

Photocrosslinkable Polynorbornene-based Block Copolymers with Enhanced Dielectric and Thermal Properties*

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Abstract Block copolymers poly(*endo*-*N*-3,5-bis(trifluoromethyl)biphenyl-norbornene-pyrrolidine)-block-poly(*exo*-*N*-(cinnamoyloxyethyl)-7-oxanorborn-5-ene-2,3-dicarboximide) (*endo*-PTNP-*b*-*exo*-PCONBI) and poly(*exo*-*N*-3,5-bis(trifluoromethyl)biphenyl-norbornene-pyrrolidine)-block-poly(*exo*-*N*-(cinnamoyloxyethyl)-7-oxanorborn-5-ene-2,3-dicarboximide) (*exo*-PTNP-*b*-*exo*-PCONBI) were synthesized by ring-opening metathesis polymerization. The *endo*- or *exo*-PTNP served as the high dielectric functional chain, and *exo*-PCONBI acted as the crosslinking segment. The *endo*-PTNP-*b*-*exo*-PCONBI, in which *endo*-PTNP has a high content of *trans* double bond and adopts isotactic configuration, shows a dielectric constant (ϵ) of 15.5, whereas *exo*-PTNP-*b*-*exo*-PCONBI, in which *exo*-PTNP has 67% *trans* double bonds and atactic microstructure, displays relatively low ϵ of 7.1. The cinnamate groups in *exo*-PCONBI were crosslinked to form three-dimensional network by cycloaddition reaction under UV irradiation. Exposed to UV-light for 10 min, the cinnamate group in polymer films has a crosslinking conversion of 36%, as determined by UV-Vis absorption measurements. By photocrosslinking, the polymer film has an increased ϵ of 16.6, a dielectric loss of 0.03, an elevated glass-transition temperature of 137 °C, and an enhanced decomposition temperature of 405 °C, compared to those of polymer films without irradiation.

Keywords: ROMP; Block copolymer; Photocrosslinking; Thermal stability; Dielectric performance.

INTRODUCTION

High-performance dielectric materials, defined as materials with dielectric constant above 7^[1], have a variety of applications in high energy and power capacitors^[2], and electric energy storage devices^[3]. Typical dielectric materials are ceramics including silicon oxide, silicon nitride, and barium titanate^[4]. These traditional materials can easily achieve very high dielectric constant at low frequency, whereas the dielectric loss is large ($>> 0.01$) and the processing of materials is expensive and complicated, moreover the high leakage current and low breakdown voltage^[5]. To overcome these disadvantages, an extensive effort has been made to develop new materials with high dielectric constant, low dielectric loss, and high breakdown voltage^[6, 7]. The common approach is the construction of composites, including the composite of polymers and ceramic or metal^[8], and the all-organic polymeric composites composed of organic fillers and polymer matrix^[9]. However, the composite approaches to form simple physical blends suffer from the adverse excessive agglomeration of the high-dielectric-constant organic fillers due to the incompatibility, which increases the dielectric loss and reduces the breakdown field^[10]. The modified approach is the chemical bonding of the filler to the backbone of polymer matrix to easily control the dispersibility of filler particulates in the materials^[11]. For example, the copper-

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phthalocyanine oligomers and/or conductive polyaniline oligomers were chemically grafted to polyurethane backbones, and the resulting materials showed an improved compatibility of the components^[12].

It is universally known that dielectric constant of polymer depends on the polarity of molecule itself^[13, 14]. The stronger is the polarity of molecules, the dielectric constant is likewise higher. Polymers may have higher dielectric constants when the polar groups are in the side position than those in the main chain, and also the polar molecules with asymmetric molecular structure have a higher dielectric constant than that of the symmetric ones. It was reported that the dielectric constant of the copolymers of propylene and hydroxylated propylene is 2 times more than that of polypropylene, due to the polarization of hydroxyl groups^[8]. The polymers obtained from ring-opening metathesis polymerization (ROMP) have versatile microstructures, which may contain the different *trans/cis* ratios of the double bonds in the backbone, various tacticities (isotactic, syndiotactic, and atactic), and monomer configuration (head-head, head-tail, *etc.*) for the unsymmetrically substituted monomers^[15, 16]. These microstructures are important to tune the dielectric constant of polymers. Polynorbornenes (PNBEs) prepared by ROMP possess physical characteristics, such as high thermal stability up to 400 °C^[17], and usually known as low-dielectric materials owing to their symmetric structure and low polarity of molecules^[18, 19]. However, if the polar side groups were introduced to PNBE backbone, the dielectric constant of polymer will greatly increase. Of such functional groups are cyano, nitro, halogen, perfluoroalkyl, and so forth. It has been demonstrated that poly(2,3-bis(trifluoromethyl)norbornadiene) with > 98% *trans*-vinylenes and highly tactic microstructure exhibited a much higher dielectric constant than half *trans*-polymer^[20]. The functional PNBEs containing large conjugated aromatic structure with polar trifluoromethyl (CF₃) group and rigid pyrrolidine moiety displayed much higher dielectric constant of above 20 than polymers commonly used in the thin film capacitors^[21, 22].

Crosslinkable polymers have been used in the areas of interpenetrating polymer networks^[23], nonlinear optical materials^[24], macro- and microlithography^[25], and the formation of outstanding thermally and chemically resistant materials^[26–28]. Film properties were a function of crosslinking in the polymer^[29]. The most prominent methods for the covalent crosslinking are the incorporation of the polymerizable or photo/UV crosslinkable groups and the introduction of crosslinking reagents. One of the most widely employed crosslinkable side chains of polymers is the cinnamate group, which undergoes controlled UV-induced [2+2] cycloaddition reaction^[30]. The three-dimensional crosslinked network of the dielectric composition could achieve higher dielectric constant and better mechanical properties compared with the materials before crosslinking. For instance, the crosslinked nitrile-functionalized carbon nanotubes and poly(arylene ether nitriles) showed higher dielectric constant and lower dielectric loss^[31]. With this contribution, herein, the crosslinkable block copolymer was synthesized by ROMP, and the polymer thin film crosslinked by the UV-induced cycloaddition reaction exhibited the enhanced thermal and dielectric properties.

