High Dielectric Performance of Tactic Polynorbornene Derivatives Synthesized by Ring-Opening Metathesis Polymerization

Zewang You, Danyi Gao, Ouyue Jin, Xiaohua He, Meiran Xie

Department of Chemistry, East China Normal University, Shanghai 200241, China Correspondence to: M. Xie (E-mail: mrxie@chem.ecnu.edu.cn)

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ABSTRACT: Functional polynorbornenes (PNBEs) containing pyrrolidine moiety and bis(trifluoromethyl)biphenyl side group were synthesized via ring-opening metathesis polymerization (ROMP), and the microstructure of polymer chain was characterized by NMR spectroscopy. Poly(*N*-3,5-bis(trifluoromethyl)biphenyl-norbornene-pyrrolidine) (PTNP) and poly(*N*-phenyl-norbornene-pyrrolidine) (PTNP) are supposed to have practically *trans* double bonds and adopt isotactic *syn* conformation, whereas poly(*N*-3,5-bis(trifluoromethyl)biphenyl-norbornene-dicarboximide) (PTNDI) has both *trans* and *cis* double bonds and atactic microstructure. PTNP, PTNDI, and PPNP have much different dielectric constants of 20, 7, and 3, respectively, which

INTRODUCTION High dielectric constant materials have been more focused lately on novel polymers because of their possible application in high density film capacitors where requiring the small volume and large energy storage density, which has long been a scientifically challenging and industrially important area.¹ Ceramics, such as silicon oxide, silicon nitride, and barium titanate, are typical high dielectric constant materials, but the dielectric loss is large and the processing of materials is very expensive and complicated. Thin film capacitors based on polymers, including polyethylene terephthalate, polypropylene, polyester, and polycarbonate,² have attracted a great deal of attention for energy storage applications due to their desirable properties, such as lightweight, low cost, and safety.³ However, these polymer film capacitors generally suffer from either low energy density^{2,4} because of a low dielectric constant (2-3) or unacceptably large energy loss⁵ that reduces storage capacity and causes big problems in capacitor stability. One popular strategy⁶ to solve these problems is to introduce ceramic fillers into polymer and try to combine the advantages of both components. For instance, polyvinylidene fluoride-based composite was usually selected as the dielectric materials because of their good dielectric properties with a relatively high dielectric constant (\sim 8), whereas the dielectric loss is high due to the interface polarization^{2,7-10} and the dielectric dispersion is

is attributed to both the polar 3,5-bis(trifluoromethyl)biphenyl group and the stereoregular chain structure. The existence of rigid pyrrolidine moiety has a positive contribution to form the tactic polymer chain during ROMP. Polymers are highly thermal stable up to ~300 °C. Having good dielectric properties and thermal stability, these functional PNBEs are expected as the potential dielectric material in thin film capacitors. © 2012 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 1292–1301

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large, which may bring problem for high frequency. In general, thin film capacitors require a good film-forming and high dielectric constant company with small dielectric loss and dielectric dispersion, so using all-organic material for high dielectric applications is reasonable.

Dielectric constant of polymer depends on the degree of polarization itself. The stronger is the polarity of molecules, the greater is the degree of polarization, and the dielectric constant is likewise higher. Polymer has a higher dielectric constant when the polar groups in the side position than that in the main chain, and also the polar molecules with asymmetric molecular structure have a higher dielectric constant than that of symmetric ones. Thus, to get high dielectric polymer, it is suitable by introducing functional groups with a large dipole moment into polymer as the side groups. Of such functional groups are cyano, nitro, halogen, perfluoroalkyl, and so forth. Kobayashi¹¹ reported that incorporation of cyano into polyvinyl alcohol or copolymerization of vinyl alcohol with acrylonitrile could improve the dielectric constant and also the dielectric constant increased with the percentage of acrylonitrile. Yuan et al.² compared the dielectric constant of isotactic polypropylene to the copolymers of propylene and hydroxylated propylene and found that the dielectric constant of copolymers was elevated from 2 to 5. Obviously, those are not effective ways to enhance the

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dielectric constant of polymers up to a desired high level. Furthermore, the dielectric constant of polymers is related to the microstructure of polymer chain, which is dependent on the stereochemical configuration and arrangement of the monomer units into the polymer chain when polymerization especially ring-opening metathesis polymerization (ROMP) happened. Polynorbornenes (PNBEs) are usually known as low-dielectric materials¹²⁻¹⁵ owed to their symmetric structure, and they have been used in the microelectronics industry.¹⁶ However, if the side groups in particular the polar groups were introduced to PNBE, the dielectric constant of polymer will greatly increase. Schrock and coworkers reported that tactic polymers prepared by Mo carbene-catalyzed ROMP of 2,3-bis(trifluoromethyl)norbornadiene exhibit a much higher dielectric constant than the corresponding atactic polymers prepared by using the catalytic system of WCl₆/SnMe₄.¹⁷ High *trans*-tactic polymer has a higher dielectric constant than that of half trans-polymer and high cispolymer, basically due to the dipolement cumulation of polar trifluoromethyl (CF₃) group on the tactic polymer chain.¹⁸

