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Highly Stereoselective Ruthenium-Catalyzed Ring-Opening Metathesis Polymerization of 2,3-Difunctionalized Norbornadienes and Their 7-Oxa Analogues

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ABSTRACT: The ring-opening metathesis polymerization (ROMP) of 2,3-difunctionalized norbornadienes and their 7-oxa analogues catalyzed by $[RuCl_2(p\text{-cymene})]_2$ in the presence of trimethylsilyldiazomethane (TMSD) yields high-trans, highly tactic polymers. A tentative mechanism involving arene loss, carbene formation, and monomer chelation is presented. The ROMP of 2,3-dicarbomethoxynorbornadiene served as a test reaction to investigate the influence of the various experimental parameters (reaction time and temperature, nature of the solvent and catalyst, and TMSD initiation conditions). An all-trans, highly tactic (>79%) polymer was obtained under a wide variety of conditions. Strikingly, the addition of tricyclohexylphosphine had a detrimental influence on the polymerization yield and stereoselectivity. The procedure was successfully applied to various other 2,3-dicarboalkoxynorbornadienes, benzonorbornadiene, and their 7-oxa analogues. In the case of the diester monomers, an increase in the alkyl substituent size led to a decrease of the polymer trans content and tacticity. Because of the ruthenium catalyst's ready availability and marked resistance to oxygen and water, reactions were very easy to set up and to carry out.

Introduction

Ring-opening metathesis polymerization (ROMP),[1] acyclic diene metathesis (ADMET),[2] and ring-closing metathesis (RCM)[3] are transition-metal-catalyzed reactions of prime importance for both cleaving and forming C=C double bonds.[4] Since the visionary proposition by Hérisson and Chauvin in 1970 that metal alkylidenes are active species in this type of reactions,[5] significant advances in the design of efficient, well-defined, one-component olefin metathesis catalysts have been achieved. A milestone was laid in the mid-1980s with the discovery by Schrock et al. of relatively stable, well-characterized alkylidene complexes based on early transition metals, in particular, molybdenum and tungsten.[6] Another strong impetus came from the development of ruthenium-based catalysts in the early 1990s. The most notorious representative of this new generation of olefin metathesis catalysts is the metal−alkylidene complex $RuCl_2(=CHPh)(PCy_3)_2$ developed by Grubbs and co-workers.[7] This complex, along with similar mono- and bimetallic species, has found numerous applications in both ROMP and RCM over the past few years.[8] At approximately the same time as Grubbs and co-workers, we have shown that readily available ruthenium complexes of the type $RuCl_2(\text{arene})(PR_3)$ are versatile and efficient promoters for the ROMP of both strained and low-strain olefins when activated by a suitable carbene precursor such as trimethylsilyldiazomethane (TMSD).[9,10] Formation of the most active ROMP catalysts was achieved by adding basic and sterically demanding phosphines (typically tricyclohexylphosphine) to dimeric $[RuCl_2(\text{arene})]_2$ complexes and, more specifically, to $[RuCl_2(p\text{-cymene})]_2$ (*p*-cymene is 1-isopropyl-4-methylbenzene). As a convenient alternative to preformed complexes, catalyst precursors were also prepared in situ by the addition of the phosphine ligand to the ruthenium dimer followed by introduction of a monomer. When a diazo compound was added to the reaction mixture, polymerization took place with no apparent induction time and high yields of polynorbornenes and polyoctenamers were obtained.[10] Strikingly, attempts to polymerize 2,3-dicarbomethoxynor-

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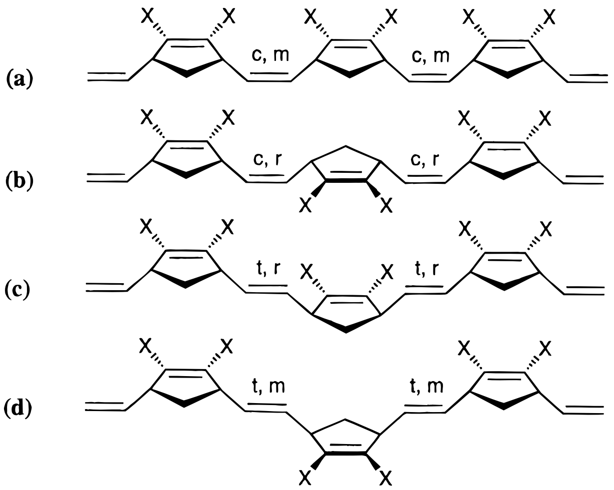


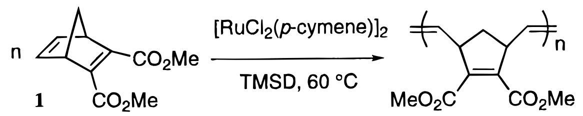
Figure 1. The four possible regular structures of 2,3-disubstituted norbornadienes: (a) cis, isotactic; (b) cis, syndiotactic; (c) trans, syndiotactic; and (d) trans, isotactic.

bornadiene (bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid dimethyl ester, **1**) gave unexpected results. Not only was the corresponding ROM polymer formed in higher yields in the absence of any phosphine, but also it had a highly stereoregular structure, as evidenced by NMR analysis.[11] To further sustain these observations, we have launched a detailed study of the polymerization of differently substituted norbornadienes in the presence of $[RuCl_2(p\text{-cymene})]_2$. In this article, we report the synthesis and the polymerization of a number of simple 2,3-difunctionalized norbornadienes and their 7-oxa analogues under a variety of experimental conditions.

2,3-Disubstituted norbornadienes are particularly suited for a systematic investigation of ring-opening polymerization for several reasons. First, experience reveals that ROMP invariably occurs by cleavage of the less hindered and more electron-rich unsubstituted double bond.[4] Second, the stereochemistry of the polymer is determined only by the cis or trans configuration about the double bond formed upon ring opening and by the meso or racemic configuration of the chiral allylic carbons in the cyclopentene rings on each side of the double bond. Meso dyads give rise to an isotactic polymer, whereas racemic dyads are responsible for a syndiotactic chain. Head/tail, tail/tail, and head/head regiochemistries are not encountered if the monomer is symmetrically substituted. Therefore, only four regular primary structures are possible for the polymer, as illustrated in Figure 1. Third, 2,3-disubstituted norbornadienes are readily synthesized by Diels−Alder reaction between cyclopentadiene (or furan in the case of their 7-oxa analogues) and an appropriate disubstituted alkyne. Depending on the substituent nature, it is possible to alter the steric and electronic properties of the monomer while keeping unchanged the bicyclic unit responsible for the polymer backbone. Thus, a set of closely related polymers can easily be prepared and used to investigate the influence of the monomer structure on the outcome of the reaction.

Results

Polymerization of 2,3-Dicarbomethoxynorbornadiene. In the course of our exploratory work on the $[RuCl_2(p\text{-cymene})]_2$ + TMSD catalytic system, we were able to polymerize **1** in tetrahydrofuran or chlorobenzene at 60 °C in the absence of any phosphine.[11] Conversions did not exceed 50%, but we deemed these results promising enough to launch a systematic study of the reaction and to investigate the influence of the various experimental parameters on the polymer yield and microstructure (see eq 1).



First, we carried out the ROMP of our probe substrate in various media. Thus, $[RuCl_2(p\text{-cymene})]_2$ (0.025 mmol) was dissolved in 4 mL of the following organic solvents under the exclusion of air and moisture: 1,2-dimethoxyethane, 1,2-dichloroethane, chlorobenzene, toluene, and tetrahydrofuran. Besides being polar, these liquids have a boiling point higher than 60 °C, a prerequisite for our system. Preliminary experiments showed indeed that temperatures within the 60−80 °C range were mandatory for observing relatively fast reaction kinetics. Next, 5 mmol of **1** was added and the reaction mixture was stirred a few min at 60 °C before 1 mL of 0.1 M TMSD diluted in the reaction solvent (0.1 mmol) was added dropwise over a 30 min period. The reaction mixture was kept at 60 °C for 6 h. It was then poured into a large volume of methanol to precipitate the poly(2,3-dicarbomethoxynorbornadiene) formed. The polymer was dried under dynamic vacuum and characterized by GPC and NMR spectroscopy. No precipitation took place when the reaction was carried out in 1,2-dimethoxyethane. Results obtained with the other solvents are gathered in Table 1. In all cases, only single sets of signals were observed for each carbon atom by $^{13}C\{^1H\}$ NMR spectroscopy. Comparison of the chemical shifts with those reported for *cis*-[12] and *trans*-poly(**1**)[13] indicated that only the trans polymer was formed under our reaction conditions. ^1H NMR spectroscopy confirmed this analysis: only trans olefinic protons and methine protons adjacent to trans double bonds (at 5.40 and 3.51 ppm in $CDCl_3$, respectively) were visible. With the exception of the sample prepared in toluene, all of the polymers obtained in this series of experiments had relatively broad molecular weight distributions. GPC traces were unimodal and PDIs ranged between 1.7 and 1.9 (see Figure 2b for a typical trace). We shall come back to these observations later, but it can be pointed out already that living ROMP does not occur under our reaction conditions. Because the highest yield of polymer was obtained in tetrahydrofuran, we elected this solvent as the reaction medium for all of our subsequent investigations.

In a second set of experiments, $[RuCl_2(p\text{-cymene})]_2$ was replaced by various other $[RuX_2(\text{arene})]_2$ catalyst precursors, where X = Cl or Br and arene = benzene or durene (durene is 1,2,4,5-tetramethylbenzene). The polymerizations were again initiated with TMSD. A separate run was also carried out with Grubbs' ruthenium−alkylidene complex $RuCl_2(=CHPh)(PCy_3)_2$. For the sake of comparison, 0.05 mmol of this catalyst dissolved in 5 mL of dry THF was reacted with the usual 5 mmol of **1** at 60 °C for 6 h in the absence of TMSD. Thus, the monomer/ruthenium molar ratio and the relative concentrations were identical for all experiments.

