the resulting neutral entity is soluble in DMA. In dried specimens, the nylon 6–$LiClO_4$ complex remains amorphous probably because CO–NH links, i.e., hydrogen bonds, are energetically less favored than NH–ClO_4^- and CO–Li^+ links. The "free" N–H stretch vibrations in the 3375–3588-cm^{-1} region support such a mechanism. Although at high salt concentrations each of the CO and NH groups may interact with separate Li^+ and ClO_4^- ions, at the limiting salt concentration in a gel, elemental analysis has shown that two amide groups are associated with one Li^+ and one ClO_4^- ion. Therefore, a single ion may coordinate with more than one amide group, and the resulting pseudo-cross-linked structures may give the complex the texture of a gel. Upon the addition of water or excess THF to the solution of nylon 6 in THF/$LiClO_4$ (or to the gel or to the amorphous dry complex), Li^+ and ClO_4^- ions are preferentially solvated by water molecules or by THF. Nylon 6 now readily forms hydrogen bonds within its own species and thus crystallizes into the α form.

In conclusion, the gelation and solubilization of nylons in THF and the formation of an amorphous nylon 6–$LiClO_4$ complex upon drying are attributed to the interaction of Li^+ and ClO_4^- ions with the CO and NH groups of nylons. Removal of Li^+ and ClO_4^- ions either by solvation with water molecules or by THF leads to the crystallization of nylon 6 in the α form. Nylons are not degraded in the presence of $LiClO_4$, the gel can be drawn into a fiber, and nonbonded N–H groups are present even in dried complexes.

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Registry No. THF, 109-99-9; $LiClO_4$, 7791-03-9; nylon 6 (SRU), 25038-54-4; nylon 6,6 (SRU), 32131-17-2; nylon 3 (SRU), 24937-14-2; nylon 3 (homopolymer), 25513-34-2; nylon 6,9 (SRU), 28757-63-3; nylon 6,9 (copolymer), 27136-65-8; nylon 6,10 (SRU), 9008-66-6; nylon 6,10 (copolymer), 26123-27-3; nylon 6,11 (SRU), 50732-66-6; nylon 6,11 (copolymer), 27967-39-1; nylon 11 (homopolymer), 25587-80-8; nylon 11 (SRU), 25035-04-5.

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Simultaneity of Initiation and Propagation in Living Polymer Systems

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Polymerization free of termination and chain transfer is referred to as living polymerization. This kind of system is often encountered in ionic polymerizations, and provided that initiation is virtually instantaneous and propagation irreversible the resulting polymers are characterized by a Poisson molecular weight distribution; i.e., for high degrees of polymerization they have nearly uniform size. Slow initiation broadens molecular weight distribution, a disturbing effect observed, e.g., in anionic polymerization of vinyl and diene monomers initiated by organolithium compounds, especially *n*-butyllithium in hydrocarbon solvents.

It was suggested in several publications[1] and again in a recent monograph[2] that such a broadening may be prevented by means of the so-called "seeding technique" based on the following concept. A *small* fraction of the monomer to be polymerized is mixed with *all* the initiator to be used in the reaction. The mixture is left to react for a while, and thereafter the bulk of the monomer is added. It is believed that *all* the initiator, however slowly initiating the polymerization, will react *quantitatively* with the *small* amount of monomer supplied initially, provided that the mixture is allowed to react for a sufficiently long time. Then, on addition of the remaining monomer, the previously formed oligomers will propagate the polymerization of the added bulk of the monomer, yielding product of uniform size because the slow initiator was already consumed.

Contrary to the published claims, this technique cannot eliminate the undesired broadening of molecular weight distribution in virtually irreversible propagation. This is proved in the present paper, and the derived conclusions are confirmed by the experiments reported here. The misconception of this approach becomes obvious by considering first a simple kinetic scheme. Let an initiator I react with a monomer M in a bimolecular fashion with rate constant k_i. The resulting living polymers P* propagate, again in a bimolecular reaction, with propagation constant k_p, smaller than the initiation constant k_i. It will be shown that, whatever the concentration of the added monomer and however large is k_i, the initiator cannot be consumed *quantitatively* in irreversible polymerization ensuing in this system.

