

## Living non-conjugated polyacetylenes

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### SUMMARY

The non-conjugated poly (3,3-dimethyl-1-butyne) and poly (1-trimethylsilyl)-1-propyne were prepared by metathesis catalysts and the polymerization was monitored for molecular weight by GPC and monomer conversion by GC. Both the 1-(trimethylsilyl)-1-propyne and 3,3-dimethyl-1-butyne gave a linear relationship with number average molecular weight versus conversion and number average molecular weight versus monomer to initiator ratio. The 1-(trimethylsilyl)-1-propyne failed to polymerize beyond 100% conversion. The 3,3-dimethyl-1-butyne, however, gave conversion to 300%, with GPC data clearly showing the continuation of propagation from the living polymer chain. The living character of these polymerizations seems to be the result of both the lack of backbiting which can occur only from a cis-cisoidal growing chain, and the lack of interchain reactions. Both the cis-cisoidal configuration and the interchain reactions are prohibited for steric reasons.

### INTRODUCTION

The generally accepted mechanism of ring opening polymerization of cycloolefins by metathesis catalysts consists of the reversible [2+2] cycloaddition of a transition metal carbene complex to a carbon-carbon double bond with the formation of a metallacyclobutane intermediate (1-3). The origin of the carbon-carbon double bond reaction with the metal carbene (i.e. from a monomer, from its own growing polymer chain and/or from a different polymer chain) leads to either propagation, backbiting with cyclics formation, and interchain reactions with broadening polydispersity. This polymerization process resembles the overall polymerization behavior of cationic ring opening polymerization of heterocyclic monomers.

The first direct observations of the simultaneous presence and of the interconversion of chain propagating metal-carbene and metallacyclobutane complexes were recently reported and these experiments have led to the discovery of the living metathesis polymerization of cycloolefins (4-6). The goal of this paper is to present some preliminary data on the living metathesis polymerization of 3,3-dimethyl-1-butyne and 1-(trimethylsilyl)-1-propyne.

### EXPERIMENTAL

#### Materials

1-(Trimethylsilyl)-1-propyne and 3,3-dimethyl-1-butyne (both from

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Farchan Labs) were distilled from calcium hydride under argon at atmospheric pressure. Purity by gas chromatography (GC) was 99.5% for the 3,3-dimethyl-1-butyne, and 97.0% for the 1-(trimethylsilyl)-1-propyne with the major impurity for the second monomer being hexamethyldisiloxane.  $\text{MoCl}_5$  (99+%) and  $\text{TaCl}_5$  (99+%) both from Morton Thiokol were used without further purification.

### Polymerizations

In a typical polymerization experiment, 0.5g (0.0061 mole) of 3,3-dimethyl-1-butyne is added to a solution of 0.026g (0.01 mmole)  $\text{MoCl}_5$  in 10ml of sodium dried toluene at 30°C. The reaction mixture is stirred for 24 hours. At various reaction intervals, aliquots were removed and added to methanol. The obtained polymer was evaluated for molecular weight by GPC and the resultant solution was monitored for monomer conversion by GC.

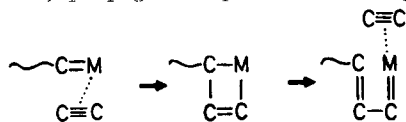
### Techniques

The relative molecular weights of polymers were measured by gel permeation chromatography (GPC) with a Perkin-Elmer Series 10 LC using THF as solvent (1ml/min at 40°C) and a calibration plot constructed with polystyrene standards. Monomer conversions were determined on an Hewlett-Packard HP 5890 GC using a 6.1m X 0.32cm column of 10% SP-1000 80/100 Supelcoport. Chemical modifications of the polymer backbone were attempted using conventional techniques. The extent of reaction was measured using an XL 200 Varian NMR spectrometer and a Perkin-Elmer 1320 infrared spectrophotometer.

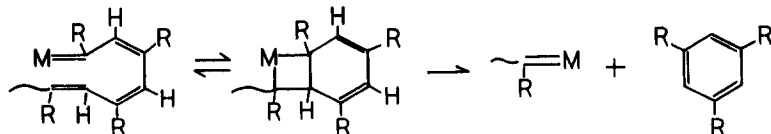
### RESULTS AND DISCUSSION

It is well documented that living ring opening cationic polymerization requires preferably a higher rate constant of propagation than backbiting or interchain reactions (i.e. termination). From a series of kinetic studies with cyclic sulfides, amines and cyclic esters of phosphonic acid, it was shown that in a given series of monomers with the same parent heterocycle, the ratio  $k_p/k_t$  increases with the bulkiness and the number of substituents on the monomer. Although the absolute rate of polymerization also decreases, the presence of substituents retards the termination more than the propagation (for a review see 7).

