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The electrochemical detection of Ru(II) in a methyl methacrylate solution

Karolien De Wael [*,1], Annemie Adriaens, Eduard Temmerman

Ghent University, Department of Analytical Chemistry, Krijgslaan 281 S12, B-9000 Ghent, Belgium

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Abstract

This article describes the voltammetric behaviour of $RuCl_2(PPh_3)_3$ in a methyl methacrylate (MMA) solution. Acquiring this type of information is only possible when the ohmic resistance can be kept sufficiently low. Therefore, the conductivity study of pure methyl methacrylate and a tetrabutylammonium tetrafluoroborate ($TBABF_4$) methyl methacrylate solution has been described as well. Impedance measurements show an increase in conductivity by adding $TBABF_4$, while a conductometric curve illustrates the presence of ion pairs, triple ions and quadrupoles depending on the $TBABF_4$ concentration. The conductivity of a 0.1 mol L^{-1} $TBABF_4$–MMA solution (formation of charged triple ions) was high enough to perform electrochemical experiments and a calibration curve could be obtained. The ability of obtaining relevant electrochemical data in low conducting media opens up new perspectives, especially for electroanalytical purposes used to monitor polymer reactions, more specific atom transfer radical polymerization (ATRP) reactions. This method employs a redox process with transition metal complexes in which a halogen ion is transferred reversibly between the transition metal and the polymer chain end. The dynamic equilibrium can be monitored by measuring the ruthenium concentration.

Keywords: Voltammetry; Non-aqueous solution; Ruthenium detection; Methylmetacrylate; Tetrabutylammonium tetrafluoroborate

1. Introduction

The Ru(III)/Ru(II) redox system is commonly used to prepare well-defined polymers, which are characterized by a reduced polydispersity, terminal functionalities and a better controlled molecular mass. One of the most successful methods to make well-defined polymers is through atom transfer radical polymerization (ATRP) [1–8]. This method employs a redox process with transition metal complexes in which a halogen ion is transferred reversibly between the transition metal and the polymer chain end.

Complexes with Ru(II) as the central metal ion are commonly used as catalysts in this kind of polymerization reactions. The metal complexes must have the capability of inter-converting between oxidation states differing by one unit. In the case of ruthenium, Ru(III), the deactivator of the process can be formed from Ru(II). Several monomers including methyl methacrylate (MMA) can be polymerized in this way, as is illustrated in Scheme 1. The transition metal complex L/M^n undergoes a one-electron oxidation into a higher oxidation state (L/M^{n+1}), via abstraction of the halogen X from the dormant species. The dynamic equilibrium of this redox system is responsible for the well-defined behaviour of this kind of polymerizations. The equilibrium can be monitored by measuring the ruthenium concentration.

This paper describes the first results concerning the voltammetric determination of Ru(II) in MMA. The electrochemical determination of ruthenium concentrations in solvents of low permittivity has, to the authors' knowledge, never been described before. Organic solvents can be important in the field of electrochemistry because very large potential windows can be achieved [9–11].

Electrochemical measurements are very useful to determine concentrations of electroactive species in solution.

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[*] Corresponding author. Tel.: +32 9 264 48 20; fax: +32 9 264 49 60.
E-mail address: Karolien.DeWael@UGent.be (K. De Wael).

[1] Postdoctoral Fellow of the Research Foundation – Flanders (FWO – Vlaanderen).

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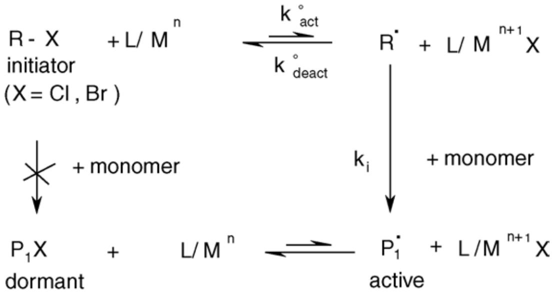

Scheme 1. Atom transfer radical polymerization reactions.

