

# Magnetic resonance study of poly(ether-block-ester) copolymers with ferrocene units



J. Typek, N. Guskos, G. Zolnierkiewicz and A. Szymczyk

Institute of Physics, West Pomeranian University of Technology, Al. Piastow 48, 70-311 Szczecin, Poland

## Abstract

The poly(ether-block-ester)s (PEEs) based on poly(butylene terephthalate) (PBT), which forms the hard phase, and poly(oxytetramethylene) (PTMO) as the soft phase is a widely known class of thermo-plastic elastomers. In this work PEE was obtained by using 1,1' ferrocenedimethoxy as catalyst. A small amount (1-2 mole %) of the ferrocene units incorporated into polyester hard block of PEE enhanced the tensile properties and thermal stability of PEE. Electron paramagnetic resonance (EPR) study of samples with different concentration of ferrocene units and different proportions of hard and soft segments (50/50 and 30/70) has been carried out in the 4-290 K temperature range. The spin spatial homogeneity of PBT-block-PTMO copolymers has been studied by registering the EPR response of a large number of samples. Different types of paramagnetic centres of low-spin and high-spin  $\text{Fe}^{3+}$  ions have been revealed. Temperature dependence of the EPR parameters (linewidth, g-factors, and integrated intensity) of PEE/50/50-type sample has been investigated and the magnetic properties of copolymer have been correlated with the electronic structure of the free radicals

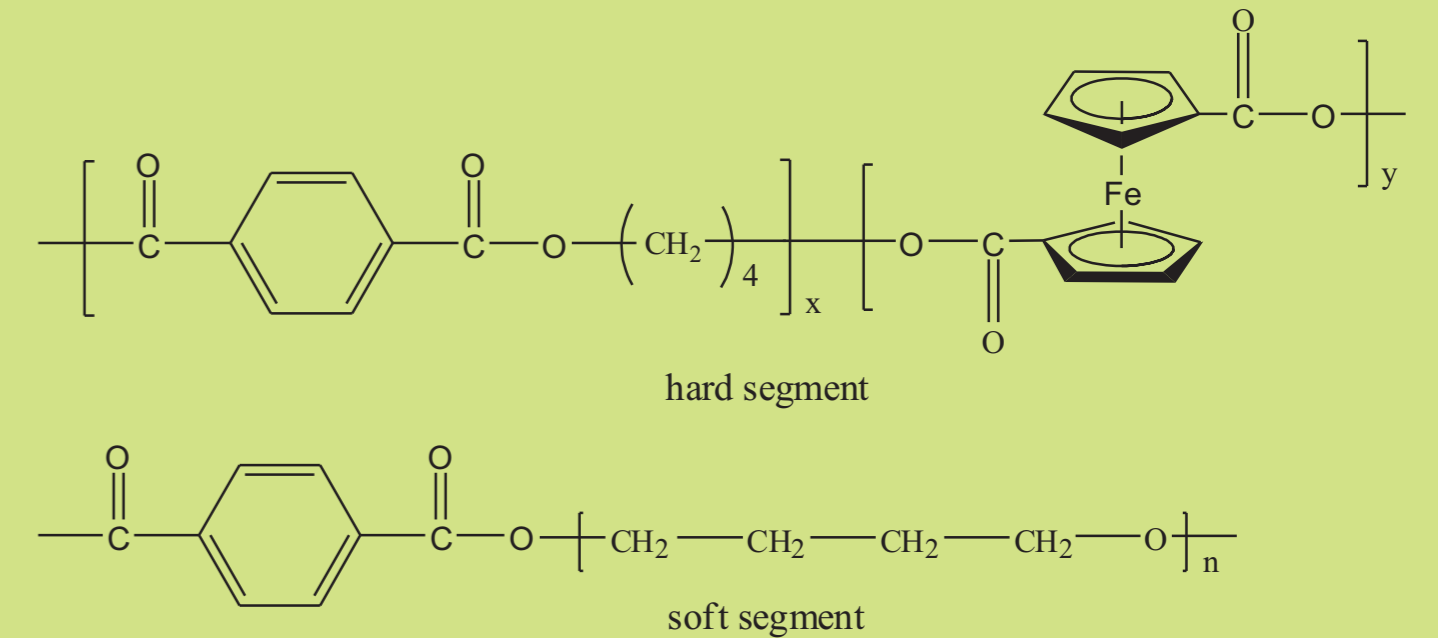


Figure 1. The structure of hard and soft segments of studied PBT-PTMO copolymers. The value of index  $n=14$ .

