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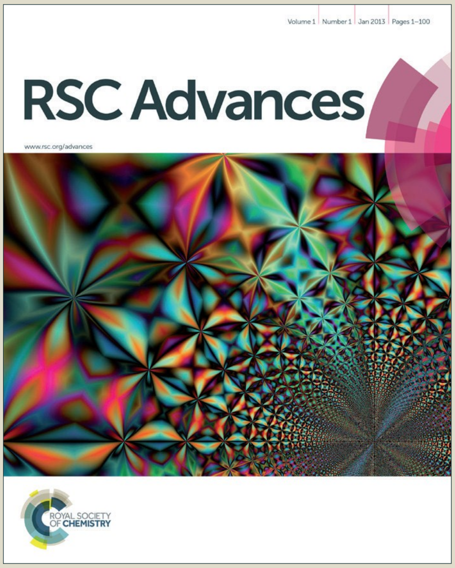

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Thermally stable transparent sol-gel based active siloxane-oligomer materials with tunable high refractive index and dual reactive groups

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In this paper, a series of novel active silicone-oligomers (PMDM) of high refractive index (RI) with dual reactive moieties (Si-H and S-H) synthesized by nonhydrolytic sol-gel condensation are reported for the first time. The RI of the oligosiloxane can be effectively increased from 1.55 to 1.65 by varying the feed ratio between methyldimethoxysilane (MDMS) and 3-mercaptopropylmethyldimethoxysilane (MMDS). Additionally, via "thiol-ene" click chemistry and the subsequent hydrosilylation reaction under Pt catalyst, a transparent siloxane-polymer film with enhanced refractive index (1.59) and excellent thermal stability ($T_{5\%}$ = 381 ^{o}C) was facilely synthesized and characterized, which in turn effectively substantiated the reactivity of the dual reactive moieties in PMDM. Such active oligomers would be useful chemical intermediates and the easily processed materials have great potential in modern optical/photonic applications such as waveguides, lasers or light emitting diodes.

Introduction

Novel optical materials with high refractive index (RI) have been more desired for their potential application in civil, medical, and military areas, where semiconductors (e.g., Ge and Si) and inorganic glasses (e.g., germinate, bismuthate, niobate, titanate and chalcogenide glasses) are desirable candidates for the components of lenses or prism due to their high refractive inde.[1-10] Recently, due to the excellent performance of light weight, high impact strength, easy processing, good flexibility and dyeability, high refractive-index polymers (HRIPs) with high transparency and highly thermal stability are attracting much attention and extending their range of applications such as prisms, waveguides, lenses or encapsulants for organic light-emitting diode devices (OLEDs).[11-17] Generally, there are two strategies to develop HRIPs, namely filling a polymer matrix with inorganic nanoparticles of high-refractive index, or altering the chemical structure of the polymer to increase its intrinsic RI.[18] Doping inorganic nanoparticles of high RI into organic polymer matrixes could easily increase RI values to more than 1.80. However, these nanocomposites often suffer from poor storage stability, high optical losses, and processing challenges because nanoparticles are prone to aggregation in the polymer due to their high specific surface energies and inherently hydrophilic character.[19-21] As a result, many researchers recently pay more attention to design polymers with high intrinsic RIs. According to the Lorentz-Lorenz theory, introduction of substituents with high molar refractions and low molar volumes, such as aromatic rings, sulfur, heavy halogens (except for fluorine) and metallic elements[22-24] could effectively increase the intrinsic RIs of polymers.[25]

Silicone-based polymers with high transmittances and excellent thermal resistances have been widely applied in the fields of computer chips, adhesives, encapsulation, aerospace, etc.[26-29] However, in consequence of the chemical structure (Si-O-Si), silicone-based polymers in general have low RI values of about 1.4, which is difficult to meet the requirements of many devices and greatly limits their practical applications.[30] Over the past few decades, great efforts have been devoted to the development of silicone-based materials with sufficiently high RI. It has been reported that substituting aromatic and conjugated systems can increase the value of RI to a great extent.[31] The RI values of several polysiloxanes synthesized by varying the content of phenyl or altering the types of aromatic groups range from 1.43–1.68.[32-35] Except for the phenyl ring, employing phenyl ethers, i.e., phenyloxyphenyl ether and phenlythiophenyl ether, as the pendant groups of silicone monomer or covalently attaching the phthalimide structure into siloxane oligomers can also significantly enhance the RI of polysiloxane.[36-40] Additionally, some other studies on a series of epoxy-functionalized polysiloxanes revealed that increasing the crosslink density would induce an increase in RI.[41] Although the silicone resins with relatively high RIs have been paid close attention, due to limited species of the silicon-based materials with multi-functionality, researches on modulation of RI values based on

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silicon-based materials are difficult to obtain the significant breakthrough.

