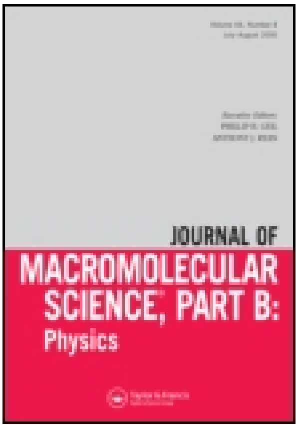

Journal of Macromolecular Science, Part B: Physics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lmsb20

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Accepted author version posted online: 04 Apr 2012.Version of record first published: 21 Sep 2012.

To cite this article: Jin Wang, Ming-Liang Du, Cong-Sheng Xu, Han Zhu & Ya-Qin Fu (2012): Synthesis of Transparent Densely Crosslinked Polysiloxane with High Refractive Index, Journal of Macromolecular Science, Part B: Physics, 51:12, 2462-2472

To link to this article: http://dx.doi.org/10.1080/00222348.2012.679140

Journal of Macromolecular Science®, Part B: Physics, 51:2462–2472, 2012
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ISSN: 0022-2348 print / 1525-609X online
DOI: 10.1080/00222348.2012.679140

Synthesis of Transparent Densely Crosslinked Polysiloxane with High Refractive Index

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Densely crosslinked polysiloxane, with high refractive index and high transparency, was synthesized via co-hydrolysis/condensation and then cured via hydrosilylation with a Pt catalyst. ^{29}Si nuclear magnetic resonance (NMR) spectra were utilized to identify the process of co-hydrolysis/condensation and characterize the structures of the prepolymers. Fourier transform infrared spectroscopy (FTIR) was used to investigate the hydrosilylation reaction. The number-average molecular weight of the prepolymers was determined to be ca. 1200 g mol^{-1}. Prepolymers with high refractive index, above 1.52, were synthesized, from which densely crosslinked polysiloxane resins, with high transmittance of about 99% and nearly no absorption in the visible range, were prepared.

Keywords condensation, high refractive index, hydrolysis, hydrosilylation, polysiloxane, transparency

1. Introduction

Optically transparent polymers have shown tremendous potential for application in many fields, such as optical glass, alkali-resistant glass fibers, microlenses, and encapsulation materials, and have attracted many researchers' attention during this decade.[1–5] Optical fibers have been manufactured using transparent polymers, such as epoxy. However, yellowing takes place when these polymers are applied at high temperature. Due to its high thermal stability, polysiloxane resin has been more and more widely used in the optical transparency area. Recently, polysiloxane with high thermal stability and refractive index has been developed by a sol-gel process, in which the siloxane monomers have hydroxyl groups and are then polymerized via polycondensation.[6] The synthesis of transparent polysiloxane with high refractive index and high thermal stability is becoming of more and more interest.[6,7] Some research has shown that an increase of disubstituted alkoxide can provide a high consolidation temperature to prevent softening when used at relatively high temperatures, which is very important for their use as encapsulation materials. However,

Received 9 November 2011; accepted 15 March 2012.

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residual hydroxyl groups induced by hydrolysis in the conventional sol-gel process are unfavorable to the optical properties.[8–10] In addition, the large shrinkage and crack formation at the sol-gel transition also limited the application of polysiloxane.[11–13]

Based on the above, some researchers have made impressive efforts to prepare polysiloxane with high transparency and refractive index by introducing several special units, such as azo chromophores, resulting in changes in the refractive index due to its trans-cis isomerization.[14–17] Other researchers have indicated that the phenyl group was significant for the optical property as the result of its high polarizability.[2] In addition, the viscoelastic properties were also considered in the phenyl-modified polysiloxane research,[18–21] they being related to the application as encapsulation materials.

In this article, because the hydrosilylation reaction can avoid the formation of bubbles and voids that occur in the conventional sol-gel process, we designed a two-step method of co-hydrolysis/condensation followed by hydrosilylation reaction to fabricate an organic–inorganic hybrid network structure. Phenyl groups were introduced to the polysilxoane to obtain a high refractive index, which was expected to lead to low optical losses for the polysiloxane resin. The structures and the optical properties of the synthesized polysilxoanes were studied and discussed.

