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Living Polymerization of 1-Trimethylsilyl-1-propyne and 4-Methyl-2-pentyne by $NbCl_5$-Based Catalysts

E. Yu. Sultanov, V. S. Khotimskiy*

Summary: Sequential homopolymerization of disubstituted acetylenes 1-trimethylsilyl-1-propyne and 4-methyl-2-pentyne by $NbCl_5$–Ph_3SiH was investigated and the main evidence of living polymerization, namely, continuation of chain propagation after addition of a new portion of monomer was observed. AB and BA type block copolymers of 1-trimethylsilyl-1-propyne and 4-methyl-2-pentyne were synthesized by sequential polymerization of these monomers in presence of $NbCl_5$–based catalytic systems.

Keywords: block copolymers; disubstituted polyacetylenes; living polymerization; poly-1-trimethylsilyl-1-propyne; poly-4-methyl-2-pentyne

Introduction

Disubstituted polyacetylenes are amorphous glassy polymers with high glass transition temperatures (>200 °C) and good mechanical characteristics. High interest to these polymers is due to their extremely high gas and vapor permeability parameters in combination with good fiber- and film-forming properties.[1] That is why disubstituted polyacetylenes are perspective materials for usage as gas separation membranes. Properties of disubstituted polyacetylenes depend on chemical and geometrical structures of polymer chain. Thus parameters of gas transport, as well as stability towards components of separating mixtures may essentially differ for membranes from these polymers. For example, poly-1-trimethylsillyl-1-propyne (PTMSP) possesses record level of permeability and selectivity to condensable hydrocarbons while separating mixtures containing common gases and hydrocarbon vapors but PTMSP isn't resistant towards many liquid hydrocarbons.[2] Whereas another disubstituted polyacetylene – poly-4-methyl-2-pentyne (PMP) is resistant towards aliphatic and aromatic hydrocarbons.[3,4]

It is obvious that combination of required properties can be obtained by synthesis of copolymers, for example block copolymers. Sequential living polymerization of different monomers is one of the main methods of synthesis of block copolymers. To obtain block copolymers by sequential polymerization it is necessary to find catalysts and conditions equally effective for both comonomers. It is known that metathesis polymerization of some substituted acetylenes induced by transition metal catalysts may have living character.[5,6] Investigation of homopolymerization of 1-trimethylsilyl-1-propyne (TMSP) and 4-methyl-2-pentyne (MP) by different catalytic systems showed that 100% conversion of monomer which is characteristic feature of living polymerization is not observed for all catalytic systems and depends on structure of monomer. Recently we determined that living polymerization of TMSP and MP proceeds in presence of $NbCl_5$–Ph_4Sn catalyst, which was indicated by linear dependence of molecular weight versus monomer conversion and by continuation of chain propagation after addition of a new portion of monomer.[7]

In this work we investigated polymerizations of TMSP and MP by $NbCl_5$–Ph_3SiH to find out if they have living

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A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences (TIPS RAS), Leninsky prospect 29, 119991 Moscow, Russia
E-mail: sultanov@ips.ac.ru

nature and to broaden range of catalytic systems available for synthesis of block copolymers on the basis of disubstituted polyacetylenes. Also we investigated possibility of synthesis of AB and BA type block copolymers of TMSP and MP by $NbCl_5$–Ph_3SiH and $NbCl_5$–Ph_4Sn catalytic systems.

Experimental Part

Materials

Monomers TMSP (99.9%) and MP (99.9%) were synthesized by techniques developed in cooperation with NPO OAO Yarsintez.[8,9] Before polymerization experiments, monomers and cyclohexane (99%, Fluka) were distilled three times over calcium hydride under high-purity argon. Catalyst niobium pentachloride $NbCl_5$ (99.5%, Fluka) and cocatalysts tetraphenyltin Ph_4Sn (97%, Fluka) and triphenylsilane Ph_3SiH (97%, Fluka) were used as received.

