Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Reactivity of Hydroxypoly(ethylene oxide) propyl-*b*-polydimethylsiloxane-*b*-propyl hydroxypoly(ethylene oxide)

Weihu Li[a]; Xingyuan Zhang[a]; Jiabing Dai[a]
[a] CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, P.R. China

To cite this Article Li, Weihu , Zhang, Xingyuan and Dai, Jiabing(2009) 'Synthesis and Reactivity of Hydroxypoly(ethylene oxide) propyl-*b*-polydimethylsiloxane-*b*-propyl hydroxypoly(ethylene oxide)', Journal of Macromolecular Science, Part A, 46: 9, 914 — 920

To link to this Article: DOI: 10.1080/10601320903078396

URL: http://dx.doi.org/10.1080/10601320903078396

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2009) **46**, 914–920
Copyright © Taylor & Francis Group, LLC
ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320903078396

Synthesis and Reactivity of Hydroxypoly(ethylene oxide) propyl−*b*−polydimethylsiloxane−*b*−propyl hydroxypoly(ethylene oxide)

WEIHU LI, XINGYUAN ZHANG* and JIABING DAI

CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, P.R. China

Received February 2009, Accepted April 2009

A series of α, ω−bishydroxyl terminated PDMS, hydroxypoly(ethylene oxide) propyl−*b*−polydimethylsiloxane−*b*−propyl hydroxypoly(ethylene oxide) (HPEO−PDMS−HPEO) was prepared by a hydrosilation reaction of monoallyloxy substituted poly(ethylene oxide) with α,ω−bishydrogen terminated PDMS (HPDMS) that obtained via acid−catalyzed ring−opening polymerization of octamethylcyclotetrasiloxane with 1,1,3,3−tetramethyldisiloxane. Chloroplatinic acid was employed as the catalyst of hydrosilation. The molecular weight of HPEO−PDMS−HPEO could be controlled easily by varying the chain length of HPDMS. FTIR and ^{1}H−NMR spectroscopy were used to identify the structure of HPEO−PDMS−HPEO and HPDMS. The conversion of Si−H bond to Si−C bond was affected by the catalyst amount, reaction time and temperature. It was found that the optimum condition of hydrosilation reaction was the catalyst amount of 22 μg/g and 5 h time at 100°C. Synthesized HPEO−PDMS−HPEO showed good storage stability at ambient temperature. Urethane reaction of OH and NCO group revealed that HPEO−PDMS−HPEO was more reactive toward to diisocyanate than α,ω−bishydroxylbutyl terminated PDMS.

Keywords: Synthesis, reactivity, hydrosilation reaction, α,ω−bishydroxyl terminated PDMS

1 Introduction

α,ω−Bishydroxyl terminated polydimethylsiloxane (PDMS) is a versatile starting material for preparing the block or graft copolymers of siloxane−urethane, siloxane−ester and siloxane−epoxy type (1−6). PDMS modified copolymers exhibit an interesting combination of oxidative stability, low surface energy and biocompatibility (7−10). Therefore, the copolymers can be used in the preparation of weatherproof and hydrophobic coating, adhesive and biomaterials. The α,ω−bishydroxyl terminated PDMS reported up to now is basically hydroxyalkyl terminated PDMS (HAPDMS) (11−12), prepared by base− or acid−catalyzed equilibration reaction of octamethylcyclotetrasiloxane (D_4) with a disiloxane endblocker and the subsequent thermal or other treatment of the resulting product (13). A major problem related to the preparation of well-defined dihydroxyalkyl terminated PDMS oligomers with controlled molecular weight was the stability of end groups. It has been shown that hydroxyalkyl groups undergo dehydration yielding vinyl type end groups under strong acid catalysis (14). In addition, because of limited commercial availability, disiloxane endblockers that can be used to prepare HAPDMS are only either 1,3−bis(3−hydroxypropyl) tetramethyldisiloxane or 1,3−bis(4−hydroxybutyl) tetramethyldisiloxane. However, these disiloxanes cyclized when subjected to high temperature in neutral conditions (15). Moreover, when HAPDMS was used in modifying polyurethanes or polyesters, synthesis of the copolymers suffered from a problem related to the solubility of PDMS with other components owing to large solubility differences between nonpolar PDMS and polar components (16). This makes organic solvent even mixing solvents necessary in the synthetic process. Thus, new synthetic methods and improvement of hydroxyl terminated PDMS still need to be addressed.

In this article, α, ω−bishydrogen terminated PDMS (HPDMS) is first obtained via acid−catalyzed equilibration reaction of D_4 with 1,1,3,3−tetramethyldisiloxane (TMS), and then α,ω−bishydroxyl terminated PDMS, hydroxypoly(ethylene oxide) propyl−*b*−polydimethylsiloxane−*b*−propyl hydroxypoly(ethylene oxide) (HPEO−PDMS−HPEO) is prepared by a hydrosilation reaction of monoallyloxy substituted poly(ethylene oxide) (MAPEO)

---

*Address correspondence to: X. Zhang, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, P.R. China. E-mail address: zxym@ustc.edu.cn

oligomer with HPDMS. Further investigation shows that HPEO−PDMS−HPEO is stable, and has good reactivity toward diisocyanates.

