Available online at www.sciencedirect.com
ScienceDirect
Journal of Photochemistry and Photobiology A: Chemistry 183 (2006) 106–110
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Ionic reactions in pulse irradiated poly(vinyl chloride) film—the effect of plasticizers

J. Mayer, M. Szadkowska-Nicze [*]

Institute of Applied Radiation Chemistry, Technical University, Wróblewskiego 15, 93-590 Łódź, Poland

Received 17 January 2006; received in revised form 23 February 2006; accepted 24 February 2006

Abstract

Poly(vinyl chloride), PVC + plasticizer (DEHP, TOTM) films were pulse irradiated using electron accelerator and the transient species generated in these matrices were analysed. The absorption spectra of plasticizers ions (anion and cation type) were identified in PVC system using as a model 2-propanol and sec-butyl chloride solutions of respective plasticizers. The mechanism of reactions is proposed and discussed.

Keywords: Poly(vinyl chloride); Pulse radiolysis; Plasticizers; Radical ions

1. Introduction

Commercial polymers contain different type of additives which allow to modify their properties. The poly(vinyl chloride), PVC, itself is a stiff and inflexible material. In order to change these properties, i.e. to make flexible and elastic product, PVC has to be plasticized. Plasticized PVC usually contains between 40 and 70 parts of plasticizer for every 100 parts of PVC. The plasticizers are mainly phthalic esters, of which bis(2-ethylhexyl)phthalate (DEHP) is the most common, commercial additive in PVC formulation for production of food packages and medical as well as pharmaceutical devices [1]. To ensure the absence of microorganisms in the above mentioned products the technique of sterilization by ionizing radiation has been applied as a international standard.

The effect of ionizing radiation on PVC has been extensively studied. It is generally assumed that the radiation induced degradation of PVC proceeds through the radical mechanism leading to the hydrogen chloride (HCl) production and polyene chains formation as the end products. The short review of the available data can be found in our recent paper [2]. We proposed novel mechanism of radiation induced decomposition of PVC where the contribution of ionic processes was underlined and proved [2]. Many authors have studied the effect of different plasticizers on gamma-irradiated PVC [3–17]. The main aim of those investigations was related to the influence of plasticizers on physical, chemical and biological properties of the system.

Nobody has been interested in the detailed mechanism of reactions contributed to the observed effects. According to the recent interpretation during irradiation of PVC plasticized films the degradation by chain scissions is mostly observed [17]. In other opinion the plasticizers: DEHP and epoxidised soybean oil are effective in stabilizing the radiolytic abstraction of HCl from PVC [13]. The improvement of radiation stability of plasticized PVC was found to be possible by application of the multicomponent, synergistic system [14] protected by patent [18].

The main aim of this study is to show the ionic reaction mechanism involved in the radiation induced transformations of PVC in the presence of typical plasticizers, i.e. DEHP and tris(2-ethylhexyl)trimelitate (TOTM). Taking into account the structure of plasticizer molecules, an important component of PVC composition, one can guess that such compounds may interfere into primary ionic steps of PVC radiolysis influencing the HCl yield, undesired final product of PVC degradation. Using pulse radiolysis technique we hope to present date concerning the reactivity of these additivies against electrons and positive ions produced in irradiated polymeric matrix.

2. Experimental details

2.1. Materials

Poly(vinyl chloride), for medical application, S-70 SM product of Anwil SA (Poland) was used as received. Tetrahydrofuran

---

[*] Corresponding author. Tel.: +48 42 631 3173; fax: +48 42 636 0246.
E-mail address: magdanis@mitr.p.lodz.pl (M. Szadkowska-Nicze).

1010-6030/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2006.02.030

(THF) HPLC grade, inhibitor free (Aldrich, product no. 27038-5) was used as a solvent for PVC film preparation; 2-propanol, spectroscopic grade (Merck) and sec-butyl chloride, G.C 99 + % (Aldrich) were used as received. All liquid solutions were deoxygenated by bubbling argon or nitrogen gas for ca. 30 min.

Two type of plasticizers, i.e. bis(2-ethylhexyl)phthalate, 99% (Aldrich, prod. 52515-4) and tris(2-ethylhexyl)trimelitate, 99% (Aldrich, prod. 53814-0) both manufactured by Eastman Chemical Comp., were used as received.