2. Experimental

2.1. Materials

Phenyltriethoxysilane (P3B, $M_n = 240$ g mol^{-1}), diethoxydiphenylsilane (2P2A, $M_n = 244$ g mol^{-1}), tetramethylsilane (HMW, $M_n = 134$ g mol^{-1}), vinylmethyldiethoxysilane (V2B, $M_n = 160$ g mol^{-1}), hexamethyl disiloxane (MW, $M_n = 162$ g mol^{-1}), vinyldimethylethoxy-silane (VB, $M_n = 130$ g mol^{-1}), methyldiethoxysilane (H2B, $M_n = 90$ g mol^{-1}), and divinyltetramethylasiloxane (VMW, $M_n = 186$ g mol^{-1}) were all purchased from Shanghai Jiancheng Industrial and Trade Co. Ltd. (China) and were of commercial grade. Pt catalyst (platinum complex with unsaturated siloxane), with a Pt concentration of 2000 ppm, was purchased from Shenzhen Junchi Technical Co. Ltd. (China). Toluene, hydrochloric acid, and absolute ethanol were all purchased from Zhejiang Eagle Chemical Reagent Co. Ltd. (China) and used with no further treatment.

2.2. Synthesis of Prepolymers

In the present study, two kinds of prepolymers were prepared from different monomers. Prepolymer A contained vinyl groups, while prepolymer B contained both vinyl groups and Si–H groups, which were used for the hydrosilylation reaction to obtain highly crosslinked structures. Prepolymer A was prepared from P3B, 2P2A, V2B, MW, and VB, with 0.463, 0.190, 0.134, 0.067, and 0.162 moles, respectively. Prepolymer B was prepared from P3B, 2P2A, H2B, HMW, VMW, and MW, with 0.435, 0.143, 0.441, 0.040, 0.040, and 0.055 moles, respectively. As shown in Fig. 1, prepolymers A and B were both fabricated via a co-hydrolysis/condensation process. Initially, all the monomers were poured into a three-neck flask at once, 200 g hydrochloric acid (3.65%, mass ratio) as a catalyst was dropped slowly using a constant pressure funnel in about 1.5 h to promote the co-hydrolysis/condensation, and the mixture was then stirred at 60°C for 2 h. Next, toluene was introduced and the

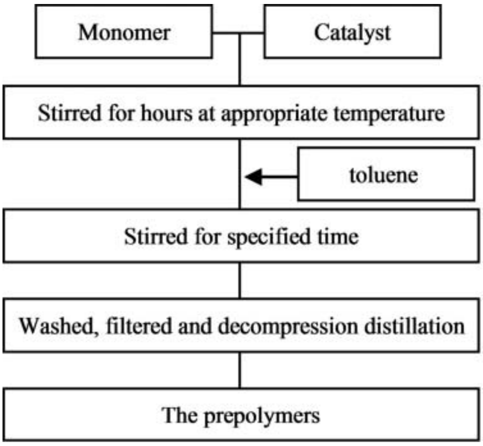

Figure 1. Flowchart describing the preparation process of polysiloxane prepolymers.

mixture was stirred for 1 h, 5 h, or 24 h, respectively. Finally, the obtained mixture was washed with deionized water prior to being filtered through a Teflon filter with pore size of 0.45 μm. The liquid prepolymers were obtained after decompression distillation to remove the solvent.

2.3. Cure of the Prepolymers to Prepare the Crosslinked Polysiloxane

Prepolymers A and B, with a mass of 5 g and 10 g, and 0.05 g Pt catalyst were mixed and stirred in a beaker uniformly and then the mixture was poured into a Teflon mold and cured for 1 h in an oven at 150°C.

2.4. Characterization

2.4.1. Nuclear Magnetic Resonance (NMR). The chemical structure of the prepolymers was characterized by ^{29}Si NMR spectra using a CMX 400 NMR spectrometer (JEOL, Japan). The prepolymers were dissolved in deuterated acetone prior to the measurement.

2.4.2. Fourier Transform Infrared Spectroscopy (FTIR). FTIR-spectra of the prepolymers and the cured polymer were recorded using a Nicolet 5700 FTIR spectrometer (Thermo Electron, USA) to analyze the chemical structure. The samples of as-prepared prepolymers were coated on KBr-pellets for the FTIR analysis.

