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# **Graphical Abstract**



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Synthesis and post-polymerization modification of polynorbornene bearing dibromomaleimide side groups

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# Abstract

We demonstrate that polynorbornene containing dibromomaleimide side group is a novel polymer platform for post-polymerization modification. Polymer **P0** was obtained through ring-opening metathesis polymerization of monomer **2** by using Grubbs third generation catalyst. Subsequently, **P0** was chemically modified with 1-butanethiol and benzyl mercaptan to generate **P1** and **P2**, respectively. In this way, the dibromomaleimide units on polymer side chain were quantitatively converted to dithiolmaleimide moieties. All the polymer samples exhibited good thermal stability and relatively high glass transition temperature. Meanwhile, the effects of substituent and solvent on fluorescent properties of the polymers were elucidated.

# Keywords

Polynorbornene; Dibromomaleimide; Post-polymerization modification

### 1. Introduction

Functional polymeric materials have attracted much attention from both academic and industrial communities. In particular, the diversity of functionality expands rapidly in recent years due to the wide applications of highly efficient organic reactions in polymer chemistry [1]. In general, functional polymers can be synthesized via polymerization of monomers that bearing functional moieties, so that the functionality of the corresponding polymers are highly predicted. However, the scope of functional groups that could be selected was usually narrowed due to the intolerance of highly reactive species such as cations, anions and transition metal catalysts to polar moieties. Moreover, monomer synthesis is the very first and indispensable step to meet the requirements of developing a specific sort of polymeric material with novel functions. On the other hand, post-polymerization modification represents another synthetic methodology to afford functional polymers always in an efficient and powerful manner [2-7]. In this way, the as-prepared polymer serves as a platform ready to be chemically modified with functional groups of a broad range. At the same time, a large number of functional polymers can be obtained simply by choosing different modification reactions. A unique chain length and molecular weight distribution of the final polymers is anticipated, which provides convenience to make a point-to-point comparison of the structure-property relationships. After modification, the microstructure of the functional polymer is highly predicted as long as the reactive sites are quantitatively converted.

Ring-opening metathesis polymerization (ROMP) is an exceptional synthetic method to obtain polymers with controlled chain length and low polydispersity index [8]. The release of monomer ring strain is the driving force of chain propagation, therefore norbornene and cyclooctene derivatives both become ideal choices for ROMP monomers. The ruthenium-based catalysts (best known as Grubbs catalysts) are not only commercially available but also highly tolerant to a variety of polar groups. In this way, functionality of a polymer chain can be well controlled and the concentration of functional groups in local environment can be facially adjusted by using ROMP. Indeed, in the last decade, tremendous research efforts have been dedicated to this chain-growth polymerization protocol, and the diversity of functional polymers that derived from ROMP was greatly enriched. Among the reported contributions, post-polymerization modification of ROMP polymer represents an increasingly appealing research field. For example, functional groups including azido [9-11], alkyne [12-14], activated ester [15-18], activated bromide [19] and pentafluorophenyl [20] have been induced to the ROMP polymer side chains for further modification. Very recently, multiple "click" reactions (e.g. activated ester nucleophilic substitution, Diels-Alder reaction, atom transfer nitroxide radical coupling, maleimide-thiol coupling, hydrazone formation, thiol-ene reaction and copper-catalyzed azido-alkyne 1,3-dipolar cycloaddition, etc) are used for orthogonal modification of ROMP polymer side chains [21-26]. At the same time, quantitative conversion of the internal alkene moieties of ROMP polymers to other functional groups was also realized upon several approaches [27-30]. However, only a single

functional moiety is induced to each repeating unit of the polymer. Moreover, although the induction of functional groups along with the construction of polymer topology such as grafted polymer and polymer brush both become successful, research on the property of the resultant polymer is rather limited.

