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ANIONIC POLYMERIZATION OF VINYLFERROCENE

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Abstract

Vinyl ferrocene was polymerized by means of typical anionic initiators, such as n-BuLi , s-BuLi and distyryl dianion. The polymerization is characterized by spontaneous initiation, control of the molar masses by the ratio of [Monomer]: [Initiator], linear molar mass-conversion-relationship and a narrow molar mass distribution.

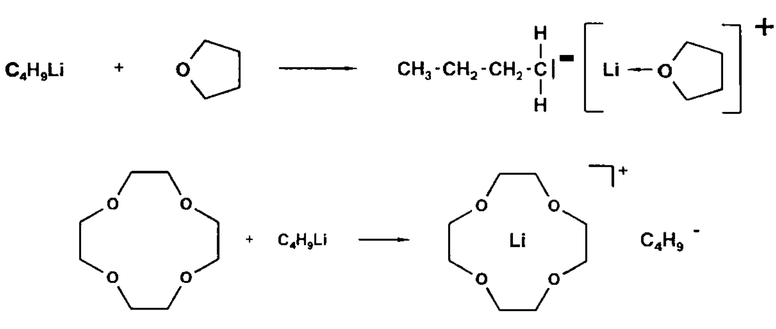
1.Introduction

Metal containing polymers have emerged as an important class of polymers in the last twenty years[1]. One of the reasons for this development is that many of them became available via conventional synthetic routes[2]. Furthermore, these polymers are expected to posses properties significantly different from those of conventional organic polymers and that they show high thermal stability, electrical and photoconductivity, magnetic behavior and last not least interesting nonlinear optical properties[3-5]. Therefore, this field of research can be seen as crossing the borderline between organic, inorganic, polymer chemistry and material science. However, there are still several synthetic problems to be solved. Although, the polymerization of vinyl ferrocene (**1**) has been studied under radical [6,7], cationic[8] and Ziegler-Natta-conditions[8] it was not possible to receive polymers with controlled molar masses. Anionic polymerization was claimed to be impossible for the electron rich compound **1**[9]. Indeed, on the basis of the e-value (Q,e-scheme) e = - 2,1 [3] it seemed to be hopeless to apply anionic initiators for the polymerization of **1**.

2.Anionic Polymerization of Vinylferrocene(1)

2.1. Reaction conditions

For the optimization of the polymerization many variations of solvent/initiator system have been applied. In addtion, temperature has been varied between -70°C and 0°C . Reaction time was extended up to 60 hrs. Finally it was found, that n-BuLi, S-BuLi and distyryl dianion in THF as solvent are most suitable for a controlled anionic polymerization of **1**. However, polymerization was not possible in toluene, methylene chloride or dioxane. The reason for these differences is propably due to the capibility of THF to form complexes with Li^+ and therefore to support the formation of naked, highly reactive carbanions, which are able to react with electron rich monomers such as **1**. This view is supported by the observation that polymerization becomes also possible in dioxane if [12]-crown-4 is added (scheme 1).



(1)

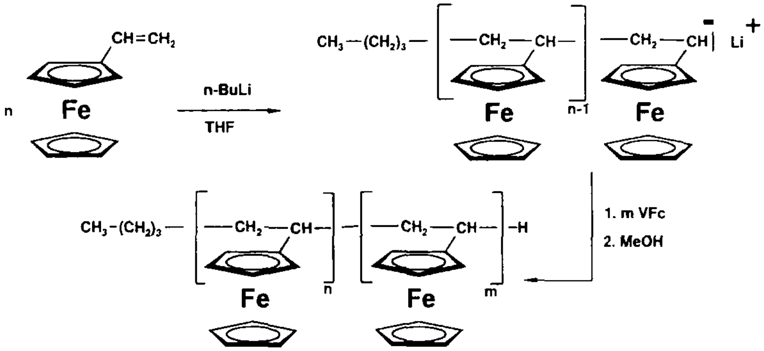
2.2. Polymerization of 1 with n-BuLi and s-Bu-Li in THF

Polymerization of **1** was initiated either by n-BuLi or s-BuLi in THF at temperatures between 0°C and -70°C. Depending on the temperature rection time varied between

4 hrs(0°C) and 80 hrs(-70°C). However, it is not advisable to work at to low temperatures due to the fact that it becomes very difficult to keep the system dry and to reach 100% conversion (results are presented in Tab. 1 and Fig. 1).