2 Experimental

2.1 Materials

1,1,3,3-Tetramethyldisiloxane and octamethylcyclotetrasiloxane (Jiangxi Xinghuo Chemical Co., Ltd.) were distilled before use. Monoallyloxy substituted poly (ethylene oxide) ($M_n = 350$, Yangzhou Chenhua Scientific Co., Ltd.) was dried over 4−Å molecular sieves. Sulfuric acid, toluene (Shanghai Chemical Reagent Corporation) and 4,4′-methylene diphenyl diisocyanate (MDI) (Degussa Corporation) are used as received. 2,4−tolylene diisocyanate (TDI) and isophorone diisocyanate (IPDI) (Junsei Chemical Co., Ltd.) were vacuum distilled before use. Chloroplatinic acid (Shanghai Chemical Reagent Corporation) was dissolved in isopropanol (50 μg/ml).

2.2 Synthesis of HPEO−PDMS−HPEO

2.2.1. *Synthesis of HPDMS*

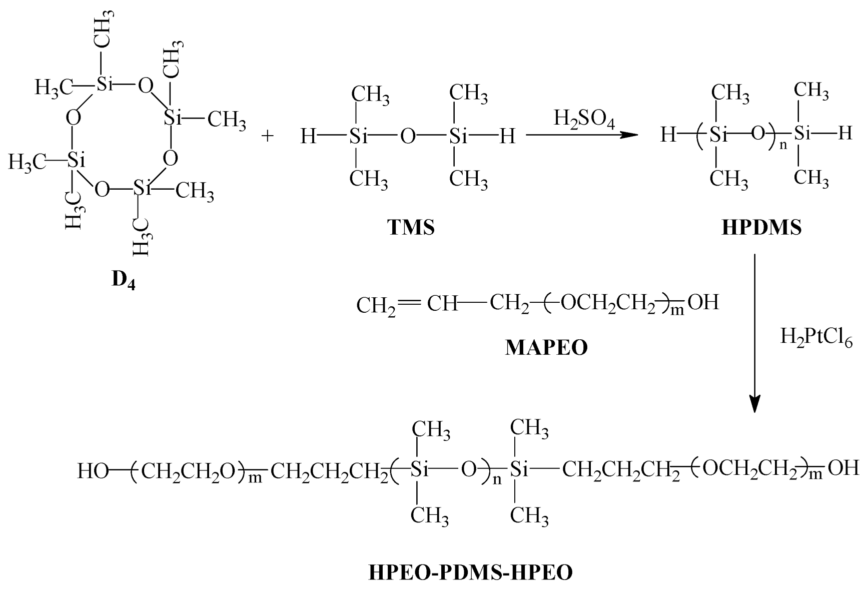
Scheme 1 shows the general synthesis process of HPEO−PDMS−HPEO. The first step is the synthesis of HPDMS. As an example (molar ratio of D_4 and TMS is 5:1), the reaction was carried out in a four-necked flask equipped with a stirrer, a nitrogen inlet, a reflux condenser and a thermometer. 119.2 g D_4, 10.7 g TMS and 1.3 g sulfuric acid were first added into the reactor. Ring−opening polymerization was carried out at 45°C under N_2 atmosphere for about 48 h until the system reached the thermodynamic equilibrium. In order to purify HPDMS, some ether as dilution agent was added into the mixture, and the mixture was then washed with deionized water repeatedly to remove the catalyst through a separating funnel until the washings were neutral (pH = 7.0). After that, upper layer organic solution was separated and dried with anhydrous sodium sulfate. Finally, the solution was treated by filtrating and distilling under reduced pressure at 120°C to remove D_4 remaining in the solution. The purified HPDMS was obtained. Changing the molar ratio of D_4 and TMS, HPDMS with different molecular weigh could be synthesized.

2.2.2. *Synthesis of HPEO−PDMS−HPEO*

The prepared HPDMS and MAPEO according to a fixed mole ratio of 1/2.3 were dissolved in toluene, suitable chloroplatinic acid as a catalyst was added at an elevated temperature. The synthesis reaction was carried out at 100°C under N_2 atmosphere for 5 h. After completion of the reaction, the product was purified by washing, drying, filtrating and distilling similar to HPDMS preparation process. The synthesized HPEO−PDMS−HPEO is a slightly yellow liquid and the molecular weight of HPEO−PDMS−HPEO can be controlled easily by changing the molecular weight of HPDMS.

2.3 Measurements

Fourier transform infrared (FTIR) spectroscopy was employed to follow and identify the structure of HPDMS and HPEO−PDMS−HPEO. FTIR spectra were recorded on a Nicolet−Nexus−FTIR spectrometer over the range of 4000−650 cm^{-1}. Nuclear magnetic resonance (^{1}H−NMR) spectroscopy was used to estimate the molecular weight (M_n) of HPDMS. The spectra were obtained using a



Sch. 1. General synthesis process of HPEO−PDMS−HPEO.

