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Cationic polymerization of 2-vinylthiophene – the polymer structure formation

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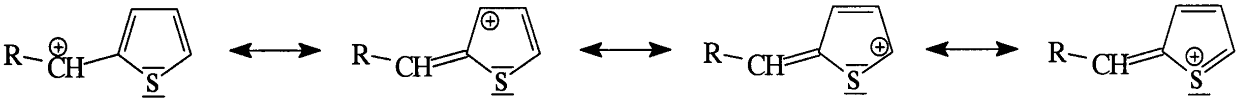
Summary

The cationic polymerization of 2-vinylthiophene (VT) has been studied in solution and on the surface of silica particles. For this purpose different cationically active initiators have been used, e.g. $SnCl_4$, CF_3SO_3H, and CF_3COOH in homogeneous solution as well as $(4\text{-}CH_3OC_6H_4)_2CH\text{-}Cl$ and $(C_6H_5)_3CCl$ in conjunction with silica nanoparticles in a slurry. For all experiments a high conversion of VT to oligomers with M_n = 1500 –2000 g/mol (M_w/M_n = 1.4) (Tg = 109 °C) and oligoVT/silica hybrid particles, respectively, have been observed. The different head and endgroups have been ascertained by means of MALDI TOF spectroscopy. Different NMR spectra analyses of the oligomers show that both the vinyl double bond and the five position of the thiophene ring are involved in the propagation reaction.

Introduction

Furan and thiophene containing polymers are important for many technical applications [1]-[5]. Five membered heterocyclic moieties are also promising functional groups for special optical and electrical properties when linked in organic/inorganic hybrid materials [6], [7]. Owing to the interesting properties of thiophene group containing polymers, [8], [9] surface functionalization of inorganic particles or flat surfaces with thiophene polymers has been studied by us using cationic polymerization as a tool for surface modification [10], [11]. In two recent papers we reported on the use of cationic polymerization in order to fix conjugated polymer structures on silica particles [12], [13].

According to former studies, we have chosen 2-vinylthiophene (VT) as monomer for cationic surface polymerization because the thiophene ring has a great electron density which stabilizes the positive charge of carbenium ions i.e by different mesomeric resonance structures (scheme 1) [14], [15].



Scheme 1 Stabilization of the carbenium ion by a thiophene substituent

Poly (2-vinylthiophene) (PVT) seems a promising polymer in order to produce novel conjugated polymer sequences on surfaces by consecutive hydride ion abstraction, in case of a regular structure (propagation via double bond) of the yielded PVT.

In spite of the predicted reactivity of VT for cationic polymerization, it has been only reported on the radical polymerization of VT until now [17] We will later see, what probably was the reason for this fact. For initiating the polymerization on silica, we used halogenoarylmethane compounds, e.g. chloro triphenylmethane (TrCl) and chloro bis(4-methoxyphenyl)methane (BMCM) as well established initiators for cationic surface polymerization [10], [11], [12], [18]. Because on the cationic polymerization of VT was still not reported, its polymerization in solution has been studied for comparison using the common cationic initiators CF_3COOH, CF_3SO_3H, and $SnCl_4$. We used silica KG 60 because of its commercial availability and high surface area. In this work we will report first results on the cationic polymerization of VT in solution and on silica and on the structure analysis of the obtained soluble oligomer fractions by different NMR techniques, GPC, and MALDI TOF spectroscopy.

