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High-efficiency approach to control network structure formation in the cross-linking radical copolymerization of ethylene glycol dimethacrylate

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A high-efficiency approach has been proposed to control network structure formation in the cross-linking radical copolymerization of ethylene glycol dimethacrylate using cobalt porphyrin, which limits polymeric chain growth owing to catalytic chain transfer, and dodecyl methacrylate as a comonomer.

In the cross-linking radical polymerization 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 the formation of branched macromolecules and microgel particles.[1] The regulation of the contribution of these reactions in general conversion of C=C bonds allows one to control the process of network structure formation in the cross-linking radical polymerization of multifunctional monomers and to synthesise polymers of various macromolecular architectures: from network ones to soluble branched low-molecular-weight polymers.

Here we propose the control of reactions leading to network structure formation under the copolymerization of ethylene glycol dimethacrylate (EGDMA) by the additions of the Co^{II} tetramethylhematoporphyrin-IX complex ($Co^{II}P$) as a catalytic chain-transfer agent limiting the polymer chain growth.[2] Unlike the conventional chain transfer agent[†] used for this purpose,[3] the $Co^{II}P$ neither consume during polymerization nor introduce in polymeric chains and its concentration is less than 0.01 mol dm^{-3}. Therefore, the structural-kinetic effect observed in cross-linking radical copolymerization in the presence of $Co^{II}P$ is a result of network structure transformation. Under short polymeric chains formation the addition of a comonomer, *i.e.*, dodecyl methacrylate (DDMA) with the bulky alkyl substituents $C_{12}H_{25}$, which produce additional steric hindrances for the interaction of a polymeric radical with pendant C=C bonds is favourable for the restriction of cyclization and cross-linking reactions. The efficiency of such an approach is demonstrated in comparative studies of the copolymerization kinetics of EGDMA with DDMA in the absence and presence of $Co^{II}P$.

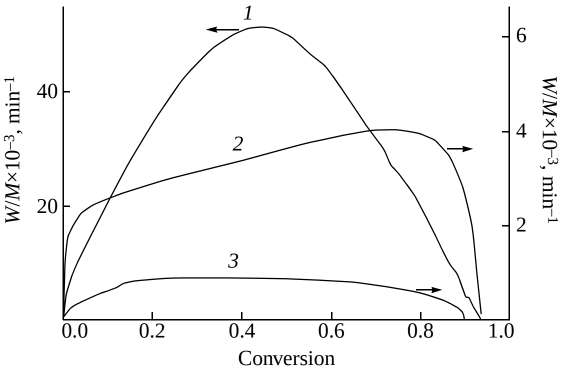

Figure 1 Kinetics of copolymerization of EGDMA with DDMA (1:1) in (*1*) the absence and (*2*) presence of 4.8×10^{-4}, (*3*) 3.9×10^{-3} mol dm^{-3} $Co^{II}P$. [AIBN] = 6.3×10^{-3} mol dm^{-3}. T = 60 °C. C is conversion.

EGDMA and DDMA (Aldrich) were used. The copolymerization was carried out in glass ampoules sealed in a vacuum after freeze–pump–thaw cycles. The kinetics of bulk copolymerization of EGDMA with DDMA was studied by precision isotermal microcalorimetry using Calve calorimeters. An equimolar mixture of the monomers (per double bond) was used in the copolymerization. The $Co^{II}P$ concentrations were varied from 4.8×10^{-4} to 3×10^{-2} mol dm^{-3}. The concentration of the initiator AIBN was 6.3×10^{-3} mol dm^{-3}. The calculation methods of double bond conversion and the copolymerization rates are described elsewhere.[1(*f*),4] The structural-physics research of final copolymers was 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 an uniaxial compression mode at very low rates of deformation ($\dot{\varepsilon} = 1\times10^{-4}$ s^{-1}). The stress–strain plots were obtained using a high-precision dynamometer of a lever type designated 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,[1(*b*)] 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 under a vacuum. The conversion of double bonds in final copolymers was determined by densitometry.