Varian DRX 500 NMR spectrometer with an operating frequency of 400 MHz and deuterated chloroform as solvent. ^{1}H−NMR spectra was also used to follow the hydrosilation process. In the synthesis process, the hydroxyl-value (OH-value) was determined by the pyridine-acetic anhydride method (ASTM−1957−86). Moreover, FTIR spectroscopy was also used to detect the remaining NCO group in the reaction system as the literature (17).

3 Results and Discussion

3.1 Synthesis of HPDMS and HPEO−PDMS−HPEO

In the first step of Scheme 1, intermediate product HPDMS was prepared by ring-opening equilibrium polymerization of D_4 with TMS as end-blocker. The polymerization can be catalyzed by both acid (*i.e.* sulfuric acid) and base (*i.e.* quaternary ammonium base) catalyst (18). However, because the Si−H group of TMS is unstable for base catalysts (19), acid catalyst, sulfuric acid was employed in this reaction. The molecular weight of HPDMS can be controlled by feeding different molar ratio of D_4 and TMS. Chosen D_4 and TMS at molar ratios of 3:1, 5:1, 7:1 and 9:1 could give the theoretical molecular weights of 1000, 1600, 2200, 2800 g/mol, respectively. Except for controlling the molecular weight, TMS also allowed the polymer to have Si−H terminals, which would be needed in the second step of the synthesis. Unreacted D_4 was separated by distilling the reaction mixture under vacuum condition. According to distilling result, D_4 remaining varies from 11% to 16%, affected by the molar ratio of D_4 and TMS. The larger the molar ratio is, the more the D_4 remains.

FTIR spectra of reactants (TMS and D_4) and intermediate product (HPDMS) are shown in Figure 1. The characteristic absorption bands locating at 2963 cm^{-1} (CH_3), 1260 cm^{-1} and about 810 cm^{-1} [$Si(CH_3)_2$] are presented in the spectra of HPDMS, D_4 and TMS. Because of ring−opening polymerization, the ambiguous double absorption peak in the range of 1095−1060 cm^{-1} (cyclic Si−O−Si) for D_4 has been converted into two clear peaks located at 1093 and 1028 cm^{-1} (linear Si−O−Si) for HPDMS, respectively. The spectrum of HPDMS showed the absorption peak at 2129 cm^{-1} (Si−H) similar to that of TMS, while there is no absorption in the spectrum of D_4.

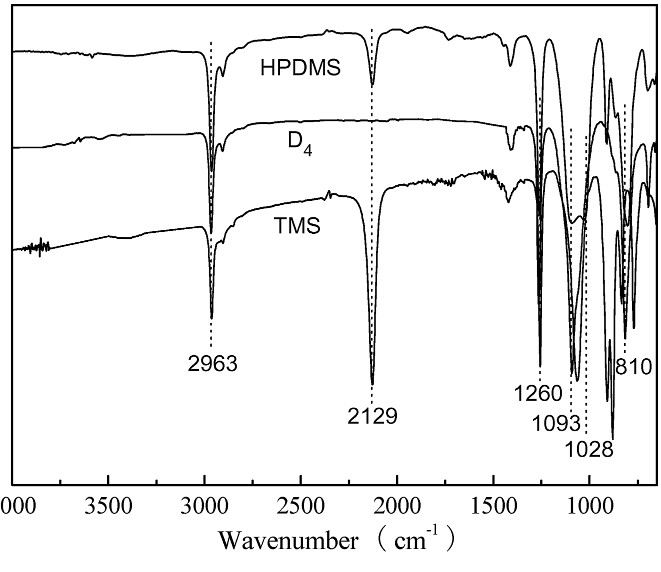


Fig. 1. FTIR spectra of TMS, D4 and HPDMS.

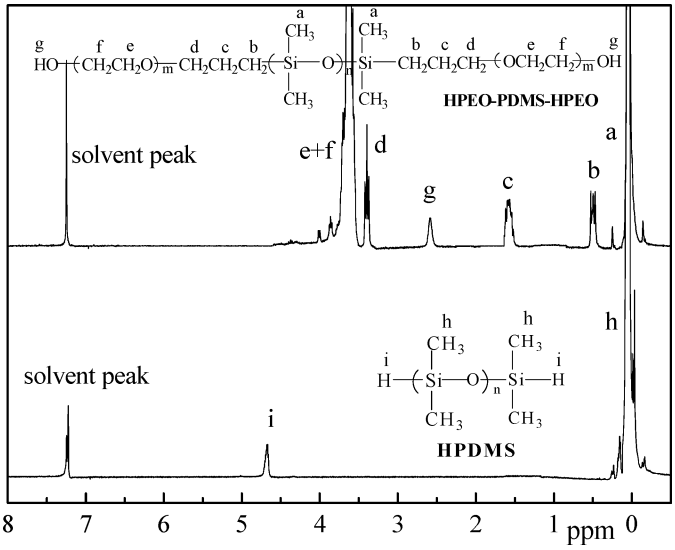


Fig. 2. ^{1}H−NMR spectra of HPEO-PDMS-HPEO and HPDMS.