It seems to be accepted that the polymerization of acetylenes initiated by metal halides or metal halide based catalysts (W, Mo, Ta, etc) proceeds through a mechanism quite similar to the metathesis polymerization of cycloolefins i.e., propagation proceeds through metal carbenes (8-13).

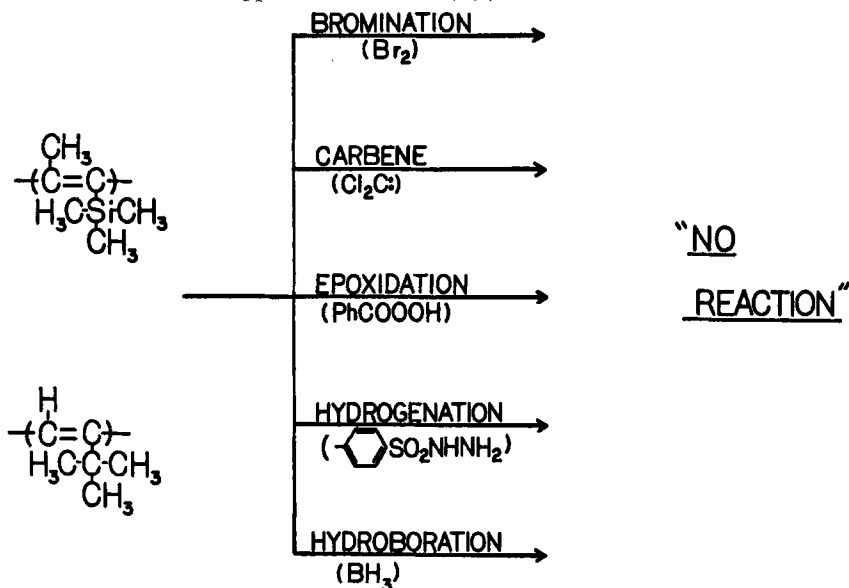


A possible termination mechanism in the polymerization of acetylenic monomers could be the backbiting of the propagating metal carbenes in a cis-cisoidal growing chain as shown below:



Evidence supporting this mechanism is going to be published elsewhere (14). We are assuming that when this backbiting reaction is avoided for steric reasons, the polymerization would have to proceed through a living mechanism. Based on the same principles as those previously discussed for the case of ring opening polymerization, bulky side groups would increase the ratio  $k_p/k_t$  and therefore lead to living polymerizations. Two monomers of potential interest in this respect are 3,3-dimethyl-1-butyne and 1-(trimethylsilyl)-1-propyne which were extensively studied by Higashimura and Masuda's group (15).

Scheme 1 outlines the synthetic procedures used to functionalize the backbone of both the poly (3,3-dimethyl-1-butyne) and the poly (1-(trimethylsilyl)-1-propyne). The polymer backbone was non-reactive. This was not an expected result for a non-conjugated polymer. Both polymers absorb in the UV below 340nm and therefore their double bonds are non-conjugated due to their non-overlapped  $\pi$  orbitals (15).



Scheme 1: Synthetic procedures used to functionalize the polymer backbone.

In addition, it was shown by molecular modeling that both polymers could not adopt a cis-cisoidal configuration due to steric reasons. These were extremely important results in that first, the propagating metal carbene could not terminate via a cis-cisoidal backbiting mechanism giving the stable aromatic derivative, and secondly, that the reactivity of the double bonds along the polymer chain was probably insufficient to react in an inter/intrachain fashion with the metal carbene, again leading to termination.

