

Formation of Initiating Systems on the Basis of Cobalt Porphyrins and Benzoyl Peroxide in Chloroform and Methyl Methacrylate

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To understand the initiating mechanism of the radical polymerization of methyl methacrylate (MMA) in the presence of porphyrin complexes the interaction of Co porphyrins [5,10,15,20-tetraphenylporphyrin (CoTPP), 5,10,15,20-tetra(4-methoxyphenyl)porphyrin (CoTP(MeO)P), 5,10,15,20-tetra(3-butoxyphenyl)porphyrin (CoTP(BuO)P)] with benzoyl peroxide in chloroform and methyl methacrylate was studied using a spectrophotometric method. Oxidation of these metalloporphyrins leads to the formation of isoporphyrins.

Keywords: Radical polymerization, initiating system, metalloporphyrin, benzoyl peroxide, isoporphyrin.

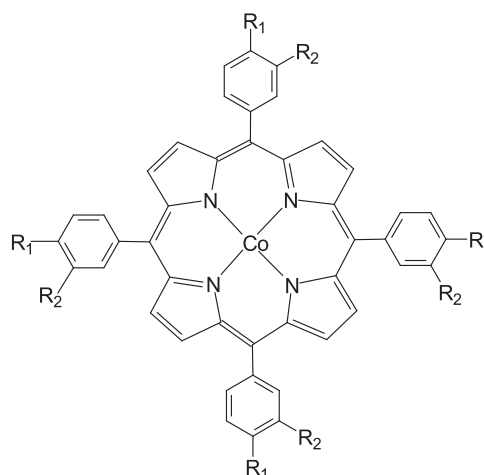
Introduction

It is known that metalloporphyrins are very effective catalysts of different processes.^[1,2] Cobalt complexes of porphyrins can be used as catalysts (initiators) of controlled ring-opening polymerization of various heterocyclic monomers^[3] and unsaturated monomers.^[3-8] There is a lot of works on the controlled radical polymerization in the presence of initiating system "metalloporphyrin – benzoyl peroxide",^[8-10] which leads to the synthesis of polymers with the specific molecular weight and chain-length distribution. But, to the best of our knowledge, there is no information about the interaction of metalloporphyrins with benzoyl peroxide during the polymerization process and the role of this type of interaction in the controlled radical polymerization is not so far revealed. Currently available data are insufficient for understanding of radical polymerization mechanism. The present work presents the first study of the interaction between Co porphyrins and benzoyl peroxide in chloroform and methyl methacrylate.

Experimental

Co complexes of 5,10,15,20-tetraphenylporphyrin (CoTPP), 5,10,15,20-tetra(4-methoxyphenyl)porphyrin (CoTP(MeO)P), 5,10,15,20-tetra(3-butoxyphenyl)porphyrin (CoTP(BuO)P) were prepared as described earlier.^[11] The model oxidation reaction of Co porphyrins was studied in chloroform (CHCl₃) and polymerization reaction in methyl methacrylate (MMA). These solvents^[12] and benzoyl peroxide (BP) were purified using known procedures.^[13]

Electronic absorption spectra of CoTPP, CoTP(MeO)P, CoTP(BuO)P and benzoyl peroxide solutions in chloroform and methyl methacrylate were recorded on Lambda 20 PERKIN ELMER and Shumadzu «UV 2550 KC» spectrophotometers. The kinetic measurements of the interaction between Co porphyrins and benzoyl peroxide in chloroform and methyl methacrylate were carried out by spectrophotometric method in hermetic quartz cuvettes.



