

Research Article

Synthesis and Ring-Opening Metathesis Polymerization of a New Norbornene Dicarboximide with a Pendant Carbazole Moiety

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A new norbornene dicarboximide presenting a pendant carbazole moiety linked by a *p*-methylene benzyl spacer is synthesized. This carbazole-functionalized monomer is polymerized via ring-opening metathesis polymerization using Grubbs third-generation catalyst. Microstructural analysis of resulting polymers performed by Nuclear Magnetic Resonance (NMR) shows that they are stereoirregular. Wide-angle X-ray diffraction (WAXD) and thermal (DSC) analysis indicate that polymers are also amorphous. With respect to the fluorescence analysis, both solution and film polymer samples exhibit only "normal structured" carbazole fluorescence, while excimer formation by overlap of carbazole groups is not detected.

1. Introduction

In the latest recent years, carbazole-containing polymers have gained importance because of their use as organic photorefractive materials, photoconductors, light-emitting materials, etc. [1–7]. From a structural point of view, carbazole-containing polymers can be divided into two groups: main chain-type and side chain-type carbazole-containing polymers [1]. As for the latter class of polymers, poly(*N*-vinylcarbazole) (PVK) was the first to be synthesized [8, 9]. It has excellent film-forming properties and a high glass transition temperature and has also been used in combination with other layers in the fabrication of white OLEDs [10–12]. As for PVK and other side chain-type carbazole-containing polymers, their photophysical and photochemical properties were widely studied and it was found that their peculiar behaviour is due to the potential ability of these polymers to form two distinct excimers: a low-energy "sandwich-like" excimer and a high-energy "partially overlapping" excimer [13–20]. Moreover, it was established that the photophysical properties and

photoconductive behaviour of polymers can be modified by the conformation of the main chain as well as the nature and length of a spacer linking carbazole moiety to polymer backbone [1].

Side chain-type carbazole-containing polymers are generally nonconjugated polymers which, depending on the starting monomer, can be synthesized by using different polymerization techniques [1, 21–23]. PVK is prepared by cationic or radical polymerization using a vinylcarbazole monomer [15–18]. Higher homologues of PVK were synthesized by stereospecific Ziegler-Natta polymerization by using vinyl monomers [2–5, 24, 25]. Styrene-based monomers were polymerized by anionic and Ziegler-Natta polymerization [23, 26, 27]. Over the past two decades, the ring-opening metathesis polymerization (ROMP) has emerged as a powerful polymerization technique for the synthesis of structurally precise polymers [28, 29]. With the development of ruthenium-based catalysts such as the commercial Grubbs catalysts [30–32] that possess an excellent functional group tolerance, a variety of functional polymeric materials with interesting architectures and useful properties have been

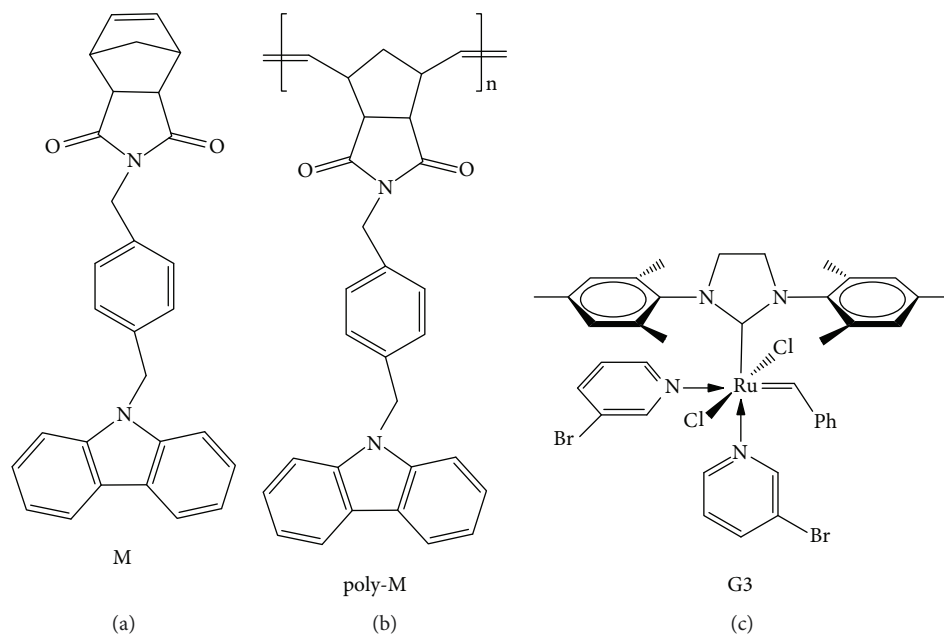


FIGURE 1: (a) Structure of (2-(4-((9H-carbazole-9-yl)methyl)benzyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione) (**M**). (b) Structure of poly(2-(4-((9H-carbazole-9-yl)methyl)benzyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione) (poly-**M**). (c) Grubbs third generation catalyst (**G3**).

synthesized via ROMP. Moreover, a high degree of control of both molecular weight and dispersity of polymers can be achieved [33]. Norbornene and its derivatives are the most commonly utilized ROMP monomers due to their high reactivity and easy incorporation of substituents in their structure that allows to introduce appropriate pendant functional groups on the polymer backbone [28, 29, 34–37]. Therefore, ROMP appears to be an interesting method also for fabricating side chain-type carbazole-containing polymers. Some examples of ROMP of norbornene-based monomers containing carbazole groups promoted by Grubbs catalysts are described in the literature [38–41]. Recently, Zeng et al. also reported the synthesis of highly efficient blue thermally activated delayed fluorescence polymers and copolymers based on side chain-type carbazole-containing polymers obtained by using Grubbs second-generation catalyst [42]. In this work, we describe the synthesis of a new carbazole-functionalized norbornene dicarboximide (**M**, Figure 1(a)) and its polymer (Figure 1(b)) obtained via ROMP using the Grubbs third-generation catalyst **G3** (Figure 1(c)) [43]. A poly(5-norbornene-2,3-dicarboximide) backbone was chosen to impart high glass transition temperature, good mechanical properties, and high thermal resistance to the resulting material [44–46], while a *p*-methylene benzyl spacer between the main chain and the carbazole moiety was introduced to reduce flexibility of the pendant arm thus favouring the formation of carbazole excimers. An accurate ^1H and ^{13}C NMR microstructural characterization of obtained polymer samples, as well as the X-ray and thermal analyses, is reported. UV-vis and photoluminescence properties were also investigated.

