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A novel stimuli-responsive fluorescent elastomer based on AIE mechanism

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Abstract: In this paper, a facile approach for the synthesis of stimuli-responsive fluorescent elastomer was developed. Tetraphenylethylene (TPE) derivant was linked to flexible polydimethylsiloxane(PDMS) polymer chains by covalent-bond with silane coupling agent, followed by condensation reaction with tetraethylorthosilicate(TEOS) as the curing agent via sol-gel reaction to obtain the fluorescent elastomer. ^{1}HNMR and FTIR spectroscopy studies showed the degree of the reaction, and the homogeneous distribution of TPE derivant in the elastomer was confirmed by SEM, XRD and PL spectra, respectively. Due to the hampered intramolecular rotation of the aryl rotors of dye molecules with the intertwined polymer chains, the cured elastomers showed intense fluorescent emission. In addition, the elastomers exhibited stimuli-sensitive fluorescence against temperature, and its responsiveness was found to be reversible.

Introduction

With the progress of the times, new requirements are presented to the people. The development of modern technologies requires the materials combination of properties that cannot be provided by just ordinary polymers. Moreover, the continuous interest on the commonly called smart materials has also been extremely stimulated by the recent European Council regulation on plastic packages that is under revision to include active and intelligent systems, the latter being able to constantly monitor the quality of the packaged material during transport and storage[1-4]. Fluorescent organic molecules have been vigorously investigated due to the interesting photophysical properties accompanied by their intrinsic softness and lightness. Many researches have focused on their applications for such as organic light-emitting diodes (OLED), semiconductor laser, and fluorescent sensors[5−7]. In general, they present prominent fluorescence in a solution, not in a solid state due to aggregation-caused quenching (ACQ) phenomenon, while the practical uses of them are based on their solid state such as film[8-9]. However, fundamental molecular design of organic molecules exhibiting highly efficient solid-state luminescence is still ambiguous.

In 2001, a novel phenomenon of aggregation-induced emission(AIE) was first found by Tang's group from propeller-like siloles, whose emission was very weak in solution but

became intense as aggregates formed[10]. Such abnormal emission behavior has drawn great research interest, for it is exactly opposite to the common belief that the emission of chromophores decreases in the aggregate state[11-13]. This intriguing finding paves a new avenue to tackle the notorious ACQ of conventional chromophores. Tetraphenylethene (TPE) is one of the typical fluorescent molecule with AIE character, and it is found to be non-emissive in dilute solutions but became highly luminescent when their molecules are aggregated in concentrated solutions or cast in solid films[14]. In detail, in a dilute solution, TPE undergoes dynamic intramolecular rotations against its double bound and renders its molecule non-luminescent. On the other hand, in the aggregate state, the molecules cannot pack through a π-π stacking process due to its propeller shape, while the intramolecular rotations of its aryl rotors are greatly restricted owing to the physical constraint. This restriction blocks the non-radiative pathway and opens up the radiative channel[15-16].

With rapid extension of the application of fluorescent materials, including biological monitoring, lithography, solar cells and selective membranes, it is very interesting to design or modify novel AIE luminogens to make them into application[17]. Xiqi Zhang et al synthesized piezofluorochromic aggregation-induced emission (PAIE) materials which possessed both piezofluorochromic and aggregation-induced emission properties[18]. Zujin Zhao et al synthesized novel 1,3,6,8-tetrakis [4-(1,2,2-triphenylvinyl) phenyl] pyrene (TTPEPy) with a novel AIEE effect, efficient solid PL (Φ_F = 70%), and excellent thermal stability (T_d = 485℃). The AIEE effect enables TTPEPy to work as a solid emitter for the construction of efficient OLEDs, with η_C , η_P and η_{ext} up to 12.3 cd A^{-1}, 7.5 lm W^{-1} and 4.95%, respectively[19]. Xiqi Zhang et al provided tetraphenylethene-based AIE FONs (TPE-Ply), with facile preparation procedure, AIE property, uniform morphology, high water dispersibility and excellent biocompatibility, they were expected to be novel and promising for cell imaging applications[20].

Taking the advantage of AIE luminogens, the fluorescence intensity of the modified polymers can be efficiently enhanced by increasing its concentration, loading without the need to avoid the aggregation of the probes. However, it is strongly necessary to figure out how the AIE luminogens and the polymer will interact with each other, and how the

interaction will impact on the products' fluorescence properties.

In this paper, we synthesized TPE derivant and knitted it to PDMS polymer chains by covalent bonds to study its fluorescence property. PDMS based elastomer is known to be rubbery material consisting of soft and flexible polymer chains with cross-linking points; thus the movement of the polymer chains seriously affect the degree of bondage to AIE luminogen. Importantly, the application of AIE luminogen functionalized elastomer may not be limited to the fluorescent material, their tunable emission wavelength and good stimuli-sensitive fluorescence properties may make them to be applied into thermal detection and so on.

Results and discussion

Compound TPE-containing dibenzyl bromide (TPE-2CH_2Br) and its synthetic process are presented in Scheme 1 and Scheme 2, respectively. Detailed procedures can be found in the supporting information.

----------Scheme 1----------

TPE-2CH_2Br was then knitted to PDMS polymer chains by covalent bond with APTES. The synthetic process is presented as follows (Scheme 3). Detailed procedures can be found in the supporting information. To study the influence of AIE luminogen content on the properties of the elastomers, the weight ratio of TPE-2CH_2Br to PDMS varied from $1:10^{-2}$ to $1:10^{-4}$ as presented in Table 1, and the corresponding oligomer were named as TPE-PDMS-A, TPE-PDMS-B, TPE-PDMS-C, TPE-PDMS-D, and TPE-PDMS-E, respectively.