In this article, by adjusting the feed ratio between MDMS and MMDS, a series of active siloxane-oligomers (PMDM) with dual reactive groups and tunable RI ranging from 1.55 to 1.65 were successfully synthesized through sol-gel condensation for the first time. Additionally, via “thiol-ene” click chemistry and the subsequent hydrosilylation reaction under Pt catalyst, a transparent siloxane-polymer film with enhanced RI and good thermal stability was facilely synthesized and characterized, which effectively confirmed the reactivity of the dual reactive groups. The resultant siloxane-oligomers (PMDM) are therefore a representative model with dual reactive groups and further reaction could derive a variety of novel functional materials.

Experimental

Materials

Methyldimethoxysilane (MDMS, >97.0%), diphenylsilanediol (DPSD, >98.0%), 1,3-divinyltetramethyldisiloxane (DVTMDS, >97.0%), and 3-mercaptopropylmethyldimethoxysilane (MMDS, >95.0%) were purchased from Tokyo Chemical Industry. $Ba(OH)_2{\cdot}H_2O$ (BH, 98%) and Pt catalyst, platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution were purchased from Sigma Aldrich. The other reagents were purchased from Energy Chemical. Tetrahydrofuran (THF) was purified by distillation with sodium and benzophenone. The solvents used were stored over 5 Å molecular sieves. All other chemicals were used as purchased without further purification.

Synthesis of PMDM by sol-gel condensation

The PMDM resin was prepared by a typical sol-gel condensation process from MDMS, DPSD, and MMDS (Scheme 1). Detailed procedures for the synthesis of PMDM-1 are given below as a typical example:

DPSD (2.60 g, 12.01 mmol), MDMS (0.57 mL, 4.62 mmol), and MMDS (0.83 mL, 4.62 mmol) with an optimal molar ratio of Si-OCH_3/Si-OH as 1.00:1.30 were mixed in toluene (12.00 mL) in a flask, then barium hydroxide monohydrate, $Ba(OH)_2{\cdot}H_2O$ (BH) (4.02 mg, 0.02 mmol) was added as a catalyst to promote the direct condensation reaction between the methoxy radical of MDMS/MMDS and the diol radical of DPSD to form the siloxane bonds. The mixture was stirred continuously and kept at 80 ^{o}C for 4 h. After the reaction, BH was removed by a 0.45 μm pore-sized Teflon filter. The residue was evaporated by reduced pressure distillation under 50 ^{o}C to remove the by-product MeOH and toluene, then it was evaporated under 70 ^{o}C for further removal of the toluene. After that, the product (PMDM-1) was dried under vacuum at 70 ^{o}C for 48h.

Other PMDM resins were prepared by using a similar method, the amount of the raw material for PMDM-2 and PMDM-3 is listed in Table 1.

Modification of PMDM-1 by “click chemistry” and the subsequent hydrosilylation reaction

Firstly, a representative vinyl monomer, 4′- (allyoxy)-biphenyl-4-carbonitrile (ABC), was efficiently synthesized by the Williams etherification reaction as the followings: 3-Bromopropene (1.46 mL, 16.89 mmol) was added dropwise to a mixture of 4′-hydroxy-4-biphenylcarbonitrile (3.00 g, 15.36 mmol), anhydrous potassium carbonate (2.76 g, 19.97 mmol), and 150.00 mL acetonitrile at room temperature and refluxed under magnetic stir for 8 h. After filtration and removal of the solvent, the crude product was purified by silica gel column chromatography with dichloromethane as the eluent and dried to give the ABC monomer as white crystal. Yield: 2.70 g (78.0%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.619 (phenyl-*H*, 2H); 7.537 (phenyl-*H*, 2H); 7.444 (phenyl-*H*, 2H); 6.928 (phenyl-H, 2H); 5.991 (HHC=C*H*-C, 1H); 5.372 (H*H*C=CH-C, 1H); 5.243 (*H*HC=CH-C, 1H); 4.528 (HHC=HC-C*HH*, 2H).

Then the oligomer PMDM-1 with dual reactive groups was modified by ABC through “thiol- ene” click chemistry. PMDM-1 (0.21 g, 0.59 mmol -SH), ABC (0.14 g, 0.59 mmol –$CH=CH_2$), AIBN (9.90 mg, 0.06 mmol), and toluene (3.00 mL) were added into a Schlenk-type flask. After degassed by three freeze-pimp-thaw cycles, the mixture was stirred continuously in a sealed flask at 65 ^{o}C for 24 h to proceed the reaction. Then, methanol was added into the mixture to precipitate the resultant product, which was further purified by dissolving in THF. This process was repeated for several times and the final precipitated product was dried under vacuum. The target product PMDM-1-ABC was obtained as an oily liquid.

Finally, the modified PMDM-1-ABC was thermally cured with the cross-linker, divinyltetramethyldisiloxane (DVTMDS), by a conventional hydrosilylation reaction under Pt catalyst in the following procedure: A mixture of PMDM-1-ABC (14.22 mmol -Si-H) and DVTMDS (3.00 mL, 14.22 mmol –$CH=CH_2$) with Pt catalyst (50 ppm) was spin-coated onto a glass plate, followed by curing at 200 ^{o}C for 6 h under air atmosphere. Then a transparent film was obtained.