EXPERIMENTAL

Materials

Bis(tricyclohexylphosphine) benzyldiene ruthenium(IV) dichloride (first-generation Grubbs catalyst, **Ru-I**) was purchased from Aldrich and used as received. *endo*- or *exo*-*N*-3,5-Bis(trifluoromethyl)biphenyl-norbornene-pyrrolidine (*endo*-**TNP** or *exo*-**TNP**) and *exo*-*N*-(cinnamoyloxyethyl)-7-oxanorborn-5-ene-2,3-dicarboximide (*exo*-CONBI) were prepared according to the literatures^[18, 20, 23]. Solvents were distilled over drying agents under nitrogen before use: dichloromethane (CH₂Cl₂) and chloroform (CHCl₃) from calcium hydride.

Polymerization was carried out in a Schlenk tube under dry nitrogen atmosphere.

Characterization

¹H- (500 MHz) and ¹³C- (125 MHz) NMR spectra were recorded using tetramethylsilane as an internal standard in CDCl₃ on a Bruker DPX spectrometer. FTIR spectra were recorded on a Perkin Elmer spectrometer using KBr pellets. UV-Vis absorption spectra were measured on a UV-1800 spectrometer, and ultraviolet (UV) irradiation was carried out with a 500 W mercury lamp (made by Blue Sky Special Lamps Development Co., Ltd, Zhuozhou County, Hebei Province, China). Gel permeation chromatography (GPC) was used to calculate

relative molecular weight and molecular weight distribution equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (7.8 mm $\times$ 300 mm, 5 mm bead size; 10^3 , 10^4 , and 10^5 Å pore size). GPC measurements were carried out at 35 °C using THF as the eluent with a flow rate of 1.0 mL·min⁻¹. The system was calibrated with polystyrene standard. The solution of polymer for GPC was filtered through a 0.22 µm poly(vinylidene fluoride) Millipore filter. The hydrodynamic diameter of polymer nanostructure was determined by means of dynamic light scattering (DLS) analysis using a Malvern Zetasizer Nano-ZS light scattering apparatus (Malvern Instruments, U.K.) with a He-Ne laser (633 nm, 4 mW). The Nano ZS instrument incorporates noninvasive backscattering (NIBS) optics with a detection angle of 173°. Differential scanning calorimetry (DSC) was performed on a Netzsch 204F1 instrument in nitrogen atmosphere. An indium standard was used for temperature and enthalpy calibrations. All the samples were first heated from 25 °C to 300 °C and held at this temperature for 3 min to eliminate the thermal history, and then, they were cooled to room temperature and heated again from 25 °C to 300 °C at a heating or cooling rate of 10 K/min. Thermal gravimetric analysis (TGA) was performed using a SDTA851e/SF/1100 TGA instrument under nitrogen flow at a heating rate of 10 K/min from 30 °C to 800 °C. Dielectric measurements were carried out by a Novo control BDS40 dielectric spectrum analyzer over the frequency range of 100 Hz to 1 MHz at room temperature, and a contacting electrode method was used. The edge side (d) of the guarded electrode is 0.3 mm. The capacitance (C_p) and the dissipation factor (dielectric loss, loss tangent) of the tested films were recorded.

Sample Preparation for Dielectric Measurement

Polymer was dissolved in CHCl₃ to form a solution of 5 wt%, and then, the solution was stirred for 12 h at room temperature, followed by sonication for 10 min. After that, the solution was spin-coated on a pre-aluminized substrate at a spinning speed of 2000–3000 r/min for 30 s, and dried in air overnight, followed by continuous heat treatment in vacuum for another 12 h to evaporate all the solvents. The thickness of films was controlled by using different solution concentration and spinning speed, and tested by the Elcometer (Veeco Dektak 6M). The typical thickness of the polymer films was about 3 µm, and then, a thin layer (50 nm) of Pt particle was sputtered on the exposure sides of the sample.

UV-crosslinking of Polymer Film and Polymer Solution

The process for crosslinking of polymer film and solution is similar to the preparation for dielectric measurement. The polymer film and solution were subjected to UV irradiation for 2–10 min using a 500 W mercury lamp, which had characteristic emission wavelengths ranging from 350 nm to 450 nm. The obtained samples were investigated by means of UV-Vis spectroscopy.

Syntheses of Block Copolymers via ROMP

The block copolymers were prepared by ROMP with the sequential addition of monomers, and a typical procedure (copolymer 2) was as follows. In a nitrogen-filled Schlenk tube, a solution of **Ru-I** (3.3 mg, 0.004 mmol) in 0.5 mL of CH₂Cl₂, which was degassed with three freeze-vacuum-thaw cycles, was added to a degassed solution of *endo*-**TNP** (84.5 mg, 0.2 mmol) in 0.5 mL of CH₂Cl₂ to give a monomer concentration of 0.2 mol·L⁻¹. After stirring for 50 min at 30 °C, a degassed solution of *exo*-**CONBI** (67.8 mg, 0.2 mmol) in 1.5 mL of CH₂Cl₂ was then added under nitrogen. After stirring for 1 h, the polymerization was quenched by adding ethyl vinyl ether with stirring for further 30 min, and the solution was then poured into an excess of methanol. The polymer was redissolved in CH₂Cl₂, and precipitated once again from methanol. The precipitate was dried under vacuum for 24 h. The corresponding block copolymer poly(*endo*-*N*-3,5-bis(trifluoromethyl)-biphenyl-norbornene-pyrrolidine)-block-poly(*exo*-*N*-(cinnamoyloxyethyl)-7-oxanorborn-5-ene-2,3-dicarboximide) was referred to as *endo*-**PTNP-*b*-exo-PCONBI**. The molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) of *endo*-**PTNP-*b*-exo-PCONBI** were 78.1 kDa and 1.14, respectively. ¹H-NMR (CDCl₃, δ): 7.94–7.27 (m, ArH + PhCH=CH), 6.74–6.49 (m, ArH), 6.37–6.20 (m, PhCH=CH), 6.06–5.15 (m, CH=CH on polymer chain), 5.06–4.10 (m, CHOCH + CH₂OCO), 3.92–3.65 (m, NCH₂CH₂O), 3.34–3.00 (m, ArNCH₂ + CHCONCOCH), 2.97–2.42 (m, CHCHCH₂N + CHCHCH₂N), 1.80–1.15 (m, CHCH₂CH). ¹³C-NMR

