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Factors Influencing the Rate of Tungsten Hexachloride/Tetramethyltin-Catalyzed Olefin Metathesis Polymerization: Monomer Ring Strain Is Not Important

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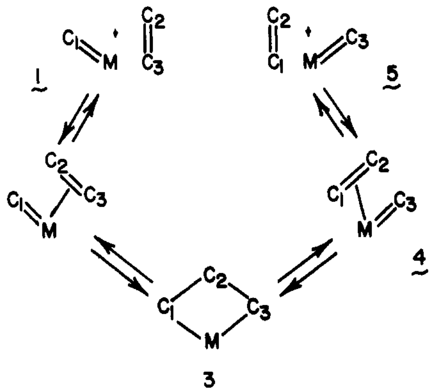
ABSTRACT: Competitive kinetics in tungsten hexachloride/tetramethyltin-catalyzed olefin metathesis copolymerizations demonstrate that monomer ring strain does little to affect reaction rates. The species in the catalytic cycle that appears to be kinetically pertinent is the metal carbene; the nature and geometry of the growing polymer chain about the catalyst and specifically the ability of the penultimate double bond to coordinate to the metal determine the reactivity of the metal carbene toward monomer. Relative reactivities for carbenes derived from cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, 1,5-cyclooctadiene, cyclodecene, cyclododecene, norbornene, bicyclo[2.2.2]oct-2-ene, and α-pinene are determined.

Introduction

Although the skeleton of the presently most widely accepted mechanism for olefin metathesis propagation was proposed in 1970,[1] certain subtleties remain undetailed. The interconversion of carbene/olefin and metallacyclobutane complexes (Scheme I) has a large amount of experimental support,[2,3] but questions such as the relative stabilities of **2**, **3**, and **4** (it has been suggested[4] that **3** is not an intermediate, but a transition state for some systems and **3** has been isolated as an intermediate in other systems[5]), the geometry of **2** and **4** (with regard to the dihedral angles between the olefin and carbene)[6] and whether a direct [2 + 2] reaction occurs instead of the formation of a distinct olefin/carbene complex[4] are still issues. Explanations of reactivity and stability differences and origins of selectivity and stereoselectivity depend on these mechanistic details; hence rational control of this catalysis depends on the answers to these questions.

Scheme I



We have been concerned with factors affecting the rate of olefin metathesis polymerization, in particular the structure of the propagating carbene and the monomer ring strain, and have published a preliminary account of this work.[7] This paper presents evidence that, contrary to popular assertions,[2,8,9] the rate of polymerization of cyclic olefins by metathesis catalysis is not a function of ring strain in the monomer and that "reactive monomers" such as norbornene[4,10] are not reactive because of their ring strain. We offer another interpretation of the kinetic data, namely that reactivity differences between different cyclic olefins can be ascribed to the relative reactivity of the propagating carbene. The geometry of the growing polymer chain about the catalyst site determines the reactivity. Our interpretations are derived by using tungsten hexachloride/tetramethyltin catalysis, and we recognize that other catalysts may have different kinetically pertinent species. Comparison with other cyclic monomers (ethers, lactones, lactams, see below) suggests that our observations are general.

Experimental Section

All manipulations were carried out under an atmosphere of prepurified nitrogen. Norbornene, cyclooctene, cyclooctadiene, cyclohexene, cyclopentene, cycloheptene, bicyclo[2.2.2]oct-2-ene, α-pinene, cyclodecene, cyclododecene, cyclohexane, cyclopentane, chlorobenzene, and tetramethyltin were obtained from Aldrich; cyclobutene was prepared by a published procedure.[11] Each was dried over calcium hydride and distilled under nitrogen. Tungsten hexachloride was zone refined under vacuum at 350–400 °C and stored under nitrogen. Gas chromatographic analyses were performed with a Hewlett-Packard 5790A gas chromatograph using a 6 ft × $^1/_8$ in. 5% OV 101 on Chromosorb W column.