Sample designation	$w_r$ wt %	$w_s$ wt %	$x$ mol/mol	$w_r$ lg/100 g	$w_s$ spins/mg
PEE/50/1	50	50	5.14	$0.785 \cdot 10^{-3}$	$5.82 \cdot 10^{17}$
PEE/50/2	50	50	5.14	$2.357 \cdot 10^{-3}$	$0.06 \cdot 10^{17}$
PEE/30/1	30	70	2.2	$4.285 \cdot 10^{-3}$	$4.91 \cdot 10^{17}$
PEE/30/2	30	70	2.2	$8.714 \cdot 10^{-3}$	$4.48 \cdot 10^{17}$

$w_r$  – content of rigid segments;  $w_s$  – weight fraction of flexible segments;  $x$  – degree of polymerization of rigid segments with reference of 1 flexible unit;  $w_r$  – content of ferrocene units per 100 g of polymer;  $w_s$  – number of spins per 1 mg of polymer.

Table 1. The composition of the synthesized PBT-PTMO copolymers

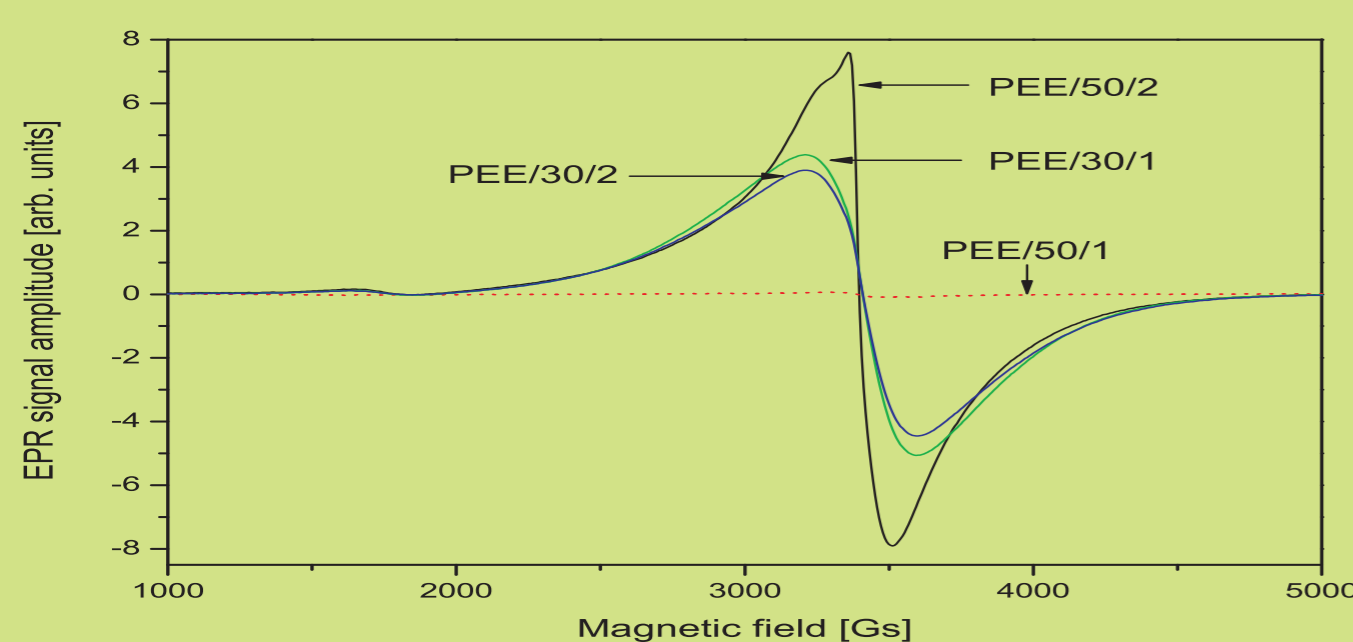


Figure 2. EPR spectra of four investigated polymer samples registered at room temperature.