All of the $[RuX_2(\text{arene})]_2$ listed in Table 2 gave very similar results. This corroborates earlier observations made while screening the catalytic activity of numerous

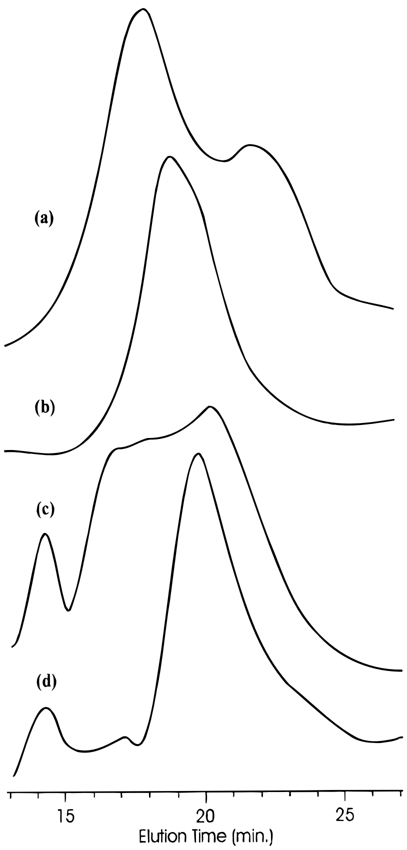


Figure 2. GPC traces of poly(**1**) prepared using as catalysts: (a) $RuCl_2({=}CHPh)(PCy_3)_2$, (b) $[RuCl_2(p\text{-cymene})]_2$ in the presence of TMSD, (c) $[RuCl_2(p\text{-cymene})]_2 + 2\ PCy_3$ in the presence of TMSD, and (d) $[RuCl_2(p\text{-cymene})]_2 + 4\ PCy_3$ in the presence of TMSD.

Table 1. Polymerization of 2,3-Dicarbomethoxynorbornadiene in Various Solvents

solvent	yield, %	M_n	M_w/M_n	% trans
1,2-dichloroethane	22	19 000	1.8	100
chlorobenzene	30	26 000	1.9	100
toluene	49	30 000	1.4	100
tetrahydrofuran	86	46 000	1.7	100

Table 2. Polymerization of 2,3-Dicarbomethoxynorbornadiene in the Presence of Various Ruthenium Catalysts

catalyst	yield, %	M_n	M_w/M_n	% trans
$[RuCl_2(benzene)]_2$	84	33 000	2.0	100
$[RuCl_2(durene)]_2$	77	53 000	1.7	100
$[RuCl_2(p\text{-cymene})]_2$	86	46 000	1.7	100
$[RuBr_2(p\text{-cymene})]_2$	89	80 000	1.9	100
$RuCl_2({=}CHPh)(PCy_3)_2$	26	25 000[a]	4.9[a]	45

[a] Global integration of a bimodal distribution; see Figure 2a.

ruthenium−arene complexes toward norbornene polymerization.[10] It confirms that the nature of the coordinated halogen and arene are of relatively minor importance and do not alter significantly the catalyst performance when the reactions are initiated by a small amount of TMSD. Recourse to the preformed ruthenium−alkylidene complex $RuCl_2({=}CHPh)(PCy_3)_2$, on the other hand, gave totally different results. The polymer was formed in low yield and had a broad bimodal molecular weight distribution as evidenced by GPC (Figure 2a). These poor results are not surprising. The experimental conditions adopted, in particular the relatively high temperature, possibly induce a rapid degradation of the initial carbene initiators, and the absence of TMSD prevents any replenishment of the reaction medium. More significant was the absence of stereocontrol. ^1H NMR analysis revealed that the trans content was reduced to 45%,[14] and the presence of three broad signals at 38.8, 37.9, and 37.1 ppm in the ^{13}C NMR spectrum indicated a lack of tacticity. Indeed, the resonance for what was C_7 in a norbornadiene monomer[15] is highly sensitive to the relative orientations of adjacent five-membered rings in a polymer chain. NMR data obtained by Schrock et al. for *all-cis*-poly(**1**) clearly show that three resonances are often observed for C_7, usually in a nonstatistical fashion.[16] If one moves downfield from TMS, these resonances are attributed to syndiotactic (*rr*), atactic (*rm*/*mr*), and isotactic (*mm*) triads, respectively. Expansion of the C_7 region for our *all-trans*-poly(**1**) reveals the presence of only one sharp peak at 37.9 ppm, with a small shoulder to lower frequency (Figure 3a). So, we can assume that we are seeing two partially resolved triad signals. Deconvolution and integration of the two overlapping peaks indicate that our polymer is 79% tactic, but it is not possible to assign the specific stereochemistry from these data only.

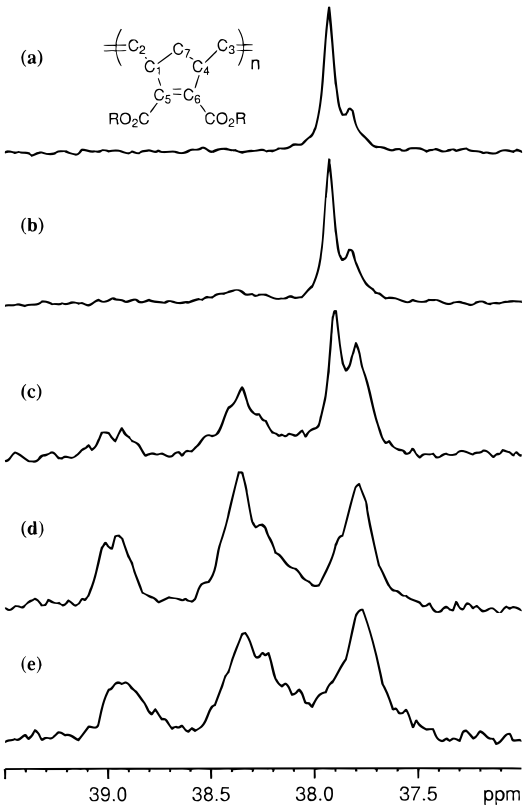


Figure 3. C_7 region of the 100.613 MHz ^{13}C NMR spectra in $CDCl_3$ of poly(**1**) prepared using $[RuCl_2(p\text{-cymene})]_2$ as catalyst in the presence of TMSD and (a) 0, (b) 0.5, (c) 1, (d) 2, and (e) 4 molar equiv of PCy_3.

A deeper insight into the problem of tacticity came from investigations on the influence of added phosphine on our ruthenium catalyst. Tricyclohexylphosphine was the ligand of choice in our previous work on cyclooctene polymerization.[10] The relative amount of PCy_3 needed to reach a maximum activity was investigated. A phosphine/ruthenium molar ratio equal to or greater than 1 was required to achieve satisfactory conversion of the monomer. Grubbs and co-workers also noted that replacing triphenylphosphine by tricyclohexylphosphine in their metal−alkylidene complexes boosted the cata-

Table 3. Influence of the Phosphine/Ruthenium Molar Ratio on the Polymerization of 2,3-Dicarbomethoxynorbornadiene

PCy_3/Ru ratio	yield, %	M_n	M_w/M_n	% trans
0	79	42 000	2.1	100
0.5	71	23 000	3.0	83
1	62	30 000[a]	3.5[a]	69
2	47	20 000[b]	2.0[b]	57
4	10	16 000	1.8	57

[a] Integration of the main peak group in a polymodal distribution; see Figure 2c. [b] Integration of the main peak in a trimodal distribution; see Figure 2d.

lytic activity toward low-strain cyclic olefins[17] as well as straight-chain alkenes.[18] To ascertain the role of the phosphine in the polymerization of norbornadienes, we have carried out the ROMP of **1** in dry THF using as catalyst a mixture of $[RuCl_2(p\text{-cymene})]_2$ and variable amounts of PCy_3 in the presence of TMSD. Table 3 describes the results obtained when the phosphine/ruthenium molar ratio was increased from 0.5 to 4. A joint control experiment in the absence of any phosphine is also reported.

Whereas PCy_3 seemed to play a crucial part in the polymerization of all of the olefins previously investigated, its influence on our test reaction is obviously detrimental. Adding 1 equiv of PCy_3/dimeric complex already has a marked influence on the outcome of the reaction. Most noticeable is the emergence of cis double bonds within the polymer structure, as reflected by significant changes in the ^1H and ^{13}C NMR spectra. The polymer yield is also slightly reduced while the molecular weight distribution broadens from 2.1 to 3.0. Further increases in the phosphine/ruthenium ratio lead to a steady drop in the yield. The trans content of the polymer, conversely, seems to reach a minimum value of 57% and no longer decreases when the PCy_3/Ru excess doubles from 2 to 4. The polymer mass profile follows yet another type of evolution. The polydispersity index first reaches a maximum value of 3.5 when the phosphine is introduced in stoichiometric proportion relative to ruthenium. The next time, when a 2- and a 4-fold excess of PCy_3 are added, a decrease of M_w/M_n occurs. The GPC trace obtained for a stoichiometric PCy_3/Ru ratio has a very distinct shape (Figure 2c). The complex mass distribution observed in this case probably arises from the coexistence of two or more types of chain initiators present in similar proportions and which grow chains independently. When the PCy_3/Ru ratio is 2, two small additional peaks, including one corresponding to high-mass polymers are still detected (Figure 2d), but the main peak has regained a unimodal profile. Only simple unimodal curves are observed when the PCy_3/Ru ratio is lower than 1 or greater than 2 (see Figure 2b for a typical GPC trace under these conditions). These experiments could be reproduced with a good fit of the GPC traces.

