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The polymerization of alkyl substituted acetylenes using metal halide based initiators: The bulky substituent effect

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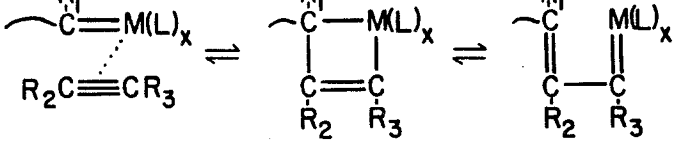
SUMMARY

The polymerization of 1-hexyne, 3,3-dimethyl-1-butyne, 2-hexyne and 1-chloro-1-hexyne by using metal halide based initiators was studied. By analogy with ionic ring opening polymerization systems, living acetylene polymerizations resulted when backbiting and interchain reactions were suppressed, i.e., k_{tr}, $k_t=0$. Large acetylenic substituents suppress the formation of cis-cisoidal propagating chains and subsequently eliminate backbiting reactions and also propagating carbene interchain reactions. Possible explanations for differences in polymer dispersities which result under different reaction conditions were also provided.

INTRODUCTION

A living polymerization represents a polymerization reaction in which the termination and transfer reaction steps are absent (i.e. $k_t=0$, $k_{tr}=0$). When the rate constant of initiation is higher than that of propagation ($k_i>>k_p$) the resulting polymers exhibit narrow molecular weight distribution. A living polymer results in a characteristic linear number average molecular weight versus conversion relationship ($k_{tr}=0$), a linear ln $[M]_0/[M]_t$ versus time relationship ($k_t=0$) and a Poisson molecular weight distribution. A Poisson molecular weight distribution is, in fact, sufficient proof that a system is living (1).

The preparation of alkyl substituted acetylenes has been extensively studied by the Higashimura and Masuda research group at Kyoto University (2). They have shown that a wide variety of alkyl and phenyl substituted acetylenes can be polymerized to high molecular weight polymers using transition metal halides or transition metal halide based initiators (WCl_6, $MoCl_6$, $TaCl_6$, etc.). The generally accepted mechanism of acetylene polymerization initiated with these initiators is believed to resemble the metathesis mechanism accepted for the ring opening polymerization of cyclic olefins, i.e. initiation and propagation through metal carbenes which are in dynamic equilibrium with metal cyclometallobutenes (3-6). There is, however, limited experimental evidence to support this mechanism of polymerization of acetylene derivatives (7-11).



As described previously, there are three approaches to the development of the living polymerization of acetylenes (12). The first, an organometallic synthetic approach, is to design a preformed metal carbene initiator complex whose reactivity can be controlled by choice of ligands and carbene substituents. The second approach to the living polymerization of acetylenes involves the use of a single, highly active generated metal

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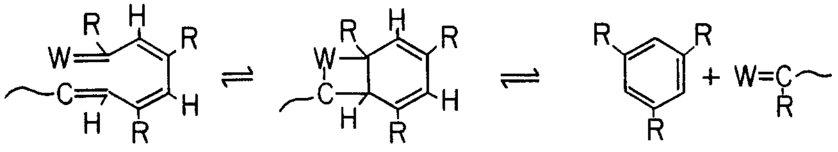
carbene initiator complex while varying the size and polarizability of the acetylenic monomer substituents. An optimum substituent size along the polymer backbone might suppress the termination and transfer reactions of the growing propagating metal carbene complex. The third approach involves preparation of polyacetylenes having rigid rod-like conformations. The propagation through a trans-cisoidal or trans-transoidal configuration, which corresponds to an extended rod-like conformation of the growing chain, is expected to suppress intrachain reactions by the back-biting of a cis-cisoidal propagating chain. This, however, does not preclude interchain type termination and transfer reactions.