2.4.3. Ultraviolet-Visible-Near Infrared Spectroscopy (UV-vis-NIR). The optical transmission spectra of the cured polymer were recorded using UV-vis-NIR spectrometer U3500 (Hitachi Co. Ltd., Japan). The spectra were measured in the range of 350–800 nm.

2.4.4. Determination of Refractive Index. The refractive indices of the prepolymer were tested using a WAY (2WAJ) Abbe's Refractometer (KeBo Co. Ltd., China) to determine the optical properties.

2.4.5. Determination of the Molecular Weight. The number-average molecular weight of the prepolymers was tested by gel permeation chromatography (GPC) method using PL-GPC50 (PL Co. Ltd., USA) and tetrahydrofuran was used as solvent.

2.4.6. Determination of the Viscosity. The viscosities of all prepolymers were measured using a Physica MCR301 (Anton Paar Co. Ltd., Germany) at 25°C.

3. Results and Discussion

3.1. Characterization of the Structure of the Prepolymers and Densely Crosslinked Polysiloxane

In this work, we fabricated transparent densely crosslinked polysiloxane by a two-step method, a co-hydrolysis/condensation process and then a hydrosilylation reaction, as shown in Fig. 2. The first reaction was co-hydrolysis/condensation of the monomers with hydrochloric acid as a catalyst, in which the alkoxy was converted to siloxane precursors (Si–OH) under a hydrolysis process and then a phenyl-oligomer (Ph–Si–O–Si) was prepared under a condensation process. The rate of co-hydrolysis/condensation has been shown to be influenced enormously by the amount of the catalyst and an excessive amount of catalyst will deteriorate the optical properties because microgels will be formed at high concentrations of catalyst.[22] Toluene was added as a thinner to promote the reaction by decreasing the viscosity. Some research has indicated that residual OH groups, induced by hydrolysis, would have a detrimental influence on the optical properties of the crosslinked siloxane.[8–10] Therefore, further condensation was achieved in the cure process of the prepolymers to reduce the residual OH groups. In addition, the hydrosilylation reaction between the vinyl group (C=C) and the hydrogen bonds (Si–H) in the curing process will make the polysiloxane more stable than that prepared by a conventional sol-gel process due to the much more densely crosslinked structure.

^{29}Si MAS NMR spectra of the prepolymers with different reaction times are shown in Fig. 3. The T^3 units were observed for all the prepolymers at a high field of −78 to −80 ppm because the silicon atom is surrounded by three oxygen atoms. The T^2 units containing the unreacted alkoxys were observed at about −70 ppm and indicated that the co-hydrolysis/condensation was not fully completed. The chemical shifts of T^3 and T^2 units varied in both A and B with the reaction time due to the continuous change of chemical environment in the co-hydrolysis/condensation process. In addition, the appearance of T^3 units in all the prepolymers indicated the formation of a crosslinked network structure. Due to the electronegativity, the V units were shifted upfield to about −31 ppm for all the prepolymers.[24] As expected, the H units containing hydrogen were only observed in prepolymer B because monomers containing the H unit were introduced, which were used to achieve the subsequent hydrosilylation reaction with the V unit in the curing stage. Similarly, the chemical shifts of the V and H units varied with the co-hydrolysis/condensation process resulting from the change of their chemical environments. As shown in Fig. 3, the P_2 units

