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Macromolecular design of the network structure of copolymers of ethylene glycol dimethacrylate with methyl methacrylate using the catalytic chain transfer reaction

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Abstract: It has been shown that catalytic chain transfer reaction is an effective instrument for the macromolecular design of the network structure of copolymers of ethylene glycol dimethacrylate with methyl methacrylate. Copolymers of various macromolecular architectures - from networks to soluble branched low-molecular-weight oligomers - have been produced using cobalt porphyrin as catalytic chain transfer agent. The influence of cobalt porphyrin on the kinetics of copolymerization, structure and properties of final copolymers has been studied.

Introduction

In the cross-linking radical homo- and copolymerization of multifunctional monomers, the growth of linear chains bearing pendant double bonds is accompanied by the reactions of primary cyclization, intra- and intermolecular cross-linking of polymer chains that lead to network structure development [1-6]. Regulation of the contribution of these reactions in the general conversion of C=C bonds allows to control the process of network structure formation in the cross-linking radical polymerization of multifunctional monomers and to synthesize polymers of various macromolecular architectures: from networks to soluble branched low-molecular-weight polymers. This is possible owing to the restriction of polymer chain growth. Conventional chain transfer agents, e.g., thiols were usually used for this purpose [7-10]. They have a chain transfer constant in the range 10^{-2} - 10^{1}, i.e., they have to be used in high concentrations. Thus, 1 - 2 mol-% of dodecanethiol is required to synthesize soluble branched copolymers of MMA with diacrylate. To avoid network structure formation, the concentration of multifunctional comonomer was only 0,5 - 2 mol-% [10]. A more efficient method for limiting polymer chain growth is based on the use of catalytic chain transfer agents, e.g., macrocycles of cobalt (II) [10-12]. The catalytic chain transfer constant C_s is equal to 10^{2} - 10^{5}, therefore, its appropriate concentration is less than 10^{-2} mol/l.

We propose to control network structure development during the copolymerization of ethylene glycol dimethacrylate (EGDMA) with methyl methacrylate (MMA) by addition of the Co^{II} tetramethylhematoporphyrin-IX complex ($Co^{II}P$) as a catalytic chain

transfer agent [11-16]. The efficiency of such an approach is demonstrated by comparative studies of the copolymerization kinetics of EGDMA with MMA in the absence and in the presence of $Co^{II}P$, and by the structural properties of final copolymers. Since the catalytic chain transfer agent is neither consumed during polymerization nor added to polymeric chains, the structural-kinetic effects observed in cross-linking radical copolymerization in the presence of $Co^{II}P$ is a result of network structure transformation.

Experimental part

EGDMA (Aldrich) was used as received. MMA was distilled in vacuum prior to reaction. The copolymerization was carried out in glass ampoules sealed in vacuum after freeze-pump-thaw cycles. The kinetics of copolymerization of EGDMA with MMA in bulk was studied by precision isothermal microcalorimetry using a Calve calorimeter. An equimolar mixture of the monomers (per double bond) was used in the copolymerization. $Co^{II}P$ concentrations were varied from $5{,}4\cdot10^{-5}$ to $2\cdot10^{-2}$ mol/l. The concentration of the initiator AIBN was $6{,}3\cdot10^{-3}$ mol/l.

Structural investigations of final copolymers were carried out by a diffusive-sorbate probing method (in water and benzene vapours at atmospheric pressure and 20°C) and by measuring their mechanical properties in a uniaxial compression mode at very low rates of deformation ($\approx 10^{-4}$ s^{-1}). Stress-strain plots were obtained using a high-precision dynamometer of a lever type designed to study small samples (≈ 0.1 g). Cylindrical copolymer samples 5 mm in length and 3 mm in diameter were used. Since the properties of network polymers depend on the conversion of double bonds [2], we studied copolymers with similar C=C bond conversions for comparison. The copolymers of low conversion were annealed by a stepwise change of temperature from 70 to 120°C in vacuum. The conversion of double bonds in final copolymers was determined by densitometry.

The low-molecular-weight oligomers were analyzed by gel permeation chromatography (GPC) using a Waters (410-996) gel chromatograph equipped with a differential refractometer and a photometric detector with a diode ruler. Measurements were made using Silacorb SPH 600 (250×4 mm) columns. Optically pure tetrahydrofuran (THF) was used as an eluent. The elution rate was 0,3 ml/min at 35°C. To calculate the molecular weights of oligomers, polystyrene calibration curves were used.