Competitive kinetics measurements were obtained by two different procedures:

Procedure A. Chlorobenzene (55 mL), 0.43 mmol of tetramethyltin (0.24 mL of a 1.8 M solution in chlorobenzene), and 1.5 mL of cyclohexane or cyclopentane (GC internal standards) are introduced via syringe to a nitrogen-purged Schlenk flask containing a stirring bar. Tungsten hexachloride (0.43 mmol) is

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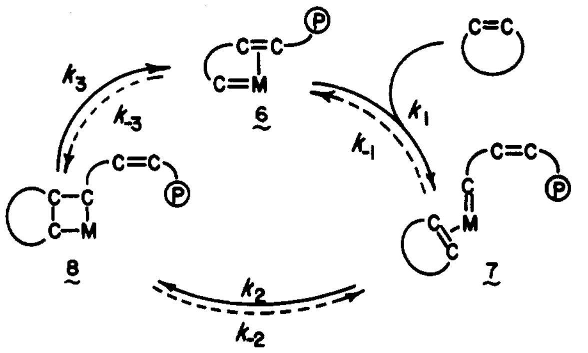
Scheme II



added via syringe as 4.3 mL of a 0.1 M solution in chlorobenzene; a bright orange-red color forms. Two 20-mL aliquots of this solution are transferred via syringe to two Schlenk flasks. Fifteen minutes after the WCl_6 is added, cyclooctadiene (COD, 1.0 mL, 8.2 mmol) is added to one flask and a mixture of cyclooctadiene (0.5 mL, 4.1 mmol) and the second monomer (0.5 mL, 2.6–5.7 mmol) is added to the other flask. Initial COD/W/Sn ratios are 57/1/1. The rate of monomer disappearance is monitored by GC analysis of periodic aliquots which are quenched with methanol. For reactions carried out at elevated temperatures, both the tetramethyltin/solvent/internal standard solution and the tungsten hexachloride solution are equilibrated at the reaction temperature prior to their mixture.

Procedure B. Chlorobenzene (15 mL), 0.24 mmol of tetramethyltin (0.1 mL of a 2.4 M solution in chlorobenzene), and 0.24 mL of cyclohexane (GC internal standard) are introduced via syringe to a nitrogen-purged Schlenk flask containing a stirring bar. Tungsten hexachloride (0.1 mmol) is added via syringe as 1.0 mL of a 0.1 M chlorobenzene solution, and, 15 min later, cyclooctadiene (0.5 mL, 4.1 mmol) is added via syringe. Initial COD/W/Sn ratios are 40/1/2.4. Aliquots are collected every 2 min and analyzed by GC. Several minutes after the cyclooctadiene is introduced, 0.25 mL (1.3–2.9 mmol) of the second monomer is added. Data points are taken over the next 20 min. All monomers are added to the reaction mixtures as neat liquids except norbornene and bicyclo[2.2.2]oct-2-ene, which are dissolved in the minimal amount of chlorobenzene to permit syringe transfer. For reactions carried out at elevated temperatures, both the tetramethyltin/solvent/cyclohexane solution and the tungsten hexachloride solution are equilibrated at the reaction temperature prior to their mixture.

Justification of First-Order Kinetics. That the reactions are first order with respect to monomer is indicated by linear first-order plots to greater than 3 half-lives and by indistinguishable first-order plots of percent monomer remaining vs. time for $[\mathrm{COD}]_0$ = 0.16, 0.33, and 0.49 M and for $[\mathrm{COE}]_0$ = 0.12, 0.23, and 0.46 M.

