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Mechanism of methyl methacrylate polymerization initiated by benzoyl peroxide and ferrocene in the presence of oxygen

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Experimental

Methyl methacrylate (Fluka) was twice distilled under reduced pressure (bp 48 °C, 140 Torr). Ferrocene (Cp_2Fe) and 2,2-diphenyl-1-picrylhydrazyl (DPPH, Fluka) were used without further purification. Benzoyl peroxide (BP) was recrystallized three times from methanol and dried at room temperature in a vacuum. Physico-chemical constants of distilled solvent (ethanol, acetonitrile, isooctane, *tert*-butanol), correspond to published data.[1]

The purity of the used reagents was tested with ^{13}C, ^{1}H NMR spectroscopy. IR spectra were recorded on a Specord M80 spectrophotometer in 4000−400 cm^{-1} as a suspension in vaseline oil. Investigation of the interaction of system components Cp_2Fe−BP−MMA was studied by spectrophotometric method on the device Carl Zeiss Jena «Specord M-40» in the 200-700 nm in the temperature range 285−303 K using a quartz cuvette l = 0.1 or 1 cm. A solution of the reaction mixture was placed in the working quartz cell, and a solvent was poured in the reference cell.

The initial concentration Cp_2Fe, BP, MMA was varied $(0.25–5.0)\times10^{-2}$ mol·dm^{-3}, $(0.12−2.0)\times10^{-2}$ mol·dm^{-3} and $(2.0−5.0)\times10^{-2}$ mol·dm^{-3}, respectively. Methanol, ethanol, acetonitrile, isooctane were used as a solvent.

The products of reaction of Cp_2Fe and BP ($[Cp_2Fe]_0$: $[BP]_0$ = 2:1) and Cp_2Fe, BP, and MMA ($[Cp_2Fe]_0$: $[BP]_0$: $[MMA]_0$ = 2:1:10) were prepared in isooctane at 293−303 K. The precipitate was filtered off, washed three times with solvent to remove impurities and Cp_2Fe, BP were dried at room temperature *in vacuo* to constant weight.

Bulk radical polymerization was performed in glass dilatometers. Standard method of bulk polymerization: calculated amounts of monomer and components of initiating systems

were placed in glass dilatometers; solution was degassed by freeze-pump-thaw cycles repeated three times to a residual pressure of 1.3 Pa; dilatometers were sealed (for studies of polymerization to low conversion) or filled up with degassed glycerin (for studies of polymerization to high conversion) and placed in a thermostat at temperature of (333.0±2.7) K and kept for until a specified degree of conversion was achieved.

The method of preparation of polymerization mixture with access for air: calculated amounts of monomer and components of initiating systems were placed in glass dilatometers; dilatometers were capped (for studies of polymerization to low conversion) or filled up with degassed glycerin (for studies of polymerization to high conversion) and placed in a thermostat at temperature of (60.0±0.1) °C and kept for until a specified degree of conversion was achieved.

The method of preparation of polymerization mixture *in vacuo*: separated round-bottom flasks containing calculated amounts of monomer and components of initiating systems were attached to dilatometer; each component of reaction mixture was degassed separately by freeze-pump-thaw cycles repeated three times to a residual pressure of 1.3 Pa. Then components of reaction mixture were mixed. Dilatometers were sealed (for studies of polymerization to low conversion) or filled up with degassed glycerin (for studies of polymerization to high conversion) and placed in a thermostat at temperature of (60.0±0.1)°C and kept for until a specified degree of conversion was achieved. The polymerization kinetics was studied by dilatometry.[2]

All geometry optimizations were carried out using the mPW1K[3] hybrid density functional which can give good results for ionic system.[4] The 6-311+G(d,p), 6-31+G(d,p) basis set[5] were used for all atoms except Fe which was treated with the Ahlrichs VDZ and Ahlrichs VTZ,[6] this basis sets give consistent and rapidly converging results.[7] All calculations were performed with the Gaussian 09 software package.[8] All studied structures were optimized without constraints. Vibrational frequencies and zero-point vibrational energies (ΔZPVE) were obtained at the same levels of theory without any scaling factors. Time–dependent DFT calculations were performed at the mPW1K/6-311+G(d,p) (except Fe, which was treated with Ahlrichs VTZ basis set) level.