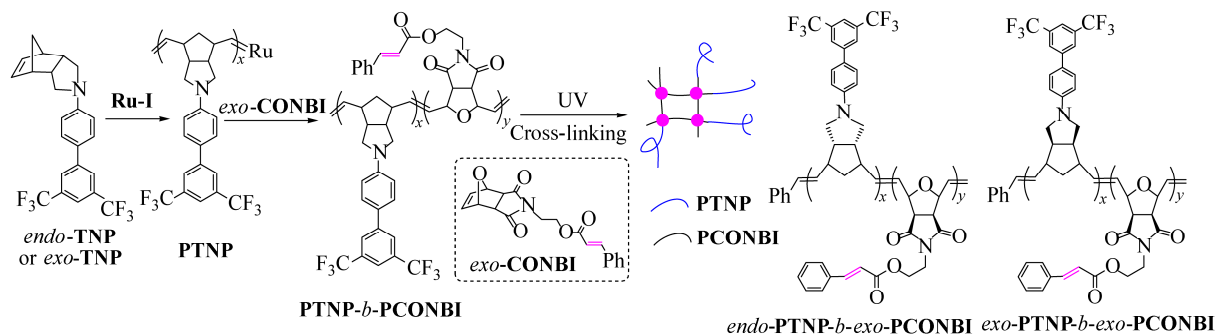
(CDCl₃, δ): 175.3 ($\underline{\text{CONCO}}$), 166.7 ($\underline{\text{OCOCH=CH}}$), 148.4 ($\underline{\text{NCCH}}$), 145.7 ($\underline{\text{CH=CHPh}}$), 143.0 ($\underline{\text{NAr-CCH}}$), 134.1 ($\underline{\text{CH=CH}}$ on polymer chain), 131.7–128.9 ($\underline{\text{HC=CHPh}}$), 128.3 ($\underline{\text{CF}_3\text{C}}$), 125.6 ($\underline{\text{NCCHCH}}$), 124.6 ($\underline{\text{NAr-CCH}}$), 122.5 ($\underline{\text{C-ArCF}_3}$), 119.2 ($\underline{\text{CHCCF}_3}$), 117.3 ($\underline{\text{HC=CHPh}}$), 113.3 ($\underline{\text{NCCH}}$), 126.7, 120.2, 115.8, 112.0 ($\underline{\text{ArCF}_3}$), 80.7 ($\underline{\text{CHOCH}}$), 58.0 ($\underline{\text{CH}_2\text{OCO}}$), 52.0 ($\underline{\text{CHCON}}$), 49.9 ($\underline{\text{CHCH}_2\text{N}}$), 46.6 ($\underline{\text{CHCHCH}_2\text{N}}$), 44.7 ($\underline{\text{CHCH}_2\text{N}}$), 38.4 ($\underline{\text{CHCH}_2\text{CH}}$), 18.1 ($\underline{\text{NCH}_2\text{CH}_2\text{O}}$).

The synthetic procedure of *exo*-PTNP-*b*-*exo*-PCONBI (copolymer 4) was the same as that of *endo*-PTNP-*b*-*exo*-PCONBI. The values of M_n and PDI were 81 kDa and 1.15, respectively. ¹H-NMR (CDCl₃, δ): 7.97–7.29 (m, $\underline{\text{ArH}}$ + $\underline{\text{PhCH=CH}}$), 6.84–6.58 (m, $\underline{\text{ArH}}$), 6.42–6.33 (m, $\underline{\text{PhCH=CH}}$), 6.05–5.30 (m, $\underline{\text{CH=CH}}$ on polymer chain), 5.12–4.90 (s, $\underline{\text{CHOCH}}$), 4.54–4.24 (m, $\underline{\text{CH}_2\text{OCO}}$), 3.90–3.72 (m, $\underline{\text{NCH}_2\text{CH}_2\text{O}}$), 3.50–3.16 (m, $\underline{\text{ArNCH}_2}$ + $\underline{\text{CHCONCOCH}}$), 2.81–2.38 (m, $\underline{\text{CHCHCH}_2\text{N}}$ + $\underline{\text{CHCHCH}_2\text{N}}$), 1.56–1.27 (m, $\underline{\text{CHCH}_2\text{CH}}$). ¹³C-NMR (CDCl₃, δ): 175.4 ($\underline{\text{CONCO}}$), 166.6 ($\underline{\text{OCOCH=CHAr}}$), 149.3 ($\underline{\text{NCCH}}$), 145.8 ($\underline{\text{CH=CHPh}}$), 143.2 ($\underline{\text{NAr-CCH}}$), 134.1 ($\underline{\text{CH=CH}}$ on polymer chain), 131.7–128.9 ($\underline{\text{HC=CHPh}}$), 128.3 ($\underline{\text{CF}_3\text{C}}$), 125.9 ($\underline{\text{NCCHCH}}$), 124.6 ($\underline{\text{NAr-CCH}}$), 122.4 ($\underline{\text{C-ArCF}_3}$), 119.3 ($\underline{\text{CHCCF}_3}$), 117.3 ($\underline{\text{HC=CHPh}}$), 114 ($\underline{\text{NCCH}}$), 126.7, 120.2, 115.8, 112.0 ($\underline{\text{ArCF}_3}$), 80.7 ($\underline{\text{CHOCH}}$), 60.7 ($\underline{\text{CH}_2\text{OCO}}$), 53.7 ($\underline{\text{CHCON}}$), 52.2 ($\underline{\text{CHCH}_2\text{N}}$), 50.3 ($\underline{\text{CHCHCH}_2\text{N}}$), 49.2 ($\underline{\text{CHCH}_2\text{N}}$), 38.4 ($\underline{\text{CHCH}_2\text{CH}}$), 18.4 ($\underline{\text{NCH}_2\text{CH}_2\text{O}}$).