Dibromomaleimide (DBM) is capable of modifying cysteine in a selective and reversible way as reported by Baker [31]. From then on, this sort of native disulfide bridging protocol was widely used in biomedical field such as protein modification including PEGylation [32] and fluorescent labeling [33] as well as bioconjugation [34]. The carbon-bromide bond can be efficiently substituted by thiols under mild condition and in a quantitative manner, and this novel sort of "click" reaction have already found wide applications in polymer chemistry. For example, O'Reilly group demonstrated that polymer chain end [35] and side chain [36] functionality could be tuned in a broad range by DBM-thiol reaction, and functional polymers were also obtained by polymerization of pre-functionalized monomers [37]. At the same time, cyclic [38] and star [39] polymers were successfully generated with the assistance of DBM-thiol reaction to control polymer topology, and even sequence-regulated polymers [40] were obtained due to the "click" nature of this reaction. Very recently, functional materials such as gene delivery vehicle [41], nanomedicine [42] and biomolecule-modified surface [43] have been fabricated to exemplify the huge potential and impact of this novel "click" reaction in materials science. Inspired by the previous works, we speculated that the marriage of ROMP and DBM will certainly provide new opportunity for post-polymerization modification. A new sort of

chemically modifiable polymer platform could be generated through the ROMP of norbornene monomer bearing DBM moiety, which contains two reactive sites in each repeating unit. After the DBM-thiol reaction, different kinds of densely functionalized polynorbornene could be obtained simply by changing the type of thiols. Importantly, the thiol-substituted maleimide has been reported to be a fluorophore, so that fluorescent polymers are anticipated. Therefore, the effect of thiols as well as environmental factors such as solvent on fluorescent properties of the polymers could be investigated, which is surely helpful for the development of polymeric fluorescent probe of next generation.

In this contribution, we provide the first example of polynorbornene bearing DBM units as side groups via ROMP and the subsequent post-polymerization modification. Monomer bearing DBM moiety was synthesized in a two-step manner and was obtained in high yield. ROMP of the monomer was catalyzed by Grubbs third generation (G-III) catalyst, and the resultant polymer was obtained with predicted chain length molecular weight distribution. Subsequently, and narrow post-polymerization modification was performed by using DBM-thiol reaction to quantitatively convert the DBM units to dithiolmaleimide (DTM) moieties. All the polymer samples exhibited good thermal stability and relatively high glass transition temperature ( $T_g$ ). Fluorescent polymers were generated after the modification, and the fluorescence intensity and the maximum emission wavelength were found to be correlated with the type of thiol and solvent.

## 2. Experimental

### 2.1. Materials

3,4-Dibromo-1H-pyrrole-2,5-dione (DBM, Ark Pharm, Inc.), methylchloroformate (MCF,  $\geq$ 99%, Xiya Reagent Co., Ltd.), *N*-methylmorpholine (NMM,  $\geq$ 99.8%, Aladdin), 5-norbornene-2-methylamine (NMA, mixture of isomers, >98.0%, TCl), G-III catalyst (Sigma-Aldrich), ethyl vinyl ether (EVE, stabilized with 0.1% *N*,*N*-diethylaniline, Alfa Aesar), 1-butanethiol (98%, Alfa Aesar) and benzyl mercaptan (99%, Alfa Aesar) were all used as received without further purification. Tetrahydrofuran (THF), chloroform (CHCl<sub>3</sub>), dichloromethane (DCM), *N*,*N*-dimethylformamide (DMF), anhydrous methanol (MeOH), petroleum ether (petrol), ethyl acetate (EtOAc), anhydrous magnesium sulfate (MgSO<sub>4</sub>) and anhydrous ammonium chloride (NH<sub>4</sub>Cl) were all purchased from Sinopharm Chem. Reagent Co., Ltd. Calcium hydride (CaH<sub>2</sub>) was bought from Tianjin Xuan'ang Trade and Industry Co., Ltd. THF, CHCl<sub>3</sub> and DCM were refluxed with CaH<sub>2</sub> for 8 h and then redistilled. DMF was vigorously stirred with CaH<sub>2</sub> for 6 h and then distilled under reduced pressure. CDCl<sub>3</sub> was obtained from J&K Chemical Co., Ltd.

# 2.2. Characterization

Bruker ARX-400 spectrometer was utilized to measure the <sup>1</sup>H (400 MHz) and <sup>13</sup>C (100 MHz) NMR spectra. ROMP monomer and polymer samples were all dissolved in CDCl<sub>3</sub> with tetramethylsilane (TMS) as the internal reference for chemical shifts. Number- and weight-average molecular weights ( $M_n$  and  $M_w$ ) and polydispersity