Studies were then completed for both polymers where the molecular weight and monomer conversion were monitored for a series of polymerizations having different monomer-initiator ratios. Figure 1 shows the number average molecular weight versus conversion for the polymerization of 1-(trimethylsilyl)-1-propyne. A linear relationship indicative of a living polymerization was observed. The high polydispersities we feel are not unexpected. The initiation process requires two steps: metal carbene formation, followed by initiation. Initiation could be fast relative to prop-

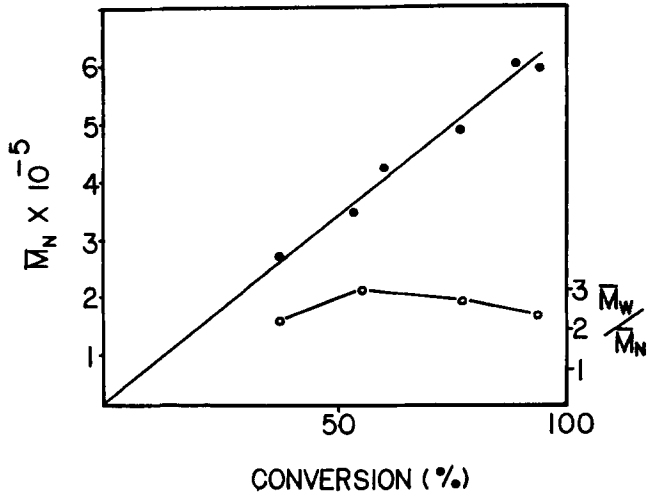


Figure 1. The dependence of number average molecular weight versus conversion for the polymerization of 1-(trimethylsilyl)-1-propyne by  $\text{TaCl}_5$  (toluene,  $80^\circ\text{C}$ ,  $[\text{M}_0] = 1.0\text{M}$ ,  $[\text{I}_0] = 20\text{mM}$ ).

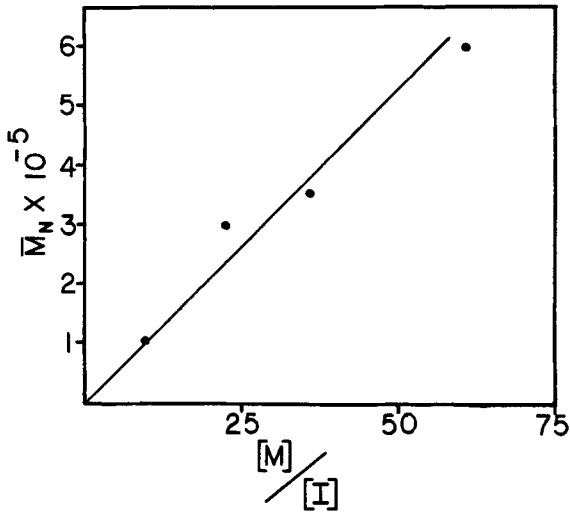


Figure 2. The dependence of number average molecular weight versus monomer-initiator ratio for the polymerization of 1-(trimethylsilyl)-1-propyne by  $\text{TaCl}_5$  (toluene,  $80^\circ\text{C}$ , 100% conversion).

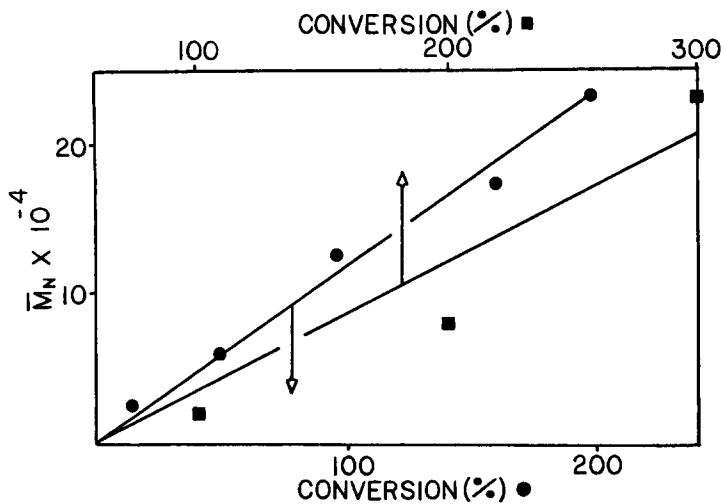


Figure 3. The dependence of number average molecular weight versus conversion for the polymerization of 3,3-dimethyl-1-butyne by  $\text{MoCl}_5$  (toluene,  $30^\circ\text{C}$ ; ●,  $[\text{M}_0] = 0.5\text{M} + 0.5\text{M}$ ,  $[\text{I}_0] = 20\text{mM}$ ; ■, data from figure 5.).