----------Scheme 2----------

----------Scheme 3----------

----------Table 1----------

Then, TPE-PDMS fluorescent elastomers were prepared by sol-gel reaction. At first, TPE-PDMS oligomers were blended with TEOS at weight ratio of 100:30; after being added into DBTDL(0.05wt%), the blends were casted onto the substrate. The fluorescent elastomers were got by being heated at 80℃ for 8h. To identity clearly, the solidified fluorescent elastomers were named as STP-A, STP-B, STP-C, STP-D and STP-E,

respectively. Because TPE molecular was knitted with PDMS chains by covalent-bond, its intramolecular rotations would be restricted with the surrounding polymer chains, and the elastomer showed a typical Aggregation Induced Emission character.

Fig.1S shows FTIR spectra of PDMS modified with APTES and TPE-PDMS-A, respectively. The peaks at 3750cm^{-1}, 2962cm^{-1} and 1100~1002cm^{-1} assign to ν_{N-H}, ν_{C-H} and ν_{Si-O}, respectively. From these two spectra, the relative intensity absorption of N-H weakened obviously for TPE-PDMS-A because -NH_2 group had been consumed during the reaction when TPE-2CH_2Br was added. In addition, 7.260(m, H-Benzene) attributes to the benzene ring of TPE is observed from ^{1}HNMR of TPE-PDMS-A(Fig.2S)($CDCl_3$ is used as the solution). These data indicate that the reaction has successfully proceeded without damaging the structures.

Table 1S summarizes Molecular Weight and Molecular Weight Distribution of TPE-PDMS oligomer. The cross-linking density of TPE-PDMS oligomer increased with the content of silane coupling agent because more content of PDMS was linked with each other during the reaction. The performance of the cured elastomer would be interfered by highly crosslinked PDMS oligomers. The result of GPC demonstrated this trend.

X-ray diffractometry (XRD) was used to characterize the dispersion of AIE luminogen in the fluorescent elastomer. No diffraction peaks from TPE-2CH_2Br were detected for STP-A elastomer, suggesting that TPE-2CH_2Br was uniformly dispersed in the elastomer without the formation of large aggregates probably due to its connection onto PDMS polymer chains with covalent bonds[21].

----------Fig.1----------

----------Fig.2----------

Typical SEM image of the surface of STP-A elastomer, as is shown in Fig.2, conformed the conclusion of XRD. TPE-2CH_2Br was uniformly dispersed in the PDMS matrix without the formation of large aggregates. A slight wrinkle might be caused by the shrinkage of polymer chains during the process of sol-gel reaction[22].

Due to high chemical-bond energy (Si-O-Si,422.5kJ/mol), it needs more energy to destruct PDMS-based elastomer[23]. From Fig.3, pure PDMS-based elastomer showed a

good heat resistant property, and the thermal decomposition temperature reached 472℃. When TPE-2CH_2Br is knitted to PDMS chains by covalent bonds, thermal stability of elastomer may be influenced by its lower chemical-bond energy. However, from the result of TGA, the heat resistant of STP-A could still be as high as 452℃. With the protection of the packed long polymer chains, thermal stability of AIE luminogen is enhanced effectively, which means that the cured fluorescent elastomer can still work at high temperature.

----------Fig.3----------

To obtain a deep insight of cross-linking in these fluorescent elastomers, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were carried out on pure PDMS-based elastomer and the fluorescent elastomers, respectively. In the literature, a DSC chart of STP-X and pure PDMS-based elastomer showed one melting point at around -45℃. By increasing the crosslink density of the fluorescent elastomers, more energy is needed to destroy the crystalline lamellae due to higher molecular weight of the elastomer, so the enthalpy of the fluorescent elastomers are increased(Seen from Table 2S). These data, substantially different from those of the starting polymers, also supported the successful process of cross-linking reaction, resulting in appropriate anchoring of the employed polymer chains [24]. In addition, the result of thermodynamics measurement conformed that the mobility of the polymer chains enhanced linearly to the increased temperature above room temperature. Due to the restricting effect of the polymer chains weakens with the increased temperature, the mobility of TPE molecular increases and a part of TPE molecular can return to ground state through non-radiative way, and the intensity of photoluminescence will weaken correspondingly[25].

----------Fig.4----------

----------Fig.5----------

Unlike DSC, DMA measurement provides a better accuracy of thermal phase transition readings, and more importantly, are capable of isolating the storage and loss moduli. As was demonstrated by Hill and Kozlowski[26], the dynamic measurements are advantageous since it is possible to simultaneously measure storage and loss moduli in a rubbery plateau region. Take STP-A as an example, from its DMA curve(Fig.6), lineally decreased storage modulus meant that the motion capability of the polymer chains

increased linearly with the temperature and no phase transition happened during the range of testing temperature. The result of DMA is consistent with DSC, so a part of TPE molecular linked with PDMS polymer chains can return to ground state through non-radiative way, and the photoluminescence intensity of the fluorescent will weaken correspondingly.