indices ( $D = M_w/M_n$ ) were determined by gel permeation chromatograph (GPC). The measurements were conducted in THF (flow rate: 1 mL/min) at 35 °C with a Waters 1525 binary HPLC pump equipped with a Waters 2414 refractive index detector and three Waters Styragel columns  $(1 \times 10^4, 1 \times 10^3 \text{ and } 500 \text{ Å pore sizes})$ . A family of narrowly dispersed polystyrenes was used as the standards, and Breeze 3.30 SPA software was applied to calculate the  $M_n$  and D values. Electrospray ionization mass spectroscopy (ESI-MS) characterization was conducted using a Bruker APEX-IV Fourier transform mass spectrometer in a positive ion mode. Thermal gravimetric analysis (TGA) was carried out using a Q600-SDT thermogravimetric analyzer (TA Co., Ltd.) with nitrogen purging rate set at 100 mL/min. Measurements were conducted from room temperature to 600 °C at a heating rate of 10 °C/min. Calorimetric measurement was performed using a Q100 differential scanning calorimeter (TA Co., Ltd.) with nitrogen purging rate set at 50 mL/min. The program was set to finish two cycles in the temperature range from 0 °C to 180 °C. The heating/cooling rate was set to 10 °C/min. Data of the endothermic curve was acquired from the second scan. TA Universal Analysis software was used for data acquisition and processing in TGA and DSC measurements. Fluorescence spectra of polymers were recorded on a Hitachi F-7000 fluorescence spectrometer at room temperature. The scanning rate was 240 nm/min and both excitation and emission slit widths were 5.0 nm.

# 2.3. Synthesis of intermediate 1

To a solution of DBM (3.00 g, 11.7 mmol) and NMM (1.30 mL, 11.7 mmol) in THF

(135 mL), MCF (0.90 mL, 11.7 mmol) was added and the mixture was stirred for 1 h at room temperature. The solvent was removed *in vacuo*, and then DCM (100 mL) was added. The organic phase was sequentially washed with water and brine, and then dried over anhydrous MgSO<sub>4</sub>. After filtration, the solvent was removed *in vacuo* to generate the intermediate **1** as a pink powder in quantitative yield. The compound **1** was directly subjected to the next synthetic step without further purification.

### 2.4. Synthesis of ROMP monomer 2

NMA (1.42 mL, 11.2 mmol) was added dropwise to a stirred solution of **1** (3.66 g, 11.7 mmol) in DCM (120 mL). After 10 h, the solvent was removed *in vacuo*, and EtOAc (100 mL) was added to dissolve the crude product. The organic phase was sequentially washed with saturated NH<sub>4</sub>Cl solution, water and brine, and then dried over anhydrous MgSO<sub>4</sub>. After filtration, the organic filtrate was concentrated to dryness, and the yellowish crude residue was purified by column chromatography (petrol/EtOAc = 50/1) to generate **2** as white solid. Yield: 79%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 6.50-5.83 (m, 2H), 3.83-3.14 (dddd, *J* = 39.3, 23.1, 13.8, 8.2 Hz, 2H), 2.98-2.30 (m, 3H), 2.10-0.40 (m, 4H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>):  $\delta$  163.93 (d, *J* = 14.7 Hz), 137.89, 137.06, 135.97, 132.34, 129.27 (d, *J* = 5.0 Hz), 49.45, 44.85 (d, *J* = 13.4 Hz), 44.22 (d, *J* = 8.8 Hz), 43.62, 42.45, 41.78, 38.04 (d, *J* = 4.7 Hz), 30.37 (d, *J* = 53.4 Hz). ESI-MS: [M + Na<sup>+</sup>] = C<sub>12</sub>H<sub>11</sub>O<sub>2</sub>NBr<sub>2</sub>Na, calcd: 383.9034, found: 383.9090.

2.5. ROMP

To a 25 mL Schlenk tube **2** (36.1 mg, 0.1 mmol) and DCM (1 mL) was added to generate solution 1. G-III catalyst (2.9 mg, 3.3  $\mu$ mol) was dissolved in DCM (1 mL) to form solution 2. Subsequently, solution 2 (1 mL) was added to solution 1 under nitrogen atmosphere by using pipette ([**2**] = 0.05 mol/L), and the resulting solution was vigorously stirred at room temperature for 0.5 h. Afterwards, an excess of EVE was added under nitrogen atmosphere, and the polymer solution was vigorously stirred for an additional 5 min with the Schlenk tube sealed. The as-prepared polymer solution was directly subjected to GPC characterization. Meanwhile, the solution was poured into cold methanol (100 mL) to rapidly generate **PO** as a white solid for NMR characterization, thermal analysis and fluorescent property investigation. At the same time, the as-prepared polymer solution was concentrated to dryness, and **PO** was obtained as brownish semi-solid in this case for the subsequent DBM-thiol reaction. The overall yield was over 95%.