It is a more convenient way to get high dielectric materials by designing a monomer with large dipole groups, and then aggregated to produce a tactic polymer. As we all known, there are two approaches to obtain a tactic polymer in ROMP. One is that by using the catalyst with different ligands to control the polymerization progress, and high trans/cis whatever isotactic or syndiotactic microstructure¹⁹⁻²⁴ is well defined; the other one is to design a monomer tending to polymerization regularly. A monomer carried with more rigid structure, such as pyrrolidine moiety, is more likely to produce a tactic polymer during the ROMP process. Luh and coworkers^{25–30} has paid more attention to polymerizing a rigid norbornene monomer catalyzed by Grubbs catalyst to get tactic polymer. In addition, the interaction, like π - π stacking interaction,³¹⁻³⁶ between the side groups of polymer is a strong driving force to make the neighbor repeat units arranged in the same direction.

It is rarely seen to increase the dielectric constant upon an introduction of strong polar conjugated aromatic structure to the chain of PNBE by now. In this article, we prepared functional PNBEs containing the large aromatic group with polar CF_3 group and rigid pyrrolidine moiety via ROMP and investigated their unique dielectric and thermal properties.

EXPERIMENTAL

Materials

Norbornene-5,6-*endo*-dicarboxylic anhydride (NDA), lithium aluminum hydride (LiAlH₄), bis(tricyclohexylphosphine) benzylidene ruthenium (IV) dichloride (**Ru-I**), tricyclohexylphosphine [1,3-bis (2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2ylidene] benzylidene ruthenium dichloride (**Ru-II**), 4-amino-3',5'-bis(trifluoromethyl)biphenyl, and aniline were purchased from Aldrich or Alfa Aesar and used as received. 4-Dimethylaminopyridine (DMAP), ethyl acetate (EtOAc), anhydrous sodium acetate, acetic anhydride, and magnesium sulfate (MgSO₄) were purchased from Shanghai Chemical Reagents Co, and used as received without purification. Solvents were distilled over drying agents under nitrogen before use: dichloromethane (CH₂Cl₂), trichloromethane (CHCl₃), and 1,2-dichloroethane (DCE) from calcium hydride; diethyl ether (Et₂O) and tetrahydrofuran (THF) from sodium/benzophenone.

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

Characterization

¹H (500 MHz), ¹³C (125 MHz), and ¹⁹F (500 MHz) NMR spectra were recorded using tetramethylsilane as an internal standard in CDCl₃ on a Bruker DPX spectrometer. Melting Point was determined by Micro melting point apparatus (Yanoco). GC/MS measurements were performed with a Varian Saturn 2100 GC/MS system with GC-3900 using a VF-5 MS, 30 m imes 0.25 mm imes 0.25 μ m diffused silica capillary column. FTIR spectra were recorded on a Nicolet Nexus 670 in the region of 4000 to 400 cm^{-1} using KBr pellets. 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 \times 300 mm, 5 mm bead size; 10³, 10⁴, and 10⁵ Å pore size). GPC measurements were carried out at 35 $^\circ$ C using THF as the eluent with a flow rate of 1.0 mL min⁻¹. The system was calibrated with polystyrene standard. Differential scanning calorimeter (DSC) was performed on a Netzsch 204F1 in nitrogen atmosphere. An indium standard was used for temperature and enthalpy calibrations. All the samples were first heated from 25 to 300 $^\circ\text{C}$ 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 to 300 °C at a heating or cooling rate of 10 °C/min. Thermal gravimetric analysis (TGA) was performed using a SDTA851e/SF/1100 TGA Instrument under nitrogen flow at a heating rate of 10 $^\circ$ C min⁻¹ from 30 to 800 $^\circ$ C. Dielectric measurements were carried out by a Novocontrol 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, or tan δ) of the tested films were recorded. The dielectric constant ε can be calculated by eq 1:

$$\varepsilon_{\rm r} = C_{\rm p} t / \varepsilon_0 A \tag{1}$$

where *t* is the thickness of the film and ε_0 , the permittivity of the free space, is 8.85×10^{-12} F/m, *A* is the guarded electrode area, $A = d^2$. Preparation of film samples: polymer was dissolved in CHCl₃ to a solution of 8–15 wt %, and then, the solution was stirred for 12 h at room temperature, followed by the sonication for extra 10 min. After that, the solution was spin-coated on a pre-aluminumed substrate at spinning speed of 1200–2500 rpm 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 3–10 μ m, and then, a thin layer (500 Å) of Pt particle was sputtered on the exposure sides of the sample.

