

SYNTHESIS AND CHARACTERIZATION OF REACTIVE GRAFT COPOLYMER PDMS-g-(PEO—OH)*

QIU Yongxing(邱永兴) YU Xiaojie(俞小洁)
and FENG Lingxian(封麟先)

(Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027)

ABSTRACT

A new reactive graft copolymer, poly (dimethyl siloxane)-graft- ω -hydroxyl-poly (ethylene oxide) (PDMS-g-(PEO—OH)), was synthesized by the hydrosilylation reaction of α , ω -bifunctional PEO macromonomer ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{PEO}-\text{OH}$) with poly (hydromethylsiloxane) (PHMS). The obtained copolymer, exhibited the expected comb-like structure as indicated by the result of detailed characterization and the needed reactivity as demonstrated by the result of esterification between PDMS-g-(PEO—OH) and aminoacetic acid. This reactive graft copolymer is expected to be very useful in the preparation of new bioactive polymer materials.

INTRODUCTION

A great deal of research effort has been devoted to the design and synthesis of truly blood-compatible polymer materials during the last few decades. The accumulative results have demonstrated that the bioactive polymer material, a type of material in which bioactive macromolecules are immobilized onto the surface of polymer substrates, may be the most promising one of possessing true blood-compatibility, although some pure polymers, such as poly (dimethylsiloxane) (PDMS), poly (ethylene oxide) (PEO) and polyetherurethane, may also exhibit good blood-compatibility^[1]. One of the best ways of synthesizing bioactive polymer materials with well-

* This work was supported by the Foundation for 863 Projects of the State Science and Technology Commission of China and the Natural Science Foundation of Zhejiang Province

Received January 31, 1994

defined structure is to immobilize covalently the bioactive macromolecules onto the surface of polymer substrates. And the bioactivity of the covalently-bound bioactive macromolecules would almost be fully kept if these molecules were immobilized onto the surface of polymer substrates via a suitable spacer (for example, PEO). Thus, in choosing PDMS as the polymer substrate and PEO as the spacer, and as the initial stage of a new bioactive antithrombogenic polymer material's research, the present paper will describe the fundamental results about the synthesis and characterization of a reactive graft copolymer: PDMS-g-(PEO—OH).

The hydrosilylation reaction of alkenes has been widely used to synthesize non-reactive block copolymers, for example, PDMS-b-PEO and PDMS-PEO-PDMS^[2,3] and PDMS-b-PS^[4], and non-reactive graft copolymers, such as PDMS-g-PEO^[5], PDMS-g-PMMA and PDMS-g-PS^[6]. This reaction was used in our Lab to synthesize the reactive graft copolymer: PDMS-g-(PEO—OH).

EXPERIMENTAL

Sodium allyl alcoholate ($\text{CH}_2=\text{CH}-\text{CH}_2\text{ONa}$) was prepared through the reaction of sodium with an excess of allyl alcohol under vacuum at room temperature. α -Allyl- ω -hydroxyl PEO macromonomer ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{PEO}-\text{OH}$) was synthesized by anionic polymerization of EO using $\text{CH}_2=\text{CH}-\text{CH}_2\text{ONa}$ as initiator, followed by termination of the alkoxide function of "living" PEO chains with a protonic acid. For details, the procedures used in the synthesis and purification of acryloyl terminated PEO macromonomer have been reported in the previous paper^[7].

PDMS-g-(PEO—OH) was prepared by the hydrosilylation reaction of $\text{CH}_2=\text{CH}-\text{CH}_2-\text{PEO}-\text{OH}$ macromonomer with commercial PHMS at about 70°C. Chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was used as catalyst and toluene as solvent. The graft copolymer was obtained by precipitating the reaction mixture with a large amount of heptane, followed by repeatedly washing the precipitate with heptane to remove the excess PHMS.

