New Functional Monomers for Well-Controlled ROMP Polymerizations

Richard Charvet and Bruce M. Novak*

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695

Received June 7, 2001

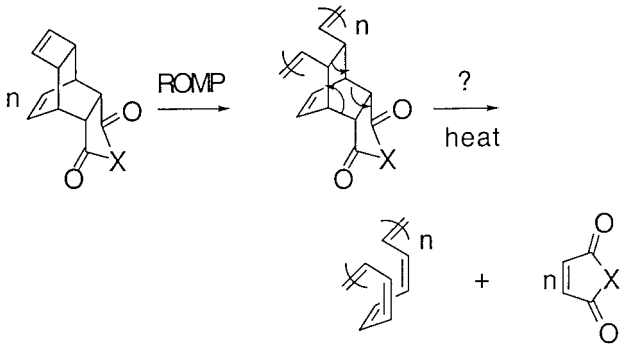
ABSTRACT: The ring-opening metathesis polymerization of cyclobutene-containing monomers based on the *endo*-tricyclo[4.2.2.0^{2,5}]deca-3,9-diene structure bearing cyclic anhydride and *N*-alkyl- or *N*-phenyl-substituted succinimides at the 7- and 8-positions was investigated. Well-defined molybdenum and ruthenium complexes were used as catalysts. $Cl_2Ru(CHPh)(PCy_3)_2$ (**III**) was shown to be the most suitable catalyst as a well-controlled and even living polymerization was observed. Mainly cis stereochemistry (≈75%) was observed in the main chain. Kinetic studies with different substituted succinimide moieties indicated that the polymerization rate depended on electronic effects in the monomer. ^{19}F NMR of fluorinated polymers suggests that through-space interactions between fluorine groups and the main polymer chain occur. These new polymers have a good thermal stability (304 °C < T_d < 344 °C). Upon hydrogenation, the *N*-methylsuccinimide functionalized polymer exhibited a T_g at 285 °C, and the thermal stability increased by about 100 °C.

Introduction

In the early 1980s, Feast et al. reported a new precursor route to polyacetylene that proceeded through a controlled retro Diels−Alder reaction on unsaturated polymers prepared via ring-opening metathesis polymerization.[1] Monomers based on the *endo*-tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene structure were polymerized with the classical WCl_6/Bu_4Sn system that gave polydisperse samples (PDI > 3). Later, well-defined oligomers were prepared in a living fashion from these same monomers using the Schrock carbene catalysts.[2] We too reported a precursor route to polyacetylene based on the retro Diels−Alder of furan derivatives from saturated polymers.[3] While both systems successfully yield polyacetylene, their utility is limited by the mass loss per double bond introduced equaling total weight losses of 60−80% and 90%, respectively.

Inspired by these promising results and determined to minimize the weight loss from these precursor polymers, we started investigating the ROMP of *endo*-tricyclo[4.2.2.0^{2,5}]deca-3,9-diene derivatives with fused functionalized rings at the 7- and 8-positions. A pericyclic elimination from the resultant materials would also yield polyacetylene (Scheme 1). The advantage here is that for each elimination three new double bonds are liberated. Because of the functionality present and our interest in controlled polymerization, only the well-defined initiators based on molybdenum and ruthenium were examined in this study.

Scheme 1

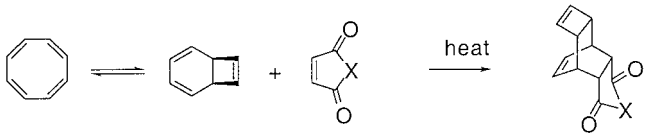


Results and Discussion

Monomer Preparation. Using a modified procedure, the *endo*-tricyclo[4.2.2.0^{2,5}]deca-3,9-diene monomers were prepared by a [4 + 2] cycloaddition reaction between 1,3,5,7-cyclooctatetraene (COT) and the desired dienophile to give exclusively the *endo*-polycyclic adduct (Scheme 2).[4] Substituted *N*-phenylmaleimides were synthesized by a one- or two-step procedure starting from maleic anhydride and functionalized aniline.[5,6]

In the [4 + 2] cycloaddition step, the yields varied from 30 to 85% depending on the electronic and steric characteristics of the dienophile. Lower yields were observed for the more electron-rich *N*-alkyldienophiles.

Scheme 2. Monomer Synthesis



monomer	X
1	O
2a	N-methyl
2b	N-tert-butyl
3	N-phenyl
4a	N-2-fluorophenyl
4b	N-4-fluorophenyl
4c	N-2,3,4,5,6-pentafluorophenyl
5	N-2-trifluoromethylphenyl
6	N-4-methoxyphenyl
7	N-2-tertbutylphenyl
8	N-2-trifluoromethoxyphenyl

Introduction of a bulky substituent at the ortho position(s) of the *N*-phenylmaleimide aromatic rings constrains the phenyl ring to a plane lying perpendicular to the maleimide ring. The steric hindrance presented by a very bulky ortho substituent appears to inhibit the cycloaddition reaction. Monomers **1**−**8** are all high melting point solids that can be purified by sublimation,

10.1021/ma0109875 CCC: $20.00
Published on Web 09/26/2001

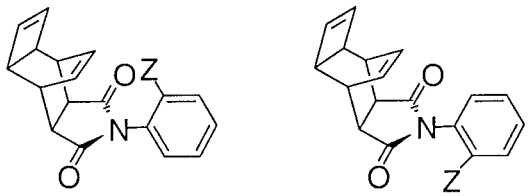


Figure 1. Endo−endo and endo−exo conformations.

recrystallization, or column chromatography. They are all soluble in chlorinated aliphatic solvents, acetone, and DMSO but poorly soluble in diethyl ether, hexane, and traditional aromatic solvents.

