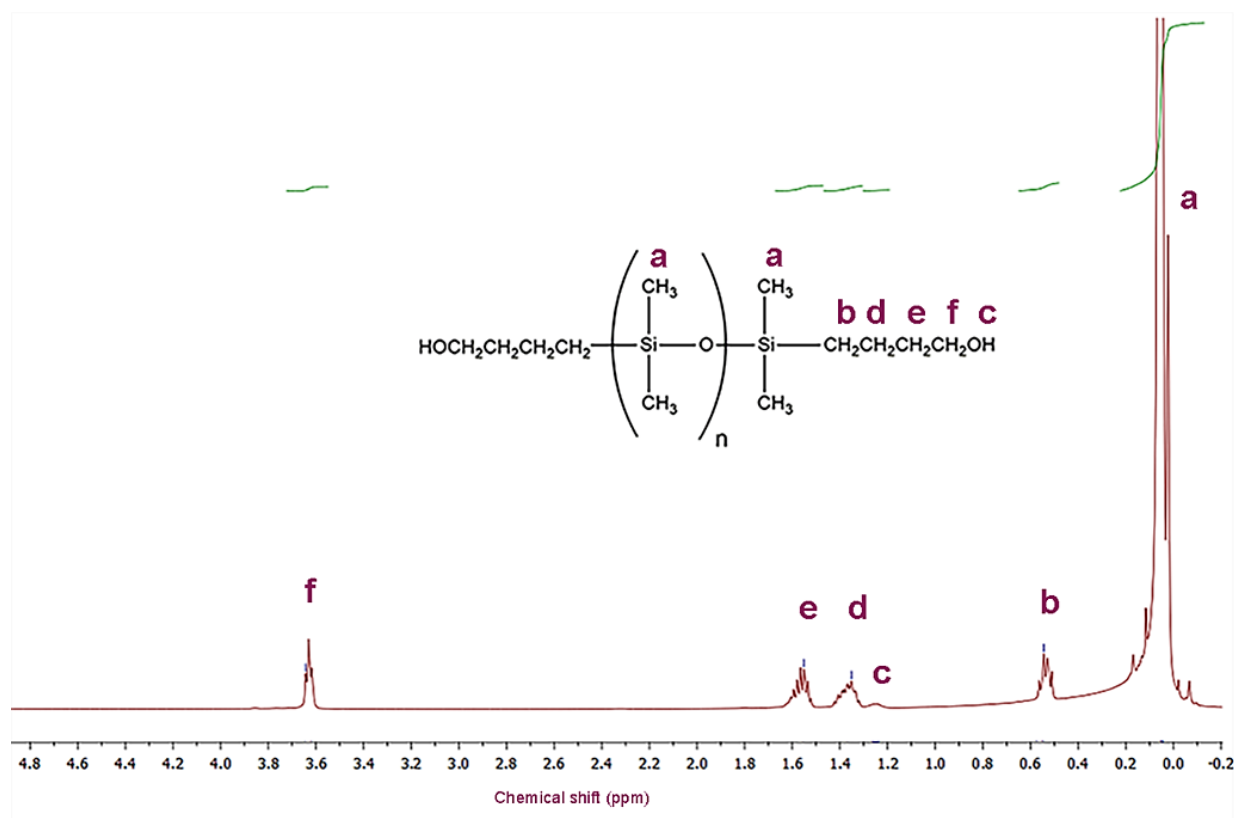


Figure 2.  $^1\text{H}$  NMR spectrum of the PDMS-30 sample.

The molecular weights of the synthesized PDMS oligomers were determined by comparing the signal intensities of the proton groups attached to the silicon atom and the protons of the terminal

methylene groups of the prepolymers attached to the hydroxyl group. Reaction conditions, viscosity, and molecular weight of the PDMS-OH samples are shown in Table 2.