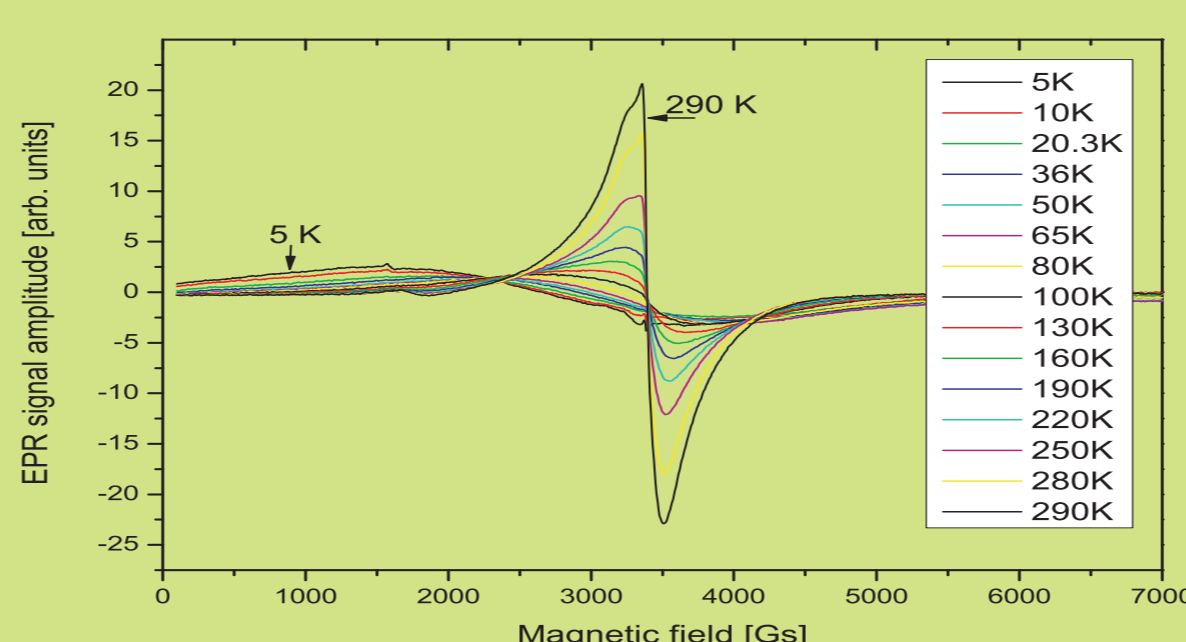


Figure 3. EPR spectra of PEE/50/2 sample at different temperatures in the 5-290 K range.