Above -45°C polymerizaion of **1** shows the characteristics of a living system:
- spontaneous initiation
- control of molar masses by [monomer] : [initiator]
- linear molar mass-conversion relationship
- increase of the molar mass with sequential addition of monomer
- narrow molar mass distribution

Polymerization takes place according to the following scheme:



(2)

Moreover the distribution of molar masses are narrow. Since the first GPC-curve was structured in the oligomer region it was possible to calibrate the GPC on the basis of a homologeous row of oligomers of **PVFc**. The calibration was completed with standards of **PVFc** synthesized during this investigation. The corectness of this calibration was strongly supported by FD-MS of **PVFc** oligomer in which homologeous between n = 3 and n = 11 were identified.

It is interesting to note that the main peaks of the FD-MS spectrum are accompanied by sattelite peaks of a mass wich corresponds with that of the oligomers plus 79. Therefore we suggest that those peaks belong to the following structure:

Table 1: Polymerzation of VFc with n-BuLi; monomer addition experiment [a]

Time /min	converted[b] VFc /mmol	$\overline{M_n}$ (calc.)[c] / g·mol^{-1}	$\overline{M_n}$[d] / g·mol^{-1}	$\overline{M_w}$[d] / g·mol^{-1}	$\overline{M_w}$ / $\overline{M_n}$
7	0.8253	295	375	430	1.15
30	2.6207	936	1070	1240	1.16
80	5.5384	1979	2070	2360	1.14
127	6.3357	2265	2340	2640	1.13
178	6.5010	2324	2400	2740	1.14
206	6.7242	2403	2400	2730	1.13
248	6.8705	2455	2450	2810	1.14
addition of monomer					
269	9.2446	3304	3110	3540	1.14
292	12.2361	4373	4180	4800	1.15
364	13.8921	4969	5030	5690	1.13
446	15.1741	5423	5650	6440	1.14
1122	18.4713	6601	6450	7546	1.17

a) in THF at -25°C [VFc] = 0.173 mol/l [n-BuLi] = 0.015 mol/l

b) determined by gas chromatography; internal standard = toluene, xylene

c) $\overline{M}_n$.cal. = C/100 · M_{VFc} · [VFc]/[n-BuLi] + M_H + M_{C4H9}

d) determined by GPC; poly(vinylferrocene) as internal standard

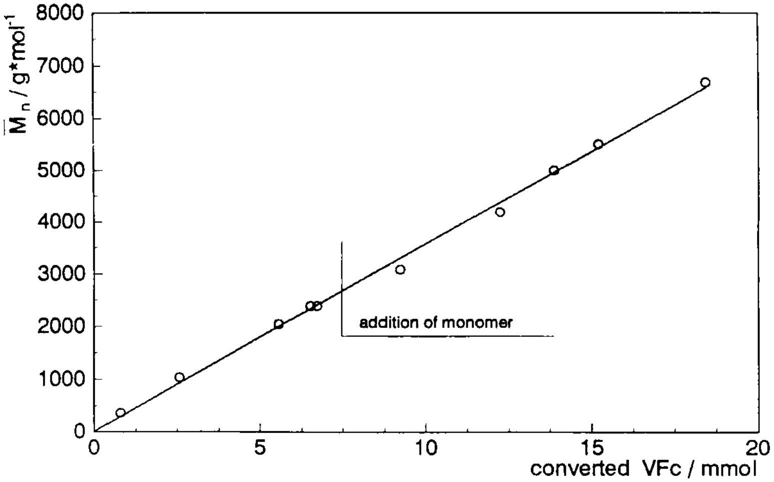


Figure 1: Monomer addition experiment; molecular weight as a function of converted Vfc in THF: 0°C; [VFc] = 0.217 mol/l [s-BuLi] = 0.009 mol/l