The NMR spectra of monomers **4a**, **4c**, **5**, **7**, and **8** bearing substituents at the ortho position(s) of the diimide ring indicated the presence of frozen rotamers resulting from the perpendicular orientation of the diimide aromatic ring relative to the plane of the succinimide ring. Therefore, two rotamers, or atropisomers, were observed, "endo−endo" or "endo−exo" (Figure 1), as indicated by the presence of two equal ^{19}F NMR signals for the ortho substituents of **4a** and **4c**. These are kinetically determined atropisomer populations, and as more bulky ortho substituents were introduced, this ratio changed and favored the "endo−exo" configuration. For **8**, a single compound was isolated by column chromatography, whereas the two atropisomers could be separated for both **5** and **7**. Nevertheless, isomerization occurs readily for **5** in chloroform at 25 °C, and therefore, polymerization could only be conducted on the thermodynamically controlled, atropisomeric mixture. After annealing **5** for 24 h at 50 °C, the rotamer ratio equilibrated to what we believe to be the thermodynamic distribution of 2.6 to 1. No isomerization was observed for **7** in solution, indicative of a higher activation energy for the rotation of the $N_{sp^2}-C_{sp^2}$ bond, and the two atropisomers could be separately characterized at room temperature (3.6:1 ratio). Interestingly, only one compound was observed upon Diels−Alder cycloaddition of cyclopentadiene and *N*-2-*tert*-butylphenylmaleimide.[6]

Polymerization Studies. The first polymerization trials were conducted with monomer **1** that was readily prepared by the Diels−Alder reaction between cyclooctatetraene (COT) and maleic anhydride.[4] The commercially available catalysts Mo(NAr)(CHCMe$_2$Ph)(OCMe$_3$)$_2$, **I**, Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$), **II** (Ar = 2,6-diisopropylphenyl), and Cl$_2$Ru(CHPh)(PCy$_3$)$_2$, **III**, were used for the polymerizations in dichloromethane. Precipitation of the white polymer occurred instantaneously with the molybdenum catalysts whereas progressive precipitation over time was observed with **III**. These first results illustrate the characteristic higher activity of the group VI catalysts for the cyclobutene ring as compared to the first generation group VIII catalyst. Yields were therefore limited by this unavoidable precipitation of the growing polymer chains (up to 60% after 24 h). The solubility of the resulting polymers was limited to DMSO, and molecular weights were not determined. All of the NMR data were consistent with the expected structure for poly-**1**, but no quantitative data on the stereochemistry could be calculated because of an unfortunate overlap between the peaks of the NMR solvent (DMSO-d_6) and the 30−40 ppm region for the allylic protons of the main chain. At low [M]/[cat.] ratios of less than 50, the poly-**1** oligomers were soluble in acetone, but only when prepared using catalyst **III**. The poly-**1** prepared with **III** and 100 equiv of monomer did not display any noteworthy features in the DSC analysis, which suggests a rigid polymer backbone and surprisingly good thermal stability. No specific decomposition pattern could be observed by thermogravimetric analysis as a continuous weight loss occurred between 300 and 500 °C (T_d = 304 °C).

The solubility problems encountered when dealing with the anhydride moiety prompted us to prepare the *N*-phenylsuccinimide functionalized adduct **3**. In this case, no precipitation problems were encountered during the polymerization of **3** using any of the different catalysts. The resulting polymer, a pale-brown powder, was soluble in chloroform but insoluble in acetone, methanol, and hexane. The molybdenum catalysts lead to uncontrolled polymerizations. A trimodal molecular weight distribution was observed with **I** whereas catalyst **II** lead to a polydisperse unimodal distribution (PDI = 1.3−1.4). This is reminiscent of the results we obtained with catalyst **II** for the ROMP of 3,4-disubstituted cyclobutenes.[7] With catalyst **I**, however, a living polymerization of the 3,4-disubstituted cyclobutenes was observed, which is distinctly different from our results in this study.

The ruthenium catalyst **III** gave much better results in terms of controlled polymerization, which is consistent with its attenuated activity relative to the molybdenum catalysts. The molecular weight of poly-**3** prepared using **III** had a narrow distribution (PDI < 1.1) and depended linearly on the monomer-to-catalyst ratio—both observations being consistent with a lack of chain transfer. The kinetic studies, however, of the polymerization showed that the monomer consumption did not strictly follow a first-order rate law (indicating possible chain termination). Also, a narrow, high molecular weight peak (approximately 3 times the M_n of the main peak) was usually observed. Polymerization studies indicated that this peak was present from the beginning of the polymerization, and its relative proportion progressively increased up to approximately 20%. This high molecular weight fraction did not increase when the reaction mixture was allowed to continuing stirring for 1 day after complete monomer consumption. This latter result argues against possible coupling reactions between active polymer chains,[8] and the origin of this second peak remains unknown.

The encouraging results achieved with the ruthenium catalyst **III** prompted us to study the ROMP of functionalized monomers similar to **3** with substituted *N*-phenylsuccinimide groups. Using the same polymerization conditions as for **3**, polymers from monomers **4** to **8** were obtained in 80−90% yields after 5 h with catalyst **III**. All the polymers were isolated as white powders. In all cases, the rate of polymerization was shown to be first order with respect to the monomer concentration, and the polymers displayed monodisperse molecular weight distributions (PDI ≈ 1.07−1.12) in most cases. The lone exception was poly-**4b**, which displayed a bimodal molecular weight distribution, with a narrow high molecular weight peak similar to poly-**3** being present.