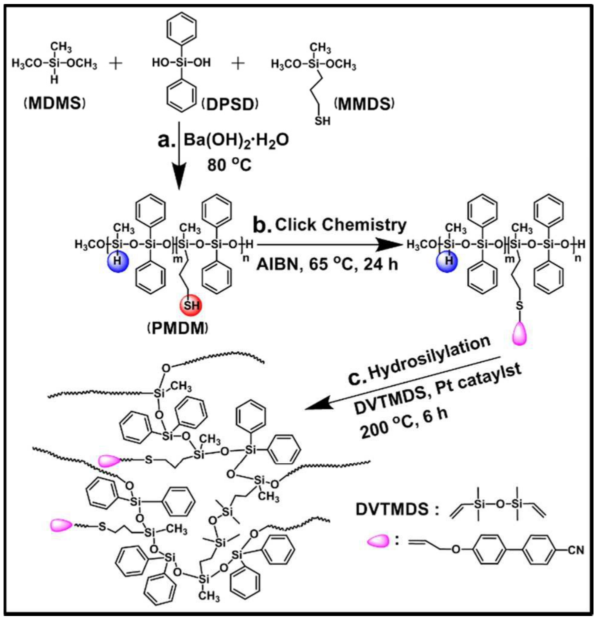
Characterization

^{1}H-NMR and ^{29}Si-NMR spectra were recorded with a Bruker AV500 MHZ (Bruker, Germany) instrument at room temperature using chloroform-*d* as solvent. FT-IR spectra were obtained on a BrukerVector-22 FT-IR spectrophotometer using a KBr pellet over a range of 4000–500 cm^{-1}. Gel permeation chromatography (GPC) was performed on a Waters 2410 instrument equipped with a Waters 2410 refractive index detector and three Waters μ-Styragel columns (103, 104, and 105 Å). The column packing allowed the separation of polymers over a wide molecular weight range of 2200-600000. All GPC data were gathered by using tetrahydrofuran (THF) (HPLC grade, Fisher Scientific) as the eluent at a flow rate of 1.0 mL/min at 35 ^{o}C and calibrated with linear polystyrene standards. Thermogravimetric analysis (TGA) was recorded on a Perkin Elmer/TGA 4000 thermal analysis system at a heating rate of 10 ^{o}C/min under nitrogen. Abbe refractometer (WYA-2S) was used to measure the RIs of the PMDM solutions with different concentrations, and the refractive indices of pure PMDM and PMDM-1-ABC at 589 nm were obtained by an extrapolating method. While the refractive index of the film at 633 nm was measured on a prism coupling device (Metricon, 2010). The optical transmittance of the film was measured by a UV/VIS/NIR spectrophotometer (Perkin Elmer, Lambda 950).

Results and discussion

Synthesis and characterization of the active Silicone-oligomers (PMDM)

A series of novel silicone-oligomers (PMDM) with Si-H/S-H molar ratios of the dual reactive groups ranging from 1.00:1.00, 1.00:3.00, to 1.00:5.00 were successfully and efficiently synthesized by a facile sol-gel condensation method, as illustrated in Scheme 1. The chemical structures of the silicone-oligomers were verified by the combination of FT-IR, ^{1}H-NMR, and ^{29}Si-NMR spectra. The molecular characteristics of the oligomers are summarized in Table 1. GPC analysis showed that the number-average molecular weights (*Mn*) and the weight-average molecular weights (*Mw*) of the silicone-oligomers were 0.9 × 10^3 g/mol and 1.1 × 10^3 g/mol, respectively, with the polydispersity of 1.22, confirmed their polymeric nature.



Scheme 1 Synthesis (a), modification (b) and curing (c) of the active silicone-oligomer

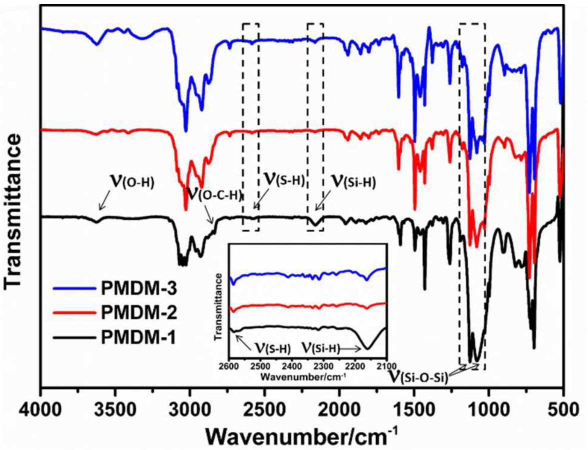


Fig. 1 FT-IR spectra of PMDM-1, PMDM-2 and PMDM-3. The insert is for enlarged details.