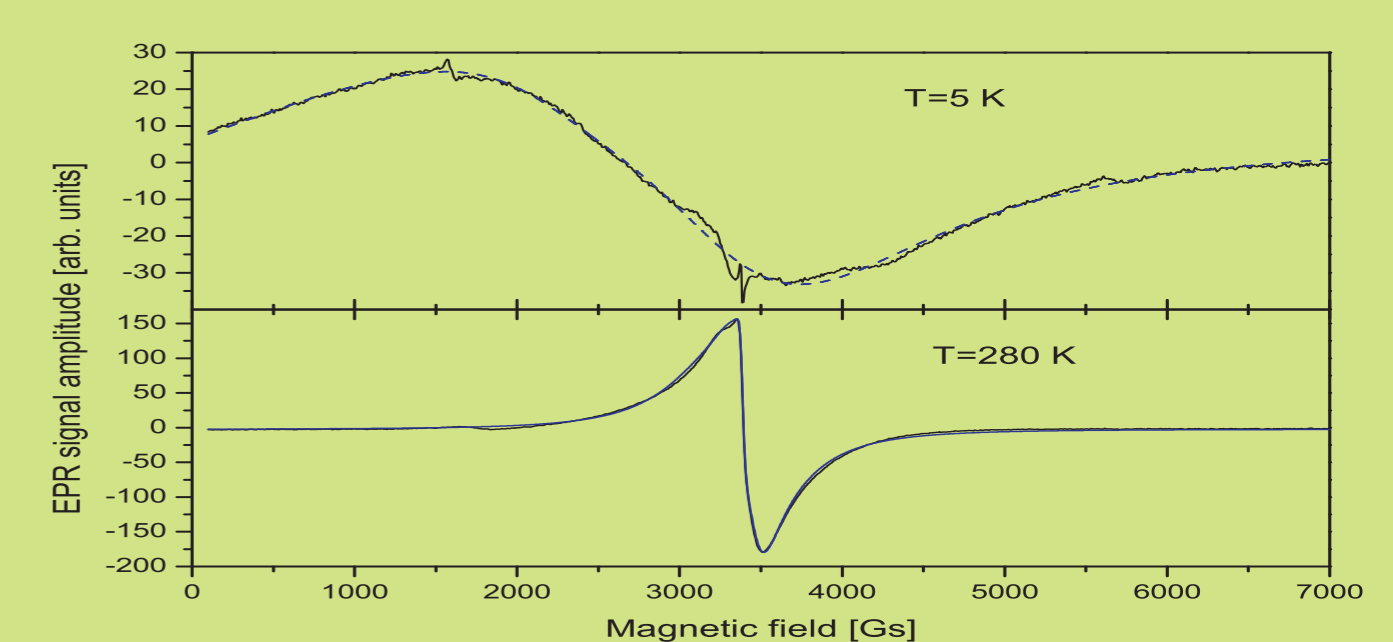


Figure 4. Experimental (black) and simulated (blue) EPR spectra of PEE/50/2 sample at 5 K (top panel) and 280 K (bottom panel).

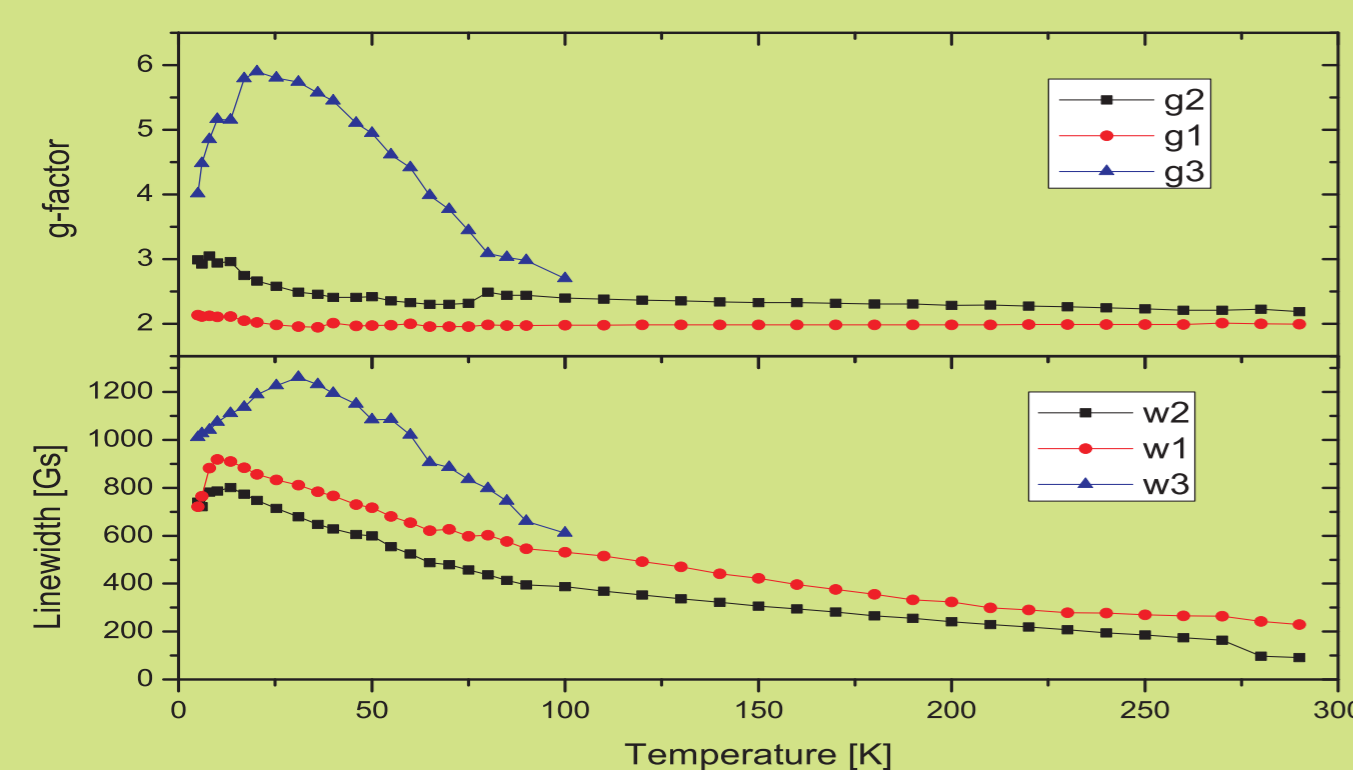


Figure 5. Temperature dependence of calculated anisotropic g-factors (top panel) and linewidths (bottom panel) of PEE/50/2 sample.