2. Materials and Methods

2.1. Materials. All manipulations involving air- and moisture-sensitive compounds were carried out under dried nitrogen stream with standard vacuum-line, Schlenk, or glovebox techniques. Glassware and vials used in the polymerization were dried in an oven at 120°C overnight and exposed to vacuum-nitrogen cycle, three times. All reagents and solvents were purchased from Sigma-Aldrich s.r.l. (Milan, Italy). Toluene was refluxed over sodium for 48 h and distilled before use. Methylene chloride (CH_2Cl_2) and tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$) were refluxed over lithium aluminium hydride (LiAlH_4) for 48 h and distilled before use. Third-generation Grubbs catalyst, dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolylidene](benzylidene)-bis(3-bromopyridine)ruthenium(II), was purchased from Sigma-Aldrich s.r.l. (Milan, Italy).

2.2. Methods

2.2.1. ^{13}C and ^1H Nuclear Magnetic Resonance Spectroscopy (^1H NMR and ^{13}C NMR). NMR spectra of monomer and polymers were recorded on a Bruker Avance 400 spectrometer (^1H , 400 MHz; ^{13}C , 100.62 MHz) operating at 298 K. Deuterated chloroform (CDCl_3) was used as the solvent to solubilize the samples, and tetramethylsilane (TMS) was used as internal chemical shift reference.

2.2.2. Electrospray Ionization Mass Spectrometry (ESI-MS). ESI-MS analysis was accomplished on a Waters spectrometer with an electrospray source.

2.2.3. Gel Permeation Chromatography (GPC). The molecular weights (M_n and M_w) and dispersity (Đ) of polymer samples

were measured by gel permeation chromatography (GPC) at 30°C, using tetrahydrofuran (THF) as a solvent, an eluent flow rate of 1 mL/min, and narrow polystyrene standards as reference. The measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four Styragel columns (range 1,000-1,000,000 Å).

2.2.4. Thermogravimetric Analyses (TGA). TGA were performed on a TGA Q500 apparatus manufactured by TA Instruments, in flowing N₂ (100 cm³/min). Polymer samples of 5 mg were placed in platinum pans and heated in the range 20-1000°C at a rate of 10°C/min.

2.2.5. Differential Scanning Calorimetry (DSC). Calorimetric measurements were carried out on a DSC Q20 apparatus manufactured by TA Instruments, in flowing N₂. Monomer and polymer samples of 5–10 mg were placed in aluminium pans and heated/cooled at a rate of 10°C/min.

2.2.6. Wide-Angle X-Ray Diffraction (WAXD). Wide-angle X-ray diffraction (WAXD) patterns of polymer powder samples were obtained by an automatic Bruker D8 Advance diffractometer, in reflection, by using the nickel-filtered Cu-Kα radiation (1.5418 Å).

2.2.7. Fourier Transform Infrared Spectroscopy (FTIR). Infrared spectra were obtained at a resolution of 2.0 cm⁻¹ with a Tensor 27 Bruker spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and a Ge/KBr beam splitter. The frequency scale was internally calibrated to 0.01 cm⁻¹ using a He-Ne laser. Thirty-two scans were signal averaged to reduce the noise. Samples were prepared by casting from a solution of polymer in chloroform.

2.2.8. Ultraviolet-Visible (UV-vis) and Fluorescence Spectroscopy. UV-vis measurement was performed by a Varian Cary 50 spectrophotometer and photoluminescence recorded by a Varian Cary Eclipse spectrophotometer. UV-vis and fluorescence measurements in solutions were performed in THF. Thin polymer films have been prepared by spin coating on a quartz slide substrate. The film thickness and roughness were measured by a KLA Tencor P-10 surface profiler. Film thickness was about 100 nm.

2.3. Monomer Synthesis

2.3.1. Synthesis of 9-(4-(Bromomethyl)benzyl)-9H-carbazole (S1). A 100 mL three-necked round-bottom flask equipped with a magnetic stir bar was charged with KH 35 wt% in mineral oil (0.72 g, 6.3 mmol). The mineral oil was removed from KH washing with dry hexane (3 × 2 mL) and solid KH then suspended in freshly distilled THF (10 mL). Subsequently, a solution of carbazole (0.79 g, 4.7 mmol) in 5 mL of THF was added dropwise at room temperature and the reaction mixture was stirred for 4 hours [47]. On completion of the reaction, the resulting brownish suspension containing the desired potassium carbazolate was filtered through a fritted glass funnel and immediately added dropwise to a THF solution of α,α'-dibromo-*p*-xylene (45 mL) previously prepared in a 250 mL three-necked round-bottom flask fitted with a

condenser. After stirring under reflux for 20 hours, the reaction mixture was cooled at room temperature, poured into water (200 mL), and extracted with CHCl₃ (3 × 100 mL). The combined organic phases were dried over Mg₂SO₄, and after removal of the solvent, the crude product was purified by silica gel column chromatography (petroleum ether/CH₂Cl₂ 2:1) to give a white solid (1.4 g, 62%). ¹H NMR (400 MHz, CDCl₃): δ 8.14 (d, 2H), 7.46-7.43 (m, 2H), 7.34 (d, 2H), 7.29-7.24 (m, 4H), 7.11 (d, 2H), 5.52 (s, 2H), 4.43 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, δ ppm): 140.75, 137.75, 137.23, 129.70, 127.02, 126.11, 123.25, 120.65, 119.53, 109.01, 46.42, 33.28. ESI+MS: m/z 375.6 (M+Na)⁺.

2.3.2. Synthesis of 3a,4,7,7a-Tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione (S2). S2 was synthesized following a previously reported procedure [48]. A mixture of urea (1.11 g, 18 mmol) and 5-norbornene-*exo*-2,3-dicarboxylic anhydride (2.50 g, 15 mmol) was introduced into a 250 mL round bottom flask, equipped with a condenser and a magnetic stirrer. The flask was heated at 145°C for 4 hours, then cooled at 90°C, and the crude product was dissolved in water (60 mL). Upon cooling at room temperature, an off-white solid precipitated. It was collected by filtration, washed with cold water, and dried *in vacuo* to obtain the desired dicarboximide S2 (1.5 g, 63%). ¹H NMR signals and ¹³C NMR signals were congruent with those reported in the literature [48].