----------Fig.6----------

The elucidation for mechanical properties of the fluorescent elastomers, including Strain-stress curve and Young's modulus (E), was conducted by tension experiment at room temperature. For the test, we prepared a dumbbell-like shaped specimen. From stress−strain curves, higher elongation at break and tensile strength can be obtained by more content of siliane coupling agent. As we know, with longer bond length and higher bond angle, PDMS polymer chains present very soft property, PDMS-based elastomer can't be applied into application only when the polymer chains is cross-linked by covalent bonds. From the result of Stress−strain curves, STP-A presented the best elongation at break property. Firstly, the increased molecular weight and the restricted movement of polymer chains can be obtained by higher cross-linking density, which is beneficial to the mechanical properties of the fluorescent elastomer. Secondly, the knitted AIE luminogen can also act as a rigid cross-linker to the fluorescent elastomers. Young's moduli were assessed from the curves between 0.479 and 0.878 of strain (Table S3). As to STP-A, when the content of silane coupling agent was the highest, the degree of cross-linking might be best to make the polymer chains be connected at a certain degree to resist on the external forces well. In addition, the elastomer didn't present brittleness property at this stage. So the enhancement of both stress and strain maxima was observed. For pure PDMS-TEOS elastomer, it might present more like a gel. The fluorescent elastomers could offset the external force by the motion of chain segment. So it exhibited longer elongation at break and lower Young's modulus than STP-E. These values are in good agreement with those of the reported PDMS elastomers[27].

Next, photophysical properties of different fluorescent oligomers and elastomers will be studied systematically. Owing to the electronic transition of the TPE unit, the absorption spectra of TPE and TPE-PDMS oligomer in diluted THF solutions (10μM) exhibited the

absorption peak at 315nm.

Photoluminescence (PL) spectra of TPE-PDMS oligomers present a strongly fluorescent property, and concentration dependent increase of intensity. We have proposed that restriction of intramolecular rotation (RIR) is the main cause for the AIE phenomenon [28]. When TPE dervriant and polymer chains were knitted together by covalent bonds, the RIR process would partially activate and thus make the oligomer&elastomer somewhat emissive. According to Fig.7, the intensity of PL spectra increased linearly to the concentration of TPE devriant. With the connection effect of covalent bonds and similar chemical environment, the intensity of PL spectra didn't present an abrupt change. These data demonstrated that TPE devriant homogeneously dispersed in the elastomeric samples without forming macroscopic aggregates or domains.

----------Fig.7----------

In addition, a slight red shift was observed from TPE-PDMS-E(475nm) to TPE-PDMS-A(491nm). It might be caused by the intramolecular charge transfer (ICT)[29-31] mechanism. Although TPE-2CH_2Br was linked to PDMS polymer chains by covalent bonds, the modified PDMS can also act as "solid-state solvent" to the AIE luminogen. With more silane coupling agent in the elastomer, higher polarity of the surrounding "solid-state solvent" will lead to a slight red-shift of the emission maximum. In the next, TPE-PDMS-A oligomer and STP-A elastomer were taken as examples because they showed the most obvious fluorescence behavior.

To identify the difference between TPE devriant and TPE-PDMS-A oligomer in photoluminescence performance, we examined the emission behaviors of TPE-2CH_2Br and TPE-PDMS-A in THF and THF-water mixtures. The PL spectrum of TPE-2CH_2Br in THF was basically a flat line parallel to the abscissa (Fig.8A). However, when a large amount of water (≥90 vol%) was added to THF solution, an emission peak emerged at 468 nm, the PL intensity was 31-fold higher than that of pure THF solution, demonstrating a typical AIE(Aggregation-Induced Emission) phenomenon[32,33]. For TPE-PDMS oligomer, on the other hand, it behaved differently. TPE-PDMS-A showed apparent fluorescent in THF solution, and the emission peak emerged at 490nm (Fig.8B). When a small amount of water was added into THF solution, obvious fluorescence enhancement was observed. The

emission became stronger progressively with increasing the amount of water in the solvent mixture. At 90 vol% water content, the PL intensity was 3.3-fold higher than that of pure THF solution, while the emission maximum was still located at 490nm. It presented a typical AEE(Aggregation-Enhanced Emission). The changes in the relative PL intensity (I/I_0) with the solvent composition of THF-water mixtures of TPE-2CH_2Br and TPE-PDMS-A oligomer are given in Fig.9.

----------Fig.8----------

----------Fig.9----------

While the PL intensity of TPE-2CH_2Br solution rose abruptly after threshold water content, a smooth emission enhancement with the water content was observed in TPE-PDMS-A. Being a low molecular weight compound, the molecule of TPE-2CH_2Br is free to rotate in pure THF solution as well as THF-water mixtures with low water contents. In contrast, TPE-2CH_2Br and PDMS polymer chains in TPE-PDMS oligomers are knitted together, which partially activate the RIR process and thus make the polymer somewhat emissive even in pure THF solution. Moreover, due to higher hydrophobicity or comparatively low solubility of TPE-PDMS in aqueous mixture, aggregates are more readily formed in THF-water mixtures with low water fractions, thus making the PL process of the polymer more sensitive to the change in its surrounding solvent medium[25,34]. In addition, the slight red-shift of the emission maximum (from ~468 to 490 nm) when TPE derivant was linked to PDMS polymer chains might be also caused by ICT mechanism and the reason had been discussed as above.

