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Synthesis and radical reaction behaviour of (1-trimethylsilyl-ethinyl)-(1-methyl-vinyl) ketone

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Dedicated to Prof. Dr. Harald Cherdron on the occassion of his 60th birthday

Summary

Monomer (1-trimethylsilyl-ethinyl)-(1-methyl-vinyl) ketone 1 was synthesized to study the reaction behaviour in radical reactions. Not only is the vinyl double bond very effective to react with radicals but also is the triple bond. At higher conversions insoluble polymers are formed. In dilatometer experiments with styrene monomer 1 proved to be an effective retarder rather than a transfer agent. To elucidate the mechanisms envolved in monomer 1 radical reactions, model compound (1-trimethylsilyl-ethinyl)-phenyl ketone 5 was synthesized and investigated in comparision.

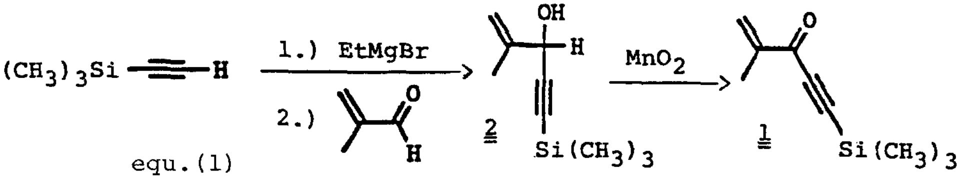
Introduction

Vinyl ketones are known to undergo radical as well as anionic or cationic polymerization reactions, also electrochemical initiation has been investigated /1-5/. They also are accessible to group transfer polymerization /6-9/. In general, radical initiation is easy and leads to high molecular weight polymers. Acetylene derivatives, on the other hand, are not very susceptible to radical initiation and in most cases benzene derivatives are formed /lo/. Ziegler type catalysts are most efficient. A monomer like (1-trimethylsilyl-ethinyl)-(1-methylvinyl) ketone 1 would be an interesting monomer with some potential of the polymer to modification via the trimethylsilyl group.

Results and discussion

Monomer synthesis

The synthesis of monomer 1 according to equ.(1) is easy to accomplish after a procedure described by Malacria et al. /11/ and the overall yield is close to 60%. The purity of the carbinol 2 prior to the oxidation reaction considerably influences the yield of monomer 1 and purification of 2 by chromatography



equ. (1)

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*To whom offprint requests should be sent is necessary. The liquid monomer 1 can be purified by distillation.

Polymerization of monomer 1

Radical polymerization was performed in bulk and in THF solution by thermal, AiBN and redox initiation, respectively, see Tab.1. According to Figs.1 and 2, the molecular weight of the reaction products from solution polymerization is considerably lower than of those polymers obtained from bulk polymeriz-

Table 1: Unipolymerization of monomer 1

Experim/ Polym No	Solvent THF	Initiator AiBN mole-%	T/°C	t/h	Convers (%)	Molec Weight	Remarks
P(1)	+	2	50	90.5	4.8	low^{1}	a
P(2)	+	5	50	90.5	15.2	low^{1}	a
P(3)	+	10	50	90.5	20.3	low^{1}	a
P(4)	-	0.9	50	25	26.3	high^{2}	a
P(4a)	-	1.0	50	72	?	-	b
P(5)	-	-	50	92	9.2	high^{2}	a
P(6)	-	-	70	64.5	13.5	high^{2}	a
P(7)	-	-	90	48.5	2.5	high^{2}	a
P(8)	MeOH	$K_2S_2O_8$/ $FeSO_4 \cdot H_2O$	4	137	0	-	c

a) pale yellow powder - P(1)-P(3) tacky; soluble in toluene, THF, $CHCl_3$; insoluble in water, MeOH
b) most insoluble
c) dark violet solution upon initiation, heterophase reaction
1) see Fig.1, 2) see Fig.2