Calculating the ratio of peak area of methyl hydrogen (Si−$\mathbf{CH_3}$, δ =0.02−0.09) and proton attaching to silicon (Si−**H**, δ = 4.71) in ^{1}H−NMR spectra, M_n of HPDMS can be determined. Figure 2 shows the ^{1}H−NMR spectra of HPDMS and HPEO−PDMS−HPEO. Based on the spectrum of HPDMS, the calculated results give the molecular weights of approximately 900, 1400, 1900, 2400 g/mol for the molar ratios of 3:1, 5:1, 7:1 and 9:1 (D_4:TMS), respectively.

In the second step of Scheme 1, HPEO−PDMS−HPEO was prepared by a hydrosilation reaction of prepared HPDMS with MAPEO. The reaction was carried out in toluene due to phase separation of the mixture. Chloroplatinic acid was chosen as the catalyst because it had been proven to be an extremely active catalyst for the hydrosilation. Comparing FTIR spectrum of HPEO−PDMS−HPEO with those of HPDMS and MAPEO shown in Figure 3, it could be found that three peaks locating at 3475 cm^{-1} (OH), 2935 and 2871 cm^{-1} (CH_2) originated from MAPEO, and other six peaks at 2963 and 2906 cm^{-1} (CH_3), 1260 and about 810 cm^{-1} [$Si(CH_3)_2$], 1093 and 1028 cm^{-1} (linear Si−O−Si) originated from HPDMS, were shown in the spectrum of HPEO−PDMS−HPEO. But the peaks at 3080 and 1645 cm^{-1} (CH_2 = CH) related to MAPEO, and at

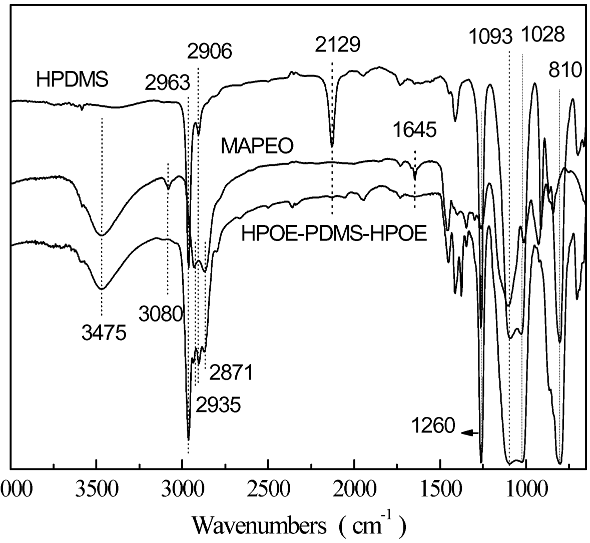


Fig. 3. FTIR spectra of HPDMS, MAPEO and HPEO−PDMS−HPEO.

2129 cm^{-1} (Si−H) related to HPDMS disappeared, respectively. Moreover, the peak at 1105 cm^{-1} (CH_2−O−CH_2) for MAPEO was overlapped by the peaks dealing with the absorption of linear Si−O−Si in the spectrum of HPEO−PDMS−HPEO. Based on the above analyses, it is confirmed that the final synthesized product is HPEO−PDMS−HPEO.

^{1}H−NMR analysis shown in Figure 2 further supported chemical structure of HPEO−PDMS−HPEO and HPDMS. For the spectrum of HPEO−PDMS−HPEO, triplet peaks appear at 0.49 ppm could be assigned to the protons of methylene attached to silicon (t, Si−$\mathbf{CH_2}$), indicating the occurrence of hydrosilation reaction. The other peaks were classified as $\delta = 0.02$−0.09 (s, Si−$\mathbf{CH_3}$), 1.58 (m, C−$\mathbf{CH_2}$−C), 2.58 (−**OH**), 3.39 (t, C−C−$\mathbf{CH_2}$), 3.57−3.68 (m, O−$\mathbf{CH_2}$−$\mathbf{CH_2}$−O). In the spectrum of HPDMS, except for the peak appear at the range of 0.02−0.09 ppm assigned to Si−$\mathbf{CH_3}$, another peak locating at 4.68 ppm could be attributed to the proton of Si−**H** (20).

By using the optimized synthetic conditions, a series of HPEO−PDMS−HPEO with different molecular weight of 1600, 2100, 2700, 3100 g/mol, estimated by ^{1}H−NMR, marked as H−1600, H−2100, H−2700, H−3100, were synthesized respectively.