Interaction between PDMS and TPE-2CH_2Br can also impact on the photophysical property of the fluorescent oligomer&elastomer. As presented in Fig.10(A), when TPE derivant was physical blended with PDMS oligomer in THF solution, no fluorescence could be observed. On the contrary, TPE-PDMS oligomer, which TPE derivant was knitted with PDMS polymer chains via covalent bond, could show obvious fluorescence in THF solution. As to the former blending solution, AIE luminogen is free to rotate in polymer solution, so the absorbed energy can be released through a non-radiative pathway. However, when intramolecular rotation of TPE derivant are restricted by the knitted polymer chains, the RIR process would activate and make TPE-PDMS oligomers emissive in pure THF

solution. The fluorescent elastomer STP-A, as presented in Fig.10(B), showed similar behavior. The STP-A elastomer displayed intensive fluorescence while the cured PDMS elastomer blended with TPE-2CH_2Br could only show extremely weak fluorescence. With good miscibility between PDMS and TPE derivant, TPE-2CH_2Br was uniformly dispersed in PDMS matrix without the formation of large aggregates. The reason for weak fluorescence intensity may be caused by low concentration of TPE-2CH_2Br in the system at first. In addition, the flexibility of the PDMS polymer chains should also be taken into account. In this state, there are no covalent links between PDMS polymer chains and AIE luminogen. TPE undergoes dynamic intramolecular rotations against its double bound and renders its molecule non-luminescent because there is no bondage action to it.

----------Fig.10----------

In addition, a slight red-shift of the emission maximum for the fluorescent elastomers (from ~490 to 500 nm) might be also caused by the ICT mechanism as was discussed above: the joint hydrolysed-TEOS will enhance the polarity of the cured elastomer[35,36].

----------Fig.11----------

PL spectra and PL intensity of STP-A varied with temperatures and are presented in Fig.11(A) and (B), respectively. The result verified the conjecture of the results of DSC and DMA. The fluorescent elastomer emitted a strong green-blue light (500 nm) at room temperature. With the raised temperature, the fluorescence intensity of the fluorescent elastomer decreased. Because TPE molecules are embedded in the polymer matrices and knitted with each other, the intramolecular motions (i.e. rotation, vibration, torsion, and bending) of the phenyl rings of TPE are restricted to some extent. The energy of the excited state is annihilated through radiation decay, and thus AIE luminogen emits efficiently. Because there was no transition temperature determined in the temperature range 0℃ ~150℃, segmental motion capability increased linearly with the increased temperature. Plots of fluorescence intensity at 500 nm against temperature showed that the fluorescence intensity dropped linearly and drastically with the increased temperature. The intramolecular motions consume the energy of the excited state, which leads to weak fluorescence emission of AIE luminogen in the rubbery state of the polymers[37,38].

----------Fig.12----------

To study the durability of the fluorescent elastomer, STP-A was selected and checked at various temperatures. From Fig.12, STP-A elastomer showed similar fluorescence image between 30℃ and 150℃. The fluorescence spectra of STP-A at 30℃ showed a distinct emission peak at 500nm, whereas the emission was considerably weaker at 150℃. The fluorescence emission was capable of reversibly switching by repeatedly altering temperature. This revealed that STP-A was stable for repeated thermal treatments.

Conclusions

In summary, we demonstrated a synthesis of fluorescent elastomer by knitting TPE-2CH_2Br with PDMS together via covalent bonds. Facile progress of the preparative reaction was confirmed by ^{1}HNMR and FTIR spectroscopy studies. The copolymerized TPE derivant didn't ruin the heat resistance of the cured fluorescent elastomer as could be confirmed by TGA; in addition, it is uniformly dispersed in the elastomer without the formation of large aggregates from the overall results of SEM, XRD and PL spectroscopy. A tensile test of the obtained sample strips showed archetypal elastomeric behavior, while the content of silane coupling agent and AIE luminogen substantially affected on their mechanical properties such as Young's modulus and maximum strain. Fluorescence of the oligomer and the cured elastomers were found to be affected by the interaction between PDMS polymer chains and TPE-2CH_2Br, only when they were knitted together with covalent bond, could activate the RIR process and make the elastomer somewhat emissive. It should partly be attributed to the hampered intramolecular rotation of the aryl rotors of dye molecules by wrapping and coiling of flexible polymer chains. Fluorescence of the elastomers was found to be stimuli-sensitive against temperature, and reversibility of this responsiveness was also confirmed. The AIE characteristics are clearly responsible for these features, which is also susceptible for the RIR process. With significant advantages, such as ease of synthesis, high and tunable sensitivity, immunity to aggregation, facile operation and data processing, TPEs offer new opportunities for combination of AIE luminogen into elastomeric polymer network to open a new horizon for material chemistry, such as sensing materials for temperature and so on.

Experimental

Materials

PDMS(M_w=1.3×10^5) was purchased from Jinan Beyond Co.,Ltd., China. Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under nitrogen. Aminopropyltriethoxysilane(APTES), 4-bromobenzophenone, zinc powder, titanium (IV) chloride ($TiCl_4$), tetraethoxysilane(TEOS), dibutyltin dilaurate (DBTDL) and other chemicals and solvents were all purchased from Aldrich and used as received without further purification.