PVC + plasticizer films were cast from the THF solution. The solvent was removed from the sample by evaporation at room temperature and at the end in vacuum (ca. 10^{-4} mmHg) for at least 10 h.

2.2. Methods

The pulse radiolysis measurements were carried out using a linear electron accelerator ELU-6 (USSR made) which delivered 17 ns (dose ca. 50 Gy), 1 μs (dose ca. 200 Gy) and 4 μs (dose ca. 500 Gy) pulses. The home-made styrofoam-copper cryostate through which cold nitrogen was passed enabled experiments at temperatures down to 100 K. The Hamamatsu R-928 photomultiplier was used as a light detector. The signals were recorded on digitizing scopes either Philips PH 3320 or Tectronix TDS 540 and transferred via interface to IBM-PC computer for storage and analysis. More details concerning detection system and the accelerator can be found elsewhere [19].

3. Results and discussion

Fig. 1 shows UV–VIS absorption spectra of pulse irradiated, deareated PVC film containing DEHP (58.6% by weight) measured at ca. room temperature and ~100 K. In general, the absorption increasing towards shorter wavelengths were detected for PVC–DEHP samples in the temperature range under consideration. The weak maxima at 340 and 425 nm can be observed for samples at low temperature, i.e. ~100 K. The value of this transient absorption is DEHP concentration dependent (tested in the range 31.5–58.6%).

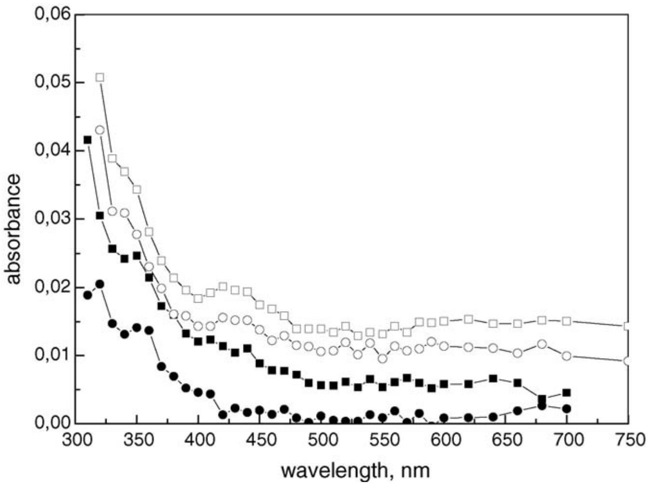

Fig. 1. Transient absorption spectra of pulse irradiated, deareated PVC film (1.0 mm thickness) containing 58.6% DEHP measured at ca.100 K (□, ○) and 295 K (■, ●) taken 5 μs (□, ■) and 500 μs (○, ●) after the 1 μs electron pulse.

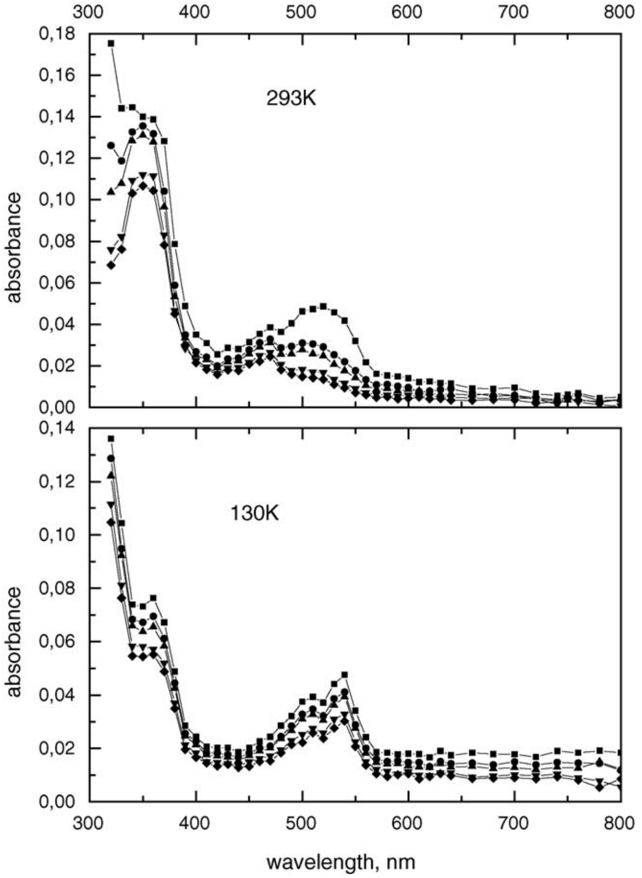

Fig. 2. Transient absorption spectra of pulse irradiated, deareated PVC film (1.0 mm thickness) containing 32.6% TOTM measured at ca.130 K (bottom) and 293 K (top), taken 10 μs (■), 50 μs (●), 100 μs (▲), 500 μs (▼) and 1 ms (♦) after the 4 μs electron pulse.