No quantitative structural data were available for the *N*-phenylsuccinimide functionalized polymers because the allylic trans carbons usually overlapped with the aliphatic carbons α to the carbonyls (around 44 ppm) in ^{13}C NMR. Therefore, we decided to prepare *N*-alkylsuccinimide functionalized polymers with the hope that

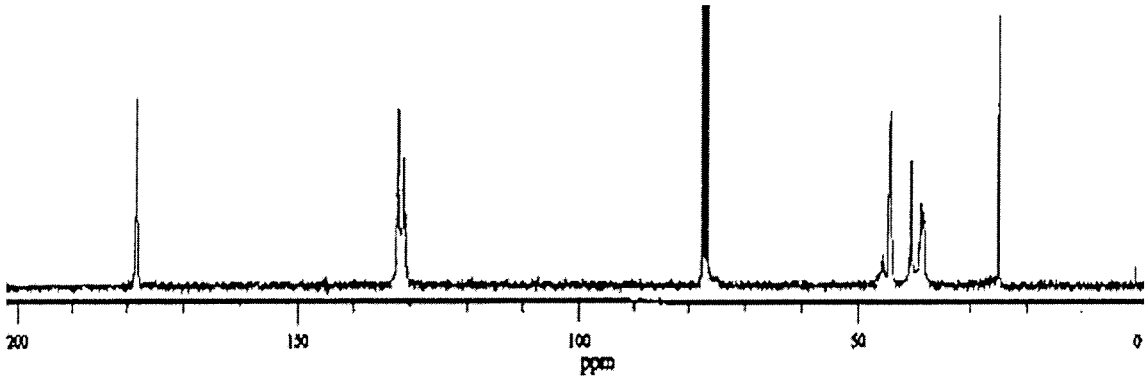


Figure 2. ^{13}C NMR spectrum of poly-**3** ($CDCl_3$).

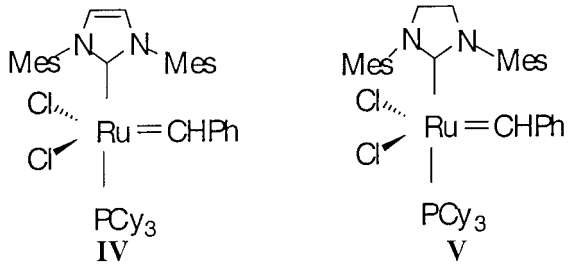


Figure 3. Ruthenium carbene catalysts **IV** and **V**.

a variation in the electronic effects of the substituent in the succinimide moiety would allow differentiation between the allylic carbons of the polymer chain. Polymers from **2a** and **2b** were readily prepared in a living fashion with **III**. The allylic trans carbons of the polymer distinctively appeared at 45.5 ppm, 5 ppm downfield from the carbons α to cis double bonds (Figure 2). Integration indicated a cis double bond content in the polymers of 75%. As a point of comparison, a 58% cis double bond configuration is observed for poly(bicyclo[3.2.0]heptene) prepared using a similar Grubbs' catalyst.[9] The high cis content contrasts with the usual high trans (>80%) content for polynorbornenes prepared with catalyst **III**.[10] No tacticity could be defined due to a lack of comparison materials, but multiple carbon resonances for most of the atoms in the repeat unit suggested an atactic structure.

With the exception of monomers **2** and **4b**, living polymerizations were achieved for all other monomers using the ruthenium catalyst **III**. This catalyst exhibits a uniquely well-controlled behavior with these potentially reactive cyclobutene monomers as illustrated by the fact that the polymerization of norbornene is not controlled at all under the same conditions.[16] Furthermore, even though the potentially reactive [2.2.2] strained ring is present within each repeat unit, they do not appear to be susceptible to attack by the active propagating species as evidenced by the lack of cross-linking or gelling phenomena. Polymerization trials with the more active ruthenium catalysts **IV**[11] and **V**[12] (Figure 3) resulted in less controlled polymerizations that produced polymers with much higher PDIs. This result is consistent with poor initiation efficiency at room temperature and significant chain transfer during the fast propagation stages.

Influence of the Succinimide Moiety. A slight variation in the yields of polymerizations performed for fixed times with monomers having different substituents on the succinimide moiety prompted us to study the influence of the substituents on the kinetics of the polymerizations. In all cases, the monomer consumption was a first-order kinetic process, which indicated a lack of chain termination. The relative polymerization rate varied from 1 for **4c** to 2.24 for **2a** (Table 1). Such influence is surprising as the succinimide group is not located next to the cyclobutene coordination site. But, the polymerization rates can be correlated to electronic effects: as the electronic donation ability of the succinimide moiety increases, polymerization proceeds faster. This result seems reasonable vis-à-vis the proposed mechanism for ROMP with catalyst **III**.[13] A more electron-rich cyclobutene certainly helps stabilize the 14-electron metallocyclobutane intermediate.

Table 1. Relative Polymerization Rates[a]

monomer	relative polymerization rate	monomer	relative polymerization rate
4c	1	**5**	1.62
8	1.16	**2b**	2.02
4a	1.29	**2a**	2.24
6	1.6		

[a] Conditions: $CDCl_3$, [M] = 0.2 M, 20 equiv.

Characterization of the Fluorinated Monomers. ^{19}F NMR of the fluorinated polymers revealed some interesting structural details. For poly-**4a** prepared with **III**, two peaks resulting from the two possible rotamers were observed in a 1:1 ratio at 42.2 and 44.7 ppm. But the peak at 44.7 ppm in the ^{19}F spectrum appeared as two overlapping peaks whereas in the monomer spectrum, it was a sharp singlet. We believe that this feature results from the interaction of the fluorine substituent with the remaining olefin double bond in the repeat unit. This double bond is itself sensitive to the main polymer chain. This explanation is also consistent with the features of the ^{19}F NMR spectrum of poly-**5a** in which a broad singlet was present at 100.5 ppm and overlapping peaks appeared around 101.0 ppm (Figure 4).