References

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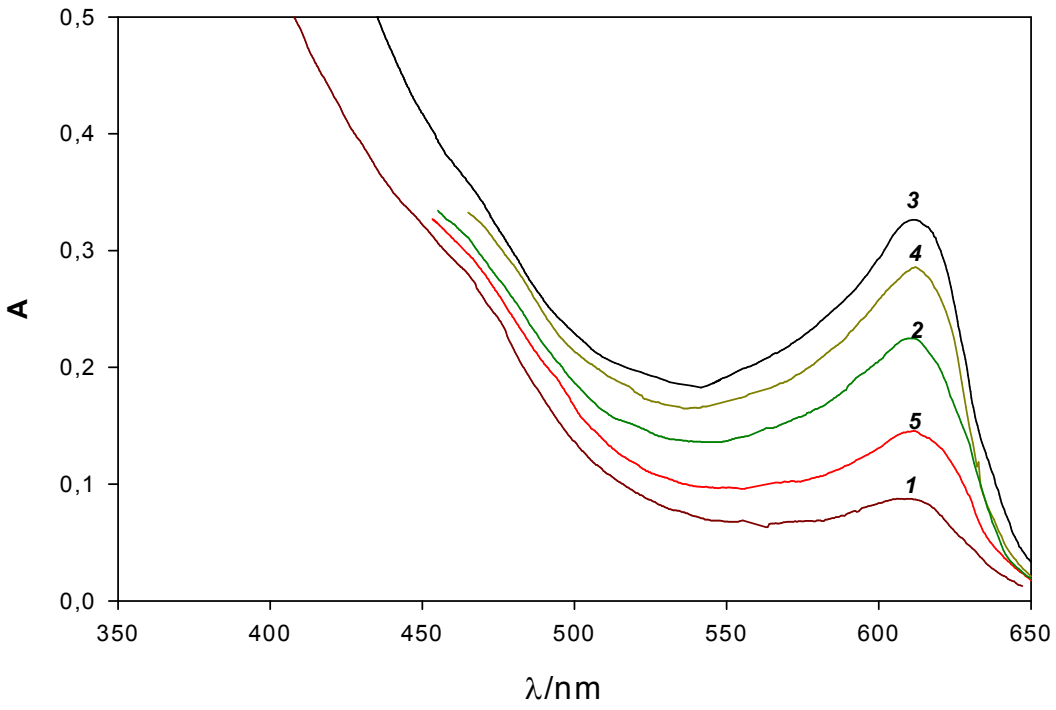

Figure 1S Absorption spectra of ferrocene–benzoyl peroxide system in ethanol at 299 K: (*1*) 4 min, (*2*) 16 min, (*3*) 29 min, (*4*) 32 min, (*5*) 40 min; $[Cp_2Fe]_0=2.50\cdot10^{-3}$ mol·dm^{-3}, $[BP]_0=1.25\cdot10^{-3}$ mol·dm^{-3}.

