GPC was found to be 56 000 and M_w/M_n (determined by GPC) = 1.17. The calculated M_n of styrene/EtLi = 52 000.

In the second experiment 5% of a solution of 4.4 mL of styrene in 26 mL of benzene was added to 7.6×10^{-5} mol of EtLi in 25 mL of benzene. The mixture was stirred for 24 h to form the "seeds", and thereafter the remaining styrene solution was added under stirring. The stirred mixture was kept at room temperature for an additional 24 h, the polymer isolated by the previously described procedure, and its molecular weight determined. The M_n obtained by GPC was 55 100, $M_w/M_n = 1.17$, and the M_n calculated from stoichiometry was 50 300.

Conclusions

The theoretical considerations discussed in this paper as well as the experimental findings given above clearly reveal the erroneous premises of the seeding technique. Neither the amount of the utilized initiator nor the molecular weight or molecular weight distribution of polymers formed by the process discussed here is affected by the order of monomer addition. The same results are obtained whether the monomer is added at once or piecemeal. To ensure sharp molecular weight distribution one has to use, as stressed by Hsieh,[4,5] a fast initiator; such a result cannot be achieved with a slow initiator.

Added Note. The seeding technique is useful in *reversible* polymerization, e.g., for monomers such as α-methylstyrene or methyl methacrylate. The depropagation of living polymers provides then the monomer needed to consume the unreacted initiator. Hence, all the initiator is utilized provided that the mixture is left for a sufficient time to allow the depropagation to produce the required amount of monomer. This point was stressed[6] as long ago as 1968 and again in a recent review.[7] For the monomers mentioned above the required time is of the order of hours or less, but for the polymerization of styrene, treated as a reversible reaction, it is of the order of years at room temperature, and still longer for the polymerization of isoprene or butadiene.

References and Notes

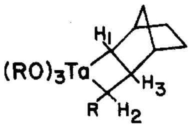
(1) Morton, M. et al. *Rubber Plast. Age* **1961**, *42*, 387.
(2) Morton, M. *Anionic Polymerization*; Academic: New York, 1983.
(3) Worsfold, D. J.; Bywater, S. *Can. J. Chem.* **1964**, *38*, 1891.
(4) Hsieh, H. L. *J. Polym. Sci., Part A* **1965**, *3*, 173.
(5) Hsieh, H. L.; Glaze, W. H. *Rubber Chem.* **1970**, *43*, 22.
(6) Szwarc, M. *Carbanions, Living Polymers, and Electron Transfer Processes*; Interscience: New York, 1968; p 57.
(7) Szwarc, M. *Adv. Polym. Sci.* **1983**, *49*, 68.

Communications to the Editor

Ring-Opening Polymerization of Norbornene by a Tantalum Catalyst: A Living Polymerization

In the next few years it should be possible to use well-characterized, high oxidation state alkylidene complexes to prepare homopolymers and block copolymers from cyclic alkenes in a controlled fashion that has not yet been possible with classical olefin metathesis catalysts. In this paper we report the ring opening of norbornene by a tantalum alkylidene catalyst that closely mimics ring-opening polymerization of norbornene by a living titanium catalyst discovered by Grubbs.[1]

Yellow-orange $Ta(CH^tBu)(OR)_3(THF)$ complexes (OR is 2,6-diisopropylphenoxide (DIPP) or 2,6-dimethylphenoxide (DMP)) can be prepared straightforwardly from $TaCl_5$ and $Zn(CH_2{}^tBu)_2$ in three high-yield steps.[2] Addition of 1 equiv of norbornene (NBE) at −30 °C to $Ta(CH^tBu)(DMP)_3(THF)$ in ether produces a yellow solution from which a yellow oil can be obtained by removing all solvent in vacuo. Very pale yellow crystals that are extremely soluble in pentane can be obtained from concentrated solutions at −30 °C in 31% yield. The NMR spectra of the oil and the crystals are identical except for minor impurity peaks in the former. The latter is shown in Figure 1. It is consistent with the product being the tantallacyclobutane complex **1a** (ring stereochemistry unknown). The most characteristic features are the resonances at 5.20 (d), 3.72 (d), and 0.85 (t), assignable to the coupled protons H_1, H_2, and H_3, respectively. (In a similar titanacyclobutane complex $(\eta^5\text{-}C_5H_5)_2\overline{\text{TiCHRCHC}_5\text{H}_8\text{C}}\text{H}$ ($R = CMe_2CH{=}CH_2$) prepared by Grubbs,[1] these signals are found at 3.72, 2.63, and 0.08 ppm.) The ^{13}C NMR spectrum of **1a** shows signals for all 15 carbon atoms, the C_α ring carbon atom resonances being observed at 132.5 ppm (J_{CH} = 132 Hz) and 135.0 ppm (J_{CH} = 142 Hz) and the C_β ring carbon resonance at 29.0 or 30.2 (probably the former with $J_{CH} \approx 150$ Hz; cf. 110.9, 104.4, and 24.2 ppm in the titanacycle above).