Additional information on the influence of PCy_3 on the polymer microstructure was obtained by examination of the C_7 region of the ^{13}C NMR spectra (Figure 3). As the phosphine proportion increases, two structural changes seem to take place. First, there is a reversal of magnitude between the two components of the original signal at 37.9 ppm. This can be related to a change of tacticity in the trans fraction of the polymer. Second, two new broad resonances emerge at ca. 38.9 and 38.3 ppm as the cis content increases. By comparison with earlier data obtained by Schrock et al. for *all-cis*-poly(**1**),[16] we tentatively assign these resonances to *mm* and *mr*/*rm* triads in cis/cis or cis/trans sequences, respectively. The corresponding *rr* resonances are expected to fall under the trans signal at 37.9 ppm, thus explaining in part its broadening. The fact that tacticity splitting results in much larger chemical shift differences for cis than for trans junctions is consistent with the fact that the cis junctions are more sterically crowded. Experimental evidence in favor of this assumption is indeed well-documented for other related norbornene and norbornadiene monomers.[19]

^1H, ^{13}C, and ^{31}P NMR analyses were also carried out on a stoichiometric mixture of monomer **1** and PCy_3 in $CDCl_3$. No sign of reaction between the ester and the phosphine could be detected even after heating the mixture for 7 h at 60 °C. The major change in solution involved partial oxidation of tricyclohexylphosphine into the corresponding oxide and subsequent degradation over prolonged reaction time.

Our next concern was to emphasize the role of the carbene precursor on the polymerization process. The standard conditions adopted so far implied the dropwise addition of a TMSD solution (0.1 mmol, TMSD/Ru = 2) to the warm reaction mixture (60 °C) over a 30 min period and stirring for an additional 5.5 h at 60 °C. No polymer was isolated when the reaction mixture was left at room temperature. This result can be attributed to a lack of reaction of the diazo compound, which prevents the formation of carbene initiators. Another control experiment was carried out at 60 °C in the absence of TMSD. In this case, *all-trans*-poly(**1**) was formed in a modest 29% yield. The polymer had a relatively low molecular weight and a rather large polydispersity (M_n = 23 000, M_w/M_n = 1.9). These figures reflect the poor efficiency of initiation when the carbene precursor is omitted. We have also varied the amount of diazo compound introduced and its rate of addition to the monomer and catalyst solution at 60 °C. It appears from these trials that the reaction is most efficient when the original standard conditions are followed (0.1 mmol of TMSD, 30 min addition time). Modifying the concentration of the TMSD solution or the rate of the syringe pusher used to add TMSD, or both, did not result in any dramatic improvement and sometimes had a detrimental influence on the polymerization outcome. Instantaneous addition of TMSD led to polymers with a relatively narrow distribution of high molecular weights (M_n = 85 000, M_w/M_n = 1.5), but the yield stagnated below 25%. As an alternative to TMSD, we have also investigated the use of ethyl diazoacetate. This diazoester is another commercially available carbene precursor which has been successfully employed in our group as a cyclopropanation reagent[20] or as an initiator for ruthenium-catalyzed ROMP of cycloalkenes.[21] When used in place of TMSD in our test polymerization of **1**, however, it did not give any polymeric products. We note in passing that in a related study on the use of vinylidene−ruthenium complexes to catalyze the ROMP of norbornene derivatives Katayama and Ozawa reported the unrivaled superiority of the trimethylsilylvinylidene species over various other aliphatic and aromatic derivatives. Although no exact reason for this superiority was given, the authors assumed that the particularly high stability of silylvinylidene complexes might account for their outstanding catalytic activity.[22]

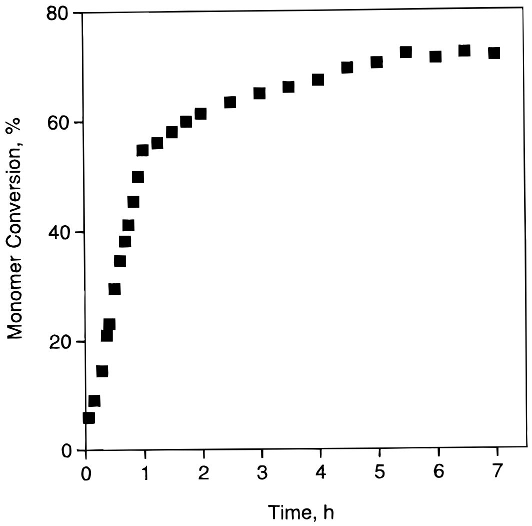


Figure 4. Time course of the polymerization of **1** (5×10^{-4} mol) in THF-d_8 (0.4 mL) at 60 °C using [RuCl$_2$(*p*-cymene)]$_2$ (2.5×10^{-6} mol) as a catalyst in the presence of TMSD (100 μL of a 0.1 M solution in hexanes/THF-d_8 added dropwise in 50 min).

Table 4. Influence of the Reaction Time on the Polymerization of 2,3-Dicarbomethoxynorbornadiene

reaction time, h	yield, %	M_n	M_w/M_n	% trans
1.5	61	38 000	2.0	100
3	78	43 000	1.8	100
4.5	84	49 000	1.9	100
6	83	49 000	1.8	100

All of the polymerizations carried out so far were terminated after 6 h by the precipitation of the poly(**1**) with methanol. In many cases, however, the reaction media became highly viscous by the end of the TMSD addition, i.e., after only 30 min, and no other sign of evolution was visible during the remaining 5.5 h. To acquire more precise information on the time course of the polymerization, we have monitored the conversion of monomer **1** into poly(**1**) by ^{1}H NMR spectroscopy of the alkene protons (Figure 4). The influence of TMSD on the reaction profile was blatant: repeated additions of 10 μL portions of the carbene initiator solution to the reaction mixture at 5 min intervals was accompanied by a steady increase of the polymer yield during the first hour of reaction. When the addition was finished and the NMR tube content was only stirred every 15 min, the monomer conversion significantly slowed and reached a maximum of 72% after 6 h.

We also have determined the yields and microstructures of polymer samples isolated after 1.5, 3, 4.5, and 6 h of reaction in dry THF at 60 °C, respectively (Table 4). It is important to stress that the data in Table 4 were not obtained by analyzing a single reaction mixture at various time intervals but came from four separate experiments run in parallel. Although the use of a syringe pusher allowed the steady addition of TMSD to the monomer and catalyst solutions, reactions frequently exhibited rather mediocre reproducibility. In general, careful repetitions of experiments led to yield variations of up to 10%, well below the 20–30%[23] or even 40%[24] ranges reported for ruthenium-catalyzed aqueous ROMP. Changes in molecular weight (M_n ±30 000) and polydispersities (M_w/M_n ±0.3) revealed the sensitivity of the polymer mass to slight variations of the reaction conditions, as already reported for related systems.[10] A potential cause for these variations is diffusion control of the reaction rate due to the high viscosities observed. The cis/trans ratios and the tacticities of the polymers obtained, on the other hand, were remarkably reproducible and remained unaffected by the weight distribution fluctuations. Keeping these observations in mind helped discriminate between significant tendencies and experimental artifacts in Table 4. Hence, one can conclude that the monomer conversion and the polymer chain length increase during the first 4.5 h of the reaction. The yield then levels off, and the molecular weights remain unchanged when the reaction time is extended to 6 h. These results nicely corroborated with those deduced from Figure 4. In this latter case, conversions were slightly lower, a likely consequence of the intermittent stirring. Polydispersities remained roughly unchanged over the time period spanned and only trans junctions were visible by NMR spectroscopy for all of the polymers isolated.

Table 5. Polymerization of 2,3-Dicarbomethoxynorbornadiene under Various Experimental Conditions

run	solvent, atm	yield, %	M_n	M_w/M_n	% trans
1	dry THF, N_2	79	42 000	2.1	100
2	99% THF, air	80	49 000	2.0	100
3	dry THF, O_2	51	46 000	1.7	100
4	dry THF + water,[a] air	56	36 000	1.8	100
5	dry THF + water,[b] air	6	26 000	1.8	89

[a] 0.0127 g, H_2O/Ru molar ratio = 14. [b] 0.0942 g, H_2O/Ru molar ratio = 103.

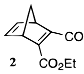
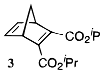
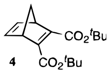
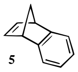
To conclude our systematic study of the polymerization of **1**, we tested the behavior of the [RuCl$_2$(*p*-cymene)]$_2$ + TMSD catalytic system in the presence of air or moisture or both. This is an important issue because it has direct implications on the scope of the reaction and its ease of setup and performance. Early ROMP catalysts suffered from severe limitations which strongly reduced their applicability. For instance, although tetrahydrofuran is a useful and valuable solvent for a wide variety of polymers, it acted as an efficient inhibitor for many of the conventional two component initiators [e.g., $WCl_6/(CH_3)_4Sn$].[25] Development by Schrock et al. of complex molybdenum and tungsten catalysts (cf. Introduction) improved the tolerance toward polar and functionalized monomers and solvents, but rigorous exclusion of air and moisture was still required.[6] Switching to ruthenium-based active species helped reduce the sensitivity to atmospheric oxygen and water, as moving to the right in the periodic table leads to softer, *d*-electron richer metal atoms which interact preferentially with olefins rather than with harder oxygen-containing derivatives.[26] The robustness of ruthenium–arene catalysts in protic solvents such as ethanol or ethanol/water was indeed evidenced by Mühlebach and co-workers for photoinduced ROMP.[27] Recourse to ruthenium–alkylidene complexes also expanded the scope of the ring-closing metathesis as Grubbs et al. demonstrated the persistent activity of $RuCl_2({=}CHCH{=}CPh_2)(PCy_3)_2$ in the presence of air and reagent-grade solvents.[28] Such a remarkable stability is also displayed by our [RuCl$_2$(*p*-cymene)]$_2$ catalyst, as evidenced by the data in Table 5. We were pleased to note that a polymerization carried out under normal atmosphere in 99% THF stabilized with 0.025% butylated hydroxytoluene taken straight from the bottle gave virtually identical results to those obtained using more cumbersome Schlenk techniques and THF distilled under argon (compare runs 1 and 2). This provides a good indication of the relative insensitivity of the reaction to oxygen, moisture, and adventitious impurities. Additional experiments under harsher conditions were also carried out in order to drive the system to its limits. The polymerization of **1** was first carried out in dry THF at 60 °C under pure oxygen (run 3). A significant reduction of yield ensued. This result seemingly contrasts with earlier observations by Rooney and co-workers.[29] While studying the polymerization of norbornene in the presence of well-defined electron-rich ruthenium complexes such as $RuCl_2(PPh_3)_4$, these authors found that the presence of oxygen significantly increased the rate of an otherwise slow ring-opening polymerization. Formation of oxometallacyclobutanes which generate metallacarbenes upon cleavage was held responsible for the initiation step, therefore explaining the beneficial role of oxygen.[29] In our system, the dropwise addition of TMSD to the reaction medium furnishes all of the necessary initiators, and the reaction proceeds quickly under inert atmosphere, as shown previously in Figure 4 and Table 4. Therefore, oxygen can only have a detrimental influence, perhaps because the resulting polymer is poorly stable under oxidative conditions (vide infra) or more likely because oxidation into Ru(III) species deactivates the catalyst. Addition of water to the ruthenium−arene dimer dissolved in dry THF also disrupts the polymerization process, but entries 4 and 5 in Table 5 clearly indicate that fairly high levels of hydration have to be reached before the reaction is almost completely thwarted.

