THE STRUCTURE AND PHOTOCHEMICAL TRANSFORMATION OF CHLORIDE COMPLEXES OF IRON IN POLYETHYLENGLYCOL

K.G. BELYAEVA, N.I. ZAITSEVA, V.K. IMSHENNIK and I.P. SUZDALEV
Institute of Chemical Physics, Academy of Sciences, Moscow, USSR

The investigation of \((C_2H_5)_4NFeCl_4\)-polyethyleneglycol (PEG) system was carried out by means of optical spectroscopy, electron spin resonance (ESR) and Mössbauer spectroscopy. We also tried to connect kinetic parameters of photoreduction process with the structure of the complex and polymer surrounding.

1. Introduction

The first row transition metallic complexes dispersed in polymer matrix are used as initiators of free-radical processes under heat or light radiation. High redox ability of iron is widely used in different polymer radical reactions.

Recently it has been shown that photoreduction processes of iron containing polymethylmethacrylate or polypropylene can be described in terms of non-equivalent redox centers in polymer matrix.

Several authors have recently investigated iron chloride doped polymers by means of Mössbauer spectroscopy [1–3]. They studied the transformation of these complexes in polymer matrixes and obtained their parameters.

The aim of this work was to study the photoreduction centers of the \((C_2H_5)_4NFeCl_4\)-PEG system and connect the structure and photochemical ability of iron-chloride complexes with polymer surrounding.

2. Experimental results and discussion

PEG was doped with \((C_2H_5)_4NFeCl_4\) \((C_{Fe} = 0.05–0.10 \text{ mmol/g})\) under rigorously anhydrous conditions. The stability of this iron complex has been studied earlier [4]. This system was studied by Mössbauer resonance, optical and ESR spectroscopies. The exposure of iron doped PEG system to air for 6 months doesn’t change the obtained parameters. The initial spectra were recorded in the temperature range 4.2 K–300 K with standard Mössbauer transmission geometry and X-band ESR spectrometer. Foil of \(\alpha\)-Fe was used for the velocity calibration and for isomer shift data.

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The kinetic photoreduction curves were observed in the ultraviolet region (\( \lambda = 365 \text{ nm} \)). The irradiation experiments were performed at 77 K, but some samples were sealed under vacuum in quartz tubes, the others were placed in a bath with liquid nitrogen. After the irradiation Mössbauer spectra were recorded at 77 K, too.

Particular feature of PEG is its amorphous-crystalline structure below \( T_g = 253 \text{ K} \). In this phase the Mössbauer spectra (fig. 1a) show the presence of an intensive singlet (\( IS = 0.30 \text{ mm/s} \)) and a quadrupole doublet with \( IS = 0.50 \text{ mm/s}; QS = 1.20-1.30 \text{ mm/s} \). The singlet can be assigned to the high symmetry tetrahedral anion \( \text{FeCl}_4^- \) [5]. The singlet is obtained in the spectra up to 300 K contrary to the doublet, which disappears above \( T_g \) (fig. 1b). Therefore, it can be assumed that the \( \text{FeCl}_4^- \) monoanion is located in the more rigid crystalline part of the polymer matrix.

The peculiarity of the iron distribution over the polymer matrix according to the Mössbauer data is the high amount (70–80%) of total iron located in the crystalline region.

At 4.2 K a slight but well resolved hyperfine structure appears in the Mössbauer spectrum (fig. 3a). The intensive ESR signal with \( g = 2.1 \) and \( \Delta H = 132 \text{ Oe} \) is obtained.

The kinetic curves of the photoreduction processes (fig. 2) give the data in agreement with the Mössbauer ones. In the amorphous-crystalline region this curve (curve I) consists of the rapid part with the quantum yield of \((1.2-3.8) \cdot 10^{-3}\)