Simple Case. First-Order Initiation and Propagation

The kinetics of this system is described by three differential equations, $-\mathrm{d}I/\mathrm{d}t = k_iIM$, $-\mathrm{d}M/\mathrm{d}t = (k_iI + k_pP^*)M$, and $\mathrm{d}P^*/\mathrm{d}t = k_pIM$, with initial conditions at $t = 0$, $I = I_0$, $M = M_0$, and $P^* = 0$. The symbols I, M, and P^* denote the respective concentrations. It follows that

$$\mathrm{d}M/\mathrm{d}I = 1 + (k_p/k_i)(I_0 - I)/I$$

because $P^* = I_0 - I$, since each molecule of I forms one P* on reaction. Hence, M is a function of I and $I_0 - I$ only, being independent of M. Thus

$$M = M_0 + (1 - k_p/k_i)(I - I_0) + (k_p/k_i)I_0 \ln (I/I_0)$$

The amount I_r of the residual initiator left after all the monomer was polymerized is given by the solution of the equation

$$M_0 = (k_p/k_i - 1)(I_r - I_0) - (k_p/k_i)I_0 \ln (I_r/I_0)$$

Therefore, contrary to the expectation of some workers, the initiator cannot be used up *quantitatively*, whatever the initial concentration of the monomer, provided that initiation and propagation are irreversible.

These conclusions are clearly revealed by Figure 1. The curves M vs. I shown in this graph have identical shape for a constant I_0, being only displaced parallel to the M axis for various initial values of M_0. They are all approaching the M axis asymptotically as I tends to zero

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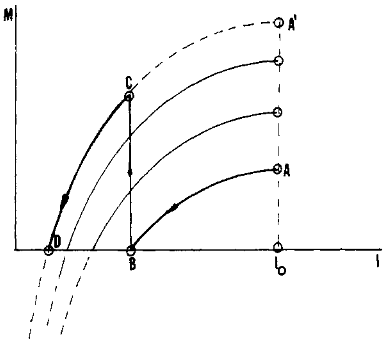

Figure 1. Plot of M as a function of I for the simple case of initiation first order in initiator and propagation first order in living polymers.

(physically an inaccessible region since M becomes negative and tends to $-\infty$). As shown by the curve ABCD the amount of residual initiator left at completion of the polymerization is the same whether all the monomer was added initially (at point A′) or consecutively (a small amount added at point A, followed by the rest added at point B, note BC = AA′).

General Case

Consider now a general case of polymerization when initiator and living polymers may exist in aggregated as well as in nonaggregated forms. This situation is typical for anionic polymerization initiated by organolithium compounds in hydrocarbon media.

Organolithium initiators and the growing lithiated polymers, denoted I and P*, respectively, form a variety of aggregates existing in a rapid equilibrium with each other. Moreover, mixed aggregates of the original organolithium compounds with the growing polymers may be formed in the course of polymerization. Thus, equilibria such as $I_4 \Leftrightarrow 4I$, K_1^{-1}, $I_2 \Leftrightarrow 2I$, K_2^{-1}, $(IP^*) \Leftrightarrow I + P^*$, K_3^{-1}, and $P^*_2 \Leftrightarrow 2P^*$, K_4^{-1}, are established if a system is composed of tetramers, dimers, and monomers of an initiator and the monomeric and dimeric growing polymers. In that case the following four equations describe the equilibrated system: $I_4 = K_1I^4$; $I_2 = K_2I^2$; $(IP^*) = K_3IP^*$; and $P^*_2 = K_4P^{*2}$. Here the symbols denote the concentrations of the respective species. The above four equations in conjunction with two stoichiometric relations, $I + 2I_2 + 4I_4 + (IP^*) = I_{\text{total}}$ and $P^* + 2P^*_2 + (IP^*) = P^*_{\text{total}}$, determine the concentrations of the six species, I, I_2, I_4, (IP^*), P^*, and P^*_2, provided that propagation does not perturb the above equilibria. This is plausible because the relaxation times of the pertinent association–dissociation reactions are very short, while the propagation is slow.

The above result is general. Whatever the complexity of the system, the concentrations of all the individual species participating in polymerization are uniquely determined by the pertinent equilibrium constants and the two stoichiometric equations involving two independent variables: I_{total} and P^*_{total}, briefly referred to as I_t and P^*_t, respectively.