Upon exposure to air and light for extended periods of time (up to 1 year), poly(**1**) became yellow and brittle. GPC analysis of aged samples showed a decrease in molecular weight and an increase in polydispersity, and IR analysis revealed the development of a new broad band at 3445 cm^{-1}. A combination of chain degradation and air oxidation is most likely responsible for this evolution, which is accelerated if the samples are kept in solution rather than in the dry state. The presence of highly reactive unsaturated C═C double bonds and tertiary allylic C−H bonds probably accounts for this behavior. Accordingly, the thermal stability of poly(**1**) was also limited. Differential scanning calorimetry (DSC) analysis indicated that the polymer had a nonreversible glass transition at 207 °C and began to degrade shortly thereafter.

Polymerization of Other 2,3-Difunctionalized Norbornadienes. Having established the influence of the various experimental parameters on the ROMP of **1**, we probed the generality of our catalytic system on other norbornadiene monomers. The diethyl (**2**), diisopropyl (**3**), and di-*tert*-butyl (**4**) esters of norbornadiene 2,3-dicarboxylic acid were prepared in a manner similar to their dimethyl counterpart (**1**), viz., by Diels−Alder reaction between cyclopentadiene and an appropriate dialkyl acetylenedicarboxylate. They were reacted with $[RuCl_2(p\text{-cymene})]_2$ + TMSD in dry THF at 60 °C using the standard experimental procedure. The ruthenium/TMSD/monomer molar ratio was 1/2/100. Reaction times of 3 or 6 h were adopted, in light of the results obtained for **1** (vide supra). The yields and characteristics of the polymers obtained are shown in Table 6.

No major change of reactivity occurred when the diethyl ester (**2**) was substituted for the usual dimethyl probe substrate (**1**). The polymerization rate was only slightly slower. The yield did not level off after 3 h but further increased from 61% to 83% when the reaction time was extended to 6 h. The molecular weight and the polydispersity also increased with the reaction time. ^1H NMR spectroscopy revealed the presence of only one sharp doublet at 5.40 ppm and one broad singlet at 3.50 ppm for olefinic and allylic resonances, respectively, in agreement with an all-trans microstructure.

Table 6. Polymerization of Various Norbornadienes

monomer	reaction time, h	yield, %	M_n	M_w/M_n	% trans
 2	3	61	71 000	1.6	100
	6	83	78 000	1.8	100
 3	3	54	87 000	1.7	85
	6	71	57 000	1.8	85
 4	3	44	99 000	1.7	61
 5	6	86	n. a.[a]	n. a.[a]	74[b]

[a] Data not available; see text for details. [b] In the soluble fraction; see text for details.

When the size of the alkyl substituent was further increased, the polymers obtained lacked a stereoregular structure and the reactions became even slower. Poly(2,3-dicarboisopropoxynorbornadiene) was formed in a satisfactory 71% yield after 6 h. The cis/trans ratio for junctions between two adjacent cyclopentene units was $^{15}/_{85}$ and remained unchanged whether the reaction was interrupted after 3 or 6 h. This ratio was calculated by the integration of the cis and trans olefinic proton resonances at 5.48 and 5.38 ppm in $CDCl_3$, respectively. Signals for methine protons adjacent to cis and trans double bonds (at 3.64 and 3.47 ppm in $CDCl_3$, respectively) gave an identical ratio. Particularly noteworthy is the *upfield* location of the olefinic trans resonance with respect to the corresponding cis signal. This is in complete contrast to the situation observed in poly(**1**) where the equivalent trans signal lies *downfield* from that of the cis. Such an inversion is not unprecedented in the poly(norbornene/norbornadiene) family, yet. For instance, a reversal of relative chemical shifts for cis and trans olefinic protons has already been reported when comparing poly(**1**) and its 7-oxa analogue.[30] We shall come back on this observation in the next section.

We also reached the conclusion that for poly(2,3-dicarbo-*tert*-butoxynorbornadiene) the correct sequence for olefinic proton resonances was cis (5.49 ppm) and trans (5.34 ppm) in $CDCl_3$. On the basis of this assignment, the cis/trans ratio in our sample is $^{39}/_{61}$. Integration of the methine protons did not bring any useful information in this case. Surprisingly, these hydrogen atoms remained unaffected by the cis or trans nature of the adjacent double bonds and gave a unique singlet at 3.41 ppm.

In contrast with *all-trans*-poly(**1**) whose C_7 resonance showed a tacticity splitting (cf. Figures 3a and 5a), the ^{13}C NMR spectrum of *all-trans*-poly(**2**) comprised only a neat singlet at 38.0 ppm for the methylene carbon resonance (Figure 5b). Peak tailing on the downfield face of C_7 resonance was first noticed for poly(**3**) and led to a distinct shoulder in the case of poly(**4**) (Figure 5c,d). This evolution, we felt, reflects the progressive appearance of cis double bonds within the polymer backbone. Deconvolution and integration of the two overlapping peaks for C_7 in poly(**4**) gave a cis/trans ratio of $^{30}/_{70}$, in moderate agreement with the $^{39}/_{61}$ value derived from

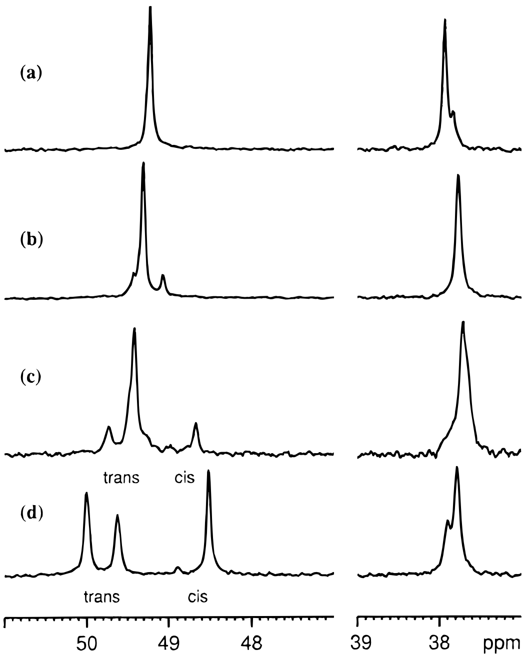


Figure 5. $C_{1,4}$ (left) and C_7 (right) regions of the 100.613 MHz ^{13}C NMR spectra in $CDCl_3$ of (a) *all-trans*-poly(**1**), (b) *all-trans*-poly(**2**), (c) 85% *trans*-poly(**3**), and (d) 61% *trans*-poly(**4**) prepared using $[RuCl_2(p\text{-cymene})]_2$ as catalyst in the presence of TMSD.[15]

^1H NMR spectroscopy. The downfield orientation of the cis signals with respect to their trans counterparts is consistent with earlier data obtained for miscellaneous other substituted polynorbornadienes, such as poly(**1**),[12,13] poly[2,3-bis(trifluoromethyl)norbornadiene],[25] or poly(7-methylnorbornadiene).[31] The chemical shift differences between cis and trans resonances are particularly small for our derivatives, however. Under these conditions, the apparent simplicity of the C_7 resonance for the poly(2,3-dicarboalkoxynorbornadienes) prepared using our ruthenium catalyst cannot be ascribed with certainty to a high degree of tacticity. Sensitivity of C_7 to structural variations at the triad level might not be visible because of overlapping between *rr*, *rm*, or *mm* signals. This is indeed a major concern, because we are dealing with high-trans polymers, and trans lines are usually sharper and less sensitive to incipient splitting than cis lines.[19]

A fine structure is however visible for $C_{1,4}$, $C_{2,3}$, $C_{5,6}$, and C=O in the high-field $^{13}C\{^1H\}$ spectra recorded for the series of poly(2,3-dicarboalkoxynorbornadienes) under consideration.[15] Examination of the $C_{1,4}$ region provided the most useful and reliable data because the various lines presented the highest chemical shift differences and were most easily assigned to cis or trans resonances. Indeed, a survey of the literature pertaining to metathesis polymers revealed that the allylic carbons adjacent to trans double bonds are always deshielded relative to their cis equivalents,[19] in agreement with earlier work on a series of linear alkenes.[32] We have therefore focused our attention on the $C_{1,4}$ (allylic) carbon resonances rather than on the $C_{2,3}$, $C_{5,6}$, or C=O signals whose positions and fine structures are more difficult to correlate with cis/trans ratios. *all-trans*-Poly(**1**) gave only a neat singlet at 49.3 ppm (Figure 5a). Reactions in the presence of tricyclohexylphosphine described previously (cf. Table 3) led to mixtures of cis and trans isomers. In these cases, a second well-shaped singlet grew concomitantly at 44.2 ppm (not shown), but no sign of tacticity splitting was ever detected for $C_{1,4}$. *all-trans*-Poly(**2**) led to a more complex pattern (Figure 5b). The presence of a predominant line strongly suggests that the polymer is highly tactic (on the basis of integration results, at least 76%), but we have no further argument to support this hypothesis at the present time. For poly(**3**) and poly(**4**), we tentatively propose a distinction between cis and trans lines in the $C_{1,4}$ region as indicated in Figure 5c,d. The assignment of the minor cis $C_{1,4}$ resonances in these spectra was not obvious given the appearance of a peak due to tacticity splitting at a similar location in *all-trans*-poly(**2**). Examination of integration data helped clear things up. Thus, for poly(**3**), the proposed separation between cis and trans lines led to a $^{14}/_{86}$ cis/trans ratio (Figure 5c), in excellent agreement with the $^{15}/_{85}$ value obtained by ^1H NMR spectroscopy. Again, one line obviously prevailed over the others, and we inferred a 85% tacticity for the trans fraction of the polymer. Signals in a cis environment were weaker and broader, so integration was less reliable, but the tacticity splitting was in the $^{20}/_{80}$ range. The cis content in poly(**4**) calculated from the four components of the $C_{1,4}$ resonance (Figure 5d) was also highly consistent with the value obtained from the olefinic protons in ^1H NMR spectroscopy ($^{38}/_{62}$ and $^{39}/_{61}$, respectively). Agreement with the ratio deduced from the partially resolved C_7 peak was far less satisfactory ($^{30}/_{70}$). The two lines observed for allylic carbons next to a trans junction were in a $^{57}/_{43}$ ratio, close to a statistical distribution. In the cis environment, conversely, a high degree of tacticity seemed to be present, because the two corresponding lines were in a $^{1}/_{99}$ ratio.