Table 2. The reaction conditions, inherent viscosities, and the number-average molecular weight of the PDMS oligomers

Sample	Reaction temperature, °C	Reaction time, h	$[\eta]$ , dL g $^{-1}$	$M_n$ (NMR) g mol $^{-1}$
PDMS-95	95	24	0.411	10490
PLLA-65	65	24	0.160	4950
PLLA-30	30	48	0.075	2090

A standard synthetic route at a relatively high temperature of 95 °C yielded a polymer whose molecular weight was significantly higher than that previously determined by the composition of the reaction mixture (10490 g mol $^{-1}$  in comparison with a predetermined value of 2000 g mol $^{-1}$ ). At a later stage of the reaction, the reaction mixture was so viscous that its mixing was prevented. It is assumed that long exposure to high temperatures has led to condensation reactions of hydroxyl groups and a significant increase in molecular weight. By reducing the temperature to 65 °C, the effect of condensation of hydroxyl groups was reduced, but

the molecular weight of the obtained oligomer was more than twice as high as previously determined (4950 g mol $^{-1}$ ). The results showed that the reaction was possible at a temperature of 30 °C and during prolonged reaction time, which enabled complete control of the molecular weight of the synthesized oligomers.

A significant increase in the molecular weight of the synthesized polymers with increasing reaction temperatures was also reflected in the values of the inherent viscosities of the synthesized PDMS. The values of the inherent viscosities of PDMS oligomers of a predetermined weight of

2000 g mol<sup>-1</sup> differ significantly and range from 0.075 to 0.411 cm<sup>3</sup> g<sup>-1</sup>. The oligomer synthesized at a temperature of 30 °C, with a molecular weight of 2090 g mol<sup>-1</sup>, has the lowest value of inherent viscosity of 0.075 cm<sup>3</sup> g<sup>-1</sup>, while samples synthesized at higher temperatures have significantly higher viscosities as well as higher molecular weights.

The thermal and thermooxidative stability of PDMS prepolymers depended on the molecular weight of the oligomer. The initial degradation temperature, expressed as a mass loss of 5%, decreased as the chain length decreased. Based on the obtained results (Tables 3 and 4), it can be concluded that all PDMS samples were more stable in an inert atmosphere.

**Table 3.** TGA analysis of PDMS samples in O<sub>2</sub> atmosphere

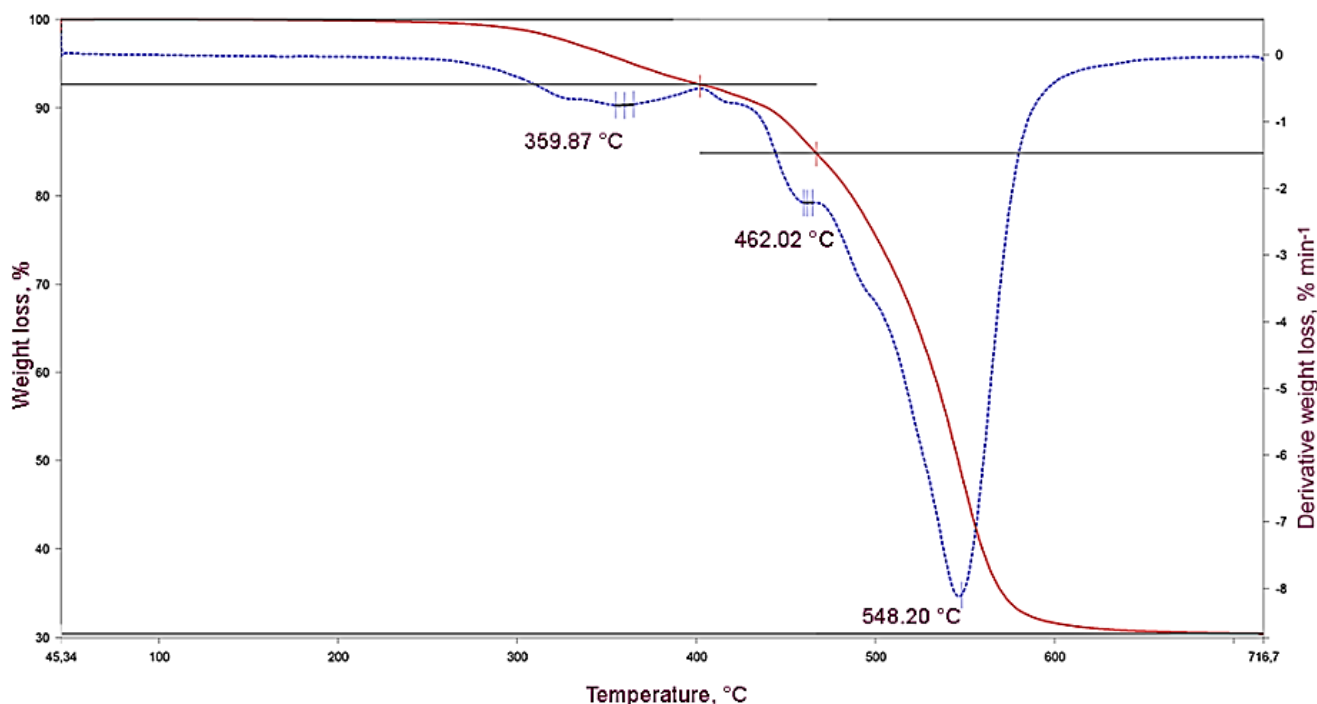
Sample	T <sub>5%</sub> , °C	T <sub>50%</sub> , °C	T <sub>max</sub> , °C	Residue at 700 °C, wt. %
PDMS-95	407	545	390/428/539	37
PLLA-65	368	538	360/462/548	31
PLLA-30	315	544	335/555	32