The same characteristics were present in the spectrum of poly-**4c** and allowed differentiation between the nonequivalent ortho fluorine groups. The multiplet around 17.8 ppm (one F from integration) accounts for the "endo−endo" ortho fluorine that interacts through space with the cyclic olefin whereas the "endo−exo" ortho fluorine is present at 20.8 ppm as a broad singlet (Figure 5).

The ^{19}F NMR spectra of poly-**4c** and poly-**5a** prepared with catalyst **III** and catalyst **V** contained a different pattern for the multiplet peak. We believe the fine structure of the fluorine resonances results from different microstructures of the polymers (cis/trans double

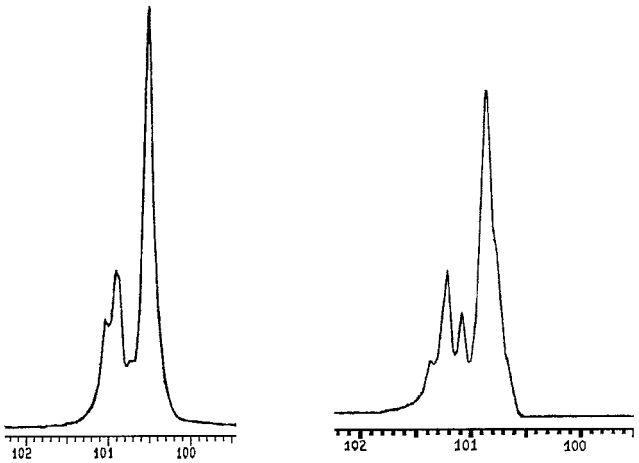


Figure 4. ^{19}F NMR spectra of poly-**5** prepared with catalysts **III** and **V**.

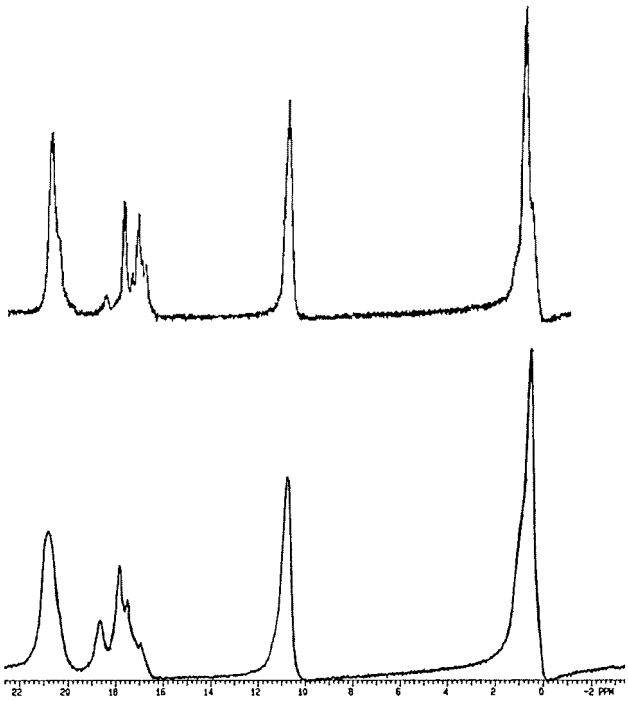


Figure 5. ^{19}F NMR spectra of poly-**4c** prepared with catalysts **III** and **V**.

bonds and/or tacticity). More detailed investigations using NMR techniques are currently underway.

Thermal Stability and Hydrogenated Polymers. For all of these unsaturated ROMP polymers, no T_g was observed from room temperature to their decomposition point (ca. 300 °C). Thermogravimetric analysis indicated that the T_d varied from 304 to 344 °C, the anhydride being less stable than the succinimide moiety. Those data are consistent with the expected rigidity of the polymer chains and indicate surprisingly good thermal stability of these polymers. This last observation runs counter to our expectation that the retro-pericyclic reaction yielding conjugated polymers will occur through ejection of the succinimide group. We are currently synthesizing monomer analogues that will eject aromatic molecules, and these results will be reported shortly.

We wanted to investigate whether a noticeable change would be observed in those properties upon hydrogenation. Using *p*-toluenesulfonhydrazide, the main chain

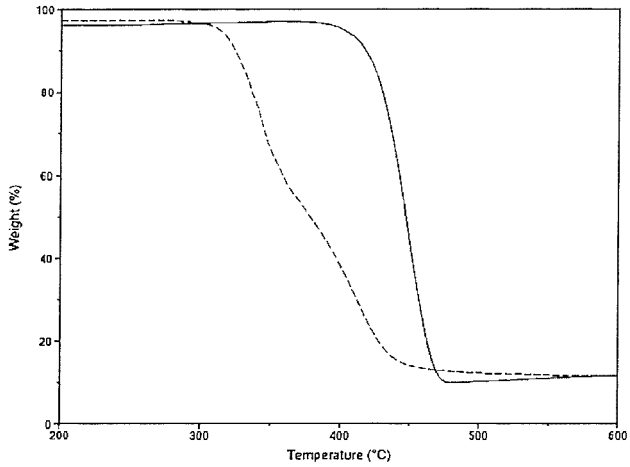


Figure 6. TGA analysis of poly-**3** (– – –) and hydrogenated poly-**3** (—).

of poly-**2a** could be fully hydrogenated while the olefin of the polycyclic structure was hydrogenated to approximately 85% as indicated by ^{1}H NMR. The resulting saturated polymer is a beige shiny solid. Consistent with the loss of a semirigid backbone, a T_g was now observed at 285 °C. Also, the T_d was increased by almost 100 °C to 423 °C, and the weight loss occurred steadily over a short-range from 400 to 470 °C (Figure 6). This remarkable improvement of the thermal stability is related to the preparation of a saturated polymer backbone less sensitive to radical decomposition.

