

## Mössbauer spectroscopic study of sulphonated poly(ether-urethane) linear ionomer doped with iron species

A. A. Kamnev · O. P. Grigoryeva ·  
E. Kuzmann · A. Vértes

Published online: 25 March 2009  
© Springer Science + Business Media B.V. 2009

**Abstract** Thermoplastic linear poly(ether-urethane) sulphonated ionomer (PEUSI), doped with natural  $\text{Fe}^{2+}$ , was studied by Mössbauer spectroscopy at  $T = 78$  and 290 K in order to monitor the chemical state of Fe species. The  $\text{Fe}^{2+}$  added was found to get only partly oxidised in the course of preparation of a dry polymer film from aqueous suspension. The oxidised part gave a ferric quadrupole doublet (over half of total Fe added) and, at  $T = 78$  K only, a small portion of magnetically split sextet (ca. 3%), whereas  $\text{Fe}^{\text{II}}$  (total over 40%) stabilised in two different forms (represented by quadrupole doublets) corresponding to two types of iron(II) microenvironments, where  $\text{Fe}^{\text{II}}$  could be coordinated involving  $-\text{CONH}-$  and  $-\text{NHNH}-$  moieties and sulphonate groups in PEUSI. The results obtained show that  $\text{Fe}^{2+}$ -doping of PEUSI-based materials may be used for probing their structural characteristics by Mössbauer spectroscopy.

**Keywords** Iron(II)-doped sulfonated poly(ether-urethane) · Thermoplastic linear ionomer ·  $^{57}\text{Fe}$  Mössbauer spectroscopy

---

A. A. Kamnev (✉)  
Laboratory of Biochemistry,  
Institute of Biochemistry and Physiology of Plants and Microorganisms,  
Russian Academy of Sciences, Saratov 410049, Russia  
e-mail: aakamnev@ibppm.sgu.ru

O. P. Grigoryeva  
Department of Heterochain Polymers and Interpenetrating Polymer Networks,  
Institute of Macromolecular Chemistry, National Academy of Sciences, Kyiv 02160, Ukraine

E. Kuzmann · A. Vértes  
Laboratory of Nuclear Chemistry, Institute of Chemistry,  
Eötvös Loránd University, Budapest 1117, Hungary

E. Kuzmann · A. Vértes  
Chemical Research Center, Hungarian Academy of Sciences, Budapest, Hungary

## 1 Introduction

A diversity of polymeric materials and blends based on poly(ether-urethane), along with their wide-range industrial applications, have also been used in medicine as synthetic biomaterials for blood contact owing to a favourable combination of their characteristics, in particular, their biocompatibility and material strength [1–5]. In order to decrease protein adsorption which, in its turn, is related to subsequent bacterial adhesion [6], it is important to enhance the hydrophilicity of polymeric biomaterials. One of the most efficient means for that is incorporating various covalently bound substituents with polar (ionic) functional groups in the polymer chains [7–9].

Incorporation of chemically bound (coordinated) metal ions can also contribute to increasing the polymer hydrophilicity and thus retarding protein adhesion [10, 11]. In this case, however, the metal has to be strongly bound to the polymer functional groups. In the case of iron, its chemical state within the polymer matrix can conveniently be probed using transmission  $^{57}\text{Fe}$  Mössbauer spectroscopy.

In this work, thermoplastic linear poly(ether-urethane) sulphonated ionomer (PEUSI) [12, 13], doped with  $\text{Fe}^{2+}$  (as  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  added to aqueous emulsion of the polymer), was studied in the form of dry films by Mössbauer spectroscopy to quantitatively monitor the chemical nature of the resulting Fe species.