2.3.3. Synthesis of 2-(4-((9H-Carbazole-9-yl)methyl)benzyl)-3a,4,7,7a-tetrahydro-1H-4,7-methano isindole-1,3(2H)-dione (M). The monomer M was prepared using a slightly modified procedure reported in the literature [49]. A 50 mL round bottom flask, equipped with a magnetic stirrer and a reflux condenser, was charged with S1 (0.62 g, 1.8 mmol), S2 (0.24 g, 1.5 mmol), and K₂CO₃ (0.22 g, 1.6 mmol) in 6 mL of dry acetone. The reaction mixture was refluxed for 45 h. After the solvent was removed under reduced pressure, the crude product was washed with water and dried under vacuum. The residue was then purified by column chromatography on silica gel using as eluent petroleum ether:CH₂Cl₂ (1:1) to give M as a white solid (0.311 g, 48%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.14 (d, 2H), 7.45-7.41 (m, 2H), 7.34 (d, 2H), 7.29-7.24 (m, 4H), 7.10 (2H), 6.26 (s, 2H), 4.56 (s, 2H), 3.24 (s, 2H), 2.66 (s, 2H), 1.40 (d, 1H), 1.03 (d, 1H). ¹³C NMR (100 MHz, CDCl₃, δ ppm): 177.78, 140.66, 138.02, 135.23, 129.29, 126.89, 125.95, 123.11, 120.52, 119.36, 108.95, 47.90, 46.37, 45.36, 42.80, 42.04. ESI+MS: m/z 455.17 (M+Na)⁺. m.p. 149.54°C.

2.3.4. Polymerization. Polymerization reactions were conducted at room temperature in a glovebox under a nitrogen atmosphere. A stirred solution of M (100 mg, 2.3 mmol) in dry CH₂Cl₂ (1 mL) was added; the Grubbs third generation catalyst (1.0 mg, 0.011 mmol) was dissolved in 0.5 mL of dry CH₂Cl₂. The polymerizations were terminated by the addition of a few drops of ethyl vinyl ether (EVE) after the prescribed time, and the solutions were poured into an excess of methanol. The polymers were precipitated from methanol,

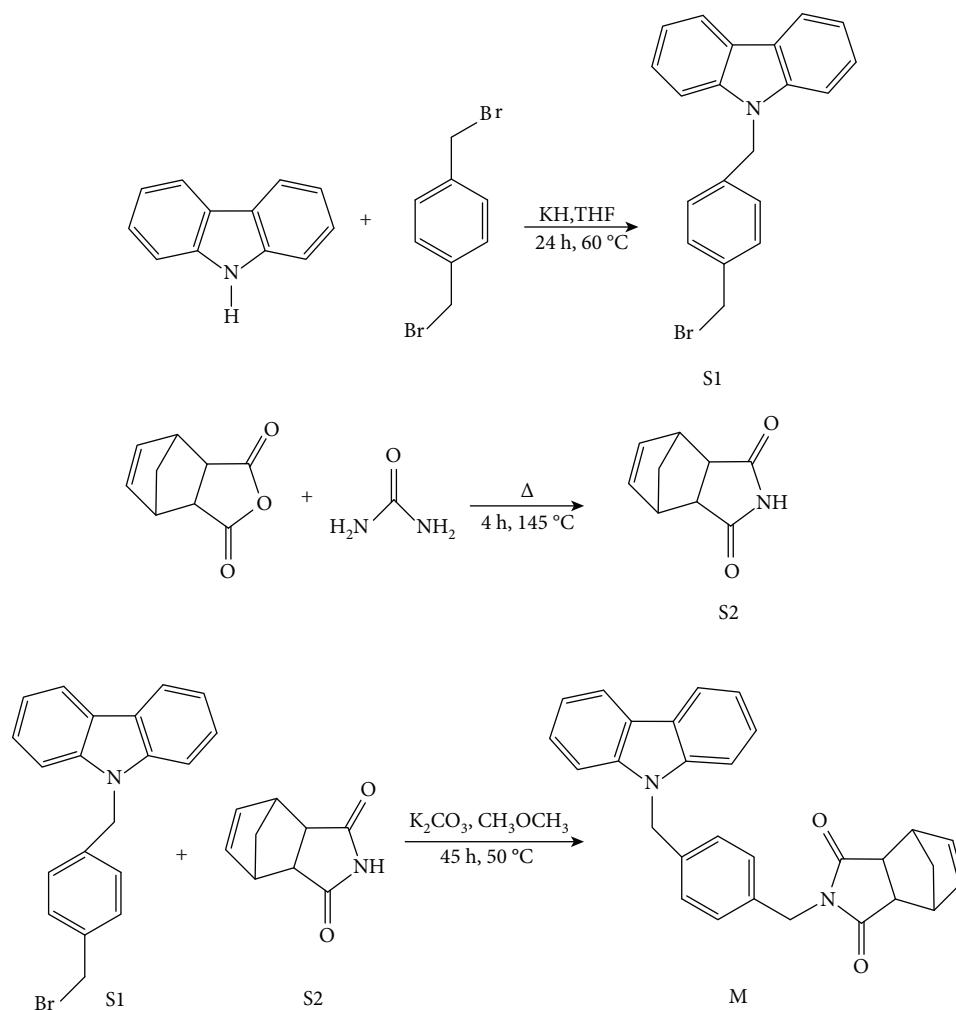


FIGURE 2: Monomer synthesis.

dissolved in CH_2Cl_2 , filtered through a pad of silica gel to remove catalyst residues, and then dried *in vacuo* at 40°C . ^1H NMR (400 MHz, CDCl_3): δ 8.10-8.04 (m, 2H), 7.39-6.93 (overlapped m, 10H), 5.63 (s, 2H, *trans*), 5.44 (s, 2H, *cis*), 5.44-5.26 (m, 2H), 4.48-4.25 (m, 2H), 3.21-2.90 (m, 2H), 2.90-2.54 (m, 2H), 2.10-1.97 (m, 1H), 1.48 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 177.87, 140.67, 137.09, 135.35, 133.65, 132.67 (*cis*), 131.79 (*trans*), 129.16, 126.93, 126.81, 125.97, 123.11, 120.53, 119.39, 109.01, 108.95, 53.28, 52.76, 52.40, 51.92, 51.09, 50.90, 46.37, 46.29, 45.73, 42.48, 41.86, 40.76.

3. Results and Discussion

3.1. Monomer Synthesis and Characterization. The synthesis of monomer 2-(4-((9H-carbazole-9-yl)methyl)benzyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione (**M**) was achieved in three steps as shown in Figure 2. The first step involved the reaction of potassium carbazolate with α,α' -dibromo-*p*-xylene to produce 9-(4-(bromomethyl)benzyl)-9H-carbazole (**S1**) [47], while the second step afforded 3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3(2H)-dione (**S2**) by the reaction of 5-norbornene-

2,3-dicarboxylic anhydride with urea [48]. Finally, **M** was obtained in 48% yield by the reaction of **S1** with **S2** [49]. The detailed procedures for the synthesis of **M** are described in the previous section. The complete characterization of **M** effected by ^1H and ^{13}C NMR, FT-IR, UV-vis, fluorescence, and mass spectroscopy, as well as by thermal analysis is reported in Supplementary Materials (see Figures S1-S10).

3.2. Polymer Synthesis and NMR Characterization. As depicted in Figure 3, target polymer samples (poly-**M**) were synthesized by ring-opening metathesis polymerization of **M** in the presence of third-generation Grubbs catalyst [43]. Polymerizations were performed under an inert atmosphere, at room temperature and using CH_2Cl_2 as solvent. Before analysis, polymer samples were purified by passing through a silica gel column. Polymerization results are summarized in Table 1.