The solvent, studied in this article, is the monomer methyl methacrylate. One of its most remarkable characteristics is the low dielectric constant ($\varepsilon = 2.9$ at 298.0 K) compared to that of water ($\varepsilon = 78$ at 298.0 K). A solvent with such a low dielectric constant corresponds to a highly resistive medium, in which voltammetric measurements are not evident. Sufficiently conducting solutions can be obtained by adding tetra-alkyl ammonium salts [12]. However, at very low salt concentrations ion association prevails because of the low dielectric constant ($\varepsilon = 2$–4). Analysis of conductivity data in solvents of low permittivity was first carried out by Fuoss and Krauss [13,14]. To our knowledge, voltammetric measurements in methyl methacrylate have not been described before. In this work the detection of ruthenium(II) in methyl methacrylate is presented. An investigation concerning the conductivity of tetrabutylammonium tetrafluoroborate ($TBABF_4$) in MMA was necessary and is described in this article.

2. Experimental

Tetrabutylammonium tetrafluoroborate, $RuCl_2(PPh_3)_3$, methyl methacrylate and acetonitrile were obtained from FLUKA (Belgium). Degassing of the solutions was obtained with nitrogen type 5.0 from Air Liquide.

The working electrode was a platinum disc with a diameter of 1 mm (Goodfellow, UK). Prior to each electrochemical experiment the electrode was pre-treated by scouring on SiC paper (Buehler) for 15 s to obtain a fresh surface followed by polishing the surface on a polishing cloth covered with alumina (Buehler) of 1, 0.3 and 0.05 μm particle size for, respectively, 5, 10 and 20 min. To remove any adherent Al_2O_3 particles the electrode surface was rinsed thoroughly with the used solvent and cleaned in an ultrasonic bath (Branson 3210) for 2 min.

A home prepared $Ag|AgNO_3|CH_3CN$ reference electrode (RE) was used for the experiments in methyl methacrylate and a double junction containing $TBABF_4$ in MMA was used in order to avoid CH_3CN entering the electrochemical cell. A platinum net (Goodfellow, UK) acted as counter electrode. For the electrochemical impedance spectroscopy (EIS) experiments a conductivity cell of Tacussel was used. The cell constant (K_{cell}) is $57.3\ m^{-1}$.

A PGSTAT20 potentiostat (ECO Chemie, NL), controlled by GPES 4.5 software package running on a Pentium II computer, was used to obtain the voltammetric data. The potentiostat was extended with a low current module to perform cyclic voltammetry in a highly resistive solvent and with a frequency response analyzer module to perform EIS (FRA 4.5).

3. Results and discussion

3.1. Conductivity measurements

In Fig. 1a, Bode (1a) and a Nyquist (1b) plot are shown, obtained by EIS using a standard conductivity cell ($K_{cell} = 57.3\ m^{-1}$), of a pure MMA solution in the absence of supporting electrolyte. The Bode plot (Fig. 1a) shows a capacitive behaviour at the highest frequencies because the phase angle is 90°. This effect can be explained by the appearance of air at the electrode surface, acting as a capacitor at high frequencies. This capacitor in parallel with a high resistance, characteristic for the solvent under study, gives rise to the capacitive behaviour at high frequencies. From the semi-circle in Fig. 1b and the wide range of frequencies where only resistive effects are observed (Fig. 1a, range where phase angle is near zero) it can be deduced that the electrical equivalent circuit consists of a resistance and capacitor in parallel. The resistance of the solution can be obtained from Fig. 1b through the diameter of the semi-circle or from Fig. 1a in the plateau of the log|Z| versus log f plot, if in the same region of frequencies no phase angle shift is observed. Because the semi-circle in Fig. 1b is not well-defined, the latter method