# 2.6. DBM-thiol reaction

Take the synthesis of **P1** as an example.

To a solution of **P0** (36.1 mg) in DMF (2 mL), 1-butanethiol (21.4  $\mu$ L, 0.2 mmol) was added by using pipette, and the resulting solution was vigorously stirred at room temperature for 10 h. The as-prepared **P1** solution was directly subjected to GPC characterization. Meanwhile, the solution was poured into cold methanol (100 mL) to rapidly generate **P1** as a yellowish solid for NMR characterization, thermal analysis and fluorescent property investigation.

Polymer **P2** was synthesized similarly with benzyl mercaptan (23.5  $\mu$ L, 0.2 mmol) as the added thiol compound. The overall yields were over 95% in both cases.

# 3. Results and discussions

### 3.1. Monomer synthesis

The synthesis of ROMP monomer 2 was conducted in two consecutive steps as shown in Scheme 1. It is reported that DBM derivatives could be obtained by treating dibromomaleic anhydride with amine. Nevertheless, a large amount of acetic acid is used as solvent and high reflux temperature is required, making the reaction condition extremely harsh and the purification rather tedious. As a result, we adopted a two-step synthetic procedure to get ROMP monomer 2 referring to the recently reported mild synthesis of N-functionalized DBM [44]. As a first step, DBM was treated with MCF and NMM to obtain the highly reactive intermediate 1 in THF at room temperature for 1 h and in quantitative yield. Subsequently, ROMP monomer **2** was generated through mixing compound **1** with 0.95 equivalent amount of NMA in DCM at room temperature for 10 h, and the overall yield of two steps reached 79% after purification. Intermediate 1 was one sort of reactive conjugate acceptor, so that no more than a stoichiometric amount of NMA was used, otherwise unwanted byproduct would be generated. The chemical structure and purity of 2 were confirmed by <sup>1</sup>H and <sup>13</sup>C NMR (Figs. 1 and S1) and ESI-MS spectra.



Scheme 1. Monomer Synthesis. Reagents and Conditions: (a) 1 equiv. MCF, 1 equiv. NMM, THF, rt,

1 h (b) 0.95 equiv. NMA, DCM, rt, 10 h.



Fig. 1. <sup>1</sup>H NMR spectrum of ROMP monomer 2 in CDCl<sub>3</sub>

# 3.2. ROMP and DBM-thiol reaction

Polymer **PO** was obtained in nearly quantitative yield through ROMP of monomer **2** with the assistance of G-III catalyst in DCM at room temperature for 0.5 h. The dose of catalyst was 3.3 mol% relative to monomer **2**, corresponding to degree of polymerization being 30, so that the theoretical molecular weights of **PO-P2** could be calculated, and the results were shown in Table 1. Gels were observed during the ROMP process if the monomer concentration was higher than 0.1 mol/L. Hence, the monomer concentration was kept 0.05 mol/L in this study.

Subsequently, as shown in Scheme 2, DBM-thiol reaction was carried out by mixing polymer **P0** with theoretical amounts of 1-butanethiol or benzyl mercaptan in DMF at room temperature for 10 h to afford DTM units functionalized polynorbornene **P1** and **P2**, respectively. The color of the solution turned bright yellow rapidly, suggesting the occurrence of nucleophilic substitution of thiols to DBM moieties.



Scheme 2. ROMP and DBM-thiol reaction. *Reagents and Conditions:* (a) G-III catalyst (3.3 mol%), DCM ([2] = 0.05 mol/L), rt, 0.5 h (b) stoichiometric 1-butanethiol or benzyl mercaptan, DMF, rt, 10 h.

All the GPC traces are unimodel as shown in Fig. 2, and the molecular weight values are summarized in Table 1. Each of the polymer samples exhibited  $M_n$  value exceeding 10,300 with narrow molecular weight distribution ( $\mathcal{D}$  values lower than 1.24 even after DBM-thiol reaction), so that efficient ROMP and post-polymerization modification was confirmed. Since GPC traces of **P1** and **P2** exhibited very similar shape to that of **P0** without the appearance of shoulder peak or significant

broadening, side reactions such as cross-linking or chain scission could be ruled out in this study. The elevated  $M_n$  values of **P1** and **P2** compared to that of **P0** could be attributed to the inherent increase of molecular weight. Meanwhile, the molecular weights of polymers measured by GPC were in high accordance with the theoretically calculated values.