The absorption spectra of pulse irradiated PVC sample containing the another plasticizer—TOTM are shown in Fig. 2. In this case, apart from the UV maxima (~360 nm), the well defined bands were detected in the visible range of the spectrum. The transient absorptions in the range 425–560 nm with two maxima (at 470 and 520 nm) were found at room temperature. In the time range 10 μs − 1 ms the red wing maximum (~520 nm) decayed much faster comparing with the 470 nm one. At lower temperature, i.e. 130 K the visible band is characterized by two maxima (~510 and 540 nm) and whole absorption band decayed similarly suggesting that only one transient intermediate is responsible for this absorption. The decay of UV absorption band (~360 nm) seems to follow the behaviour of visible absorption in particular at low temperature. The transient signals connected with TOTM intermediates were also detected for PVC samples containing small amount of TOTM, i.e. 0.34%.

In order to identify the origin of the species under discussion the following hypothesis has to be taken into account. Since the content of both plasticizers in the polymer matrix has been rather high (30–60% by weight) we have to consider the possibility of the electron scavenging by the additive molecules despite of the fact that the main component of the matrix—PVC

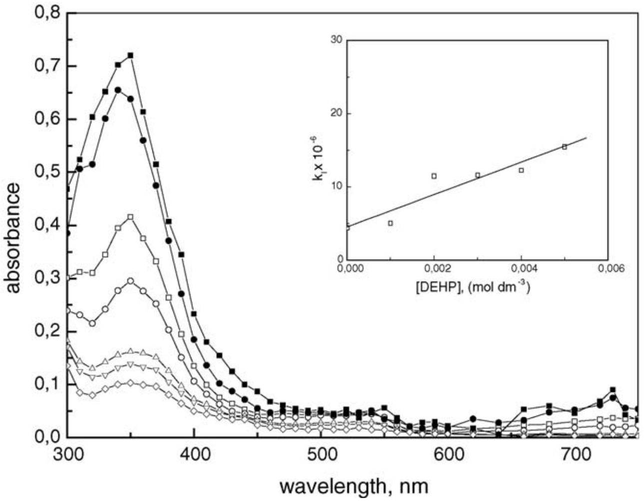

Fig. 3. The transient absorption spectra of pulse irradiated 2-propanol containing DEHP (10^{-2} mol dm^{-3}) measured at room temperature, taken 5 μs (■), 10 μs (●), 50 μs (□), 100 μs (○), 500 μs (△), 1 ms (▽), and 5 ms (◇) after the 1 μs electron pulse. Inset: the dependence of 1st order rate constants of e^-_{solv} + DEHP reaction vs. DEHP concentration, 17 ns pulse experiments.

is known as the well scavenger of the negative charges [2]. The positive charge scavenging in plasticized PVC has to be taken into account too.

Using 2-propanol as a solvent, the rate constants of e^-_{solv} reaction with DEHP and TOTM were found to be equal to 2.2×10^9 and 3.4×10^9 mol^{-1} dm^3 s^{-1}, respectively (Figs. 3 and 4, insets). These values are much higher than the rate constant of e^-_{aq} with vinylchloride, i.e. 2.5×10^8 mol^{-1} dm^3 s^{-1} [20]. The corresponding value of e^-_{solv} reaction with PVC itself has not been found because of bad solubility of PVC in common solvents.

Following the above hypothesis the transient spectra of DEHP and TOTM radical anions were measured in 10^{-2} mol dm^{-3} solutions of these plasticizers in 2-propanol at room temperature using pulse radiolysis technique (Figs. 3 and 4).

Pulse radiolysis spectra of 2-propanol–DEHP solution detected in the time scale 5 μs–5 ms are shown in Fig. 3. One can find strong UV band with maximum at ca. 360 nm and very broad absorption tail in the range 450–560 nm. The resemblance of the above spectra with that one shown in Fig. 1 is rather poor if any.