Figure 1 shows the kinetic curves of EGDMA with DDMA copolymerization 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 subsequent 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]

According to isothermal calorimetry and IR spectroscopy, the conversion of double bonds in the copolymer of EGDMA with DDMA is ~90%. Only 10% of C=C bonds remain unreacted, perhaps, owing to the freezing of the molecular mobility of reagents. In the case of EGDMA homopolymerization, the limiting conversion of C=C bonds was no higher than 55% under similar conditions.[2(*f*)] Thus, the DDMA units introduced into a polymeric chain promote the increase of polymer network mobility and effective reactivity of pendant methacrylic groups (internal plastification) despite of possible steric restrictions of polymeric chains growth due to a shielding effect of bulky alkyl substituents of DDMA.

Figure 1 (curves *2*, *3*) shows that the addition of $Co^{II}P$ results in a pronounced decrease in the rates of copolymerization and in a change in the shape of kinetic curves. This indicates the restriction of polymeric chain growth in the presence of $Co^{II}P$ owing to catalytic chain transfer reactions (CCTR).[2] A powerful kinetic effect is observed at 4.8×10^{-4} mol dm^{-3} $Co^{II}P$ (Figure 1, curve *2*). The influence of $Co^{II}P$ on the kinetics of EGDMA homopolymerization is much less pronounced.[2(*f*)] The high efficiency of CCTR is apparently caused by DDMA addition as

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[†] As conventional chain transfer agents, thiols having a chain transfer constant in the range 10^{-2}–10^{1} (the catalytic chain transfer constant is $C_s = 10^2$–10^5) were used. Consequently, high concentrations of thiols are required to significantly reduce the molecular weight of the polymers. Thus, to synthesise soluble branched copolymers of MMA with diacrylate the dodecanethiol content of 1–2 mol% was used.[3(*c*)] To inhibit the network structure formation, the concentration of a multifunctional comonomer was limited by 0.5–2 mol%.

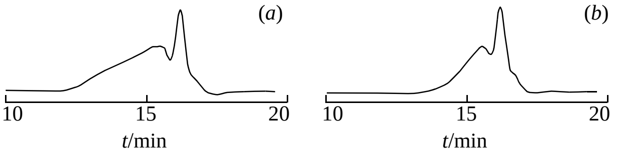

Figure 2 Chromatograms of the products of copolymerization of EGDMA with DDMA obtained in the presence of (*a*) 1×10^{-2} and (*b*) 3×10^{-2} mol dm^{-3} $\mathrm{Co^{II}P}$. [AIBN] = 6.3×10^{-3} mol dm^{-3}. [DMF] = 20 wt%. T = 60 °C.

a comonomer despite the catalytic chain transfer constant C_s varies in a number of linear alkyl methacrylates according to the equation $C_s k_p \eta^\alpha \approx$ const,[5] where k_p is the propagation rate coefficient, η is the viscosity of the reaction medium, and α = 0.5–1.

The kinetic curves changed in the presence of $\mathrm{Co^{II}P}$ because of the *in situ* formation of low-molecular-weight intermediates having pendant methacrylic groups.[2(*b*),(*e*),(*f*)] These intermediates change the course of cross-linking radical polymerization in comparison to conventional polymerization *via* microgel formation. The cyclization and cross-linking reactions are partially or completely suppressed by CCTR. As a result, the formation and growth of microgel particles are limited.

The shielding effect of long alkyl substituents in DDMA promotes this change, too. Under short polymer chain formation, the $C_{12}H_{25}$ alkyl groups of DDMA produce additional steric hindrances to interact the growing the polymeric radical with pendant C=C bonds impeding the reactions of cyclization and cross-linking of polymer chains. The combination of these factors results in the suppression of a gel effect[‡] and in a decrease in the microheterogeneity of cross-linking radical copolymerization.