RESULTS AND DISCUSSION

Preparation of Block Copolymers by Ring-opening Metathesis Polymerization

As shown in Scheme 1, the compounds *endo*-TNP, *exo*-TNP, and *exo*-CONBI were simply synthesized according to the previous procedures^[21, 22, 32], and were then used as monomers for ROMP with the sequential addition of *endo*-TNP or *exo*-TNP and *exo*-CONBI to generate the diblock copolymers *endo*-PTNP-*b*-*exo*-PCONBI and *exo*-PTNP-*b*-*exo*-PCONBI, respectively, by using **Ru-I** as catalyst. Ruthenium alkylidene complexes have been proven to be the effective catalysts for ROMP because of inherent stability toward many polar functional groups^[33].



Scheme 1 Synthesis of functional monomers and polymers

The polar monomer *endo*-TNP or *exo*-TNP was polymerized in CH₂Cl₂ to yield the first block *endo*-PTNP or *exo*-PTNP with high conversion of 95% or more at 30 °C for 50 min, which was used as the living macroinitiator to react with the second monomer *exo*-CONBI under nitrogen, resulting in the formation of *endo*-PTNP-*b*-*exo*-PCONBI (copolymers 1, 2, and 5) or *exo*-PTNP-*b*-*exo*-PCONBI (copolymer 4) with good yields (Table 1). It was evidenced by the earlier results^[21, 22] that the longer is the *endo*-PTNP block, the dielectric constant is likewise higher, thus it is necessary for functionality to broaden the length of PTNP block in copolymer. In the first case (copolymer 1), copolymerization of *endo*-TNP and *exo*-CONBI was performed at the feed molar ratio of 25:50 to afford the copolymer with relatively low M_n (26.6 kDa), which increased obviously as extending the feed molar fraction of *endo*-TNP to 50 (copolymer 2, M_n = 78.1 kDa). However, if the feed molar fraction of *endo*-TNP further increases to 75, the analysis for M_n suggested that the GPC curves showed two broadening peaks (Fig. 1), the one corresponded to the copolymer 5 with high M_n (127.9 kDa), and

the other belonged to the unreacted *endo*-PTNP block ($M_n = 43.3$ kDa). This result may be ascribed to the too long chain length of *endo*-PTNP block^[34], because the long chain of *endo*-PTNP will probably influence the activity of the living macrospecies and diffusion of monomers, which retarded the effective collision between the living *endo*-PTNP block end and *exo*-CONBI monomer, and therefore the long living macroinitiator *endo*-PTNP can not react well with the second monomer *exo*-CONBI to form the desired copolymer. The random copolymer *endo*-PTNP-*co*-*exo*-PCONBI (copolymer 3) was also synthesized under the similar condition as that of copolymer 2. When the monomer *exo*-TNP was copolymerized with *exo*-CONBI at the feed molar ratio of 50:50, copolymer 4 was obtained with a closed M_n value to that of copolymer 2.

Table 1. Characteristics of block copolymers by ring-opening metathesis polymerization^a

Copolymer	TNP:CONBI:Cat ^b	Yield ^c (%)	M_n ^d (kDa)	PDI ^d
1	25:50:1	99	26.6	1.15
2	50:50:1	98	78.1	1.14
3	50:50:1 ^e	99	78.9	1.06
4	50:50:1 ^f	98	81.0	1.15
5	75:50:1	97	43.3, 127.9	1.31, 1.44

^a Polymerization conditions: TNP = *endo*-TNP, temperature = 30 °C, solvent = CH₂Cl₂;

^b The feed molar ratios of the first monomer (TNP) to the second monomer (CONBI) and catalyst (Cat);

^c Measured by gravimetric method based on the total mass of monomers;

^d The number-average molecular weight (M_n) and polydispersity index (PDI) were determined by gel permeation chromatography (GPC) in THF relative to monodispersed polystyrene standards;

^e Random copolymer;

^f TNP = *exo*-TNP

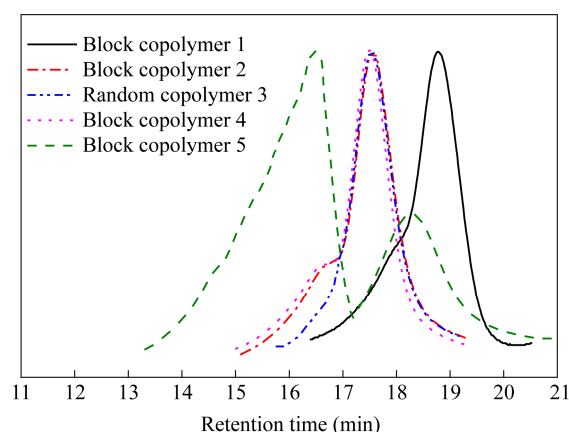


Fig. 1 GPC curves of copolymers

In addition, except for the major elution peak from the unimolecular copolymers, there is a shoulder peak at the higher molecular weight region in each GPC curve (Fig. 1), this might due to the aggregation of copolymers in THF. Because THF is a selective solvent for the copolymer PTNP-*b*-PCONBI, PTNP is soluble in common solvents, such as CH₂Cl₂, CHCl₃, toluene, and THF, whereas PCONBI is insoluble in THF or toluene^[32]. The solubility discrepancy between the PTNP and PCONBI blocks in PTNP-*b*-PCONBI block copolymer provides a possibility of micelles formation, so the block copolymers could self-assemble into micelles with the PCONBI blocks as the core and the PTNP blocks as the shell in THF or toluene, which was determined by DLS measurements as shown in Fig. 2. For the block copolymer 2, it could not self-assemble into micelles but dissolved completely in the good solvent of CHCl₃, existing as the single polymer chains with the average hydrodynamic diameter of 9 nm (Fig. 2a), while there are only aggregates in the selective solvent of toluene with the average diameters of 85 nm and 420 nm (Fig. 2b), and is no single polymer chain. It is worthy to note that the random copolymer 3 displayed only unimodal peak in GPC curve, which is consistent with the random

distribution of **CONBI** units and no **PCONBI** block formed in copolymer chains. The DLS results confirmed that the random copolymer 3 existed only as the single polymer chains with the average diameters of 22 nm in CHCl_3 (Fig. 2c) and 16 nm in toluene (Fig. 2d).

