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A cobalt(II)–porphyrin complex as a regulator of cross-linking radical copolymerization

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The additions of a porphyrin cobalt complex diminished the rate of cross-linking copolymerization of ethylene glycol dimethacrylate (EGDMA) and styrene, shifted the autoacceleration process towards higher degrees of monomer conversions and modified the structure and properties of resulting cross-linked copolymers owing to catalytic chain transfer reaction, catalytic inhibition reaction and chain regeneration as a result of the reversible breakdown of a Co–C bond.

Control over the kinetics of cross-linking radical polymerization and copolymerization of multifunctional vinyl compounds and the structure of the resulting polymer networks is a complex problem. The cross-linking polymerization is characterised by autoacceleration early in the reaction due to the hindered mobility of growing radicals attached to hyperbranched macromolecules and microgel particles bearing pendant vinyl groups.[1,2] As a result, intramolecular cyclization causes the polymer–monomer microphase separation.[3] The vitrification of the reaction medium adds complexity to copolymerization reaction and copolymer structure development. It gives rise to diffusion control over the propagation chain constant and leads to a rate autoretardation. At this stage, distinctions between comonomers in mobility can lead to a deviation of local comonomer concentrations in the vicinity of growing macroradicals from global concentrations and thereby affect the copolymer composition.[4] As a consequence, the resulting polymeric networks are always heterogeneous. This structural heterogeneity has a dramatic impact on the properties of the final cross-linked materials.[1,5]

Here, we propose the control of cross-linking radical copolymerization by the addition of the Co^{II} tetramethyl hematoporphyrin IX complex [$Co^{II}P$], which is known as a catalytic chain transfer agent and a catalytic inhibitor in the linear radical polymerization of methyl methacrylate[6] and styrene.[7] The capabilities of $Co^{II}P$ as a regulator of cross-linking copolymerization are evident from a comparison of conventional and $Co^{II}P$-controlled copolymerization of ethylene glycol dimethacrylate (EGDMA) and styrene with respect to the kinetics of copolymerization and the structure and properties of the resulting copolymers.

Commercial styrene was distilled in a vacuum after the removal of an inhibitor by a 10% NaOH solution. EGDMA (Aldrich) was used without further purification. The copolymerizations were conducted at 60 °C in glass ampoules sealed in a vacuum after freeze–pump–thaw cycles. The concentrations of $Co^{II}P$ were 3.5×10^{-4} and 4.1×10^{-3} mol dm^{-3}. The concentration of an initiator (AIBN) was 6.4×10^{-3} mol dm^{-3}.

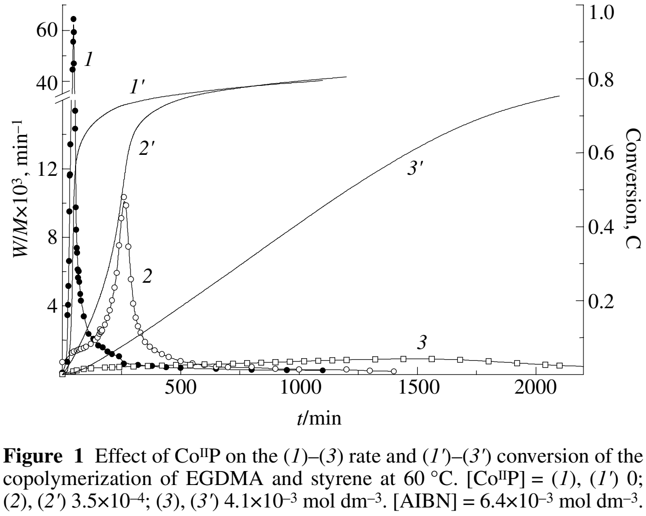


Figure 1 Effect of $Co^{II}P$ on the (*1*)–(*3*) rate and (*1′*)–(*3′*) conversion of the copolymerization of EGDMA and styrene at 60 °C. [$Co^{II}P$] = (*1*), (*1′*) 0; (*2*), (*2′*) 3.5×10^{-4}; (*3*), (*3′*) 4.1×10^{-3} mol dm^{-3}. [AIBN] = 6.4×10^{-3} mol dm^{-3}.