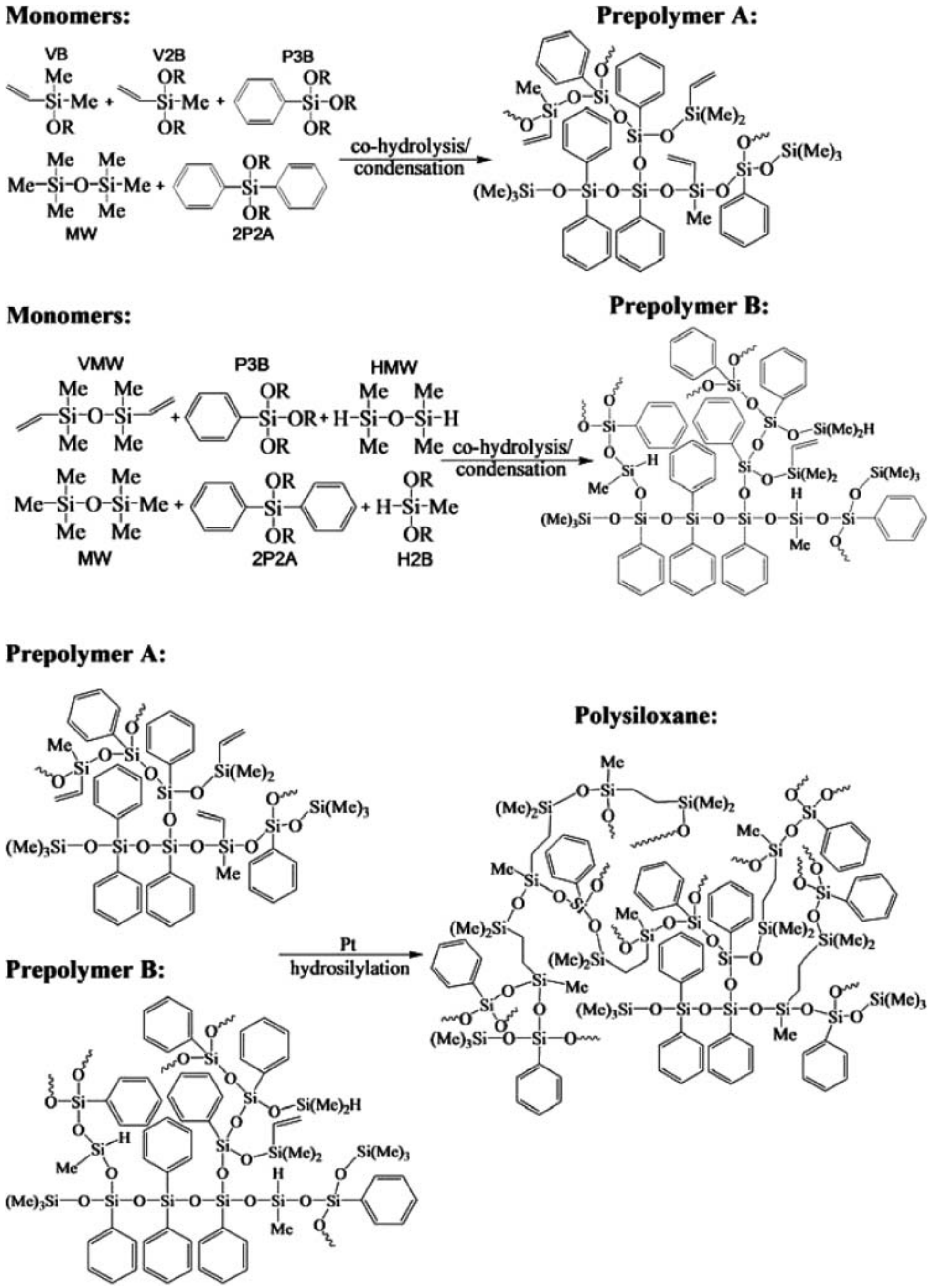

Figure 2. Synthesis of polysiloxane via co-hydrolysis/condensation and final hydrosilylation reaction with a Pt catalyst (“R” in the figure represents a methoxy or ethoxy group, “Me” represents a methyl group. “〰” represents a repeated structure with a Si-O-Si backbone.).