Experimental

Materials

VT was synthesized from 2-hydroxyethylthiophene (Acros) by a base catalysed elimination reaction. The crude product was distilled under argon using a short Vigreux column. A small portion of hydroquinone was added. Chloro triphenylmethane (TrCl) was recrystalized from toluene in the presence of a small amount of acetyl chloride (2-4 %). Chloro bis(4-methoxyphenyl)methane (BMCM) was synthesized from the corresponding carbinol and HCl in the presence of anhydrous $CaCl_2$ in dichloromethane.
Silica 60 (particle diameter: 40 - 60 µm; specific surface (BET): 423 m2/g; high porosity; pore volume: 0.71 - 0.78 ml/g) was kindly supplied by Merck (Darmstadt). CH_2Cl_2 and $CDCl_3$ were used as solvents. They were freshly distilled under Argon over CaH_2 bevor use.
The trifluoroacetic acid (TFA) (Merck), the trifluormethansulfonic acid (TFMS) (Merck) and the tin tetra chloride (Aldrich) were used as received.

General procedure for the synthesis of PVT (poly-2-vinylthiophene) modified silica particles:

Samples of silica were heated for 8 h at 400 °C to remove physisorbed water. After cooling to room temperature the solvent was added. Adding of the initiators TrCl or BMCM resulted in immediate formation of the carbenium ion as indicated by the resulting colour. The mixture was then cooled to the desired reaction temperature and the monomer added with a syringe. After the reaction was finished the silica particles were fritted off and washed five times with CH_2Cl_2 and the filtrate was dripped into a large surplus of methanol. The immediately appearing precipitate was settled and fritted of. The yielded poly-2-vinylthiophene hybrid (PVTH) particles were dried under vacuum at room temperature. The products were stored under normal conditions.

Spectroscopy

The ^1H and ^{13}C NMR spectra were measured at room temperature with a Bruker Avance 250 MHz spectrometer at 250 MHz (^1H NMR) and 62.9 MHz (^{13}C NMR). Gel permeation Chromatography (GPC) was performed in THF using a Knauer device with a three column system (MZ-SDV-10^3, MZ-SDV-10^5 and a MZ-SDV-10^6 column) and refractive index detector. Polystyrene standards were used for calibration and 2,6-di-*tert*-butyl-4-methylphenol (BHT) as standard for flow correction.
MALDI TOF spectra were recorded on a Bruker Biflex III instrument (Bruker Daltonik GmbH, Bremen) in reflector – mode. As matrix Dithranol (1, 8, 9-trihydroxyanthracen) was used. As solvent for polymer (10 g/l), matrix (20 g/l) and salt (K-trifluoro acetate, 0,1 mol/l) served tetrahydrofuran. Approx. 1 µl of this mixture was dropped onto the steel sample-holder.

Results and Discussion

The peculiarities for the cationic polymerization of VT obviously result from the bifunctionality of the monomer itself due to the two different nucleophilic sites: the five position of the thiophene ring and the vinyl double bond. A similar reactivity behavior towards electrophiles is observed for 2-vinylfuran (VF) as monomer (see

Tab. 1 Representative yield and mass balance for the cationic polymerization of VT with various heterogeneously and homogeneously active initiators, (solvent: dichloromethane)