Conclusion

In conclusion, a new family of functionalized cyclobutenes were prepared and could be polymerized by controlled ring-opening metathesis polymerization using the Grubbs' catalyst $Cl_2Ru(CHPh)(PCy_3)_2$. The polymerization rate is surprisingly dependent on the electronic character of the succinimide moiety despite their remote position relative to the reactive cyclobutene.^{19}F NMR suggests that through-space interactions occur between fluorine groups and the main polymer chain. It is possible that ^{19}F NMR could be used as a probe to specify the stereochemistry (cis/trans ratio or tacticity) of the fluorinated polymers presented. All polymers exhibit a good thermal stability with a T_d above 300 °C. The already good thermal stability could be improved by another 100 °C upon hydrogenation of the side and main polymer chains, and a high T_g was then observed.

Experimental Section

General. All polymerizations were carried out in a MBraun UNILab drybox under an argon atmosphere at ambient temperature using dry and degassed solvents (MBraun solvent system). Unless otherwise stated, materials were obtained from commercial suppliers and used without further purification. Catalysts **I**, **II**, and **III** were purchased from Strem Chemicals, Inc., whereas **IV**[14] and **V**[15] were prepared according to the literature. Maleimides for the synthesis of **2a** and **3** were commercialy available. Maleimides for the preparation of **2b**, **4b**, **4c**, **5**, **6**, and **8** were prepared in a two-step procedure similar to the reported one for the maleimide precursor of **4a**.[5] The maleimide precursor to **7** was prepared in one step.[6] Purified monomers were dried for 24 h under high vacuum at 40 °C before being transferred and stored under argon in the drybox. Melting points were measured using a DSC 2920 TA Instrument. ^{1}H and ^{13}C {^{1}H} NMR spectra were recorded using a 300 MHz GE NMR Omega spectrometer using $CDCl_3$ or DMSO-d_6 containing 1% TMS as an internal standard. ^{19}F

NMR experiments were performed using a 300 MHz Varian-Gemini spectrometer in $CDCl_3$, and C_6F_6 was used as an internal 0 ppm reference. Infrared spectra were acquired on a Jasco FT/IR-410 spectrometer; wavenumbers in cm^{-1} are reported for characteristic peaks. Molecular weight and molecular weight distribution were measured via gel permeation chromatography using a Jasco PU-1580 pump and a Jasco RI-1530 refractive index detector. The stationary phase consisted of two PL-Gel mixed C columns. Chloroform was used as the mobile phase. Molecular weights are relative to narrow molecular weight polystyrene standards (Pressure Chemical, Inc.). Thermal analyses were performed using Hi-Res TGA 2950 and DSC 2920 TA instruments using a nitrogen purge and heating rates of 10 °C/min. Elemental analysis were performed by Atlantic Microlab, Inc.

Monomer Synthesis: 7,8-*N*-Methylsuccinimide *endo*-Tricyclo[4.2.2.0$^{2.5}$]deca-3,9-diene (2a). To 1,3,5,7-cyclooctatetraene (2.08 g, 0.02 mol) under argon was added *N*-methylmaleimide (2.11 g, 0.02 mol), and the resulting neat mixture was progressively heated with an oil bath. It was kept at 155−165 °C for 1$^1/_2$ h as TLC indicated complete disappearance of the maleimide. The mixture solidified upon cooling. It was titrated with a small amount of diethyl ether, and the crude product was recovered by filtration and dried under vacuum. Recrystallization from hexane/ethyl acetate yielded a white, flocculent solid of **3** (3.19 g, 74%); mp 175−176 °C. ^{1}H NMR δ: 5.87 (m, 4H), 3.17 (br, 2H), 2.90 (s, 3H), 2.82 (br, 2H), 2.79 (s, 2H). ^{13}C {^{1}H} NMR δ: 179.05, 138.17, 128.41, 44.27, 43.56, 36.74, 24.72. IR: 3032 (w), 2947, 2912, 1771, 1689, 1556 (w), 1434, 1374, 1280, 1241, 1134, 1001, 970, 850, 792, 762, 680, 643. Anal. Calcd for $C_{13}H_{13}O_2N$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.62; H, 6.18; N, 6.47.

7,8-*N*-*tert*-Butylsuccinimide *endo*-Tricyclo[4.2.2.0$^{2.5}$]-deca-3,9-diene (2b). By a procedure similar to **2a**, in 3 mL of chlorobenzene, shiny white flakes of **2b** (0.70 g, 27%) were obtained; mp 201−202 °C. ^{1}H NMR δ: 5.89 (m, 4H), 3.12 (br, 2H), 2.78 (br, 2H), 2.63 (m, 2H), 1.51 (s, 9H). ^{13}C {^{1}H} NMR δ: 180.14, 138.14, 128.38, 58.33, 44.34, 43.24, 37.16, 28.50. IR: 3051 (w), 3021 (w), 2971, 2933, 1770 (w), 1690, 1458, 1365, 1355, 1340, 1259, 1161, 1001, 852, 812, 712, 683, 651. Anal. Calcd for $C_{16}H_{19}O_2N$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.39; H, 7.51; N, 5.41.

7,8-*N*-Phenylsuccinimide *endo*-Tricyclo[4.2.2.0$^{2.5}$]deca-3,9-diene (3). By a procedure similar to **2a**, **3** (5.0 g, 90%) was obtained as a white powder; mp 241−242 °C. ^{1}H NMR δ: 7.38 (m, 3H),7.19 (d, J = 7.5 Hz, 2H), 6.01 (m, 2H), 5.92 (s, 2H), 3.27 (br, 2H), 2.95 (s, 2H), 2.87 (br, 2H). ^{13}C {^{1}H} NMR δ: 178.04, 138.17, 132.10, 129.25, 128.74, 128.61, 126.70, 44.24, 43.53, 37.19. Anal. Calcd for $C_{18}H_{15}O_2N$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.80; H, 5.57; N, 5.02.

