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Oxidative Coupling of Poly (2-Vinylthiophene) Chains by $FeCl_3$

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Summary

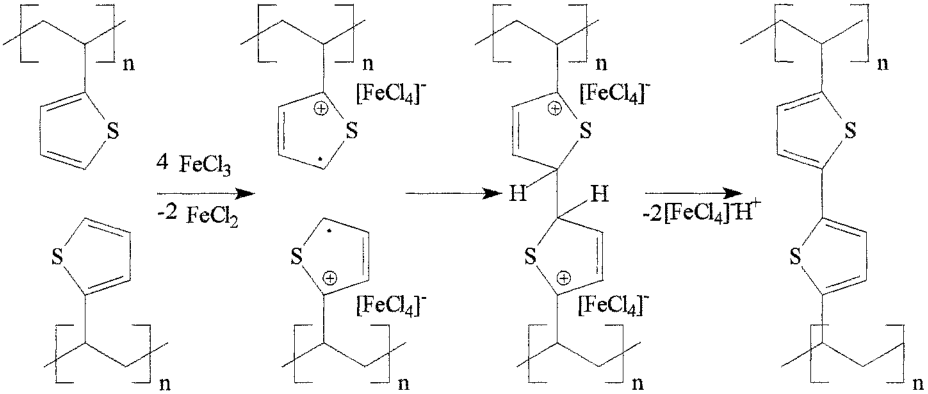
Poly(2-vinylthiophene) (PVT) can be cross linked with $FeCl_3$ either in dichloromethane solution or when immobilized on silica particles. Extend of cross linking is strongly dependent on the $FeCl_3$/PVT ratio used for the reaction as shown by GPC plots and gravimetric analyses of the formed insoluble polymer fraction. A stoichiometric $FeCl_3$/PVT ratio of about four is necessary to achieve complete conversion, because consecutive formations of thiophene$H^+FeCl_4^-$ and bisthiophene$H^+FeCl_4^-$ sigma complexes take place. PVT can be also cross linked when adsorbed on silica using the same procedure. The cross-linking is proved by IR and ^{13}C CP/MAS NMR spectroscopy.

Introduction

Poly(2-Vinylthiophene) (PVT) can be synthesized by a radical [1], electrochemical [2], or cationic polymerization of 2-vinylthiophene [3,4]. Radical polymerization is less suitable due to the low reactivity of the monomer for this purpose [1]. Cationic polymerization gives high yield of the polymer with $M_w/M_n \approx 2$ and a well defined glass transition temperature [3, 4]. However, the molecular weight of cationically produced PVT seldom exceeds $M_n > 2000$ gmol^{-1} which makes the polymer disadvantageous for several applications to nano-composite production or surface coating [4]. To fix a thiophene polymer at an interface, oxidative cross linking between soluble chains is suitable for this purpose, which has been applied to various polythiophenes at the water/benzene interface using $HClO_4/Fe(ClO_4)_3$ as the catalytic system [5]. Poorly defined insoluble polymeric films are obtained by this procedure. However, the rate of dimerization of the radical cation of alkyl substituted thiophene is in the order of about 10^5 M^{-1} s^{-1} [6] which makes this reaction even suitable for adjustable cross linking of soluble PVT chains.

In this communication we report on the controlled redox coupling of cationically produced PVT chains via the five position of the two alkyl substituted thiophene rings according to Scheme 1. $FeCl_3$ has been well established as an effective reagent to link thiophene rings together via the 2 and 5 position, because it is an effective catalyst to produce linear polythiophene chains in different environments [7-12].

For the experiments in this work, two different procedures have been applied: ***A***: PVT as soluble polymer and ***B***: PVT when immobilised on silica particles alone and with a



Scheme 1 Oxidative coupling reaction of two PVT chains in the five position with Iron III chloride.

mixture of dissolved PVT, respectively. The soluble PVT fraction as well as the PVT/silica hybrid particles have been simultaneously synthesized by a cationic surface polymerization of 2-VT in conjunction with silica particles using chloro triphenylmethane or chloro bis(4-methoxyphenyl)methane (BMCM) as the initiator, respectively [3,4]. To adjust the optimal conditions for the coupling reaction, the molar ratio of PVT to $FeCl_3$ (n_{PVT}/n_{FeCl3}) has been varied from 10 to about 0.2.

