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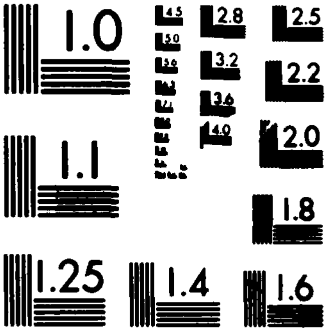

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by

John S. Murdzek and Richard R. Schrock*

Contribution from

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Abstract

Addition of 50-200 eq of norbornene to $Mo(CH^{t}Bu)(NAr)(O^{t}Bu)_2$ yields living polymers, $Mo\{[CH(C_5H_8)CH]_xCH^{t}Bu\}(NAr)(O^{t}Bu)_2$ (55% *trans*), that are stable for days in the absence of water and oxygen with essentially no isomerization of the double bonds in the chain. Addition of benzaldehyde cleaves off the polymer in a Wittig-like reaction to yield polynorbornenes with polydispersities in the range 1.04-1.11. Analogous reactions involving 50-200 eq of *endo,endo*-5,6-dicarbomethoxynorbornene yields homopolymers with polydispersities in the range 1.11-1.22. Block copolymers containing 50 eq of *endo,endo*-5,6-dicarbomethoxynorbornene and 200 eq of norbornene prepared by adding one or the other monomer first are virtually identical (polydispersities 1.06 and 1.09 with $\bar{M}_n$ 57200 and 59900, respectively). These results suggest that the molybdenum catalyst will not react significantly with up to 100 eq of ester functionality during the time of a typical polymerization reaction (~15 m at 25°).

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John S. Murdzek and Richard R. Schrock

Submitted for Publication

in

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Massachusetts Institute of Technology
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Abstract

Addition of 50-200 eq of norbornene to Mo(CH^{t}Bu)(NAr)(O^{t}Bu)$_2$ yields living polymers, Mo{[CH(C$_5$H$_8$)CH]$_x$CH^{t}Bu}(NAr)(O^{t}Bu)$_2$ (55% *trans*), that are stable for days in the absence of water and oxygen with essentially no isomerization of the double bonds in the chain. Addition of benzaldehyde cleaves off the polymer in a Wittig-like reaction to yield polynorbornenes with polydispersities in the range 1.04-1.11. Analogous reactions involving 50-200 eq of *endo,endo*-5,6-dicarbomethoxynorbornene yields homopolymers with polydispersities in the range 1.11-1.22. Block copolymers containing 50 eq of *endo,endo*-5,6-dicarbomethoxynorbornene and 200 eq of norbornene prepared by adding one or the other monomer first are virtually identical (polydispersities 1.06 and 1.09 with M$_n$ 57200 and 59900, respectively). These results suggest that the molybdenum catalyst will not react significantly with up to 100 eq of ester functionality during the time of a typical polymerization reaction (~15 m at 25°).

In general, classical metathesis catalysts will not tolerate functionalities such as the carbonyl group.[1] In some cases it has proven possible to ring-open polymerize functionalized norbornenes, although it has never been shown that none of a given catalyst is destroyed during the course of the reaction.[1d] Recently we have shown that catalysts of the generic type W(CHR')(NAr)(OR)$_2$ (Ar = 2,6-diisopropylphenyl; R and R' = alkyl groups[2]) will react with norbornene when OR = t-butoxide to give polynorbornene with a polydispersity approaching 1,[3] and that analogous molybdenum complexes of the type Mo(CHR')(NAr)(OR)$_2$ are active for the metathesis of ordinary olefins at rates that vary from very fast when OR = OCMe(CF$_3$)$_2$ to virtually zero when OR = t-butoxide.[4] We have found that W(CH^{t}Bu)(NAr)(O^{t}Bu)$_2$ will polymerize *endo,endo*-5,6-dicarbomethoxynorbornene, but the catalyst is destroyed rapidly and molecular weight therefore cannot be controlled. We suspected that the metal-carbon bond in Mo(CHR)(NAr)(O^{t}Bu)$_2$ might not be as strongly polarized as it is in W(CHR)(NAr)(O^{t}Bu)$_2$, and therefore that molybdenum complexes would not react as readily with the ester functionality as tungsten complexes. We show here that Mo(CH^{t}Bu)(NAr)(O^{t}Bu)$_2$ is an initiator in a living polymerization reaction in which at least 100 eq of the ester carbonyl (50 eq of monomer) is tolerated on the time scale of a typical polymerization reaction (~15 m).