7,8-*N*-2-Fluorophenylsuccinimide *endo*-Tricyclo-[4.2.2.0$^{2.5}$]deca-3,9-diene (4a). By a procedure similar to **2a**, in 0.5 mL of chlorobenzene, **4a** (4.5 g, 75%) was recovered as a white powder; mp 220−221 °C. ^{1}H NMR δ: 7.38 (m, 1H), 6.03 (t, J = 3.6 Hz, 2H), 5.93 (s, 2H), 3.28 (br, 2H), 3.01 (br, 2H), 2.88 (s, 2H). ^{13}C {^{1}H} NMR δ: 177.27, 138.17, 131.06, 130.96, 129.41, 128.64, 128.48, 124.70, 116.97, 116.72, 44.17, 44.04, 43.92, 43.75, 37.10. ^{19}F NMR δ: 42.65, 44.58. IR: 3046, 2978, 2916, 2900, 1778, 1714, 1595, 1504, 1463, 1385, 1287, 1272, 1242, 1182, 818, 808, 793, 766, 742, 719, 676. Anal. Calcd for $C_{18}H_{14}O_2NF$: C, 73.21; H, 4.78; N, 4.74. Found: C, 73.00; H, 4.86; N, 4.86.

7,8-*N*-4-Fluorophenylsuccinimide *endo*-Tricyclo-[4.2.2.0$^{2.5}$]deca-3,9-diene (4b). By a procedure similar to **2a**, in 5 mL of chlorobenzene, **4b** (4.4 g, 70%) was recovered as a white crystalline powder; mp 227−228 °C. ^{1}H NMR δ: 7.18 (m, 4H), 6.00 (m, 2H), 5.92 (s, 2H), 3.27 (br, 2H), 2.95 (br, 2H), 2.88 (s, 2H). ^{13}C {^{1}H} NMR δ: 177.98, 163.99, 138.17, 128.61, 128.48, 127.93, 116.42, 116.13, 44.21, 43.50, 37.16. ^{19}F NMR δ: 49.84. IR: 3048, 2941, 2912, 1772, 1704, 1601, 1507, 1396, 1291, 1234, 1218, 1192, 1150, 844, 820, 787, 713. Anal. Calcd for $C_{18}H_{14}O_2NF$: C, 73.21; H, 4.78; N, 4.74. Found: C, 73.26; H, 4.95; N, 4.88.

7,8-*N*-2,3,4,5,6-Pentafluorophenylsuccinimide *endo*-Tricyclo[4.2.2.0$^{2.5}$]deca-3,9-diene (4c). By a procedure similar to **2a**, in 2 mL of chlorobenzene, **4c** (1.20 g, 70%) was recovered as a white powder; mp 218−219 °C. ^{1}H NMR δ: 6.02 (m, 2H), 5.93 (s, 2H), 3.27 (br, 2H), 3.07 (s, 2H), 2.88 (s, 2H). ^{13}C {^{1}H} NMR δ: 175.75, 143.68 (dm, J = 255 Hz), 142.27 (dm, J = 257 Hz), 138.20, 138.04 (dm, J = 248 Hz), 128.61, 107.41 (td, J = 14.5, 4.9 Hz), 44.30, 43.95, 37.10. ^{19}F NMR δ: 20.75 (dt, J = 16.6, 5.4 Hz, 1F), 18.92 (dt, J = 22, 5.6 Hz, 1F), 10.75 (t, J = 22 Hz, 1F), 1.02 (m, 2F). IR: 3044, 2978, 2958, 2924, 1780, 1724, 1662, 1520, 1481, 1364, 1304, 1289, 1179, 1148, 1132, 1021, 991, 822, 805, 697, 683. Anal. Calcd for $C_{18}H_{10}O_2NF_5$: C, 58.86; H, 2.74; N, 3.81. Found: C, 58.94; H, 2.73; N, 3.92.

7,8-*N*-2-Trifluoromethylphenylsuccinimide *endo*-Tricyclo[4.2.2.0$^{2.5}$]deca-3,9-diene (5). By a procedure similar to **2a**, an atropisomeric mixture of **5** (2.56 g, 74%) was recovered after column chromatography purification (hexane/ethyl acetate); mp 171−172 °C. ^{1}H NMR δ: 7.78 (d, J = 7.5 Hz, 2H), 7.61 (m, 2H), 7.17 (d, J = 7.8 Hz, 0.15H), 7.10 (d, J = 7.8 Hz, 0.85H), 6.08 (m, 1.8H), 6.02 (m, 0.2H), 5.93 (s, 2H), 3.29 (br, 2H), 3.05 (m, 1.8H), 2.99 (m, 0.2H), 2.88 (br, 2H). ^{13}C {^{1}H} NMR δ: 177.79, 138.17, 133.36, 130.84, 130.74, 130.09, 129.06, 128.83, 128.41, 127.57 (q, J = 4.8 Hz), 128.25, 126.52 (q, J = 259 Hz), 44.46, 44.34, 44.14, 43.69, 36.94, 36.74. ^{19}F NMR δ: 101.07 (s, 0.26F), 100.54 (s, 2.74F). IR: 3041, 2944, 2908, 1780, 1719, 1607, 1588, 1502, 1457, 1381, 1319, 1274, 1179, 1163, 1129, 1111, 1060, 1033, 850, 793, 763, 744, 680. Anal. Calcd for $C_{19}H_{14}O_2NF_3$: C, 66.09; H, 4.09; N, 4.06. Found: C, 66.11; H, 4.12; N, 4.17.