Experimental

Materials

PVT (M_n = 2000 $gmol^{-1}$, M_w/M_n = 1.4) was synthesized by a cationic polymerization reaction as described previously [3]. PVT/silica hybrid particles have been synthesized by a related procedure using silica/chloro arylmethane as both component and catalyst [4]. Typical experimental conditions for synthesis of PVT were: Initiator BMCM, silica: KG 60, solvent: dichloromethane (DCM), T = 0 °C, reaction time = 48 h, M / I = 10, m_{BMCM}/m_{Silica} = 0.266.

Procedures for the reaction of PVT with $FeCl_3$

A: oxidative coupling of soluble PVT

PVT is dissolved in dichloromethane (DCM) at room temperature. Then, $FeCl_3$ dissolved in DCM (for the UV Vis measurements) or in acetonitrile (c = 0.15-0.25 g/ml) was added. In dependence on the amount of $FeCl_3$ used, a cross linked polymer precipitate is formed during the reaction. It is filtered off at the end of the reaction and washed with DCM and methanol. For the GPC investigations the remained soluble polymer fraction is precipitated in methanol, sucked off, washed with methanol, and dried under vacuum (0.5 Torr) at room temperature.

B: oxidative coupling using PVT/silica composites

PVT/silica hybrid particles are used as slurry in DCM at room temperature. Then

$FeCl_3$ dissolved in acetonitrile (c = 0.15-0.25 g/ml) was added. For the post grafting experiments, a desired amount of PVT dissolved in DCM was added afterwards. After the reaction is finished, the composite is sucked off and washed five times with DCM and methanol, respectively. For the GPC investigations the soluble polymer (in the remaining solution) is precipitated in methanol, sucked off, and washed with methanol. Both the composite and the soluble polymer were dried under vacuum (0.5 Torr) at room temperature.

Spectroscopy and Gel Permeations Chromatography

The ^1H and ^{13}C NMR spectra in solution were measured at room temperature with a Bruker Avance 250 MHz spectrometer at 250 MHz (^1H NMR) and 62.9 MHz (^{13}C NMR). $CDCl_3$ served as solvent and residual protons from $CHCl_3$ and natural abundant ^{13}C from $^{13}CDCl_3$ were used as internal references. Solid state NMR spectra under magic angle spinning (MAS) and cross polarization (CP) conditions were run on a Bruker Model Avance 400 Digital spectrometer at room temperature using 4 and 7 mm ZrO_2 rotors, the contact time was always 5 ms and the relaxation time was 3 s. For decoupling the TPPN method was applied.

The UV/VIS-transmission spectra were recorded in the slurry by a diodenarry spectrometer MCS 400 by Carl Zeiss Jena GmbH connected with an immersion cuvette TS 5A

EPR experiments were performed at room temperature with a BRUKER ESP 300 E spectrometer (X-band, ν = 9.783 GHz). The modulation frequency and amplitude was 100 kHz and 5 G, respectively.

IR measurements were run on an IR spectrometer FTS 165 by Biorad in diffuse reflection.

The elemental analysis was done with a Vario EL device of the company Elementar Analysensystem GmbH.

Gel permeation chromatography (GPC) was performed in THF using a Knauer device with a three column system (MZ-SDV-103, MZ-SDV-105and a MZ-SDV-106 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.

Results and Discussion

The soluble PVT was transformed to partially cross-linked PVT by reaction with $FeCl_3$ using different PVT/$FeCl_3$ ratios. Soluble and an insoluble polymer part is yielded in dependence on the amount of $FeCl_3$ a. With increasing the $FeCl_3$ concentration, the molecular mass of the soluble fraction increases as shown by the GPC plots (Figure 1). Since a PVT/$FeCl_3$ ratio > 2 has been used the main part of PVT remains soluble. If the PVT/$FeCl_3$ ratio is < 5, additionally a high molecular weight fraction is formed indicating the coupling between more then 4 different chains. Mainly an insoluble product is formed when a PVT/$FeCl_3$ ratio < 0.5 is used, because high conversion of cross linking between PVT chains takes place (Figure 2). As expected, the amount of cross linked insoluble polymer increases when a larger concentration of the polymer in the solution is used. The oxidative coupling process is associated with the formation of an intense red-violet coloured solution. A UV/vis spectra series is shown in Figure 3.