Fig. 1 and Fig. 2 show the FT-IR and NMR spectra of the PMDM, respectively. As shown in Fig. 1, the appearance of the vibrational bands at 1020-1120 cm^{-1} (assigned as the representative siloxane network stretching, $\nu_{Si-O-Si}$), 3627 cm^{-1} and 2849 cm^{-1} (assigned as the terminal-group of silanol (ν_{Si-OH}) and methoxy groups on silicon atoms ($\nu_{Si-OCH3}$), repectively), as well as the vibrational bands at 2580 cm^{-1} and 2160 cm^{-1} (attributed to the stretching vibration of –SH and –SiH, respectively), indicated the successful preparation of the PMDM resin.

Furthermore, in ^{1}H NMR spectrum shown in Fig. 2(a), the appearance of the representative signals of –SH, -SiH, and –OCH_3 in PMDM-1 at 1.54, 2.40, and 3.37 ppm, respectively, confirmed the success of the sol-gel condensation reaction. The ^{29}Si-NMR spectrum of PMDM-1, which presented highly condensed Si species as shown in Fig. 2(b), further verified the formation of the siloxane network.[30,42] Based on the ^{29}Si-NMR measurements, the degree of condensation (DOC) of the siloxane network was calculated as 80.7%.[43] Additionally, the actual molar fraction of two active groups of –SiH and –SH in a specified oligomer was calculated according to the integral area of the signals at 1.54 ppm (-SH moiety) and 2.40 ppm (-SiH moiety) (as remarked in Figure 2a). The results were listed in Table 1, which was in accordance with the feed ratio.

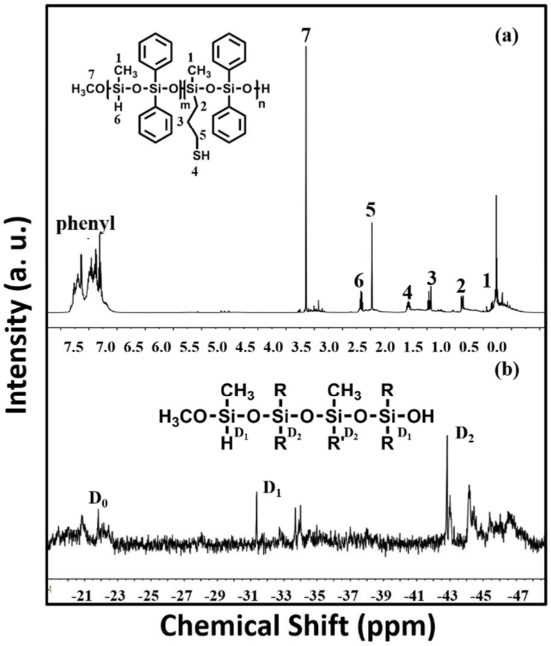


Fig. 2 ^{1}H NMR (a) and ^{29}Si NMR (b) spectra of PMDM-1.

Modification of the oligomers (PMDM) by "click chemistry" and the subsequent hydrosilylation reaction

In order to verify the stability of the Si-H and S-H groups and their independent reactivity, PMDM-1 was selected as a raw material for the subsequent reaction. As shown in Scheme 1, firstly, a typical vinyl monomer was grafted onto PMDM-1 via thiol-ene click chemistry and the target product, PMDM-1-ABC, was obtained as a

Table 1 The molecular characterizations of the oligomers and silicone-based film.

Sample	$m_{(MDMS)}$ [mol]	$m_{(MMDS)}$ [mol]	$m_{(DPSD)}$ [mol]	m(BH) [$\times 10^2$mol]	$m_{(\text{-SiH})}$:$m_{(\text{-SH})}$ theoretical	calculated[a]	Refractive Index (*n*)	$T_{1\%}$[d] [°C]	$T_{5\%}$[e] [°C]
PMDM-1	1.00	1.00	2.60	0.23	1.00:1.00	1.00:0.97	1.55[b]	201	286
PMDM-2	1.00	3.00	5.20	0.92	1.00:3.00	1.00:2.76	1.64[b]		
PMDM-3	1.00	5.00	7.80	1.38	1.00:5.00	1.00:4.77	1.65[b]		
PMDM-1-ABC							1.62[b]		
PMDM-1-ABC-DVTMDS							1.59[c]	324	381

[a] Calculated according to the ^{1}H-NMR results. [b] Evaluated by Abbe refractometer at 589 nm. [c] Measured by prism couping device at 633 nm.
[d] 1% weight loss temperature was evaluated by TGA at a rate of 10 °C/min. [e] 5% weight loss temperature was evaluated by TGA at a rate of 10 °C/min.

transparent oily intermediate. Fig. 3 and Fig. 4 show the FT-IR and ^{1}H-NMR spectra of PMDM-1 and PMDM-1-ABC.