We have also polymerized benzonorbornadiene (**5**) using $[RuCl_2(p\text{-cymene})]_2$ + TMSD in dry THF at 60 °C (Table 6). The reaction medium quickly became highly viscous. When the polymerization was terminated after 6 h, the resulting thick gel could not be fully solubilized in chloroform before precipitation. The polymer was nevertheless isolated in a satisfactory 86% yield. Attempts to dissolve the dry solid in tetrahydrofuran or chloroform for GPC analysis gave only suspensions which turned dark yellow upon standing a few hours at room temperature. Such a color change and limited solubility were also observed by El-Saafin and Feast using the catalytic system $WCl_6/SnPh_4$ in toluene.[33] IR and ESCA analyses showed that poly(benzonorbornadiene) is rapidly oxidized by molecular oxygen.[33] This can be easily rationalized because each monomer unit contains two tertiary C−H bonds which are both allylic and benzylic. Therefore, a high susceptibility to direct oxidation is not surprising. The percentage of trans double bonds in the soluble fraction of our sample was 74%, judging from the ratio of the resonances for trans and cis olefinic protons (at 5.64 and 5.57 ppm in $CDCl_3$, respectively) or methine protons adjacent to cis and trans double bonds (at 4.12 and 3.72 ppm, respectively). This value should however be treated with care, as the properties of the soluble fraction may not reflect those of the bulk. Carbon NMR spectra were very similar to that recorded by Hamilton et al. for *high-trans*-poly(**5**) prepared using $RuCl_3 \cdot xH_2O$ as a catalyst.[34] In particular, the C_7 and $C_{2,3}$ regions revealed a complex set of overlapping peaks attributed to an atactic structure. This lack of stereoselectivity contrasts with the results obtained for 2,3-diesters of norbornadiene and will be discussed further when we consider the reaction mechanism.

In an attempt to elucidate the iso- or syndiotactic bias of our polymerization process, we have investigated the reaction of 2,3-bis(trifluoromethyl)norbornadiene. The ROMP of this monomer has been extensively studied and both the all-cis and high-trans (>98%) polymers were prepared and characterized using molybdenum-based catalysts.[12,13] The trans polymer had an unusually high relaxed dielectric constant ϵ_R which could be related to a predominantly syndiotactic structure in an elegant work by Hubbard and co-workers.[35] Because the $[RuCl_2(p\text{-cymene})]_2$ + TMSD-initiated ROMP of 2,3-dicarboalkoxynorbornadienes gave essentially trans products, we carried out a similar reaction with 2,3-bis(trifluoromethyl)norbornadiene. Applying our standard experimental procedure (with no phosphine added) gave a very disappointing result. Only a few percent of a tarry material was recovered after 6 h at 60 °C. NMR analysis of this residue indicated that it contained a mixture of *cis*- and *trans*-poly[2,3-bis(trifluoromethyl)norbornadiene] along with various impurities. When a 2-fold molar excess of tricyclohexylphosphine to ruthenium was added to the reaction mixture, initiation took place in a more satisfactory way, and an 86% yield was reached after 6 h. However, the polymer obtained under these conditions lacked stereoregularity. As found already for poly(**1**) (cf. Table 3 and Figures 2 and 3), the presence of phosphine led to a complex trimodal weight distribution. The cis/trans ratio derived from ^{1}H NMR analysis was $^{28}/_{72}$, and the C_7 region of the ^{13}C spectrum did not include any prominent feature and closely reflected earlier literature data.[25]

Norbornadiene itself also failed to react with $[RuCl_2(p\text{-cymene})]_2$ + TMSD in the absence of phosphine. When 2 equiv of tricyclohexylphosphine to ruthenium were added, a thick gel formed within minutes, and a quantitative yield of polynorbornadiene was isolated after 6 h at 60 °C. As expected, the opening of the second unsubstituted double bond present in the monomers led to cross-linking of the polymer and rendered the product completely insoluble in most organic solvents, thus preventing any NMR or GPC characterization.

Polymerization of 2,3-Difunctionalized-7-Oxanorbornadienes. We have prepared the dimethyl (**6**), diethyl (**7**), diisopropyl (**8**), and di-*tert*-butyl (**9**) esters of 7-oxanorbornadiene-2,3-dicarboxylic acid by Diels–Alder reaction between furan and the corresponding dialkyl acetylenedicarboxylates. As expected, the aromatic heterocycle was a less reactive diene than cyclopentadiene. Longer reaction times and higher temperatures were therefore required to achieve completion of the cycloadditions, particularly in the case of the bulky di-*tert*-butyl derivative. The monomers obtained were reacted with $[RuCl_2(p\text{-cymene})]_2$ + TMSD in dry THF at 60 °C using the standard experimental procedure (see eq 2). In all cases, the polymerizations were allowed to proceed for 6 h before the macromolecular products were precipitated from *n*-heptane. They were characterized by GPC and NMR spectroscopy, as described in Table 7.

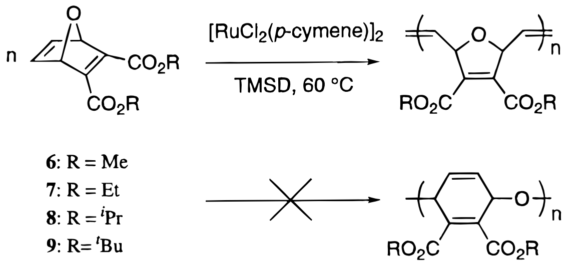
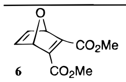
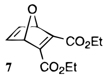
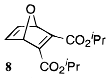
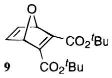
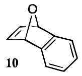


Table 7. Polymerization of Various 7-Oxanorbornadienes

monomer	solvent	yield, %	M_n	M_w/M_n	% trans
 6	THF	54	1700	1.6	98
	PhCl	20	2700	1.8	92
	CCl4	18	1000	1.4	98
 7	THF	48	9800	2.2	96
 8	THF	72	13 000	1.6	100
 9	THF	72	14 000	1.6	63
 10	THF	78	3500	2.9	89

Upon addition of TMSD, the solution of 2,3-dicarbomethoxy-7-oxanorbornadiene (**6**) and $[RuCl_2(p\text{-cymene})]_2$ quickly turned into a brown ocher suspension. Hence, the formation of oligomers insoluble in tetrahydrofuran can be invoked to justify the modest 54% yield and the low molecular weights obtained. We have tried to circumvent the problem by replacing tetrahydrofuran with chlorobenzene or carbon tetrachloride, but precipitation of poly(2,3-dicarbomethoxy-7-oxanorbornadiene) also occurred in these solvents, and results were even less satisfactory. In the case of 2,3-dicarboethoxy-7-oxanorbornadiene (**7**), the reaction medium quickly became viscous and a thick gel was obtained, but no sign of precipitation was visible. GPC analysis revealed that higher and broader molecular weights were attained, but the yield did not exceed 50%. Solutions of 2,3-dicarboisopropoxy-7-oxanorbornadiene (**8**) and 2,3-dicarbo-*tert*-butoxy-7-oxanorbornadiene (**9**) remained fluid throughout the reaction and behaved in very similar ways. In both cases, the polymer yield climbed to 72%, and the molecular weights passed the 10 000 threshold with a polydispersity index of 1.6. We note that in both the 7-methylene and the 7-oxa series polymers derived from dicarbomethoxynorbornadienes **1** or **6** had substantially lower molecular weights than those derived from all of the esters with larger alkoxy groups, but we have no satisfactory explanation for this observation so far.