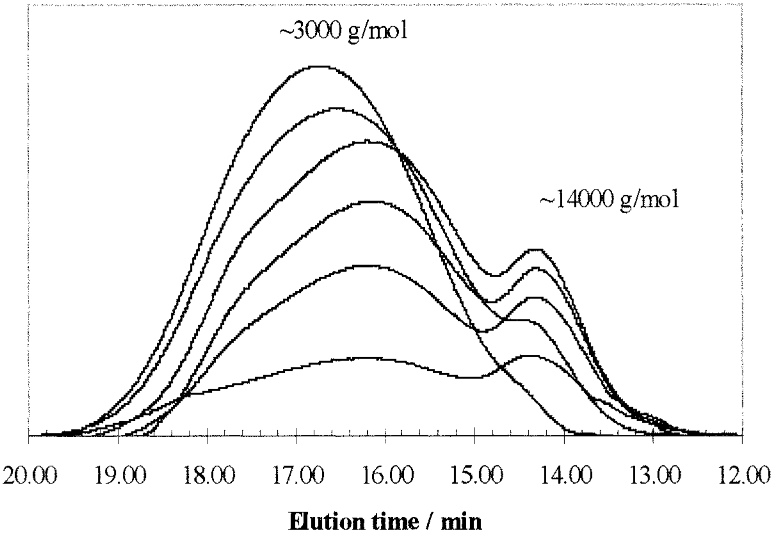


Figure 1 GPC traces of the soluble PVT fraction after reaction with $FeCl_3$ in dependence on the ratio of n_{PVT}/n_{FeCl3}, curves top to bottom: n_{PVT}/n_{FeCl3} = 9.2; 5.1; 3; 2; 1; 0.5, T = 293 K, c_{PVT} = 0.01 g/ml.

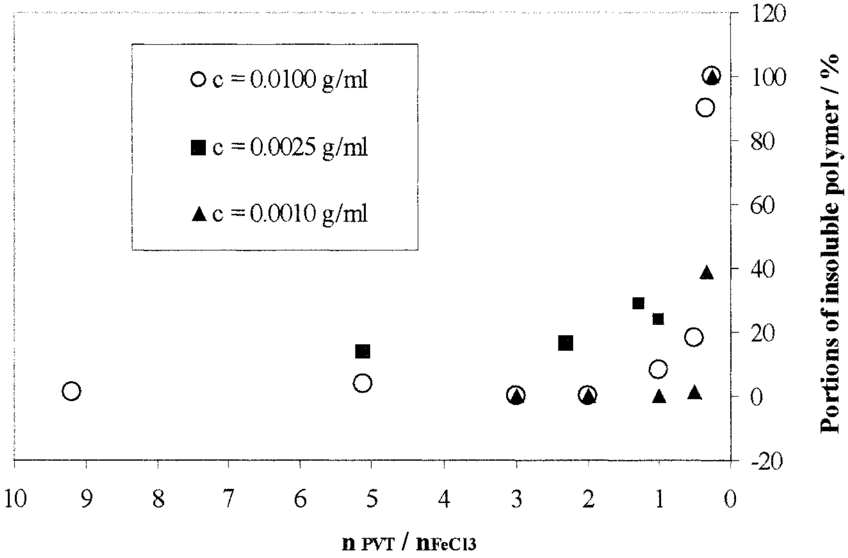


Figure 2 Part of insoluble polymer formed during the reaction of PVT with $FeCl_3$ as function of the n_{PVT}/n_{FeCl3} ratio using different start concentrations of PVT (inset).

The colour disappears immediately when a strong base is added. These results indicate the formation of sigma-complexes between $H^+FeCl_4^-$ and bisthiophene or thiophene moieties [13]. Related complexes are observed during the cationic polymerisation of 2-VT [4] and when thiophene derivatives are treated with strong Broensted acids such as $TiCl_4/HCl$ [13] or HY zeolite [14]. Proton transfer reactions to 2-substituted thiophene rings induce the formation of further species which makes the assignment to a specific structure difficult.