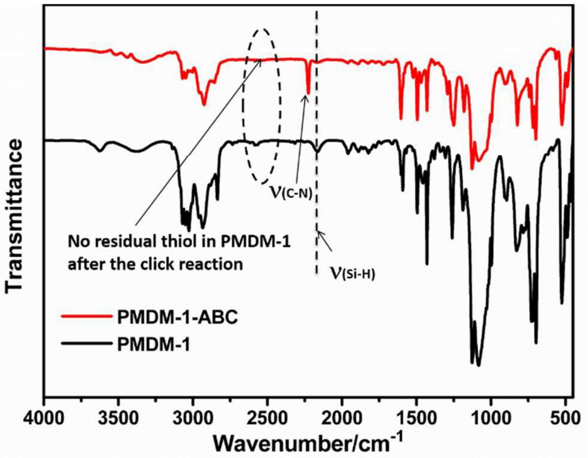


Fig. 3 FT-IR spectra of the oligomer PMDM-1 and PMDM-1-ABC

As shown in Fig. 3, it can be clearly seen that the vibrational bands of siloxane network ($\nu_{Si\text{-}O\text{-}Si}$) (at around 1020-1120 cm^{-1}) and the Si-H ($\nu_{Si\text{-}H}$) (at around 2160 cm^{-1}) in PMDM-1 were still presented after the thiol-ene click reaction. The disappearance of the vibrational band of thiol group at 2580 cm^{-1} and the appearance of the vibrational band of cyano group at 2228 cm^{-1} indicated that "thiol-ene" click reaction was fully completed. Additionally, the appearance of the representative signal of Ar-O-CH$_2$ in PMDM-1-ABC at about 4.00 ppm in ^{1}H-NMR spectrum further confirmed the success of the grafting reaction of the ABC moiety onto PMDM-1 (as shown in Fig. 4).

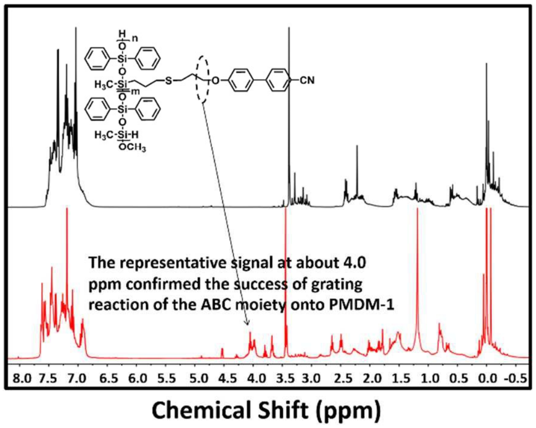
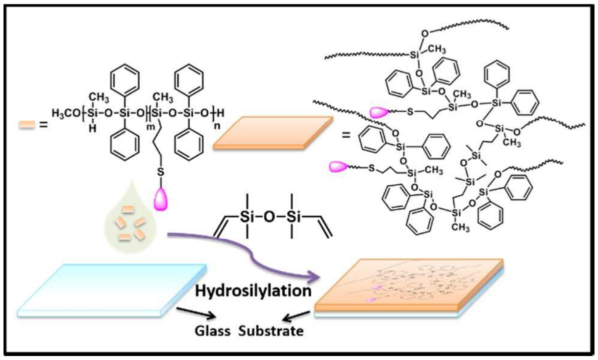


Fig. 4 ^{1}H NMR spectra of the PMDM-1 and PMDM-1-ABC.

Then, as shown in Scheme 1c and Scheme 2, the PMDM-1-ABC was facilely cured in the presence of cross-linker and Pt catalyst through hydrosilylation reaction. Finally, a transparent film of PMDM-1-ABC-DVTMDS with a highly cross-linked network structure was successfully obtained.



Scheme 2 Schematic of the preparation of the transparent film PMDM-1-ABC- DVTMDS through hydrosilylation reaction.

FT-IR analysis was employed to monitor the hydrosilylation reaction process. As illustrated in Fig. 5, the disappearance of the vibrational band at 2160 cm^{-1} assigned as Si-H stretching in PMDM-1-ABC-DVTMDS film showed that the Si-H groups were reacted

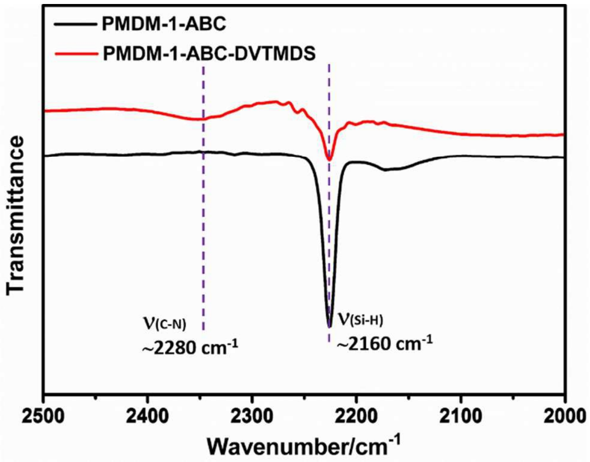


Fig. 5 FT-IR spectra of the PMDM-1-ABC and PMDM-1-ABC-DVTMDS film.

completely. Therefore, it firmly substantiated that the S-H and Si-H groups reacted independently in each step of the reaction, namely the thiol-ene click reaction and the subsequent hydrosilylation reaction, which demonstrated the independent reactivity of the Si-H and S-H groups in the active siloxane-oligomer of PMDM.