Under the bulk copolymerization of EGDMA with DDMA using high concentrations of $\mathrm{Co^{II}P}$, the network structure formation was not suppressed completely; it was only restricted. Thus, the EGDMA–DDMA copolymer obtained by bulk copolymerization in the presence of 1×10^{-2} mol dm^{-3} $\mathrm{Co^{II}P}$ is a slightly cross-linked insoluble copolymer rather than a monolithic polymer body. However, it is possible in the polymerization of EGDMA with DDMA in the presence of $\mathrm{Co^{II}P}$ in the aprotic solvent dimethylformamide (DMF). In this case, the soluble low-molecular-weight oligomers of EGDMA with DDMA are formed. Thus, the network structure formation processes are completely suppressed under the copolymerization of EGDMA with DDMA in the presence of catalytic chain transfer in a polar solvent, prevented the aggregation of polymer chains.

After reaction has finished due to initiator consumption, the soluble low-molecular-weight oligomers of EGDMA with DDMA were isolated and characterised by GPC and IR spectroscopy. Figure 2 demonstrates the molecular weight distributions of EGDMA with DDMA copolymerization products obtained at different $\mathrm{Co^{II}P}$ concentrations. Their molecular weight characteristics are given in Table 1. To calculate the molecular weights of oligomers, polystyrene calibration curves were used. A Waters (410–996) gel chromatograph equipped with Silacorb SPH 600 (250×4 mm) and Lichrospher 500 columns was used for GPC analysis. Optically pure THF was used as an eluent. The elution rate was 3 ml min^{-1} at 25 °C.

A broad maximum in the chromatograms was attributed to the copolymerization product of EGDMA with DDMA. With increasing $\mathrm{Co^{II}P}$ concentration, the molecular weight characteristics of EGDMA with DDMA oligomers diminished. Thus, an increase in the concentration of $\mathrm{Co^{II}P}$ by a factor of 3 resulted in a decrease in the polydispersity index M_w/M_n of synthesised oligomers from 2 to 1.3.

It is of interest to compare GPC data for the products of EGDMA homopolymerization and copolymerization with DDMA synthesised under similar conditions (Table 1). In the polymerization of EGDMA, oligomers with higher values of M_n and broader molecular weight distributions are produced as compared with the copolymerization of EGDMA with DDMA. This indicates an increase in the diffusion control[6] of CCTR in the polymerization of EGDMA owing to a decrease in the molecular mobility of bulky $\mathrm{Co^{II}P}$ complexes during the accumulation of a network polymer and the glass transition of the reaction medium. The decrease of the multifunctional monomer content of a mixture with DDMA up to 50 mol% can lead to a decrease in the diffusion control of CCTR and an increase in its efficiency. As a result, the polymerization products of EGDMA and DDMA with a lower molecular weight can be obtained.

Table 1 Molecular weight characteristics of EGDMA and EGDMA with DDMA oligomers depending on reaction conditions.

Oligomer	[$\mathrm{Co^{II}P}$]/ mol dm^{-3}	[DMF] (wt%)	M_n	M_w	M_w/M_n
EGDMA	1×10^{-2}	20	4060	41200	10.2
	3×10^{-2}	20	2200	3500	1.6
EGDMA–DDMA	1×10^{-2}	20	1450	2900	2.0
	3×10^{-2}	20	980	1270	1.3

The oligomers of EGDMA with DDMA were characterised by IR spectroscopy. Because of high concentrations 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,[2(*e*)] methacrylates and acrylates) enables one to extend the range of low-molecular-weight polymers on the basis of dimethacrylates. Soluble oligomers of dimethacrylates with structures ranged from linear to super branched ones modified by comonomer units allocated in polymeric chains depending on the reactivity ratios r_1 and r_2 can be produced.

In the cross-linking homo- and copolymerization of multifunctional monomers, the reaction kinetics is closely associated with network structure formation.[1(*b*)–(*f*)] Therefore, it should be expected that the additives of $\mathrm{Co^{II}P}$ affect the resulting