The esterification of PDMS-g-(PEO—OH) with aminoacetic acid was carried out at room temperature, using 1, 3-dicyclohexylcarbodiimide (DCCI, $\text{C}_6\text{H}_{11}\text{N}=\text{C}=\text{NC}_6\text{H}_{11}$) as catalyst.

RESULTS AND DISCUSSION

1. *Synthesis and characterization of α,ω -bifunctional PEO macromonomer*

The IR spectrum of PEO macromonomer exhibited the characteristic strong absorption of ether linkages at 1120cm^{-1} and that of hydroxyl groups at 3500cm^{-1} . The characteristic peak of double bond at 1640cm^{-1} was also observed.

In the $^1\text{H-NMR}$ spectrum, a strong peak at 3.6ppm due to the methylene groups in $-\text{CH}_2\text{CH}_2\text{O}-$ appeared. Moreover, the characteristic peak of hydroxyl groups at 2.8ppm was also presented. The IR and $^1\text{H-NMR}$ figures were not presented here for the reason that they have some similarity with that of acryloyl terminated PEO macromonomer as presented in Ref. [7].

The above results, together with the fact that the obtained PEO macromonomer has high mole percentage of end double-bonds (as listed in the last column of Table 1), confirm that the obtained PEO macromonomer do have the following expected structure:
 $\text{CH}_2=\text{CH}-\text{CH}_2-(\text{OCH}_2\text{CH}_2)_n\text{OH}$.

Table 1 Quantitative results of $(\text{CH}_2=\text{CH}-\text{CH}_2-\text{PEO}-\text{OH})$ macromonomers

Sample	$\bar{M}_n$ (theoretical)	$\bar{M}_n$ (VPO)	Relative deviation	H*	Mole% of allyl group
93-4-12	1160	1360	17.2%	1.4	80.2%
93-4-15	2020	2300	13.9%	1.3	96.1%
93-4-24	1800	2780	54.4%	1.4	52.7%
93-5-14	1080	1980	83.3%	/	20.5%

* Polydispersity index

As indicated in Table 1, $(\text{CH}_2=\text{CH}-\text{CH}_2-\text{PEO}-\text{OH})$ macro monomers with different PEO chain length and double-bond functionality were obtained. An interesting results can be observed by comparing the four samples in Table 1. For samples 93-4-12 and 93-4-15, which were synthesized by using the freshly-prepared $\text{CH}_2=\text{CH}-\text{CH}_2\text{ONa}$ as initiator, the $\bar{M}_n$ of these samples determined by VPO were found to be close to those predicated theoretically, and the double-bond functionality was quite high.

2. Synthesis and structural identification of PDMS-g-(PEO—OH)

It is obvious that the needed PDMS-g-(PEO—OH) graft copolymer can really be obtained if the hydrosilylation reaction occurs only between the end double bond of $(\text{CH}_2=\text{CH}-\text{CH}_2-\text{PEO}-\text{OH})$ and the Si—H bonds of PHMS, while at the same time the end hydroxyl remains non-reactive towards the Si—H bonds of PHMS. However, besides the desired hydrosilylation reaction, it seems also possible that the end hydroxyl may react with the Si—H bonds of PHMS. Therefore, the reaction between polyethylene glycol (PEG, $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$, $\bar{M}_n=1000$) and PHMS was studied in order to clarify the effect of end hydroxyl on the hydrosilylation reaction. Fortunately, the hydroxyl was confirmed to be non-reactive towards PHMS from the result that no copolymer can be detected from the mixture of PHMS and PEG under the same experimental conditions used in the hydrosilylation reaction. Thus, it is reasonable to conclude that the expected PDMS-g-(PEO—OH) will be obtained if the hydrosilylation reaction can occur between $\text{CH}_2=\text{CH}-\text{CH}_2-\text{PEO}-\text{OH}$ and PHMS.