OR = DMP: **1a**, R = ^{t}Bu; **1b**, R = polymer
OR = DIPP: **2a**, R = ^{t}Bu; **2b**, R = polymer

Table I
Kinetic Data for the Consumption of NBE by $\overline{\text{TaCH}^t\text{BuCHC}_5\text{H}_8\text{C}}\text{H(DIPP)}_3$ (2a) in C_6D_6

[Ta], mM	[NBE]$_0$, mM	*T*, K	$k \times 10^3$, s^{-1}
5.59	80	317.9	2.02
5.59	55	323.3	3.51
6.84	183	323.3	3.86
7.98	189	323.3	3.92
2.91	46	323.3	3.78
5.59	45	330.0	7.05
5.70	177	330.0	7.58
9.32	87	333.1	11.9
5.59	200	337.8	23.3

The reaction between $Ta(CH^tBu)(DIPP)_3(THF)$ and NBE produces more crystalline, colorless **2a** (64% from ether) whose ^1H NMR and ^{13}C NMR spectra are analogous as far as the TaC_3 ring is concerned (e.g., H_1 at 5.32 ppm, H_2 at 3.88 ppm, and H_3 at 0.88 ppm).[3] However, the DIPP resonances are broad, characteristic of a slowing down of a fluxional process that interconverts them in a tantallacyclobutane complex in which they are not all equivalent; some restricted rotation of these bulky ligands is also possible. After 1 day in C_6D_6 **2a** decomposes to the extent of 10–20% to as yet unidentified products.

When excess NBE is added to **2a** and the mixture is heated to 50 °C, the doublet at 3.88 ppm disappears and olefin proton resonances characteristic of polynorbornene[4] (~55% trans) appear (Figure 2). One hour after com-