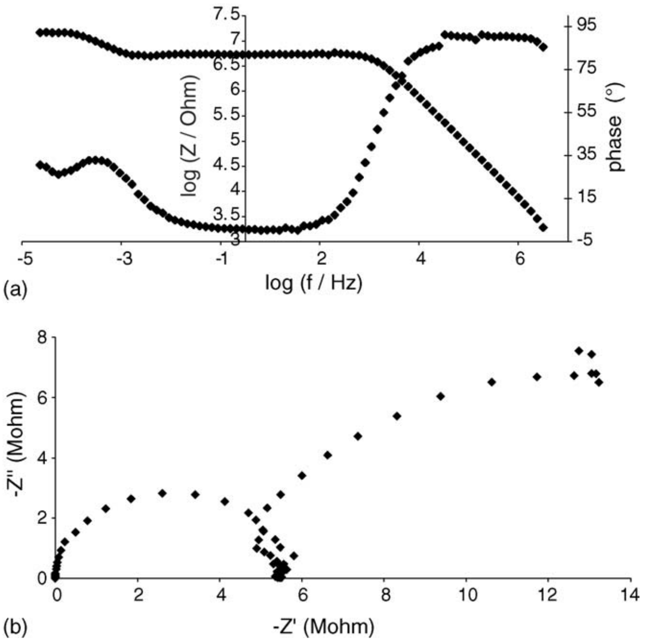

Fig. 1. (a) Bode and (b) Nyquist plots recorded in methyl methacrylate using a platinum conductivity cell with $K = 1$ at 298.0 K.

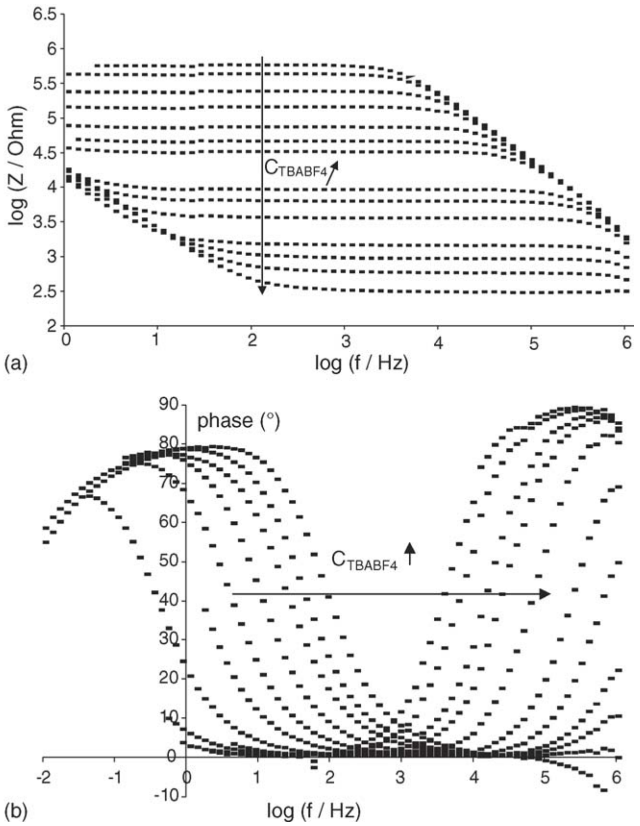

Fig. 2. Bode plots ((a) log *Z* vs. log *f* and (b) phase vs. log *f*) recorded in methyl methacrylate containing different $TBABF_4$ concentrations using a platinum conductivity cell at 298.0 K. The $TBABF_4$ concentrations are listed in Table 1.

was used to determine the resistance of the pure MMA solution. In that MMA solution a resistance of 5.9 MΩ was found.

One of the requirements to perform voltammetric experiments in a highly resistive solution is the presence of a supporting electrolyte. Tetrabutylammonium tetrafluoroborate is commonly used as electrolyte in organic solutions. The bode plots obtained in a MMA solution with different concentrations of $TBABF_4$ are shown in Fig. 2a and b, which show the behaviour of, respectively, $\log|Z|$ and the phase angle versus $\log f$. As expected the resistance drops by adding $TBABF_4$.

The Bode plots show a resistive behaviour in the complete region of frequencies. Only at the lowest frequencies for the highest $TBABF_4$ concentrations signs of capacitive behaviour became visible. This can be explained by the fact that only at very low frequencies the double layer can be built up. This is evident because MMA is less polar than water, which implies that water molecules are not able to form a monolayer at the surface to build up the double layer. In the case of an organic solvent, only the ions of the electrolyte are capable of doing so. It is also known that dissociation of the electrolyte is small in organic solvents with low permittivity. Therefore, the probability that an ion is released is very small. The measured values obtained for the resistance (Fig. 2a), conductivity κ and molar conductivity Λ are summarized in Table 1. As expected the conductivity decreases by adding more supporting electrolyte. In contrast, the molar conductivity shows a completely different behaviour. Fig. 3 represents the conductometric curve in which the molar conductivity is plotted against the square root of the electrolyte concentration. Four distinct regions [12] can be observed in this figure. Starting at zero concentration, there is a steep decrease of the molar conductivity, proportional with the square root of the concentration in accordance with Onsager's equation [15], characteristic for solutions with a small value of their dielectric constant. This decrease represents the formation of ion pairs. Another characteristic is the occurrence of a minimum in the curve. This is a result of the equilibrium between triple ions and ion pairs. The third part in the curve is the increase in the region between 8.5×10^{-3} and $0.2\,\mathrm{mol\,L^{-1}}$ $TBABF_4$. This increase can be explained by the formation of charged triple ions. The last part, starting at a concentration of $0.2\,\mathrm{mol\,L^{-1}}$ $TBABF_4$, represents a slow decrease of the molar conductivity due to viscosity effects and/or formation of quadrupoles.