Preparation of Monomers N-3,5-bis(trifluoromethyl)biphenyl-norbornene-

dicarboximide (TNDI)

A solution of 4-amino-3',5'-bis(trifluoromethyl)biphenyl (4.88 g, 16 mmol) in 80 mL of DCE was added dropwise to the stirred solution of NDA (3.15 g, 19.2 mmol) in 80 mL of DCE for 1 h in an ice bath, DMAP (0.195 g, 1.6 mmol) was then added at room temperature, and the mixture was further refluxed for 20 h. The solution was washed by dilute hydrochloric acid (5 \times 30 mL), followed by water, and dried with anhydrous MgSO₄. After filtration and removing the solvent, a white needle crystal was obtained by recrystallization twice from ethanol (6.13 g, 85% yield).

mp 153 °C; ¹H NMR (500 MHz, CDCl_3 , δ): 7.97 (s, 2H, o-ArH-CF₃), 7.87 (s, 1H, p-ArH-CF₃), 7.65-7.64 (d, J = 8.35 Hz, 2H, m-ArH-NC=0), 7.32-7.30 (d, 2H, o-ArH-NC=0), 6.29 (s, 2H, CHCH=CHCH), 3.53 (s, 2H, CHC=0), 3.47 (s, 2H, CHCHC=0), 1.82-1.80 and 1.65-1.63 (d, I = 8.75 Hz, 2H, CHCH₂CH); ¹³C NMR (125 MHz, CDCl₃, δ): 176.6 (ArNC=0), 142.4 (NCCH), 138.4 (NAr-CCH), 134.7 (CHCH=CHCH), 132.5 (C-ArCF₃), 132.1 (CF₃C), 127.9 (NCCHCH), 127.3 (NAr-CCH), 124.3 (CHCCF₃), 122.2 (NCCH), 121.3 (ArCF₃), 52.3 (CHCH₂CH), 45.9 (CHC=0), 45.6 (CHCHC=O); ¹⁹F NMR (500 MHz, CDCl₃, δ): -62.85 (CF₃); ESI/MS: Calcd. for C23H15F6NO2: 451.3, Found: 451.1; IR (KBr): *v* = 2987, 2929, 2861, 1773, 1709, 1649, 1518, 1460, 1381, 1272, 1177, 1126, 1101, 1054 cm⁻¹.

N-3,5-bis(trifluoromethyl)biphenyl-norbornenepyrrolidine (TNP)

To a slurry of $LiAlH_4$ (1.22 g, 32 mmol) in Et_2O (40 mL), TNDI (3.6 g, 8 mmol) in CH₂Cl₂ (40 mL) was added slowly under nitrogen atmosphere at 0 °C, and the mixture was stirred at room temperature for 6 h. EtOAc (5 mL) was added, and then water (2 mL) was carefully introduced. The resulting suspension was filtered, and the residue was washed with CH₂Cl₂ repeatedly. The organic phase was dried with MgSO₄ and the solvent was removed in vacuo to give the crude product as a yellow color solid. After recrystallization from ethanol for three times, the product was obtained in a white flake (2.4 g, 72% yield).

mp 110 °C; ¹H NMR (500 MHz, CDCl₃, δ): 7.93 (s, 2H, o-ArH-CF₃), 7.70 (s, 1H, p-ArH-CF₃), 7.48-7.47 (d, J = 8.65 Hz, 2H, m—ArH—NCH₂), 6.55–6.53 (d, I = 8.6 Hz, 2H, o-ArH-NCH₂), 6.19 (s, 2H, CHCH=CHCH), 3.32-3.28 (m, J = 17.9, 3.8 Hz, 4H, ArNCH₂), 3.12-2.96 (m, 4H, CHCHCH₂N + CHCH₂N), 1.64–1.63 and 1.55–1.53 (d, J = 8.6 Hz, 2H, CHCH₂CH); ¹³C NMR (125 MHz, CDCl₃, δ): 147.8 (NCCH), 143.4 (NAr-CCH), 135.8 (CHCH=CHCH), 131.9 (CF₃C), 127.8 (NCCHCH), 125.7 (NAr-CCH), 124.7 (C-ArCF₃), 122.5 (CHCCF₃), 118.9 (ArCF₃), 112.4 (NCCH), 52.1 (CHCH₂N), 50.6 (CHCH₂CH), 46.6 (CHCHCH₂N), 45.5 (CHCH₂N); ¹⁹F NMR (500 MHz, CDCl₃, δ): -62.84 (CF₃); GC: single peak observed at the retention time of 7.9 min; EIMS: Calcd. for $C_{23}H_{19}F_6N$: 423.4, Found: 423.5; IR (KBr): v = 2969, 2883, 2836, 1602, 1532, 1459, 1374, 1271, 1198, 1167, 1107, and 1061 cm⁻¹.

General Ring-Opening Metathesis Polymerization Procedures

Typically, polymerization was carried out in a Schlenk tube under dry nitrogen atmosphere for a preset time. After terminating polymerization by addition of a small amount of ethyl vinyl ether and stirring for 1 h, the solution was poured into an excess of methanol. Polymer was dissolved in CHCl₃ or THF, and precipitated once again from methanol. The obtained polymer was dried in a vacuum oven at 40 °C to a constant weight.

Polymerization of TNDI

Monomer TNDI (0.676 g, 1.5 mmol) and Ru-II (12.3 mg, 0.015 mmol) were stirred in 7.5 mL of CHCl₃ at 50 °C for 1 h. The number-average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) of poly(N-3,5-bis(trifluoromethyl)biphenyl-norbornene-dicarboximide) (PTNDI) were 32,200 and 1.3, respectively.