Results and Discussion

Scheme II depicts the generally accepted mechanism for the propagation step in cyclic olefin metathesis polymerization. Several details of this mechanism are not well established for any monomer–catalyst system and probably differ for different monomers, different catalysts, and different polymerization conditions: In addition to the questions indicated in the introduction concerning Scheme I, whether the coordination step is association–dissociation or dissociation–association, whether the penultimate and/or other chain double bond(s) is (are) coordinated, and whether a cocatalyst is involved are issues. These issues have frequently been addressed[12] with selectivity and stereoselectivity data, but very little information concerning the kinetics of these processes is available.[4]

In this paper we present competitive kinetics data for several cyclic olefins that give insight into the structures and reactivities of the intermediates in Scheme II. In particular, we have examined the effects of ring strain in the monomer and in **6** on relative propagation rates. It is not a priori obvious whether monomer ring strain should increase or decrease the rate of propagation; an a priori analysis is difficult. The extent to which ring strain manifests itself in transition states as opposed to ground states of intermediates is difficult to predict. It has been pointed out[2] that differences in energy between **6**, **7**, and **8** and the transition states between them must be small to explain the observed rates and activation parameters.

The relative rates of ring-opening polymerizations of other types of cyclic monomers (ethers, lactones, lactams) do not suggest that monomer ring strain is important. In the cationic polymerization of cyclic ethers in nonpolar media, tetrahydrofuran (23 kJ/mol strain energy)[13] polymerizes with a rate constant 2 orders of magnitude larger than that of ethylene oxide (114 kJ/mol)[13] and 3 orders of magnitude larger than that of oxepane (33 kJ/mol).[13,14] In lactam polymerizations, the correlation between ring size and reactivity differs for different types of polymerization (anionic, cationic, hydrolyic) and often also varies with temperature and catalyst.[15–17] The reactivity ratios of cyclic ethers or lactams in copolymerization do not correlate with strain energy.[18–20] Kinetic investigations of the metathesis of acyclic olefins and the cometathesis of cyclic and acyclic olefins show that the acyclic olefins (lacking any strain energy) react at rates comparable to those of the cyclic olefins.[21–25]

Experiments detailed below suggest that monomer ring strain does little to affect propagation rates in metathesis polymerization and that the rate is principally a function of the structure of **6**.

Much of the data and discussion that follows concerns differences in the rate of metathesis of cyclooctadiene (COD). We compare the rate of COD disappearance in homometathesis reactions with the rate of COD disappearance in cometathesis (with another cyclic olefin) reactions; tungsten hexachloride/tetramethyltin is the catalyst. The rate expressions for COD homometathesis and cometathesis are given by eq 1 and 2, respectively, where

$$-\mathrm{d}[\mathrm{COD}]/\mathrm{d}t = k_{cc}[\mathrm{W{=}(COD)}][\mathrm{COD}] \qquad (1)$$

$$-\mathrm{d}[\mathrm{COD}]/\mathrm{d}t = k_{cc}[\mathrm{W{=}(COD)}] + k_{mc}[\mathrm{W{=}(M)}][\mathrm{COD}] \qquad (2)$$

W=(COD) represents the COD-derived carbene, W=(M) represents the comonomer-derived carbene, k_{cc} is the rate constant for the reaction of COD with COD-derived carbene and k_{mc} is the rate constant for the reaction of COD with comonomer-derived carbene. By comparing the rates of COD disappearance in the presence and absence of comonomer, we can measure the relative reactivity of W=(COD) and W=(M), and assuming that [W=(COD)] in eq 1 is equal to [W=(COD)] + [W=(M)] in eq 2, and we carry out the reactions so that this is so. COD is a convenient monomer for such comparisons: it polymerizes to high conversions (has a low equilibrium monomer concentration) and exhibits first-order kinetics for several half-lives.