The copolymerization kinetics of EGDMA and styrene was monitored by isothermal calorimetry. An equimolar monomer mixture feed was used. The computations of C=C bond conversion and copolymerization rate were described elsewhere.[8] The final conversions of C=C bonds in EGDMA and styrene copolymers were determined by IR spectroscopy.[9] The structure of copolymers was probed by the sorption of benzene and water vapour at atmospheric pressure and 20 °C. The mechanical properties of the copolymers were investigated in an uniaxial compression mode. A modernised Hepplers consistometer and cylindrical copolymer samples 5 mm in length and 3 mm in diameter were used to obtain the stress–strain plots.

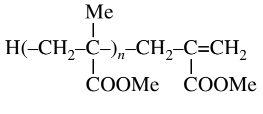
Figure 1 shows a significant difference in the kinetics between the conventional copolymerization of EGDMA and styrene and the copolymerization in the presence of $Co^{II}P$. On adding 3.5×10^{-4} mol dm^{-3} $Co^{II}P$, the beginning of a gel effect shifts to higher conversion and the rate of copolymerization at a maximum is lowered by a factor of 6. An increase in the concentration of the additive to 4.1×10^{-3} mol dm^{-3} eliminates the gel effect almost completely. Thus, $Co^{II}P$ can be used as a regulator of cross-linking radical copolymerization.

To understand how $Co^{II}P$ affects cross-linking radical copolymerization of EGDMA and styrene, data on the impact of $Co^{II}P$ upon linear homopolymerizations of methyl methacrylate (MMA) and styrene should be taken into account. It is known[6] that in the course of MMA polymerization $Co^{II}P$ catalyses chain transfer reaction from a tertiary propagating radical to a monomer *via* the consecutive steps

$$R_n^* + Co^{II}P \longrightarrow P_n + HCo^{III}P, \qquad (1)$$

$$HCo^{III}P + M \longrightarrow Co^{II}P + R_1^* \qquad (2)$$

producing unsaturated macromonomers P_n[10]



$$H(-CH_2-\underset{COOMe}{\overset{Me}{C}}-)_n-CH_2-\underset{COOMe}{C}=CH_2 \qquad (A)$$

In styrene polymerization, the chain transfer coefficient from a secondary propagating radical to a monomer is 10 times smaller than that in MMA polymerization.[7] This decrease in chain transfer coefficient was attributed to the concurrent catalytic inhibition reaction

$$HCo^{III}P + R_m^* \longrightarrow P_m + Co^{II}P \qquad (3)$$

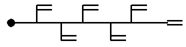
and to the reversible cobalt–carbon bond formation

$$R_n^* + Co^{II}P \rightleftharpoons R_n\text{–}Co^{III}P. \qquad (4)$$

The reversible dissociation of a cobalt–carbon bond can result in polystyrene growing chain regeneration,[7] which gives rise to a ‘living’ polymerization mechanism.[11–13]

By analogy with the linear homopolymerization of MMA and styrene, a $Co^{II}P$ additive will reduce the rate of cross-linking copolymerization of EGDMA and styrene because of reactions

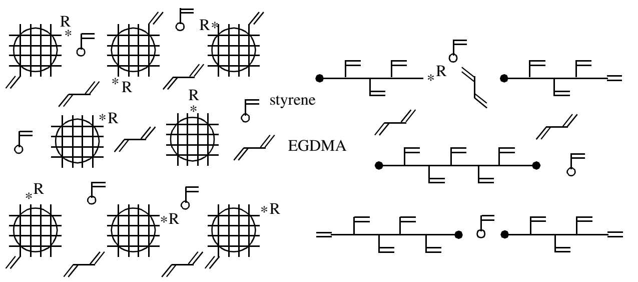
(3) and (4), and such a decrease was observed experimentally (Figure 1). At the same time, there is one more pathway unique to the polymerization of dimethacrylates whereby $\mathrm{Co^{II}P}$ transforms the kinetics of crosslinking copolymerization and the development of a polymer network structure. Unlike MMA, the polymerization and copolymerization of dimethacrylates produce multifunctional oligomers bearing pendant reactive methacrylic groups



(B)

as an alternative to macromonomers A.

Note that the multifunctional oligomers of type B are intermediate species synthesised *in situ* as a result of catalytic chain transfer reactions (1) and (2) on the way from the initial dimethacrylates to the resulting cross-linked copolymer. They radically alter the course of reaction in comparison to conventional copolymerization. The conventional reaction proceed through the formation and growing of microgel particles (C)



(C) (D)

Because of a hindered mobility of radicals R* attached to microgel particles, the rate of termination reaction diminishes, the gel effect arises, and the resulting cross-linked copolymer becomes heterogeneous. In the presence of $\mathrm{Co^{II}P}$, the reaction medium has another structure (D) because catalytic chain transfer reaction prevents the formation of large microgel particles, suppresses the gel effect and produces a network copolymer of more homogeneous structure.