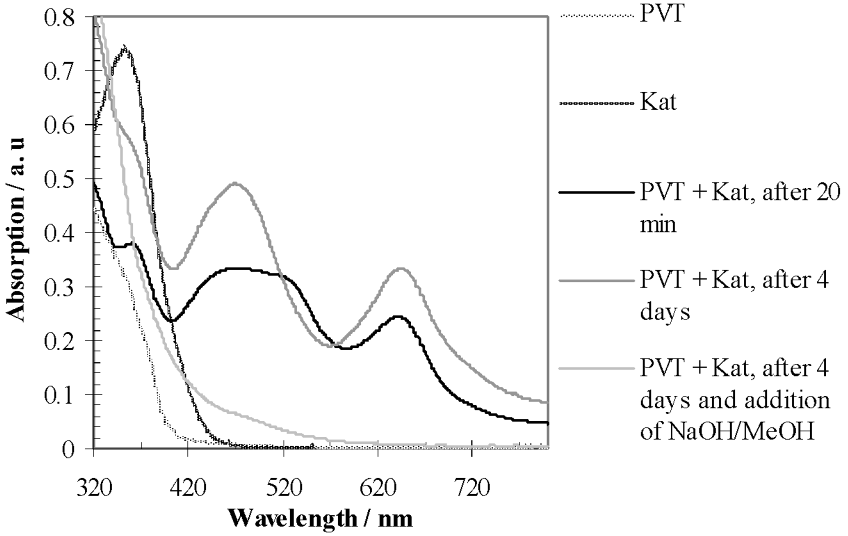


Figure 3 UV-Vis absorption spectra series monitored during the reaction of PVT with $FeCl_3$ (Kat), reaction conditions: room temperature, solvent: dichloromethane, $n_{PVT}/n_{FeCl3} = 29$, $c_{PVT} = 0.0014$ g/ml, $c_{FeCl3} = 8.07 * 10^{-5}$ g/ml.

Already the pure $FeCl_3$ solution shows the characteristic UV/vis absorption band of the tetrachloroferrate anion at $\lambda = 363$ nm [15] which is attributed to the autodissociaton of $FeCl_3$ into $FeCl_2^+$ and $FeCl_4^-$ in organic solvents like acetonitrile [16]. The intensity of the $FeCl_4^-$ UV/vis absorption band increases rapidly when PVT or 2-methylthiophene as model compound is treated with $FeCl_3$. Thus, a part of the catalyst remains as the tetrachloroferrate complex (thiophene-H^+ or bisthiophen-H $^+$ $FeCl_4^-$), because $FeCl_3$ serves as both oxidation- and Lewis acid-catalyst. A new UV/vis absorption band at about $\lambda_{max} = 470$ nm appears immediately after mixing the components. The UV/vis absorption band at $\lambda_{max} = 620$ nm increases with reaction time, which is likely caused by CT-complex formation. We conclude that the UV/vis absorption band at $\lambda_{max} = 470$ nm is due to the bisthiophene complex which agrees with UV/vis data of similar complexes [13, 14]. The UV/vis spectra of 2-methylthiophene and 2-methoxythiophene after treating with $FeCl_3$ show comparable absorption bands at $\lambda_{max} = 434$, 518, 627 nm and 430, 600 nm, respectively.

The UV/vis spectrum of an $FeCl_3$ treated PVT after purification shows absorption bands at $\lambda_{max} = 303$ nm and 350 nm indicating the occurrence of bisthiophene units.

ESR experiments have been performed in order to proof the presence of persistent radical cations. However, even traces of radicals could not be detected. Therefore we suggest that radical cations of the alkylthiophene units originate as intermediate (scheme 1) but are not stable enough to be detected by ESR [17].

Table 1 Mass balance results of PVT/silica composite particles when treated with $FeCl_3$ and $FeCl_3$/PVT mixture, respectively. T = 298 K, Solvent: DCM/acetonitrile.

g PVT (composite)	(weight % C)	g PVT (soluble)	PVT/$FeCl_3$	weight % C after $FeCl_3$ treatment
0.007	5.67	-	1.84	4.84
0.066	12.80	0.068	0.25	11.30
0.050	1.30	0.050	0.74	14.50
0.050	13.30	0.050	0.37	14.50
0.050	12.20	0.050	0.25	15.20
0.107	17.45	0.107	0.17	23.38

Hence, the formation of bisthiophene sigma-complexes occurs very fast. As a consequence, the work up procedure requires the neutralisation of this sigma-complex by a weak base. PVT/silica particles show the same UV/vis absorption bands when treated with a $FeCl_3$ solution. Coloured PVT/silica hybrid particles are obtained by this procedure. Results for the post cross linking of PVT on silica and post-grafting of PVT on silica with soluble PVT induced by $FeCl_3$ are given in Table 1.