According to GPC analysis, polymers showed monomodal curves and molecular weight distribution values suggesting that ROMP polymerization reactions could proceed in a living way [33].

Polymer microstructures were evaluated by ^1H and ^{13}C NMR analysis. As expected, catalyst **G3** produced polymers

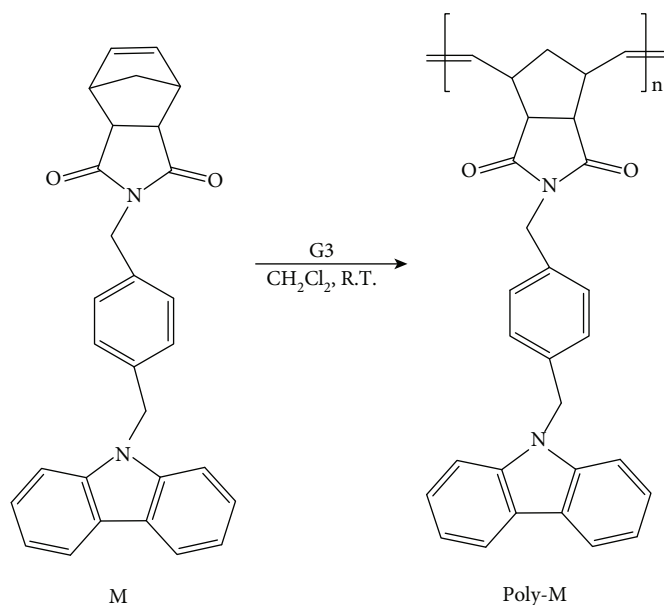


FIGURE 3: Polymerization scheme.

TABLE 1: Polymerization results.

Sample ^a	Time ^b (h)	Yield (%)	M_n^c (kDa)	\bar{D}	T_d^d (°C)	T_g (°C)
1	2	70	15.1	1.27	423	189
2	3	99	24.8	1.15	423	195

^aPolymerization conditions: $[M] = 0.15$ M, $G3 = 1.1 \times 10^{-3}$ mol, $M/G3 = 200$, solvent = CH_2Cl_2 , room temperature. ^bReaction time. ^cMolecular weights of soluble fractions of polymers in THF. ^dDecomposition temperature was evaluated by TGA at 5% weight loss.

with a mixture of *cis* and *trans* double bonds. Figure 4 shows the 1H NMR spectra of monomer **M** (A) and of its polymer (**B**, sample **2** in Table 1). In Table 2, the complete shift assignments are also reported.

As can be observed, the monomer olefinic signals at $\delta = 6.26$ ppm (Figure 4(a)) were replaced by two new resonances centered at $\delta = 5.63$ and 5.44 (Figure 4(b)), which correspond to the *trans* and *cis* double bonds of the polymer, respectively. The fraction of double bonds with *cis* configuration in the polymer backbone was estimated to be 45%. The ^{13}C NMR spectra of **M** and its polymer are displayed in Figures S2 and S8 of the Supplementary Material, respectively. The characteristic signals attributed to the olefinic carbons of the norbornene ring were observed at 138.02 ppm, while the resonances of the olefinic carbons of polymer chain were observed at 133.65-132.67 (*cis*) and 131.79 (*trans*).

3.3. X-Ray, DSC, and Optical Characterization. The X-ray diffraction pattern of both polymer samples (see Figure 5) shows an intense and broad amorphous peak centered at $2\theta = 19.2^\circ$ with a weak shoulder at $2\theta = 14.2^\circ$. This pattern result is very similar to that recently reported for poly(4-(N-carbazolyl)methyl styrene) (PSK) which is a polyolefin

leading similar side group of our polymer samples [26]. For PSK, it was assumed that the most intense peak of the X-ray spectrum has to be associated with correlation distances among face to face arranged carbazole groups [26]. Likewise, the maximum of the X-ray pattern of both our polymer samples should be associated with the stacking formation of carbazole units having an average relative distance of 4.5 Å.

To thermal analysis, both polymer samples show thermal stability with a decomposition temperature (T_d , with 5% weight loss) of 423°C (see Figure 6(a)). Consistent with the X-ray diffraction results, the DSC curves of both polymer samples show only the glass transition (T_g), ~189 and ~195°C for samples **1** and **2** in Table 1, respectively (see Figure 6(b)). The lower T_g value observed for sample **1** with respect to that for sample **2** is consistent with the lower molecular weight of **1** with respect to that of **2**. It is worth noting that the thermal behaviour of amorphous polymers presenting the same main chain of our polymer samples (poly(5-norbornene-2,3-dicarboximide) but different N-substituted groups on N (i.e., phenyl and adamantyl) was already reported in the literature [45, 50, 51].

As expected, decomposition temperatures close to those of our polymers were detected, while slightly higher T_g values were instead reported [45, 50, 51]. This last result is expected taking into account not only the higher molecular weights of reported N-substituted poly(5-norbornene-2,3-dicarboximide)s with respect to our polymers (about ten times more) but also the minor ability of the N-substituted side group (9H-carbazole-9-yl)methyl)benzyl) of our polymer samples to decrease the chain mobility and to increase the rotational barrier of the polymer main chains respect to phenyl or more rigid adamantyl side groups.

UV-vis spectrum of polymer sample **2** in Table 1 is showed in Figure 7. The peaks which characterize the