Fig. 2. GPC traces of PO-P2 using THF as the eluent.

NMR characterization was carried out to manifest the chemical structures of polymer samples. Polymers **P0-P2** all exhibited good solubility in CDCl<sub>3</sub>, and the related <sup>1</sup>H NMR spectra were shown in Fig. 3. Signals of internal alkene (5.1-5.5 ppm), methylene spacer (3.3-3.7 ppm) and cyclopentane of polymer backbone (1.0-3.2 ppm) protons were clearly distinguished for **P0**, respectively. At the same time, signals corresponding to internal alkenes could be seen for polymer samples of **P1** and **P2** as well, suggesting the absence of side reaction between thiols and those moieties. Meanwhile, signals of *n*-butyl protons (for **P1**) and benzyl protons (for **P2**) were clearly observed and depicted in Fig. 3, confirming the successful DBM-thiol reaction. Importantly, the integration ratios between the signals of *n*-butyl or benzyl

groups and those of the internal alkene moieties matched well with the theoretical values, which solidly confirm the quantitative manner of DBM-thiol reaction for post-polymerization modification.



Fig. 3. <sup>1</sup>H NMR spectra of PO-P2 in CDCl<sub>3</sub>.

# Table 1

Molecular weights and thermal data of polymer samples.

Polymer	$M_{n, thero}^{a}$	M <sub>n, GPC</sub> <sup>b</sup>	${\cal D}^{\sf b}$	<i>T</i> <sub>g</sub> <sup>c</sup> ( <sup>o</sup> C)	𝕶 <sup>d</sup> (°C)
PO	10 900	<mark>10 300</mark>	1.17	153	241
P1	11 500	10 800	1.23	126	207
P2	<mark>13 500</mark>	12 700	1.24	174	231

<sup>a</sup> Calculated according to the feed ratio [2]/[G-III] = 100/3.3 (degree of polymerization being 30).

Then  $M_{n, \text{thero}}$  = (theoretical repeating unit mass) × 30 + terminuses.

<sup>b</sup> Determined by GPC (1 mL/min in THF at 35 °C) using polystyrene calibration.

<sup>c</sup> Determined by DSC (10 <sup>o</sup>C/min scan rate, nitrogen purging rate at 50 mL/min), the values recorded from the second scan data.

<sup>d</sup> Determined by TGA (10  $^{\circ}$ C/min scan rate, nitrogen purging rate at 100 mL/min).  $T_{d}$  is defined as the temperature at 5 % weight loss.

# 3.3. Thermal properties

Thermal stability of all the polymer samples was examined by TGA, and the photograph of solid **P0-P2** could be seen in Fig. S2. All the data are collected in Table 1.  $T_d$  is defined as the temperature at 5% weight loss. Fig. 4A depicts the TGA curves of **P0-P2** with the onset  $T_d$  values ranging from 207 °C to 241 °C, indicating the thermal stability of these polymers is suitable for common use. Multi-step catastrophic decomposition was detected above 200 °C, suggesting the complicated mechanism of thermal degradation. Although polynorbornene was commonly regarded as thermal resistant polymeric material [45], induction of DBM or DTM moieties as side groups severely diminished the thermal stability. Finally, all the polymer samples decomposed completely at about 600 °C.

Thermal transition behaviors of all the polymer samples were measured by DSC. Polymers **PO-P2** only exhibited typical glass transition stages in the DSC thermograms of Fig. 4B, and no melting peaks or other transition was observed even when heated to 180 °C. The polymers decompose before they melt owing to the moderate thermal stability, resulting in the absence of melting peaks. The as-prepared polymer **P0** 

exhibited glass transition stage at 153 °C, and this result could be explained as the stiffness of polymer main chain and the structural rigidity of DBM moieties. P1 showed lower  $T_g$  value (126 °C) compared with P0 due to the flexibility of butyl chains. Meanwhile, the glass transition stage of P2 appeared at 174 °C since the aromatic phenyl ring elevated the rigidity of polymer side chain. These results indicate that the thermal transition behaviors of this family of functional polymers can be potentially adjusted over a broad temperature range simply by altering the type of thiol compound for substitution.



Fig. 4. (A) TGA curves of PO-P2. (B) Endothermic DSC thermograms of PO-P2.