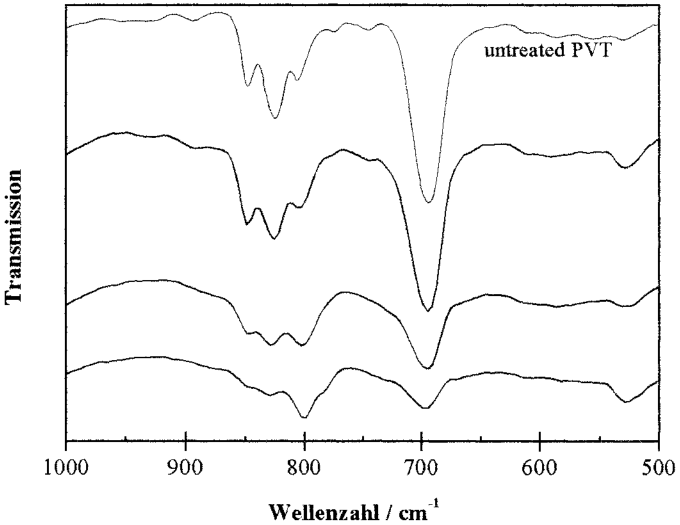


Figure 4 IR spectra of PVT and $FeCl_3$-treated PVT at room temperature after reaction with $FeCl_3$ in dependence on the ratio of n_{PVT}/n_{FeCl3}, from top to buttom: n_{PVT}/n_{FeCl3} = 1/0, 1/1, 1/2, 1/4, spectra were taken in diffuse reflection, the samples were diluted with KBr (m_{PVT}/m_{KBr} = 0.01/1)

Because $FeCl_3$ acts both as Lewis-acid and cross linking reagent, acidically induced degradation reaction are observed when PVT/silica particles are used with a low content of immobilized PVT. The post-grafting reaction of PVT onto PVT/silica particles with $FeCl_3$ as catalyst is less effective as indicated by the only few increase of the carbon content of the PVT/silica particles. However, the procedure is suitable to fix PVT chains irreversibly on silica particles because the former linking based on Si-O-C bonds [4] is hydrolytically unstable. Structure investigations of the PVT/silica hybrid particles and of the soluble fractions have been carried out with IR spectroscopy and different NMR techniques. By means of IR spectroscopy it is possible to distinguish between monosubstituted and disubstituted thiophene rings in the fingerprint region [5]. Characteristic vibration bands at 850, 825, and 690 cm^{-1} (monosubstituted thiophene) and a small band at 800 cm^{-1} (disubstituted thiophene) are already present in the IR spectrum of the untreated polymer (see figure 4) which indicates the complex structure of cationically produced PVT [3, 4].

The IR spectra of the polymer after reaction with $FeCl_3$ (see Figure 4) clearly show an increase of the band at 800 cm^{-1} with reaction time indicating coupling reactions in the 5 position of monosubstituted thiophene rings.