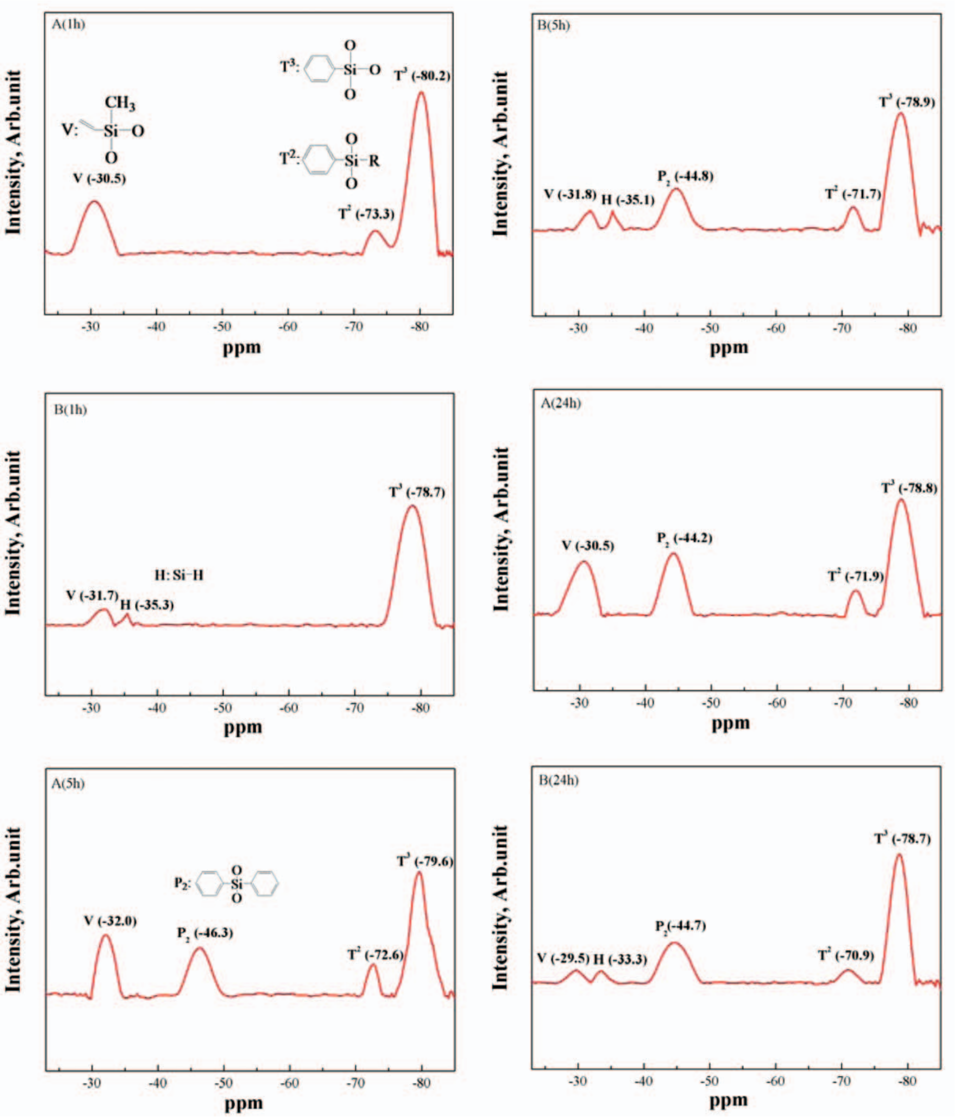

Figure 3. ^{29}Si MAS NMR spectra recorded for prepolymers with different reaction times (1 h, 5 h, and 24 h; the peaks were assigned according to refs. [6] and [23]) (color figure available online).

were observed in all prepolymers A and B with reaction times of 5 h and 24 h; however, they were absent in the prepolymers with reaction time of 1 h, indicating that the 2P2A had relatively lower co-hydrolysis/condensation reactivity than that of V2B, H2B, P3B, and VB. In addition, the steric effect of phenyl groups also caused the absence of the P_2 unit in 1 h.[6] With increase of reaction time, the P_2 units were observed at about −45 ppm, suggesting the P_2 unit was then introduced into the polysiloxane.

The hydrosilylation reaction was also studied by FTIR and the results are shown in Fig. 4. In accordance with the results derived from ^{29}Si MAS NMR spectra, the absorption