The cis/trans ratio for all four poly(2,3-dicarboalkoxy-7-oxanorbornadienes) was deduced from their ^{1}H NMR spectra based on earlier assignments for poly(**6**).[36] Poly(**7**) displayed a main resonance at 5.81 ppm in $CDCl_3$ for trans olefinic protons, together with a small shoulder at 5.76 ppm for their cis counterparts. Methine protons adjacent to double bonds were better separated, with the main trans singlet lying at 5.37 ppm and a broad weak cis multiplet at ca. 5.47 ppm. In addition to the isopropyl group multiplets, poly(**8**) afforded only two sharp singlets at 5.77 and 5.33 ppm, indicative of an all-trans microstructure. The spectrum of poly(**9**) was more difficult to interpret. There was no obvious separation between cis and trans components within the two broad signals centered at 5.74 and 5.27 ppm for olefinic and allylic resonances, respectively. Deconvolution of these complex resonances and cross-examination with

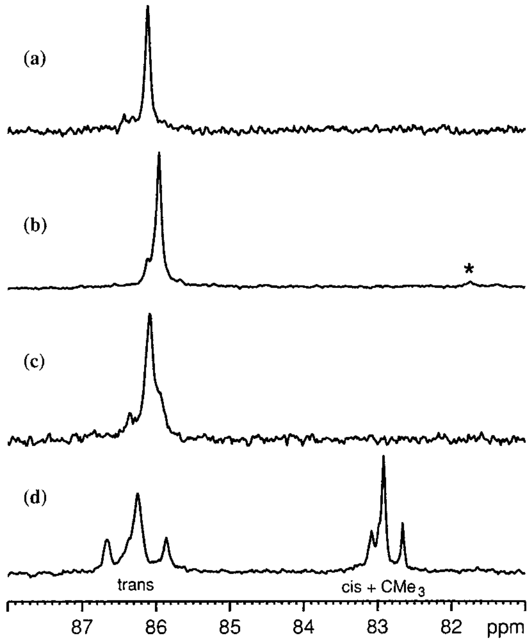


Figure 6. $C_{1,4}$ region of the 100.613 MHz ^{13}C NMR spectra in $CDCl_3$ of (a) 98% *trans*-poly(**6**), (b) 96% *trans*-poly(**7**), (c) *all-trans*-poly(**8**), and (d) 63% *trans*-poly(**9**) prepared using $[RuCl_2(p\text{-cymene})]_2$ as catalyst in the presence of TMSD.[15]

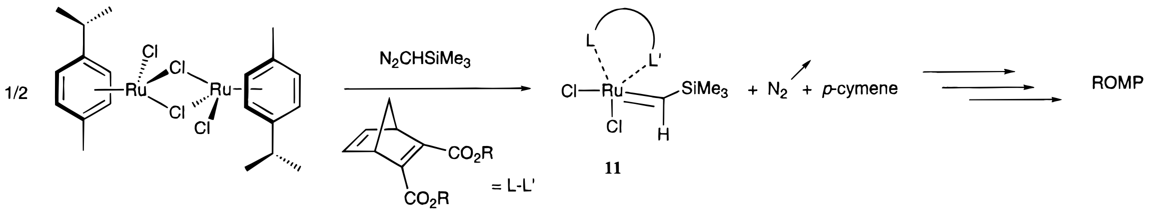
other ^1H and ^{13}C NMR data at hand allowed us to infer a $^{37}/_{63}$ cis/trans ratio.

The ^{13}C spectrum of our 98% *trans*-poly(**6**) comprised only one main resonance in the 81−88 ppm region, assigned to $C_{1,4}$ in a trans environment (Figure 6a). The corresponding cis line did not emerge from the baseline noise but is known to fall at 81.8 ppm. Both lines were observed by Hamilton and co-workers in the 93% trans polymer prepared using a $RuCl_3$ catalyst in chlorobenzene/ethanol at 60 or 100 °C.[30] The British group also observed two supplementary lines in the same region. These were assigned to poly(1,4-dihydrophenoxide) units present in a separate polymer formed by ring-opening of the oxa bridge (see eq 2). Such a side reaction was first reported by Novak and Grubbs when they employed highly Lewis acidic transition-metal catalysts for the ROMP of 7-oxanorbornenes.[37] Obviously, species such as WCl_6, $WOCl_4$, or to a lesser extent $RuCl_3$ preferentially coordinate to and cationically open the 1,4-bridging epoxide moiety. $[RuCl_2(p\text{-cymene})]_2$, on the other hand, is a weaker Lewis acid and exclusively cleaves the $C_2{=}C_3$ double bond. In the high-trans polymer prepared by Hamilton et al., the carbonyl carbon signal was basically a 1:2:1 triplet with further splitting of the downfield component. Because the polymer was known to be atactic from the spectra of its hydrogenated derivative, the primary triplet splitting was attributed to a sensitivity at the triad level, i.e., *mm*, *rr*, and *mr*/*rm*. With the same logic, the further splitting of the downfield component was assigned to a higher order sensitivity, e.g., *rmm*, *mmm* or *rrr*, *mrr*.[30] The C=O resonance for our 98% *trans*-poly(**6**) comprised only two overlapping components. Deconvolution and integration of these signals showed that they were in a $^{86}/_{14}$ ratio. Again, this result is indicative of a high stereoselectivity, but the exact iso- or syndiotactic bias of the polymer cannot be determined from NMR experiments only. If the change from a methyl to an ethyl resonance is disregarded, the ^{13}C spectrum of 96% *trans*-poly(**7**) closely matched that recorded for 98% *trans*-poly(**6**). The trans $C_{1,4}$ resonance at 86.0 ppm was slightly distorted, and the presence of 4% cis double bonds within the macromolecular chain led to a hardly visible new line at 81.8 ppm (marked with an asterisk in Figure 6b). The $^{13}C{=}O$ resonance at 162.2 ppm also included two overlapping peaks in a $^{88}/_{12}$ ratio. *all-trans*-Poly(**8**) displayed a very simple ^{13}C NMR spectrum. The apparent broadening and partial splitting of the $C_{1,4}$ resonance in Figure 6c is due most likely to the presence of monomer impurities in the starting material. GC and NMR analyses indeed revealed that the diisopropyl acetylenedicarboxylate used as a reagent to prepare 2,3-dicarboisopropoxy-7-oxanorbornadiene contained a few percent of the dimethyl and methylisopropyl diesters. Careful purification of the Diels−Alder adduct **8** failed to remove the last traces of the accompanying 7-oxanorbornadiene impurities which were therefore incorporated into the polymer and could induce local perturbations of the NMR signals. Genuine tacticity effects were observed when the more bulky di-*tert*-butyl ester **9** was polymerized with the $[RuCl_2(p\text{-cymene})]_2$ catalyst. Cis and trans exocyclic C=C double bonds were clearly visible in the $C_{1,4}$ region (Figure 6d). Their fine structures proved to be complex enough to prevent a more detailed assignment, particularly in the case of the cis signals, which coincided with the quaternary carbon resonance of the *tert*-butyl groups. Resonances for $C_{2,3}$, $C_{5,6}$, and C=O were even more complex and did not bring any further information. Thus, there was no easy way to quantify the change of tacticity induced by the replacement of smaller alkyl substituents with the *tert*-butyl group. This was a foreseeable conclusion. Contrary to the situation in high-trans (or high-cis) polymers, carbon atoms in a polymer sample of intermediate cis/trans content are subject to the influence of more remote structural variations and give more complex chemical shifts which often resist a rigorous assignment.

We terminated the experimental part of our study with the $[RuCl_2(p\text{-cymene})]_2$ catalyzed ROMP of 7-oxabenzonorbornadiene **10** (Table 7). The polymerization was carried out at 60 °C in dry THF according to the general procedure. The initial solution became a solid mass upon addition of TMSD. The reaction was interrupted after 3 h by addition of chloroform and precipitation from methanol. Contrary to the behavior of poly(benzonorbornadiene), poly(7-oxabenzonorbornadiene) remained soluble in chloroform. Thus, a GPC analysis was feasible. It revealed that the polymer formed had a low molecular weight ($M_n = 3500$, relative to polystyrene standards) and a broad unimodal polydispersity ($M_w/M_n = 3.5$). The observed solidification of the reaction mixture could possibly prevent monomer diffusion to the active polymerization sites and favor chain transfer instead. Polymer degradations can also result from oxidation processes. As pointed out by other groups for poly(**10**)[27,36] and already discussed for poly(**5**) in this article (cf. previous section), the presence within the polymer microstructure of both allylic and benzylic tertiary C−H bonds is a cause of instability.

To the best of our knowledge, the only NMR data available for poly(**10**) were published by Schrock et al. in 1991.[36] They concerned a 50% trans sample, so discrimination between cis and trans resonances was not achieved. This led to incomplete and erroneous assignments. One stereoisomer was clearly predominant in the product that we have obtained using the $[RuCl_2(p\text{-cymene})]_2$ + TMSD catalytic system, and we were

Scheme 1



able to clear up proton assignments using a combination of ^{1}H, ^{13}C, and H−C heteronuclear correlation spectroscopies. Two singlets at 79.5 and 84.0 ppm in the ^{13}C spectrum served as starting points. These were assigned to cis and trans $C_{1,4}$ resonances, respectively. Both their relative positions (trans being downfield of cis) and intensities (trans major, cis minor) were consistent with the various other data acquired during the course of this study and corroborated the fact that allylic carbons adjacent to trans double bonds are always deshielded relative to their cis equivalents, as discussed in the previous section. Correlation spectroscopy helped us to distinguish the allylic protons among the four signals present between 5.5 and 6.2 ppm. Therefore, the correct assignments for allylic protons are $\delta_{\mathrm{cis}} = 6.12$ and $\delta_{\mathrm{trans}} = 5.57$ ppm, and for olefinic protons $\delta_{\mathrm{cis}} = 5.74$ and $\delta_{\mathrm{trans}} = 5.94$ ppm in $CDCl_3$. A $^{89}/_{11}$ cis/trans ratio was calculated from both sets of integrals for our sample of poly(**10**). Aromatic protons resonated between 7.05 and 7.23 ppm. In ^{13}C NMR spectroscopy, the chemical shift difference between cis and trans lines was largest for the $C_{1,4}$ resonance. Tacticity splitting was observed for $C_{2,3}$ but seemed to affect only the cis part of the signal. Because the replacement of the C_7 methylene bridge of poly(**5**) by an oxygen in poly(**10**) had removed the most sensitive ^{13}C NMR probe, it was not possible to conclude with certainty the degree of tacticity of our sample.