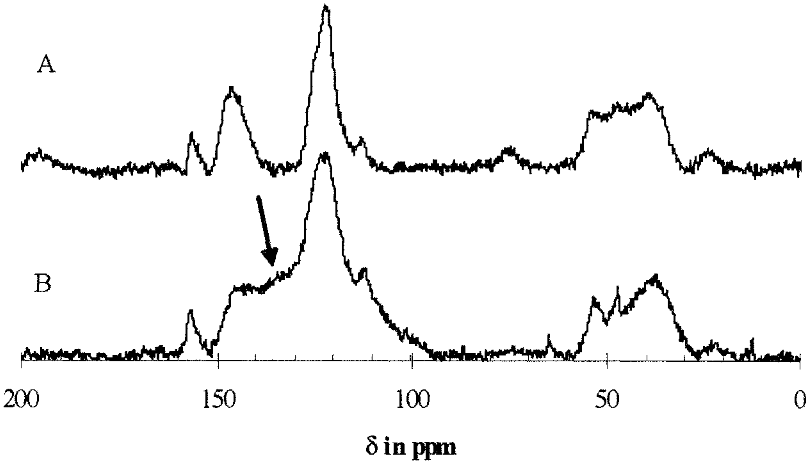


Figure 5 Solid state $\{^1H\}^{13}C$ CP MAS NMR spectra of: A: a PVT/silica composite at room temperature, rotational frequency: 7.5 kHz, number of scans: 4031 and B: a $FeCl_3$-treated PVT/silica composite at room temperature, rotational frequency: 11 kHz, number of scans: 7575, $n_{PVT}/n_{FeCl3} = 1/6$, the →marked Signal is at 135 ppm

The ^1H spectrum of the soluble polymer only shows little changes after the PVT has been treated with $FeCl_3$ indicating a low conversion (< 5 %) which agrees with the GPC results. The ^1H NMR spectra are poorly resolved, all signals are very broad. This is surely due to the poor solubility of the polymers after treatment with $FeCl_3$. However, it was impossible to take ^{13}C NMR of the soluble fractions. Thus, the PVT/silica hybrid particles were investigated by means of solid state ^{13}C NMR spectroscopy. The solid state $\{^1H\}^{13}C$ CP MAS NMR spectrum of a $FeCl_3$ treated PVT/silica composite is shown in Fig 5.

In the ^{13}C NMR spectrum of the $FeCl_3$ treated PVT/silica hybrid, compared to that of the former PVT/silica hybrid, a new signal is detected at approximately δ = 135 ppm (indicated in figure 5B). This signal indicates 2,2′-linked bithiophene moieties according to the ^{13}C NMR spectrum of 2,2′-bithiophene [18]. The other signals at δ = 125, 146 ppm and 30 – 50 ppm relate well to the expected structure.

Conclusion

The results have shown that the thiophene ring of PVT chains can be used as cross linking group when $FeCl_3$ is used as the catalyst. Because the linking of two thiophene rings produces HCl, sigma complexes are really formed which requires an additional stoichiometric equivalent of $FeCl_3$ to achieve high conversion, because the reaction of $FeCl_3$ with a chloride ion source like HCl takes place quantitatively [19].

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References

1. Trumbo DL, Suzuki T, Harwood HJ (1981) Polym Bull 4:677
2. Randazzo M, Toppare L, Fernandez JE (1994) Macromolecules 27:5102
3. Höhne S, Spange S, Schrepp W (2001) Polym Bull 47:31
4. Höhne S, Seifert A, Friedrich M, Holze R, Spange S (2004) Macromol Chem Phys accepted
5. Marani DA, Entezami AA (1994) Iran Polym Journal 3:2
6. Smie A, Synowczyk A, Heinze J, Alle R, Tschunky P, Götz G, Bäuerle PJ (1998) Electroanal Chem 452:87
7. Nalwa HS (1997) Handbook of organic conductive molecules and polymers. Wiley & Sons, Chichester New York Weinheim Brisbane Singapore Toronto
8. Sato M, Hiroi M (1994) Chem Lett:745
9. Andersson MR, Mammo W, Olinga T, Svensson M, Theander M, Inganäs O (1999) Synth Met 101:11
10. Matsumoto A., Kitajima T, Tsutsumi K (1999) Langmuir 15:7626
11. Choi JR, Kim Y, Yoon M (2001) Bull Korean Chem Soc 22:1045
12. Li G, Bhosale S, Wang T, Zhang Y, Fuhrhop JH (2003) Angew Chem 115:3948, Int Ed 42:3818
13. Feng Q, Luo S, Olmstead M, Rauchfuss TB, Stafford PR (1997) Chem Mat 9:641 and references therein
14. Geobaldo F, Palomino GT, Bordiga S., Zecchina A, Areán CO (1999) Phys Chem Chem Phys 1:561
15. Swanson TB, Larie VW (1965) J Phys Chem 69:244
16. Gao Y, Guery J, Jacoboni C (1993) Acta Cryst C49:147
17. Aleman C, Brillas E, Davies AG., Fajari L, Giro D, Julia L, Perez JJ, Rius J (1993)J Org Chem 58(11):3091
18. SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/(acces date)
19. Gutmann V, Hampel W (1961) Monatsh Chem 92:1048