0024-9297/87/2220-0448$01.50/0

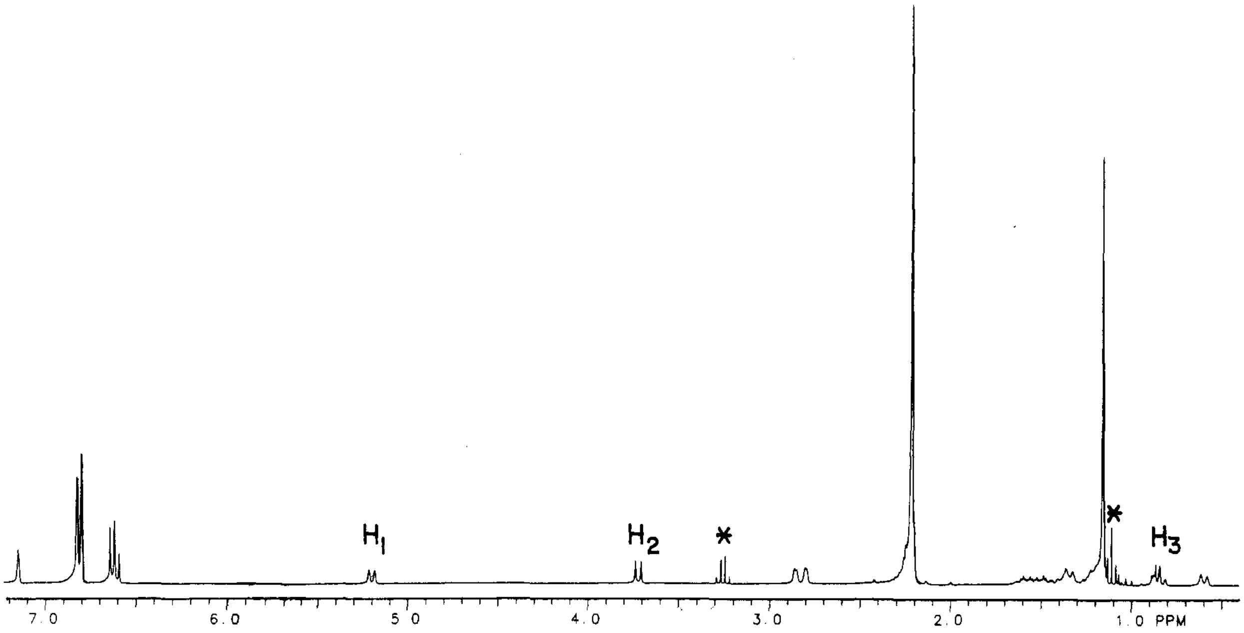


Figure 1. ^{1}H NMR spectrum of $\overline{\mathrm{TaCH^tBuCHC_5H_8C}}\mathrm{H(O\text{-}2,6\text{-}C_6H_3Me_2)_3}$ (**1a**) in $\mathrm{C_6D_6}$ (asterisks mark diethyl ether peaks).

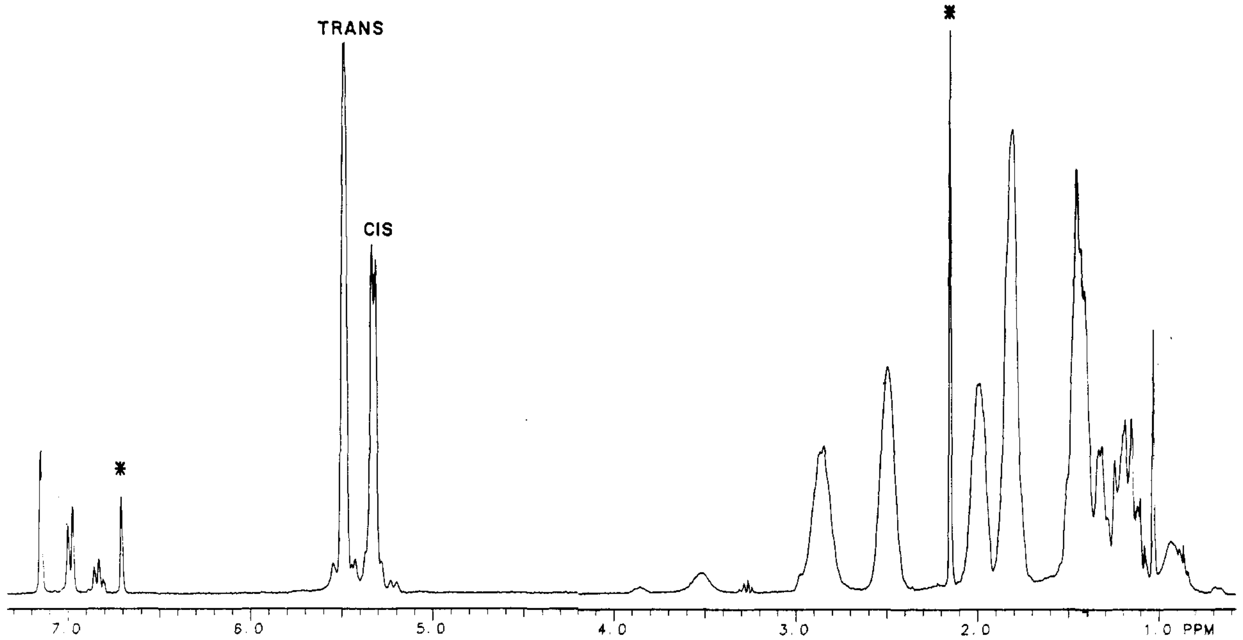
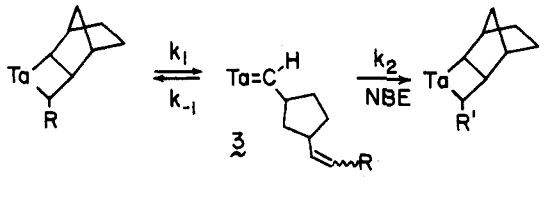


Figure 2. ^{1}H NMR spectrum of $\overline{\mathrm{TaCH^tBuCHC_5H_8C}}\mathrm{H(O\text{-}2,6\text{-}C_6H_3{}^iPr_2)_3}$ (**2a**) in $\mathrm{C_6D_6}$ after addition of NBE and heating for 1 h at 50 °C ([Ta] = 5.59 mM; $[\mathrm{NBE}]_0$ = 74.3 mM; asterisks mark mesitylene internal standard peaks).