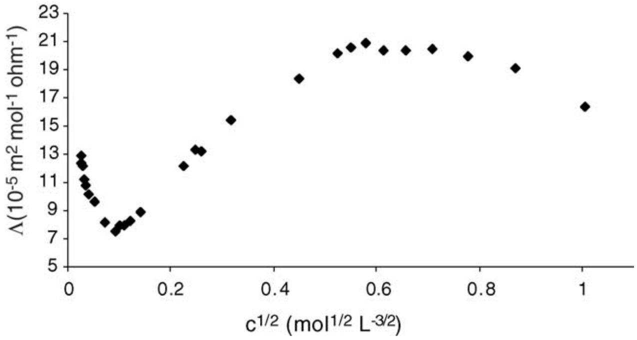

Fig. 3. Conductometric curve for all $TBABF_4$ concentrations listed in Table 1.

These conductivity measurements were carried out to obtain an estimate of the conductivity of the $TBABF_4$ solution in which the voltammetric experiments will be performed. In the presence of $0.1\,\mathrm{mol\,L^{-1}}$ $TBABF_4$, the measured resistance of the MMA solution drops to circa 3700 Ω instead of 5.9 MΩ for pure MMA. All voltammetric experiments described in this article were performed in a $0.1\,\mathrm{mol\,L^{-1}}$ $TBABF_4$ MMA solution, characterized by the presence of charged triple ions.

3.2. *Electrochemical determination of ruthenium(II) in MMA*

Experiments were performed to study the voltammetric behaviour of MMA containing $TBABF_4$ at a platinum disc electrode. The formation of radical species by oxidation and reduction of MMA limits the usable potential window. Since these reactions disturb the voltammetric detection of $RuCl_2(PPh_3)_3$, the potential window used in this study reaches from −1 to 0.7 V versus RE. In this potential range where $RuCl_2(PPh_3)_3$ is electroactive, additional reactions of the solvent or electrolyte were not observed.

Table 1
Resistance R_Ω, conductivity κ and molar conductivity Λ measured, respectively, calculated for different TBABF$_4$ concentrations

C_{TBABF4} (mol L^{-1})	$R_{\Omega,\mathrm{measured}}$ (Ω)	κ (10^{-3} Ω^{-1} m^{-1})[a]	Λ (10^{-5} m^2 Ω^{-1} mol^{-1})
6.377E−04	696626.5	8.225E−05	12.90
7.289E−04	638263.5	8.977E−05	12.32
8.503E−04	553350.1	0.0001036	12.18
1.020E−03	501187.2	0.0001143	11.20
1.276E−03	414954	0.0001381	10.83
1.701E−03	331131.1	0.0001730	10.17
2.551E−03	232273.7	0.0002467	9.670
5.102E−03	138356.6	0.0004141	8.117
8.503E−03	88920.1	0.0006444	7.578
9.921E−03	72276.9	0.0007928	7.991
1.190E−02	60673.6	0.0009444	7.936
1.488E−02	46558.6	0.001231	8.271
1.984E−02	32508.7	0.001763	8.884
5.056E−02	9332.54	0.006140	12.14
6.068E−02	7079.5	0.008094	13.34
6.681E−02	6516.3	0.008793	13.16
0.1002	3698.3	0.01549	15.46
0.2023	1541.7	0.03717	18.38
0.2747	1032.8	0.05548	20.20
0.3022	920.4	0.06225	20.60
0.3357	816.6	0.07017	20.90
0.3777	743.0	0.07712	20.42
0.4317	653.1	0.08773	20.32
0.5036	555.9	0.1031	20.47
0.6043	475.3	0.12055	19.95
0.7554	396.3	0.1446	19.14
1.007	346.7	0.1653	16.41

[a] κ, $K_{\mathrm{cell}}/R_{\Omega,\mathrm{measured}}$ with $K_{\mathrm{cell}} = 57.3\,\mathrm{m}^{-1}$.