 $^{1}\mathrm{H}$ NMR (500 MHz, CDCl_3, δ): 7.96–7.87 (s, $o\text{--}\mathrm{Ar}H\text{--}\mathrm{CF}_3$ + *p*-Ar*H*-CF₃), 7.68-7.54 (d, *m*-Ar*H*-NC=0), 7.39 (d, o—ArH—NC=O), 5.89–5.69 (s, CH=CH on polymer chain), 3.41-3.06 (s, CHC=0 + CHCHC=0), 1.84 and 1.53 (d, CHCH₂CH); ¹³C NMR (125 MHz, CDCl₃, δ): 175.4 (ArNC=0), 142.1 (NCCH), 138.0 (NAr-CCH), 134.8 (C-ArCF₃), 132.7-132.2 (*C*H=*C*H on polymer chain), 129.5 (*C*F₃*C*), 127.5 (NCCHCH), 127.0 (NAr-CCH), 124.6 (NCCH), 121.2 (CHCCF₃), 119.0 (ArCF₃), 49.0 (CHC=0), 45.3 (CHCHC=0), 40.65 (CHCH₂CH).

Polymerization of TNP

Monomer TNP (0.634 g, 1.5 mmol) and Ru-I (12.3 mg, 0.015 mmol) were stirred in 7.5 mL of CH_2Cl_2 at 30 °C for 1 h. The values of M_n and PDI of poly(N-3,5-bis(trifluoromethyl)biphenyl-norbornene-pyrrolidine) (PTNP) were 27,200 and 1.21, respectively.

¹H NMR (500 MHz, CDCl₃, δ): 7.92 (m, *o*—Ar*H*—CF₃), 7.88 (m, *p*—Ar*H*—CF₃), 7.43 (m, *m*—Ar*H*—NCH₂), 6.74–6.67 (m, o-ArH-NCH₂), 5.46 (d, CH=CH on polymer chain), 3.27-3.23 (m, ArNCH₂), 2.92–2.72 (m, CHCHCH₂N + CHCH₂N), 1.80 and 1.45 (d, CHCH₂CH); ¹³C NMR (125 MHz, CDCl₃, δ): 157.2 (NCCH), 148.5 (NAr-CCH), 135.5 (CH=CH on polymer chain), 127.8 (CF₃C), 125.6 (NCCHCH), 124.6 (NAr-CCH), 122.7 (C-ArCF₃), 119.5 (CHCCF₃), 126.7, 120.2, 115.8, 112.0 (ArCF₃), 113.8 (NCCH), 49.9 (CHCH₂N), 47.5-46.5 (CHCHCH₂N), 45.0-44.7 (CHCH₂N), and 37.5-35.7 (CHCH₂CH).

RESULTS AND DISCUSSION

Synthesis of Functional Monomers

Synthesis of norbornene-based monomers TNDI and TNP was carried out by using the commercial chemicals in a simple procedure as shown in Scheme 1.

TNDI was prepared readily by the reaction of NDA with 4-amino-3',5'-bis(trifluoromethyl)biphenyl in the presence of catalyst DMAP in DCE at refluxed temperature, and the



SCHEME 1 Synthesis of functional monomers and polymers.

reaction was monitored by thin layer chromatography analysis. The crude product was purified by recrystallization from ethanol to give a white needle crystal. TNDI was characterized by MS and NMR spectroscopy. ¹H NMR spectrum [Fig. 1(A)] indicates that the presence of methylene group (proton b) at 1.80-1.65 ppm and double bond (proton a) at 6.29 ppm on the norbornene ring, and the phenyl groups (protons e, f, g, and h) at 7.30-7.87 ppm. The molecular weight of TNDI from MS analysis was in good accordance with the calculated value, and the product has a high purity estimated from the single peak of GC chromatogram. Also, the ¹⁹F NMR spectrum of TNDI (Supporting Information Fig. S1A) shows the resonance signal of CF_3 group at -62.85 ppm. All of these points assured that 3,5-bis(trifluoromethyl)biphenyl group has been successfully connected to the norbornene ring.

TNP was obtained by reduction of TNDI with LiAlH₄, and the reaction was monitored by thin layer chromatography analysis. ¹H NMR spectrum [Fig. 1(C)] showed the new resonance signals appeared at 3.32–3.28 ppm from two groups of methylene (proton i) adjacent to the norbornene ring, meant carbonyl group was completely reduced to methylene. GC/ MS also indicated that the product has a high purity and the exact molecular weight. Additionally, IR spectrum showed the disappearance of typical, characteristic C=0 stretch band of TNDI at 1773 and 1709 cm⁻¹, confirming the transformation of carbonyl into methylene successfully. The ¹⁹F NMR spectrum of TNP (Supporting Information Fig. S1B) showed the resonance signal of CF₃ group at -62.84 ppm, which further confirmed the successful preparation of TNP.

PNDI was synthesized by two steps (Supporting Information Scheme S1) in a similar procedure of literature.³⁷ The ¹H NMR spectrum of PNDI (Supporting Information Fig. S2A) showed the resonance signals of methylene (proton b) at 1.60–1.50 ppm, and double bond (proton a) at 6.14 ppm on the norbornene ring. Moreover, the resonance signals of phenyl (protons e, f, and g) at 7.22, 6.63, and 6.45 ppm can be clearly observed, which correspond to the chemical structure of PNDI. GC/MS also indicated that the product has a high purity and the exact molecular weight.