The suggestion that catalytic chain transfer reactions (1) and (2) restrict the growth of copolymer chains producing mainly terminal C=C bonds of methacrylic groups was supported through the determination of the concentration of residual double bonds in resulting copolymers by calorimetry and IR spectroscopy. The total concentration of C=C bonds in the copolymers obtained in the presence of 4.1×10^{-3} mol dm^{-3} $\mathrm{Co^{II}P}$ determined from IR spectra was 10% higher than the value determined by calori-metry. This is because IR spectroscopy, contrary to calorimetry, detects not only C=C bond consumption in copolymerization but also the production of new terminal C=C bonds in oligomers B as a result of catalytic chain transfer reaction. In accordance with these data, the average concentration of methacrylic units in intermediate oligomers of type B may be evaluated as ~10%. The direct evidence for the formation of multifunctional oligo-mers B was obtained by the analysis of soluble products of the copolymerization of EGDMA and styrene in the presence of 20% of dimethylformamide. According to IR spectra, the products contain a lot of pendant methacrylic groups. The average molecular weights of these multifunctional oligomers were determined to be $M_n = 2270$ and $M_w = 14350$ by gel permeation chromatography using polystyrene as a standard.

A considerable disadvantage of the conventional cross-linking polymerization is the incompleteness of shrinkage (contraction). The problem is that during the polymerization of multifunctional methacrylates the rate of volume shrinkage is lower than the rate of polymerization because the chemical reaction requires merely the single oligomer and growing macroradical to be mobile whereas shrinkage requires a concerted movement of the entire reactive medium.[14] The incomplete shrinkage gives rise to undesirable results such as internal stresses, microporosity, micro-cracks, and poor mechanical properties.[1] The additives of $\mathrm{Co^{II}P}$ solve the problem through the suppression of a gel effect and the increasing mobility of a reactive medium. The equalization of the rates of copolymerization and volume relaxation can lead to profound changes in the structure and properties of resulting copolymers.

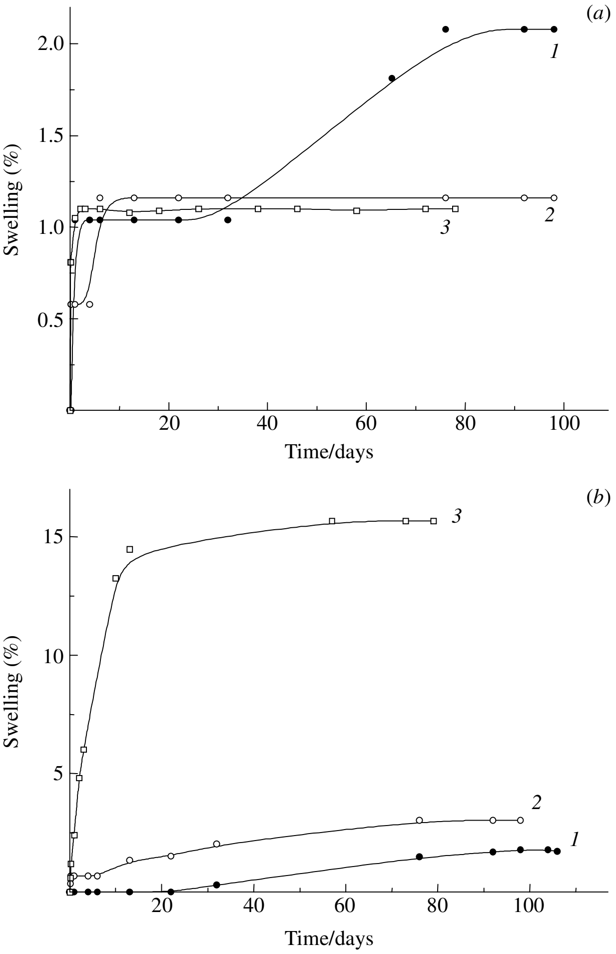


Figure 2 The kinetics of (*a*) water and (*b*) benzene vapour sorption by EGDMA and styrene copolymers (*1*) I, (*2*) II, (*3*) III. The final conversions of C=C bonds in copolymers I, II and III are 88.5, 88.3 and 89%, respectively.