Results and discussion

Fig. 1 shows the dependences of the reduced rate W/[M] of the copolymerization of EGDMA with MMA versus total conversion of comonomers under conventional conditions and in the presence of various amounts of $Co^{II}P$. The kinetics of copolymerization (curve 1) obeys the common law of cross-linking radical polymerization, and the reaction occurs through autoacceleration (gel effect) and autoretardation stages. Its origin is the microheterogeneous mechanism of cross-linking copolymerization accompanied by the formation of branched macromolecules and microgel particles bearing pendant methacrylic groups [1-6]. As a result, elementary reactions become diffusion-controlled and the effective rate constants of chain propagation (k_p) and chain termination (k_t) decrease with growing diffusive hindrance [3,6].

The addition of $Co^{II}P$ results in a pronounced decrease of the copolymerization rate, in a shift of the beginning of the gel effect to higher conversion, and in a change in

the shape of the kinetic curves (Fig. 1, curves 2 - 5). A powerful kinetic effect is already observed at $5{,}4\cdot10^{-5}$ mol/l $Co^{II}P$ (curve 2). Thus, the maximum rate of copolymerization decreased approximately by a factor of 1/7. The copolymerization reaction proceeded at constant rate up to high conversion (≈ 60%) in the presence of $3{,}9\cdot10^{-3}$ mol/l $Co^{II}P$ (curve 5).

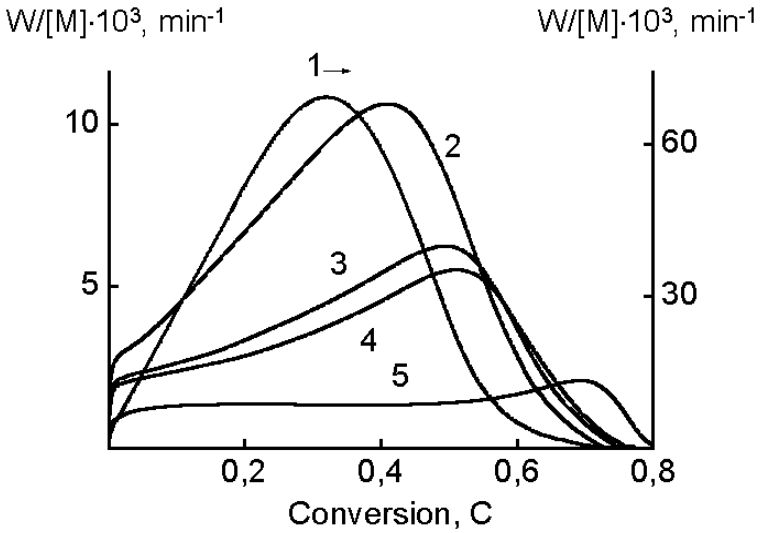


Fig. 1. Kinetics of copolymerization of EGDMA with MMA in bulk in the absence (1) and presence of $5{,}4\cdot10^{-5}$ (2), $3{,}4\cdot10^{-4}$ (3), $5\cdot10^{-4}$ (4) and $3{,}9\cdot10^{-3}$ (5) mol/l $Co^{II}P$. [AIBN] = $6{,}3\cdot10^{-3}$ mol/l. *T* = 60°C. W/[M] is the reduced rate. Curve 1 corresponds to the right axis

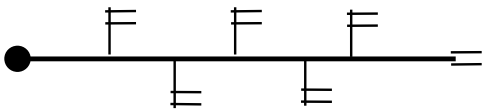
This indicates the restriction of polymeric chain growth owing to catalytic chain transfer reaction (CCTR) [11-16]. A two-step catalytic mechanism has been proposed for the chain transfer from the growing radical R_n^* to the monomer

$$R_n^* + Co^{II}P \longrightarrow P_n + HCo^{III}P$$

$$HCo^{III}P + M \longrightarrow Co^{II}P + R_1^*$$

where R_n^* and R_1^* are polymer and monomer radicals, respectively, M is the monomer, $HCo^{III}P$ is hydride, P_n is oligomer or polymer with a terminal double bond, formed as a result of abstraction of the hydrogen atom from the methyl groups of the C-tertiary radical R_n^*.

The kinetic curves changed in the presence of $Co^{II}P$ because of the *in situ* formation of low-molecular-weight intermediates having pendant methacrylic groups [14-16].



These intermediates change the course of cross-linking radical polymerization in comparison to conventional polymerization proceeding via microgel formation. The formation of short polymeric chains promotes the suppression of cyclization and cross-linking reactions leading to the development of a network structure. It results in the growth of diffusive mobility of reagents and a decrease of diffusion control of chain termination. As a consequence, the polymerization rate diminishes with an

increase of k_t. Furthermore, these changes cause a decrease in the microheterogeneity of cross-linking radical copolymerization and lead to the formation of more homogeneous polymers [15,16].