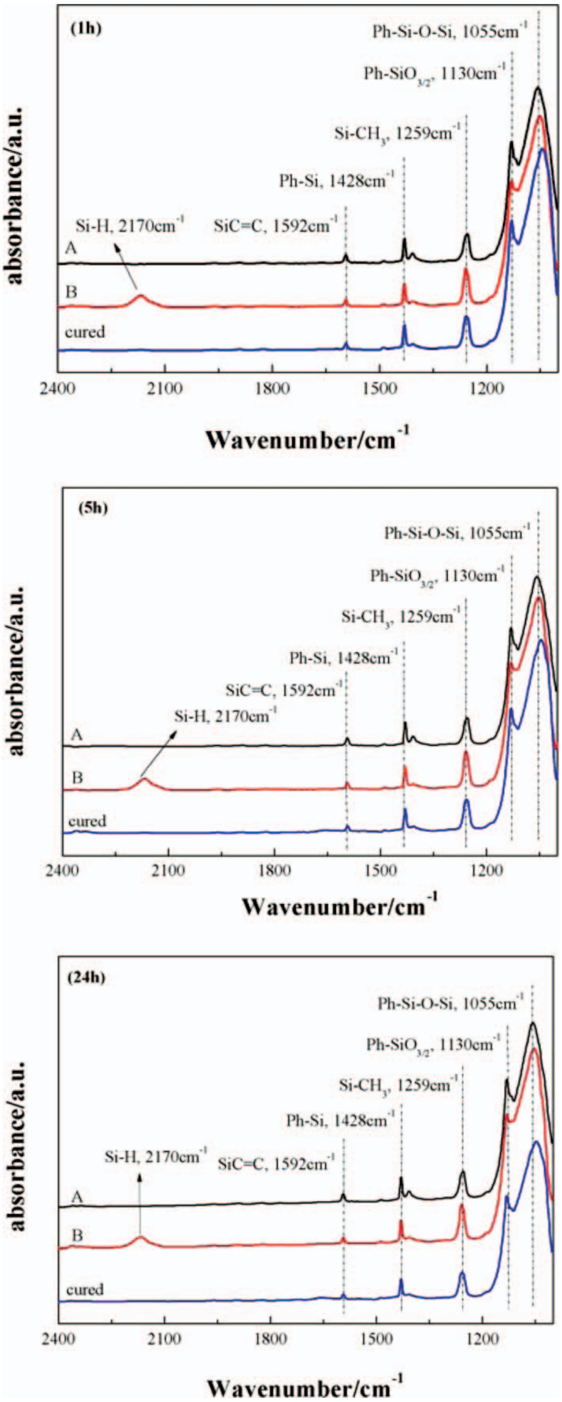

Figure 4. FTIR-spectra of prepolymers with different reaction time (1 h, 5 h, and 24 h) and the corresponding cured polymers (1 h/150°C) (color figure available online).

Table 1
The molecular weight, polydispersity index (PDI), and viscosity of the prepolymers

	M_n	M_w	PDI	η/pa.s
A (1 h)	1043	1200	1.1510	1.00
B (1 h)	1224	1828	1.4931	1.90
A (5 h)	1046	1207	1.1538	1.01
B (5 h)	1203	1803	1.4993	2.06
A (24 h)	1074	1449	1.3492	1.18
B (24 h)	1347	2162	1.6050	2.17

peaks of Si–C=C and Si–H, at 1592 cm^{-1} and 2170 cm^{-1} respectively, were observed. After the cure process had taken place, the peaks at 2170 cm^{-1}(Si–H) for prepolymer B disappeared, which corresponds to the hydrosilylation reaction of the two prepolymers. However, the weaker Si–C=C bonds' peaks at 1592 cm^{-1} were still observed, indicating a large amount of residue of the C=C groups in the cured polysiloxane. The absorption peaks at 1055 cm^{-1} (Si–O–Si) and 1130 cm^{-1} (Ph-SiO$_{3/2}$) simultaneously existed, suggesting the incomplete co-hydrolysis/condensation for both prepolymers.

As well known, the viscosity of prepolymers is directly related to the number-average molecular weight. As shown in Table 1, the number-average molecular weights for the prepolymers determined by GPC were ca. 1050–1350 g mol^{-1}, which are similar to a previous report.[24] The number-average molecular weights of the prepolymers prepared in 24 h were slightly higher than those of the prepolymers prepared in 1 h and 5 h because the co-hydrolysis/condensation reaction was more exhaustive. Besides, the number-average molecular weight of prepolymer B was higher than that of prepolymer A owing to the higher reactivity of the B monomers. The value of the polydispersity index (PDI) was used to evaluate the molecular weight distribution of the prepolymers. The results suggest that slightly smaller PDI values can be obtained with 1 h and 5 h reaction, indicating that the prepolymers prepared in shorter reaction time show a narrower molecular weight distribution, which may be beneficial to the thermal stability since the low molecular weight molecules are expected to be less stable. The viscosity became higher with the increase of reaction time due to the increased molecular weight. However, a high viscosity is a disadvantage to the second cure step and we found that the prepolymers prepared in 5 h seemed to be the optimal ones in this work.