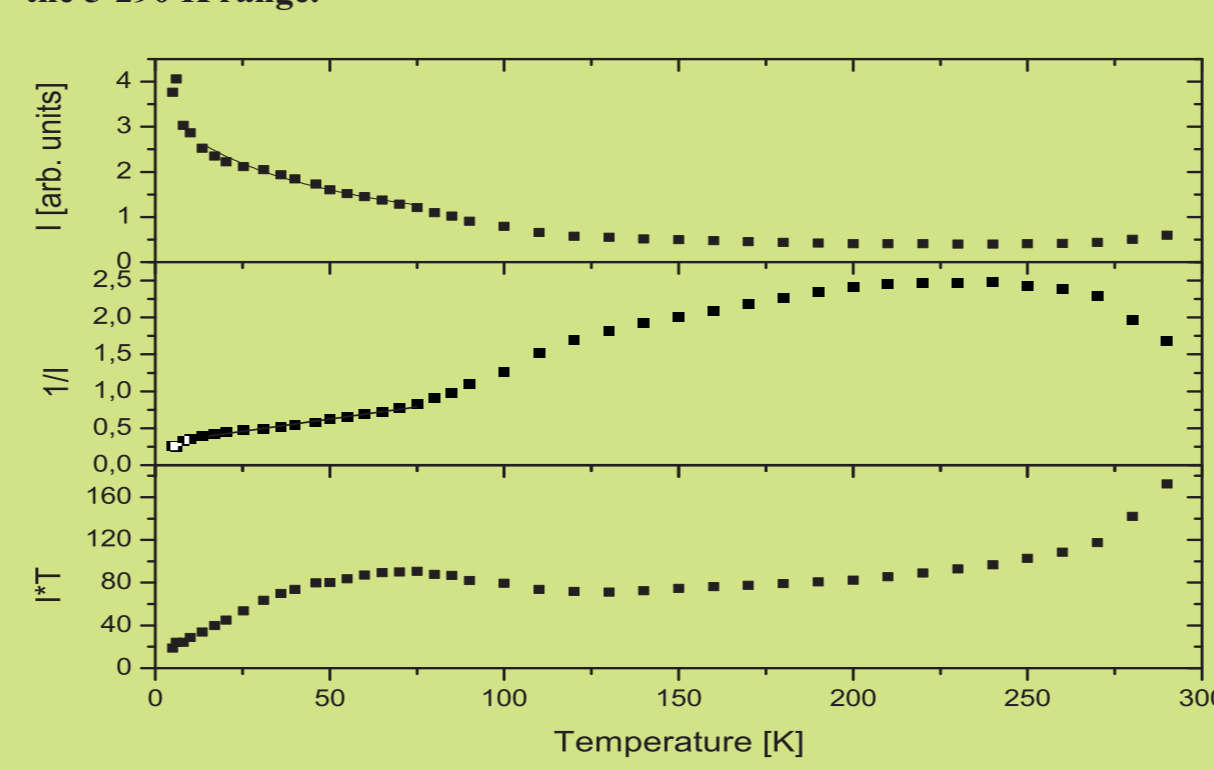


Figure 6. Temperature dependence of the EPR integrated intensity (top panel), reciprocal of integrated intensity (middle panel) and the product of temperature and integrated intensity (bottom panel) of PEE/50/2 sample.