Thermal stability of the film

The thermal properties of the film were evaluated by thermogravimetric analysis (TGA) and Fig. 6 shows the TGA curve of the non-oxidative thermal degradation of the oligomer PMDM-1 and the cured film PMDM-1-ABC-DVTMDS at the temperature ranges of 30-850 ^{o}C. As shown in Fig. 6, the temperatures at *1%* and *5%* weight loss of the oligomer PMDM-1 are 201 ^{o}C and 286 ^{o}C under nitrogen, respectively. While the temperatures of the cured film PMDM-1-ABC-DVTMDS are 324 ^{o}C and 381 ^{o}C, respectively, which are much higher that the oligomer. This obvious enhancement indicated that the introduction of rigid phenyl groups and the crosslinked structure provided great thermal stability to the film.[35]

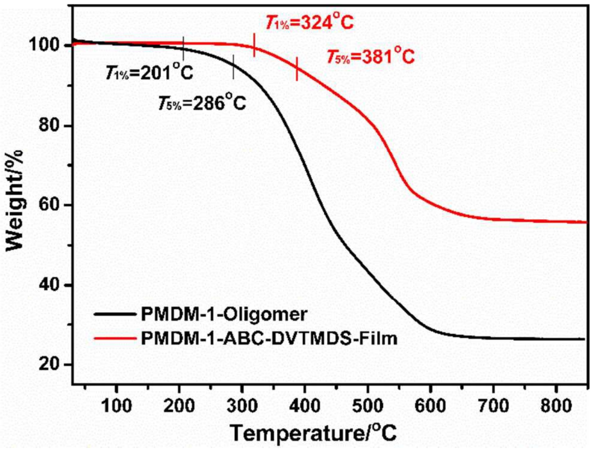


Fig. 6 TGA curves of the oligomer PMDM-1 and the cured film PMDM-1-ABC-DVTMDS (under a nitrogen atmosphere, 10 ^{o}C/min)

Optical performance of the oligomers and film

The refractive index (*n*) of the active oligomers, which is one of the most important parameters to evaluate the performance of silicon-based materials, was estimated by an extrapolating method with Abbe refractometer.[44] During the measurement, a series of PMDM/toluene mixtures with the PMDM fractions ranging from 0.2 to 1.2 wt% were prepared and their refractive indices were tested (as shown in Fig. 7). By comparing the results of the mixtures with their concentrations, the *n* values of the pure PMDM can be extrapolated.

The *n* values of the synthesized active oligomers are listed in Table 1. It can be seen that attributing to the introduction of sulfur atom and aromatic ring with both low molar volumes and high molar refractions,[18] the *n* values of the three silicone-oligomers were in the range between 1.54 and 1.65, which were higher than the commercially available silicon-based materials.[31] These results confirmed that the RIs can be enhanced due to the higher sulfur content per repeat unit. Furthermore, due to the reactivity of the –SH and –SiH groups, the refractive index of the active silicone-oligomer can be further regulated and improved. Via "thiol-ene" click chemistry, a transparent oily intermediate PMDM-1-ABC was prepared and its refractive index could be measured using the same method above. The subsequent hydrosilylation reaction could obtain a transparent PMDM-1-ABC-DVTMDS film. And the refractive index of the film was measured by a prism coupling device at 633 nm at 20 ^{o}C. As illustrated in Table 1, the refractive index of PMDM-1 sample was increased effectively from 1.55 to 1.62 by the introduction of vinyl monomer ABC. While after the hydrosilylation reaction with the crosslinker DVTMDS, the refractive index value of the PMDM-1-ABC-DVTMDS film decreased to 1.59 due to the low refractive index of the cross-linker ($n_{(DVTMDS)}$ = 1.41).