The addition of norbornene to a solution of Mo(CH^{t}Bu)(NAr)(O^{t}Bu)$_2$[4] (1) under standard reaction conditions[5] yielded low dispersity polynorbornenes with molecular weights proportional to the quantity of monomer employed (Table I, entries 1-3). If only 10 eq of norbornene is added to an NMR sample of 1 in C_6D_6 (H_α at 11.23 ppm) a new alkylidene H_α signal can be observed at 11.52 ppm, a doublet characteristic of Mo{[CH(C$_5$H$_8$)CH]$_x$CH^{t}Bu}(NAr)(O^{t}Bu)$_2$ (2) (cf. H_α at 8.05 ppm in W(CH^{t}Bu)(NAr)(O^{t}Bu)$_2$ and 8.36 ppm in W{[CH(C$_5$H$_8$)CH]$_x$CH^{t}Bu}-(NAr)(O^{t}Bu)$_2$[3]); the ratio of 1 to 2 is 1:9, and the total is equal to the initial amount of 1 (vs. an internal standard). If only one equivalent of norbornene is employed then 83% 1 remains. These results suggest that the rate of initiation by 1 is slightly slower than the rate of propagation by 2,[6] presumably for steric reasons. All polynorbornene obtained employing 1 at 25° is ~55% *trans*. A sealed NMR sample that had been prepared with 20 eq of norbornene (91:9 ratio of 2 to 1; 54% *trans*) changed little in two weeks (93:7 ratio of 2 to 1; 57% *trans*), signifying that the living polymer does not isomerize C=C bonds in the polymer chain. (Isomerization of *cis* to *trans* (~85%) in such polymers is observed if catalysts that are active for metathesis of ordinary olefins, e.g., $Mo(CH^tBu)(NAr)[OCMe(CF_3)_2]_2$,[4] are added; 1 is virtually inactive for the metathesis of *cis*-2-pentene.)

We first showed that norbornene could be polymerized in the presence of 10 eq of ethyl acetate. Entry 4 in Table I shows that polynorbornene prepared from 100 eq of NBE is virtually identical to that obtained in the absence of ethyl acetate, good evidence that the Mo=C bonds are not destroyed to any significant extent by 10 eq of the ester during the polymerization reaction (10-15 m).

Addition of 20 eq of *endo,endo*-5,6-dicarbomethoxynorbornene (DCNBE) to 1 in C_6D_6 quantitatively converted it (vs. an internal standard) into a living polymer (3; Figure 1a) that has an alkylidene H_α signal at 11.64 ppm. The olefinic proton resonances in what we presume to be a mixture of *cis* and *trans* polymer at 5.75 ppm could not be resolved. If only 1 eq of DCNBE is added to 1, 68% 1 remains. Therefore we can say that 1 is converted more efficiently to the living polymer in the case of DCNBE than in the case of NBE, although initiation is the slower step in both cases.[6,8] When 50 and 100 eq of DCNBE are added to 1 in a manner analogous to the reactions in which polynorbornene is prepared, the resulting polymer has a low polydispersity, characteristic of a living polymerization catalyst system (Table I). The fact that the polydispersity with 100 eq is not quite as good as that for the analogous polynorbornene suggests that there may be some slow destructive reaction between the catalyst and the ester carbonyl group. This is supported by the fact that the polymer prepared using 200 eq of DCNBE, although it has the expected molecular weight relative to the polymer prepared employing 100 eq of DCNBE, has an even higher polydispersity. Poly-DCNBE is much less viscous that polynorbornene, and systems in which it is prepared therefore more easily manipulated. Full characterization of it and related polymers will be reported in due course.

If a living polymer containing 20 eq of NBE is prepared and 20 eq of DCNBE is added to it, an ^1H NMR spectrum shows that the H_α resonance for 2 is completely replaced by one characteristic of 3, and that the remainder of the spectrum is a virtual composite of that for 2 and that for 3 (Figure 1b). An analogous sample prepared by adding 20 eq of DCNBE first, followed by 20 eq of NBE has an identical spectrum, except the chemical shift of the H_α resonance is close to that of 2. The carbon NMR spectra of the 2/3 and 3/2 block copolymers also are virtual composites of the spectra for the individual homopolymers when the chain is relatively long (>20 units).