pletion of a typical run the spectrum is essentially unchanged, a fact that suggests **2b** does not degrade in this time period. The rate of consumption of NBE is linear vs. time after an initial induction period and until ~1 equiv of NBE remains (Figure 3). The data shown in Table I confirm that the rate of consumption of NBE during the major part of the reaction is zero order in NBE and first order in catalyst concentration, consistent with rate-limiting ring opening followed by trapping of the incipient alkylidene complex **3** (eq 1) by norbornene.[5] An



(1)

Arrhenius plot of the data in Table I yields values of $\Delta H^{\ddagger}$ = 24.9 (1.5) kcal/mol, $\Delta S^{\ddagger}$ = 7.5 (4.6) eu, and $\Delta G^{\ddagger}_{338}$ = 22.4 (2.2) kcal/mol with a correlation factor R = 0.995. These results are remarkably similar to those observed by Grubbs[1] in the titanium system ($\Delta H^{\ddagger}$ = 27.1 (0.5) kcal/mol, $\Delta S^{\ddagger}$ = 9 (4) eu, and $\Delta G^{\ddagger}_{338}$ = 24 (1) kcal/mol. If a polymerization run is cooled to room temperature, polymerization essentially halts. When the sample is warmed again to 50–60 °C, the rate of polymerization increases to what it was before cooling.

The approach to linearity in the beginning of the reaction (Figure 3) can be ascribed to the somewhat *slower* reaction of **2a** with NBE vs. the reaction of **2b** with NBE. We checked this proposal by following the rate of disappearance of the 3.88 ppm peak in the NMR spectrum of **2a** at 35.0 °C. We find that **2a** is consumed at a rate with $k \approx 4 \times 10^{-4}$ s^{-1} (two runs yielded values of 3.7×10^{-4} and 4.1×10^{-4} s^{-1}); at 35.0 °C the calculated rate constant for consumption of NBE is 5.37×10^{-4} s^{-1}. If k_2[NBE] > k_{-1} when R = ^{t}Bu (and there is no reason to suspect that this

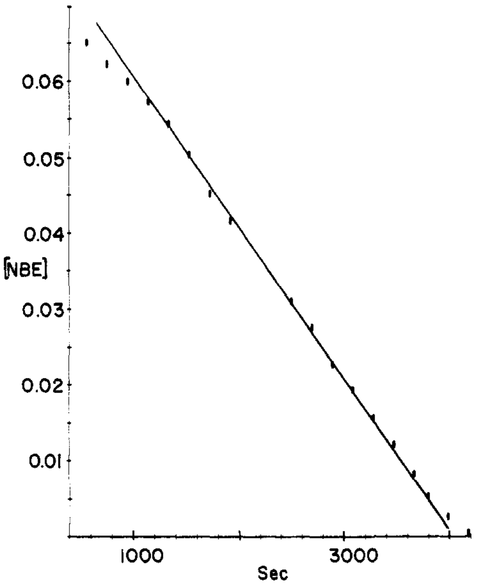


Figure 3. Plot of the consumption of 20 equiv of NBE by **2a** at 50 °C in C_6D_6.

Table II
GPC Analysis of Polynorbornene Prepared at 65 °C Using 2a as the Catalyst[a]

run	equiv of NBE	$\bar{M}_n$(uncor)	$\bar{M}_w/\bar{M}_n$
1	100	22 000	1.63
2	200	48 000	1.66
3	500	127 000	1.73
4	200 (~75% complete)	32 100	1.04[b]

[a] A -30 °C solution of 20 mg of **2a** in toluene was mixed with a -30 °C solution of norbornene in toluene such that the total volume was ~15 mL. The resulting solution was heated in an oil bath and checked by GLC to ensure that norbornene was completely consumed. The reactions were heated for an additional 30 min to 1 h and cooled to 25 °C. Acetone (~1 mL) was added, and the mixture was heated to 65 °C for approximately 15 min. The solvent was removed in vacuo, and the polymer was rinsed with methanol and dried in vacuo. In run 4 the reaction was taken to only ~75% completion. The polynorbornene was analyzed in toluene at 25 °C on a Waters 150C instrument vs. polystyrene standards using three Styragel columns. [b] The polymer with the expected molecular weight made up ~94% of the sample; ~6% of a fraction with a relatively high molecular weight could be resolved as a separate peak in this GPC spectrum.

is not the case), then k_1 is smaller when R = ^{t}Bu than when R is the growing polymer chain. This result is surprising until one considers that the steric congestion probably is greater out near the isopropyl groups of the phenoxide ligands than it is in the region where the *tert*-butyl group is found; i.e., the growing chain exerts a greater steric effect.