**Table 4.** TGA analysis of PDMS samples in O<sub>2</sub> atmosphere

Sample	T <sub>5%</sub> , °C	T <sub>50%</sub> , °C	T <sub>max</sub> , °C	Residue at 700 °C, wt. %
PDMS-95	450	580	510/620	0
PLLA-65	402	562	473/612	0
PLLA-30	340	502	458/537	0

Also, based on the shape of the differential TGA curve and the number of maxima, it can be concluded that the degradation process was more complex and took place in several phases in an

oxygen atmosphere, which is consistent with the results of other authors [6]. The thermogravimetric curves of the PDMS-30 sample in a nitrogen and oxygen atmosphere are shown in Figures 3 and 4.



**Figure 3.** TGA curves of PDMS-30 sample in O<sub>2</sub> atmosphere

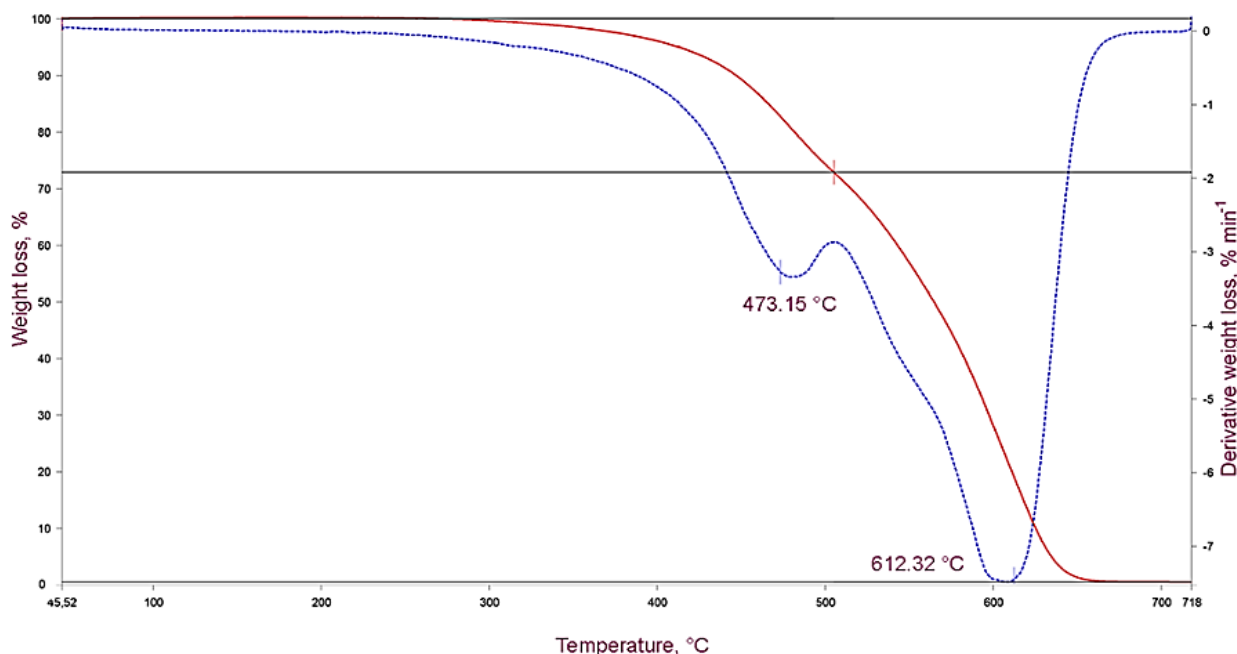


Figure 4. TGA curves of PDMS-30 sample in  $N_2$  atmosphere

Under oxidative conditions of thermal degradation of PDMS, free radicals are formed in the side groups and free radical reactions take place in which gaseous compounds of carbon, carbon monoxide, carbon dioxide, formaldehyde, methane acid, hydrogen, and water are formed, and silicon dioxide remains. Degradation of PDMS by depolymerization reactions in an inert atmosphere takes place practically without residue, thanks to the increased thermal stability of cyclic monomers compared to linear polymers. As siloxane degradation takes place by different mechanisms in an

inert and oxidative medium, the residue of poly (ester-siloxane) copolymers in an oxidative medium increase, and decreases in an inert atmosphere with increasing content of PDMS blocks [6,7].

Figure 5 shows a comparative TG-FTIR analysis of degradation products of all synthesized PDMS samples. As can be seen, TG-FTIR analysis showed that the degradation of all PDMS samples proceeds by similar mechanisms independent of the length of the PDMS segments.