Figure 1 displays first-order plots of monomer concentration vs. time for three $WCl_6/SnMe_4$-catalyzed reactions: COD and norbornene (NBE) homopolymerizations and a COD polymerization to which NBE (0.5 equiv) was added at t = 8 min. Accurate rate constants cannot be determined from this data, but several better-than-qualitative points can be made: In separate, side-by-side reactions, NBE homopolymerizes greater than 100 times faster than does COD, but in a competitive experiment (NBE–COD copolymerization) NBE reacts at essentially the same rate as COD. The addition of NBE to a COD polymerization in progress dramatically increases the rate of COD me-

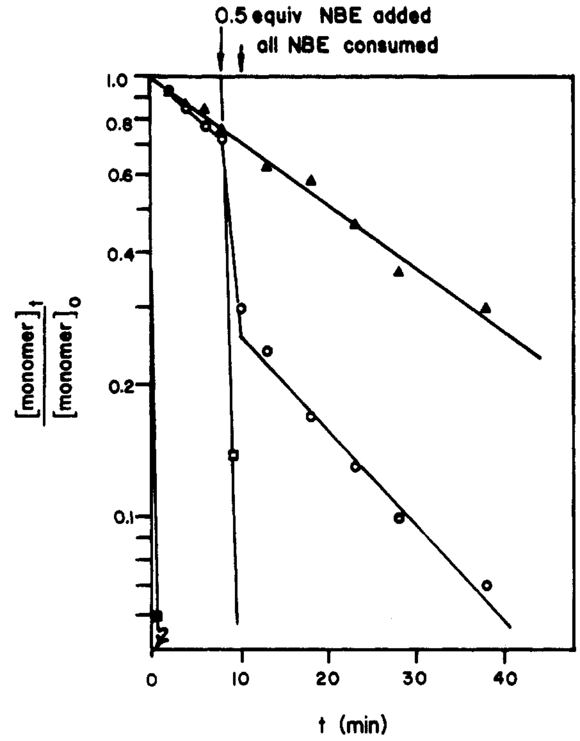
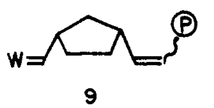


Figure 1. Homopolymerization of COD (▲) ([COD)]$_0$ = 0.35 M) and NBE (■) ([NBE]$_0$ = 0.35 M). Polymerization of COD (○) ([COD]$_0$ = 0.17 M) to which 0.5 equiv of NBE was added at t = 8 min, T = 35 °C.

tathesis: COD had polymerized to 30% conversion when NBE was added at 8 min; in the following 3 min an additional 45% is consumed—a 5.5-fold rate increase. Over this 3-min period the NBE is completely consumed, and afterward the COD consumption returns to its initial rate.

The greater than 100-fold rate difference between NBE and COD homopolymerizations would normally be rationalized by differences in monomer ring strain. Clearly this cannot be an important effect as it hardly manifests itself in the competitive experiment and does not explain why COD polymerizes faster in the presence of NBE than it does in its absence. We interpret these data in terms of the relative reactivity of the NBE- and COD-derived carbenes (**9** and **10**, respectively), generically represented



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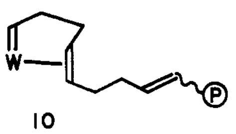


10

by **6** in Scheme II; that is, k_{mc} is greater than k_{cc} is eq 1 and 2. The olefin in **9** cannot coordinate with the tungsten (the planar cyclopentane ring holds them apart) with the ease that the olefin in **10** can, making **9** the more exposed and more reactive carbene. The initial rate of COD conversion (Figure 1) can be ascribed to the rate of reaction of **10** with COD. The intermediate greater rate is due to the combined rates of reaction of **9** and **10** with COD. After the NBE is consumed, **9** no longer is present, and the reaction returns to its initial rate.

The same type of experiment has been performed with NBE and cyclooctene (COE). Figure 2 shows the analogous data and we interpret the results identically.

We recently reported that the "metathesis-inert" monomer cyclohexene (which is virtually strain-free) can be copolymerized with NBE.[26] The reactive NBE-derived carbene **9** increases the rate of cyclohexene polymerization relative to its depolymerization, and the copolymer is isolated as a kinetic product.