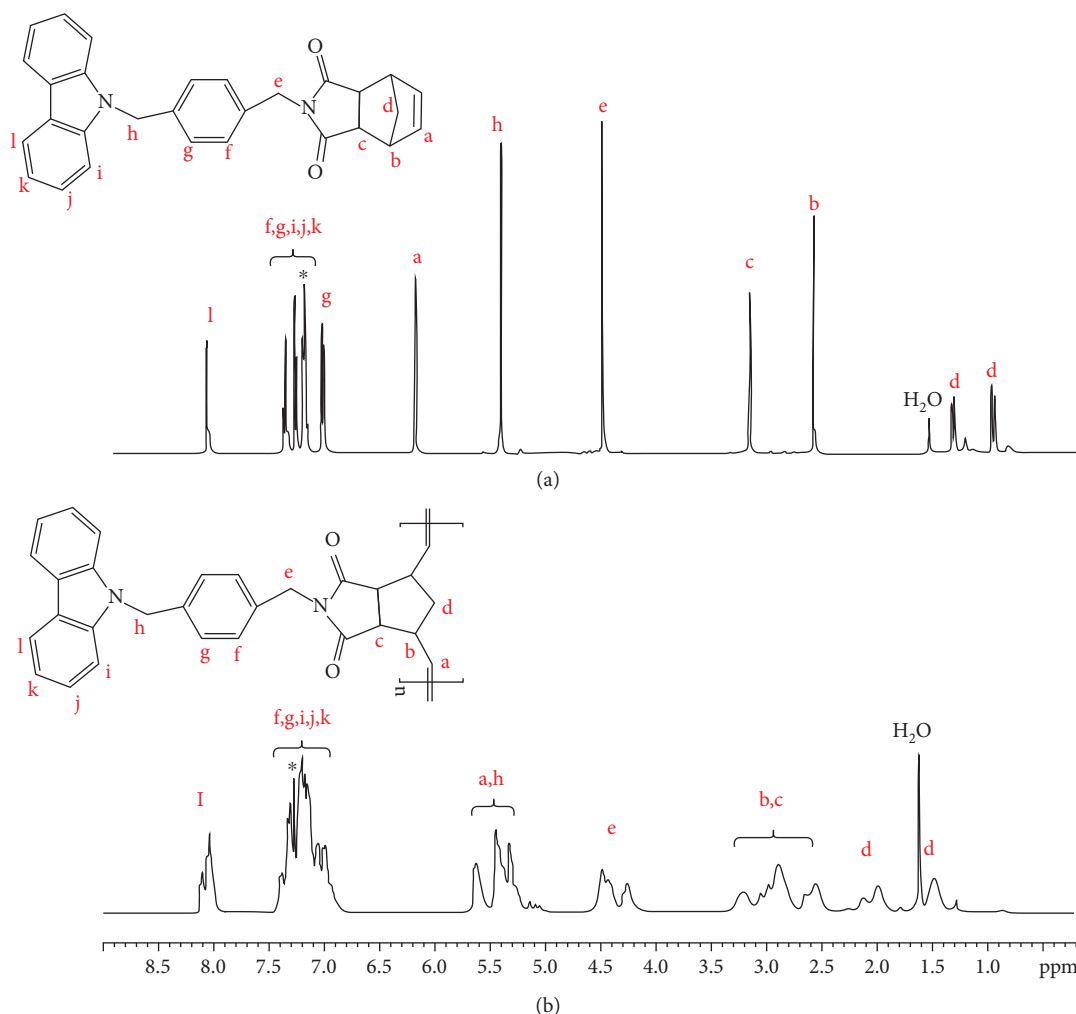


FIGURE 4: ^1H -NMR spectra of **M** (a) and its polymer (b, sample 2) in CDCl_3 . The residual protio impurity of CDCl_3 is marked with an asterisk.

TABLE 2: ^1H NMR chemical shift assignments for **M** and its polymer.

Monomer (M)		Polymer	
Proton	Chemical shift (ppm)	Proton	Chemical shift (ppm)
a	6.26	a	5.63 (<i>t</i>), 5.44 (<i>c</i>)
b	2.66	b	2.90-2.54
c	3.24	c	3.21-2.90
d	1.03	d	1.48
d	1.40	d	2.10-1.97
e	4.56	e	4.48-4.25
f,i,j,k	7.45-7.24	f,g,i,j,k	7.29-6.93
g	7.10	h	5.44-5.26
h	5.49	l	8.10-8.04
l	8.14		

carbazole groups are those at 332 and 346 nm, and they are always present in the absorption spectra of carbazole-containing polymers [52, 53]. Fluorescence measurements of polymer sample 2 both as film and in dilute tetrahydrofuran (THF) solution at room temperature were also

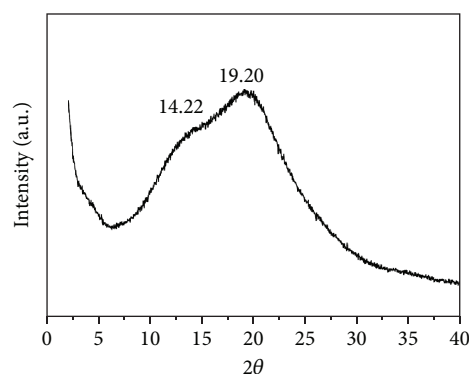


FIGURE 5: X-ray diffraction patterns of polymer sample 2 in Table 1.

performed. Both fluorescence spectra measured under an excitation wavelength of 300 nm are reported in Figure 8. They only show in the high-energy region two bands assigned to carbazole group emission and currently named “normal structured” monomer fluorescence [52, 53]. For the sake of clarity, the fluorescence spectra of THF monomer solution are also showed in Figure 8, for comparison.

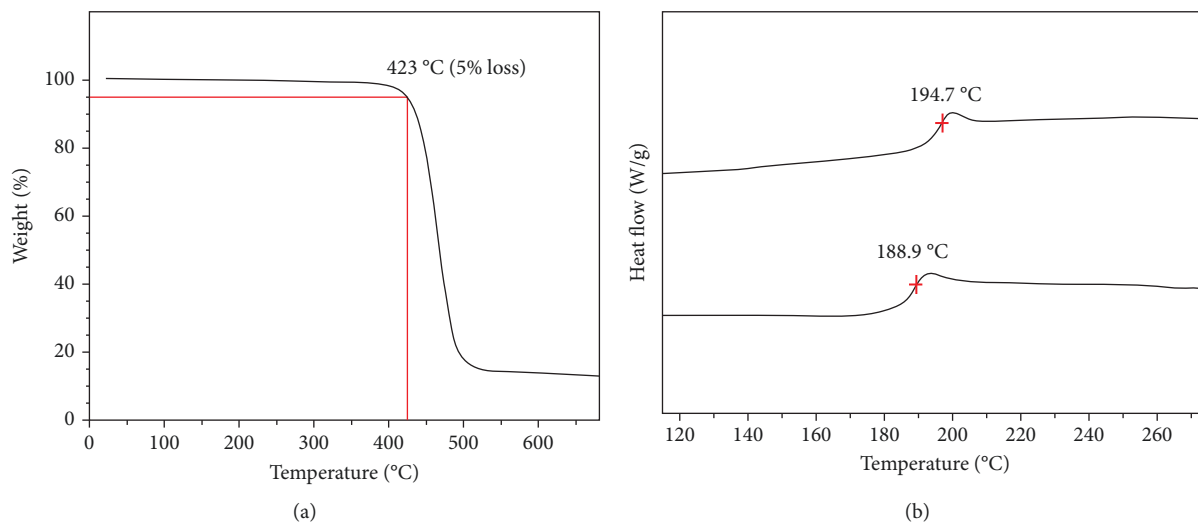


FIGURE 6: (a) TGA curve of polymer sample 2. (b) DSC curves of polymer samples 1 (A) and 2 (B).