Cross-linking can be completely inhibited under copolymerization of EGDMA with MMA in the presence of $Co^{II}P$ in the aprotic solvent dimethylformamide (DMF). Apparently, the polar solvent prevents the aggregation of polymer chains. As a result, soluble low-molecular-weight oligomers of EGDMA with MMA are formed. After reaction had finished due to initiator consumption, the soluble low-molecular-weight oligomers of EGDMA with MMA were isolated and characterized by GPC. According to gravimetry and GPC, the yield of oligomers was 35 - 40%. This can be improved by addition of a new portion of initiator to continue the copolymerization reaction. However, with increasing monomer conversion the efficiency of CCTR diminishes. It is caused by a decrease of the values of C_s with increasing viscosity of the reaction medium [17,18].

Fig. 2 demonstrates the molecular weight distribution of the copolymerization product of EGDMA with MMA. As can be seen, the molecular weight distribution shows a bimodal pattern.

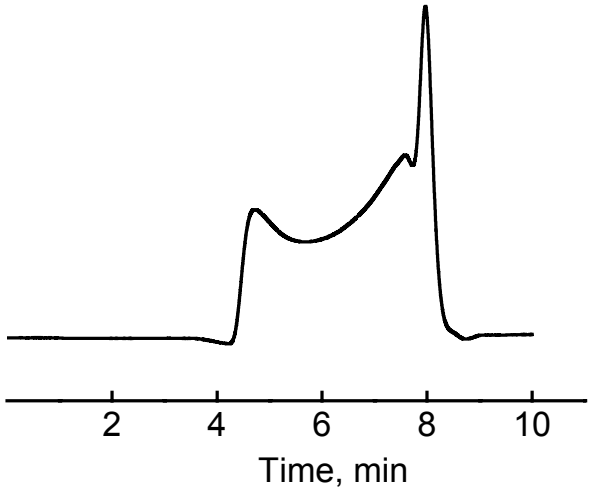


Fig. 2. Chromatogram of the copolymerization product of EGDMA with MMA obtained in the presence of $2 \cdot 10^{-2}$ mol/l $Co^{II}P$. [AIBN] = $6{,}3 \cdot 10^{-3}$ mol/l. [DMF] = 20 wt.-%. T = 60°C. The narrow peak is residual EGDMA

Molecular weight characteristics of synthesized oligomers are given in Tab. 1. The influence of DMF concentration on the molecular weight characteristics of oligomers of EGDMA with MMA is insignificant (Tab. 1).

Tab. 1. Molecular weight characteristics of oligomers of EGDMA with MMA depending on the reaction conditions

Oligomer	$[Co^{II}P] \cdot 10^2$ in mol/l	[DMF] in wt.-%	M_n	M_w	M_w/M_n
EGDMA-MMA	2	20	1060	5260	5
EGDMA-MMA	2	40	940	4490	4,8

After removal of residual comonomers, the oligomers of EGDMA with MMA were characterized by IR spectroscopy. In IR spectra of the oligomers the intensity of the absorption bands related to stretching vibrations of double bonds at 1638 cm^{-1} is high. Therefore, it was concluded that the studied oligomers contain a large amount of pendant methacrylic groups. According to a rough estimation, the content was ≈30%. Because of the high numbers of pendant methacrylic groups, they can be used as precursors for the synthesis of new polymers: star or hyperbranched systems, graft and block-copolymers. Using various comonomers (styrene, methacrylates and acrylates) makes it possible to extend the range of low-molecular-weight oligomers on the basis of dimethacrylates. Thus, soluble oligomers of dimethacrylates can be produced with structures ranging from linear to super-branched ones modified by comonomer units allocated in polymeric chains depending on the reactivity ratios r_1 and r_2 [15,19,20].

In the cross-linking homo- and copolymerization of multifunctional monomers, the reaction kinetics is closely associated with network structure formation [2,3,6]. Therefore, it should be expected that the additives of $Co^{II}P$ affect the resulting copolymer structure on topological and morphological levels. To test this assumption, a comparative structural study of the copolymers obtained by bulk copolymerization in the absence and in the presence of $Co^{II}P$ was carried out.