In the case of the 2-propanol–TOTM system the results (Fig. 4) seem to be more promising. The absorption spectra of TOTM anionic species in μs time scale (5 μs–1 ms, Fig. 4 bottom) are very similar to the transient spectra of PVC–TOTM system at 293 K (Fig. 2). In both cases the ~360 nm maxima were detected as well as the visible bands in the range 425 nm–560 nm. The fast time scale (100 ns–2 μs) spectra of 2-propanol–TOTM system (maxima at 510 and 540 nm, Fig. 4 top) are very similar to the transient absorptions measured for pulse irradiated PVC–TOTM matrix at 130 K (Fig. 2). These observations are in good agreement with the common interpretation that at lower temperatures one can slow down the fast time events (nanosecond scale) to the ms–s time range.

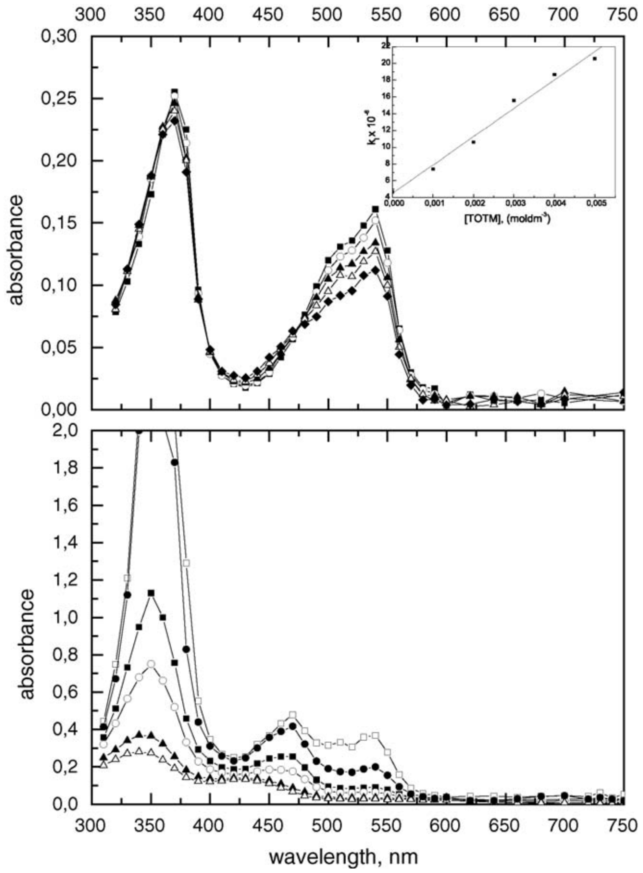

Fig. 4. The transient absorption spectra of pulse irradiated 2-propanol containing TOTM (10^{-2} mol dm^{-3}) measured at room temperature after the 17 ns pulse (top), taken at 100 ns (■), 200 ns (○), 500 ns (▲), 1 μs (△) and 2 μs (♦), and after the 1 μs electron pulse (bottom) taken at 5 μs (□), 10 μs (●), 50 μs (■), 100 μs (○), 500 μs (▲) and 1 ms (△). Inset: the dependence of 1st order rate constants of e^-_{solv} + TOTM reaction vs. TOTM concentration.

The time and temperature dependent spectral changes found for TOTM radical anions may be explained likewise it was proposed for poly(ethylene terephthalate) ions [21]. In the first step TOTM molecules can scavenge electrons producing transient TOTM$^{\bullet-}$. These species like PET$^{\bullet-}$ are thermally unstable and are observed at low temperature (130 K) in PVC–TOTM system (Fig. 2) and in ns–μs times in the case of 2-propanol–TOTM (Fig. 4).

The maxima at 510 and 540 nm might be responsible for TOTM$^{\bullet-}$ primary intermediate. In the next step, the negative charge, i.e. electron is transferred to the ester group of the side chain—in position 4 generating ester radical anion with absorption maximum at 470 nm observed in μs–ms time scale for PVC–TOTM system at room temperature (Fig. 2) and 2-propanol–TOTM solution (Fig. 4). The formation of this peak can be detected as isobestic point (λ~470 nm) in fast events data for the latter system (Fig. 4).