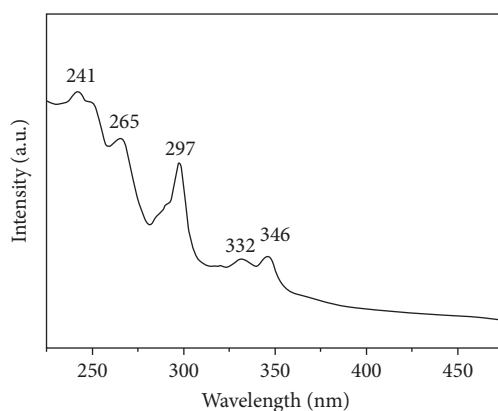


FIGURE 7: UV-vis absorption spectra of polymer sample 2 films.

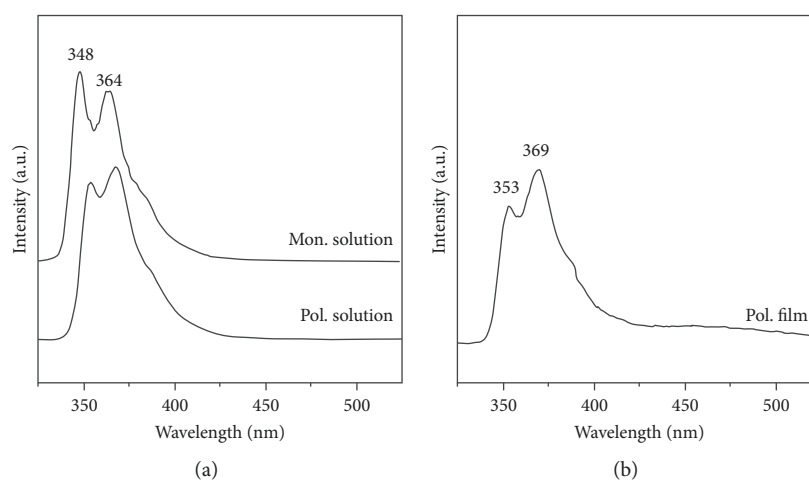


FIGURE 8: (a) Fluorescence spectra of polymer solution (sample 2, THF 10^{-4} M) and monomer solution (THF 10^{-4} M). (b) Fluorescence spectrum of polymer film. ($\lambda_{exc} = 300\text{nm}$).

It is worth nothing that bands attributable to “sandwich-like” or “partially overlapping” excimers usually formed by carbazole-containing polymers like poly(N-vinylcarbazole)

(PVK) [15, 18, 54] or stereoregular higher homologues of PVK [2–5, 23, 24] are not observed. For solution emission spectra, this result can be easily explained assuming that the

presumed main chain conformational freedom in solution prevents excimer formation. As for the lack of excimer emission in film spectra, it could be justified by the presence of the *p*-methylene benzyl spacer linking the poly(5-norbornene-2,3-dicarboximide) chain and the carbazole groups that increases the conformational freedom of carbazole groups preventing excimer formation. Very likely, the *p*-methylene benzyl spacer is not rigid enough to induce the stacking of carbazole groups and therefore excimer formation. Furthermore, the lack of excimer emission in the film spectra of our polymer samples could be also related to lack of conformational order of the main chain. In this regard, it is worth recalling that for carbazole-containing polymer, excimer formation can be induced by main chain stereoregularity [2–5, 15, 18, 24, 25, 54]. As an example, both isotactic and syndiotactic PSK film fluorescence spectra present bands attributable to low-energy “sandwich-like” and/or high-energy “partially overlapping” excimers which are not observed in atactic PSK [26]. Since our polymer samples do not present any stereoregularity degree due to the lack of stereospecificity of catalyst **G3**, their optical behaviour could be expected.

4. Conclusion

Herein, a new norbornene dicarboximide presenting a pendant carbazole moiety linked by a *p*-methylene benzyl spacer was prepared and utilized in polymerization by ROMP using Grubbs third generation catalyst **G3**. Consistent with a controlled living polymerization mechanism, the obtained polymer samples show narrow dispersities. They were fully characterized by NMR spectroscopy disclosing a stereoirregular microstructure of the main chain presenting random distribution of *cis* and *trans* double bonds. TGA analyses showed that polymer samples have high thermal stability with a decomposition temperature of 423°C. The X-ray patterns of polymer samples present a broad amorphous halo centered at $2\theta = 19.2^\circ$ and a not too well-defined hump at $2\theta = 14.2^\circ$. The maximum of the X-ray pattern was tentatively associated to stacking formation of carbazole units having an average relative distance of 4.5 Å. According to the WAXD data, polymer DSC traces only present glass transition ($T_g \sim 190^\circ\text{C}$). With respect to the optical analysis, both solution and film polymer samples showed similar fluorescence spectra with two weak shoulders in the high-energy region which are due to carbazole emission, while excimer emission was not observed. In particular, as for polymer film samples, the presence of a *p*-methylene benzyl spacer connecting carbazole with the main chain as well as the stereoirregularity of the polymer chain could avoid excimer formation. However, starting from this new monomer, stereoregular polymers with more interesting optical properties could be prepared by using stereoselective ROMP catalysts, thus leading to the development of attractive materials for optoelectronic applications.

Data Availability

The data used to support the findings of this study are available in the text and in the Supplementary Material.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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Supplementary Materials

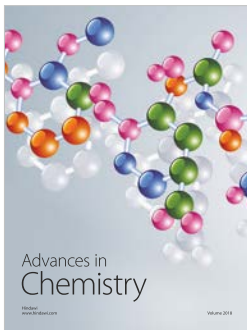
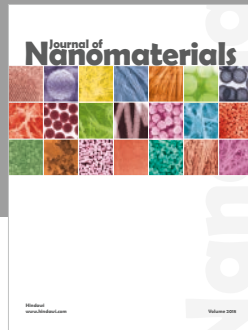
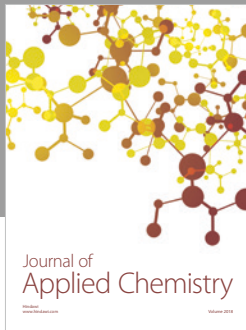
NMR spectra, mass spectroscopy, FT-IR, UV-vis, fluorescence, and thermal analysis of **M** and NMR spectra, mass spectroscopy, FT-IR, UV-vis, fluorescence, and thermal analysis of poly-**M**. (*Supplementary Materials*)