Discussion

The procedure devised in this study affords easy access to highly stereoregular poly(2,3-dicarboalkoxynorbornadienes) and their 7-oxa analogues using commercially available air-stable catalyst precursors. Indeed, under appropriate activation conditions, ruthenium−arene dimers such as $[RuCl_2(p\text{-cymene})]_2$ are highly efficient yet very selective initiators for the ROMP of various norbornadiene derivatives. Highly stereoselective polymerization of this class of monomers had already been achieved by Schrock et al. using much more sophisticated molybdenum- and tungsten-based alkylidene catalysts, such as $Mo({=}CHCMe_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(O\text{-}t\text{-}Bu)_2$.[6] In sharp contrast, reactions with our ruthenium-based catalysts are very easy to set up and to carry out even in the presence of oxygen or water traces or both. Because the actual catalysts are generated in situ, the price to pay for the ease of implementation is a rather poor control over molecular weight and polydispersity. It is also difficult under these conditions to know the exact nature of the catalytic center and to provide a clear picture of the mechanistic pathway. It can be assumed, nevertheless, that activation of the ruthenium−arene dimer proceeds via arene loss and carbene formation. The intermediacy of a monometallic ruthenium trimethylsilylvinylidene chloride is indeed consistent with earlier literature results. Support in favor of a thermal arene displacement is provided by NMR observations[10] and DSC measurements[38] for the related $RuCl_2(p\text{-cymene})(PR_3)$ system, and the notorious metathesis activity of well-defined ruthenium alkylidene complexes, such as the Grubbs catalyst $RuCl_2({=}CHPh)(PCy_3)_2$[7] or the new N-heterocyclic carbene complexes developed by Herrmann et al.[39] strongly sustain the in situ formation of a ruthenium trimethylsilylvinylidene carbene from TMSD and our catalyst precursor. Chelation of the monomer to complete the coordination sphere of the ruthenium initiator is also very likely. The data that we have acquired for 2,3-dicarboalkoxynorbornadienes and their 7-oxa analogues strongly suggest that ester coordination to the metal center is of prime importance and results in highly ordered transition states, the key to the high stereoselectivity observed. If ester coordination is hindered or impossible, the polymers obtained lack stereoregularity. This was unambiguously evidenced when (i) the strongly coordinating tricyclohexylphosphine ligand was added to the reaction mixture, (ii) the bulky *tert*-butyl groups (and to a lesser extent the isopropyl groups) were substituted for the methyl or the ethyl substituents in 2,3-dicarboalkoxynorbornadienes, or (iii) other non-ester 2,3-difunctionalized norbornadienes and unsubstituted norbornadiene itself were polymerized.

At this point of our research, the exact nature of the active species remains, however, elusive, and we have no further indication of the ligand distribution around the metal center. In particular, all of our attempts to highlight coordination of monomer **1** with various ruthenium catalyst precursors have remained inconclusive so far. We nevertheless assume that the norbornadiene diesters can act as bidentate ligands and form chelates with ruthenium. Thus, we tentatively propose the hypothetical structure **11** as the initial 16-electron active species formed upon addition of TMSD and a diester monomer (symbolized by L−L′ in Scheme 1) to the $[RuCl_2(p\text{-cymene})]_2$ dimer. Initiation by a closely related complex was already postulated in our previous work on cyclooctene polymerization catalyzed by $[RuCl_2(p\text{-cymene})]_2$ in the presence of TMSD and tricyclohexylphosphine. In that case, the alkene could only act as a η^2 ligand and a monophosphine ruthenium−carbene complex was supposed to be formed in the presence of PCy_3.[10] Starting from the stable methylidene diphosphine complex $RuCl_2({=}CH_2)(PCy_3)_2$, Grubbs et al. also reached the conclusion that the major pathway for olefin metathesis involved olefin binding and phosphine dissociation to generate the actual carbene initiator.[40] This assumption was later substantiated by Snapper and co-workers who isolated and characterized a metathesis active complex derived from $RuCl_2({=}CHPh)(PCy_3)_2$ and cyclobutenes. X-ray diffraction confirmed that only one PCy_3 ligand was present.[41] Thus, the main difference between the present system and that of the previously described phosphine-containing ruthenium catalysts consists of the presence of a η^4 chelating monomer in place of the usual monophosphine ligand. This chelation imposes a severe steric constraint on the ruthenium complex. The subsistence of a vacant coordination site in intermediate **11** allows the possible coordination of a second monomer unit cis to the carbene moiety to afford an 18-electron species. We do not know at the present time if such a ligation is involved in the polymerization process or if the metallacyclobutane formation takes place via ring opening of the chelated monomer. As a matter of fact, all of the active ruthenium carbene complexes identified so far are 16-electron rather than 18-electron species.

Another important question which remains unanswered so far is whether the trans polymer chains prepared have an iso- or a syndiotactic bias. Because neither the monomers nor the catalysts used in this study are optically active, direct NMR methods could not be employed to argue for a given tacticity of the polymers formed. An absolute assignment of tacticity would be possible only if all-trans, highly tactic polymers could be prepared from enantiomerically pure monomers. Future work will be aimed toward the synthesis of 2,3-dicarboalkoxynorbornadienes derived from chiral alcohols and the structural analysis of their polymers. We are also currently investigating the solution equilibria resulting from the addition of TMSD to $[RuCl_2(p\text{-cymene})]_2$ to enlighten the intimate reaction mechanism, and we shall report our findings in due course.

Experimental Section

General Information. All reactions were performed under nitrogen using standard Schlenk techniques unless otherwise specified. NMR spectra were recorded on a Bruker AM400 spectrometer. ^1H and ^{13}C chemical shifts are listed in parts per million downfield from TMS. Infrared spectra were recorded on a Perkin-Elmer 1720X series FT-IR spectrometer with a selected resolution of 4 cm^{-1}. Gel permeation chromatography (GPC) was carried out on a Waters 600/610 HPLC system equipped with a Waters 410 differential refractometer detector and a battery of 3 Styragel HR columns fitted in series. Chloroform served as the eluent at a flow rate of 1.0 mL/min and a temperature of 40 °C. The molecular weights (not corrected) and polydispersities are reported versus monodisperse polystyrene standards. DSC analyses were performed with a DuPont 9000 DSC apparatus. The heating rate was 20 °C/min.

Materials. All of the solvents were freshly distilled from standard drying agents and kept under argon. 7-Oxabenzonorbornadiene was supplied by Acros under the name 1,4-epoxy-1,4-dihydronaphthalene. Norbornadiene, dimethyl, diethyl, and di-*tert*-butyl acetylenedicarboxylates were purchased from Aldrich. Diisopropyl acetylenedicarboxylate[42] and the ruthenium complexes $[ArRuX_2]_2$ (Ar = benzene, *p*-cymene, durene; X = Cl, Br)[43] were prepared as described in the literature. $RuCl_2(=CHPh)(PCy_3)_2$ was purchased from Strem. Trimethylsilyldiazomethane[44] (TMSD, from Aldrich) came as a 2 M solution in hexanes. This solution was further diluted by addition of a suitable solvent.

Synthesis of Monomers. The following monomers were prepared according to literature: 2,3-dicarbomethoxynorbornadiene,[45] 2,3-dicarbomethoxy-7-oxanorbornadiene,[46] benzonorbornadiene,[33] and 2,3-bis(trifluoromethyl)norbornadiene.[47]

2,3-Dicarboethoxynorbornadiene (2). Freshly distilled cyclopentadiene (4.3 g, 65 mmol) was added dropwise to cold (ice−water bath) diethyl acetylenedicarboxylate (8.5 g, 50 mmol) with stirring. The resulting mixture was slowly brought back to room temperature over a 4 h period. The solution was concentrated on a rotary evaporator, and the residue was distilled under reduced pressure to afford the pure product as a colorless oil (11.7 g, 99% yield): bp 115 °C/0.6 mmHg; IR (neat) ν 2983, 2943, 1708, 1626, 1369, 1260, 1152, 1055, 864 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.85 (d, 2H, CH=CH), 4.16 (q, 4H, OCH_2CH_3), 3.86 (m, 2H, =CHC*H*), 2.21 and 2.02 (dd, 2H, $CHCH_2CH$), 1.24 (t, 6H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 165.3 (C=O), 152.2 (=*C*−CO), 142.5 (=CH), 72.9 (OCH), 61.0 (OCH_2), 53.5 (CH_2), 14.2 (CH_3).

2,3-Dicarboisopropoxynorbornadiene (3). A mixture of cyclopentadiene (1.7 g, 26 mmol) and diisopropyl acetylenedicarboxylate (4.0 g, 20 mmol) was reacted as described above to afford **3** as a colorless oil becoming solid in the freezer (5.0 g, 95% yield): bp 112 °C/0.6 mmHg; IR (neat) ν 2982, 2942, 1708, 1627, 1362, 1266, 1158, 1095, 1049, 711 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.83 (t, 2H, CH=CH), 5.0 [m, 2H, $OCH(CH_3)_2$], 3.84 (m, 2H, =CHC*H*), 2.19 and 1.98 (dd, 2H, $CHCH_2CH$), 1.21 [d, 12H, $OCH(CH_3)_2$]; ^{13}C NMR ($CDCl_3$) δ 164.8 (C=O), 151.9 (=*C*−CO), 142.4 (=CH), 72.8 (OCH), 68.5 [$OCH(CH_3)_2$], 53.4 (CH_2), 21.8 (CH_3).

2,3-Dicarbo-*tert*-butoxynorbornadiene (4). Freshly distilled cyclopentadiene (0.9 g, 13 mmol) was added dropwise to cold (ice−water bath) di-*tert*-butyl acetylenedicarboxylate (2.3 g, 10 mmol) dissolved in dichloromethane (5 mL) with stirring. The resulting mixture was slowly brought back to room temperature over an 8 h period. The solution was concentrated on a rotary evaporator, and the residue was recrystallized from *n*-pentane to afford white needles of **4** (2.3 g, 80% yield): mp 86−87 °C; IR (KBr) ν 2986, 1735, 1698, 1630, 1368, 1342, 1273, 1147, 1098, 851 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.19 (t, 2H, CH=CH), 3.77 (m, 2H, =CHC*H*), 2.16 and 1.94 (dd, 2H, $CHCH_2CH$), 1.43 [s, 18H, $OC(CH_3)_3$]; ^{13}C NMR ($CDCl_3$) δ 164.7 (C=O), 152.2 (=*C*−CO), 142.6 (=CH), 81.6 (OC), 72.5 (OCH), 53.7 (CH_2), 28.4 (CH_3).