Sequential Polymerization Procedures

The sequential polymerization of TMSP was performed according to the following technique. A glass reactor was loaded with a solution of $NbCl_5$ (0.14 g, 0.5 mmol) and Ph_3SiH (0.12 g, 0.5 mmol) in cyclohexane (25 ml). The resulting mixture was vigorously stirred at 25 °C for 30 min in a flow of high-purity argon. Then, TMSP (2.8 g, 25 mmol) was added to the catalytic solution. After 24 h (during this time, 100% conversion of the first portion of monomer was achieved) more 2.8 g (25 mmol) TMSP in 25 ml of cyclohexane was added to the reaction mixture. After more 72 h the reaction mixture was treated with methanol (50 ml) to deactivate the catalyst. The polymer was dissolved in CCl_4 (300 ml), precipitated into methanol (1.5 l), filtered out, and dried in the air for 24 h. The resulting polymer was redissolved in CCl_4 and reprecipitated into methanol. After vacuum drying, the yield of the product was determined.

The sequential polymerization of MP was carried out in a similar manner.

The synthesis of block copolymers was performed in a similar manner but after 24 h instead of second portion of the same monomer another monomer was added.

Measurements

The intrinsic viscosity of polymer solutions in CCl_4 was measured at 25 °C using an Ostwald–Ubbelohde viscometer.

Molecular weight characteristics were determined by GPC. Measurements were performed in cyclohexane at 20 °C using a Waters chromatograph equipped with a Waters R401 refractometric detector and a system of $2 \times$ PLgel 5 μ MiniMix-C columns. The molecular weight parameters were estimated from the calibration plot constructed on the basis of samples of PTMSP and PMP with known molecular weights (these samples were characterized by GPC with light scattering and refractometric detectors).

The composition of poly[1-trimethylsilyl-1-propyne]-block-[4-methyl-2-pentyne] (poly(TMSP)-b-(MP)) was calculated from elemental analysis data obtained by pyrolysis chromatography on a Carlo Erba instrument. Elemental analysis found for AB type block copolymer (here and everywhere block A is accepted as PTMSP and block B as PMP) synthesized by $NbCl_5$–Ph_4Sn: C, 74.4%; H, 11.3%; Si, 14.3%. Elemental analysis found for AB type block copolymer synthesized by $NbCl_5$–Ph_3SiH: C, 73.9%; H, 11.3%; Si, 14.8%. Elemental analysis found for BA type block copolymer synthesized by $NbCl_5$–Ph_4Sn: C, 66.7%; H, 10.8%; Si, 22.5%. Elemental analysis found for BA type block copolymer synthesized by $NbCl_5$–Ph_3SiH: C, 67.6%; H, 10.9%; Si, 21.5%.

A method based on IR measurments described in the work [10] was also used for calculating the composition of copolymers.

Results and Discussion

Sequential polymerization of TMSP by $NbCl_5$–Ph_3SiH showed that conversion of the second portion of monomer is 85%

(here and everywhere conversion of first portion of monomer during sequential polymerization is accepted as 100% because polymerization is carried out in conditions in which 100% yield of polymer is observed) after 72 h. As a result increase of molecular weight of polymer and unimodal molecular weight distribution (MWD) is observed (Fig. 1). PTMSP which forms after 100% monomer conversion has $M_n = 2.5 \times 10^5$ and $M_w/M_n = 1.75$ whereas PTMSP obtained by sequential polymerization has $M_n = 5.3 \times 10^5$ and $M_w/M_n = 2.4$.

Sequential polymerization of MP proceeds with 40% conversion of the second portion of MP after 72 h. As a result polymer with unimodal MWD is formed (Fig. 2). PMP which forms after 100% conversion has $M_n = 4 \times 10^5$ and $M_w/M_n = 2.0$ whereas PMP obtained by sequential polymerization has $M_n = 4.9 \times 10^5$ and $M_w/M_n = 2.5$.