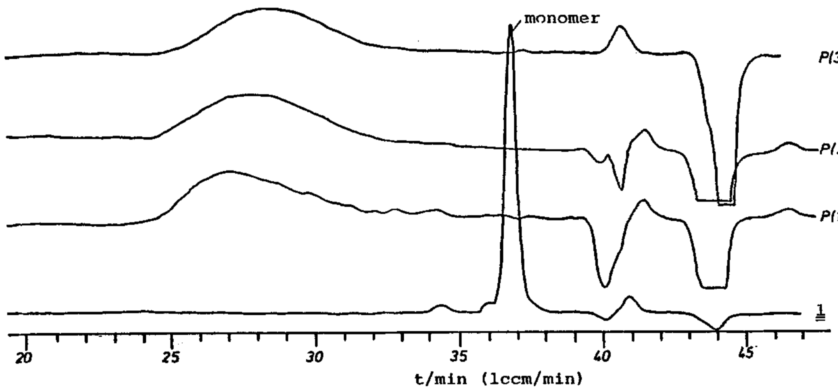


Fig.1: Gelpermeation chromatograms of monomer 1 and products of solution polymerization P(1)-P(3), see Tab.1. Low molecular weight column PL-gel 10 µm, 500-10^3-10^4-10^5 Å, THF, 55°C, detector 250 nm

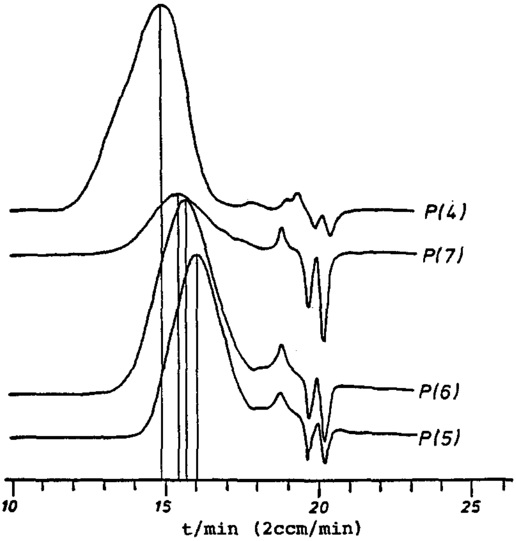
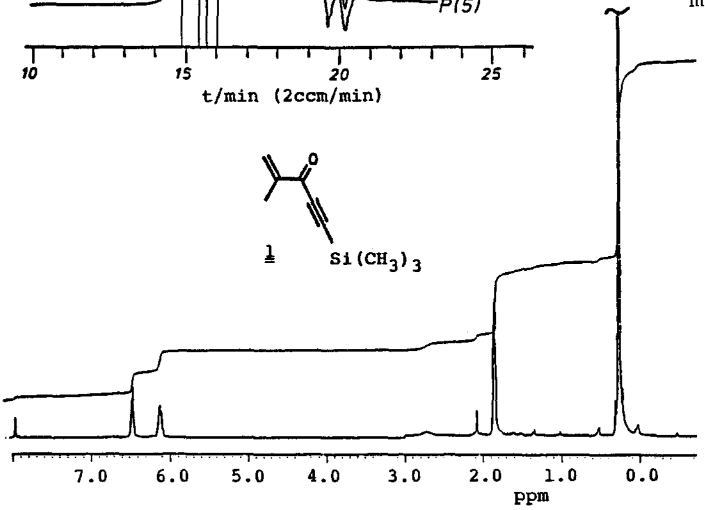


Fig.2: Gelpermeation chromatograms of polymer products of bulk polymerization P(4)-P(7), see Tab. 1. High molecular weight column PL-gel 10 µm, 10^6-10^5-10^4-10^3 Å, THF, 55°C, detector 250 nm

Fig.3: 80 MHz ^{1}H-nmr spectrum of monomer **1**, acetone-d_6, no TMS as internal standard