References

- [1] J. V. Grazulevicius, P. Stroehriegl, J. Pielichowski, and K. Pielichowski, “Carbazole-containing polymers: synthesis, properties and applications,” *Progress in Polymer Science*, vol. 28, no. 9, pp. 1297–1353, 2003.
- [2] A. Botta, S. Pragliola, V. Venditto et al., “Highly isotactic poly(N-pentenyl-carbazole): a challenging polymer for optoelectronic applications,” *AIP Conference Proceedings*, vol. 1599, pp. 493–497, 2014.
- [3] A. Botta, S. Pragliola, V. Venditto et al., “Synthesis, characterization, and use as emissive layer of white organic light emitting diodes of the highly isotactic poly(N-pentenyl-carbazole),” *Polymer Composites*, vol. 36, no. 6, pp. 1110–1117, 2015.
- [4] A. Botta, V. Venditto, A. Rubino, and S. Pragliola, “Highly isotactic poly(N-butenyl-carbazole): synthesis, characterization, and optical properties,” *Journal of Chemistry*, vol. 2016, Article ID 1656459, 8 pages, 2016.
- [5] R. Liguori, A. Botta, S. Pragliola et al., “Study of the electroluminescence of highly stereoregular poly(N-pentenyl-carbazole) for blue and white OLEDs,” *Semiconductor Science and Technology*, vol. 32, no. 6, article 065006, 2017.
- [6] T. Michinobu, K. Okoshi, H. Osako, H. Kumazawa, and K. Shigehara, “Band-gap tuning of carbazole-containing donor–acceptor type conjugated polymers by acceptor moieties and π -spacer groups,” *Polymer*, vol. 49, no. 1, pp. 192–199, 2008.
- [7] Y. Zou, D. Gendron, R. Badrou-Aïch, A. Najari, Y. Tao, and M. Leclerc, “A high-mobility low-bandgap poly(2,7-carbazole) derivative for photovoltaic applications,” *Macromolecules*, vol. 42, no. 8, pp. 2891–2894, 2009.
- [8] W. Reppe and E. Keyssner, “N-VinylCompounds,” DRP618120, 1935.
- [9] W. Reppe, E. Keyssner, and E. Dorrer, “Polymerized Vinyl Compounds,” DRP664231, 1938.
- [10] X. Yang, G. Zhou, and W. Y. Wong, “Recent design tactics for high performance white polymer light-emitting diodes,” *Journal of Materials Chemistry C*, vol. 2, no. 10, pp. 1760–1778, 2014.

- [11] C. Fan, Y. Li, C. Yang, H. Wu, J. Qin, and Y. Cao, "Phosphoryl/sulfonyl-substituted iridium complexes as blue phosphorescent emitters for single-layer blue and white organic light-emitting diodes by solution process," *Chemistry of Materials*, vol. 24, no. 23, pp. 4581–4587, 2012.
- [12] P.-L. T. Boudreault, S. Beaupré, and M. Leclerc, "Polycarbazoles for plastic electronics," *Polymer Chemistry*, vol. 1, no. 2, pp. 127–136, 2010.
- [13] G. E. Johnson, "Emission properties of vinylcarbazole polymers," *The Journal of Chemical Physics*, vol. 62, no. 12, pp. 4697–4709, 1975.
- [14] A. Rivaton, B. Mailhot, G. Derderian, P. O. Bussiere, and J. L. Gardette, "Investigation of the photophysical processes and photochemical reactions involved in PVK films irradiated at $\lambda > 300$ nm," *Macromolecules*, vol. 36, no. 15, pp. 5815–5824, 2003.
- [15] A. Itaya, K. Okamoto, and S. Kusabayashi, "Singlet excitation energy transfer in the vinyl polymers with pendant carbazolyl groups," *Bulletin of the Chemical Society of Japan*, vol. 50, no. 1, pp. 22–26, 1977.
- [16] C. E. Hoyle, T. L. Nemzek, A. Mar, and J. E. Guillet, "Time resolved fluorescence studies of poly(N-vinylcarbazole), poly(1-vinylnaphthalene), and 1,3-bis(N-carbazolyl) propane," *Macromolecules*, vol. 11, no. 2, pp. 429–431, 1978.
- [17] F. Evers, K. Kobs, R. Memming, and D. R. Terrell, "Intramolecular excimer emission of poly(N-vinylcarbazole) and rac and meso-2,4-di-N-carbazolylpentane. Model substances for its syndiotactic and isotactic dyads," *Journal of the American Chemical Society*, vol. 105, no. 19, pp. 5988–5995, 1983.
- [18] K.-I. Okamoto, M. Yamada, A. Itaya, T. Kimura, and S. Kusabayashi, "Polymerization of N-vinylcarbazole, N-vinyl-5H-benzo[b]carbazole, and N-vinyl-7H-benzo[c]-carbazole," *Macromolecules*, vol. 9, no. 4, pp. 645–649, 1976.
- [19] T. Kawamura, M. Sakuma, and K. Matsuzaki, "Stereoregularity in poly(N-vinylcarbazole)," *Die Makromolekulare Chemie, Rapid Communications*, vol. 3, no. 7, pp. 475–481, 1982.
- [20] D. R. Terrell and F. Evers, "Stereocontrol in the cationic polymerization of N-vinylcarbazole," *Journal of Polymer Science: Polymer Chemistry Edition*, vol. 20, no. 9, pp. 2529–2543, 1982.
- [21] B. Wang, F. Shen, P. Lu et al., "New ladder-type conjugated polymer containing carbazole and fluorene units in backbone: synthesis, optical, and electrochemistry properties," *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 46, no. 9, pp. 3120–3127, 2008.
- [22] N. Blouin, W. Mitchell, C. Wang, and S. Tierney, "Polymers of 8,9-dihydrobenzo[def]carbazole and their use as organic semiconductors," U.S. Patent 20130001476A1, 2013.
- [23] Y.-S. Cho, S.-W. Kim, C.-S. Ihn, and J.-S. Lee, "Anionic polymerization of 4-(9-carbazolyl)methylstyrene," *Polymer*, vol. 42, no. 18, pp. 7611–7616, 2001.
- [24] R. Liguori, A. Botta, A. Rubino, S. Pragliola, and V. Venditto, "Stereoregular polymers with pendant carbazolyl groups: synthesis, properties and optoelectronic applications," *Synthetic Metals*, vol. 246, pp. 185–194, 2018.
- [25] A. Botta, C. Costabile, V. Venditto et al., "Optoelectronic properties of poly(N-alkenyl-carbazole)s driven by polymer stereoregularity," *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 59, pp. 242–251, 2018.
- [26] A. Botta, S. Pragliola, C. Capacchione et al., "Synthesis of poly(4-(N-carbazolyl)methyl styrene)s: tailoring optical properties through stereoregularity," *European Polymer Journal*, vol. 88, pp. 246–256, 2017.
- [27] S. J. Jeong, I. T. Jung, and K. B. Yoon, "Intra-/intermolecular excimer emission of syndiotactic polystyrene having carbazole substituents," *Polymer Korea*, vol. 35, no. 4, pp. 314–319, 2011.
- [28] R. H. Grubbs, A. G. Wenzel, D. J. O'Leary, and E. Khosravi, *Handbook of Metathesis*, Wiley-VCH, Weinheim, second edition, 2015.
- [29] K. Grell, *Olefin Metathesis: Theory and Practice*, John Wiley & Sons, Inc, Hoboken, NJ, USA, 2014.
- [30] S.-T. Nguyen, L.-K. Johnson, R. H. Grubbs, and J.-W. Ziller, "Ring-opening metathesis polymerization (ROMP) of norbornene by a group VIII carbene complex in protic media," *Journal of the American Chemical Society*, vol. 114, no. 10, pp. 3974–3975, 1992.
- [31] E.-L. Dias, S.-T. Nguyen, and R. H. Grubbs, "Well-defined ruthenium olefin metathesis catalysts: mechanism and activity," *Journal of the American Chemical Society*, vol. 119, no. 17, pp. 3887–3897, 1997.
- [32] M. Scholl, S. Ding, C. W. Lee, and R. H. Grubbs, "Synthesis and activity of a new generation of ruthenium-based olefin metathesis catalysts coordinated with 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene ligands," *Organic Letters*, vol. 1, no. 6, pp. 953–956, 1999.
- [33] C. W. Bielawski and R. H. Grubbs, "Living ring-opening metathesis polymerization," *Progress in Polymer Science*, vol. 32, no. 1, pp. 1–29, 2007.
- [34] C. Slugovc, "The ring opening metathesis polymerisation toolbox," *Macromolecular Rapid Communications*, vol. 25, no. 14, pp. 1283–1297, 2004.
- [35] R.-R. Schrock, "Synthesis of stereoregular polymers through ring-opening metathesis polymerization," *Accounts of Chemical Research*, vol. 47, no. 8, pp. 2457–2466, 2014.
- [36] S. Sutthasupa, M. Shiotsuki, and F. Sanda, "Recent advances in ring-opening metathesis polymerization, and application to synthesis of functional materials," *Polymer Journal*, vol. 42, no. 12, pp. 905–915, 2010.
- [37] S. Shao, J. Hu, X. Wang, L. Wang, X. Jing, and F. Wang, "Blue thermally activated delayed fluorescence polymers with non-conjugated backbone and through-space charge transfer effect," *Journal of the American Chemical Society*, vol. 139, no. 49, pp. 17739–17742, 2017.
- [38] D.-J. Liaw, K.-L. Wang, K.-R. Lee, and J.-Y. Lai, "Ring-opening metathesis polymerization of new norbornene-based monomers containing various chromophores," *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 45, no. 14, pp. 3022–3031, 2007.
- [39] A. Meyers, A. Kimyonok, and M. Weck, "Infrared-emitting poly(norbornene)s and poly(cyclooctene)s," *Macromolecules*, vol. 38, no. 21, pp. 8671–8678, 2005.
- [40] M.-C. Choi, J.-C. Hwang, C. Kim, Y. Kim, and C.-S. Ha, "Synthesis of poly(N-9-ethylcarbazole-exo-norbornene-5,6-dicarboximide) for hole-transporting layer in hybrid organic light-emitting devices," *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 48, no. 22, pp. 5189–5197, 2010.
- [41] N. S. Saleesh Kumar, M. D. Gujrati, and J. N. Wilson, "Evidence of preferential π -stacking: a study of intermolecular and intramolecular charge transfer complexes," *Chemical Communications*, vol. 46, no. 30, pp. 5464–5466, 2010.
- [42] X. Zeng, J. Luo, T. Zhou et al., "Using ring-opening metathesis polymerization of norbornene to construct thermally activated