I R₁=R₂=H
Co^{II}TPP

II R₁=OCH₃, R₂=H
Co^{II}TP(MeO)P

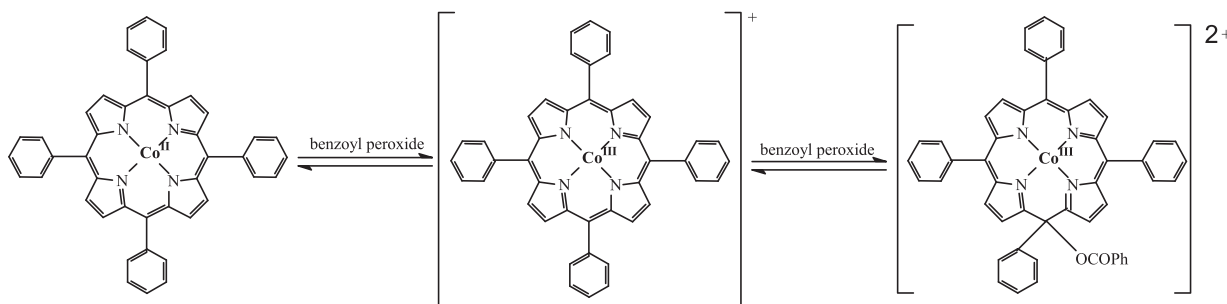
III R₁=H, R₂=OC₄H₉
Co^{II}TP(BuO)P

Results and Discussion

In order to reveal some fundamental patterns of the formation of initiating systems on the basis of cobalt porphyrins and benzoyl peroxide in chloroform and methyl methacrylate we have studied the influences of the solvent nature and the porphyrin structure.

The mechanism of interaction of Co porphyrins and benzoyl peroxide may be presented by Scheme 1.

The interaction of cobalt(II) porphyrins with benzoyl peroxide was investigated in CHCl₃ and MMA at different ratio – at equimolar quantity (1:1), in excess (1:10) and deficit (5:1) of benzoyl peroxide. In all cases the characteristic



Scheme 1. The possible mechanism of interaction of Co porphyrins with benzoyl peroxide.

spectral changes were observed (Figure 1). Two groups of well-defined isosbestic points are indicative about the two consecutive steps: the first one is the oxidation of Co^{2+} to Co^{3+} (Figure 1a),^[14,15] and the second one is the formation of Co^{3+} isoporphyrin (Figure 1b).^[16-18] In the ^1H NMR spectrum of Co^{3+} isoporphyrin in CDCl_3 the β -pyrrole protons appear at 6.36, 6.62, 7.04, 7.24 ppm; the phenyl protons appear in the 7.4 – 7.8 ppm region.^[15] The kinetic curves for the process of $\text{CoTP}(\text{BuO})\text{P}$ oxidation by benzoyl peroxide are presented in Figure 2. The character of the observed curves corresponds to the two consecutive reactions.^[19]

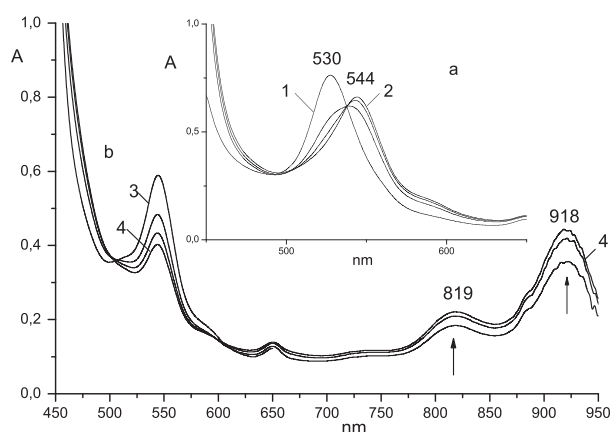


Figure 1. a) Change of the electronic absorption spectra of $\text{CoTP}(\text{BuO})\text{P}$ ($5 \cdot 10^{-5}$ mol/l) in CHCl_3 during oxidation by benzoyl peroxide ($5 \cdot 10^{-5}$ mol/l) at 25°C : 1 – $\text{Co}^{\text{II}}\text{TP}(\text{BuO})\text{P}$; 2 – $\text{Co}^{\text{II}}\text{TP}(\text{BuO})\text{P} + \text{BP}$ after 2 min; 3, 4 – $\text{Co}^{\text{III}}\text{TP}(\text{BuO})\text{P} + \text{BP}$ ($\tau = 2$ min 30 sec and 2 h 25 min).

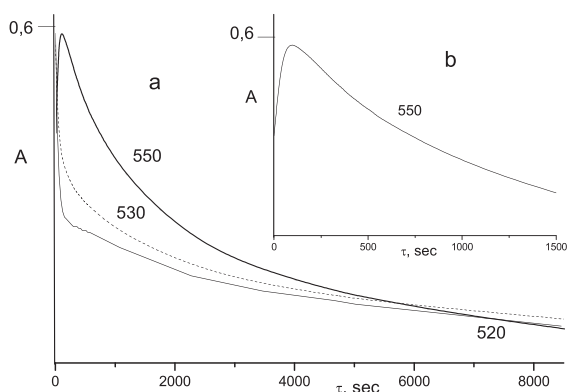


Figure 2. The kinetic curves for oxidation of $\text{CoTP}(\text{BuO})\text{P}$ ($5 \cdot 10^{-5}$ mol/l) by benzoyl peroxide ($5 \cdot 10^{-5}$ mol/l) at 25°C (a). Insert (b) shows enlarged initial part of the kinetic curve.