In Fig. 4, current potential curves are shown obtained by performing cyclic voltammetry at a platinum disc electrode in MMA solutions containing 0.1 mol L^{-1} TBABF$_4$ and different concentrations of RuCl$_2$(PPh$_3$)$_3$. The potential was swept from −1 to 0.7 V versus RE (forward sweep direction) and back to −1 V versus RE (backward sweep direction) with a scan rate of 50 mV s^{-1}. In the range of 0–0.7 V, two oxidation waves at 0.31 (I$_a$) and 0.46 (II$_a$) V versus RE and two reduction processes at 0.2 (I$_c$) and 0.36 (II$_c$) V versus RE are observed. Based on several literature data [16–20], these reactions can be attributed to redox processes of the ruthenium metal ion. The following reactions are suggested:

$$\mathrm{Ru(II)Cl_2(PPh_3)_3} \rightarrow [\mathrm{Ru(III)Cl_2(PPh_3)_3}]^{+} + \mathrm{e}^{-} \quad \text{(I)}$$

$$[\mathrm{Ru(III)Cl_2(PPh_3)_3}]^{+} \rightarrow [\mathrm{Ru(IV)Cl_2(PPh_3)_3}]^{2+} + \mathrm{e}^{-} \quad \text{(II)}$$

Both redox couples behave quasi-reversibly. In the potential range from −1 to 0 V four poorly defined redox couples are observed and indicated as III to VI in Fig. 4. The oxidation reactions occur at potentials of −0.76, −0.55, −0.33

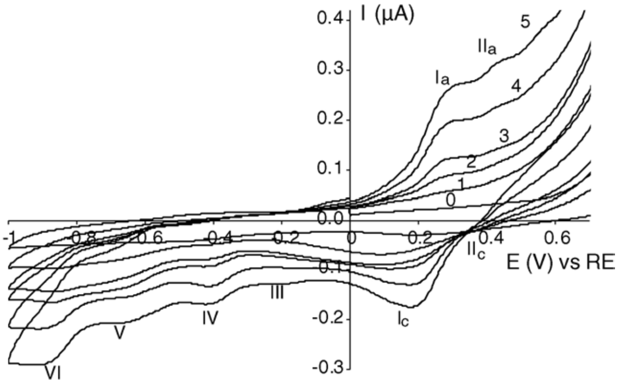

Fig. 4. Cyclic voltammetric curves recorded at a platinum disc electrode in a methyl methacrylate solution containing 0.1 mol L^{-1} TBABF$_4$ and different concentrations of Ru(II)Cl$_2$(PPh$_3$)$_3$. Concentrations are: (0) 0, (1) 1.48×10^{-4}, (2) 2.91×10^{-4}, (3) 4.28×10^{-4}, (4) 7.49×10^{-4} and (5) 0.00104 mol L^{-1}; T = 298.0 K, v = 50 mV s^{-1}.

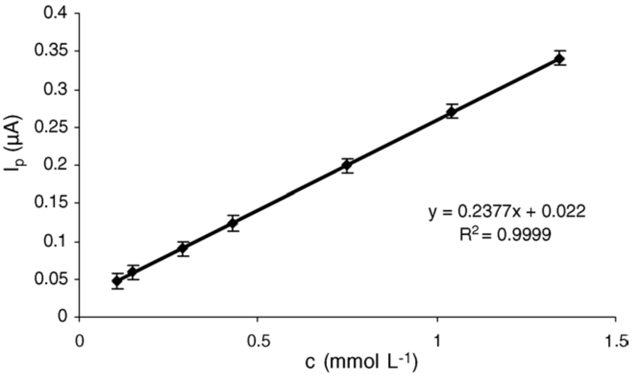

Fig. 5. Calibration plot for the detection of Ru(II) concentrations in 0.1 mol L^{-1} TBABF$_4$ methyl methacrylate solution based on the peak current at 0.31 V vs. RE, obtained from cyclic voltammetric curves shown in Fig. 4; T = 298.0 K, v = 50 mV s^{-1}.

and −0.04 V versus RE. The reduction processes are located at −0.92, −0.66, −0.41 and −0.2 V versus RE. These quasi-reversible processes can be explained as reactions of the triphenylphosphine ligand [21]. The authors suggest that stable radicals are formed which can be detected electrochemically in methyl methacrylate.