3.2 Effects of Time, Temperature and Catalyst on the Hydrosilation Yield

In order to optimize the synthesis condition, the effects of reaction time, temperature and catalyst on the hydrosilation yield were investigated by following ^{1}H−NMR spectrum of reaction mixture (21−23). Figure 4 shows ^{1}H−NMR spectra for the mixture of HPDMS and MAPEO at different hydrosilation time. Peaks located at 7.26 ppm, 7.24−7.11 and 2.36 ppm could be attributed to the solvent of chloroform-*d* and toluene, respectively. As the increase of reaction time, peak area of Si−**H** (δ =4.71) decreases and that of Si−$\mathbf{CH_2}$ (δ =0.49) increases, but Si−$\mathbf{CH_3}$ (δ =0.02−0.09) does not change. The hydrosilation yield of Si−H to Si−CH_2 at *t* time could be calculated using the equation:

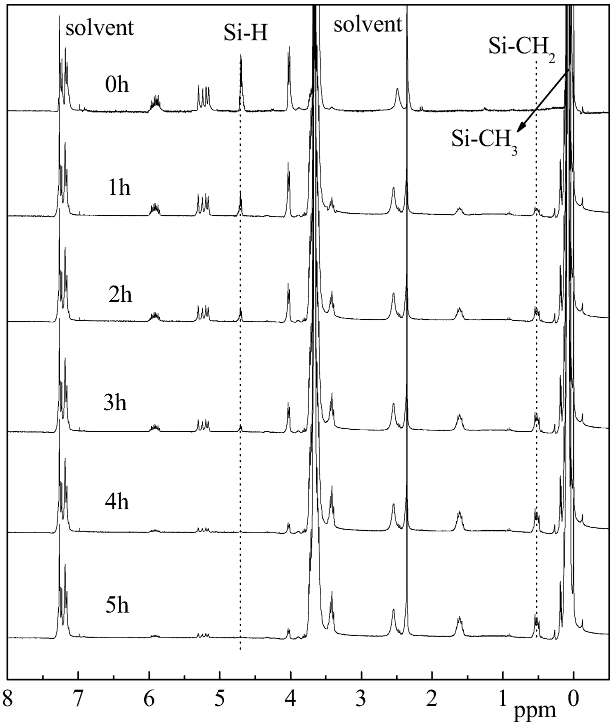


Fig. 4. ^{1}H−NMR spectra of the hydrosilation process at different time for the mixture of HPDMS and MAPEO. Reaction temperature is 100°C, and catalyst amount is 22 μg/g.

$$\text{hydrosilation yield (\%)} = \left[1 - \frac{(A_{\mathrm{SiH}} / A_{\mathrm{SiCH3}})_t}{(A_{\mathrm{SiH}} / A_{\mathrm{SiCH3}})_0}\right] \times 100\%$$

Where A_{SiH} and A_{SiCH3} are the peak areas of Si−H and Si−CH_3, respectively. Through investigating the change of A_{SiH} and A_{SiCH3} at different reaction temperature and catalyst amount, the effects of temperature and catalyst amount on the hydrosilation yield were also followed by NMR spectra.

Reaction time plays a significant role for the hydrosilation yield. As expected, the hydrosilation yield increases with the increase of reaction time. It could be seen from Figure 5 that the hydrosilation yield increased rapidly from 0 to 3 h, and then increased slowly. The hydrosilation yield became a constant gradually when the reaction time increased to about 5 h. The result showed that prolonging the reaction time led to a direct consequence of the favorable effect on diffusion of the reactants between HPDMS and MAPEO molecules. However, as the decrement of reactants the probability of collision between reactive groups

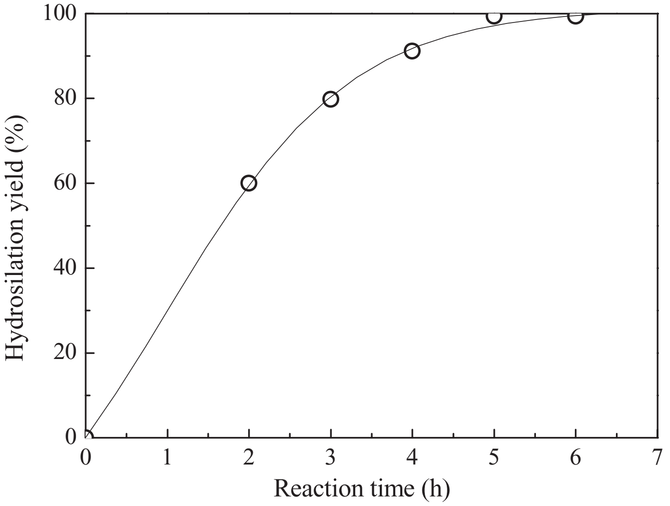


Fig. 5. Hydrosilation yield increases with the increase of reaction time.