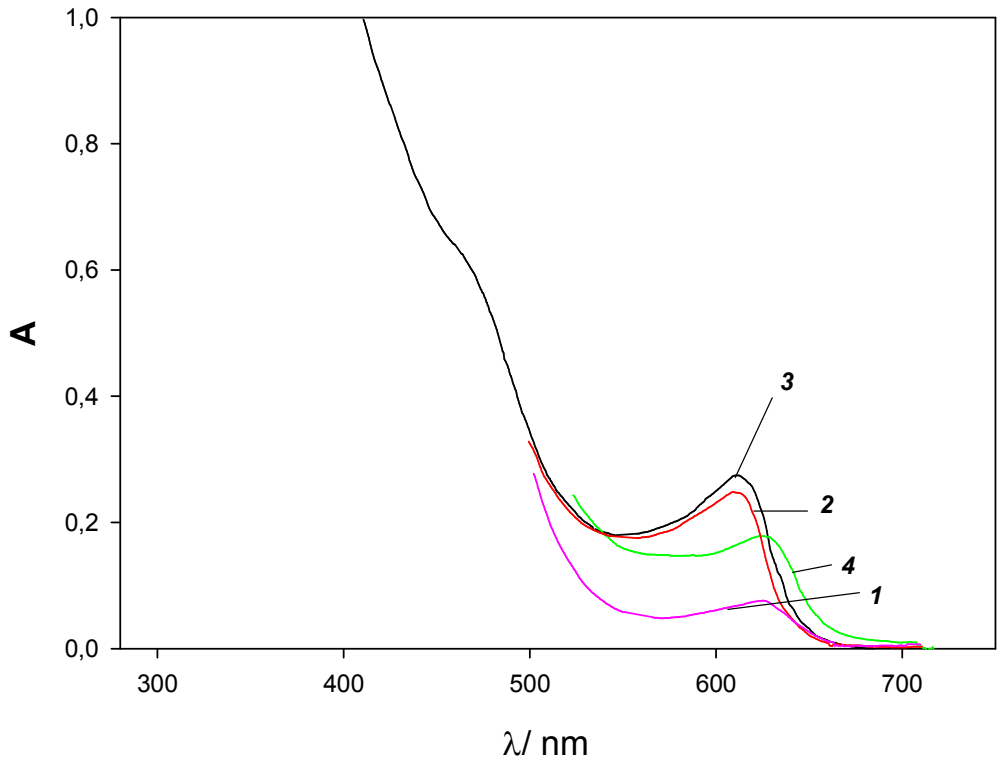

Figure 2S Absorption spectra of ferrocene– benzoyl peroxide system in acetonitrile at 285 K: (*1*) 4 min, (*2*) 7 min, (*3*) 29 min, (*4*) 32 min, $[Cp_2Fe]_0$= $5.00 \cdot 10^{-3}$ mol·dm^{-3}, $[BP]_0$=$1.25 \cdot 10^{-3}$ mol·dm^{-3}.