7,8-*N*-4-Methoxyphenylsuccinimide *endo*-Tricyclo-[4.2.2.0$^{2.5}$]deca-3,9-diene (6). By a procedure similar to **2a**, in 7 mL of chlorobenzene, **6** (4.50 g, 75%) was recovered as white shiny flakes; mp 213 °C. ^{1}H NMR δ: 7.11 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 6.01 (br, 2H), 5.92 (s, 2H), 3.82 (s, 3H), 3.27 (br, 2H), 2.94 (s, 2H), 2.88 (s, 2H). ^{13}C {^{1}H} NMR δ: 178.33, 159.66, 138.17, 128.61, 127.93, 124.73, 114.58, 55.64, 44.27, 43.46, 37.16. IR: 3055, 2976, 2938, 2900, 2840, 1771, 1703, 1605, 1511, 1436, 1397, 1294, 1255, 1195, 1163, 1026, 844, 810, 787, 710, 683. Anal. Calcd for $C_{19}H_{17}O_3N$: C, 74.25; H, 5.57; N, 4.56. Found: C, 74.22; H, 5.65; N, 4.46.

7,8-*N*-2-*tert*-Butylphenylsuccinimide *endo*-Tricyclo-[4.2.2.0$^{2.5}$]deca-3,9-diene (7). By a procedure similar to **2a**, the two isomers of **7** (0.154 g, 46%) were recovered as white powders. They were separated using silica gel column chromatography (hexane/ethyl acetate, 2/1).

Endo−Exo Isomer (78%) R_f = 0.68. ^{1}H NMR δ: 7.54 (d, J = 8.1 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.24 (t, J = 7.2 Hz, 1H), 6.73 (d, J = 7.2 Hz, 1H), 6.08 (m, 2H), 5.92 (s, 2H), 3.30 (br, 2H), 2.98 (s, 2H), 2.87 (br, 2H). ^{13}C {^{1}H} NMR δ: 179.34, 148.03, 138.17, 131.03, 130.74, 129.83, 129.06, 128.70, 127.54, 44.30, 43.72, 36.94, 35.71, 31.77.

Endo−Endo Isomer (22%) R_f = 0.45. ^{1}H NMR δ: 7.52 (dd, J = 8.1, 1.5 Hz, 1H), 7.35 (td, J = 7.5, 1.5 Hz, 1H), 7.25 (td, J = 7.8, 1.5 Hz, 1H), 6.73 (dd, J = 7.8, 1.5 Hz, 1H), 6.04 (m, 2H), 5.92 (s, 2H), 3.30 (br, 2H), 2.97 (s, 2H), 2.88 (br, 2H). IR: 3037, 2959, 2914, 1771, 1703, 1491, 1445, 1381, 1291, 1239, 1184, 1073, 850, 793, 756, 700, 682. Anal. Calcd for $C_{22}H_{23}O_2N$: C, 79.25; H, 6.95; N, 4.20. Found: C, 79.36; H, 6.99; N, 4.15.

7,8-*N*-2-Trifluoromethoxyphenylsuccinimide *endo*-Tricyclo[4.2.2.0$^{2.5}$]deca-3,9-diene (8). By a procedure similar to **2a**, **8** (2.15 g, 80%) was recovered as a beige solid after silica gel chromatography purification (R_f = 0.67, hexane/ethyl acetate (2:1)). One single compound is observed on TLC, but two isomers can be seen in solution. Atropisomeric mixture mp 102−103 °C. ^{1}H NMR δ: 7.41 (m, 3H),7.21 (m, 0.58H), 7.15 (m, 0.42H), 6.04 (m, 2H), 5.93 (s, 2H), 3.28 (br, 2H), 3.04 (s, 0.44H), 2.99 (s, 0.56H), 2.88 (br, 2H). ^{13}C {^{1}H} NMR δ: 177.07, 145.12, 144.92, 138.17, 130.80, 130.09, 129.93, 128.67, 128.48, 127.48, 127.38, 124.83, 124.66, 121.43, 121.01, 120.37 (q, J = 257 Hz), 44.17, 43.62, 37.07, 36.90. ^{19}F NMR δ: 104.88 (s, 1.74F), 104.41 (s, 1.26F). IR: 3047, 2948, 2911, 1780, 1718, 1504, 1460, 1386, 1291, 1255, 1217, 1180, 791, 764, 748, 720, 683. Anal. Calcd for $C_{19}H_{14}O_3NF_3$: C, 63.16; H, 3.90; N, 3.88. Found: C, 63.17; H, 3.93; N, 3.94.

Typical Polymerization of 3 Using III. To **3** (262 mg, 200 equiv) dissolved in 2.5 mL of CH_2Cl_2 was added a solution of **III** (5.4 mg, 0.5 mL of CH_2Cl_2) under vigorous stirring. The mixture progressively turned from purple/pinkish to dark yellow and was stirred for 5 h at room temperature. The polymerization was quenched by adding few drops of ethyl vinyl ether and stirred for 30 min. It was taken out of the drybox, slightly concentrated, and added dropwise to methanol under vigorous stirring. The precipitated polymer was recovered by filtration and dried under vacuum. It was further purified by redissolution with CH_2Cl_2 and subsequent precipitation with methanol. A brown pale flocculent solid was recovered (225 mg, 86%). ^{1}H NMR δ: 6.32 (br, 2H), 5.16 (br, 2H), 3.15, 3.10, 2.95, 2.88, 2.85, 2.69 (br, 9H). ^{13}C {^{1}H} NMR δ: 178.43, 132.13, 131.13, 130.84, 45.63, 44.37, 44.11, 40.52, 38.68, 38.20, 24.79.