The peak current of oxidation process I_a (Ru(III)/Ru(II)) can be used for electroanalytical purposes. Fig. 5 shows a linear relationship between peak current at 0.31 V versus RE and the ruthenium(II) concentration. This calibration curve can be used for the electrochemical detection of ruthenium(II) in MMA solution. A stable background current was found, which resulted in a detection limit of $7.5 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ for Ru(II). The ability of measuring ruthenium on line in low conducting media, such as MMA, opens up new perspectives, especially for electroanalytical purposes in the monitoring of polymer reactions.

4. Conclusion

It can be concluded that it is possible to detect $\mathrm{Ru(II)Cl_2(PPh_3)_3}$ in methyl methacrylate with a detection limit of $7.5 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ when $0.1\,\mathrm{mol\,L^{-1}}$ $\mathrm{TBABF_4}$ is added as a supporting electrolyte. A conductometric study has shown that charged triple ions are formed when $0.1\,\mathrm{mol\,L^{-1}}$ $\mathrm{TBABF_4}$ is added to methyl methacrylate. This result opens up new perspectives for further studies such as the possibility for continuous and on line detection of Ru(II) during ATRP polymerization reactions.

References

[1] K. Matyjaszewski, T.E. Patten, J. Xia, J. Am. Chem. Soc. 119 (1997) 674.
[2] K. Matyjaszewski, A. Kajiwara, Macromolecules 31 (1998) 548.
[3] A. Kajiwara, K. Matyjaszewski, Macromolecules 31 (1998) 5695.
[4] J. Wang, T. Grimaud, K. Matyjaszewski, Macromolecules 30 (1998) 6507.
[5] A. Kajiwara, K. Matyjaszewski, Polym. J. 31 (1999) 70.
[6] G. Odian, Principles of Polymerization, third ed., John Wiley, New York, 1991.
[7] C.H. Bamford, Radical Polymerization in Encyclopedia of Polymer Science and Engineering, vol. 13, John Wiley, New York, 1990.
[8] G. Moad, D.H. Solomon, The Chemistry of Free Radical Polymerization, Pergamon, Oxford, 1995.
[9] K. De Wael, P. Westbroek, J. De Strycker, E. Gasana, E. Temmerman, Microchem. J. 77 (2004) 85.
[10] M.D. Geraldo, M.I. Montenegro, D. Pletcher, Talanta 42 (1995) 1725.
[11] M.D. Geraldo, J. Electroanal. Chem. 439 (1996) 41.
[12] A.P. Abbott, D.J. Schiffrin, J. Chem. Soc., Faraday Trans. 86 (1990) 1453.
[13] R.M. Fuoss, C.A. Krauss, J. Am. Chem. Soc. 55 (1933) 21.
[14] R.M. Fuoss, C.A. Krauss, J. Am. Chem. Soc. 79 (1957) 3304.
[15] R.A. Robinson, R.H. Stokes, Electrolyte Solutions, Butterworths, London, 1959.
[16] U. Kölle, R. Görissen, A. Hörnig, Inorg. Chim. Acta 281 (1994) 33.
[17] E.T. Bell-Loncella, C.A. Bessel, Inorg. Chim. Acta 303 (2000) 199.
[18] W.-H. Chiu, S.-M. Peng, C.-M. Che, Inorg. Chem. 35 (1996) 3369.
[19] T. Ando, M. Kamigaito, M. Sawamoto, Macromolecules 33 (2000) 5825.
[20] T. Ando, M. Kamigaito, M. Sawamoto, Macromolecules 33 (2000) 6732.
[21] V.T. Kasumov, Spectrochim. Acta Part A 60 (2004) 915.