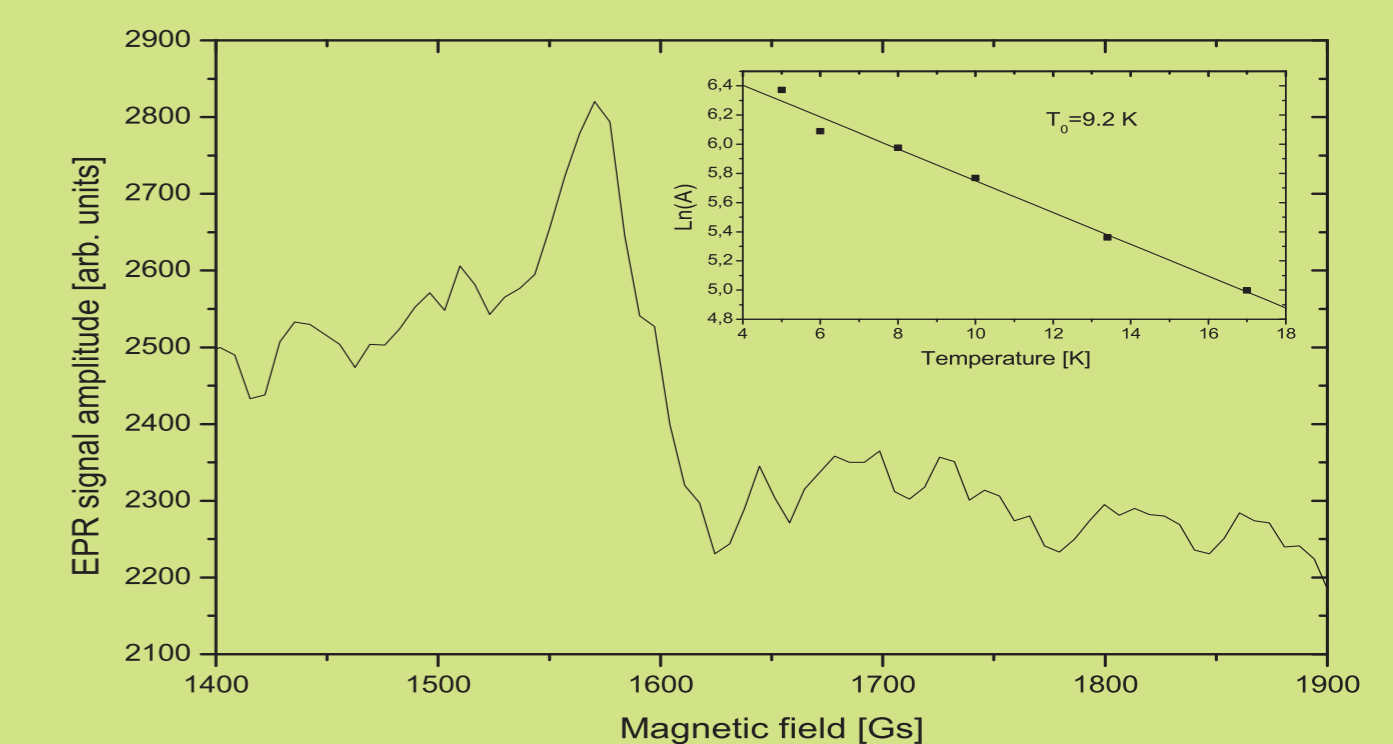


Figure 7. Low-field, low-temperature EPR line of PEE/50/2 sample. The inset shows the decrease of this line amplitude with increasing temperature.