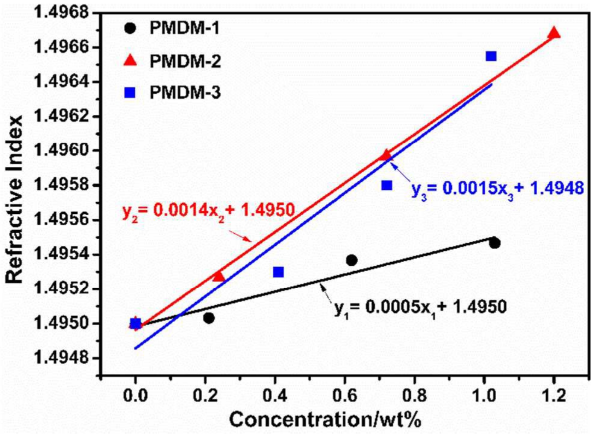


Fig. 7 The fitted curves between refractive index and PMDM concentration

The optical transparency of the PMDM-1-ABC-DVTMDS film (~10 μm) on a glass substrate was investigated by UV-vis transmittance spectroscopy (as shown in Fig. 8). The PMDM-1-ABC-DVTMDS film maintained good transmittance in the visible range (400-800 nm) and the transmittance was above 80% at 550 nm, which was attributed to the effective prevention of inter-chain molecular packing deriving from the asymmetric substituent groups and rigid aromatic rings in the side chain and the introduction of branched chain. As expected, the silicon-based polymers in this study with

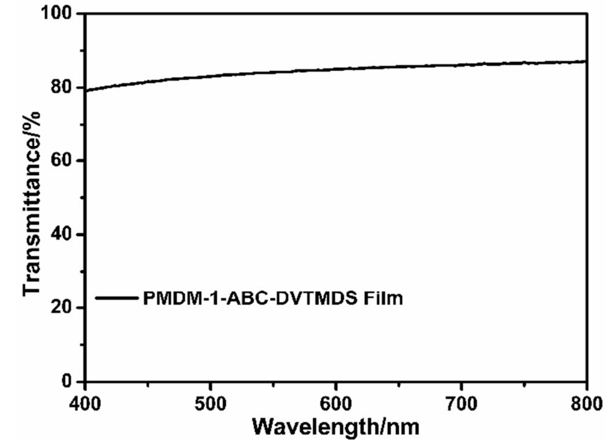


Fig. 8 Visible transmittance spectrum of the PMDM-based film (PMDM-1-ABC-DVTMDS)

high transmittance, excellent thermal resistance, and enhanced refractive index are strongly desired in practical applications.

Conclusions

In summary, by efficient sol-gel condensation reaction, a series of novel active silicone-oligomers (PMDM) with different molar ratios of -SiH and -SH reactive moieties were rationally designed and successfully synthesized for the first time. Moreover, through "thiol-ene" click chemistry and a subsequent hydrosilylation reaction, the stability and the independent reactivity of the -SiH and -SH moieties were reasoningly verified. Therefore, the resultant siloxane-oligomers (PMDM) with dual reactive groups are representative models and useful chemical intermediates, and multifarious novel functional materials could be produced by further reaction. Interestingly, due to the reactivity of the –SH and –SiH moieties, the RIs of the active silicone-oligomer can be arbitrarily regulated and further improved. It is believed that the newly synthesized active silicone-oligomer with tunable high RIE and dual reactive groups will possess more interesting properties and great potential applications. Future work will be focused on the performance of these materials in terms of their mechanical properties and long-term stability, such as photostability and oxidative stability.