Instruments

^{1}HNMR spectra were measured on Bruker ARX 400 NMR spectrometers using $CDCl_3$ as the deuterated solvent and tetramethylsilane (TMS; δ=0ppm) as the internal standard. FTIR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Relative number (M_n) and weight-average (M_w) molecular weights and polydispersity indices (PDI or M_w/M_n) of the TPE-PDMS oligomers were estimated by a Waters Associates gel permeation chromatography (GPC) system equipped with RI and UV detectors. THF was used as the eluent at a flow rate of 1.0 mL min^{-1}. A set of monodispersed linear polystyrenes covering the molecular weight range of 10^3~10^7 was used as the standard for the molecular weight calibration. X-ray diffraction (XRD) measurements were performed using an XRD diffractometer(D-MAX 2200 VPC) equipped with Ni-filtered Cu Kα radiation, having a wavelength of 0.154nm. Images of scanning electron microscopy were taken on a JSM-6700F electron microscope. Thermogravimetric analysis (TGA) measurements were carried out under nitrogen or in air on a Perkin-Elmer TGA 7 analyzer at a heating rate of 10℃ min^{-1}. DSC measurements were carried out using DSC Q100 (TA Instruments) (TA Instruments, USA) over the temperature of -80℃ to 200℃ at a scan rate of 10℃ min^{-1} . All the thermograms were base line corrected and calibrated using Indium metal. The experimental specimens (8–10 mg) were dried at 60℃ under vacuum for 24h, before being measured. All the samples were firstly annealed at 120℃ for 3 min, and cooled to -80℃ by using liquid nitrogen and then scanned for the measurement. Tensile properties of were measured through a 10 kN electromechanical tensile testing machine (CMT5104, China) at room temperature, and the tensile speed was 50 mm min^{-1}. UV-vis absorption and light transmission spectra were measured on a Milton Roy Spectronic 3000

array spectrophotometer. Dynamic mechanical analysis (DMA) was done by DMA242，(NETZSCH, Germany) measurement. It was carried on from room temperature to 150℃ at a scan rate of 10℃ min^{-1}, with 80μm amplitude of vibration and 1Hz frequency of the alternating stress. Fluorescence spectra were recorded using a steady state spectrometer (Edinburgh Instrument Ltd, FLSP920) equipped with a temperature control system (Oxford instruments). To eliminate the interference of heating rates on the thermal properties of the fluorescent elastomer, heating rate was fixed at 1 min^{-1} for all specimens. Fluorescence spectra were scanned every 1 min.

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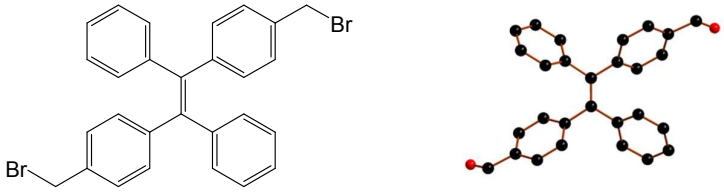
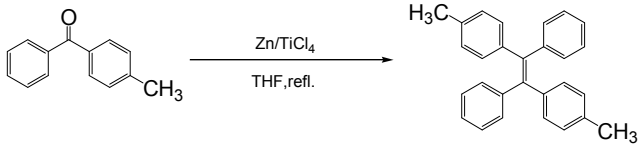


Scheme 1. Chemical structure and ball-rod modelling of TPE-2CH_2Br

Step 1



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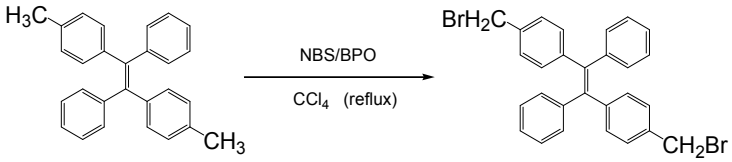
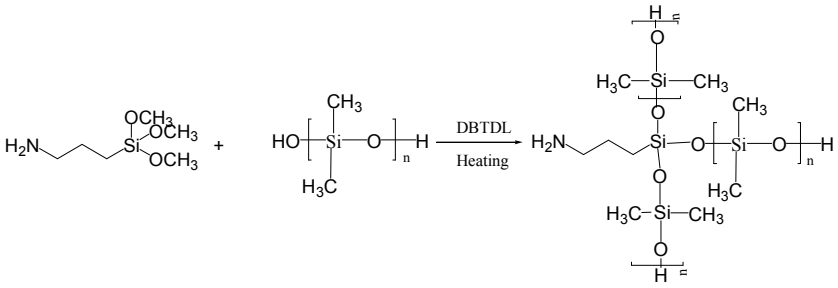
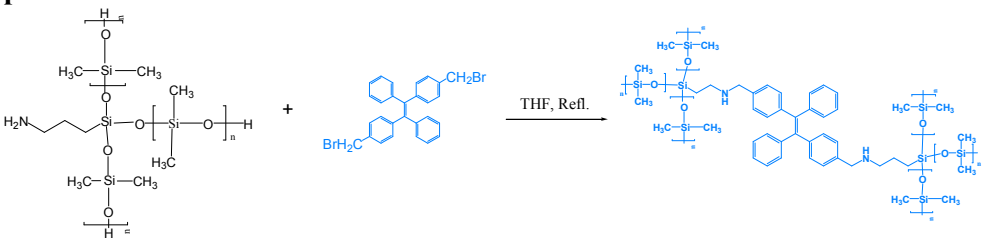