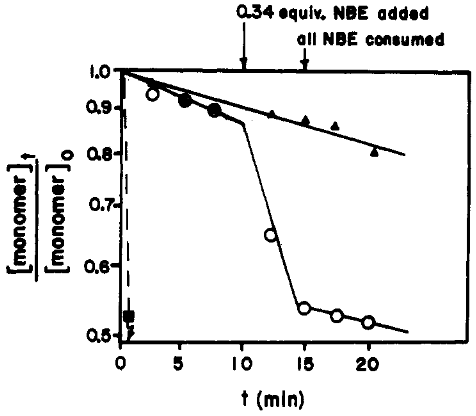


Figure 2. Homopolymerizations of NBE (■), COE (▲); polymerization of COE to which 0.34 equiv of NBE was added at t = 10 min (○). [NBE]$_0$ (homopolymerization) = 0.13 M, [COE]$_0$ = 0.37 M, T = 25 °C.

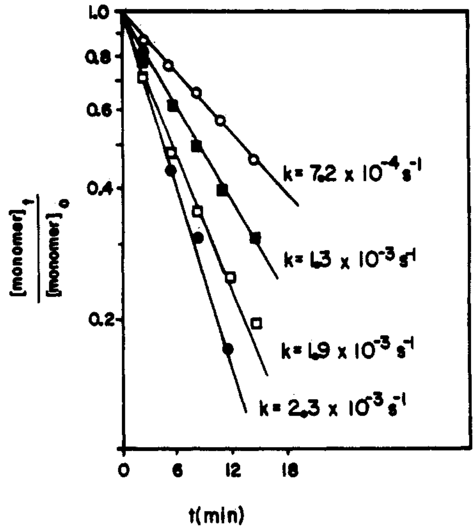
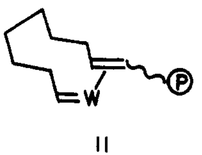


Figure 3. Homopolymerizations at COE (□) and COD (○); copolymerization of COE (■) and COD (●): [monomer]$_0$ = 0.4 M, T = 80 °C.

On the basis of this interpretation of NBE copolymerization kinetics, it is reasonable to expect that the presence of any monomer should affect the polymerization kinetics of another monomer given that the reactivities of the resultant carbenes differ. Consider, for example, COD and COE homo- and copolymerizations. The carbenes generated by COD and COE are **10** and **11**, respectively.



11

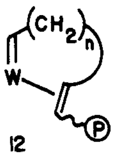
The double bond in **11** is separated from the carbene by six methylene carbons, while there are only two methylene carbons separating the carbene and olefin in **10**. To determine the relative reactivity of these two carbenes, the experiments detailed in Figure 3 were performed. In side-by-side homopolymerizations, COE reacts 2.7 times faster than COD, but in a copolymerization the reactivity inverts; COD reacts 1.8 times as fast as COE. The COE-derived carbene is clearly the more reactive carbene. That COD polymerizes approximately twice as fast as COE in copolymerization can be rationalized by the fact that COD has two double bonds for every one of COE.

Table I
Relative (to COD-Derived) Carbene Reactivities

monomer	k(rel)[a]	temp, °C	method[b]
cyclobutene	1.0	25	B
cyclopentene	2.2	25	B
	2.4[c]	70	A
cyclohexene	1.3[c]	25	A
	1.2	70	A
cycloheptene	0.52[c]	25	A, B
	0.58	70	A
cyclooctene	3.0[d]	70	A, B
cyclodecene	1.4[c]	70	A
cyclododecene	1.1[c]	70	A
norbornene	24	25	B
	41	35	B
	48	70	B
bicyclo[2.2.2]oct-2-ene	1.2[c]	25	B
α-pinene	1.2	25	B
	1.2	70	B

[a] The ratio of COD disappearance rates in homo- and copolymerization. [b] See Experimental Section. [c] Average of two experiments (deviations less than 5%). [d] Average for four experiments.