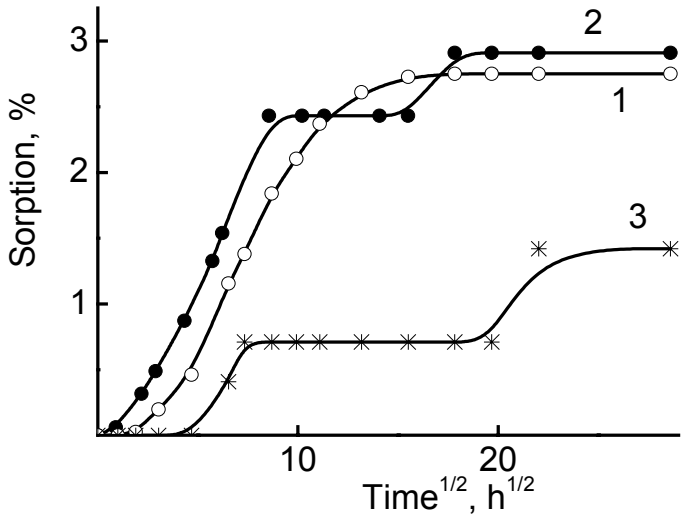


Fig. 3. The kinetics of water vapour sorption by copolymers of EGDMA with MMA obtained in the absence (1) and in the presence of $3{,}4 \cdot 10^{-4}$ (2), and $3{,}9 \cdot 10^{-3}$ (3) mol/l $Co^{II}P$, respectively

Sorption curves of benzene and water can characterize the structure of copolymers. The values of limiting sorption by copolymers and of the diffusion rate depend essentially on the thermodynamic affinity and size of sorbate molecules. In the case of water, the diffusive-sorbate properties of copolymers are defined by both structural defects, i.e., microfractures due to internal stresses, and the formation of H-bonds with ester groups [2,5]. Water sorption by a copolymer of EGDMA and MMA obtained in the absence of $Co^{II}P$ is a one-stage process (Fig. 3, curve 1). Sorption of water by copolymers of EGDMA and MMA obtained in the presence of $Co^{II}P$ is a two-stage process. In a copolymer obtained in the presence of $3{,}9 \cdot 10^{-3}$ mol/l $Co^{II}P$, a decrease of sorption capacity and a limiting level of sorption of 1,5% were observed. The latter indicates that the formed copolymer has fewer defects. This can be caused by less

volume shrinkage owing to equalization of the rates of copolymerization and volume relaxation. Thus, addition of $Co^{II}P$ solves the important problem of cross-linking radical copolymerization of multifunctional monomers, namely, the incomplete shrinkage that gives rise to undesirable results such as internal stresses, micro-porosity, and micro-cracks [2,3,5,6].

Fig. 4 shows the curves of benzene sorption by the copolymers of EGDMA with MMA. The amount of benzene absorbed by the copolymer obtained in the presence of $3{,}9\cdot10^{-3}$ mol/l $Co^{II}P$ is much higher than that obtained without CCTR agent.

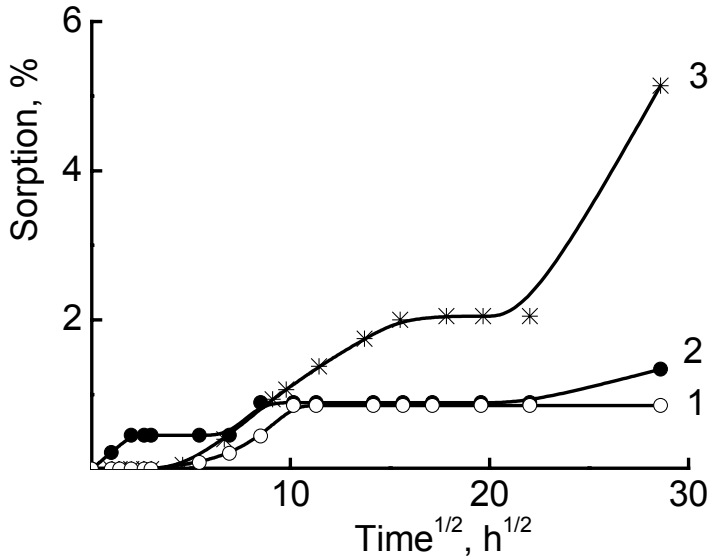


Fig. 4. The kinetics of benzene vapour sorption by copolymers of EGDMA with MMA obtained in the absence (1) and in the presence of $3{,}4\cdot10^{-4}$ (2), and $3{,}9\cdot10^{-3}$ (3) mol/l $Co^{II}P$, respectively