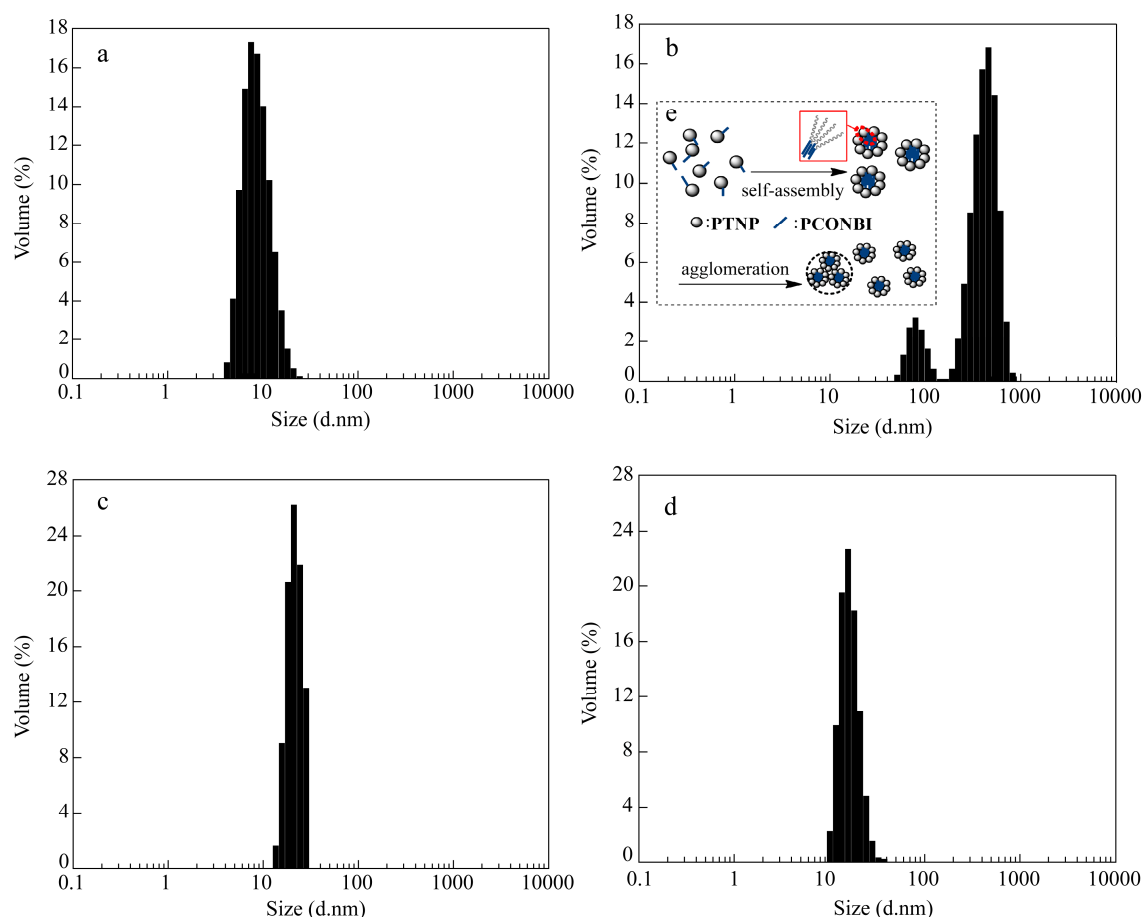


Fig. 2 Sizes of block copolymer 2 (a and b) and random copolymer 3 (c and d) at the concentration of 2 mg/mL in CHCl_3 (a and c) and in toluene (b and d) determined by means of DLS; (e) The schematic process of core-shell nanostructure from a single chain of block copolymer 2 in toluene

The ^1H -NMR spectra confirmed the formation of the block copolymer 2 and copolymer 4 as shown in Fig. 3. The resonance signals of alkene protons on the oxanorbornene and norbornene ring approximately at $\delta = 6.30$ completely disappeared after ring opening, whereas these signals of alkene protons on the backbone came at $\delta = 5.90$ – 5.40 , which pointed out polymerization was processed successfully. The block copolymer composition could be estimated by the ^1H -NMR analysis of the specific group^[34, 35]. The molar ratio of the repeating units in the block copolymer 2 or copolymer 4 was determined by means of the peak integration ratio of the phenyl proton ($-\text{NCCH}-$, H_f) at $\delta = 6.63$ in the *endo*-PTNP or *exo*-PTNP block to the methylene protons ($-\text{NCH}_2\text{CH}_2\text{O}-$, H_m) at $\delta = 3.80$ in the *exo*-PCONBI block, and thus the molar composition ratio of the repeating units in the *endo*-PTNP or *exo*-PTNP block to those in the *exo*-PCONBI block was found to be 1:1, which is close to the feed molar ratio of monomers.

Microstructure of Block Copolymers

The *trans/cis* ratio of as-synthesized copolymers can be analyzed by integration of the ^1H -NMR signals related to the protons of the $\text{C}=\text{C}$ double bond^[36, 37] on the backbone of *endo*-PTNP or *exo*-PTNP at $\delta = 5.43$ to 5.87 in

Fig. 3. Because the *trans* and *cis* signals of copolymer 2 were not well separated, then the exact ratio was hard to be determined. In the case of copolymer 4, the *exo*-PTNP block has a *trans/cis* ratio of 67:33. Additionally, IR spectroscopy was also used to characterize the *trans/cis* content of the copolymers using the characteristic bands for *trans*- at 965 cm^{-1} and for *cis*-vinylene at 720 cm^{-1} . The copolymers have strong absorption of *trans* double bond and weak absorption of *cis* double bond in Fig. 4, but the data are only qualitative.