Such ester radical anion seems to be not generated in the case of side chains in position 1, 2 of TOTM and in DEHP as it was observed.

Fig. 5 shows the absorption spectra of pulse irradiated sec-butyl chloride (positive charge donor)—plasticizer samples at room temperature. In both cases (DEHP, TOTM) the UV bands with maxima at 340–350 nm were found. In addition for TOTM

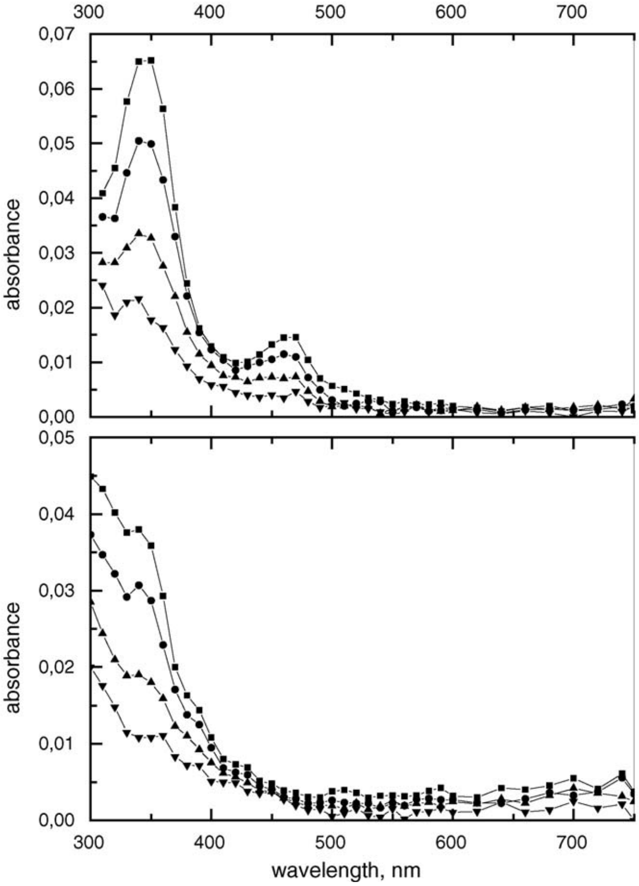

Fig. 5. The transient absorption spectra of sec-butyl chloride containing DEHP (10^{-2} mol dm^{-3}, bottom) and TOTM (10^{-2} mol dm^{-3}, top) pulse irradiated at room temperature taken 5 μs (■), 10 μs (●), 50 μs (▲) and 500 μs (▼) after the 1 μs pulse.

containing system the well defined band with maximum at ∼470 nm is observed. The transient absorptions under consideration can be attributed to the DEHP$^{\bullet+}$ and TOTM$^{\bullet+}$ radical cations and may contribute to the UV absorption results shown in Figs. 1 and 2. The ionization potentials (IP) for PVC and above mentioned plasticizers have not been available. The IP for vinylchloride was found to be equal to 9.99 ± 0.02 eV [22] whereas for dimethylphthalate and terephthalic acid equaled 9.64 ± 0.07 and 9.86 ± 0.2 eV, respectively [22]. All these numbers are quite similar but taking into account the spectral evidences (Figs. 1, 2 and 5) one may suggest that in PVC–plasticizer system the formation of DEHP$^{\bullet+}$ and TOTM$^{\bullet+}$ cations is possible.

Taking into account the results described above the following, main reactions may be suggested:

$$\text{PVC} \quad \text{—}\wedge\wedge\wedge\wedge\!\rightarrow \quad e^- + \text{PVC}^{\bullet+}$$

$$e^- + \text{PVC} \rightarrow \text{PVC}^{\bullet-} \qquad (2)$$

$$e^- + \text{Plast.} \rightarrow \text{Plast.}^{\bullet-}(\text{DEHP}^{\bullet-}, \text{TOTM}^{\bullet-}) \qquad (3)$$

$$\text{PVC}^{\bullet+} + \text{Plast.} \rightarrow \text{Plast.}^{\bullet+}(\text{DEHP}^{\bullet+}, \text{TOTM}^{\bullet+}) \qquad (4)$$

where Plast. denotes plasticizer (DEHP or TOTM).