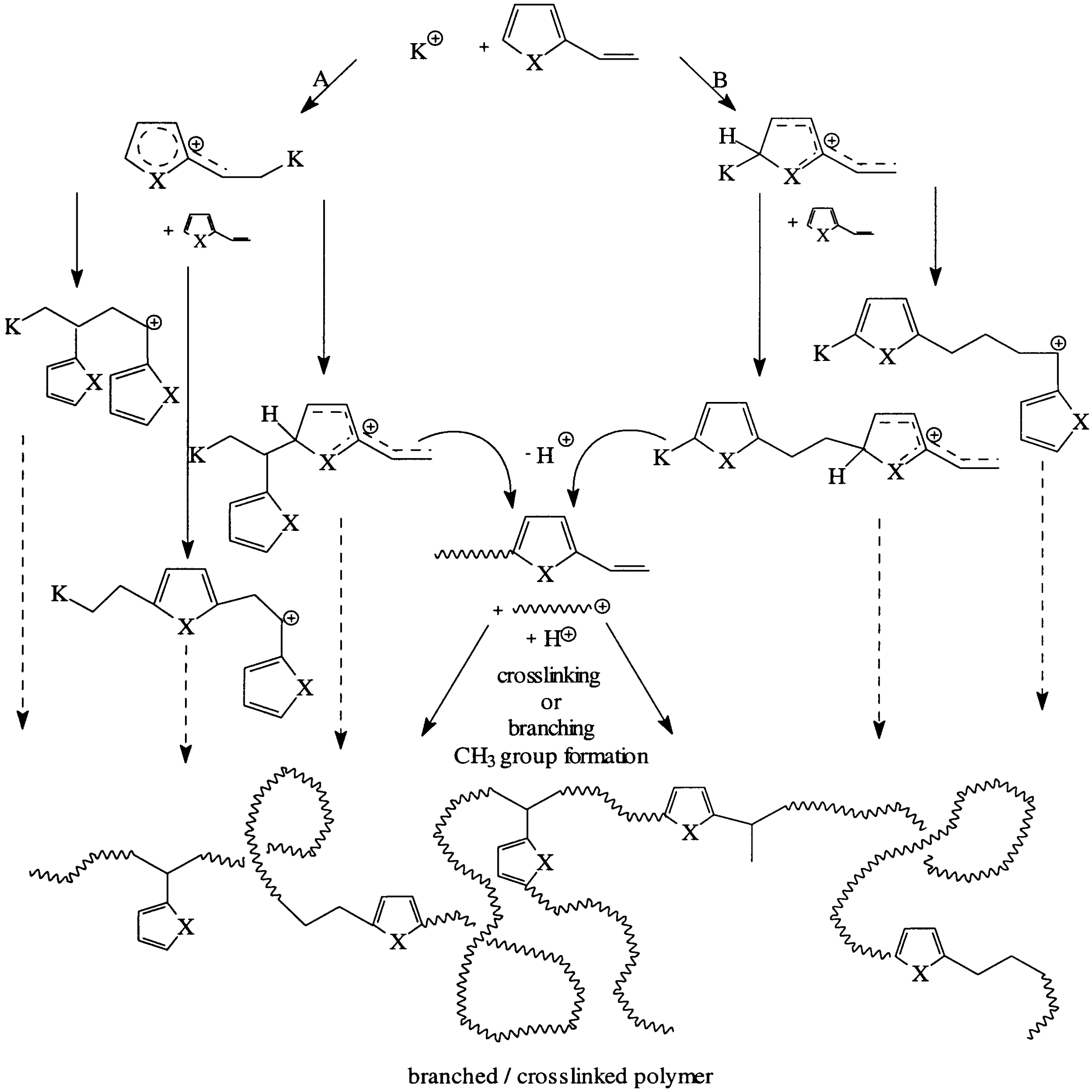
initiator	T / °C	reaction time / h	total yield (with respect to the monomer) / %	M_n	M_w / M_n	PVTH / PVT [a]
TrCl/silica [b]	0	24	76	1850	1.66	0.45
TrCl/silica [b]	0	48	85	2280	1.63	0.32
TrCl/silica [b]	-20	48	61	1900	1.55	0.23
BMCM/silica [b]	0	24	87	2060	1.90	0.68
BMCM/silica [b]	0	48	85	1906	1.63	0.57
BMCM/silica [b]	-20	48	73	2140	1.71	0.31
BMCM/silica [b]	20	24	95	2850	2.10	0.35
TFA [c]	0	24	100	3280	1.86	-
TFA [d]	0	24	64	2820	1.71	-
TFMS [d]	0	24	100	3760	2.53	-
tin tetra chloride [d]	-20	24	100	3890	2.44	-

a) PVTH / PVT denotes the amount ratio of yielded PVT/silica to the soluble PVT fraction
b) $m_{Silica} / n_{Initiator} / n_{Monomer} / V_{solvent}$ = 1g / 0.001 mol / 0.01 mol / 10 ml
c) $n_{Initiator} / n_{Monomer} / V_{solvent}$ = 0.001 mol / 0.01 mol / 10 ml
d) $n_{Initiator} / n_{Monomer} / V_{solvent}$ = 0.001 mol / 0.02 mol / 10 ml

scheme 2). Usually, for cationic polymerization of VF cross-linking and isomerization reactions are observed causing broad MWD's (molecular weight distribution) and colored polymers [19], [20]. Thus, cationic surface polymerization of VF on silica yields mainly a functionalized silica particle rather than a soluble polymer fraction [13b].