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Notes and references

1 H. Ma, A. K. Y. Jen and L. R. Dalton, *Adv. Mater.,* 2002, **14**, 1339.
2 M. Pagliaro and R. J. Ciriminna, *Mater. Chem.*, 2005, **15**, 4981.
3 L. W. Shacklette, *Opt. photonics News*, 2004, **15**, 22.
4 J. S. Sanghera, L. B. Shaw, and I. D. Aggarwal, *C. R. Chimie,* 2002, **5**, 873.
5 J. Lucas and X. H. Zhang, *J. Non-Cryst. Solids,* 1990, **125**, 1.
6 M. Peng, N. Zhang, L. Wondraczek, J. Qiu, Z. Yang and Q. Zhang, *Opt. Mater.,* 2011, **19**, 20799.
7 T. Hashimoto, Y. Shimoda, H. Nasu and A. Ishihara, *J. Am. Ceram. Soc.,* 2011, **94**, 2061.
8 A. Masuno, S. Kohara, A. C. Hannon, E. Bychkov, and H. Inoue, *Chem. Mater.,* 2013, **25**, 3056.
9 J. Yu, S. Kohara, K. Itoh, S. Nozawa, S. Miyoshi, Y. Arai, A. Masuno, H. Taniguchi, M. Itoh, M. Takata, T. Fukunaga, S. Koshihara, Y. Kuroiwa, and S. Yoda, *Chem. Mater.,* 2009, **21**, 259.
10 X. Zhang, B. Bureau, P. Lucas, C. Boussard-Pledel and J. Lucas, *Chem. Eur. J.,* 2008, **14**, 432.
11 S. Katayama, The Latest Technology of Nano Hybrid Materials. CMC, Tokyo, 2005, 327.
12 C. Sanchez and B. Lebeau, *Mrs Bull.*, 2001, **26**, 377.
13 J. Choi, S. G. Kim and R. M. Laine, *Macromolecules*, 2004, **37**, 99.
14 B. J. Scott, G. Wirnsberger and G. D. Stucky, *Chem. Mater.*, 2001, **13**, 3140.
15 Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito, *J. Mater. Res.*, 1993, **8**, 1185.
16 J. N. Hay and H. M. Raval, *Chem. Mater.*, 2001, **13**, 3396.
17 C. Gao, B. Yang and J. Shen, *J. Appl. Polym. Sci.,* 2000, **75**, 1474.
18 J. Liu and M. Ueda, *J. Mater. Chem.*, 2009, **19**, 8907.
19 F. M. Pavel and R. A. Mackay, *Langmuir*, 2000, **16**, 8568.
20 C. H. Hung and W. T. Whang, *J. Mater. Chem.*, 2005, **15**, 267.
21 W. Caseri, *Macromol. Rapid Commun.*, 2000, **21**, 705.
22 J. G. Liu, Y. Nakamura, C. A. Terraza, Y. Shibasaki, S. Ando and M. Ueda, Macromol. *Chem. Phys.*, 2008, **209**, 195.
23 J. Liu, Y. Nakamura, T. Ogura, Y. Shibasaki, S. Ando and M. Ueda, *Chem. Mater.*, 2008, **20**, 273.
24 M. C. Choi, J. Wakita, C. S. Ha and S. Ando, *Macromolecules*, 2009, **42**, 5112.
25 S. Ando, T. Fujigaya and M. Ueda, *Jap. J. Appl. Phys.*, 2002, **41**, L105.
26 P. R. Dvornic and R. W. Lenz, *Macromolecules*, 1992, **25**, 3769.
27 D. C. Hofer, ACS Proc. Polym. *Mat. Sci. Chem.*, 1986, **55**, 85.
28 I. Hägglund, K. Janak, L. Blomberg, A. Bemgard, S. G. Claude, M. Lymann and R. Tabacchi, *J. Chromatogr. Sci.*, 1991, **29**, 396.
29 O. I. Umanskaya, Y. L. Ishchuk, R. N. Abadzheva and V. B. Smerechinskii, *Chem. Tech. Fuels Oils*, 1990, **26**, 151.
30 Y. H. Kim, J. Y. Bae, J. Jin and B. S. Bae, *ACS Appl. Mater. Interfaces*, 2014, 6, 3115.
31 Z. Ahmad, High refractive index silicone. Concise Encyclopedia of High Performance Silicones 65-74.
32 Q. G. Gu and Q. L. Zhou, Eur. Polym. J., 1998, 34, 1727.
33 S. Kohjiya, K. Maeda, S. Yamashita and Y. Shibata, J. Mater. Sci., 1990, 25, 3368.
34 P. M. Chevalier and D. L. Ou, US Pat., 7,429, 638, 2008.
35 J. S. Kim, S. C. Yang and B. S. Bae, Chem. Mater., 2010, 22, 3549.
36 D. W. Mosley, G. Khanarian, D. M. Conner, D. L. Thorsen, T. Zhang and M. Wills, J. Appl. Polym. Sci., 2014, 131, 39824.
37 R. N. Lewis. US Pat., 3,114,759, 1963.
38 W. J. Schnabel. US Pat., 3,013,044, 1961.
39 T. C. Wu. US Pat., 3,385,878, 1968.
40 H. Cai, L. Zhang, Y. Xiong, Q. Qu and H. Tang, J. Inorg. Organomet. Polym. Mater., 2014, 24, 780.
41 S. N. Yahya, C. K. Lin, M. R. Ramli, M. Jaafar and Z. Ahmad, Mater. Design, 2013, 47, 416.
42 K. H. Jung, J. Y. Bae, S. J. Park, S. Yoo and B. S. Bae, J. Mater. Chem., 2011, 21, 1977.
43 S. Sepeur, N. Kunze, B. Werner and H. Schmidt, Thin Solid Films, 1999, 351, 216.
44 H. Saveyn, D. Mermuys, O. Thas and P. Van Der Meeren, Part. Part. Syst. Char., 2002, 19, 426.

Thermally stable transparent sol-gel based active siloxane-oligomer materials with tunable high refractive index and dual reactive groups

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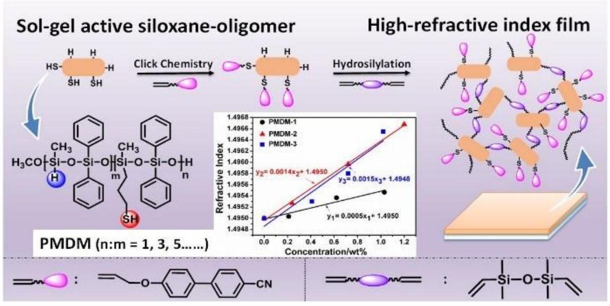

A novel active silicone-oligomers used as chemical intermediates in optical applications were synthesized and one of their derivatives, a transparent film with high refractive index, were presented.