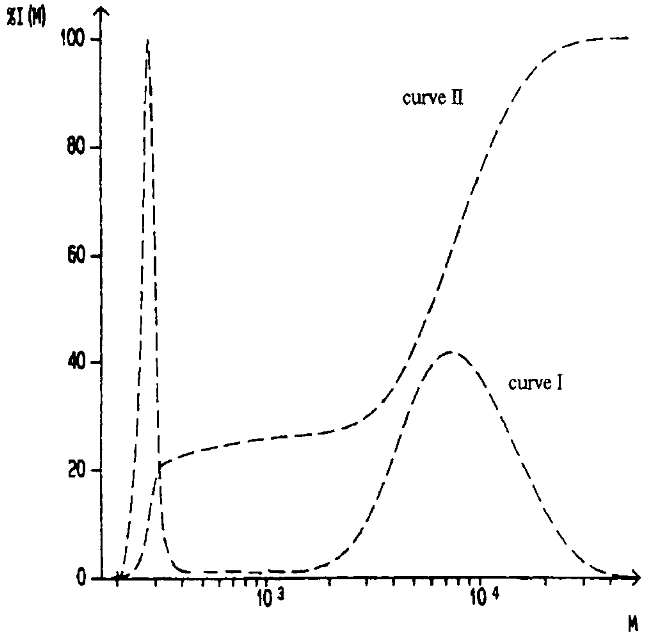
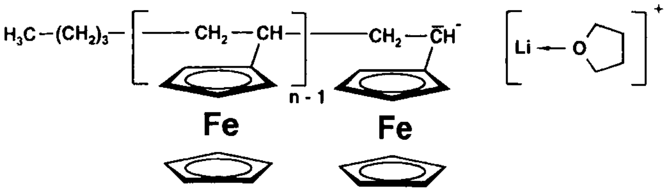


Figure 2: Determination of conversion by GPC (UV-detection) in THF; -25°C [VFc] 0.175 mol/l [n-BuLi = 0.0.15 mol/l



(3)

2.3. Reaction Kinetics

The conversion of the monomer was followed either by gas chromatography or by GPC. A typical GPC is shown in Fig. 2.

Curve I the elution curve of a sample (UV-detection) in which the integral UV-absorption is shown as function of log M. Curve II is the differential UV absorption

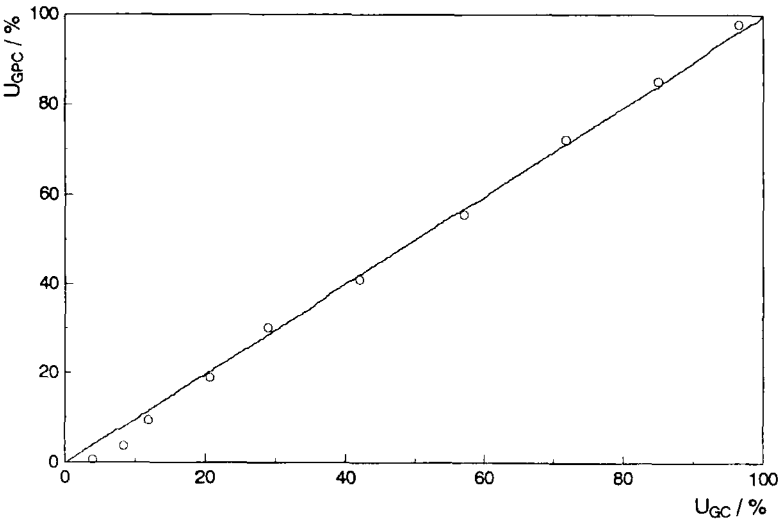


Figure 3: Correlation of the conversion(C) determined by GC (C_{GC}) with the conversion determined by GPC (C_{GPC})

of monomer and polymer. The area below curve II represents the concentration of monomer and polymer assuming that their absorption coefficients are identical. This assumption was controlled by GC and shown to be fullfilled by the following graph in which the slope is shown to be equal to one (Fig. 3).