The IR spectrum of the purified copolymer (Fig. 1) exhibited the characteristic absorption of hydroxyls at 3500cm^{-1} and that of $\text{Si}(\text{CH}_3)_2$ and SiCH_3 groups at 800cm^{-1} . The peak at 1120cm^{-1} due to the overlapping absorptions of the C—O—C and Si—O—Si linkages was also present. $^1\text{H-NMR}$ spectrum (Fig. 2) showed a single peak at 3.6ppm arising from the methylene groups in $-\text{CH}_2\text{CH}_2\text{O}-$ units and a single peak at 2.8ppm contributed by hydroxyl groups, while the peak of Si—H bonds at 4.7ppm disappeared. These results indicated that the hydrosilylation reaction had occurred between the end double bond of $(\text{CH}_2=\text{CH}-\text{CH}_2-\text{PEO}-\text{OH})$ and the Si—H bonds of PHMS, and the obtained copolymer did exhibit the expected comb-like structure with hydroxyl groups at the free ends of PEO side chains: PDMS-g-(PEO—OH).

3. Control of copolymerization

The effects of Si—H content of PHMS, $\bar{M}_n$ of PEO macromonomer and feed ratio of macromonomer to PHMS ($\text{C}=\text{C}/\text{Si}-\text{H}$) on the hydrosilylation were investigated.

As indicated in Table 2, in order to obtain non-crosslinking products, PHMS with low Si—H content should be used in the hydrosilylation.

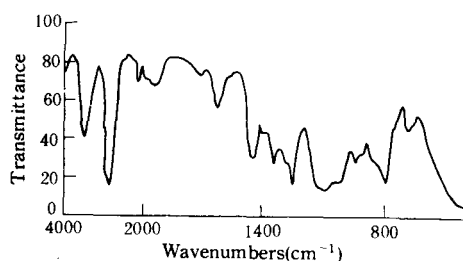
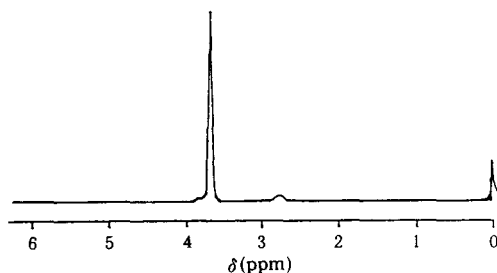


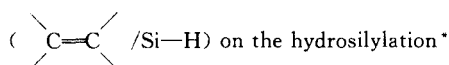
Fig. 1 IR spectrum of PDMS-g-(PEO—OH) copolymer

Fig. 2 ¹H-NMR spectrum of PDMS-g-(PEO—OH) copolymer**Table 2** Effect of Si—H content of PHMS on the hydrosilylation (70°C)

Sample	PHMS		Phenomenon
	$\bar{M}_n$	Si—H mol %	
1	3120	96.2	Crosslinking after 5 minutes
2	2910	82.6	Crosslinking after 90 minutes
3	2140	10.3	No crosslinking phenomenon appeared throughout the reaction of more than 5 hours

Little effect of $\bar{M}_n$ of PEO macromonomer on the hydrosilylation was observed (Table 3), which meant that the hydrosilylation reactivity of the end double bonds of the macromonomer was almost not affected by the $\bar{M}_n$ of macromonomer and thereby PDMS-g-(PEO — OH) copolymers with different PEO side chain lengths could be prepared.

As shown in Table 3, the feed ratio has some remarkable influence on the hydrosilylation. For the case of $\text{C}=\text{C} / \text{Si—H}$ bigger than 1, the hydrosilylation can be carried out completely and the product can be obtained by precipitating the reaction mixture with heptane. However, it should be pointed out that the product may include both the genuine graft copolymer and some excessive PEO macromonomer, for the reason that the amphiphilic PDMS-g-PEO may easily emulsify if trying further purification by washing the excessive PEO macromonomer with some solvent. For example, PDMS-g-PEO emulsified easily in methanol, a solvent for PEO and a precipitant for PDMS. Kiraly et al. [8] encountered the same problem when they tried to purify PDMS-PEO diblock copolymer.