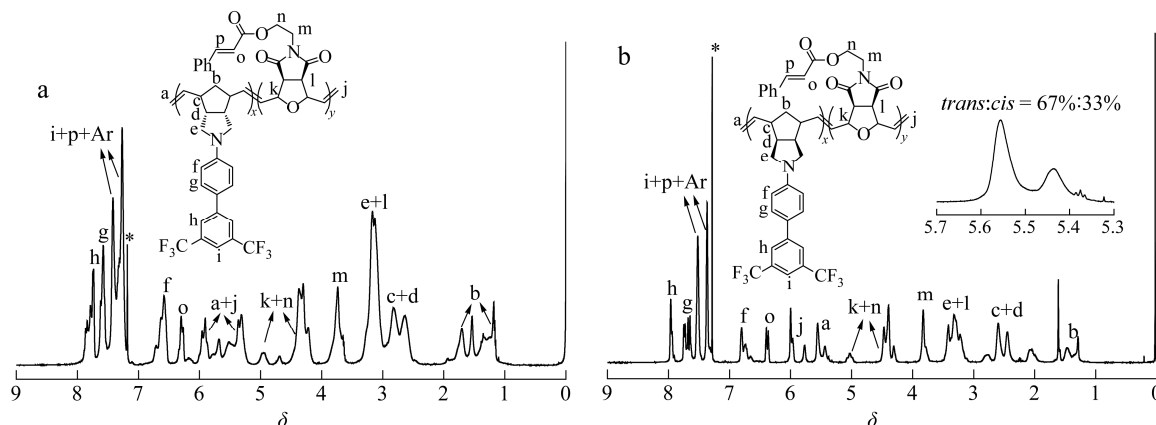


Fig. 3 ^1H -NMR spectra of (a) copolymer 2 and (b) copolymer 4

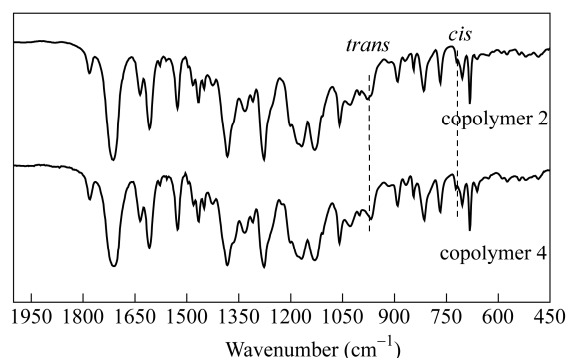


Fig. 4 IR spectra of copolymer 2 and copolymer 4

It is known that ^{13}C -NMR is the most powerful tool for the characterization of polymer microstructures, such as the *trans/cis* ratio of double bond and the tacticity of polymer. According to the previous assignment^[15, 38, 39], the *trans/cis* ratio of *endo*-PTNP or *exo*-PTNP can be analyzed by integration of the ^{13}C -NMR signals related to the vinyl group at $\delta = 131\text{--}133$, and the results showed that the most *trans endo*-PTNP was formed (Fig. 5a), but it was hard to get the *trans/cis* ratio of *exo*-PTNP from the ^{13}C -NMR spectrum (Fig. 5b), because of the multiple peaks. If the tacticity of substituted polymers is isotactic or syndiotactic, there are four possible microstructures containing two conformations *syn/anti*, which means the orientation of side groups attached to the polymer chain in both isotactic and syndiotactic styles. Therefore, the peaks of methylene carbon (C_b) would be clear as in one or two sets of signals. The resonance of methylene would be affected and splitted to corresponding peaks depending on the proportion of *trans/cis* ratio. As shown in the ^{13}C -NMR spectrum at $\delta = 34\text{--}38$, there are two sets of peaks for methylene carbon (C_b) in *endo*-PTNP. It seems that *endo*-PTNP adopts highly *trans* double bond and isotactic stereochemistry, whereas the C_b peaks of *exo*-PTNP showed the multiplet at $\delta = 38\text{--}40$, which means that *exo*-PTNP has a lower tacticity.

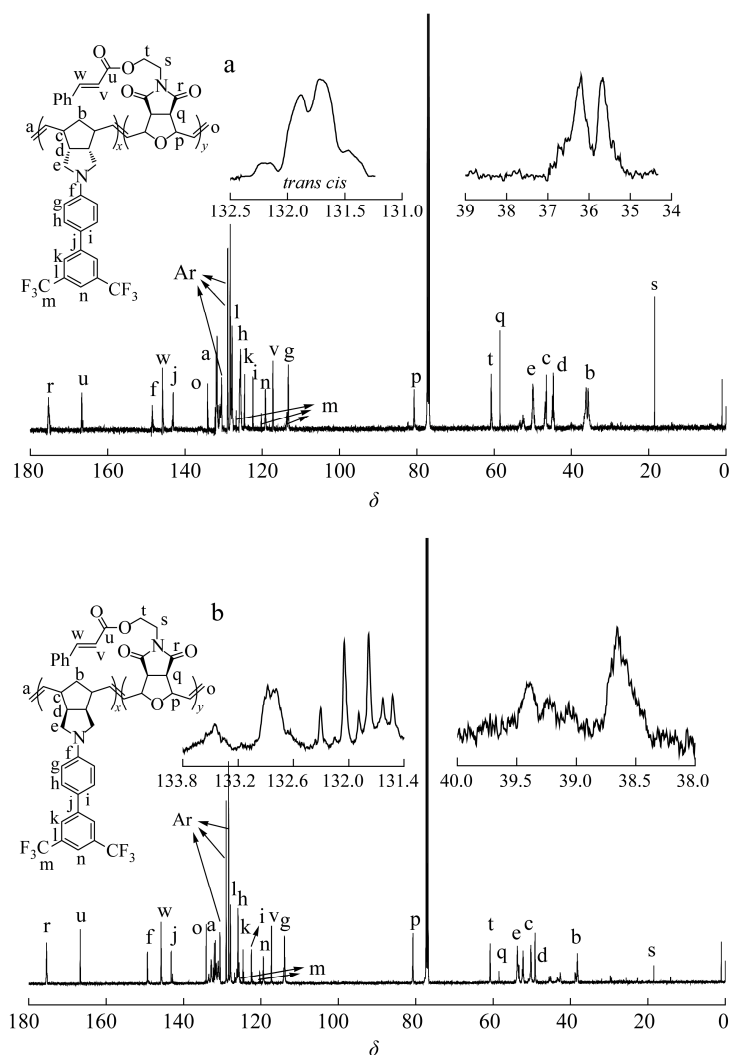


Fig. 5 ^{13}C -NMR spectra of (a) copolymer 2 and (b) copolymer 4

Crosslinking Behavior of Copolymer by UV Irradiation

In our previous work, a straightforward approach to form permanent nanoparticles was provided without the additional crosslinking reagents or initiators, which was crosslinked by the UV-induced cycloaddition reaction of cinnamate groups^[32]. For copolymer, the *exo*-PCONBI block bearing cinnamyl group was crosslinked by UV irradiation for 2, 4, 6, 8, and 10 min, and the results are summarized in Table 2. The reaction progress was monitored by UV-Vis spectroscopy. The UV-Vis spectra of copolymer 2 in film were recorded before and after irradiation, respectively. As seen in Fig. 6, the absorbance at $\lambda_{\text{max}} = 289$ nm significantly weakened after irradiation, which showed that the crosslinking reaction had occurred. According to the UV-Vis spectra, a conversion of 15% for the cinnamyl double bond was estimated from the absorbance decrease after 2 min irradiation, while after 10 min irradiation the conversion was found to be 36%, and the absorbance could not decline anymore by the extension of the irradiation time further.