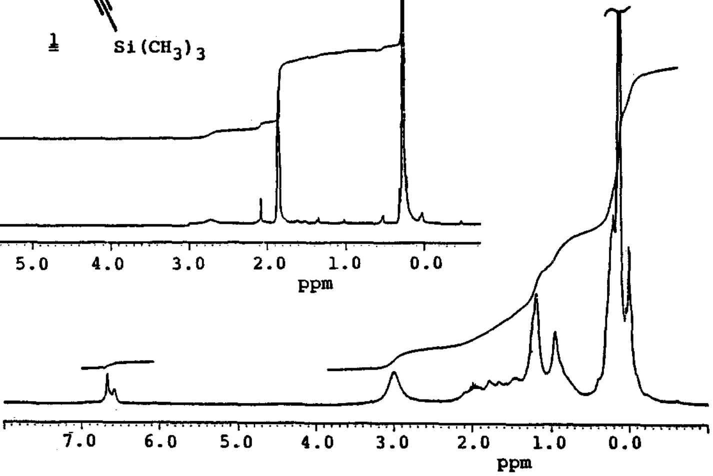
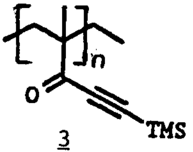


Fig.4: 80 MHz ^{1}H-nmr spectrum of polymer P(4), acetone-d_6, no TMS as internal standard

ation; from GPC data both seem to have a broad molecular weight distribution.

A comparison of the ^{1}H-nmr spectra of monomer **1** and polymer P(4) reveals differences which cannot be explained from a normal vinyl polymerization. The most striking effect is in Fig.4 the splitting of the trimethyl (TMS) protons at 0 - 0.5 ppm of the polymer whereas these protons give the expected single signal at 0.22 ppm in monomer **1**. The splitting of the TMS protons lets us suggest that the triple bond of **1** is also involved in



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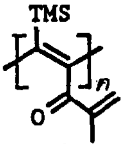
TMS = $Si(CH_3)_3$



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the polymerization process and structures 3 and 4 both may occur. The sp^2 bound TMS group in structure 4 is likely to have the splitting pattern as a result of cis-trans isomers of the substituent in the polymer main chain. In addition, in Fig.4 there is a doublet at 6.68 and 6.75 ppm, respectively, which may result from some residual vinyl protons. The low molecular weight (GPC) polymers P(1)-P(3) and polymer P(4) show the same nmr spectra.

A contribution of the triple bond in the polymerization process could explain, the formation of almost insoluble polymer P(4a) at high initiator concentration.

UV-vis and mass spectra of low molecular weight oligomers which were prepared separately at moderate and high AiBN concentrations did not elucidate the product structure sufficiantly.

Investigation of model compound (1-trimethylsilyl-ethinyl)-phenyl ketone 5

Model compound 5 was synthesized according to equ.(1). Since in the polymerization experiments of monomer 1 we presumed the participation of the triple bond, polymerization experiments of styrene in the presence of 5 upon radical initiation were carried out. As compiled in Tab.2, one observes a decrease of conversion and of molecular weight as well when the concentration of 5 is increased. From ^{1}H-nmr investigations the polymers obtained are pure polystyrene and do not contain compound 5 as comonomer even in very low content. But from dilatometer experiments with styrene in bulk and different low concentrations of 1 and 5, respectively, it is obvious that both compounds act as retarders, monomer 1 much more effectively than compound 5 in comparison, see Figs.5 and 6. Even at high concentrations of AiBN in solution with only 5 no reaction products of 5 with AiBN fragments are found using GC-MS coupling after the work-up. We assume that if a radical generated from AiBN

Table 2: Styrene polymerization experiments in the presence of compound 5

Experim/ Polym No	5 mole-%	Convers (%)	Molecular Weight (GPC)
P (9)	0	65.0	70.000
P(10)	2.35	47.7	64.000
P(11)	4.77	42.9	53.000
P(12)	9.39	38.2	40.000