Recently, it has been shown that living polymers can be obtained in the polymerization of alkyl substituted acetylenic monomers using transition metal halides (12-15). The living nature of these polymers is thought to be due to the steric nature of the backbone where an optimum substituent size is required to suppress interchain and intrachain termination and transfer reactions, i.e., k_{tr}, $k_t = 0$. The large substituents suppress the isomerization of cis-transoidal sequences to cis-cisoidal sequences and subsequently propagating carbene interchain and intrachain reactions are also suppressed (12-13).

This paper will summarize our results on the polymerization of 1-hexyne, 3, 3-dimethyl-1-butyne, 2-hexyne and 1-chloro-1-hexyne and will demonstrate that bulky acetylene substituents eliminate the intramolecular cyclization reactions and suppress transfer and termination reactions leading to a living mechanism of polymerization.

EXPERIMENTAL

1-Hexyne, 3,3-dimethyl-1-butyne and 2-hexyne were purchased from Farchan Chemical Co. The 1-chloro-1-hexyne was synthesized by reacting 1-lithio-1-hexyne with p-toluenesulfonyl chloride (16). The purity of the 1-hexyne, 3,3-dimethyl-1-butyne and 2-hexyne was greater than 99.0% as determined by GC. All monomers were distilled from calcium hydride prior to use. $MoCl_5$, and WCl_6 (99.9+%) were purchased from Aldrich Chemical Co. and used without further purification. Tetramethyltin, $(CH_3)_4Sn$, (Aldrich) was stored over activated 4Å molecular sieves prior to use. Toluene used as polymerization solvent was washed with 10% sulfuric acid, 10% sodium hydroxide and distilled water, followed by drying over magnesium sulfate and distillation from sodium. All transfers were done under dry argon. All other solvents and reagents were used as received. Analytical techniques and polymerization procedures were identical to previously reported work (12-13).

RESULTS AND DISCUSSION

There are a number of polymerization reactions where one can manipulate the polymerization kinetics to increase the ratio k_p/k_t and k_p/k_{tr} so that the polymerization approaches a living-like character. One example is the cationic ring opening polymerization of heterocyclic monomers like sulfides, amines and esters of phosphonic acid. It has been shown that in a given series of monomers based on the same parent heterocycle, the ratio k_p/k_t increases dramatically with increasing the size and number of the substituents (17). This is the consequence of the fact that the large substituent along the polymer backbone suppresses termination and transfer reactions. The rate constant of propagation also decreases, but the bulky substituent decreases the rate constants of termination and/or chain transfer processes more than the rate constant of the propagation step.

An analogous situation could be considered for the polymerization of substituted acetylenes, i.e bulky substituents suppress termination and transfer reactions leading to living polymers. A review of the literature on the polymerization of acetylenes by transition metal halides and their combinations with reducing agents clearly indicates that their polymerizability is directly related to the size of the monomer substituent (13, 15, 18-21).

In addition, attempts to functionalize the backbone of the poly (3,3-dimethyl-1-butyne) and poly [(1-trimethylsilyl)-1-propyne] using a variety of synthetic procedures failed (13). The backbone of these polymers was non-reactive even to generated carbenes suggesting that during the polymerization of acetylenic bulky monomers the propagating metal carbene can not terminate because it can not react in either an intrachain or interchain fashion. The double bonds from the polymer chain are not accessible for steric reasons.

This study describes the polymerization of a series af alkyl substituted acetylenes possessing varying substituent sizes. The polymerization studies were performed for 1-hexyne, 3,3-dimethyl-1-butyne, 2-hexyne and 1-chloro-1-hexyne using metal halide based initiators. The initiators used in this study included $MoCl_5$, $MoCl_5/(CH_3)_4Sn$, $MoCl_5/(CH_3)_4Sn/EtOH$ and $WCl_6/(CH_3)_4Sn$. A mechanism for carbene generation using these initiation systems with substituted acetylenes has been proposed by several research groups (2, 22-31).