## 2 Materials and methods

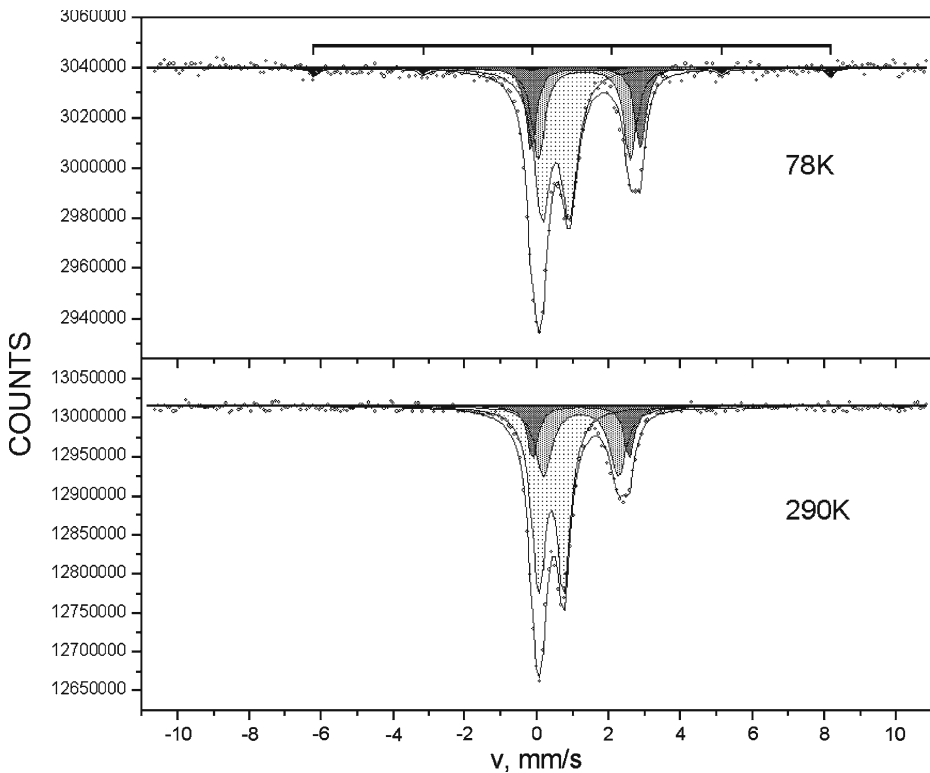
### 2.1 Preparation of the polymer sample

Thermoplastic linear poly(ether-urethane) sulphonated ionomer (PEUSI; sulphonation degree ca. 3%), was synthesized as described earlier (see, e.g. [12, 13]). In Fig. 1, the structure of the title polymer is schematically shown. The polymer was prepared in the form of a dry film ( $0.7 \pm 0.1$  mm thick) from aqueous emulsion stirred at  $45 \pm 5^\circ\text{C}$  for 1 h, spread onto an inert polytetrafluoroethylene (PTFE) support, dried in air at ambient temperature and then at  $45 \pm 5^\circ\text{C}$  to a constant weight. The polymer film had been doped with natural, non-enriched  $\text{Fe}^{2+}$  (as  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  added to aqueous emulsion of the polymer before stirring and drying) at the equivalent of  $0.1 \text{ mg} \cdot \text{cm}^{-2}$  of  $^{57}\text{Fe}$  (abundance ca. 2.2% in natural iron) to ensure the applicability of Mössbauer spectroscopic measurements up to a good statistics within a reasonable time.

### 2.2 Mössbauer spectroscopic measurements

Mössbauer spectra of the dry  $\text{Fe}^{2+}$ -doped polymer film were measured at  $T = 78$  K (in a cryostat) and at 290 K using a conventional constant-acceleration Mössbauer spectrometer with a  $^{57}\text{Co}(\text{Rh})$  source kept at room temperature. Statistical treatment of the spectra was performed using the MOSSWINN 3.0 program [14], with the assumption of Lorentzian line shapes. The calculated parameters were the isomer shift ( $\delta$ , in millimeters per second), quadrupole splitting ( $\Delta$ , in millimeters per second), experimentally observed line width (full width at half maximum,  $\Gamma_{\text{exp}}$ , in millimeters per second) and partial resonant absorption area ( $S_r$ , in percent) for each spectral component. The latter ( $S_r$ ) is used to represent the relative content of





**Fig. 2** Mössbauer spectra of  $\text{Fe}^{2+}$ -doped partly sulphonated poly(ether-urethane) dry films measured at  $T = 78$  and  $290$  K, as indicated beside the spectra. The positions of the magnetically split sextet lines (observed for  $T = 78$  K only; weak *black* peaks) are shown above the relevant spectrum. For both the spectra, doublets 1 and 2 (see also Table 1), representing two different  $\text{Fe}^{\text{II}}$  forms, are depicted as more and less *dark shaded areas*, respectively; *lightly shaded* doublet 3 (see Table 1) represents the contribution of an  $\text{Fe}^{\text{III}}$  form

in an early work [15] for the system containing 98% poly(vinylpyrrolidone) + 1%  $\text{H}_2\text{O}$  + 1%  $\text{FeCl}_2$  prepared from diluted aqueous solutions of the iron(II)-containing polymer by drying under vacuum (at  $70^\circ\text{C}$  to  $80^\circ\text{C}$ ). Note that under the conditions of air-drying applied in this work, the possibilities for iron(II) oxidation were more evident, as compared with those in [15].