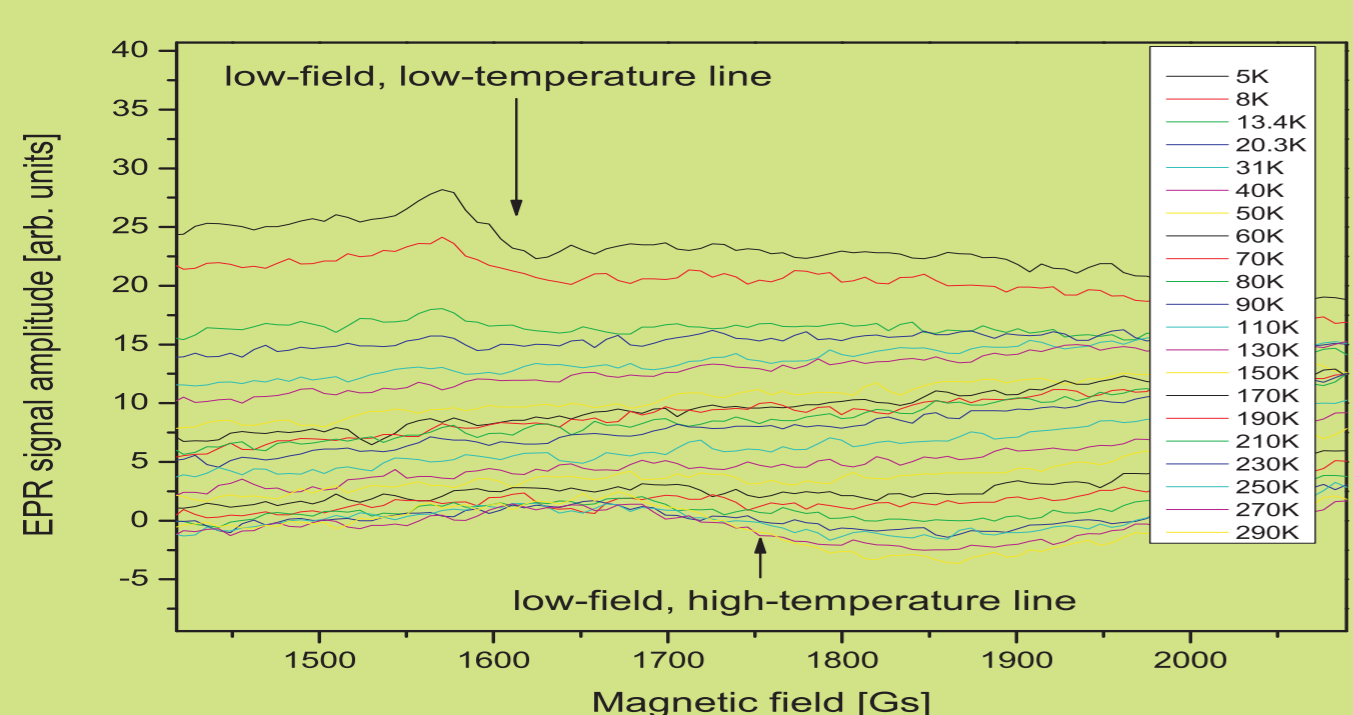


Figure 8. Two types of low-field lines in the EPR spectrum of PEE/50/2 sample: the low-temperature line is observed only at  $T < 15$  K, the high-temperature line at  $T > 170$  K.

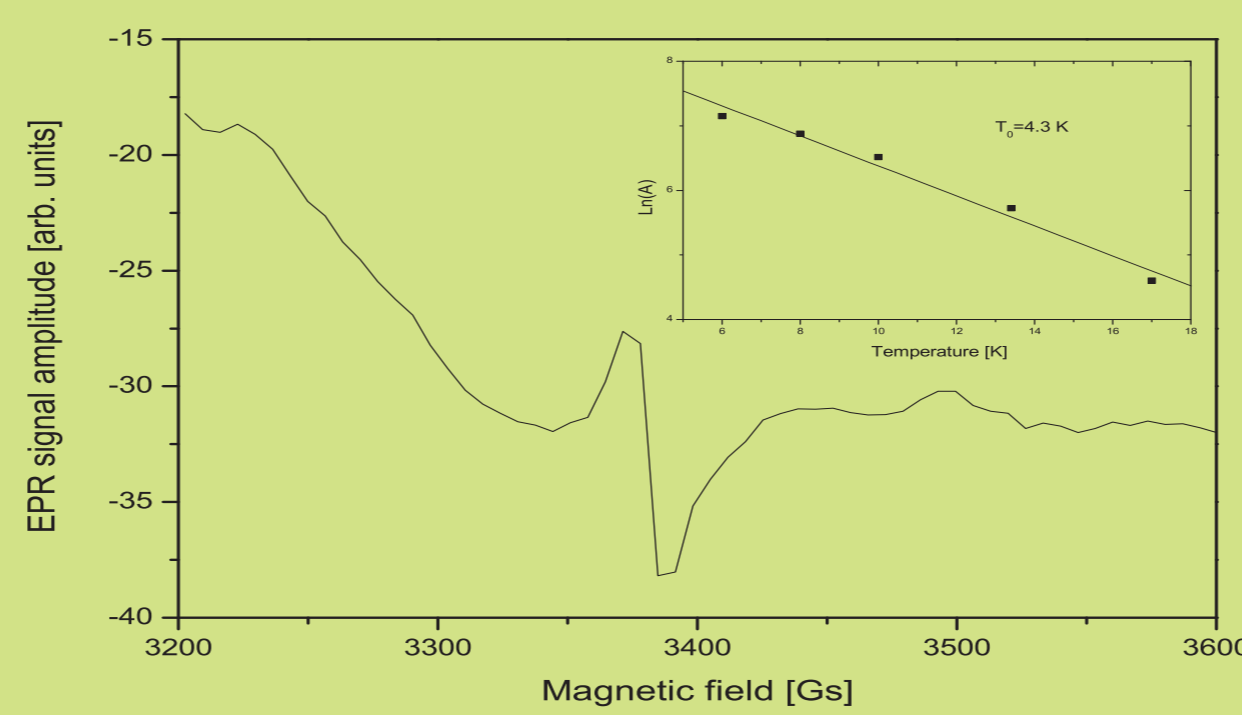


Figure 9. Low-temperature EPR line at  $g=2$  of PEE/50/2 sample. The inset shows the decrease of this line amplitude with increasing temperature