To determine whether the conversion of cinnamyl double bonds was limited in polymer film or not, the copolymer is dissolved in solvents, such as CHCl_3 and toluene, and crosslinked by UV irradiation. A conversion of 12% was obtained after 2 min in CHCl_3 , and then increased to 31% after 6 min. The conversions were similar to those in film at the same irradiation time. After irradiation for 8 min, the solution became gel, and no solvent

was left. As described in the previous part, the polymer film was produced by dissolving the block copolymer in CHCl_3 , and the solvent is the same as the solution here. It can be concluded that the conversion of the double bond of cinnamyl group has not obviously increased in solution compared with that in film.

Table 2. Crosslinking conversion of cinnamyl groups of block polymer 2 in film and in solution by UV irradiation

Time (min)	Conversion in film (%)	Conversion in chloroform (%)	Conversion in toluene (%)
2	15	12	23
4	23	30	45
6	29	31	57
8	33	gel	61
10	36	gel	62

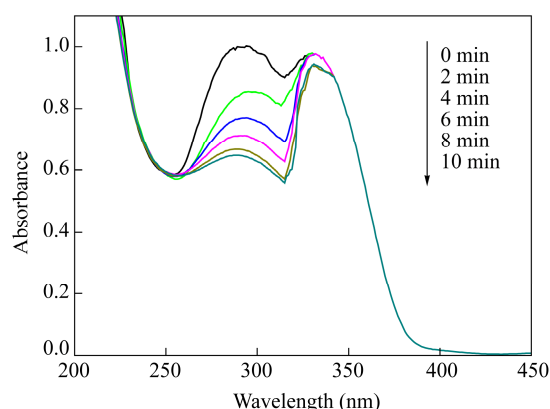


Fig. 6 UV-Vis absorption spectra of copolymer 2 in polymer film before and after irradiation

Toluene is the selective solvent, in which the block copolymers may self-assemble into micelles consisting of *exo*-**PCONBI** blocks as the core and *endo*-**PTNP** blocks as the shell as depicted in Fig. 2(e), and the conversion of cinnamyl groups in the *exo*-**PCONBI** core could be achieved to 23% in 2 min. As time went on 10 min, it increased to 62%, which was almost doubled the values in film and in CHCl_3 with the same irradiation time. The results demonstrated that the micellar structure was propitious to improve the conversion of the crosslinkable group due to the high concentration of the aggregated **PCONBI** blocks in the core of micelle.

Dielectric Performance of Copolymers

As described in our previous work^[21, 22], the dielectric response is determined by not only the polar group, but also the chain microstructure and chain length of polymers. The stronger is the polarity of side chain in polymer and the longer is the functional chain, the greater is the degree of polarization, and the higher is the dielectric constant. The dielectric spectroscopy of the polymer thin films with the thickness of about 3 μm is shown in Fig. 7. The observed value of dielectric response for copolymer 2 displayed an attractive dielectric constant of about 15.5 at frequencies of 100 Hz to 1 MHz at room temperature, while the dielectric constant of copolymer 1 decreased to 13.5 as the polar *endo*-**PTNP** block became shorter, and these values were significantly higher than those of copolymer 3 (about 11.5) and copolymer 4 (about 7.1). Generally, if the polar side group was attached to the polymer backbone regularly, the dipole moment would increase. Therefore, copolymer 2 with high *trans* and isotactic microstructures has a much higher dielectric constant than those of random copolymer 3 and atactic copolymer 4, which contained both *trans* and *cis* isomers and the microstructure with a poor tacticity. That is to say, the polar groups on the polymer chain are arranged irregularly, and the dipole moment is cancelled out, therefore, the dielectric constant of these polymers decreased.

The dielectric properties of polymers could be tuned by the crosslinking treatment because the crosslinking can decrease the free volume of polymers and increase the polarization by increasing the number of polarizable groups per unit volume, and thus lead to a higher dielectric constant^[7]. The effect of irradiation time varying

from 2 min to 6 min on the dielectric constant of the copolymer films was evaluated. After being irradiated for 2 min, the dielectric constant of the film increased to 16.2, which is higher than that of the unirradiated one (the original dielectric constant = 15.5). The dielectric constant could reach up to 16.5 after 4 min irradiation, and the value would stay stable (dielectric constant = 16.6) as the irradiation time went on 6 min, which is almost the same as that of the crosslinked polymer for 4 min irradiation. It means the dielectric constant has nearly no further increase even though extending the irradiation time. These results indicated that the formation of ring structure improved the polarizability through crosslinking reaction^[31, 40], which is a useful method to improve the dielectric properties of polymer film in some extent.