2,3-Dicarboethoxy-7-oxanorbornadiene (7). To a solution of diethyl acetylenedicarboxylate (8.5 g, 50 mmol) in dry benzene (20 mL) was added freshly distilled furan (5.1 g, 75 mmol). The resulting mixture was refluxed for 20 h in an oil bath at 90 °C using a capped efficient reflux condenser. The solution was concentrated on a rotary evaporator, and the residue was distilled under reduced pressure to afford the pure product as a yellow oil (10.2 g, 86% yield): bp 112 °C/0.7 mmHg; IR (neat) ν 2985, 2941, 1709, 1641, 1393, 1260, 1109, 1020, 882 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13 (s, 2H, CH=CH), 5.58 (s, 2H, =CHC*H*), 4.19 (q, 4H, OCH_2CH_3), 1.24 (t, 6H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 163.0 (C=O), 152.7 (=*C*−CO), 143.2 (=CH), 85.0 (OCH), 61.3 (OCH_2), 14.1 (CH_3).

2,3-Dicarboisopropoxy-7-oxanorbornadiene (8). A mixture of furan (2.0 g, 30 mmol) and diisopropyl acetylenedicarboxylate (4.0 g, 20 mmol) in dry benzene (10 mL) was reacted as described above to afford **8** as a pale yellow oil becoming solid in the freezer (4.6 g, 87% yield): bp 121 °C/0.9 mmHg; IR (neat) ν 2984, 2939, 1708, 1640, 1375, 1270, 1211, 1182, 1099, 907, 881 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13 (d, 2H, CH=CH), 5.57 (s, 2H, =CHC*H*), 5.04 [m, 2H, $OCH(CH_3)_2$], 1.23 [d, 12H, $OCH(CH_3)_2$]; ^{13}C NMR ($CDCl_3$) δ 162.7 (C=O), 152.5 (=*C*−CO), 143.2 (=CH), 85.1 (OCH), 69.2 [$OCH(CH_3)_2$], 21.8 (CH_3).

2,3-Dicarbo-*tert*-butoxy-7-oxanorbornadiene (9). To a solution of di-*tert*-butyl acetylenedicarboxylate (2.3 g, 10 mmol) in dry benzene (10 mL) was added freshly distilled furan (1.4 g, 20 mmol). The resulting mixture was refluxed for 6 days in an oil bath at 90 °C using a capped efficient reflux condenser. The solution was concentrated on a rotary evaporator, and the residue was recrystallized from *n*-pentane to afford **9** as an off-white microcrystalline powder (1.3 g, 43% yield): mp 90−91 °C; IR (KBr) ν 2983, 2936, 1737, 1702, 1643, 1368, 1341, 1258, 1158, 1110, 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13 (s, 2H, CH=CH), 5.52 (s, 2H, =CHC*H*), 1.44 [s, 18H, $OC(CH_3)_3$]; ^{13}C NMR ($CDCl_3$) δ 162.5 (C=O), 152.8 (=*C*−CO), 143.4 (=CH), 85.3 (OCH), 82.6 (OC), 28.3 (CH_3).

General Polymerization Procedure. Unless otherwise specified in the tables, $[RuCl_2(p\text{-cymene})]_2$ (0.0153 g, 2.5×10^{-5} mol) was dissolved in 4 mL of dry THF under nitrogen. A norbornadiene monomer (5×10^{-3} mol) was added with a syringe, and the reaction mixture was stirred in an oil bath at 60 °C. After a few minutes, a 0.1 M solution of TMSD in hexanes/THF (1 mL, 10^{-4} mol) was added dropwise with a syringe pusher over a 30 min period. The resulting mixture was kept at 60 °C for an additional 5.5 h. It was then cooled to room temperature, diluted with chloroform (5 mL), and added dropwise to 500 mL of vigorously stirred methanol (or *n*-heptane in the case of 7-oxanorbornadienes). The precipitated polymer was separated by filtration, washed twice with small portions of methanol (or *n*-heptane in the case of 7-oxanorbornadienes), and dried overnight under vacuum.

ROM Polymer of 2,3-Dicarbomethoxynorbornadiene (1). ^{1}H NMR ($CDCl_3$) δ 5.40 (d, 2H, =CH), 3.66 (s, 6H, OCH_3), 3.51 (br, 2H, =CHC*H*), 2.36 and 1.43 (m, 2H, $CHCH_2CH$); ^{13}C NMR ($CDCl_3$)[15] δ 165.6 (C=O), 142.3 ($C_{5,6}$), 132.5 ($C_{2,3}$), 52.1 (OCH_3), 49.3 ($C_{1,4}$), 38.0 (C_7).

ROM Polymer of 2,3-Dicarboethoxynorbornadiene (2). ^{1}H NMR ($CDCl_3$) δ 5.40 (br, 2H, =CH), 4.11 (q, 4H, OCH_2CH_3), 3.50 (br, 2H, =CHC*H*), 2.39 and 1.44 (m, 2H, $CHCH_2CH$), 1.19 (t, 6H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$)[15] δ 165.1 (C=O), 142.1 ($C_{5,6}$), 132.3 ($C_{2,3}$), 61.0 (OCH_2), 49.3 ($C_{1,4}$), 38.0 (C_7), 14.3 (CH_3).

ROM Polymer of 2,3-Dicarboisopropoxynorbornadiene (3). ^{1}H NMR ($CDCl_3$) δ 5.48 and 5.38 (br, 2H, cis and trans =CH), 4.98 [m, 2H, $OCH(CH_3)_2$], 3.64 and 3.47 (br, 2H, cis and trans =CHC*H*), 2.33 and 1.44 (m, 2H, $CHCH_2CH$), 1.18 [d, 12H, $OCH(CH_3)_2$]; ^{13}C NMR ($CDCl_3$)[15] δ 164.7 (C=O), 142.1 ($C_{5,6}$), 132.5 ($C_{2,3}$), 68.7 (OCH), 49.5 ($C_{1,4}$), 37.8 (C_7), 22.1 (CH_3).

ROM Polymer of 2,3-Dicarbo-*tert*-butoxynorbornadiene (4). ^{1}H NMR ($CDCl_3$) δ 5.49 and 5.34 (br, 2H, cis and trans =CH), 3.41 (br, 2H, =CHC*H*), 2.26 (m, 1H, $CHCH_2CH$), 1.39 [br, 18H + 1H, $OC(CH_3)_3$ and $CHCH_2CH$]; ^{13}C NMR ($CDCl_3$)[15] δ 164.8, 164.4, 164.1 (C=O), 143.3, 142.0, 139.7 ($C_{5,6}$), 132.7, 132.6, 131.8 ($C_{2,3}$), 81.8 (OC), 50.0, 49.7, 48.6 ($C_{1,4}$), 37.8 (C_7), 28.5, 28.3, 28.3 (CH_3).

ROM Polymer of Benzonorbornadiene (5). ^{1}H NMR ($CDCl_3$) δ 7.19 (m, 4H, H_{ar}), 5.64 and 5.57 (br, 2H, trans and cis =CH), 4.12 and 3.72 (br, 2H, cis and trans =CHC*H*), 2.56 and 1.76 (m, 2H, $CHCH_2CH$); ^{13}C NMR ($CDCl_3$)[15] δ 146.2 ($C_{5,6}$), 134.3 ($C_{2,3}$), 126.9 (C_{ar}), 124.4 (C_{ar}), 47.0 ($C_{1,4}$), 42.9, 42.4 (C_7).

ROM Polymer of 2,3-Dicarbomethoxy-7-oxanorbornadiene (6). ^{1}H NMR ($CDCl_3$) δ 5.82 and 5.75 (br, 2H, trans and cis =CH), 5.50 and 5.39 (br, 2H, cis and trans =CHC*H*), 3.70 (s, 6H, OCH_3); ^{13}C NMR ($CDCl_3$)[15] δ 162.7 (C=O), 138.0 ($C_{5,6}$), 131.4 ($C_{2,3}$), 85.9 ($C_{1,4}$), 52.7 (OCH_3).

ROM Polymer of 2,3-Dicarboethoxy-7-oxanorbornadiene (7). ^{1}H NMR ($CDCl_3$) δ 5.81 and 5.76 (br, 2H, trans and cis =CH), 5.47 and 5.37 (br, 2H, cis and trans =CHC*H*), 4.15 (q, 4H, OCH_2CH_3), 1.20 (t, 6H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$)[15] δ 162.2 (C=O), 137.9 ($C_{5,6}$), 131.6 ($C_{2,3}$), 86.0 (trans $C_{1,4}$), 81.8 (cis $C_{1,4}$), 61.7 (OCH_2), 14.2 (CH_3).

ROM Polymer of 2,3-Dicarboisopropoxy-7-oxanorbornadiene (8). ^{1}H NMR ($CDCl_3$) δ 5.77 (br, 2H, =CH), 5.33 (br, 2H, =CHC*H*), 5.02 [m, 2H, $OCH(CH_3)_2$], 1.19 [d, 12H, $OCH(CH_3)_2$]; ^{13}C NMR ($CDCl_3$)[15] δ 161.9 (C=O), 138.0 ($C_{5,6}$), 131.6 ($C_{2,3}$), 86.1 ($C_{1,4}$), 69.7 (OCH), 21.9 (CH_3).

ROM Polymer of 2,3-Dicarbo-*tert*-butoxy-7-oxanorbornadiene (9). ^{1}H NMR ($CDCl_3$) δ 5.74 (br, 2H, =CH), 5.27 (br, 2H, =CHC*H*), 1.40 [s, 18H, $OC(CH_3)_3$]; ^{13}C NMR ($CDCl_3$)[15] δ 161.4 (C=O), 138.2 ($C_{5,6}$), 131.7 (br, $C_{2,3}$), 86.7, 86.3, 85.9 (trans $C_{1,4}$), 83.0, 82.7 (cis $C_{1,4}$ and OC), 28.3 (CH_3).

ROM Polymer of 7-Oxabenzonorbornadiene (10). ^{1}H NMR ($CDCl_3$) δ 7.06–7.23 (m, 4H, H_{ar}), 6.12 and 5.57 (br, 2H, cis and trans =CHC*H*), 5.94 and 5.74 (br, 2H, trans and cis =CHC*H*); ^{13}C NMR ($CDCl_3$)[15] δ 141.1 ($C_{5,6}$), 133.0 ($C_{2,3}$), 128.1 (C_{ar}), 122.1 (C_{ar}), 84.0 (trans $C_{1,4}$), 79.5 (cis $C_{1,4}$).

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