Nevertheless, it is of special interest that yet a substantial part of the total iron(II) added, over 40%, was evidently found to have got firmly chemically bound to functional groups of the polymer matrix and stabilised in the  $\text{Fe}^{\text{II}}$  form represented by two different microenvironments. Note that for ferrous sulphate heptahydrate used in this work as an additive, the Mössbauer parameters at room temperature were reported as  $\delta = 1.31$  mm/s vs.  $\alpha\text{-Fe}$ ;  $\Delta = 3.20$  mm/s [16], which is far from those given in Table 1 for either doublet 1 or doublet 2. It may be reasonably assumed that the less intensive doublet 1 refers to the iron(II) form coordinated to sulphonate groups, giving a somewhat larger  $\Delta$  and corresponding to a relatively small sulphonation degree of the polymer, while the other iron(II) form represented by doublet 2 is coordinated by  $\text{CO-NH}$  and  $\text{NH-NH}$  moieties (see Fig. 1), with

**Table 1** Mössbauer parameters for Fe<sup>2+</sup>-doped partly sulphonated poly(ether-urethane) dry films measured at different temperatures (see also Fig. 2)

<i>T</i> , K	Multiplet	Fe oxidation state	Magnetic field, T	$\delta$ , mm/s	$\Delta$ , mm/s	$\Gamma_{\text{exp}}$ , mm/s	$S_r$ , %
78	Sextet	+3	44.6 (2)	0.98 (3)	–	0.3 (1)	3.2
	Doublet 1	+2	–	1.35 (1)	3.03 (3)	0.35 (3)	19.5
	Doublet 2	+2	–	1.31 (1)	2.56 (3)	0.42 (3)	26.4
	Doublet 3	+3	–	0.52 (1)	0.76 (1)	0.54 (1)	50.9
290	Doublet 1	+2	–	1.22 (1)	2.68 (3)	0.34 (3)	13.4
	Doublet 2	+2	–	1.22 (1)	2.08 (3)	0.55 (2)	27.9
	Doublet 3	+3	–	0.40 (1)	0.71 (1)	0.47 (1)	58.7

Errors (in the last digits) are indicated in parentheses

$\delta$  isomer shift (vs.  $\alpha$ -Fe at room temperature),  $\Delta$  quadrupole splitting,  $\Gamma_{\text{exp}}$  experimentally observed line width at half maximum,  $S_r$  the relative area of a relevant spectral component (relative error  $\pm 5\%$ ) representing the relative content of the related form, assuming a common recoilless fraction for all forms in a sample contributing to the spectrum

possible water molecules as additional ligands in both cases. The somewhat higher linewidth for doublet 2, as compared with that for doublet 1 (see Table 1), may well be a consequence of some non-uniformity of its microenvironments.

Thus, the PEUSI polymer matrix-stabilised ferrous species coordinated to the relevant polymer moieties may be used for probing the structural characteristics of the related polymeric materials, as well as their changes induced by external factors and additives, by Mössbauer spectroscopy. Such studies, involving Fe-doped complex PEUSI-based polymer materials, are underway and will be reported elsewhere.

## 4 Conclusions

Mössbauer study has shown that the Fe<sup>2+</sup>, added as a salt to the linear poly(ether-urethane) sulphonated ionomer (PEUSI), got only partly oxidised in the course of polymer film preparation and air-drying. The oxidised part gave a quadrupole doublet of iron(III), comprising over half of the total iron, most probably representing finely disperse ferric (oxy)hydroxide phase, a small portion of which, visible at  $T = 78$  K only, transformed into a magnetic phase (ca. 3%). The other part of Fe<sup>II</sup> (over 40% of total Fe added) stabilised in two different forms (doublets 1 and 2), which could be ascribed to two types of iron(II) microenvironments, with Fe<sup>II</sup> coordinated by sulphonate groups and/or by the CONH and NHNH moieties of the polymer chains. Thus, Fe<sup>II</sup>-doping of PEUSI-based materials may be used for probing their structural characteristics by means of Mössbauer spectroscopy.