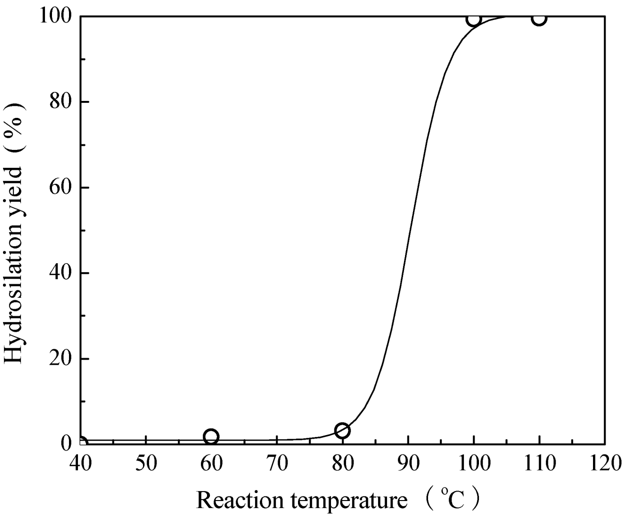


Fig. 7. Hydrosilation yield increases with the increase of reaction temperature.

(Si–H of HPDMS and vinyl of MAPEO) decreased, the increment of the hydrosilation yield reduced.

Chloroplatinic acid had been proved to be an extremely active catalyst for the hydrosilation of HPDMS and MAPEO. The experiment showed that the hydrosilation yield was affected markedly when the catalyst amount was lower than 20 μg/g. Figure 6 shows a relationship between the hydrosilation yield and catalyst amount. The hydrosilation yield increased linearly with the increase of catalyst amount when the amount was less than 18 μg/g, and became nearly a constant when the amount was higher than 22 μg/g. The result indicated that 22 μg/g was a rather efficient amount of catalyst.

Similarly, the reactive temperature also affected the hydrosilation yield. The dependence of hydrosilation yield on reaction temperature was shown in Figure 7. The hydrosilation yield was below 10% when the temperature was lower than 80°C, but there was a great leap between 80°C and 110°C. Those indicated that the catalyst was almost inactive below 80°C, and the reaction would react rapidly after the catalyst was activated. It may be explained that the catalyst could not contact the reactive group efficiently below 80°C, meanwhile, because hydrosilation reaction is a rapid exothermic reaction, the temperature would accelerate the hydrosilation reaction once the reaction was begun. In addition, according to the experiment, the reaction would be gelatinated above 120°C as the result of violent reaction. When the temperature was 100°C, total hydrosilation could be achieved with the catalyst amount of 22 μg/g for 5 h.

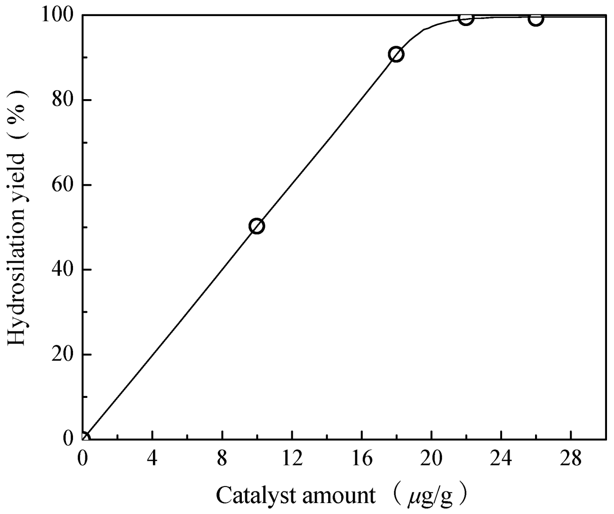


Fig. 6. Hydrosilation yield increases with the increase of catalyst amount.

3.3 Stability of HPEO–PDMS–HPEO

Normally hydroxyalkyl terminated PDMS, especially hydroxypropyl and hydroxybutyl terminated PDMS are not stable because of the cyclization (13, 15). Compared with hydroxyalkyl terminated PDMS, HPEO–PDMS–HPEO have long polyether chains at the ends of PDMS, which is not thermodynamically favorable for the formation of ring structure. Hydroxyl is the most important functional group of hydroxyl terminated PDMS, so the change of hydroxyl value reflect the stability of HPEO–PDMS–HPEO. Table 1 shows the OH–value at different temperature and time for the samples of H–1600 and H–3100. From Table 1, the following results can be observed easily:

1. Two samples are stable for at least 3 months at 25°C;

Table 1. OH−Value of HPEO−PDMS−HPEO at different temperature and time

Sample code	*Temperature (°C)*	*Time*	*OH− Value (mgKOH/g)*
H−1600	25	0	67.6
		1 months	67.5
		3 months	67.6
H−3100		0	35.2
		1 months	35.2
		3 months	35.2
H−1600	60	4 h	67.6
		8 h	67.6
H−3100		4 h	35.2
		8 h	35.1
H−1600	100	4 h	67.6
		8 h	67.4
H−3100		4 h	35.2
		8 h	35.2
H−1600	130	4 h	67.3
		8 h	66.9
H−3100		4 h	35.1
		8 h	35.0

2. The samples have good stability below 100°C for 4 h. As the rise of temperature and increase of time, the hydroxyl values decreases slightly due to the condensation of hydroxyl over 100°C;
3. Molecular weight affects the stability. The sample with large molecular weight is more stable than the smaller one. For example, the hydroxyl value of H-3100 decreases 0.7%, but that of H-1600 decreases 1.0% at 130°C for 8 h.