Monitoring the $MoCl_5$ initiated polymerization of 1-hexyne for number average molecular weight and conversion resulted in deviation from linearity even at low conversions. An initial rise in molecular weight followed by a slow decrease occurs. The polymerization was stopped at 90% conversion and resulted in a 70% yield of trisubstituted aromatics, and other cyclics and a 30% yield of low molecular weight oligomers.

This polymerization was monitored by ^{1}H-NMR spectroscopy directly in the NMR sample tube. At low conversion we observed the formation of 1,3,5-trihexylbenzene ($\delta=6.8$) and 1,2,5-trihexylbenzene ($\delta=7.0,7.1$). These cyclic compounds theoretically can result from either a direct cyclotrimerization reaction when three molecules of acetylene monomer are coordinated by the catalyst (32-34) or from the back-biting of a cis-cisoidal growing chain. A metathesis mechanism can explain the formation of cyclic trimers through a back-biting reaction only. If this assumption is valid, it means that the rate constant of back-biting is higher than that of propagation.

In contrast to these results, by increasing the size of the monomer substituent a significant decrease in proportion of side reactions occurs. For example, in the $MoCl_5$ initiated polymerization of 3,3-dimethyl-1-butyne, a linear dependence between polymer molecular weight and conversion up to 200% occurred (Figure 1)(13). That is, at the time of 100% monomer conversion, a second portion of monomer was added to the reaction mixture and the molecular weight-conversion dependence remains linear for this second polymerization process. The linear relationship is indicative of a living-like polymerization free of transfer reactions. The relationship between ln $[M]_0/[M]_t$ versus time also gave a linear plot (correlation=0.864) indicating the absence of termination reactions during the polymerization. It is important to note that a significant decrease in polymer molecular weight occurs when the polymerization is allowed to continue beyond 100% conversion.

The analysis of the 3-3,dimethyl-1-butyne polymerization reaction by ^{1}H-NMR spectroscopy has provided some insight into this polymerization. The monitoring of the $WCl_6/(CH_3)_4Sn$ initiated polymerization of 3,3-dimethyl-1-butyne shows the metal carbene signal $[W]=CH_2$ which is observed twenty minutes following the addition of $(CH_3)_4Sn$ to a WCl_6/CD_2Cl_2 solution. The ^{1}H-NMR spectrum of this reaction agrees with that reported by Ivin for a similar experiment (27). On addition of 3,3-dimethyl-1-butyne, the carbene is immediately consumed and poly (3,3-dimethyl-1-butyne) precipitates from the reaction mixture. A signal at $\delta=7.2$ ppm which is due to 1,3,5-tri-t-butylbenzene appears only after complete monomer conversion. This suggests that the cyclic trimer results from a back-biting reaction which does not take place in the presence of monomer. This demonstrates that in the case of 3,3-dimethyl-1-butyne the rate constant of propagation is much higher than the rate constant of back-biting. The broad polydispersities of these polymers is, therefore, most likely the result of a slow initiation step. The slow initiation is due to either the slow rate of carbene formation or the slow carbene-acetylene complexation rate due to the presence of the bulky t-butyl group.