The results of two critical experiments are shown as the last two entries in Table I. Living copolymers were prepared via the sequential addition of 50 equivalents of DCNBE and 200 eq of NBE (and *vice versa*) to 1 over a period of ~15 m, cleaved off with benzaldehyde, and characterized in the standard manner.[5] The number average molecular weights and the polydispersities of the two block copolymers are virtually identical. (The slightly higher M_n and polydispersity in the 50/200 block could be ascribed to a small amount of distruction of alkylidene catalyst centers since chain propagating species are exposed to ester for a longer period.) Therefore no significant amount of catalyst is destroyed in either experiment, and we must conclude on the basis of these and the results described above that at least 100 eq of ester functionality (in 50 eq of monomer) is tolerated absolutely on the time scale of a typical experiment (15 minutes).

To our knowledge this is the first report of a controlled polymerization of a norbornene that is derivatized with a relatively reactive functionality. We believe these results have important practical implications for the preparation of functionalized homo- and block copolymers, and are in the process of determining what other functionalities can be tolerated. These results also point out that differences in reactivity between analogous molybdenum and tungsten alkylidene complexes can be relatively important from the practical point of view of being able to prepare low polydispersity polymers.

Acknowledgment RRS thanks the Office of Naval Research for support (N00014-87-K-0099).

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(1) (a) Ivin, K.J. "Olefin Metathesis," Academic Press, London, 1983. (b) Grubbs, R.H. in "Comprehensive Organometallic Chemistry," Wilkinson, G.; Stone, F.G.A.; Abel, E.W.; Eds., Vol 8, Pergamon, 1982. (c) Dragutan, V.; Balaban, A.T.; Dimonie, M. "Olefin Metathesis and Ring-opening Polymerization of Cyclo-Olefins," 2nd Ed., Wiley-Interscience, 1985. (d) It has been stated (reference 1a, p. 260) that *exo,endo*-5,6-dicarbomethoxynorbornene has been polymerized. To our knowledge this was not a controlled polymerization analogous to that we report here for the *endo,endo* monomer. Polymerization of the *endo,endo* monomer has never been reported.

(2) Schaverien, C.J.; Dewan, J.C.; Schrock, R.R. *J. Am. Chem. Soc.* **1986**, *108*, 2771.

(3) Schrock, R.R.; Feldman, J.; Cannizzo, L.F..; Grubbs, R.H. *Macromolecules* **1987**, *20*, 1169.

(4) Murdzek, J.S.; Schrock, R.R. *Organometallics* **1987**, *6*, 1373.

(5) All reactions were performed under an atmosphere of dinitrogen. A standard reaction consisted of adding the monomer dissolved in 7-10 mL of toluene dropwise over 5 minutes to a vigorously stirred solution of 10 mg of **1** in 25 mL of toluene. Stirring was continued for 5 minutes and then 10 μL of benzaldehyde was added in order to cleave off the polymer through a Wittig-like reaction (confirmed by ^{1}H NMR to be complete in seconds, even at these low concentrations). The solution was then concentrated to 10mL and the polymer precipitated by addition of 50 mL of methanol containing ~1% 2,6-di-t-butyltoluene (BHT) as an antioxidant. The polymer was collected, dried *in vacuo* , and analyzed by standard gel permeation chromatography in toluene on a Waters 150C instrument equipped with three styragel columns calibrated with polystyrene standards. A single, smooth, symmetrical peak was observed in all cases. Very occasionally a small amount (~5%) of a relatively high molecular weight material was observed. It was not included in the dispersity calculations. Similar sporadic high molecular weight polymer was observed also in the tungsten-based system.[3] The high molecular weight material has not yet been identified. The possibility that it is an artifact cannot be excluded.

(6) If one assumes that the rate of propagation equals the rate of initiation, then addition of one equivalent of monomer should leave only 37% of 1 behind.[7] The difference in rate of propagation versus rate of initiation evidently is not great enough to raise significantly the polydispersity of polymers containing more than 50 eq of monomer.

(7) Peebles, L.H., Jr. "Molecular Weight Distributions in Polymers," Wiley-Interscience, New York, 1971.

(8) Kinetic studies at low temperatures confirm these proposals. Full details will reported in due course.

Table I. Polymers prepared from norbornene and *endo,endo*-5,6-dicarbomethoxynorbornene.[a]

Eq monomer	M_n(theory)	M_n(found)	Polydispersity
50 NBE	4870	13500	1.11
100 NBE	9580	22100	1.06
200 NBE	19000	48600	1.04
100 NBE	9580	21900	1.07[a]
50 DCNBE	10700	17400	1.11
100 DCNBE	21200	37700	1.12
200 DCNBE	42200	63300	1.22
50 + 200[b]	29500	59900	1.09
200 + 50[c]	29500	57200	1.06

[a] All reactions were performed in the same manner.[5] Molecular weights are relative to polystyrene; approximate true molecular weights can be obtained by dividing by 2.2.[1a,3]

[b] Reaction performed in the presence of 10 eq of ethyl acetate.