It was shown that the consumption of monomer follows a first order kinetics and can be described by the following equations:

$$-\frac{d[VFc]}{dt} = k_{app} \cdot [VFc]$$

$$[VFc] = [1-C] \cdot [VFc]_0$$

$$\Rightarrow \ln[1-C] = -k_{app} \cdot t$$

The ln(1-C) = f(t) plot is a straight line up to very high conversion for temperatures between -40°C and 0°C. From the ln k = f(1/T) plot an activation energy of 40 kJ mol^{-1} was determined.

3.Experimental

Instruments:

IR was taken with BioRad Digilab FTS-40. Bruker AC 250 was applied for ^{1}H and ^{13}C NMR. A Varian GC 3500, equipped with a capillar column Chrompack CP Sil 5 CB, 25m, was used for the conversion studies. For the mass spectrometry a Varian MAT 312 (80 eV) was applied. FD-MS was taken at Universität Regensburg. Zentrale Analytik. The GPC was a Waters model, containing pump 510, RI 410, PL-gels for polymers and oligomers. THF was used as eluent. Elemental analysis was carried out by the "Mikroanalytisches Labor" Ilse Beetz Kronach.

Solvents and Chemicals

Toluene, dioxane and tetrahydrofurane(THF) were carefully cleaned by rectification and dried over potassium. Vinyl ferrocene was synthesized(details see below) and sublimed twice before use. Argon was applied as inert atmosphere and dried over basic Al_2O_3, covered with potassium.

Synthesis of Vinyl ferrocene

Ferrocene aldehyde

112g(0.6 mol) of powdered ferrocene were dissolved in 107g(0.7 mol) $POCl_3$ were stirred and heated up to 50°C. 81g(0.6 mol) N-methyl formanilide were added to this solution dropwise in about 3 hrs. The reaction is exothermic, therefore it is essential to apply an effective stirrer. After further 30 min the mixture is cooled to room temperature, stirred for further 3 hrs, then it was poured onto ice/water and extracted with diethyl ether. The ether phase was washed neutral, dried, filtered and distilled off. The residual black oil started crystallization by rubbing the glass wall with a spatulus. It was sublimed twice (70°C/ 0.1 Torr) resulting in 71g (90%) yellow-orange crystalls, which melted at 130°C.

$C_{11}H_{10}FeO$ (214.04)	Calcd.	C 61.67	H 4.67	Fe 26.09
	Found	C 61.69	H 4.72	Fe 26.15

IR(KBr): in cm^{-1}; 3093(CH, aromat.), 2833, 2762(CH, aliphat.) 1680(CO), 1631(C,Caromat.), 1454, 1410, 1388, 1369, 1350, 1246, 1201, 1107, 1004, 825, 744, 619, 525, 499, 457

^1H NMR ($CDCl_3$). δ in ppm vs TMS : 9.93(1H,CHO); 4,81(2H, H-2,5 in C_5H_4); 4.60(2H,H-3,4 in C_5H_4); 4.29(5H, C_5H_5)

^{13}C NMR($CDCl_3$) δ in ppm vs TSM : 192.0(CHO); 78.7(C-1 in C_5H_4), 72.6(C-3,4 in C_5H_4); 68.7(C_5H_5); 68.0(C-2,5 in C_5H_4)