PNP was obtained from PNDI by the same procedure as that of TNP. The ¹H NMR spectrum of PNP (Supporting Information Fig. S2B) indicates the new resonance signals of



FIGURE 1 ¹H NMR spectra of (A) TNDI, (B) PTNDI, (C) TNP, and (D) PTNP.

 $\label{eq:constraint} \begin{array}{l} \textbf{TABLE 1} \ \text{Ring-Opening Metathesis Polymerization of} \\ \text{Monomers}^a \end{array}$

Monomer ^a	Cat.	Sol.	<i>T</i> (°C)	<i>t</i> (h)	Yield (%)	М _n ь (kDa)	PDI
TNDI	Ru-l	CH_2CI_2	30	1	-	-	-
TNDI	Ru-I	CHCl ₃	50	6	36	10.9	1.22
TNDI	Ru-II	CHCl ₃	50	1	80	32.2	1.30
TNDI	Ru-II	$CHCI_3$	50	2	90	37.7	1.51
TNP	Ru-I	CH_2CI_2	30	1	81	27.2	1.21
TNP	Ru-l	CHCl₃	50	1	93	35.1	1.48
PNP	Ru-I	CH_2CI_2	30	1	85	17.0	1.35
PNP	Ru-l	CHCI ₃	50	1	95	-	-
PNP ^c	Ru-I	CHCI ₃	50	1	95	7.83	1.29
	Monomer ^a TNDI TNDI TNDI TNDI TNP TNP PNP PNP PNP°	Monomer Cat. TNDI Cat. TNDI Cat. TNDI Cat. TNDI Cat. TNDI Cat. TNDI Cat. TNPI Cat. TNPI Cat. TNPI Cat. TNPI Cat. TNPI Cat. TNPI Cat. Cat. Cat. Cat. Cat. Cat. Cat. Cat.	MonomerCat.Sol.TNDIRu-ICH2Cl2TNDIRu-ICHCl3TNDIRu-ICHCl3TNDIRu-ICHCl3TNDIRu-ICHCl3TNPRu-ICH2Cl2TNPRu-ICH2Cl2PNPRu-ICH2Cl2PNPRu-ICH2Cl2PNPRu-ICH2Cl2PNPRu-ICHCl3PNPRu-ICHCl3	AnonomeCas.Sol.A cTNDIRu-ICH2C130TNDIRu-ICHC1350TNDIRu-ICHC1350TNDIRu-ICHC1330TNPIRu-ICH2C1230TNPRu-ICH2C1350TNPRu-ICH2C1350PNPRu-ICH2C1350PNP ^c Ru-ICHC1350	AnonomeCas.Sol.Zes.Ses.TNDIRu-ICH2Cl2301TNDIRu-ICHCl3502TNDIRu-ICHCl3502TNDIRu-ICHCl3502TNDIRu-ICHCl3502TNPIRu-ICHCl3301TNPIRu-ICHCl3301TNPARu-ICH2l2301PNPRu-ICHCl3501PNP°Ru-ICHCl3501	AnomoreCar.Sol.TensSuperimetryTNDIRu-ICH2C1301-TNDIRu-ICHC13506036TNDIRu-IICHC1350130TNDIRu-IICHC1350130TNDIRu-IICHC1350131TNDIRu-IICHC1350131TNPRu-IICH2C130131TNPRu-IICH2C330135PNPRu-IICHC1350135	AnonomeCas.Sol.ToptopMohTNDIRu-ICH2C1301-TNDIRu-ICHC1350630.10.TNDIRu-ICHC1350180.32.TNDIRu-ICHC1350180.32.TNDIRu-ICHC1350180.37.7TNDIRu-ICHC1350181.37.7TNPRu-ICH21330.181.37.7TNPRu-ICH21350.181.31.PNPRu-ICHC1350.195.7.83

 $^{a}~[M]_{0}/[Cat]_{0}=$ 100:1 (mol/mol), M = monomer, Cat = catalyst.

^b Determined by GPC in THF relative to monodispersed polystyrene standards.

 $^{c} [M]_{0}/[Cat]_{0} = 50:1 \text{ (mol/mol)}.$

proton h belong to methylene at 3.2–3.0 ppm, which means carbonyl group has been reduced by LiAH₄. GC/MS shows that the molecular weight matched to the calculated value. The structure was further confirmed by IR, which shows the complete disappearance of bands corresponding to carbonyl group (1714 cm⁻¹) in PNDI after the reaction. All of these points affirmed the successful preparation of PNP with the expected structure.