Toward the end of the reaction the plot of NBE consumption deviates from linearity. A plot of ln [NBE] vs. time in this region is linear; i.e., the rate depends on [NBE] at low values of [NBE]. Using the steady-state approximation for **3**, one finds that the reactions shown in eq 1 yield the expression $-d[NBE]/dt = k_1k_2[Ta][NBE]/(k_{-1} + k_2[NBE])$, where [Ta] is the catalyst concentration. Evidently $k_2[NBE] > k_{-1}$ until toward the end of the run. From the slope of the ln [NBE] vs. time plot we can show that $k_2/k_{-1} \approx 150\ M^{-1}$ at 57.0 °C.

Analysis of the polynorbornene prepared with **2a** as the catalyst in toluene (Table II) confirms that the molecular weight is directly proportional to the amount of monomer employed. The higher than desired polydispersities can be ascribed to slow secondary metathesis reactions after all norbornene has been consumed. In one case (run 4) the polymerization was stopped at ~75% completion. The polydispersity in that case was what one would expect from an essentially monodispersed polymer. These results suggest that this polymerization is truly living and that the slightly slower initiation step relative to propagation has a negligible adverse effect on polydispersity.

Acknowledgment. R.R.S thanks the National Science Foundation for support through Grants CHE 84-02892 and DMR 84-17818. K.C.W. thanks the Central Research Department of Dow Chemical Co. for support in the form of a predoctoral fellowship.

Registry No. **1a**, 105945-15-1; **2a**, 105945-16-2; NBE, 498-66-8; NBE (homopolymer), 25038-76-0; Ta(CH*t*-Bu)(DMP)$_3$THF, 105969-47-9; Ta(CH*t*-Bu)(DIPP)$_3$THF, 106034-24-6.

References and Notes

(1) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.
(2) For preparation of the DIPP derivative, see: Wallace, K. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 2162. The DMP derivative is prepared in an analogous fashion.
(3) Anal. Calcd for $TaC_{48}H_{71}O_3$: C, 65.72; H, 8.18. Found: C, 65.90; H, 8.36.
(4) Ivin, K. J. *Olefin Metathesis*; Academic: New York, 1983.
(5) We have seen no evidence that **2b** loses NBE in the time period of a typical run. Therefore we assume that this step is slow, as one might expect for this highly strained olefin.

Kevin C. Wallace and Richard R. Schrock*
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received August 25, 1986

Dopant-Induced Ablation of Poly(methyl methacrylate) by a 308-nm Excimer Laser

Recently, excimer laser ablation of polymeric materials has been the subject of many studies,[1] and some lithographic[2] and medical applications[3] have been reported. Because the ablation is initiated by absorption of laser photons, a necessary condition is that the target materials have an appreciable absorption at the appropriate wavelengths. Some reports have dealt with the effect of absorbance upon ablation, correlating the etched depth with the absorbance of the films.[3-6] However, in these studies both absorbance and wavelength were varied simultaneously so that it is difficult to analyze independently the effects of these two parameters. In the present work, the wavelength remains constant at 308 nm while the absorbance at 308 nm is varied. This is accomplished by varying the concentration of π-electronic chromophores in PMMA films. The dopants used in this work are pyrene and benzophenone; the photophysical data of these dopants are well documented.[7]

PMMA (ultrapure, Eastman Organic Chemicals), pyrene (Aldrich), and benzophenone (Aldrich) were used as received. PMMA and the dopant were dissolved in chlorobenzene and spin-coated on a quartz plate at a thickness of 1.5 μm. A Lambda Physik EMG 201 XeCl excimer laser was used as an exposure source. Its beam was focused into a 1 × 2 mm^2 spot by using a lens with a focal length of 12 in. and an aperture. The laser fluence was measured with a Scientec 362 power meter. A copper mesh mask made photolithographically was used in contact with the polymer films. All ablation experiments were single-shot exposures. Depth profiles were measured by a Tencor Alpha-Step 200. Scanning electron micrographs were recorded with a Philips 500 SEM instrument after argon ion metal sputter deposition.