- delayed fluorescence polymers: high-efficiency blue polymer light-emitting diodes,” *Macromolecules*, vol. 51, no. 5, pp. 1598–1604, 2018.
- [43] T.-L. Choi and R. H. Grubbs, “Controlled living ring-opening-metathesis polymerization by a fast-initiating ruthenium catalyst,” *Angewandte Chemie, International Edition*, vol. 42, no. 15, pp. 1743–1746, 2003.
- [44] J. Asrar, “High-Temperature Metathesis Polymers: Structure-Property Relationships,” *Macromolecules*, vol. 27, no. 15, pp. 4036–4042, 1994.
- [45] A. P. Contreras, A. M. Cerda, and M. A. Tlenkopatchev, “Synthesis of high-Tg polymers by ring-opening metathesis polymerization of N-cycloalkylnorbornene dicarboximide,” *Macromolecular Chemistry and Physics*, vol. 203, no. 12, pp. 1811–1818, 2002.
- [46] J. Vargas, E. S. Colin, and M. A. Tlenkopatchev, “Ring-opening metathesis polymerization (ROMP) of N-cycloalkyl-7-oxanorbornene dicarboximides by well-defined ruthenium initiators,” *European Polymer Journal*, vol. 40, no. 7, pp. 1325–1335, 2004.
- [47] R. Dinnebier, H. Esbak, F. Olbrich, and U. Behrens, “Structure determination of unsolvated potassium, rubidium, and cesium carbazoles,” *Organometallics*, vol. 26, no. 10, pp. 2604–2608, 2007.
- [48] B. Yang, B. A. Abel, C. L. McCormick, and R. F. Storey, “Synthesis of polyisobutylene bottlebrush polymers via ring-opening metathesis polymerization,” *Macromolecules*, vol. 50, no. 19, pp. 7458–7467, 2017.
- [49] M. T. Proetto, C. R. Anderton, D. Hu et al., “Cellular delivery of nanoparticles revealed with combined optical and isotopic nanoscopy,” *ACS Nano*, vol. 10, no. 4, pp. 4046–4054, 2016.
- [50] J.-C. Hwang, M.-C. Choi, Y. Ha et al., “Effect of side groups in polynorbornene films for transparent conductive substrates,” *Journal of Nanoscience and Nanotechnology*, vol. 11, no. 1, pp. 550–554, 2011.
- [51] K.-H. Yoon, K. O. Kim, M. Schaefer, and D. Y. Yoon, “Synthesis and characterization of hydrogenated poly(norbornene endo-dicarboximide)s prepared by ring opening metathesis polymerization,” *Polymer*, vol. 53, no. 11, pp. 2290–2297, 2012.
- [52] I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, NY, USA, 1971.
- [53] P. C. Johnson and H. W. Offen, “Excimer fluorescence of poly(N-vinylcarbazole),” *The Journal of Chemical Physics*, vol. 55, no. 6, pp. 2945–2949, 1971.
- [54] H. Sakai, A. Itaya, H. Masuhara, K. Sasaki, and S. Kawata, “Fluorescence dynamics of poly(N-vinylcarbazole) in solution as revealed by multicomponent analysis of picosecond time-resolved fluorescence spectra: dependence on tacticity and molecular weight,” *Polymer*, vol. 37, no. 1, pp. 31–43, 1996.



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