Preparation of Functional Polynorbornenes by Ring-Opening Metathesis Polymerization

ROMP of monomers was conducted by using Ru-I or Ru-II as the catalyst and produced the corresponding polymers in an acceptable yield (Table 1). Catalyst Ru-I was the first selection to initiate ROMP of TNDI on the basis of its character to well control the polymerization process and the molecular weight of polymers. Unfortunately, PTNDI was not formed by Ru-I under the mild conditions of 1 h and 30 °C likely because of the low reactivity of such endo-configuration cyclic olefin of TNDI, and this was similar with that case of polymerization of endo-PNDI by using Ru-I to achieve the polymer PPNDI in a low yield.³⁸ Raising temperature and prolonging the reaction time, polymerization was really occurred while the yield of PTNDI was only 36%. There have been some reports on that the reactivity of exo isomers of norbornene derivatives is higher than the endo ones due to the steric interactions between the propagating ruthenium-center and the endo-ring of an incoming monomer.³⁸⁻⁴⁰ Therefore, a more active catalyst Ru-II was chosen to improve the polymerization behavior of endo-TNDI and to give the corresponding polymer. As expected, polymerization of endo-TNDI was well conducted by Ru-II with a good yield at 50 °C for 1 h. As the reaction time prolonged to 2 h, the yield of polymer increased, and also the value of PDI became wide in some extent.

Monomer TNP can be polymerized by Ru-I at 30 °C, probably because of the difference of electronic effect between

imide and pyrrolidine when carbonyl group transformed into methylene group. The yield of PTNP increased as raising the polymerization temperature from 30 to 50 °C; however, PDI is also broad under the similar conditions. What is more important, PTNP and PTNDI are completely soluble in common organic solvents such as CHCl₃, THF, and so forth, and this feature favored the possibility of their application as thin film. Similar with TNP, polymerization of monomer PNP was carried out readily by Ru-I at 30 °C for 1 h. Nevertheless, poly(N-phenyl-norbornene-pyrrolidine) (PPNP) is only little soluble in CHCl₃ and THF, and this may be related to the rigid phenyl rings in the side chain of polymer. When the polymerization temperature raised to 50 °C, polymer was found to be insoluble in all the common solvents even in decalin. A reduced ratio of monomer to catalyst from 100:1 to 50:1 was then used, and the corresponding polymer with a lower molecular weight was soluble in THF and CHCl₃. Of course, the poor solubility of PPNP has a limitation to affording a high molecular weight polymer and its application to the thin film capacitors.

The occurred polymerization was confirmed by ¹H NMR spectra [Fig. 1(B,D) and Supporting Information Fig. S2C] on the basis of the varied olefinic proton signals. The signal of olefinic protons on the norbornene ring at about 6.19 ppm is completely disappeared after ring opening, whereas the new signal of olefinic protons on the backbone comes at 5.90-5.40 ppm, which points out polymerization is processed successfully. According to the previous assignments,^{19,41} the *trans/cis* ratio of as-synthesized polymers can be analyzed by integration of the ¹³C NMR signals related to the vinyl group at 131-133 ppm in Figure 2(B,C), and the results suggested that the most trans PTNP and PPNP formed, whereas PTNDI seems to be that the quantitative difference of *trans* to *cis* from Figure 2(A) is reduced, or the content of cis PTNDI increased significantly. When getting these highly *trans* polymers, the tacticity is supposed to be determined by ¹³C NMR. When it comes to the tacticity of endo-type substituted polymers, there are four possible microstructures as it can be seen from Scheme 2 for the representative case of PTNP. It would be two conformations syn/anti, which means the orientation of side groups attached to polymer chain in both isotactic and syndiotactic styles.²⁶ For the isotactic structures, syn conformation has a plane of symmetry perpendicular to the polymeric backbone and bisecting each monomeric unit. However, the two planes of symmetry (σ and σ') in two neighboring units are different; therefore, two sets of ¹³C NMR signals would be anticipated. On the other hand, anti conformation has the center of inversion (i) at the center of the carbon-carbon double bond, it is expected that it would show only one set of ¹³C NMR signals. For the syndiotactic structures, syn conformation has a C2 symmetry axis bisecting the C=C double bond, whereas the anti form has the C2 rotation axis perpendicular to the polymeric backbone and orthogonal to the corresponding C2 axis of the syn conformation. Each of the neighboring monomeric units have the same environments, and only one set of ¹³C NMR signals would be expected in both syn and anti conformations.



FIGURE 2 ¹³C NMR spectra of (A) PTNDI, (B) PTNP, and (C) PPNP.

Specifically, in the *endo*-type substituted PNBE derivatives, the signals of methylene carbon can provide undoubtedly evidence. As shown in the ¹³C NMR spectra at 35–42 ppm, there are two sets of peaks [Fig. 2(B)] for methylene carbon (C_b) in PTNP, whereas the counterpart of C_b in PPNP presents one set of signal [Fig. 2(C)]. The electron withdrawing and donating side groups contribute to the difference of the peaks of methylene carbon in PTNP and PPNP, which is similar to that of literature.²⁶ However, PTNDI shows a multiplicity of C_b peaks [Fig. 2(A)]. On the basis of the analysis, it seems like that PTNP adopts isotactic stereochemistry showing two sets of signals in methylene carbon, which have practically *trans* double bond and the dipolar pendant

groups are coherently arranged in the *syn* conformation. PPNP having one set of signals may be isotactic *anti* or syndiotactic *syn* and *anti* conformations. By contrast, PTNDI is supposed to be atactic because of the multiple peaks of methylene carbon, which is in accordance with *trans* and *cis* isomers.