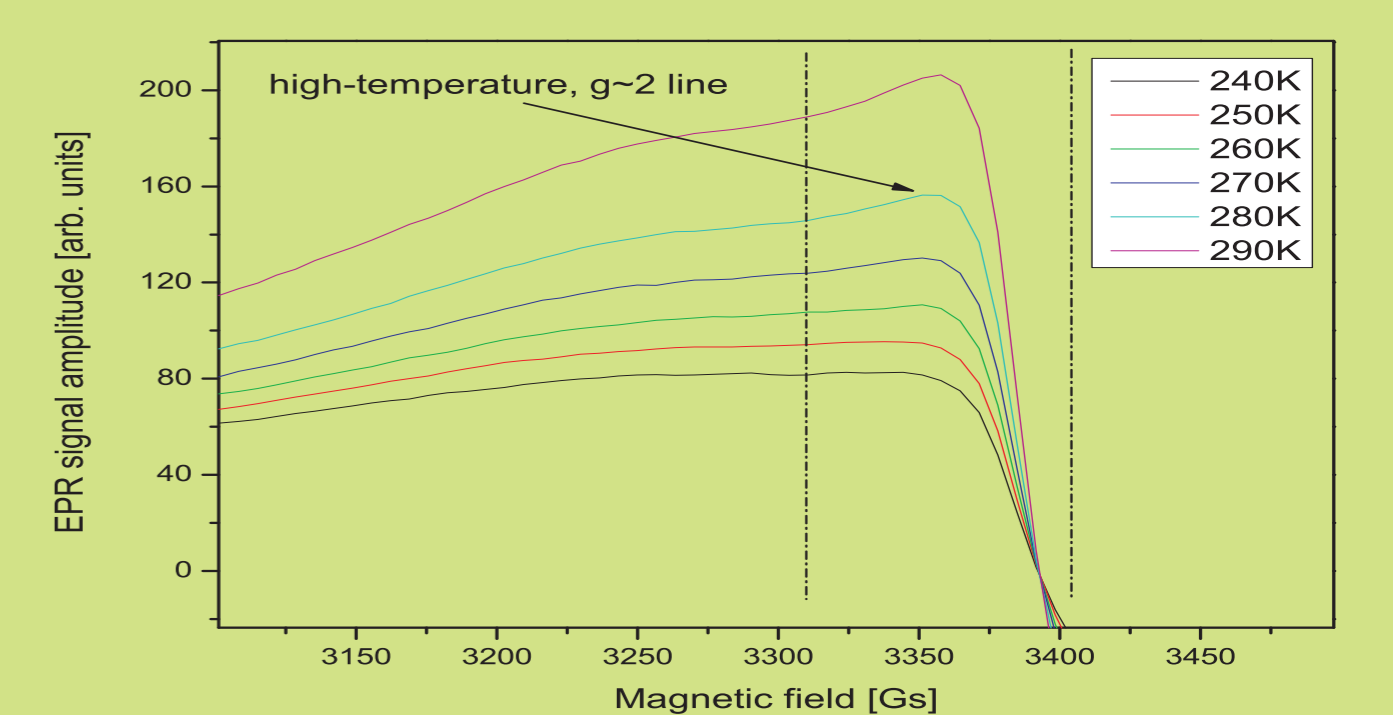


Figure 10. Part of the EPR spectrum of PEE/50/2 sample in the high temperature range showing the high-temperature  $g=2$  line.

## Conclusions

- The spin spatial homogeneity in the polymer has been studied by registering EPR signal from many different samples cut from the same polymer thread and was found to be rather low (spin concentration variation were up to 20% calculated on a polymer mass unit).
- The correlation between ferrocene content and the number of paramagnetic centers is weak indicating on a crucial role of oxygen in the process of copolymer formation.
- The following paramagnetic centers have been identified:
  - The main paramagnetic centers  $S=1/2$  visible in the whole temperature range. At room temperature it has an axial symmetry, but its magnetic anisotropy increases below 100 K (to rhombic symmetry),
  - Low-field, low-temperature paramagnetic centers of high-spin  $\text{Fe}^{3+}$  at low-symmetry site, strongly coupled to the lattice,
  - Low-field, high-temperature paramagnetic centers of high-spin  $\text{Fe}^{3+}$  at low-symmetry site, weakly coupled to the lattice,
  - Low-temperature EPR centers with  $g \sim 2$  of low-spin  $\text{Fe}^{3+}$  at high-symmetry site,
  - High-temperature EPR centers with  $g \sim 2$  of high-spin  $\text{Fe}^{3+}$  at high-symmetry site