Vinyl ferrocene

4.03g (36 mmol)K tert.butylate were added in small portions to a suspension of 12.15g(34 mmol) methyltriphenyl phosphonium bromide in 100ml dry THF under Argon at room temperature. A strong yellow colour indicates the formation of the ylide. After the ylide formation is completed a solution of 6.85g(32mmol) ferrocene aldehyde in 50ml dry THF was added dropwise. After further stirring of 30 min at RT the solution was hydrolyzed carefully by addtion of 100ml of oxygen-free dest. water. Then THF was distilled off in vacuo. The residual water phase was extracted with 5x 50ml methylene chloride. The organic phase was dried over $MgSO_4$ and finally the solvent was distilled off. The residual product was cleaned by chromatography over Al_2O_3 with n-hexane followed by sublimation at 50°C in vacuo. 5.1g (76%) orange coloured crystals of vinyl ferrocene melt at 48 -49°C.

$C_{12}H_{12}Fe$(212,06)	Calcd.	C 67.91	H 5.66	Fe 26.34
	Found	C 67.95	H 5.59	Fe 26.31

IR(KBr) in cm^{-1} : 3103, 3080(CH, arom.), 3007(CH, vinyl) 1631, 1620(CC, vinyl), 1408, 1384, 1367, 1240, 1197,1103, 1045, 1026, 1016, 999, 912, 855, 823, 812, 727, 636, 518, 480

^1H NMR(in $CDCl_3$) δ in ppm vs. TSM: 6.49(dd, 1H, ^3J = 17.6 Hz), 5.31(dd, 1H, ^3J = 7.6 Hz, ^2J = 1Hz), 5.01(dd, 1H, ^3J = 17.6 Hz, ^2J = 1Hz), 4.34(m, H-2,5 in C_5H_4), 4.18(m, H-3,4 in C_5H_4), 4.08(s, C_5H_5)

^{13}C NMR(in $CDCl_3$) δ in ppm vs. TSM: 134.1(CH), 110.6(CH_2), 69.1(C_5H_5), 68.8(C-1 in C_5H_4), 68.3 and 66.2(C-2,3,4,5 in C_5H_4)

Polyvinylferrocene

Anionic Polymerization

1.5g(7mmol) of vinylferrocene(double sublimed and freece-dried) were directly sublimed into a 100 ml thermostated glass reactor, equipped with a thermostated dropping funnel, magnetic stirring barr, septum and a three-way-stop cock. Then 50ml dry THF and 1ml dry toluene(internal standard for the analysis) were added. The solution was cooled to the reaction temperature and then the polymerization was started by addition of a precooled initiator solution (n-BuLi or s-BuLi dissolved in n-hexane or cyclohexane) through the septum. The progress of the polymerization was followed via gas chromatography for which 0.5 ml samples(taken through the septum) were poured into methanol (-78 °C).

$$U_{GC}\% = \frac{(A_{VFC}\ A_{TOL})_0 - (A_{VFc}\ A_{TOL})_t}{(A_{VFc}\ A_{TOL})_0} \times 100$$

A_{VFc} = area of the VFc-peak ; A_{Tol} = area of the toluene peak
index o at time t = 0; index t: at time t = t

After the first portion of monomer is completely converted into polymer, a second portion of monomer (dissolved in THF) , stored and precooled in the dropping funnel, was added into the reaction mixture. Its consumption was followed by GC again. Moreover, the resulting polymer precipitating in methanol was filtered off, redissolved in THF and precipitated in methanol again and dried in high vacuum at 60°C. Weight and molar mass of each sample were determined and correlated with the conversion of monomer.

Analytical Data

IR(KBr) in cm^{-1}: 3091, 3008(CH, aromat.), 2854(CH, aliphat.), 1653, 1464, 1411, 1219, 1105, 1022, 1001, 815, 756, 667, 508, 484

^{1}H NMR($CDCl_3$) δ in ppm vs.TMS: 4.58 -3.3(C_5H_5, C_5H_4), 2.69 -0.5($CHCH_2$),

^{13}C NMR($CDCl_3$) δ in ppm vs.TMS: 68.4 -66.9(C_5H_5, C_5H_4), 45.9 -40.3($CHCH_2$)

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