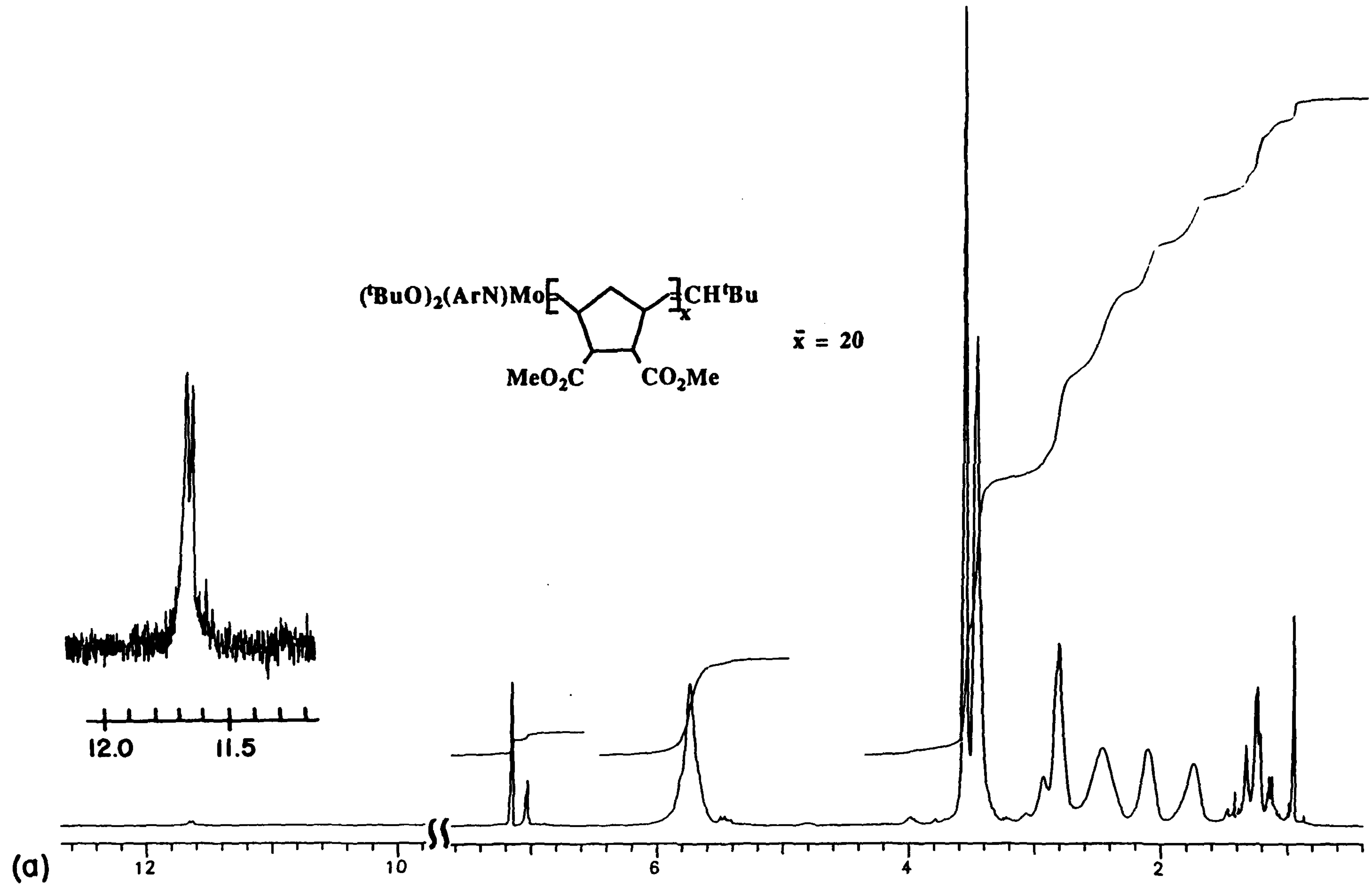
[c] 50 eq of *endo,endo*-5,6-dicarbomethoxynorbornene followed by 200 eq of norbornene.

[d] 200 eq of norbornene followed by 50 eq of *endo,endo*-5,6-dicarbomethoxynorbornene.