In the case of VT-polymerization the soluble polymer fraction is the main product. However, for thiophene also the 3 position of the ring can be involved in electrophilic reactions because of its high tendency to reactions with electrophiles [15]. But there is still no indication that this reaction occurs.

Despite the problems predicted, a white, soluble oligomer with narrow MWD is obtained after cationic polymerization of VT with the various initiators used, e.g. halogenoarylmethanes/silica, CF_3COOH, CF_3SO_3H, and $SnCl_4$. From all experiments it can be concluded that VT readily polymerizes cationically to high conversion (see experimental). The results are briefly summarized in Tab. 1.



Scheme 2 Possible alternative cationic propagation reactions for electron rich 2 vinyl substituted five ring heterocycles

However, the real problem arises from the bifunctionality of the monomer. Therefore, the resulting polymer structure consists of different main units reflecting this problem – chain polymerization of the vinyl group versus step growth by friedel crafts polymerization involving the thiophene ring. This is dramatically observable in the ^{1}H NMR spectra of any soluble oligo VT sample fraction obtained. A representative ^{1}H NMR spectrum is shown in Fig. 1. The NMR spectra of the PVT started with various initiators do not significantly differ concerning the chemical shift and the intensity of the polymer signals (see Tab. 2). Compared to the ^{1}H NMR spectrum of a PVT obtained by a radical polymerization (then only the vinyl double bond polymerizes) [17a], a lot of