#### 3.4. Fluorescent properties

The fluorescent properties of all the polymer samples were evaluated by fluorescence spectra. We selected CHCl<sub>3</sub>, DMF and MeOH as three representative organic solvents to carry out the experiment. All the polymer samples exhibited solvent-dependent fluorescent properties. As shown in Fig. 5A-C, the fluorescence intensity as well as the maximum emission wavelength of polymer **P0-P2** is a function of the type of organic solvent. For example, the fluorescence emission of **P0** 

was not only obviously bathochromic-shifted but also drastically diminished as increasing the polarity of organic solvent. Polymers P1 and P2 exhibited the similar trend but differed in maximum emission wavelength. This phenomenon can be explained as the sensitivity of intra-molecular electron transfer to environmental factor such as solvent. The electron shifted away from the sulfur or bromide atom (electron donor) in the excited state to carbonyl group (electron acceptor) [46]. The significant decrease of fluorescence intensity and the phenomenon of bathochromic-shift in protic solvent such as methanol could be ascribed to the hydrogen bond between organic solvent and imide moiety of maleimide group [47]. On the other hand, due to the difference in fluorescence emission energy resulting from the alteration of substitution, the maximum emission wavelengths of P1 and P2 are bathochromic-shifted compared to that of PO. For a specific sort of organic solvent, as summarized in Fig. 5D, polymers bearing DTM moieties (P1 and P2) exhibit relatively strong fluorescence while the as-prepared polymer PO shows much weaker emission. This result coincided well with the previously reported ON-OFF switch between DTM and DBM units [48]. Meanwhile, the weaker fluorescence intensity of P2 compared to that of P1 is due to the negative effect of aromatic moieties such as benzyl group on fluorescence emission [49].

Overall, the fluorescent properties of **P0-P2** are determined by organic solvent and substituent. The maximum emission wavelength is bathochromic-shifted and the fluorescence intensity is diminished as increasing the polarity of organic solvent. Converting DBM to DTM group has a significant effect on bathochromic-shift of

maximum emission wavelength and enhancement of fluorescence intensity of the polymer. The variation of fluorescent property is the synergistic outcome of chemical structure and organic solvent. It is worth mentioning that polymer concentration of 2  $\mu$ M was sufficient for fluorescent property characterization, and the homogeneous sample solutions were generated in this case. However, increasing the concentration of polymer solution (e.g. 5  $\mu$ M) may result in opaque suspension especially when protic solvent such as methanol was selected. The maximum excitation ( $\lambda_{ex}$ ) and emission ( $\lambda_{em}$ ) wavelengths of all the polymer samples were collected in Table S1.



**Fig. 5.** (A)-(C) Fluorescence emission spectra of **P0**, **P1** and **P2** in different solvents, respectively. All the spectra were recorded at polymer concentration of 2  $\mu$ M. (D) Comparison of the relative fluorescence intensity of **P0-P2** in different solvents.

#### 4. Conclusions

The first example of polynorbornene containing DBM side groups via ROMP was provided in this study. Monomer 2 was obtained in high yield by means of two consecutive synthetic steps. Subsequently, ROMP of monomer 2 was successfully conducted by using G-III catalyst to generate polymer **P0** with predicted chain length and narrow molecular weight distribution. Thiol-DBM reaction was utilized for post-polymerization modification to quantitatively convert DBM units to DTM moieties, and polymers P1 and P2 were generated after treatment of P0 with stoichiometric amount of 1-butanethiol and benzyl mercaptan, respectively. Polymers **P0-P2** were stable up to 200  $^{\circ}$ C and exhibited  $T_{g}$ s higher than 125  $^{\circ}$ C, and all the solid samples were re-dissolvable in common organic solvents even after selective precipitation. The fluorescence intensity and the maximum emission wavelength of the polymers were determined by substituent and solvent. Specifically, the fluorescence intensity of the polymer was greatly enhanced after the thiol-DBM reaction but significantly diminished as increasing the polarity of organic solvent. The present work not only provides an alternative of chemically modifiable polymer platform but also sheds light on the exploration of novel polymeric fluorescent probe.

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# Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.201X.XX.XXX.

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# Highlights

- Polynorbornene containing DBM side groups was synthesized by means of ROMP.
- Thiols were used for quantitative conversion of DBM units to DTM moieties.
- Fluorescent properties of the polymers were governed by substituent and solvent.