The addition of a monomer molecule to the initiator, in whatever form, converts one I into one P*, hence, like in the previous case, the total concentration of living polymers at time t, denoted by $P^*_{t_t}$, is given by

$$P^*_{t_t} = I_{t_0} - I_t$$

where I_{t_0} and I_t denote the concentration of the initiator at $t = 0$ (initial) and at time t.

In spite of all the complexities of these systems, their treatment is greatly simplified by accepting the implicitly introduced assumption, namely, that the kinetics of each elementary step of initiation or propagation is first order in monomer. Therefore, the rate of the initiator consumption is

$$-dI_t/dt = F(I_t, I_{t_0} - I_t)M$$

with an analogous expression for the rate of monomer consumption

$$-dM/dt = \{F(I_t, I_{t_0} - I_t) + G(I_t, I_{t_0} - I_t)\}M$$

both functions being determined by two variables only, namely, I_t and $I_{t_0} - I_t$. Hence

$$dM/dI_t = 1 + G(I_t, I_{t_0} - I_t)/F(I_t, I_{t_0} - I_t)$$

is independent of the monomer concentration provided that the previously mentioned two assumptions are retained, namely, the equilibria between all the species participating in the polymerization are not perturbed by propagation, and the kinetics of each elementary step of the process is first order in monomer. Integration of the above differential equation gives M as a function of I_t and $I_{t_0} - I_t$.

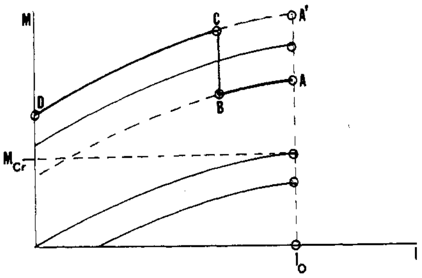

Figure 2. Plot of M as a function of I for the general case. Note: I does not reach zero for $M_0 < M_{cr}$. For $M_0 = M_{cr}$, $M = 0$ as $I = 0$.

It may be helpful to provide examples showing the forms acquired by the functions $F(I_t, I_{t_0} - I_t)$ and $G(I_t, I_{t_0} - I_t)$. For the previously treated system involving the six variables I, I_2, I_4, (IP^*), P^*, and P^*_2 we find

$$F(I_t, I_{t_0} - I_t) = k_1I + k_2I_2 + k_3I_4 + k_4(IP^*)$$

and

$$G(I_t, I_{t_0} - I_t) = k_5P^* + k_6P^*_2 + k_4(IP^*)$$

where k_1, k_2, k_3, k_4, k_5, and k_6 refer to the respective reactions

$$I + M \rightarrow P^* \qquad k_1$$

$$I_2 + M \rightarrow (IP^*) \text{ or } I + P^* \qquad k_2$$

$$I_4 + M \rightarrow I_2 + (IP^*) \qquad k_3$$

$$(IP^*) + M \rightarrow 2P^* \text{ or } P^*_2 \qquad k_4$$

$$P^* + M \rightarrow P^* \qquad k_5$$

$$P^*_2 + M \rightarrow P^*_2 \qquad k_6$$

Some of the k's may be zero, e.g., if I_4 and P^*_2 are inert, then k_3 and k_6 are equal to zero.

The independence of dM/dI_t of M and therefore of its initial concentration, M_0, implies that the curves giving M as functions of I_t and $I_{t_0} - I_t$ have identical shapes for constant I_0 but, like in the simple case, are displaced parallel to the M axis, depending on the value of M_0. Such curves are exemplified by Figure 2. Note the two kinds of systems: (a) for $M_0 > M_{cr}$ the initiator is consumed quantitatively prior to the completion of polymerization; (b) for $M_0 < M_{cr}$ some residual initiator is left at the completion of polymerization.

Integration of $\mathrm{d}M/\mathrm{d}I_t$ and substitution by zero of M and I_t in the resulting expression provides the equation yielding the value of M_{cr}. The simple system, discussed previously, is of type b as pointed out earlier.