5 ccm styrene, 5 ccm toluene, 40.0 mg (1.4 mole-%) AiBN, 50°C, 65 h, Ar; 5 does not undergo unipolymerization under these conditions

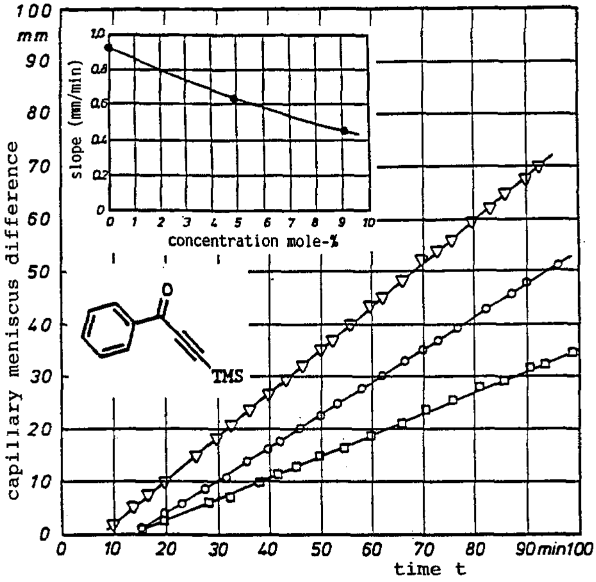


Fig.5:

Dilatometer experiments in bulk of styrene with compound 5 upon radical initiation;
∇ P(14) [5] = 0
o P(16) [5] = 5 mole-%
□ P(15) [5] = 10 mole-%

Gelpermeation chromatograms of polymers P(18) and P(19) are shown in Fig.7

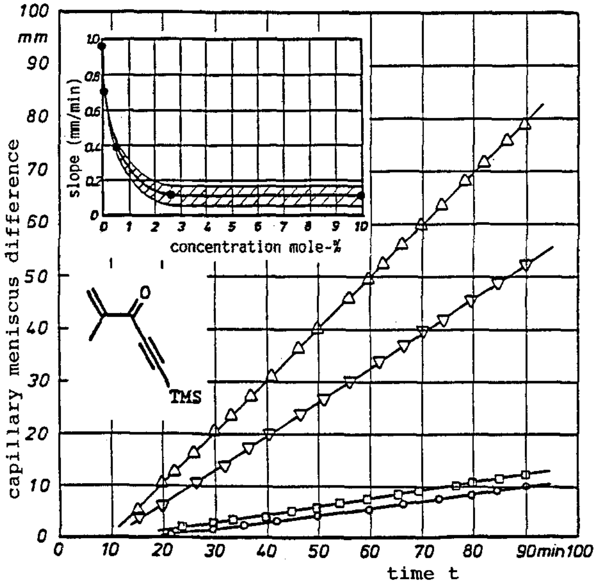
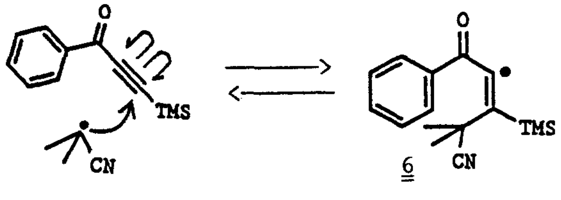


Fig.6:

Dilatometer experiments in bulk of styrene with monomer 1 upon radical initiation;
Δ P(19) [1] = 0
∇ P(21) [1] = .006 m.-%
□ P(20) [1] = .3 mole-%
o P(17), P(18) [1] = 2.8 res. 10 mole-%



equ.(2)

supposed reversible reaction of 2-cyanopropyl radical with compound 5 attacks 5 - the same counts for a growing polymer radical chain - the radical 6 is formed according to equ.(2). The half occupied p-orbital can move into a planar position with the phenyl-carbonyl-π system by rotation around the single bond from which a stabilization of the radical may be achieved. We do not know the reason why 6 does not initiate styrene. Presumably the radical attack to 5 is a dead end reaction from which both the radical and compound 5 are set free again in a back reaction. The blocking of active growing polymer chains by 5 results in a decrease of the rate of polymerization but does not decrease the number of chain termination steps and therefore lowers the degree of polymerization of the polymer in regard.