3.4 Reactivity of HPEO−PDMS−HPEO Towards Diisocyanate

Urethane reaction of OH and NCO groups in bulk was carried out to investigate the reactivity of HPEO−PDMS−HPEO, and $\alpha,\omega-$bishydroxylbutyl terminated PDMS (DHB−PDMS, $M_n = 2000$) used as a reference. Generally, the concentration of NCO group decreases with the increase of reaction time in the urethane reaction of OH and NCO groups, and the progressive decrease of absorption intensity for NCO group (2261 cm^{-1}) in FTIR spectrum with the time could be carefully monitored to calculate the relative concentration of reactants. Figure 8 shows the absorbance of NCO group for the reaction of H−2100 with MDI at 80°C. The absorbance decreases gradually with the increase of reaction time. Using the second−order kinetics model for the urethane reaction of OH and NCO groups, the reaction rate constant k could be calculated according to the slope of linear relationship between $(A_0 - A_t)/A_t$ and the time (24−25), here A_0 and A_t were the absorbance at initial time and t, respectively.

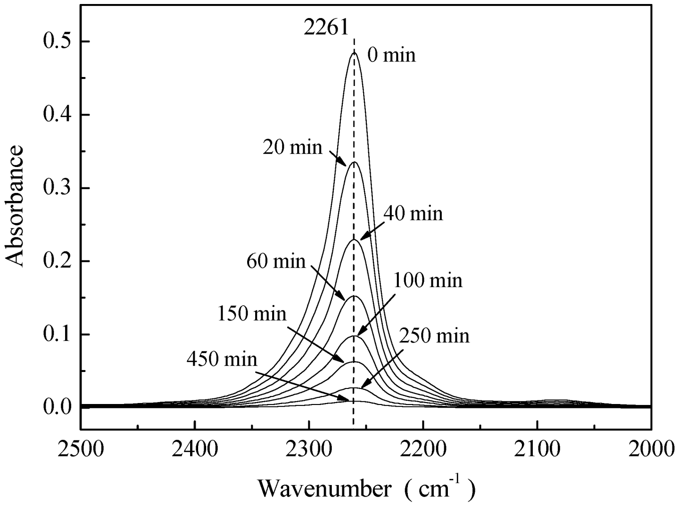


Fig. 8. Absorbance of NCO group decreases with the increase of reaction time.

The second−order reaction rate constant k for stoichiometric reactions between hydroxyl−terminated PDMS and diisocyanates at 60 and 80°C is shown in Table 2. As expected, k increases with increasing reaction temperature. Table 2 shows that H−2100 is more reactive than DHB−PDMS. In the same conditions, k of H−2100 towards MDI is 2.4 times larger than DHB PDMS at 60°C and 4.0 times at 80°C, respectively, indicating H—2100 has the reactivity more than two times higher than that of DHB−PDMS. Similar reactivity can be found by comparing k of two kinds of hydroxyl−terminated PDMS with IPDI and TDI. The reaction rate constant of H−2100 with IPDI at 60°C is 3.0 times as large as DHB−PDMS, while that of H−2100 with TDI at 80°C is 3.7 times larger than DHB−PDMS. All the data show that H−2100 is

Table 2. Reaction rate constant for NCO and OH groups in contrastive reactions

Reaction temperature (°C)	*Reactants*	*k (L·mol^{-1}·s^{-1})*
60	H−2100 + MDI	2.7×10^{-4}
	DHB−PDMS + MDI	1.2×10^{-5}
	H−2100 + IPDI	4.0×10^{-5}
	DHB−PDMS + IPDI	1.3×10^{-5}
	H−2100 + TDI	3.3×10^{-4}
	DHB−PDMS + TDI	1.4×10^{-4}
80	H−2100 + MDI	9.7×10^{-4}
	DHB−PDMS + MDI	2.5×10^{-4}
	H−2100 + IPDI	1.8×10^{-4}
	DHB−PDMS + IPDI	1.3×10^{-4}
	H−2100 + TDI	1.1×10^{-3}
	DHB−PDMS + TDI	3.0×10^{-4}

more reactive towards to diisocyanate than DHB−PDMS. For other samples of HPEO−PDMS−HPEO, similar result could be observed at different reaction temperature. It may be explained in terms of a relative small difference of solubility for HPEO−PDMS−HPEO and diisocyanates compared with DHB-PDMS. The part of poly(ethylene oxide) capping at both ends of HPEO−PDMS−HPEO chain enhances the polarity of the chain, leading to the HPEO−PDMS−HPEO chain is easier to attack NCO group of the polar diisocyanates according to the principle that a similar substance is more likely to dissolve each other.