Dielectric Properties

The dielectric spectroscopy of a thin film was shown in Figure 3. The thickness of film was about 3 μ m. PTNP displayed an attractive dielectric constant of about 20 even at frequency up to 1 MHz at room temperature, and this value is significant higher than that of common polymer dielectrics,



isotactic syn



isotactic anti



SCHEME 2 Possible conformations of isotactic and syndiotactic PTNP.

which is usually in the range of 2–6. Surprisingly, the dielectric response of PTNDI is about 7, and it is only one-third of that of PTNP. Also, the observed value of dielectric response for PPNP is only 3 at frequencies of 100 Hz to 1 MHz.

The dielectric performance of polymers is closely related to their chemical component and chain microstructure. The stronger is polarity of side chain in polymer, the greater is the degree of polarization, the higher is the dielectric constant. PTNP has two CF_3 substituents in each side chain, which definitely increases the dipolement of the side chain in a great content.¹⁸ Therefore, PTNP has a much more higher dielectric constant about 20 than that of PPNP about 3. However, the existence of the polar group is not the only reason for the high dielectric response. If the polar groups were attached to the polymer chain irregularly, such as atactic polymer, the dipolement would be cancelled out,^{17,18} as depicted in the case of atactic PTNDI, its dielectric constant decreased to about 7, although bearing two CF_3 groups in each TNDI unit. These results indicated that the dielectric



FIGURE 3 Dielectric constant of polymers versus frequency from 100 Hz to 1 MHz.



FIGURE 4 Dielectric loss of polymers versus frequency from 100 Hz to 1 MHz.

response is determined not only by the polar group but also by the chain microstructure of polymer. It has been reported that metathesized polymers catalyzed by Ru-I easier to take mainly *trans* conformation.²⁴ The pyrrolidine moiety in the side chain of PTNP is attributed to the stereochemistry²⁶ and the dipolement. Because of the rigidity of pyrrolidine, all rigid side groups aligned coherently in one orientation during the ROMP process,^{28,29} which makes the most TNP units arranged in the same direction, and tends to adopt the high trans configuration and afford a syn conformation isotactic polymer [Fig. 2(B)], resulting in a highly asymmetry of PTNP chain and, hence, the high dielectric constant. On the other hand, pyrrolidine is an electron-donating moiety, whereas CF_3 is an electron-withdrawing group, and the dipolement will increase tremendously by this intramolecular asymmetric structure and the large conjugated biphenyl group in PTNP. By contrast, the dicarbonimide-based polymer PTNDI has both *trans* and *cis* isomers, tending to be an atactic polymer chain and the dipolement counteracted, and finally lowered the dielectric response in a great extent.

Furthermore, the presence of large aromatic group in PTNP may be an important factor because they may interact with the neighboring aryl pendant group. The existence of two aromatic rings between the side groups of PTNP would introduce strong π - π interactions.^{31,32} These π - π interactions between the neighboring aromatic rings, especially with the electron-withdrawing substituents,²⁶ would be essential for controlling the stereochemistry of polymerization during the course of ROMP. These interactions induce the side chains of polymer probably to take the homogeneous direction predominantly, and two CF₃ groups in the side chain greatly increase the dipolement of polymer, so the dielectric constant of PTNP can reach a high level of 20. As a result, the dielectric constant of isotactic PTNP is high and better than those of atactic PTNDI and isotactic or syndiotactic PPNP. Combined the high dielectric constant with the data of ¹³C NMR spectrum, we believed that both the dipolar groups and the tactic microstructure of polymer chain do play key roles in the dielectric property of polymers.

It can also be noted in Figure 3 that the dispersion of dielectric constant is reasonable small. That is to say, the polymers exhibited a relatively high dielectric constant in the low frequency, and followed by a little reduction in the high frequency. Such a slight dispersion may be a result of the formation of large polar moieties⁴² and the strong electron-withdrawing CF₃ groups.

Figure 4 showed the dielectric loss of PTNP, PTNDI, and PPNP. All these polymers exhibited a small dielectric loss in the range of 0.01–0.05 at the frequencies of 100 Hz to 0.1 MHz. PPNP has the lowest dielectric loss of about 0.01 at frequency below 0.1 MHz, and further down to 0.004 as the frequency up to 0.1–1 MHz. PTNP has a more stable dielectric loss of 0.045 without an obvious fluctuation in all the frequency range. The dielectric loss of PTNDI is about 0.04 at the frequency of less than 0.1 MHz; however, it increases sharply toward 0.1 near the frequency of 1 MHz. A low dielectric loss is necessary for high performance devices as it may result in higher efficiency and lower noise,⁴² which is especially critical for high frequency applications. In general, PTNP with high dielectric constant and relative low dielectric loss is a suitable candidate for thin film capacitors.