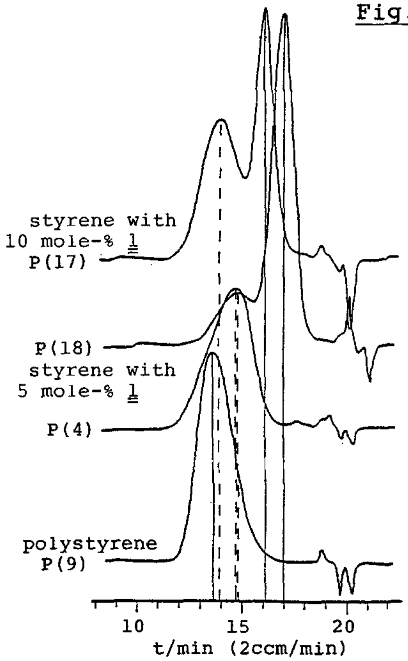


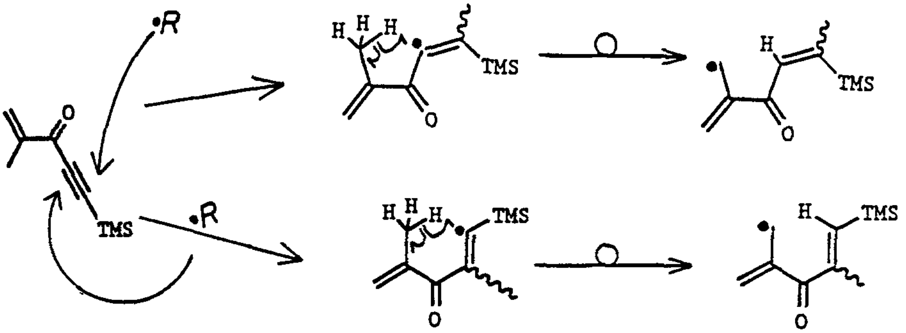
Fig.7:

Gelpermeation chromatograms of polymers P(4), P(9), P(17) and P(18) see Tabls. 1 and 2. High molecular weight column PL-gel 10µm, 10^6-10^5-10^4-10^3 Å, THF, 55°C, detector 250 nm

From copolymerization experiments of 1 with styrene in toluene solution at higher conversions almost insoluble materials are obtained. At lower conversions and the usual work-up the ^{1}H-nmr spectra of the copolymers reveal a block structure rather than a random copolymerization precess indicating that the copolymerization parameters for the system styrene/1 under these conditions are >1. In Fig.7 the gelpermeation chromatograms of polymers P(17) as well as P(18) both show a strongly marked bimodal molecular weight distribution. We suppose that at initial high monomer 1 concentrations primary radicals can react with both monomers styrene and 1, respectively. Since monomer 1 has a retarding effect on styrene polymerization all those growing chains with terminal styrene active radical units which add monomer 1 in a cross reaction propagate much slower by further addition of 1. As the styrene concentration decreases with conversion the then started polymer chains increasingly become rich in 1 units and chemical heterogeneity results.