**Acknowledgements** This work was supported in part under the NATO “Security Through Science” Programme (Expert Visit Grant CBP.NR.NREV 981748, Collaborative Linkage Grant ESP.NR.NRCLG 982857), by the Hungarian Science Foundation (OTKA; Grants K62691, K68135), as well as under the Agreement on Scientific Cooperation between the Russian and Hungarian Academies of Sciences for 2005–2007 (Protocol, Thematic Plan, Item 37) and for 2008–2010 (Protocol, Thematic Plan, Item 45).

## References

1. Santerre, J.P., Brash, J.L.: Methods for the covalent attachment of potentially bioactive moieties to sulfonated polyurethanes. *Macromolecules* **24**, 5497–5503 (1991)
2. Lamba, N.M.K., Woodhouse, K.A., Cooper, S.L., Lelah, M.D.: Polyurethanes in Biomedical Applications, 277 pp. CRC, Boca Raton, FL (1997)
3. Wang, Y.-X., Robertson, J.L., Spillman, W.B., Claus, R.O.: Effects of the chemical structure and the surface properties of polymeric biomaterials on their biocompatibility. *Pharm. Res.* **21**, 1362–1373 (2004)
4. Tanzi, M.C.: Bioactive technologies for hemocompatibility. *Expert Rev. Med. Devices* **2**(4), 473–492 (2005)
5. Santerre, J.P., Woodhouse, K., Laroche, G., Labow, R.S.: Understanding the biodegradation of polyurethanes: from classical implants to tissue engineering materials. *Biomaterials* **26**(35), 7457–7470 (2005)
6. Jansen, B., Peters, G., Pulverer, G.: Mechanisms and clinical relevance of bacterial adhesion to polymers. *J. Biomater. Appl.* **2**(4), 520–543 (1987)
7. Bamford, C.H., Middleton, I.P.: Studies on functionalizing and grafting to poly(ether-urethanes). *Eur. Polym. J.* **19**(10–11), 1027–1035 (1983)
8. Graser, T.G., Cooper, S.L.: Properties and biological interactions of polyurethane anionomers: effect of sulfonate incorporation. *J. Biomed. Mater. Res.* **23**(3), 311–338 (1989)
9. Zdrachala, R.J.: Small caliber vascular grafts. Part II: polyurethanes revisited. *J. Biomater. Appl.* **11**(1), 37–61 (1996)
10. Acharya, V., Ratna Prabha, C., Murthy, C.N.: Synthesis and characterization of polyurethane-metal complexes for biomedical applications. *J. Polym. Mater.* **20**, 83–90 (2003)
11. Acharya, V., Ratna Prabha, C., Narayanamurthy, C.: Synthesis of metal incorporated low molecular weight polyurethanes from novel aromatic diols, their characterization and bactericidal properties. *Biomaterials* **25**, 4555–4562 (2004)
12. Slisenko, O., Lebedev, E., Pissis, P., Spanoudaki, A., Kontou, E., Grigoryeva, O.: Novel polymer blends based on poly(ether-urethane) ionomer and ion-containing styrene copolymer. *J. Therm. Anal. Calorim.* **84**(1), 15–19 (2006)
13. Grigoryeva, O., Slisenko, O., Bismarck, A., Sergeeva, L.: Effect of specific interactions on structure–property relationships of thermoplastic IPNs based on polyurethane and styrene-co-acrylic acid ionomers. *Macromol. Symp.* **254**, 233–239 (2007)
14. Klencsár, Z., Kuzmann, E., Vértes, A.: User-friendly software for Mössbauer spectrum analysis. *J. Radioanal. Nucl. Chem.* **210**, 105–118 (1996)
15. Vértes, A., Nagy, M.: Mössbauer study of the interaction of some polymers with  $\text{FeCl}_2$ . *Radiochem. Radioanal. Lett.* **9**(3), 221–224 (1972)
16. Vértes, A., Zsoldos, B.: A study on thermal decomposition of iron(II)-salt hydrates by Mössbauer spectroscopy. *Acta Chim. Acad. Sci. Hung.* **65**(3), 261–271 (1970)