We found that the sorption and mechanical properties of EGDMA and styrene copolymers obtained in the presence of 3.5×10^{-4} and of 4.1×10^{-3} mol dm^{-3} $\mathrm{Co^{II}P}$ (samples II and III)

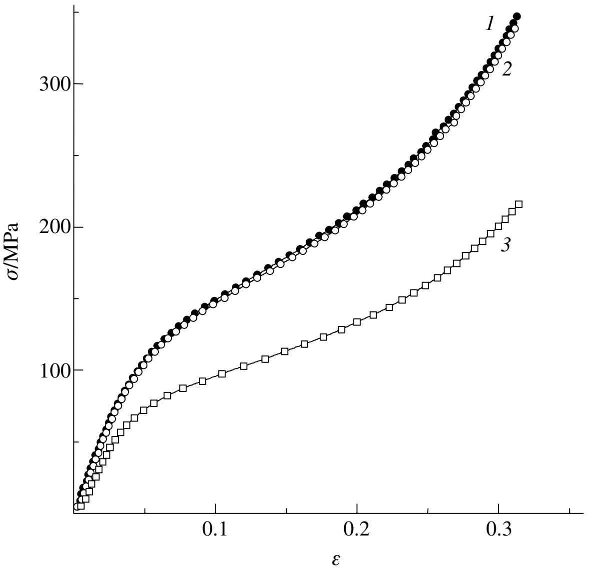
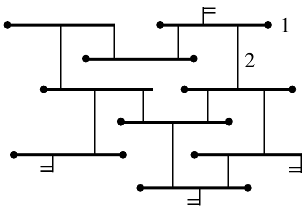


Figure 3 The plots of strain *vs.* stress for EGDMA and styrene copolymers (*1*) I, (*2*) II, (*3*) III. The final conversions of C=C bonds in copolymers I, II and III are 88.5, 88.3 and 89%, respectively.

differ significantly from the properties of a conventional copolymer (sample I). It is known that the C=C bond conversion is of fundamental importance to the properties of network polymers. Because of this, we tried to match the copolymers with equal C=C bond conversions. For this purpose, the low conversions of copolymers I and II were brought up to the conversion of copolymer III by a stepwise change in temperature from 70 to 120° under IR-spectroscopic control.

Figure 2(*a*) shows that the sorption of water by a conventional copolymer of EGDMA and styrene (I) occurs in two successive steps. We believe that the first step of sorption is determined by the formation of H-bonds between ester groups and H_2O molecules and the second step, by water condensation in the micropores. The absence of this step of water sorption in case of copolymers II and III confirms that $\mathrm{Co^{II}P}$ contributes to the development of a more homogeneous copolymer structure in comparison to conventional copolymerization.

Figure 2(*b*) shows benzene sorption curves. The sorption rate increases in copolymers arranged in a sequence I, II, III. The maximal sorption levels increase in the same sequence. Thus, the copolymers obtained in the presence of $\mathrm{Co^{II}P}$ have higher molecular mobility and elasticity as compared to a conventional copolymer. This is obviously a result of the fragmentation of copolymer chains due to catalytic chain transfer and catalytic chain inhibition reactions and formation of a specific network of short styrene–methacrylate chains (1) cross-linked by oligomer spacers (2)



Note that a variation in $\mathrm{Co^{II}P}$ concentration allows us to vary the number and size of chains (1) over a wide range and thereby to control the contributions from components (1) and (2) to copolymer properties.

An example of the effect of $\mathrm{Co^{II}P}$ concentration on the stress–strain properties of copolymers is presented in Figure 3. The addition of 3.5×10^{-4} mol dm^{-3} $\mathrm{Co^{II}P}$ has almost no effect on the properties. An increase in $\mathrm{Co^{II}P}$ concentration up to 4.1×10^{-3} mol dm^{-3} significantly diminishes the modulus of elasticity and forced elasticity. These data confirm the conclusion based on benzene sorption [Figure 2(*b*)] that a $\mathrm{Co^{II}P}$ additive is favourable to the production of more elastic copolymer networks.

The copolymerization of triethylene glycol dimethacrylate and styrene was also studied. The influence of $\mathrm{Co^{II}P}$ on the kinetics of copolymerization and the properties of the resulting copolymers were generally the same as in the case of the EGDMA–styrene system.

Thus, $\mathrm{Co^{II}P}$ is a promising regulator of cross-linking radical copolymerization and network structure development. It can be used as an effective tool for macromolecular design.

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