As shown in the Table 1 in same conditions during synthesis of PMP polymers with higher molecular weights are formed than during synthesis of PTMSP. This is evidently concerned with that in case of polymerization of TMSP more active species are formed. Initiation efficiency of polymerization of monomers TMSP and MP can be calculated from formula $[P^*]/[Cat] = [M]_{consumed}/(DP \times [Cat])$ and presented in Table 1. According to this can be concluded that efficiency of polymerization by $NbCl_5$–Ph_4Sn and $NbCl_5$–Ph_3SiH for TMSP is higher than for MP. In the work [10] it was also shown that TMSP is more active than MP which authors related with steric accessibility of C≡C bond. Such difference in initiation efficiencies of TMSP and MP means that properties of their AB and BA type block copolymers may considerably vary due to different length of blocks in formed block copolymers.

Polymers formed by ideal living polymerization have very narrow MWD ($M_w/M_n > 1.2$). Noticeably wide MWD of obtained disubstituted polyacetylenes probably related to that because of low initiation efficiency process is performed in conditions in which polymers with high molecular weights ($M_n > 2 \times 10^5$) and high intrinsic viscosities ($[\eta] > 0.5$ dl/g) are formed. Thus sufficiently vigorous stirring cannot be achieved as a result constant concentration of monomer throughout the bulk cannot be met. Consequently, stirring and heat exchange decreases as viscosity of polymerization mixture increase and as a result synthesis of polymer with high molecular weight and narrow MWD is complicated. It is significant that in case of

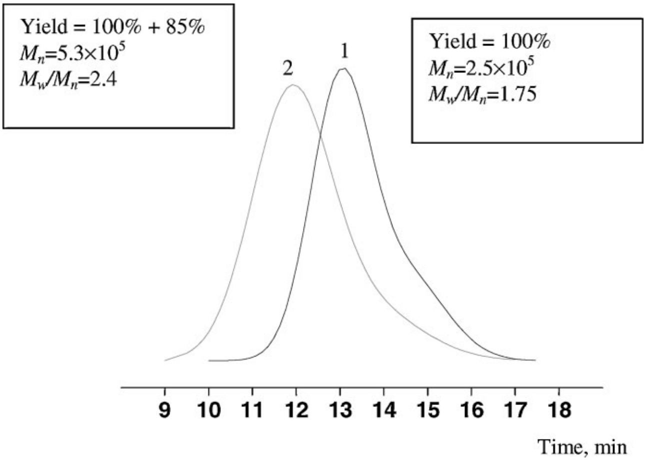

Figure 1.
GPC traces of PTMSP formed with $NbCl_5$–Ph_3SiH by one stage polymerization (1) and sequential polymerization (2).

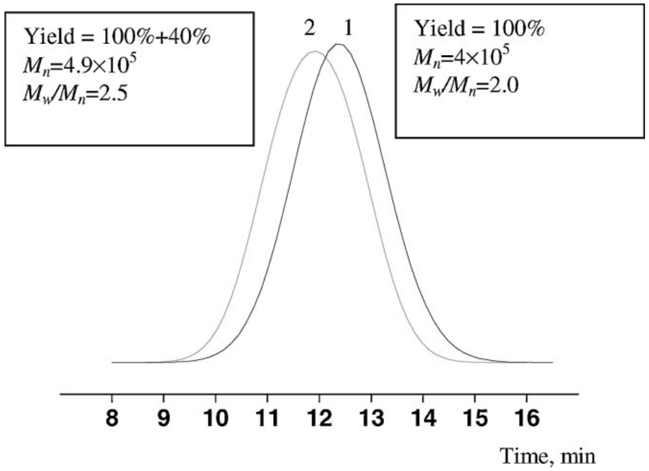

Figure 2.
GPC traces of PMP formed with $NbCl_5$–Ph_3SiH by one stage polymerization (1) and sequential polymerization (2).

sequential polymerization second stage proceeds in heterogeneous conditions where also diffusion factor plays a big role. Although it isn't ideal living polymerization however we consider that polymerization of TMSP and MP by these catalytic systems nevertheless has living nature because for polymers obtained by sequential polymerization molecular weights increase and MWD is unimodal.