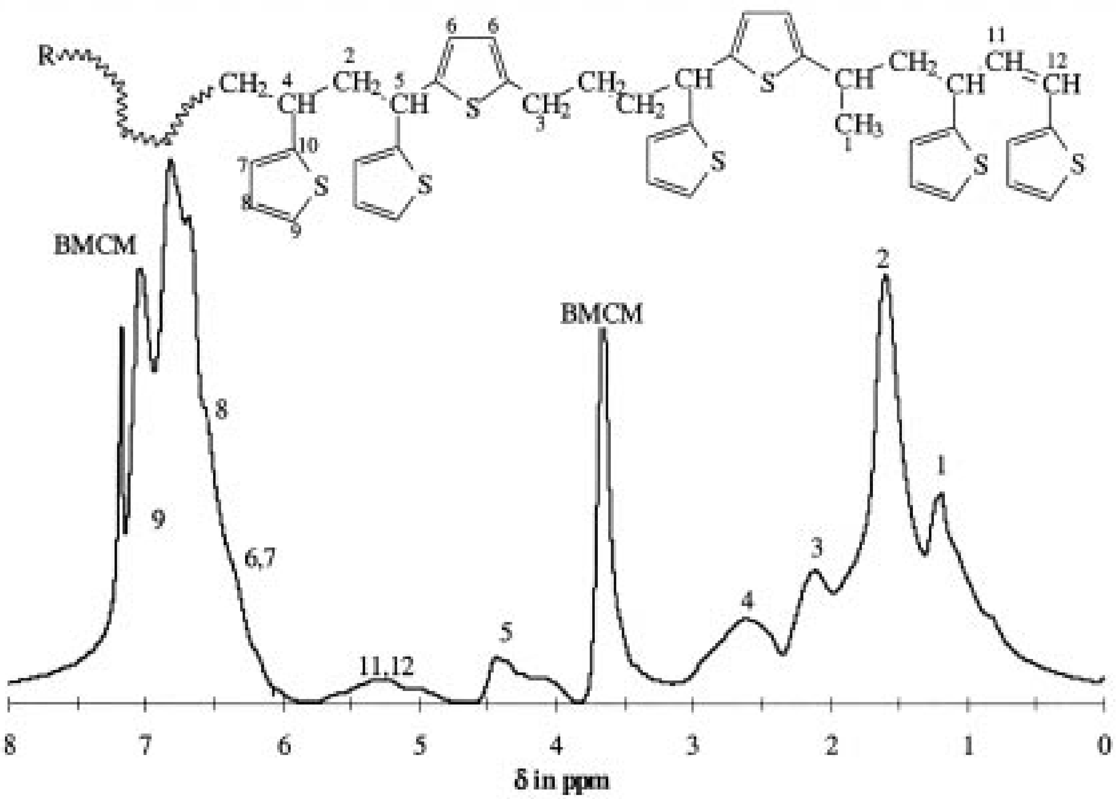


Fig. 1 ^{1}H NMR spectrum of a representative oligo VT sample in CDCl$_3$ (polymerization conditions: Initiator BMCM, T = 0 °C, reaction time: 48 h)

additional ^{1}H NMR signals are observed. In the high field region between δ = 0.9 and 1.4 ppm one sizable signal and one or two little ones appear which may be assigned to different methyl groups. A ^{13}C signal (see Fig. 2) at 24.46 verifies one methyl group. At δ ~ 1.65-1.75 ppm a large signal can be assigned to the methylene group