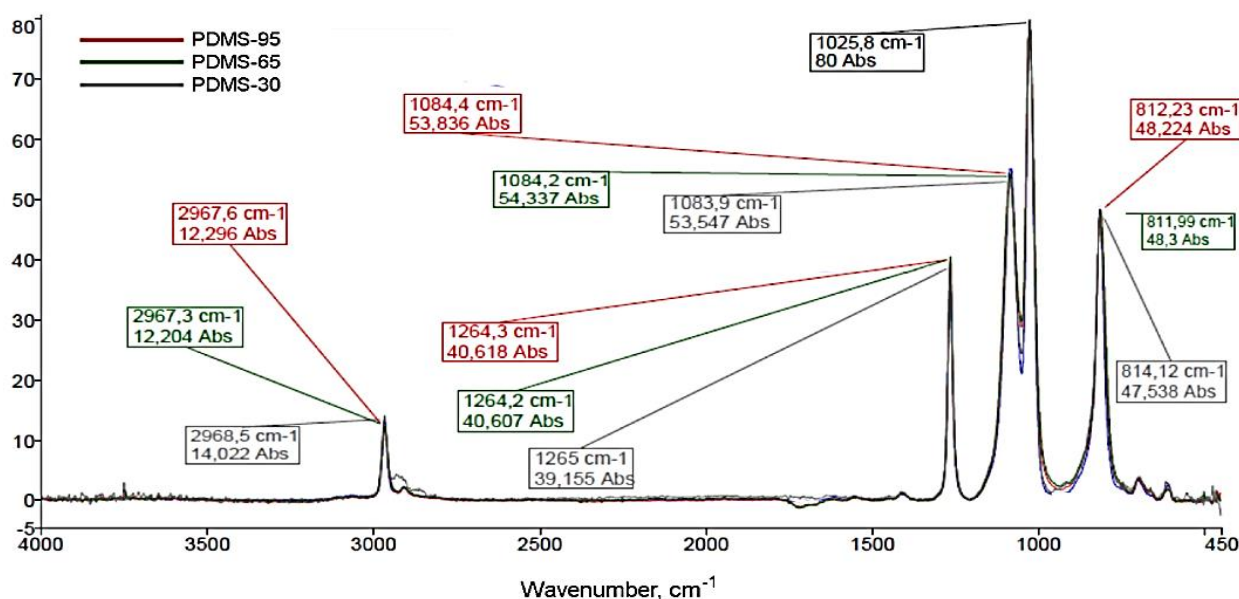


Figure 5. FTIR spectra of PDMS samples during TGA in the  $N_2$  atmosphere

#### 4. CONCLUSION

A series of hydroxybutyl-terminated PDMS oligomers were synthesized by siloxane equilibration reaction at various temperatures. The conventional synthetic route at a relatively high temperature of 95 °C gave a polymer whose molecular weight was unexpectedly higher than the one predetermined by the composition of the reaction mixture. The results showed that it was possible to perform the reaction at a low temperature of 30 °C and prolonged the time of reaction, which allowed complete control of the molecular weight of the synthesized oligomers. The thermal and thermooxidative stability of the PDMS oligomers was dependent on molecular weight. The temperature of onset of the degradation, expressed as 5% of the weight loss, decreased with the decrease in the polymer chain length. Generally, the PDMS samples were more stable in an inert atmosphere. TG-FTIR analysis showed a similar mechanism of the degradation for all examined samples regardless of the polymer chain length.

#### 5. ACKNOWLEDGEMENT

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Development of the Republic of Serbia (451-03-68/2020-14/200116).

#### 6. REFERENCES

- [1] I. Yilgör, J. E. McGrath, *Polysiloxane containing copolymers: A survey of recent developments*, Advances in Polymer Science, Vol. 86 (1988) 1–86.
- [2] M. Balaban, V. Antić, M. Pergal, D. Godjevac, I. Francolini, A. Martinelli, J. Rogan, J. Djonlagić, *Influence of the chemical structure of poly (urea-urethane-siloxane) s on their morphological, surface and thermal properties*, Polymer Bulletin, Vol. 70 (2013) 2493–2518.