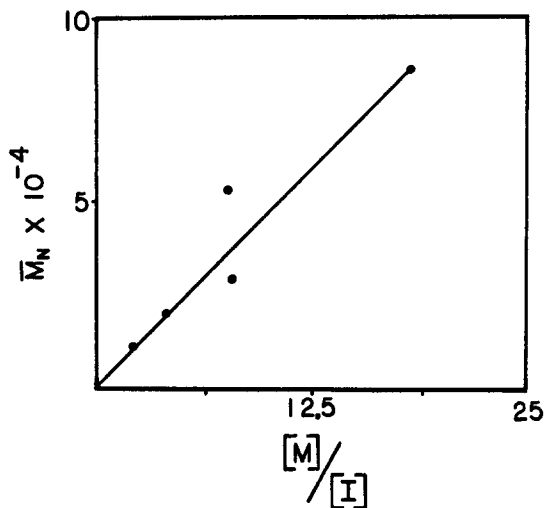


Figure 4. The dependence of number average molecular weight versus monomer-initiator ratio for the polymerization of 3,3-dimethyl-1-butyne by  $\text{MoCl}_5$  (toluene,  $30^\circ\text{C}$ , 100% conversion).

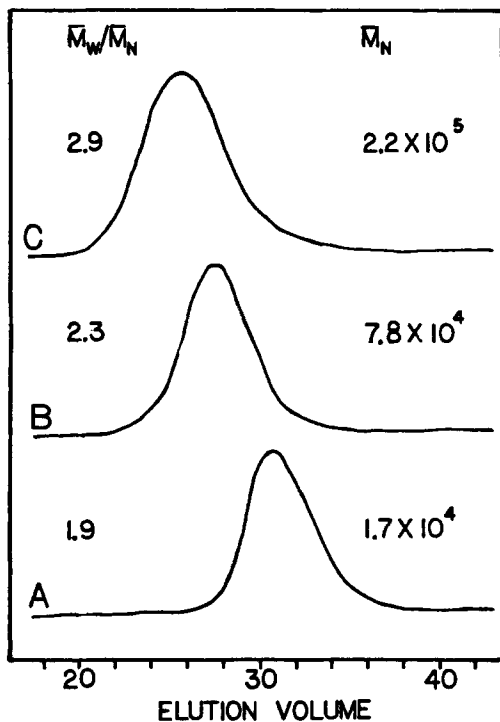


Figure 5. GPC traces for the polymerization of 3,3-dimethyl-1-butyne. A)  $[M_0] = 0.2M$ , 100% conversion; B)  $[M_0] = 0.2M + 0.5M$ , 200% conversion C)  $[M_0] = 0.2M + 0.5M + 0.5M$ , 300% conversion;  $[I_0] = 20mM$ .

agation (i.e. addition of carbene to triple bond), yet carbene formation may be slow and therefore it represents the rate determining step. Actually the mechanism of this step and the nature of the metal carbene formed are unknown (14). Therefore, although the real rate of initiation could be even faster than propagation, the apparent rate of initiation is lower than propagation and this leads to polymers with broad polydispersity. Figure 2 presents the number average molecular weight versus monomer-initiator ratio for the same polymer, again giving a linear relationship as one would expect for a living polymerization. Repeated attempts however to continue the polymerization beyond 100% conversion have failed. Our present best explanation is that the growing metal carbene chain is reacting with the hexamethyldisiloxane and therefore terminates the polymerization. Polymerizations monitored under the same conditions with added hexamethyldisiloxane gave low conversions. Figure 3 shows the number average molecular weight versus conversion for the polymerization of 3,3-dimethyl-1-butyne by  $MoCl_5$ . A linear relationship was achieved. Figure 4 gives the relationship of number average molecular weight versus monomer to initiator ratio obtained at 100% conversion. In Figure 5 is presented the GPC traces of a polymerization monitored to 100% conversion (curve A), with subsequent monomer addition and monitoring to 200% conversion (curve B), and again to 300% conversion (curve C). These curves clearly demonstrate the continuation of propagation from the living polymer chain.

In conclusion, we can state that these polymerizations follow a living

mechanism. The living character seems to be the result of both the lack of backbiting which can occur only from a cis-cisoidal configuration and the lack of interchain reactions. Both the cis-cisoidal configuration and the interchain reactions are prohibited for steric reasons.

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