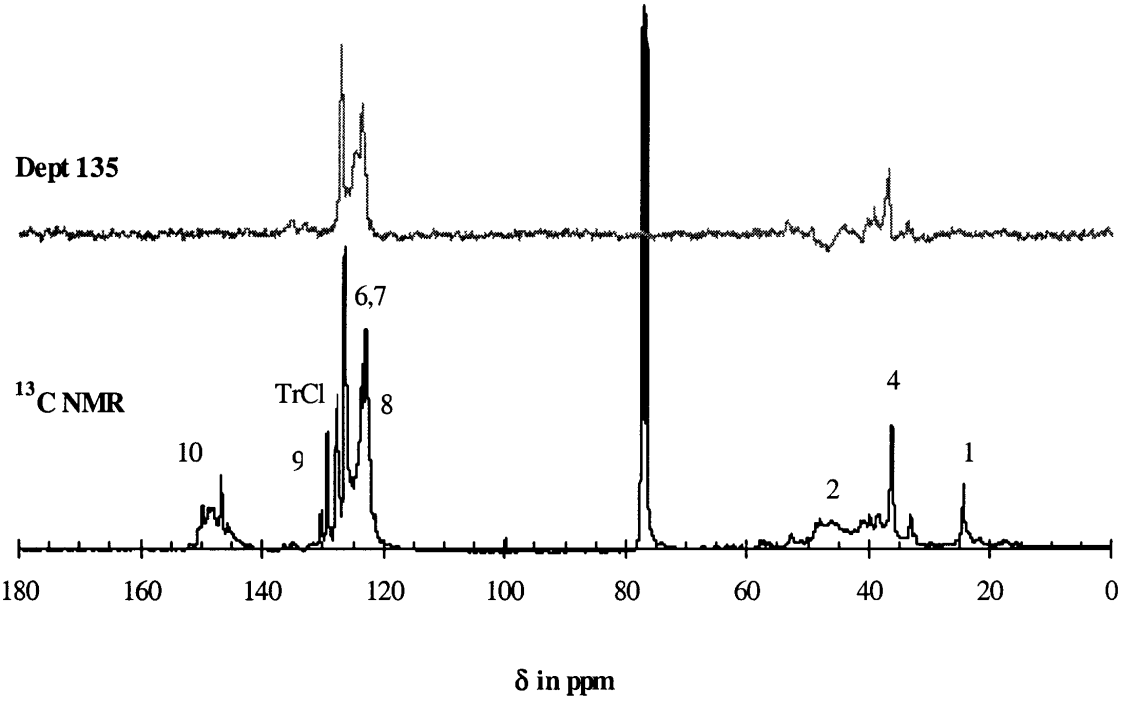


Fig .2 ^{13}C NMR spectrum of a representative oligo VT sample in CDCl$_3$, structure is according to assignment in Fig. 1 (polymerization conditions: ^{13}C NMR: Initiator TrCl, T = 0 °C, reaction time: 96 h; Dept 135: Initiator TFA, T = 0 °C, reaction time: 24 h)

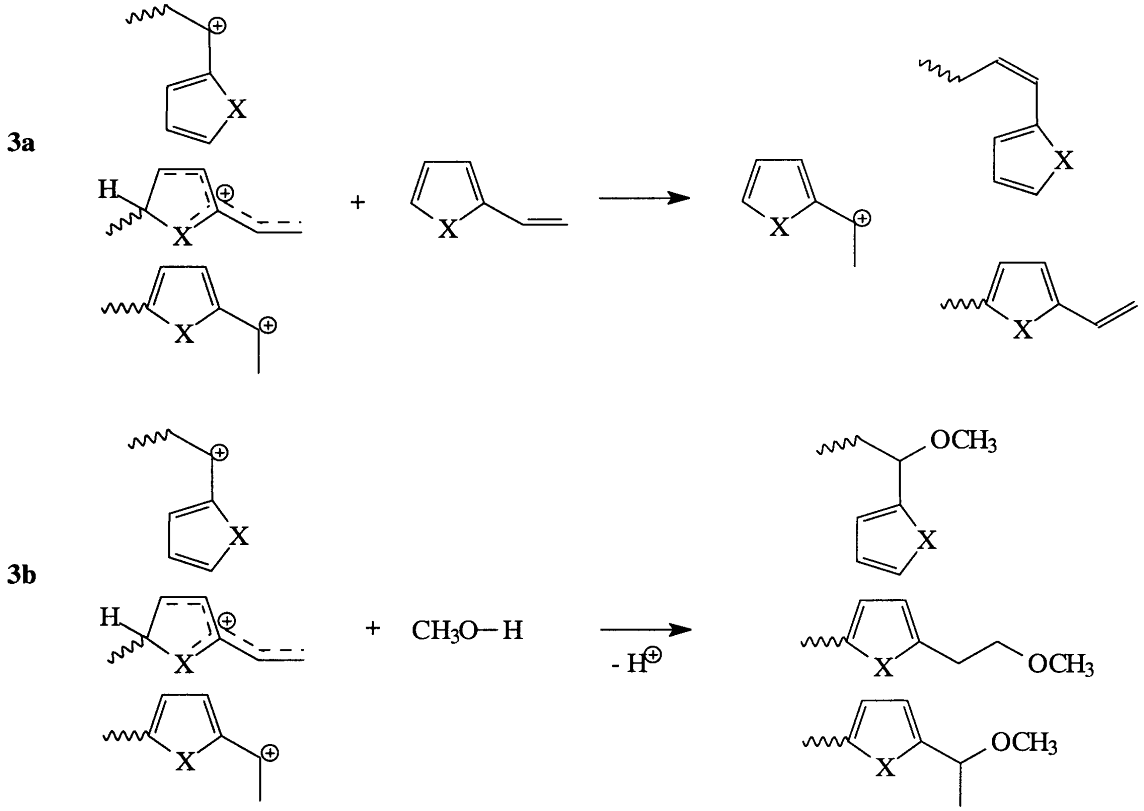
deriving from the chain polymerization according to the literature data from radically polymerized VT [17a].
In the ^{13}C NMR spectrum a signal at δ = 46-48 ppm could be recognized as a methylene group according to a DEPT 135. Aside we find a signal at δ = 2.2-2.4 ppm which has a lower intensity. This indicates the presence of another methylene group. Between δ = 2.5 and 2.9 ppm a broad signal with a shoulder is detectable. It correlates to the methine group signal of radically polymerized VT and is in accord to the literature data [17a]. In addition the ^{13}C NMR spectrum provides the expected signal at δ = 36.2 ppm for the methine carbon. The signal at δ = 3.77 ppm is due to the initiator BMCM. In the region between δ = 4.0-4.6 ppm one or two smaller signals are detectable which can be assigned to methine signals in vicinity to two thiophene rings. This structure can only be built since both propagation mechanisms (see scheme 2) contribute to the growing chain.