Scheme 2. Synthetic process of TPE-2CH_2Br

Step 1



Step 2



Scheme 3. Synthetic process of TPE-PDMS oligomer

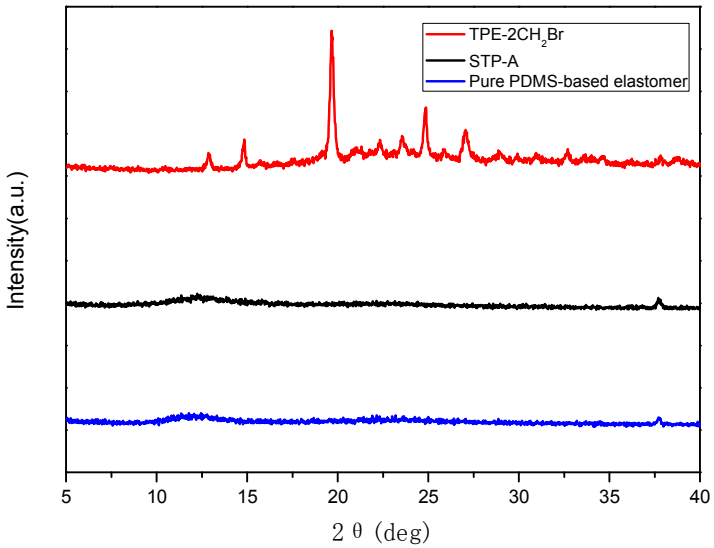


Fig.1 XRD curves of TPE-2CH_2Br, STP-A and pure PDMS-based elastomer

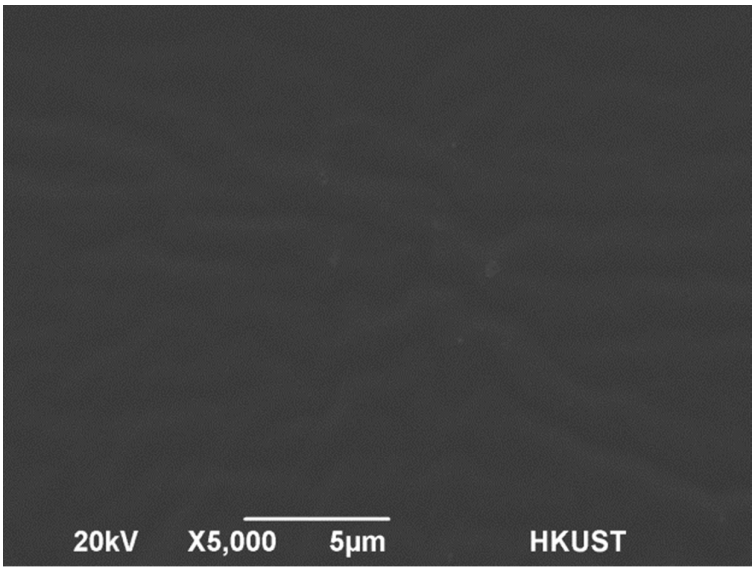


Fig.2 SEM image of STP-A elastomer

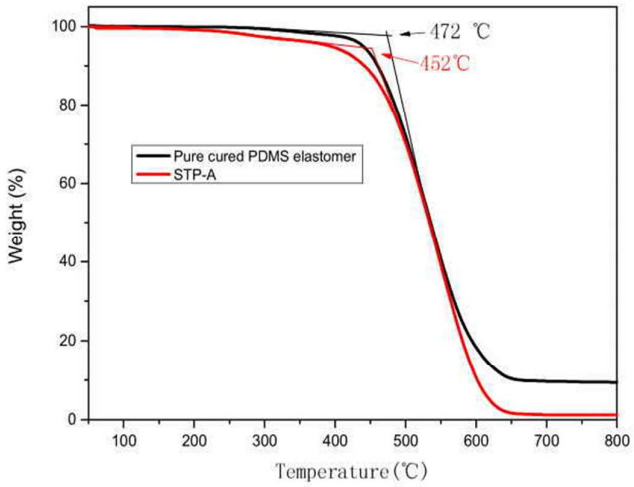


Fig.3 Heat resistant of pure PDMS-based elastomer and STP-A elastomer

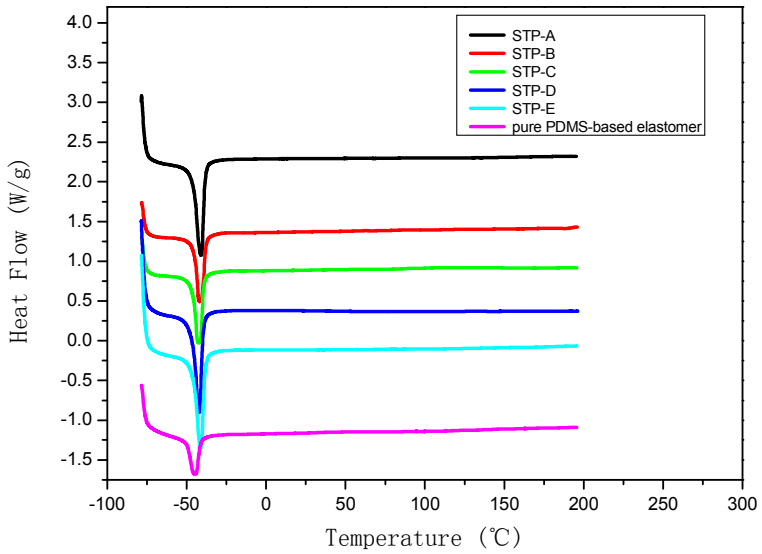


Fig.4 DSC charts of STP-X and pure PDMS based elastomers