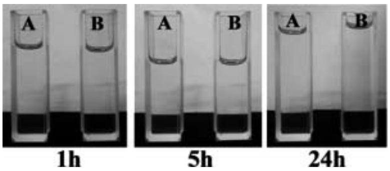

Figure 5. Pictures of the prepolymers.

Table 2
The refractive index of prepolymers

	Prepolymer A	Prepolymer B
1 h	1.531	1.519
5 h	1.532	1.523
24 h	1.532	1.524

3.2. Optical Properties of the Prepolymers and the Densely Crosslinked Polysiloxane

As shown in Fig. 5, the prepolymers exhibited high transparency. Based on our previous research, we knew that the Ph/Si ratio was crucial to the refractive index for the prepolymers;[22] higher Ph/Si ratio yields higher refractive index. However, an excessively high Ph/Si ratio decreases the transparency of the prepolymer since the phenyl groups will induce the formation of microgel. Table 2 shows that the refractive indices of the prepolymers were above 1.52, which indicates high purity, high stability, and excellent optical properties. The refractive indices of prepolymers A were higher than B because more phenyl groups were introduced in prepolymer A, as shown in Fig. 3, and they were essentially independent of reaction time. It is expected that the refractive indices of the cured polymers will be similar to that of their prepolymers. The optical transmission spectra for the cured polymer samples are shown in Fig. 6, which show a high transmittance of about 99% recorded in the 350–800 nm range and nearly no absorption in the visible range. The inset photograph of the polysiloxane resins intuitively displays a high transparency. In addition, the transmittances of polysiloxane resins fabricated from prepolymers with different reaction times were nearly the same. The excellent optical transmission property indicates the prepared densely crosslinked polysiloxane resin has potential for application as high performance light emitting diode (LED) encapsulant and in other related areas.

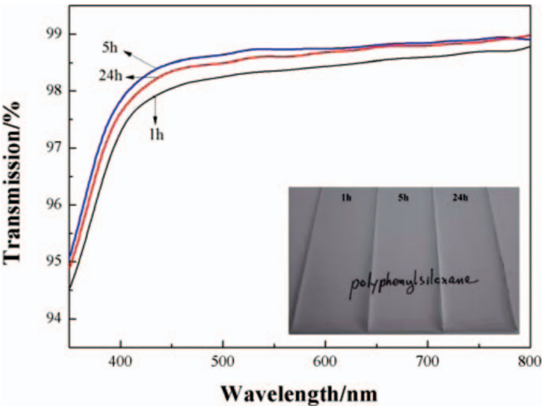

Figure 6. Optical transmission spectra for the cured samples (1 h, 5 h, and 24 h; the inset shows a photograph of polysiloxane resin) (color figure available online).

4. Conclusions

Transparent densely crosslinked polysiloxanes with high transparency and expected high refractive index were synthesized via co-hydrolysis/condensation and then cured via hydrosilylation with a Pt catalyst. The ^{29}Si NMR spectra permitted characterization of the process of co-hydrolysis/condensation and indicated the formation of densely crosslinked structures in the prepolymers. The hydrosilylation reaction was studied by FTIR and the results suggested that the absorption peak of Si–C=C and Si–H at 1592 cm^{-1} and 2170 cm^{-1} nearly disappeared with the achievement of the hydrosilylation reaction. The number-average molecular weights of the prepolymers were ca. 1050–1350 g mol^{-1} and those of the prepolymers prepared in 24 h were slightly higher than those of prepolymers prepared in both 1 h and 5 h. The number-average molecular weight of prepolymer B was higher than that of prepolymer A owing to the reactivity of the monomers. The investigation also showed that the viscosity became higher with the increase of reaction time due to the increased molecular weight. The optical transmission spectra of the cured polymer showed a high transmittance of about 99% and nearly no absorption in the visible range, indicating the polymer has potential for application as high performance LED encapsulant and in other related areas.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (NSFC; Grant No. 50903072), Zhejiang Province Natural Science Foundation (Grant No. Y4100197), and Science Foundation of Zhejiang Sci-Tech University (ZSTU) under No. 0901803-Y.

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