Figure Captions

Figure 1. The ^{1}H NMR spectrum of a sample of Mo(CH^{t}Bu)(NAr)(O^{t}Bu)$_2$ after addition of 20 eq of *endo,endo*-5,6-dicarbomethoxynorbornene.

Figure 2. The ^{1}H NMR spectrum of a sample of Mo(CH^{t}Bu)(NAr)(O^{t}Bu)$_2$ after addition of 20 eq of norbornene followed by 20 eq of *endo,endo*-5,6-dicarbomethoxynorbornene.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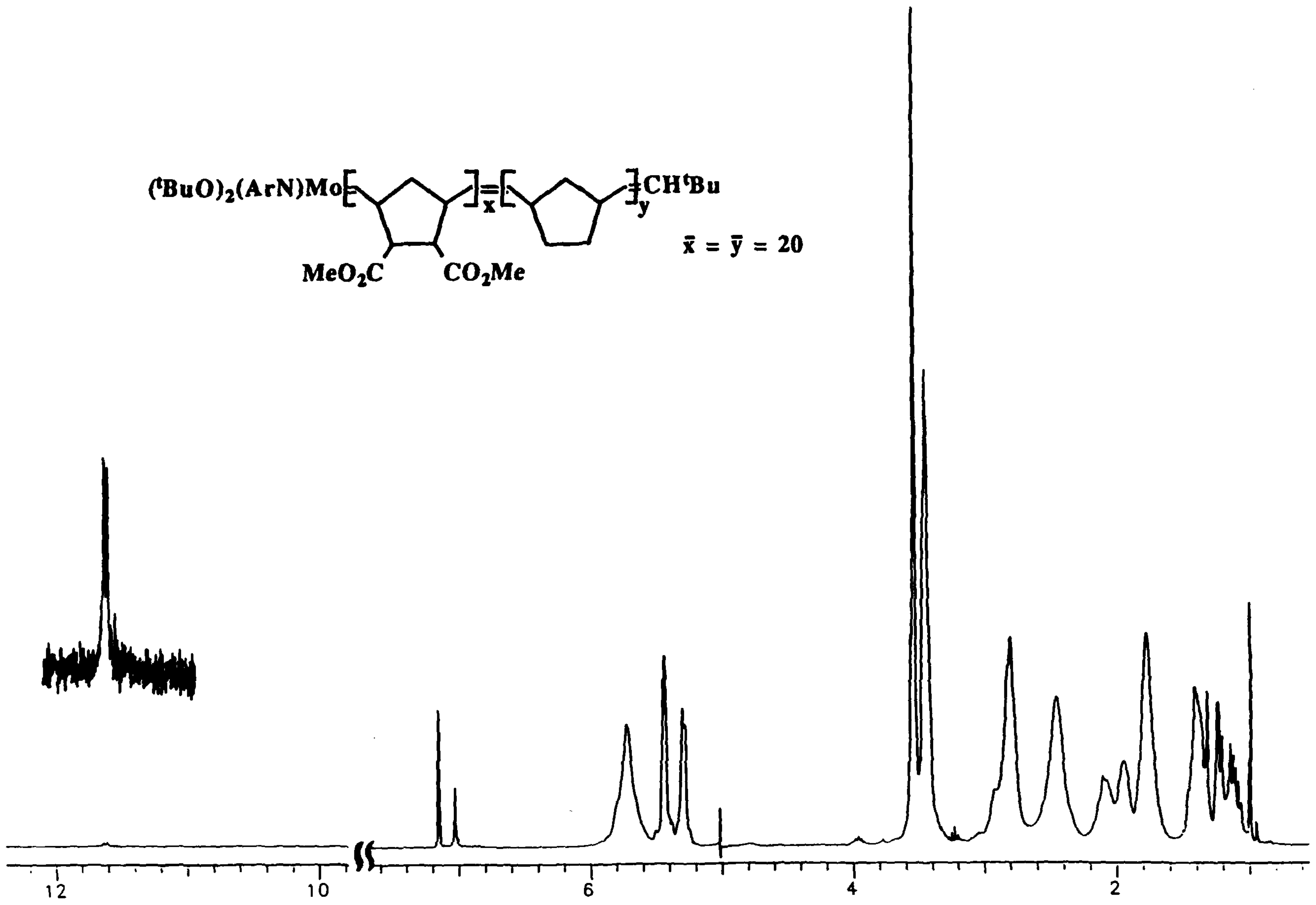

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