The character of changes in the observed electronic absorption spectra is similar for all studied complexes (CoTPP , $\text{CoTP}(\text{MeO})\text{P}$, $\text{CoTP}(\text{BuO})\text{P}$). When Co^{III} complex is formed at the first stage, the band in the visible region exhibits a weak bathochromic shift (530 nm $\rightarrow$ 547 nm). This process is very fast. At the second stage, the intensity of the band in visible region decreases sharply, and the new long-wave bands (820 nm and 920 nm) appear. These spectral changes correspond to the formation of isoporphyrin^[16-18] on the rate-limiting stage.

The interaction between of Co^{II} porphyrins with benzoyl peroxide in methyl methacrylate was studied for the first time. Experimental data show that the oxidation of Co^{II} porphyrins in methyl methacrylate is slower than in chloroform. The character of electronic absorption spectra changes during the oxidation in MMA is similar to that in CHCl_3 (Figure 4). The oxidation of $\text{CoTP}(\text{BuO})\text{P}$ in the excess of benzoyl peroxide during 3 hours at 45°C in the presence of oxygen (Figure 3) and after nitrogen blowing (Figure 4) leads to polymerization of MMA. It was noticed, that isoporphyrin is formed in both cases. The oxidation of CoTPP and $\text{CoTP}(\text{MeO})\text{P}$ by the excess of benzoyl peroxide in the presence of oxygen for 3 hours at 45°C does not lead to formation of polymer. The polymerization of MMA in the presence of CoTPP and $\text{CoTP}(\text{MeO})\text{P}$ was observed only after several days. So the most effective initiating system is 3-butoxy substituted complex $\text{CoTP}(\text{BuO})\text{P}$ in the presence of benzoyl peroxide.

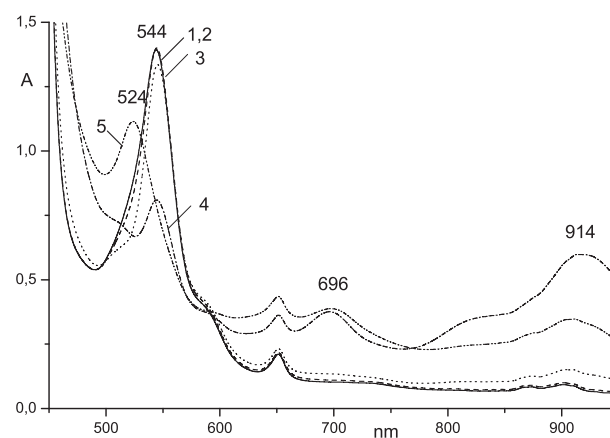


Figure 3. Changes of the electronic absorption spectra of $\text{CoTP}(\text{BuO})\text{P}$ ($5 \cdot 10^{-5}$ mol/l) during the oxidation by benzoyl peroxide ($2 \cdot 10^{-4}$ mol/l) in methyl methacrylate: 1 – $\text{CoTP}(\text{BuO})\text{P}$ in MMA at 25°C ; 2 – $\text{CoTP}(\text{BuO})\text{P}$ at 45°C ; 3 – $\text{CoTP}(\text{BuO})\text{P} + \text{BP}$ at 45°C ($\tau = 0$ min); 4 – $\text{CoTP}(\text{BuO})\text{P} + \text{BP}$ in MMA ($\tau = 30$ min) at 45°C ; 5 – $\text{CoTP}(\text{BuO})\text{P} + \text{BP}$ in MMA ($\tau = 3$ h) at 45°C .