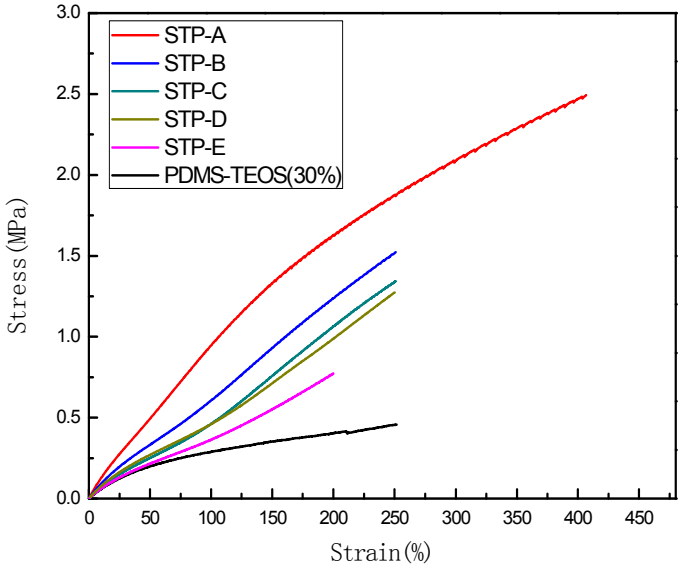


Fig.5 Stress−strain curves measured at room temperature for different elastomers

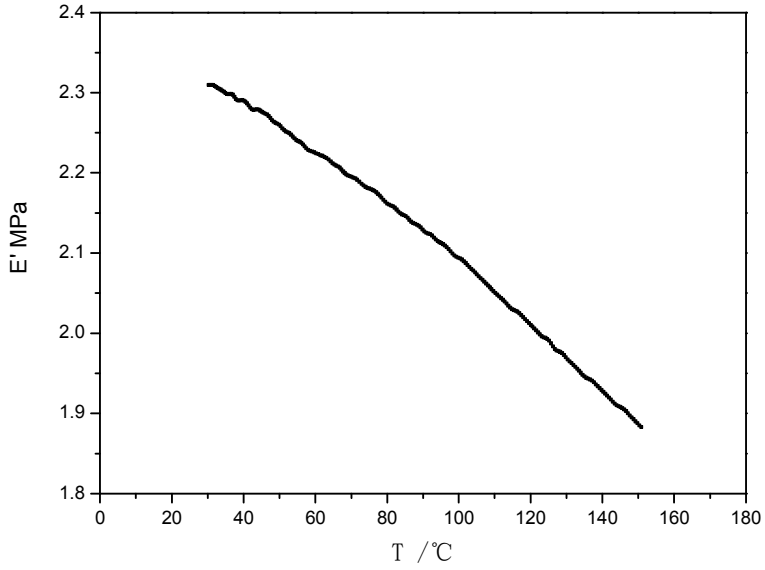


Fig.6 DMA curve of STP-A(log E')

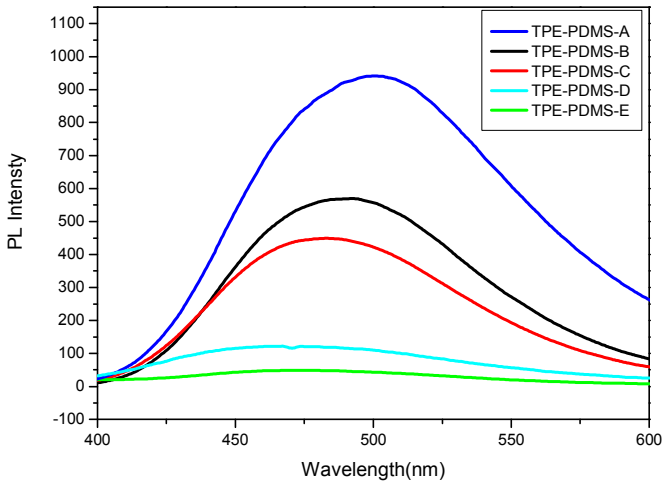


Fig.7 PL spectra of TPE-PDMS varied with the content of TPE, λ_{ex}=315 nm

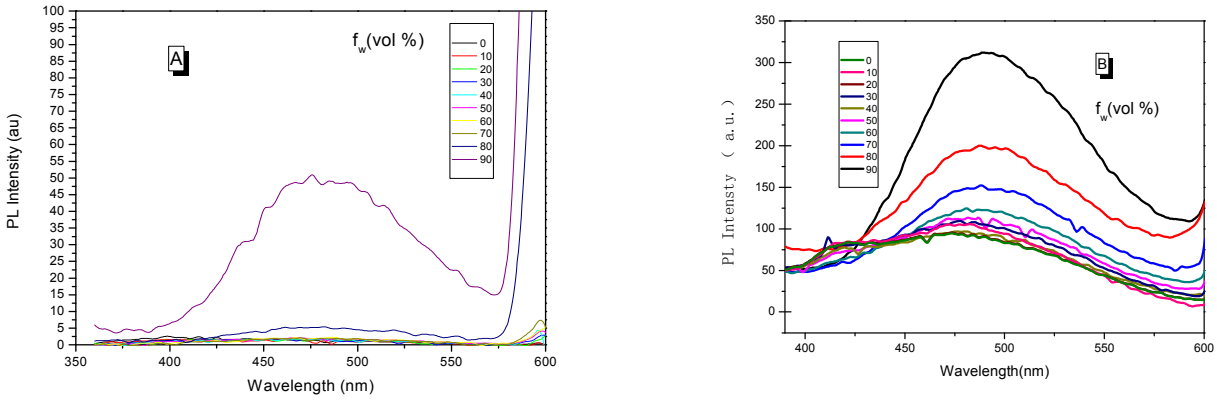


Fig.8 PL spectra of (A) $2CH_2Br$-TPE and (B) TPE-PDMS-A in THF–water mixtures with different water contents (f_w),10μM, λ_{ex}=315 nm