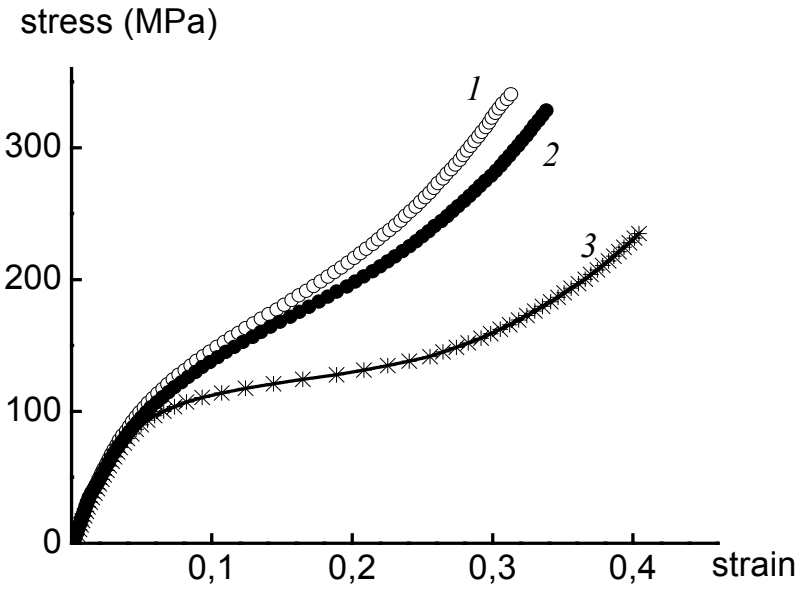


Fig. 5. Stress-strain curves for copolymers of EGDMA with MMA. *T* = 20°C. The curve numbers correspond to the copolymer sample numbers given in Tab. 2

Apparently, a large amount of defects like 'free ends' is produced under copolymerization in the presence of $Co^{II}P$. Therefore, the effective density of the polymer network is decreased and its swelling is raised according to the theory of Flory and Rener. The copolymer network formed owing to the fragmentation of polymeric chains under CCTR has a higher molecular mobility and elasticity as compared to a conventional copolymer.

Fig. 5 shows the stress-strain plots for copolymers of EGDMA with MMA obtained in the absence and in the presence of $Co^{II}P$. Deformation of test samples is completely reversible and, at a certain stress, the relaxation transition starts. As a result, the copolymer transforms from a glass state with the modulus of elasticity E_1 into a forced elasticity state with modulus $E_2 << E_1$. E_2 characterizes the contribution of the chemical network better than E_1 [2]. The values of E_1 and E_2 were determined from the slopes of the linear parts of the curves (Tab. 2).

Tab. 2. Physico-mechanical characteristics of copolymers of EGDMA with MMA (prepared in bulk) obtained in the absence and presence of $Co^{II}P$. Conversion of C=C bonds is 84,5% (1), 85% (2), and 84,9% (3), respectively

Samples	$[Co^{II}P]$ in mol/l	$E_1 \cdot 10^{-2}$ in MPa	$E_2 \cdot 10^{-2}$ in MPa	E_1/E_2
1	-	22,4	3,51	6,55
2	$3{,}4 \cdot 10^{-4}$	21,4	5,59	3,82
3	$3{,}9 \cdot 10^{-3}$	20,95	1,55	13,5

The addition of $Co^{II}P$ affects the mechanical properties of the copolymers of EGDMA with MMA. The value of E_1 for copolymers obtained in the presence of $Co^{II}P$ is decreased compared to conventional one. The E_2 value of copolymer obtained in the presence of $3{,}9 \cdot 10^{-3}$ mol/l $Co^{II}P$ is significantly diminished. Apparently, the change of mechanical properties of copolymer of EGDMA with MMA is caused by the appearance of a great deal of 'free ends' due to CCTR and formation of a polymer network consisting of short polymeric methacrylate chains cross-linked by oligomer units. These data confirm the conclusion, based on benzene sorption, that $Co^{II}P$ is favourable to the production of more elastic copolymer networks.

Conclusion

It has been shown that CCTR is an effective instrument for macromolecular design. The addition of $Co^{II}P$ allows modifying the network structure of copolymers of EGDMA with MMA significantly. The gelation process was completely suppressed under copolymerization of EGDMA with MMA in the polar solvent DMF. As a result, soluble low-molecular-weight oligomers were produced. The latter having pendant methacrylic groups can be used as precursors for synthesis of new polymers of different architectures. The addition of $Co^{II}P$ affects the kinetics of copolymerization and structural properties of final copolymers essentially.

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