- [3] P. R. Dvornic, R. W. Lenz, *High temperature siloxane elastomers*, Hüthing & Wepf, Heidelberg and New York 1990.
- [4] I. Yilgor, E. Yilgor, *Thermal stabilities of end groups in hydroxyalkyl terminated polydimethylsiloxane oligomers*, Polymer Bulletin, Vol. 40 (1998) 525–532.
- [5] J. L. Speier, M. P. David, B. A. Eynon, *Dehydration of 1,3-Bis(hydroxyalkyl)tetramethyl disiloxanes*, The Journal of Organic Chemistry, Vol. 25 (1960) 1637–1640.
- [6] A. Tasić, M. Pergal, M. Antić, V. Antić, *Synthesis, structure and thermogravimetric analysis of  $\alpha,\omega$ -telechelic polydimethylsiloxanes of low molecular weight*, Journal of the Serbian Chemical Society, Vol. 82 (2017) 1395–1416.
- [7] F. S. Chuang, H. Y. Tsi, J. D. Chow, W. C. Tsen, Y. C. Shu, S. C. Jang, *Thermal degradation of poly(siloxane-urethane) copolymers*, Polymer Degradation and Stability. Vol. 93 (2008) 1753–1761.

## СВОЈСТВА ТЕЛЕХЕЛИЧНИХ СИЛОКСАНА СИНТЕТИСАНИХ РЕАКЦИЈОМ ЕКВИЛИБРАЦИЈЕ НА НИСКИМ ТЕМПЕРАТУРАМА

**Сажетак:** Силоксанска еквилибрација у присуству одговарајућих функционалних дисилоксана уобичајена је метода за синтезу телехеличних силоксанских олигомера. Због високе реакционе температуре синтеза хидрокси-терминираних полисилоксана праћена је великим бројем споредних реакција. У овом раду оптимизована је синтеза хидрокси-терминираних силоксанских олигомера на релативно ниским температурама. Олигомери контролисане молекулске масе добијени су у присуству хетерогеног катализатора и карактерисани су спектроскопским и термичким методама, као и инфрацрвеном анализом (TG-FTIR) и вискозиметријом разблажених раствора.

**Кључне ријечи:** хидрокси-терминирани PDMS, реакција силоксанске еквилибрације,  $^1\text{H}$  NMR спектроскопија.

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