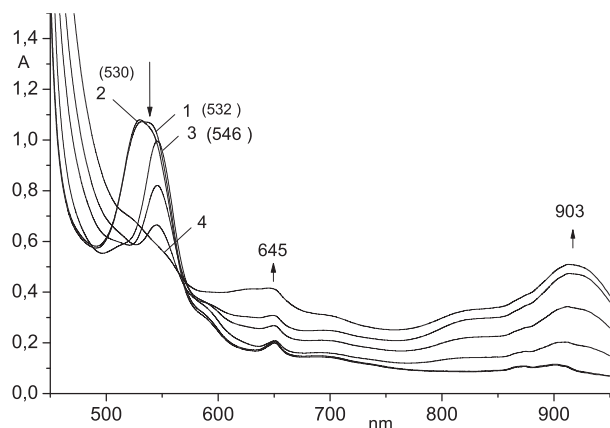


Figure 4. Changes of the electronic absorption spectra of CoTP(BuO)P ($5 \cdot 10^{-5}$ mol/l) during its oxidation by benzoyl peroxide ($2 \cdot 10^{-4}$ mol/l) in methyl methacrylate under N_2 : **1** – CoTP(BuO)P in MMA at 25°C; **2** – CoTP(BuO)P at 45°C; **3** – CoTP(BuO)P+BP at 45°C ($\tau = 0$ min); **4** – CoTP(BuO)P+BP in MMA at 45°C ($\tau = 3$ h).

Kinetic Measurements

The reaction of oxidation in an excess of benzoyl peroxide can be considered to be of the pseudo first order.^[20] The rate constants of cobalt isoporphyrin formation were calculated using Equations (1) and (2):

$$k_{obs} = \frac{2.3}{\tau} \lg \frac{C_0}{C} \quad (1)$$

$$k_v = \frac{k_{obs}}{C_{BP}} \quad (2)$$

k_{obs} – observed constant, τ – time of the reaction, C_0 and C – initial concentration of cobalt(III) porphyrin and its concentration during the process, C_{BP} – concentration of benzoyl peroxide ($\tau = 0$ min).

The dependence of $\lg(C_0/C)$ vs. τ for oxidation of Co porphyrin ($5 \cdot 10^{-5}$ mol/l) by benzoyl peroxide ($5 \cdot 10^{-4}$ mol/l) in $CHCl_3$ at 25 °C is linear (Figure 5) which is typical for the first order reactions.

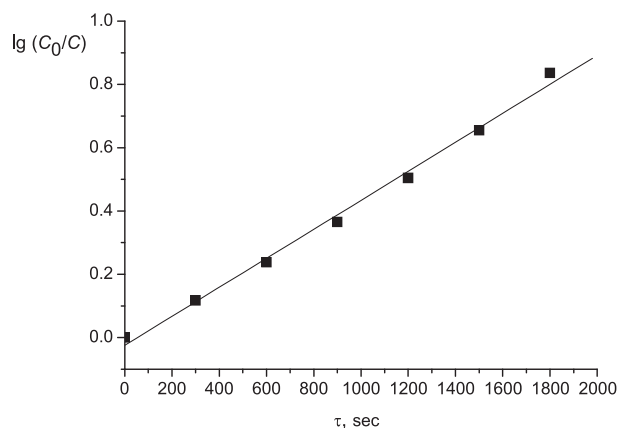


Figure 5. Dependence $\lg(C_0/C)$ vs. τ for CoTPP ($5 \cdot 10^{-5}$ mol/l) +BP ($5 \cdot 10^{-4}$ mole/l) in $CHCl_3$ at 25 °C.

Table 2. The constants of cobalt isoporphyrins formation in $CHCl_3$ ($C_{CoP} : C_{BP} = 1:10$).

Cobalt porphyrin	$k_{obs} \cdot 10^4, \text{sec}^{-1}$	$k_v, \text{mol}^{-1} \cdot \text{sec}^{-1}$
CoTPP	10.4 ± 0.5	2.0 ± 0.1
CoTP(MeO)P	18.3 ± 1.1	3.7 ± 0.1
CoTP(BuO)P	8.2 ± 0.5	1.6 ± 0.08

Conclusions

The oxidation of cobalt complexes of 5,10,15,20-tetraphenylporphyrin, 5,10,15,20-tetra(4-methoxyphenyl)porphyrin, 5,10,15,20-tetra(3-butoxyphenyl)porphyrin by benzoyl peroxide in chloroform and methyl methacrylate was studied using spectrophotometric method. These processes consist of two stages: the first is oxidation of Co^{II} to Co^{III} , and the second is the formation of Co^{III} isoporphyrin. Change of chloroform by methyl methacrylate leads only to the slower reaction process. The most effective initiating system consists of 5,10,15,20-tetra(3-butoxyphenyl)porphyrin and benzoyl peroxide.

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