It is desired to provide examples of some systems of type a. Consider polymerization for which the rate of initiation is proportional to $1/n$th power of the initiator's concentration ($n > 1$), while the propagation is proportional to the concentration of the growing polymers. This is the case of an inert initiator I_n in equilibrium with a minute amount of an active monomeric initiator, I, forming nonassociated living polymers P*. The pertinent differential equations are

$$-\mathrm{d}I_t/\mathrm{d}t = k_i I_t^{1/n} M \qquad \text{with } n > 1$$

$$-\mathrm{d}M/\mathrm{d}t = \{k_i I_t^{1/n} + k_p(I_{t_0} - I_t)\}M$$

leading to

$$\mathrm{d}M/\mathrm{d}I_t = 1 + (k_p/k_i)(I_{t_0} - I_t)/I_t^{1/n}$$

Integration gives

$$M = M_0 + I_t - I_{t_0} - n(k_p/k_i)\{I_t^{2-(1/n)}/(2n - 1) - I_{t_0} I_t^{1-(1/n)}/(n - 1)\} + \{n^2/(2n - 1)(n - 1)\}(k_p/k_i)I_{t_0}^{2-(1/n)}$$

and

$$M_{cr} = I_{t_0} + \{n^2/(2n - 1)(n - 1)\}(k_p/k_i)I_{t_0}^{2-(1/n)}$$

A more complex system was discussed by Worsfold and Bywater,[3] namely, an initiation $^1/_6$ order in the initiator and propagation $^1/_2$ order in living polymers. An approximate solution was reported. The results resemble qualitatively those discussed above; i.e., all the initiator is consumed whenever the concentration of the monomer exceeds some critical value M_{cr} that depends on I_{t_0}, while some residual initiator is left at completion of polymerization when $M_0 < M_{cr}$. For example, in the polymerization discussed in their paper 30% of the initiator was left unreacted at the completion of the quantitative conversion of the monomer into polymers.

It is interesting to consider the situation depicted in Figure 2 by the line described by ABCD. Polymerization starts with a relatively low concentration of the monomer corresponding to point A on the curve shown in Figure 2. At some stage, say, at a point denoted by B, fresh monomer is added, increasing the amount of monomer by the equivalence of BC. The reaction continues then along the curve CD. It follows from our discussion that the polymer obtained at point D has the same degree of polymerization and the same distribution of molecular weights as the polymer produced by starting with the higher initial concentration of the monomer corresponding to point A′. Note AA′ = BC. Hence, we conclude again that the mode of monomer addition does not influence the outcome of polymerization.

The last statement requires elaboration. Approximate molecular weight distribution is derived by the following reasoning. Let us assume that $\mathrm{d}M$ moles of monomer polymerized at that stage of the process when the concentration of living polymers = P^*, is evenly distributed between all the available polymers. Then the degree of polymerization of each of these polymers increases by $\mathrm{d}n = \mathrm{d}M/P^*$. Each polymer grows from the time of its formation when the concentration of the available monomer is M and the concentration of initiator is I_t until the completion of polymerization. We are concerned here only with this stage of the process when initiator is still available. Since $\mathrm{d}M = (1 + G/F)\mathrm{d}I_t$ and $P^* = I_{t_0} - I_t$, we find $\mathrm{d}n = \{(1 + G/F)/(I_{t_0} - I_t)\}\ \mathrm{d}I_t$ to be independent of M. The integrated molecular weight distribution is given by

$$\mathrm{d}P^*/\mathrm{d}n = -(I_{t_0} - I_t)/(1 + G/F)$$

and therefore it is independent of M and hence of the mode of monomer addition. Exact treatment should take into account the Poisson type of broadening of each n-mer, a correction we neglect. After all the initiator is consumed, provided that the monomer is still available, we are dealing with the conventional Poisson type of growth.