Tab. 2: Intensities of the signals in the high field region of the ^{1}H NMR spectra

	Structure unit (δ in ppm) according to Fig. 1				
	1 (0.9-1.4)	2 (1.65-1.75)	3 (2.2-2.4)	4 (2.5-2.9)	5 (4.0-4.6)
Relative intensity (RI)$^{a)}$	4.8	10.1	2.2	5.0	1.0

a) average values from eight different NMR experiments using the initiators described in Tab. 1, $RI = I_{Signal}/I_5 * \text{number of H}$

The formation of methyl head groups (δ = 1.0-1.4 ppm) and vinyl double bonds at the end of the polymer chain (δ = ~5.3 ppm) are clear evidences for proton transfer reactions to the monomer among the propagation reaction according to scheme 3a. However, this is expected for cationic polymerization. The other signals in the region between δ = 1.0 –1.4 ppm indicate the presence of one or two additional methyl groups which are probably located in the main chain. They may be formed by the Friedel Crafts attack of the cationically active chain end upon the five position of the thiophene ring and subsequent proton attack upon the remaining double bond (see scheme 2). According to the two different possible propagation steps and the initiation by arylmethylium and proton, respectively, four different head groups are expected. These head groups and two different kinds of end groups according to scheme 3 have been clearly verified by a MALDI TOF experiment (see Fig. 3 and scheme 3). But there is no differentiation possible concerning the two possible reaction pathways A or B (see scheme 2). Despite the correspondence of the results from the NMR (see Fig. 1 and 2) and MALDI TOF experiments, a clear assignment of all NMR signals to structure elements is difficult to do because the signals are rather broad and poorly resulted. This may be due to free radicals in the produced VT polymers. Some ESR experiments (not shown) indicated the existence of organic radicals in the VT polymers and hybrid materials after neutralization and cleaning of the products. Their formation may be due to exposure to oxygen and light as they were stored under non-inert conditions. Further studies concerning this fact are in progress [21].



Scheme 3: Possible proton transfer reactions of cationically active propagating oligoVT chains to the VT monomer (3a) and end group formation (3b)