So sequential homopolymerization of TMSP and MP by $NbCl_5$–Ph_3SiH showed that in presence of this catalyst propagation of polymer chain is observed after addition of new portion of monomer to the reaction mixture with fully consumed monomer. Thus obtained polymer keeps reactivity due to still active polymerization species. This is the direct evidence of living polymerization. So this behavior is similar to the case of catalyst $NbCl_5$–Ph_4Sn.[7]

Using this data we performed synthesis of poly(TMSP)-b-(MP) by sequential polymerization of monomers TMSP and MP.

Table 1.
Polymerization of TMSP and MP by $NbCl_5$–based catalysts in cyclohexane ($[M]_0 = 1$ mol/l, [Cat] = [Cocat] = 20 mmol/l; T = 25 °C; polymer yield in all cases is ~100%).

Polymer	Catalyst	$M_n \times 10^{-5}$	M_w/M_n	$[P^*]/[Cat]$, %	[η], dl/g
PTMSP	$NbCl_5$–Ph_4Sn	2.2	1.6	2.5	0.55
PTMSP	$NbCl_5$–Ph_3SiH	2.5	1.75	2.2	0.75
PMP	$NbCl_5$–Ph_4Sn	5.2	1.9	0.8	2.8
PMP	$NbCl_5$–Ph_3SiH	4.0	2.0	1.1	2.2

Table 2.
Synthesis of poly(TMSP)-b-(MP) by $NbCl_5$–Ph_3SiH and $NbCl_5$–Ph_4Sn in cyclohexane.

Catalyst	M_1	f_1, %	F_1, %*	Yield, %	$M_n \times 10^{-5}$	M_w/M_n
$NbCl_5$–Ph_4Sn	TMSP	50	57/57	80	3.1	2.1
$NbCl_5$–Ph_3SiH	TMSP	50	60/59	80	3.5	2.15
$NbCl_5$–Ph_4Sn	MP	50	88/90	20	5.8	2.2
$NbCl_5$–Ph_3SiH	MP	50	85/86	25	4.6	2.5

f_1 – ratio of M_1 in polymerization mixture; F_1 – ratio of M_1 in polymer product; Yield – yield of second block (conversion of first monomer is accepted as 100%).

*The copolymer composition was determined by IR spectroscopy (numerator) and pyrolysis chromatography (denominator).

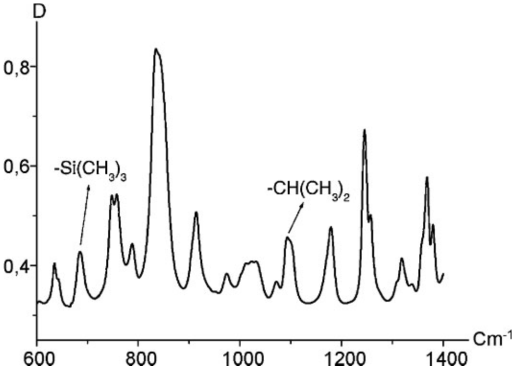

Figure 3.
IR spectrum of poly(TMSP)-b-(MP).

Results are presented in Table 2. The block copolymers have unimodal MWD and higher molecular weights than homopolymers PMP and PTMSP formed in the same conditions (see Tables 1 and 2). The IR spectra of obtained block copolymers contain analytical bands of PTMSP and PMP which are 687 and 1097 cm^{-1}, respectively (Fig. 3).

Conclusion

Direct evidences of living polymerization were obtained for polymerization of TMSP and MP by $NbCl_5$–Ph_3SiH. The possibility of synthesis of AB and BA type block copolymers poly(TMSP)-b-(MP) by sequential polymerization was shown using catalytic systems $NbCl_5$–Ph_3SiH and $NbCl_5$–Ph_4Sn. This is the first report involving synthesis of block copolymers of TMSP with MP via sequential living polymerization. A more detailed study of synthesis and properties of block copolymers poly(TMSP)-b-(MP) will be reported separately.

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