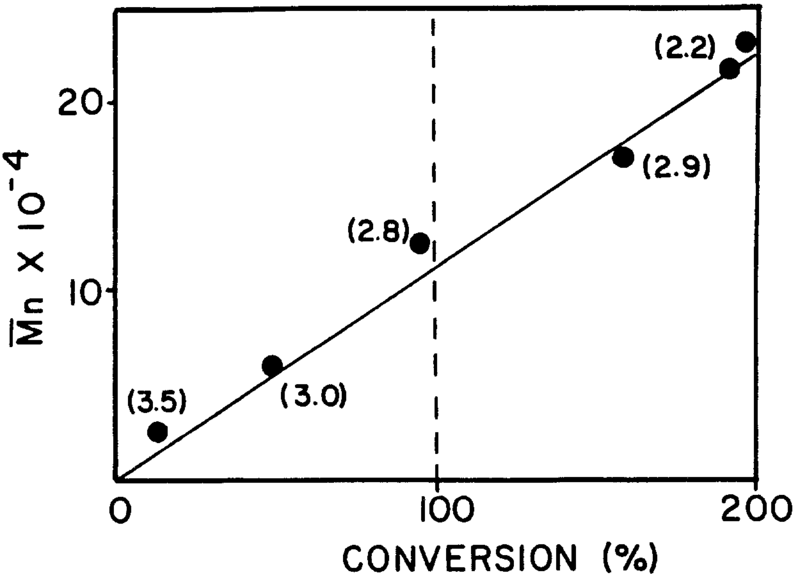


Figure 1. Dependence of number average molecular weight vs. time for the $MoCl_5$ initiated polymerization of 3,3-dimethyl-1-butyne (in toluene at 25°C; $[M]_0 = 1.0$ mole/l; $[I] = 20$ mmole/l, (Mw/Mn)).

The polymerization of 2-hexyne was monitored in a similar fashion using the $MoCl_5/(CH_3)_4Sn$ initiating system. Initially, we attempted to monitor the monomer conversion following the addition of one monomer equivalent, however, under the reaction conditions used in this experiment, the polymerization was complete within one minute and it was impossible to obtain reaction samples from the polymerization mixture at low monomer conversion. This reaction was attempted at -15°C and 0°C in a similar fashion, however, no polymer formed with at present no explanation. A series of monomer-feed experiments were then completed. Figure 2 shows the number average molecular weight-conversion plot obtained to 400% conversion for a $MoCl_5/(CH_3)_4Sn$ initiated polymerization, ie. after the addition of four equivalents of 2-hexyne monitored to complete conversion. This resulted in a high molecular weight polymer, obtained in a quantitative yield. This plot clearly demonstrates the continuation of propagation from the living polymer chain end. The living polymer does not change its molecular weight if allowed to stay for several days in the polymerization system following complete monomer conversion. This polymerization reaction was also monitored by ^1H-NMR spectroscopy directly in the NMR sample tube. There were no signals attributable to 1,3,5-trimethyl-2,4,6-tripropyl benzene (δ 2.2-2.6) either before complete monomer conversion or several days following complete monomer conversion. The 1,3,5-trimethyl-2,4,6-tripropyl benzene can theoretically result from either a direct cyclotrimerization reaction or from the back-biting of a cis-cisoidal growing chain. These data indicate that degradative chain transfer reactions are not occurring in the $MoCl_5/(CH_3)_4Sn$ initiated polymerization of 2-hexyne. The high polydispersities for these polymers is therefore, most likely due to a slow initiation step.

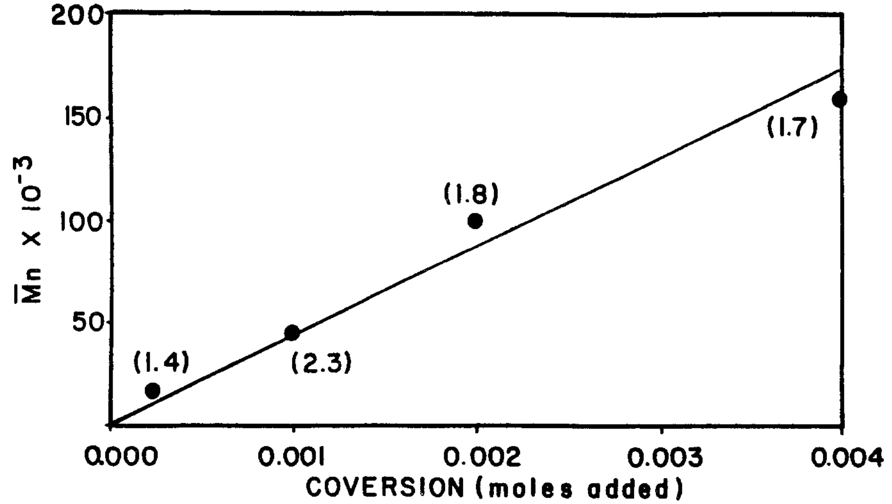


Figure 2. Dependence of number average molecular weight vs. conversion for the $MoCl_5/(CH_3)_4Sn$ (1:1) initiated polymerization of 2-hexyne (in toluene at 25°C; final [M] = 0.8 mole/l; [I] = 20 mmole/l, (Mw/Mn)).