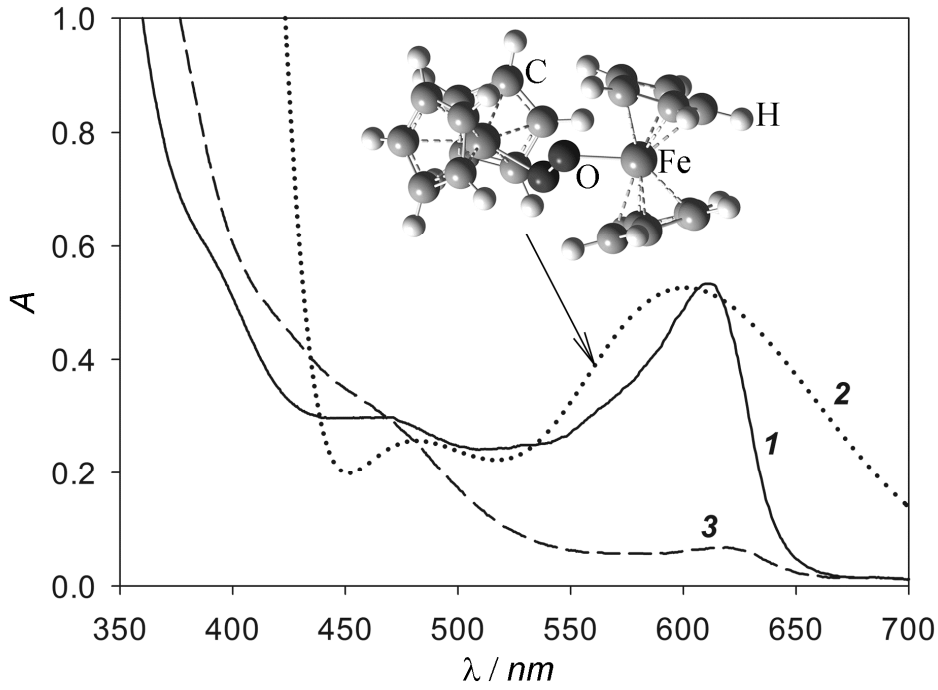

Figure 3S Absorption spectra of (*1*) ferrocenium radical cation $[Cp_2Fe^{+\bullet}]PhCO_2^-$, $C_0 = 1.1 \cdot 10^{-2}$ mol·dm^{-3}; (*2*) calculated spectra for [μ-(peroxy-O:O′)]diferrocenium at the TD-mPW1K/6-311+G(d,p) level of theory; (*3*) recorded after 60 h (l = 1 mm) in ethanol.

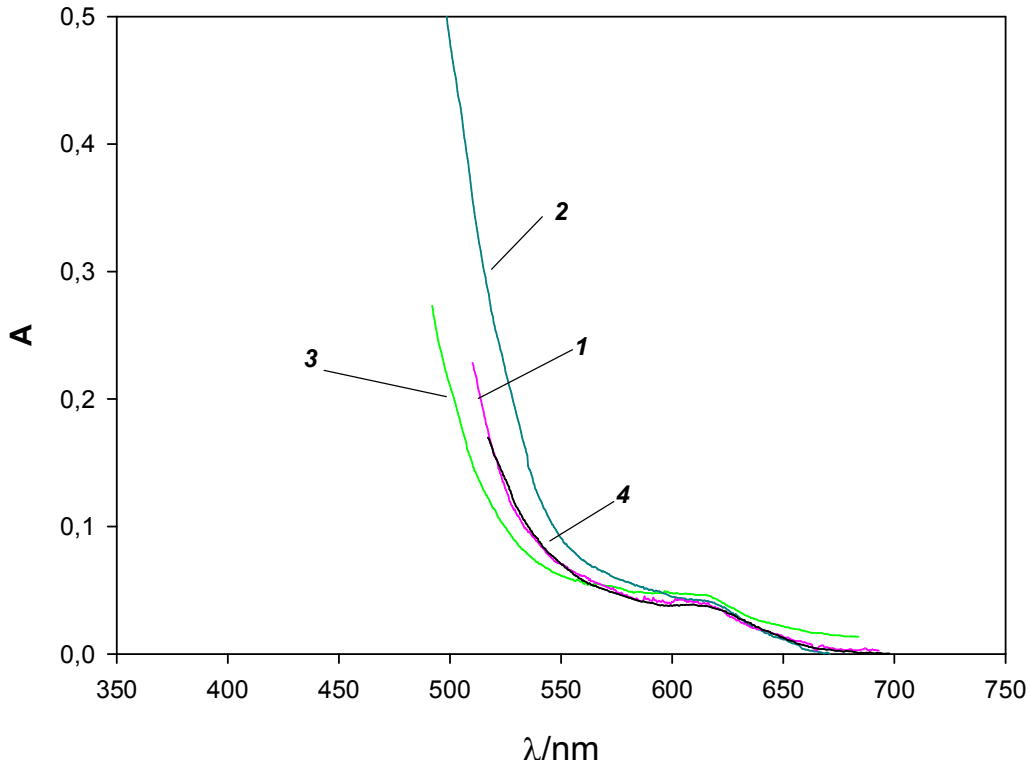

Figure 4S Absorption spectra of ferrocene - benzoyl peroxide system in MMA at 299 K: (*1*) - 10 min, (*2*) – 22 min, (*3*)- 55 min, (*4*)- 120 min, $[Cp_2Fe]= 5.00 \cdot 10^{-3}$ mol·dm^{-3}, $[BP]=1.25 \cdot 10^{-3}$ mol·dm^{-3}.