Typical Polymerization of 4c Using III. To **4c** (223 mg, 100 equiv) dissolved in 2.5 mL of CH_2Cl_2 was added a solution of **III** (5.0 mg, 0.5 mL of CH_2Cl_2) under vigorous stirring. The mixture progressively turned from purple/pinkish to dark yellow and was stirred for 5 h at room temperature. The polymerization was quenched by adding few drops of ethyl vinyl ether and stirred for 30 min. It was taken out of the drybox, slightly concentrated, and added dropwise to methanol or hexane under vigorous stirring. The precipitated polymer was recovered by filtration and dried under vacuum. It was further purified by redissolution with CH_2Cl_2 and subsequent precipitation with methanol. A white powder was recovered (171 mg, 77%). ^{1}H NMR δ: 6.40 (br, 2H), 5.19 (br, 2H), 3.47, 3.33, 3.24, 3.01, 2.75 (br, 8H). ^{13}C {^{1}H} NMR δ: 174.90, 143.55 (d of m, J = 255 Hz), 142.67 (dm, J = 183.8 Hz), 137.95 (dm, J = 262 Hz), 132.26 (m), 131.09, 107.00, 44.92−44.69 (m), 40.23, 39.29−38.20 (m). ^{19}F NMR δ: 20.85 (br, 1F), 18.7, 17.9, 17.5, 16.95 (br, 1F), 10.87 (br, 1F), 0.65 (br, 2F).

Kinetic Studies Experiment Using Catalyst III. In a Teflon-valve NMR tube, 100 μL of a stock solution of **III** (23.2 mg, 400 μL of $CDCl_3$) was added to a solution of the desired monomer (20 equiv, 600 μL of $CDCl_3$) and 1,2-tetrachloroethane (5 μL) used as an internal reference. In those conditions, [monomer] = 0.02 M. The chronometer was started, and the monomer disappearance was followed by ^{1}H NMR for a total time of $2^1/_2$ h′ at 22.5 °C. Evolution of the cyclobutene peak or the cyclobutene and side olefin peaks with respect to the reference were recorded over time.

Hydrogenation of Poly-3. 2 g (10-fold excess) of *p*-toluenesulfonhydrazide was added to 95 mg of poly-**3** (D_p = 200) in xylene (10 mL). The mixture was heated at 120 °C for 6 h under vigorous stirring. It was then poured in methanol, and a yellow pale solid was recovered by filtration. It was centrifuged several times in acetone to remove traces of the byproduct. After drying under vacuum, a shiny yellow pale solid (60 mg) was recovered. ^{1}H NMR δ: 5.68 (br, 0.29H), 3.02, 2.96, 2.90 (br, 5H), 2.17, 2.12, 1.88, 1.65, 1.45, 1.36, 1.17 (br, 10H). ^{13}C {^{1}H} NMR δ: 180.18, 131.50 (m), 45.60−44.75 (m), 39.45−39.30 (m), 38.70−38.20 (m), 29.30−29.00 (m), 27.30−27.20 (m), 27.00−26.30 (m), 24.85, 16.75−15.75 (m).

Acknowledgment. The authors acknowledge financial support of this work from the NSF.

References and Notes

(1) Edwards, J. H.; Feast, W. J.; Bott, D. C. *Polymer* **1984**, *25*, 395. Feast, W. J.; Taylor, M. J.; Winter, J. N. *Polymer* **1987**, *28*, 593. Jones, C. A.; Lawrence, R. A.; Martens, J.; Frien, R. H.; Parker, D.; Feast, W. J.; Logdlund, M.; Salaneck, W. R. *Polymer* **1991**, *32*, 1200.
(2) Park, L. L.; Schrock, R. R.; Stiegliz, S. G.; Crowe, W. E. *Macromolecules* **1991**, *24*, 3489.
(3) Safir, A. L.; Novak, B. M. *Macromolecules* **1993**, *26*, 4072.
(4) Reppe, V. W.; Schlichting, O.; Klager, K.; Toepel, T. *Liebigs Ann. Chem.* **1948**, *560*, 1.
(5) Barrales-Rienda, J. M.; Gonzales Ramos, J.; Sanchez Chaves, M. *J. Fluorine Chem.* **1977**, *9*, 293.
(6) Curran, D. P.; Geib, S.; DeMello, N. *Tetrahedron* **1999**, *55*, 5681.
(7) Perrott, M. G.; Novak, B. M. *Macromolecules* **1995**, *28*, 3492. Perrott, M. G.; Novak, B. M. *Macromolecules* **1996**, *29*, 1817.
(8) Ivin, K. J.; Mol, C. In *Olefin Metathesis and Metathesis Polymerization*; Academic Press: London, 1997.
(9) Wu, Z.; Benedicto, A. D.; Grubbs, R. H. *Macromolecules* **1993**, *26*, 4975.
(10) Amir-Ebrahimi, V.; Corry, D. A.; Hamilton, J. G.; Thompson, J. M.; Rooney, J. J. *Macromolecules* **2000**, *33*, 717.
(11) Weskamp, T.; Kohl, F. J.; Hieringer, W.; Gleich, D.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2416. Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674.
(12) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903.
(13) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887.
(14) Arduengo, A. J. III U.S. Patent 5 077 414, 1991. Scholl, M.; Trnka, T. M.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247.
(15) Hutchins, R. O.; Su, W.; Sivakumar, R.; Cistone, F.; Stercho, Y. P. *J. Org. Chem.* **1983**, *48*, 3412. Saba, S.; Brescia, A.; Kaloustian, M. K. *Tetrahedron Lett.* **1991**, *32*, 5031. Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953.
(16) The ROMP of norbornene with **III** is characterized by a slow initiation but a very fast propagation with chain transfer reactions occurring. Polydisperse samples are achieved (example: [**III**] = 0.003 M, [norbornene]/[**III**] = 500, M_n = 11 200, PDI = 7.1).

MA0109875