The polymerization of 1-chloro-1-hexyne was then monitored in a similar fashion. This monomer has recently been shown to follow a living mechanism of polymerization (35). We included this monomer in our study because of the unusual effects the chloro substituent has on the polymerization kinetics. The polymerization of 1-chloro-1-hexyne initiated with $MoCl_5/(CH_3)_4Sn/EtOH$ was monitored for both monomer conversion and polymer molecular weight and the results are presented in Figure 3. A linear relationship to 100% conversion was observed. This polymerization resulted in a quantitative yield of high molecular weight polymer which did not undergo any change in its molecular weight if left for several days in the polymerization system. In addition, the polydispersity of this polymer approaches that of a classical living polymer! The addition of another equivalent of monomer results in a polymer possessing a bimodal molecular weight distribution suggesting that a portion of the propagating metal carbene complex underwent termination prior to the second monomer feed. This bimodal distribution also occurs for the polymerization of 2-hexyne and 3,3-dimethyl-1-butyne when using the $MoCl_5/(CH_3)_4Sn/EtOH$ initiation system. The low polydispersities for the $MoCl_5/(CH_3)_4Sn/EtOH$ initiated 1-chloro-1-propyne, we believe, is due to the stabilization of the propagating metal carbene. The chlorocarbene is stabilized through inductive and resonance effects. A highly stabilized propagating metal carbene will result in a faster initiation rate and the suppression of inter- and intrachain termination and transfer reaction (less prone to backbone attack), i.e. increased k_p/k_{tr}. Scheme 1 shows the predicted route for carbene formation when using the 1-chloro-1-hexyne/ternary initiation system.

Table 1 summarizes the polymerization results for 3,3-dimethyl-1-butyne, 2-hexyne and 1-chloro-1-hexyne. The $MoCl_5$ initiated polymerization of 3,3-dimethyl-1-butyne provides a relatively slow polymerization process which requires 1-2 hours for complete monomer conversion. This is due to an induction period caused by the metal halide-acetylene reaction. The binary (metal halide and reducing agent) initiating polymerizations are usually complete within one minute. The ternary (metal halide,

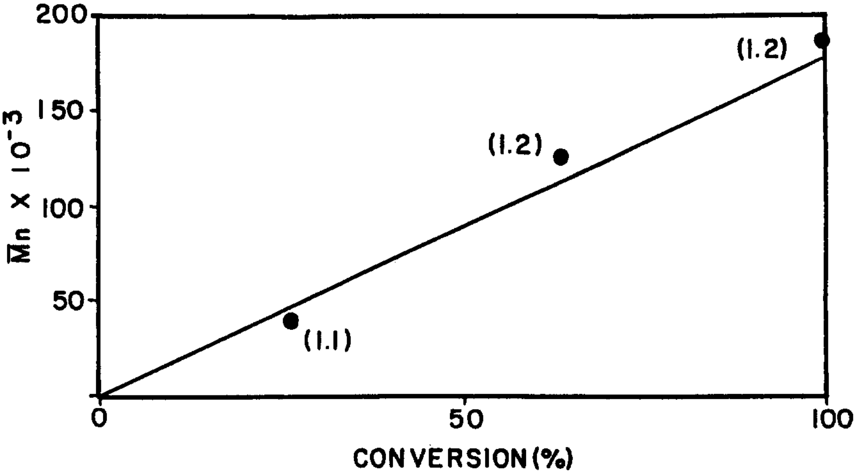


Figure 3. Dependence of number average molecular weight vs. conversion for the $MoCl_5/(CH_3)_4Sn/EtOH$ initiated polymerization of 1-chloro-1-hexyne (in toluene at 25°C; $[M]_0 = 1.0$ mole/l; $[I] = 20$ mmole/l, (Mw/Mn))