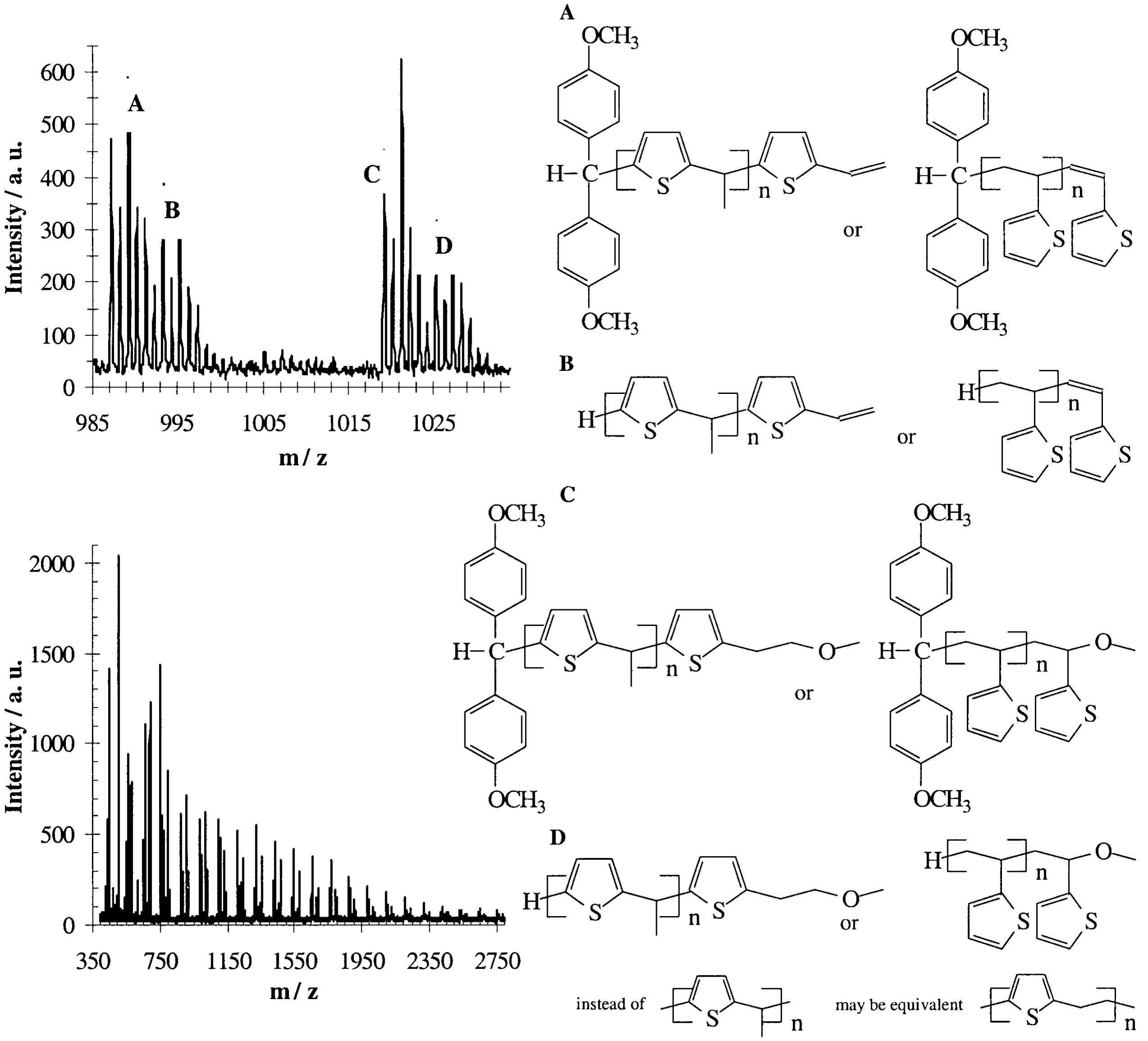


Fig. 3 MALDI TOF spectrum of a oligoVT with structure proposals assigned to the appropriate mass signals, (polymerization conditions: Initiator BMCM, T = -20 °C, reaction time: 96 h)

As mentioned (see Tab. 1), the cationic polymerization of VT initiated with freshly prepared BMCM/silica particles yields a soluble fraction (about 60 – 70 %) and PVT-functionalized silica particles. However, in comparison with the cationic surface polymerization of VF on silica [13b], [21], where mainly coated particles are yielded due to high cross-linking it can be assumed that the coating efficiency of the VT is lower. This permits the conclusion that the tendency of the VT to cross-linking reactions is much smaller than of the VF and the real structure is very probably linear but some branchings cannot be excluded. This explanation is suggested by the ^{1}H NMR spectra, the small M_w/M_n ratios and the Tg point which was determined to be approximately 110 °C.

A investigation of the hydride ion abstraction from the PVT should be promising because of the relatively regular structure of the PVT and is under study in our group.

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