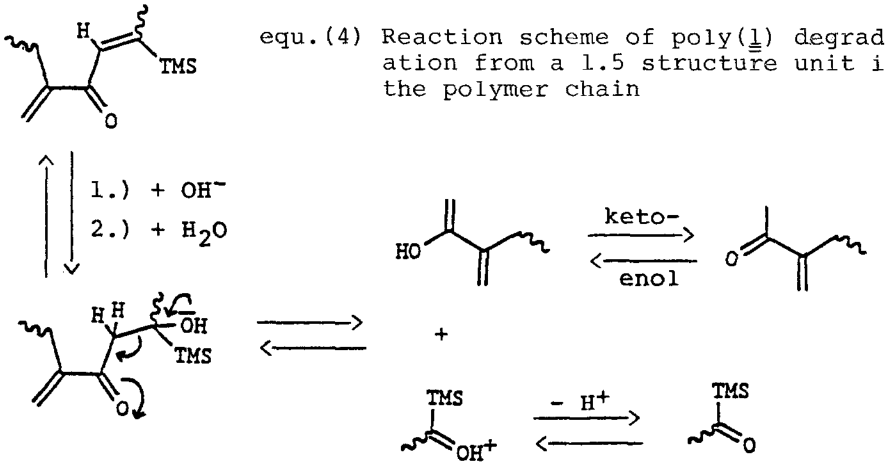
Structure of poly(1)

From the ^{1}H-nmr spectra of different unipolymers from 1 and from the formation of insoluble polymers at high conversions the participation of the triple bond to some degree in the polymerization reactions was suggested. The addition of a radical to the triple bond of monomer 1 in equ.(3) leads to a vinyl radical (see also equ.(2)) which may rearrange either by



equ.(3) Formation of vinyl radical originated from monomer 1 and followed by 1.4- and/or 1.5-rearrangement

1.4 or 1.5 hydrogen transfer to an allyl radical of low activity. For this rearrangement the half occupied orbital has to turn out of conjugation and therefore this rearrangement affords a considerable amount of activation energy. The formation of the allyl radical is an autoinhibition process of monomer 1 and chain propagation will occur only occasionally. It is known from low molecular weight acetylene derivatives that vinyl radicals out of these strongly tend to undergo hydrogen abstraction /12/. However, addition of $K_2CO_3/KHCO_3$ buffer to a THF solution of polymer P(4) under reaction conditions usually applied to cleave the trimethylsilyl bond in low molecular weight acetylene derivatives leads to polymer degradation as monitored by GPC. Reaction equ.(4) demonstrates this chain degradation reaction in which all reaction steps are reversible but under the alkaline conditions the equilibrium is shifted towards the stable ketones.



equ.(4) Reaction scheme of poly(1) degradation from a 1.5 structure unit in the polymer chain

Experimental

^{1}H-nmr spectra were recorded on a 80 MHz FT Bruker spectrometer type WP 80 SY.

A Spectra Physics SP 8100 GPC instrument was used with UV detector (Kronwald) and RI detector R 401 Waters.

Monomer 1 synthesis

(1-Trimethylsilyl-ethinyl)-(1-methyl-vinyl)-carbinol 2. In a three-necked Flask with reflux condenser and P_2O_5 tube, septum and nitrogen inlet a Grignard solution is prepared under magnetic stirring from 4.6 g Mg and 15.6 ccm bromoethane in 50 ccm of dry THF. After 30 min at reflux temperature 28 ccm of trimethylsilyl acetylene are added at 0°C; ethane is evolved. After 2 hrs at reflux temperature and cooling to 0°C 16 ccm of methacrolein are added, the solution comes to room temperature and is refluxed for additional 2 hrs. After work-up with aqueous NH_4Cl and ether extraction the carbinol 2 is purified by chromatography in $CHCl_3$ on silicagel. 21.9 g (66.6 % yield) of a pale yellow liquid is obtained.
(1-Trimethylsilyl-ethinyl)-(1-methyl-vinyl) ketone 1. 2.2 g of carbinol 2 are oxidized with 1.8 g pH-neutral MnO_2 in 150 ccm of dry CH_2Cl_2 under stirring at room temperature for 17 hrs. The solution usually gets warm on reactant mixture or should be warmed up smoothly. MnO_2 is filtered off and the solution is filtered over a short silicagel column. After solvent evaporation i.v. 1 is yielded in 91 % in usually pure form.

Acknowledgement

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