$$MoCl_5 + EtOH \rightarrow Cl_4Mo(OEt) + HCl$$

$$Cl_4Mo(OEt) + (CH_3)_4Sn \rightarrow Cl_3Mo(OEt)CH_3 + (CH_3)_3SnCl$$

$$Cl_3Mo(OEt)CH_3 + (CH_3)_4Sn \rightarrow Cl_2Mo(OEt)(CH_3)_2 + (CH_3)_3SnCl$$

$$Cl_2Mo(OEt)(CH_3)_2 \rightarrow Cl_2Mo(OEt)=CH_2 + CH_4$$

$$Cl_2Mo(OEt)=CH_2 + ClC\equiv C(CH_2)_2CH_3 \rightarrow Cl_2Mo(OEt)=C(Cl)\text{-}C\sim$$

Scheme 1 Proposed mechanism for the polymerization of 1-chloro-1-hexyne using the $MoCl_5/(CH_3)_4Sn/EtOH$ initiation system

reducing agent and alcohol) initiated polymerizations are usually complete within five minutes. For 3,3-dimethyl-1-butyne, we consistently observe the formation of a polymer of lower polydispersity when using the ternary initiating system. A similar trend is not observed for the 2-hexyne polymers while the 1-chloro-1-hexyne polymers show a significant drop in polydispersity.

In conclusion, by analogy with ionic ring opening polymerization systems, acetylenes having bulky substituents can follow a living mechanism of polymerization by suppressing backbiting and interchain reactions, i.e. k_{tr}, $k_t = 0$. The polymerization of 3,3-dimethyl-1-butyne may approach a living-like character but it is likely that some transfer and/or termination reactions are occurring, particularly in the absence of monomer. The polymerization of 2-hexyne appears to lead to true living polymers free of degradative chain transfer and termination reactions. The high polydispersity of the polymers, we believe, is a result of a slow initiation rate. The 1-chloro-1-hexyne polymers exhibit characteristics of classical living polymers when the ternary initiation system is used. The low polydispersity of these polymers, we believe, is due to an increase in the initiation rate as a result of the chloro substituent.

Table 1 Summary of results for the metal halide induced polymerization of 3,3-dimethyl-1-butyne, 2-hexyne and 1-chloro-1-hexyne[a]

		Monomer Conc.	Polymer	
Monomer	Initiator	(mole/1)	Mn	Mw/Mn
$H-C\equiv C-C_4H_9$	$MoCl_5$	0.50	200,000	2.20
	$MoCl_5/(CH_3)_4Sn/EtOH$	0.20	100,000	1.68
$CH_3-C\equiv C-(CH_2)_2-CH_3$	$MoCl_5/(CH_3)_4Sn$	0.05	17,710	1.38
	"	0.20	48,520	2.27
	"	0.40	105,700	1.76
	"	0.80	157,746	1.65
	$MoCl_5/(CH_3)_4Sn/EtOH$	0.05	107,343	1.91
	"	0.20	147,693	1.83
$Cl-C\equiv C-(CH_2)_2-CH_3$	$MoCl_5/(CH_3)_4Sn$	0.20	170,000	1.70
	$MoCl_5/(CH_3)_4Sn/EtOH$	0.20	85,000	1.14

[a] polymerization solvent, toluene; polymerization temperature, 25°C; initiator concentration, 20mmole/l; polymerization time, 1 hour for the $MoCl_5$ polymerization, 10 min. for all others; conversion 100%

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