The content of plasticizer in the polymer matrix is quite high. In such a systems the “direct” effect of irradiation on plasticizer has to be considered because the system is not totally homogenous. The “direct” effect should result in formation of additional radical ions generated via radiolysis of plasticizer molecules themselves.

Following the mechanism (reaction (1)–(3)) one may expect that, in particular, TOTM should decrease the yield of HCl formation in the PVC system [2] and ought to influence the processes leading to the radiation stability of the matrix.

Hutzler et al. [13] found that common plasticizers like DEHP, epoxy soybean oil (ESO) prevent the yellowing of the PVC and the authors concluded that these additives “are effective in stabilizing the radiolytic abstraction of HCl from PVC”. Similar conclusions can be found in other papers [10,14] although the evidences include rather indirect results like the changes of UV absorptions and pH of aqueous extracts obtained after interaction of the aqueous solution with irradiated PVC systems of different compositions.

4. Conclusions

- In the pulse irradiated PVC–plasticizer systems the primary ionic reactions involving the charges (electrons and positive ones) scavenging by plasticizer molecules (DEHP, TOTM) have to be taken into account.
- These ionic reactions have contributed to the yield of end-products (i.e. HCl) of PVC matrix radiolysis during sterilization of respective medical items.

Acknowledgements

The present work was partly supported by KBN Grant no. 3T09A 149 26. We thank Dr. K. Hodyr for keeping the accelerator faithful and Anvil SA company for supplying the medical PVC.

References

[1] R.M. David, L.K. Lockhart, K.M. Ruble, Food Chem. Toxicol. 41 (2003) 589.
[2] J. Mayer, M. Szadkowska-Nicze, J. Photochem. Photobiol. A: Chem. 177 (2006) 185, and literature cited there.
[3] C. Wippler, J. Polym. Sci. 29 (1958) 585.
[4] S.H. Pinner, Nature 183 (1958) 1108.
[5] Z. Kum, J. Polym. Sci. 43 (1960) 570.
[6] S.H. Pinner, Plastics 25 (1960) 35.
[7] S.V. Krylova, A.Ye. Kulikova, Yu.V. Ovchinnikov, S.M. Berlyant, Plast. Massy 1 (1973) 16.
[8] S.V. Krylova, A.Ye. Kulikova, Yu.V. Ovchinnikov, T.M. Lyntova, S.M. Kozenko, Plast. Massy 5 (1976) 23.
[9] A.H. Zahran, F.M. Ezz-Eldin, Radiat. Phys. Chem. 27 (1986) 175.
[10] E. Wojtyńska, Z. Bułhak, B. Szabłowska, Polimery 42 (1997) 200 (in Polish).
[11] Ch.T. Ratnam, K. Zaman, Polym. Degrad. Stabil. 61 (1998) 47.
[12] R. Buchalla, Ch. Boess, K.W. Bögl, Radiat. Phys. Chem. 56 (1999) 353.
[13] B.W. Hutzler, L.D.B. Machado, A.B. Lugâo, A.-L.C.H. Villavicencio, Radiat. Phys. Chem. 57 (2000) 381.

[14] M.B. Świerz-Motysia, Polimery 48 (2003) 434.
[15] G. Dlubek, V. Bondarenko, J. Pionteck, M. Supej, A. Wutzler, R. Krause-Rehberg, Polymer 44 (2003) 1921.
[16] G.M. Vinhas, R.M. Souto-Maior, Y.M.B. de Almeida, Polym. Degrad. Stabil. 83 (2004) 429.
[17] G.M. Vinhas, R.M. Souto-Maior, Y.M.B. de Almeida, B.B. Neto, Polym. Degrad. Stabil. 86 (2004) 431.
[18] Pol. Pat. Appl. P-344204 (2000).
[19] S. Karolczak, in: J. Mayer (Ed.), Properties and Reactions of Radiation Induced Transients. Selected Topics; Pulse Radiolysis – Experimental Features Polish Scient. Publ. PWN, Warszawa, 1999, p. 11 (Chapter 1).
[20] R. Koester, A.-D. Asmus, Z. Naturforsch, Teil B26 (1971) 1108.
[21] M. Szadkowska-Nicze, J. Mayer, J. Polym. Sci. Part A: Polym. Chem. 37 (1999) 2853.
[22] D.V. Lide, H.P.R. Frederikse (Eds.), CRC Handbook of Chemistry and Physics, 77th ed., CRC Press, 1996–97.