Table 3 Effect of $\bar{M}_n$ of macromonomer and mole feed ratio

Sample	$\bar{M}_n$ of PEO	Feed ratio $\left(\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array} \right) / \text{Si}-\text{H}$	$\bar{M}_n$	Copolymer H	PEO(wt %)
1	2780	5/3	/	/	73.5
2	1980	5/3	11240	1.48	79.6
3	1450	5/3	11810	1.65	67.0
4	1450	1/1	7720	1.37	67.0
5	1450	1/2	* *	/	* *

* 70°C, 5hr., Pt/Si-H=1/750, Si-H mol% of PHMS=10.3%, toluene as solvent

* * No copolymer could be recovered from the reaction mixture

For the case of $\left(\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array} \right) / \text{Si}-\text{H}$ smaller than 1, surprisingly no product can be obtained by precipitating the reaction mixture either with heptane or with methanol.

4. Reactivity of PDMS-g-(PEO—OH)

The esterification of PDMS-g-(PEO—OH) with aminoacetic acid was studied primarily. The IR spectrum of the product was shown in Fig. 3. In addition to the characteristic peaks of PDMS and PEO, the IR spectrum also showed a strong peak at 1735cm^{-1} arising from ester groups and the splitting peaks at 3300cm^{-1} contributed by $-\text{NH}_2$, while at the same time, the characteristic peak of hydroxyl groups at 3500cm^{-1} disappeared. These results indicated that the esterification was completed under the experimental conditions, which meant that the PDMS-g-(PEO—OH) do exhibit the expected reactivity.

CONCLUSION

α -Allyl- ω -hydroxyl PEO macromonomer ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{PEO}-\text{OH}$) was synthesized successfully. A new reactive graft copolymer PDMS-g-(PEO—OH), which exhibited the comb-like structure with hydroxyl groups at the free ends of PEO side chains, was prepared by the hydrosilylation reaction of $\text{CH}_2=\text{CH}-\text{CH}_2-\text{PEO}-\text{OH}$ macromonomer with

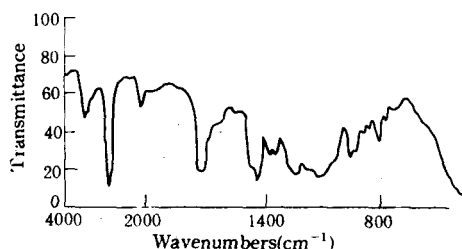


Fig. 3 IR spectrum of product obtained from the esterification of PDMS-g-(PEO—OH) with aminoacetic acid

commercial PHMS. As expected, this graft copolymer possessed the required reactivity. These results provide the basis for the further study of the reaction between PDMS-g-(PEO—OH) and bioactive macromolecules, which will led to the formation of bioactive polymer materials.

Keywords:

α -Allyl- ω -hydroxyl polyethylene oxide; Macromonomer; Reactive graft copolymer; Hydrosilylation

REFERENCES

- [1] Engbers, C. H. M. and Feijen, J., *Intern. J. Artif. Organs*, **1991**, 14(4), 199.
- [2] Galin, M. and Mathis, A., *Macromol.*, **1981**, 14, 677.
- [3] Haesslin, H. W., *Makromol. Chem.*, **1985**, 186, 357.
- [4] Chaumont, P.; Beinert, G.; Herz, J., et al., *Polymer*, **1981**, 22, 663.
- [5] Ni, J. L.; Lin, Y. Q. and Wang F. S., *Applied Chem.* (in Chinese), **1992**, 9(3), 7.
- [6] Chujo, Y.; Murai, K. and Yamashita, Y., *Makromol. Chem.*, **1985**, 186, 1203.
- [7] Qiu Y. X.; Yu X. J.; Feng L. X., et al., *Chinese J. Polym. Sci.*, **1993**, 11(1), 67.
- [8] Kiraly, Z. and Vincent, B., *Polymer International*, **1992**, 28, 139.