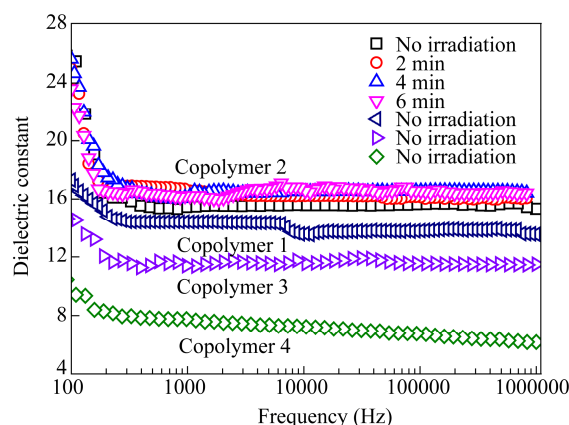


Fig. 7 Dielectric constant of copolymers with different irradiation time versus frequency from 100 Hz to 1 MHz

Figure 8 shows the dielectric loss of polymer films. The polymers exhibited a small dielectric loss in the range of 0.02 to 0.05 at the frequencies of 100 Hz to 0.1 MHz. The dielectric loss of copolymer 1 and copolymer 2 is about 0.03 at the frequency of less than 0.1 MHz; however, it increases sharply toward 0.07 near the frequency of 1 MHz. It has a stable dielectric loss ranging from 0.03 to 0.055 for copolymer 3, and from 0.025 to 0.045 for copolymer 4 without an obvious fluctuation in all the frequency range. A low dielectric loss is necessary for high performance capacitors, because it may result in higher efficiency and lower noise. In general, copolymer 2 with high dielectric constant and relative low dielectric loss is a suitable candidate for thin film capacitors.

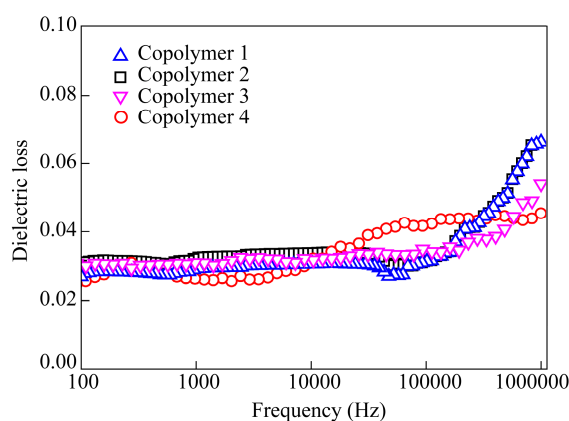


Fig. 8 Dielectric loss of copolymers versus frequency from 100 Hz to 1 MHz

Thermal Properties of Copolymers

Thermal properties of copolymers under different irradiation time were systematically investigated by TGA and DSC measurements. The DSC technique is invited to obtain the glass transition temperature (T_g) of copolymers, and in order to erase any previous thermal history, two steps were performed. First, the polymer was heated to 300 °C and then cooled to 25 °C at a rate of 10 K/min. Second, it was heated once again to 300 °C and cooled to 25 °C with the same heating and cooling rate, and the values were obtained from the second heating cycle. From the DSC curves in Fig. 9(a), the values of T_g of copolymer 2 for 0, 2, 4, and 6 min irradiation were 115, 130, 133, and 137 °C, respectively. Any structural features that reduce free volume or segmental motion will increase T_g . The crosslinking behavior of cinnamyl double bonds in side chains restricted segmental motion by forming three-dimensional network and thus enhanced T_g . Compared with the unirradiated polymer film, the T_g of the film irradiated for 6 min showed a significant improvement (increased by about 22 K).

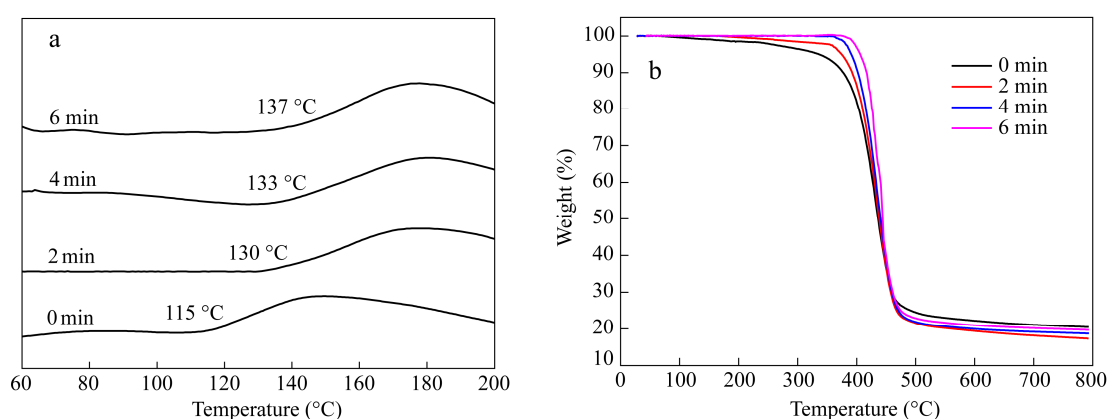


Fig. 9 DSC (a) and TGA (b) curves of copolymer 2 with different irradiation time

Besides, the decomposition temperatures (T_d) for 5% weight loss of the films were 335, 375, 390 and 405 °C after UV-irradiation for 0, 2, 4, and 6 min (Fig. 9b), respectively, which revealed an increase of T_d about 70 K compared with that of the unirradiated film, and the results indicated that the crosslinking structure is benefit to promote the thermal stability of copolymer.

CONCLUSIONS

Novel dielectric block copolymers *endo*-PTNP-*b*-*exo*-PCONBI and *exo*-PTNP-*b*-*exo*-PCONBI were synthesized by Grubbs catalyst-initiated ROMP under the mild reaction conditions, the block *endo*-PTNP or *exo*-PTNP worked as the high dielectric functional chain, and *exo*-PCONBI was used for crosslinking. The microstructure of polymer chain was characterized by NMR and IR spectroscopy. The block copolymer *exo*-PTNP-*b*-*exo*-PCONBI, which contains both *trans* and *cis* double bonds and lacked tacticity, has a lower dielectric constant ($\epsilon = 7.1$) compared with that of highly *trans* and isotactic *endo*-PTNP-*b*-*exo*-PCONBI ($\epsilon = 15.5$). Therefore, the conformation of monomer has a significant impact on the microstructure and dielectric properties of polymers. According to the UV-Vis, TGA, and DSC analysis, the copolymer was successfully crosslinked by UV-irradiation. After crosslinking, the dielectric constant of polymer film increased to 16.6, and dielectric loss almost kept about 0.03. The value of T_g or T_d of the polymer film processed for 6 min irradiation was higher than that of film before the treatment. Therefore, in view of the outstanding dielectric performance and high thermal stability of *endo*-PTNP-*b*-*exo*-PCONBI film, it is considered to be a good potential high dielectric material in a wide range of applications.

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