It is apparent from the above discussion that the relative reactivity of metal carbene–olefin complexes of the general structure **12** can be determined by measuring the change in polymerization rate of one monomer (in these cases, COD) upon the addition of an appropriate second monomer **13**. That many of the monomers represented by **13** establish a monomer–polymer equilibrium at low monomer conversion and that the relative concentration of each carbene cannot be determined makes quantitating the relative reactivities impossible, but if the resultant carbenes do form and do affect the polymerization rate of COD, then whether the resultant carbene is more or less reactive than the COD-derived carbene is apparent. We have carried out this type of experiment with a range of monomers and the data are presented in Table I. Several points warrant amplification:



12

13

Cyclobutene (CBE) has essentially no effect on the rate of COD polymerization and the two monomers polymerize at virtually identical rates (Figure 4). This is compelling evidence that (1) monomer ring strain is not an important rate-determining factor and (2) the structure of the propagating carbene is important to rate. COD and CBE form essentially the same carbene (**10**) but have drastically different ring strain. The carbenes are slightly different: the coordinated double bond of the COD-derived carbene is always cis, but the double bond in the CBE-derived carbene can be cis or trans. It also follows that CBE should retard the rate of COE polymerization (as COD does), and it does (Figure 5).

The presence of cyclohexene increases the rate of COD polymerization but is not consumed in the reaction. The cyclohexene-derived carbene is present in the reaction as a kinetically important species, but the monomer–polymer equilibrium lies far toward monomer at this temperature.[26]

The cycloheptene-derived carbene is the only one in the series found to be less reactive than **10** and the following order of reactivity can be drawn: NBE ≫ COE > cyclopentene > cyclodecene > bicyclo[2.2.2]oct-2-ene ≈ α-pinene ≈ cyclohexene > cyclododecene ≈ cyclobutene ≈ cyclooctadiene > cycloheptene.

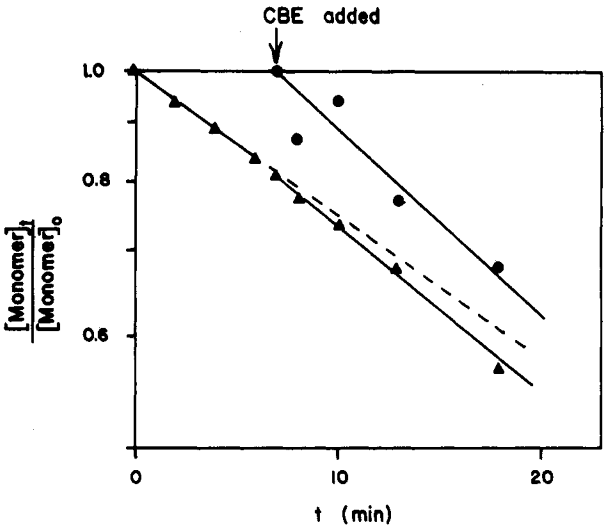


Figure 4. Polymerization of COD (▲) to which 0.5 equiv of CBE (●) is added at t = 6.5 min. Dashed line extrapolates initial rate of COD (homo)polymerization. $[\mathrm{COD}]_0$ = 0.3 M, T = 25 °C.

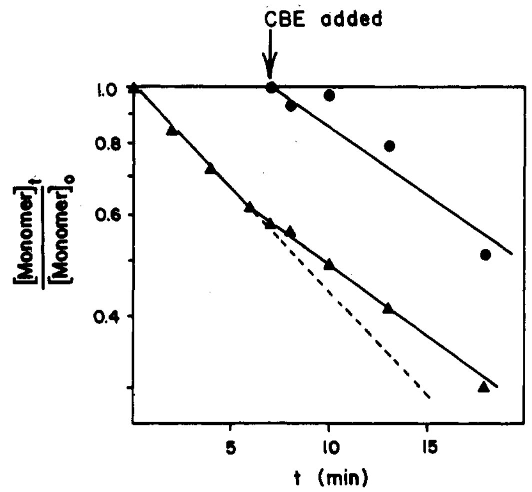
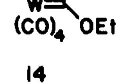


Figure 5. Polymerization of COE (▲) to which 0.5 equiv of CBE (●) is added at t = 6.5 min. Dashed line extrapolates initial rate of COE (homo)polymerization. $[\mathrm{COE}]_0$ = 0.3 M, T = 25 °C.