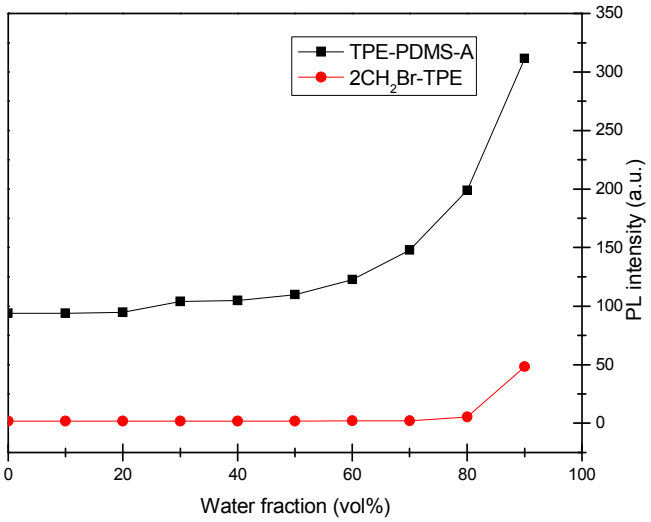


Fig.9 PL spectra of $2CH_2Br$-TPE and TPE-PDMS-A in THF–water mixtures with different water contents (f_w)

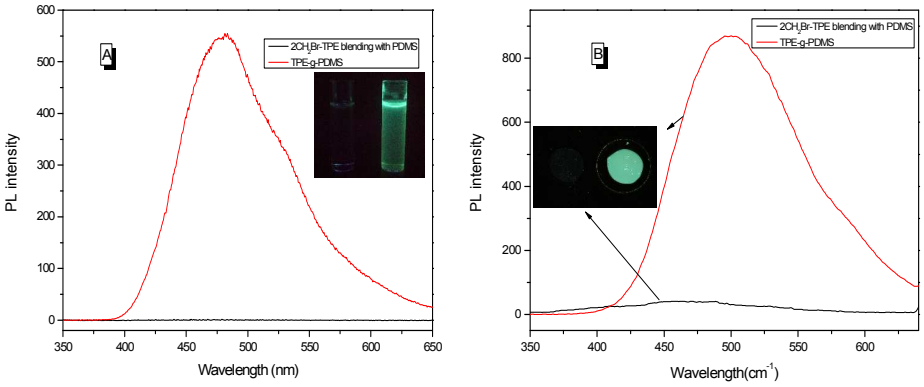


Fig.10 (A) PL spectra of PDMS blended with TPE-2CH_2Br and TPE-PDMS-A in THF solution, 10μM,; (B) PL spectra of the cured PDMS elastomer blended with TPE-2CH_2Br and STP-A elastomer, λ_{ex}= 315 nm

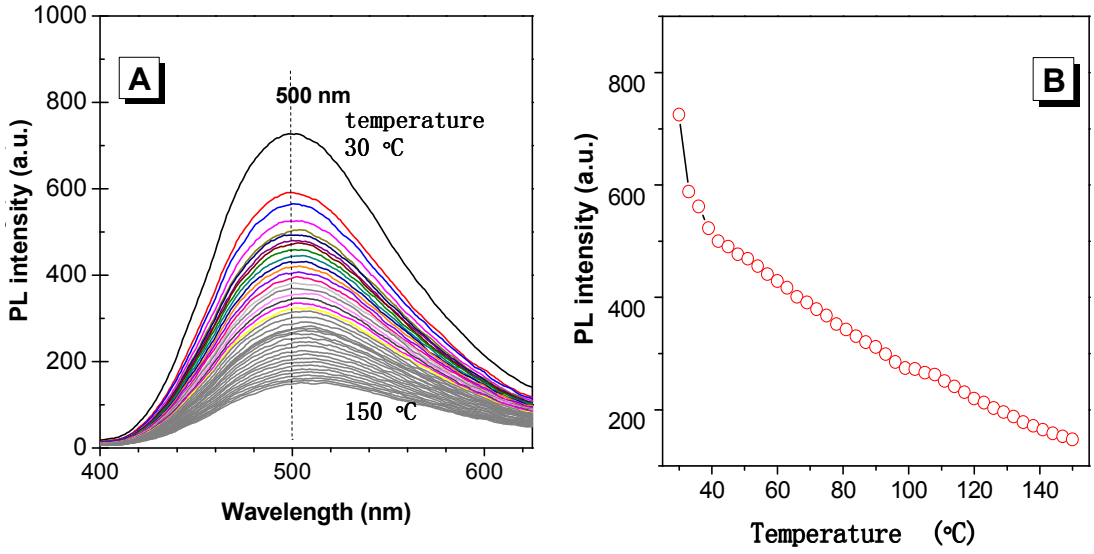


Fig.11 (A) PL spectra of STP-A varied with temperature; (B) PL intensity varied with temperature of STP-A, λ_{ex}=315 nm

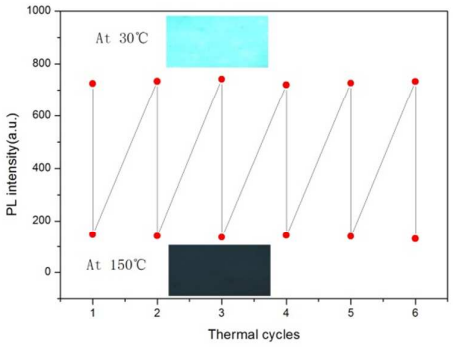


Fig.12 Fluorescence image and its intensity (500 nm) of STP-A elastomer at 30 °C and 150 °C

Table 1. Preparation Condition of TPE-PDMS oligomer

Materials	PDMS:APTES:TPE-2CH_2Br *
TPE-PDMS-A	10^2:1:1
TPE-PDMS-B	5×10^2:1:1
TPE-PDMS-C	10^3:1:1
TPE-PDMS-D	5×10^3:1:1
TPE-PDMS-E	10^4:1:1

*By weight