To check if there is a thickness dependence of the dielectric performance for polymer, the dielectric measurement of polymers with various thicknesses has been carried out. The results have been shown in Table 2. It is clearly demonstrated that the dielectric constant of these polymers has no obvious correlation to the sample thickness ranged from 3 to 10 μ m. All of them just show a slight change of dielectric constant when the sample thickness is altered. Specifically, the values for PTNP are 20–21, PPNP has still relatively low values of 3–3.2, and the dielectric constant of PTNDI remains 6–7.5. When it referred to the relationship between the dielectric constant and polymerization degree of polymer, the situation is no longer the same among these polymers. The dielectric constant of PTNP has positive correlation to the polymerization degree, and the values are 16–22 with

TABLE 2 Dielectric Constant of Polymer Versus Molecular

 Weight and Thickness of Film

Polymer	n ^a	<i>М</i> _n ^ь (kDa)	PDI	d ^c (μm)	ε ^d
PTNDI-1	84	37.7	1.51	3	7.5
PTNDI-2	51	23.0	1.28	3–10	6–7.5
PTNDI-3	31	14.0	1.16	3	7
PTNP-1	83	35.0	1.48	3	22
PTNP-2	64	27.2	1.21	3–10	20–21
PTNP-3	30	12.7	1.12	3	16
PPNP-1	81	17.0	1.35	3	3.5
PPNP-2	57	12.0	1.22	3–10	3–3.2
PPNP-3	37	7.83	1.29	3	2.6

^a The polymerization degree.

^b Determined by GPC in THF relative to monodispersed polystyrene standards.

^c The thickness of polymer films.

^d The dielectric values of polymer films.



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FIGURE 5 DSC traces of polymers.

FIGURE 6 TGA curves of polymers.

different polymerization degree ranging from 30 to 83. The values for PPNP have also a slightly increase from 2.6 to 3.5 with increased polymerization degree of 37–81. However, there is a little change of dielectric constant (7–7.5) existed in the case of PTNDI, and its variation is below 1 with various polymerization degree of 31–84. Therefore, the impressive dielectric response we have observed should be the intrinsic behavior of PTNP, and it is contributed by the collaborated tactic microstructure of polymer and the dipolement of side groups. The different microstructures of PTNP and PTNDI introduce such discrepancy in their dielectric constants. As for PPNP, there is still an enhancement of dielectric constant with the increased polymerization degree. Because of the low dipole of phenyl group in PPNP, the values are changed in a relative low range.

Thermal Properties

The DSC technique is invited to obtain the glass transition temperature ($T_{\rm g}$), in order to erase any previous thermal history, two steps were performed. First, the polymers were heated to 300 °C and then cooled to 25 °C at a rate of 10 °C min⁻¹. Second, they were heated once more to 300 °C and cooled to 25 °C with the same heating and cooling rate. During the second heating cycle, we obtained the values. From the curves (Fig. 5), $T_{\rm g}$ s for PTNP, PPNP, and PTNDI were observed at 161, 181, and 244 °C, respectively (Table 3). $T_{\rm g}$ is depended on the *trans* content of polymer, and decreased as the higher *trans* existed. The lower $T_{\rm g}$ of PTNP compared with PTNDI is probably because of the higher content of *trans* double bond, which indicates a fairly typical manifestation of variation in chain microstructure.¹⁷ As for the pyrroli-

TABLE 3 Thermal Properties of Polymers

Polymer	<i>T</i> _{d5%} (°C)	<i>T</i> _{d10%} (°C)	<i>T</i> g (°C)
PTNP	315	380	161
PPNP	250	355	181
PTNDI	365	408	244

dine-containing PTNP and PPNP, because the presence of CF_3 moieties inhibits packing of the phenyl ring and decreases the temperature to attain the relaxation process, so the T_g of PTNP was lower than that of PPNP.

The thermal properties of polymers were affected by the chain structure and the side substitutions and evaluated by TGA (Fig. 6). The decomposition temperatures (T_{ds}) of PTNP and PTNDI at 5% weight loss are 315 and 365 °C, respectively, whereas that the counterpart of PPNP is just 250 °C, suggesting the thermal stability of PTNP and PTNDI is much better than that of PPNP with analogous structure, and that is because of the two CF3 groups in the side chain of PTNP and PTNDI.³⁸ PPNP presents the lower T_d value at 10% weight loss of polymer although $T_{\rm d}$ s are all above 350 °C, which indicates that all these functional PNBEs are of relatively high thermal stability. PTNDI displayed the highest values of $T_{\rm d}$ and $T_{\rm g}$ among these polymers because of the dicarbonimide-based structure and CF3 substitutions on the pendant phenyl ring. Having the excellent thermal stability and high T_{g} make the functional PNBEs more likely to fabricate the thin film capacitors.

CONCLUSIONS

Novel dielectric functional PNBEs with different side groups and dipolement were synthesized by ROMP using Grubbs catalyst under the mild reaction conditions, and the microstructure of polymer chain was characterized by NMR spectroscopy. Isotactic PTNP with large dipolement group 3,5bis(trifluoromethyl)biphenyl and pyrrolidine moiety possesses a high dielectric constant of 20, whereas isotactic or syndiotactic PPNP with phenyl group and pyrrolidine moiety has a dielectric constant of only 3. By comparison of the dielectric constant about 7 of atactic PTNDI with 3,5-bis(trifluoromethyl)biphenyl group and imide moiety, we believe that the pyrrolidine moiety is an essential element to control the stereoregularity of polymers. The thermal properties of polymers were also investigated. Having high dielectric properties and thermal stability, PTNP is expected to be a good potential dielectric material in the thin film capacitor.

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