We ascribe the differences in reactivities to the ease of coordination of the double bond closest to the carbene or more specifically to the structure of the group in between the carbene and first chain olefin. Several literature references in this regard are noteworthy: complexes **14**[27] and **15**[28] have recently been isolated as stable crystalline solids. The authors point out that other species of the general structure **16** with $n < 2$ or $n > 2$ are less stable. Ofstead, et al.[29] reported that hepta-1,6-diene is a much more effective chain transfer agent than hexa-1,5-diene or octa-1,7-diene for $\mathrm{WF_6/EtAlCl_2}$-catalyzed cyclopentene and interpret this result in terms of the relative stability of **17**



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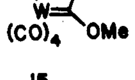

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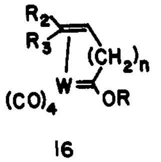

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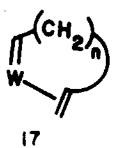


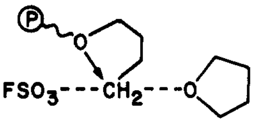
17

for $n = 2, 3, 4$. Ivin[30] has interpreted the stereospecificity of several polymerizations in terms of two propagating species **18** and **19**. **18** leads to cis product and **19** leads to trans product. The relative rates of dissociation for several olefins were reported to be NBE > cyclopentene > COE ~ COD.

18

19

Finally, the higher rate of cationic polymerization of THF compared with other cyclic ethers has been attributed to the geometry of the transition state: the oxygen is in the proper position to stabilize the transient oxionic species **20**.[14]



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Conclusions

We have demonstrated that the rate of tungsten hexachloride/tetramethyltin-catalyzed olefin metathesis polymerization is independent of ring strain in the monomer but very dependent on the structure of the propagating carbene. The ease with which the closest double bond in the growing polymer chain can coordinate to the metal center determines the carbene reactivity. Relative reactivities of carbenes can be determined by measuring the change in rate of COD polymerization upon introduction of a second olefin.

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Plasma-Initiated Polymerization of Hexachlorocyclotriphosphazene

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ABSTRACT: The polymerization of $(NPCl_2)_3$ to $(NPCl_2)_n$ has been carried out via the recently developed technique of plasma-initiated polymerization. Samples were polymerized following plasma exposure using a radio-frequency generator and capacitive coupling. Plasma initiation leads to significant rates of polymerization at lower temperatures than those required for the thermal reaction, but temperature sensitivity is less extreme. Cross-linking is encountered only after total conversion at high temperatures. At lower temperatures, a limiting conversion is reached. Polymer yield goes through a maximum with plasma power and increases linearly with plasma duration. Though thermally obtained polymers have molecular weights in excess of 10^6, plasma initiation leads to much smaller molecular weights. Molecular weight, as measured by dilute solution viscometry, rises with polymerization time but is insensitive to polymerization temperature.

Introduction

The polyphosphazenes are an important family of polymers which have attracted much interest in the past 20 years. The reasons behind this interest include the unique nature of the inorganic –P=N– skeleton and the vast range of properties attainable through a wide variety of pendant groups.[1,2] A major problem in research on polyphosphazenes is the difficulty of their syntheses. Although halogenated cyclic triphosphazenes polymerize by ring-opening, the poly(dihalophosphazenes) that result are hydrolytically unstable[3,4] and hence of little practical use. On the other hand, poly(organophosphazenes) exhibit

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