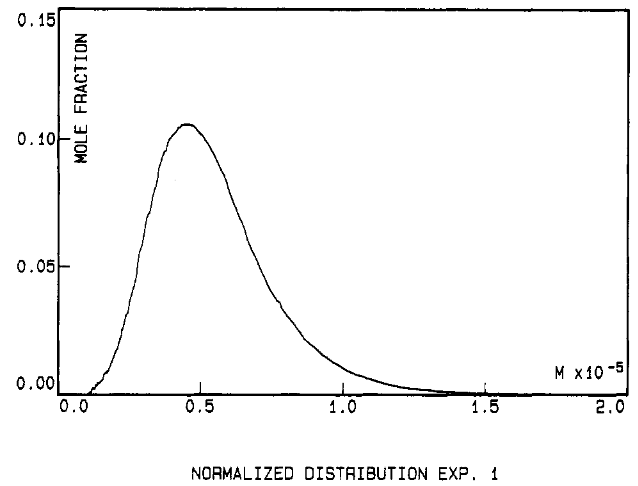

Figure 3. Molecular weight distribution for the polymer obtained on "at once" addition of all the monomer to the initiator.

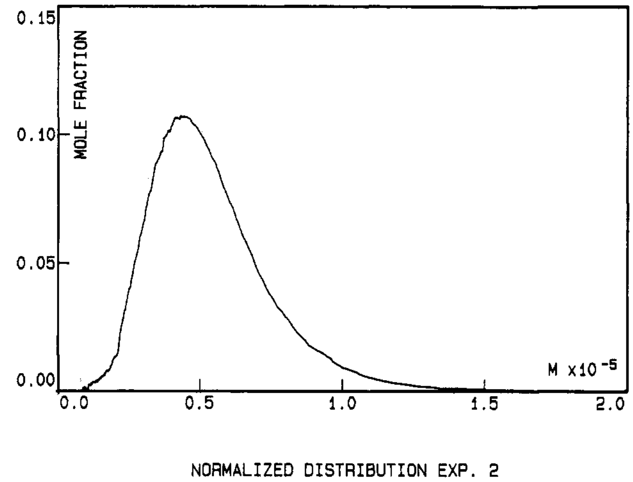

Figure 4. Molecular weight distribution for the polymer obtained by sequential monomer addition (seeding technique). Note: the sequential addition leads to the same molecular weight distribution as the "at once" addition of all the polymer.

Experimental Evidence

The conclusions drawn in the previous sections were confirmed by the following experiments. Styrene in benzene solution was polymerized with freshly recrystallized ethyllithium. Two experiments were performed. In the first one, 3.7 mL of styrene, degassed and carefully dried, was dissolved in 26 mL of rigorously purified and dried benzene. That solution was then added *at once* to a stirred solution of 6.46 × 10^{-5} mol of EtLi in 23 mL of benzene. Stirring was continued for 24 h at room temperature, and thereafter 1 mL of methanol was added to quench the reaction mixture. All these operations were performed under high vacuum.

After evaporation of benzene the residue was dissolved in 100 mL of 2-butanone, and the polymer was precipitated by dropwise addition of its solution to 300 mL of methanol, filtered off, and then dried. Its number-average molecular weight determined by

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.

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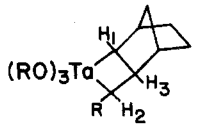
Communications to the Editor

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 $\mathrm{Ta(CH^tBu)(OR)_3(THF)}$ complexes (OR is 2,6-diisopropylphenoxide (DIPP) or 2,6-dimethylphenoxide (DMP)) can be prepared straightforwardly from $\mathrm{TaCl_5}$ and $\mathrm{Zn(CH_2{}^tBu)_2}$ in three high-yield steps.[2] Addition of 1 equiv of norbornene (NBE) at −30 °C to $\mathrm{Ta(CH^tBu)(DMP)_3(THF)}$ 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 $(\eta^5\text{-}\mathrm{C_5H_5})_2\overline{\mathrm{TiCHRCHC_5H_8CH}}$ ($\mathrm{R = CMe_2CH{=}CH_2}$) 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 $\overline{\mathrm{TaCH^tBuCHC_5H_8}}\mathrm{CH(DIPP)_3}$ (2a) in $\mathrm{C_6D_6}$

[Ta], mM	$[\mathrm{NBE}]_0$, 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 $\mathrm{Ta(CH^tBu)(DIPP)_3(THF)}$ and NBE produces more crystalline, colorless **2a** (64% from ether) whose ^{1}H NMR and ^{13}C NMR spectra are analogous as far as the $\mathrm{TaC_3}$ 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 $\mathrm{C_6D_6}$ **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-

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