4 Conclusions

A series of novel HPEO−PDMS−HPEO was synthesized by a hydrosilation reaction of MAPEO with HPDMS that was obtained via an acid−catalyzed ring-opening equilibration reaction of D_4 with TMS. The molecular weight of HPEO−PDMS−HPEO could be controlled easily in the range of 1600−3100 g/mol by varying the molecular weight of HPDMS. FTIR and ^{1}H−NMR spectroscopy confirmed the structure of HPEO−PDMS−HPEO and HPDMS. The conversion of Si−H bond to Si−C bond was affected by the catalyst amount, reaction time and temperature. The optimum condition for hydrosilation reaction was the catalyst amount of 22 μg/g, reaction time of 5 h and reaction temperature of 100°C. The measurement of the OH−value at different temperature showed that HPEO−PDMS−HPEO had good storage stability. Urethane reaction of OH and NCO group indicated that HPEO−PDMS−HPEO was more reactive towards to diisocyanates such as MDI, IPDI and TDI than α,ω−bishydroxylbutyl terminated PDMS.

Acknowledgments

Financial support from the National Natural Science Foundation of China (No. 20073041) and Anhui Provincial Education Department (No.2006KJ047A) are acknowledged.

References

1. Bai, C.Y., Zhang, X.Y., Dai, J.B. and Wang, J.H. (2008) *J. Coat. Technol. Res.*, 5: 251.
2. Liao, S.K., Jang, S.C. and Lin, M.F. (2005) *J. Polym. Res.,* 12: 103–112.
3. Antic, V.V., Govedarica, M.N. and Djonlagic, J. (2004) *Polym. Int.*, 53: 1786–1794.
4. Bai, C.Y., Zhang, X.Y. and Dai, J.B. (2007) *Prog. Org. Coat.*, 60: 63–68.
5. Zhou, C., Zhang, X.Y., Dai, J.B. and Zhang, H.P. (2005) *Chin. J. Chem. Phys.*, 18: 448–452.
6. Ahmad, S., Gupta, A.P., Sharmin, E., Alam, M. and Pandey, S.K. (2005) *Prog. Org. Coat.*, 54: 248–255.
7. Bai, C.Y., Zhang, X.Y. and Dai, J.B. (2007) *J. Macromol. Sci., Pure Appl. Chem.*, 44: 1203–1208.
8. Zhang, C.Y., Zhang, X.Y., Dai, J.B. and Bai, C.Y. (2008) *Prog. Org. Coat.*, 63(2): 238–244.
9. Bai, C.Y., Zhang, X.Y., Dai, J.B. and Zhang, C.Y. (2007) *Prog. Org. Coat.*, 59: 331–336.
10. Dabagh, M., Abdekhodaie, M.J. and Khorasani, M.T. (2005) *J. Appl. Polym. Sci.*, 98: 758–766.
11. Yilgor, I. and McGrath, J.E. (1988) *Adv. Polym. Sci.*, 86: 1–88.
12. Yu, X.H., Nagarajan, M.R., Li, C., Gibson, P.E. and Cooper, S.L. (1986) *J. Polym. Sci., Polym. Phys.*, 24: 2681–2702.
13. Yilgor, I. and Yilgor, E. (1998) *Polym. Bull.*, 40: 525–532.
14. Kojima, K., Gore, C.R. and Marvel, C.S. (1966) *J. Polym. Sci., Polym. Chem.*, 4: 2325–2327.
15. Lai, Y.C., Ozark, R. and Quinn, E.T. (1995) *J. Polym. Sci., Polym. Chem.*, 33: 1773–1782.
16. Yu, X.H., Nagarajan, M.R., Grasel, T.G., Gibson, P.E. and Cooper, S.L. (1985) J. *Polym. Sci., Polym. Phys.*, 23: 2319–2338.
17. d'Arlas, B.F., Rueda, L., Stefani, P.M., CaBa, K. De la, Mondragon, I. and Eceiza, A. (2007) *Thermochimica Acta*, 459: 94–103.
18. Voronkov, M.G. Mileshkevich, V.P. and Yuzhelevskii, Y.A. The Siloxane Bond (Physical Properties and Chemical Transformations), Plenum Publishing Corporation: New York, 159–175, 1991.
19. E.A.V. Ebsworth, Voltile Silicon Compounds, Pergamon Press: Warsaw, 26–37, 1963.
20. Nair, B.R., Osbourne, M.A.R. and Hammond, P.T. (1998) *Macromolecules*, 31: 8749–8756.
21. Ciobanu, L., Jayawickrama, D.A., Zhang, X., Webb, A.G. and Sweedler, J.V. (2003) *Angew. Chem. Int. Ed.*, 42: 4669–4672.
22. Morgenstern, M., Cline, J., Meyer, S. and Cataldo, S. (2006) *Energy and Fuels*, 20: 1350–1353.
23. Ge, Z, Zhang, X.Y., Dai, J.B. and Li, W.H. (2007) *J. Macromol. Sci., Pure and Appl. Chem.*, 44: 223–227.
24. Boufi, S., Belgacem, M.N., Quillerou, J. and Gandini, A. (1993) *Macromolecules*, 26: 6706–6717.
25. Cordeiro, N., Belgacem, M.N., Gandini, A. and Neto, C.P. (1997) Ind. Crop. Prod., 6: 163–167.