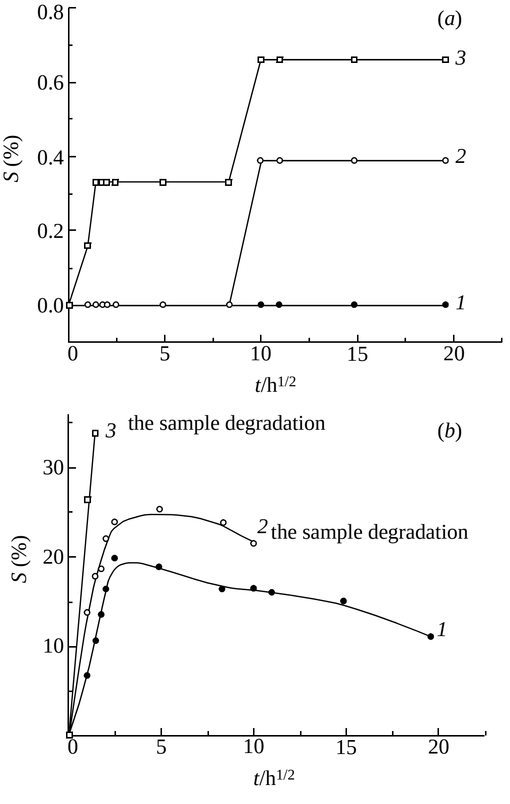

Figure 3 The kinetics of (*a*) water and (*b*) benzene vapours sorption by EGDMA–DDMA copolymers obtained (*1*) in the absence and (*2*) in the presence of 4.8×10^{-4} and (*3*) 3.9×10^{-3} mol dm^{-3} $\mathrm{Co^{II}P}$. The final conversions of C=C bonds in copolymers: (*1*) 87, (*2*) 84.8 and (3) 80%. S is the sorption.

[‡] The occurrence of a gel effect in the cross-linking radical polymerization of multifunctional monomers is caused by the network structure formation and the microheterogeneity of a reaction medium.[1(*b*)]

copolymer structure on topological and morphological levels.[1(*b*)] In this case, DDMA units statistically distributed in polymer chains, on the one hand, diminish the effective density of a network preventing chemical links formation, and, on the other hand, favour the occurrence of physical network junctions due to cooperative dipole–dipole and dispersion interactions of $C_{12}H_{25}$ groups. To test this assumption, a comparative structural-physics study of the copolymers obtained by bulk copolymerization in the absence or presence of $Co^{II}P$ was carried out.

Figure 3 shows the kinetic curves of sorption of water and benzene vapours by EGDMA and DDMA copolymers. The values of limiting sorption by copolymers and diffusion rates depend essentially on the thermodynamic affinity and size of sorbate molecules. The sorption curves of benzene and water can characterise the structure of copolymers. 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 capability of H-bonding with ester groups.[1(*e*),2(*f*)]

The EGDMA and DDMA copolymer practically does not absorb water, apparently, owing to its high hydrophobicity [Figure 3(*a*)]. However, in copolymers obtained in the presence of $Co^{II}P$, an increase of sorption capacities and a growth of the limiting levels of sorption up to 0.8% were observed. The sorption of water by the EGDMA and DDMA copolymer is a two-stage process. It is caused by the relaxation of internal stresses in a polymer matrix due to sorbate diffusion.[7]

Figure 3(*b*) shows the curves of benzene sorption by the copolymers of EGDMA with DDMA. The amount of benzene absorbed by the copolymers at the beginning of the process exceeds an equilibrium value; therefore, a part of the sorbate was removed from the copolymers (curves *1*, *2*). The sorption of benzene by the EGDMA–DDMA copolymer obtained by conventional polymerization is lower than by that obtained in the presence of $Co^{II}P$. Apparently, a large amount of defects like ‘free ends’ are produced under copolymerization in the presence of $Co^{II}P$. Therefore, the effective density of a polymer network is decreased and its swelling is raised according to the Flory and Rener theory. The EGDMA–DDMA copolymers obtained in the presence of $Co^{II}P$ degraded due to internal stresses occurred under benzene sorption.

Figure 4 shows stress–strain plots for the copolymers of EGDMA with DDMA obtained in the absence and presence of $Co^{II}P$ and a copolymer of EGDMA with styrene. 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 the modulus $E_2 << E_1$. The values of E_1 and E_2 were determined from the slopes of $\sigma = f(\varepsilon)$ curves (Table 2).

The physico-mechanical properties of the EGDMA–DDMA copolymer essentially differ from that of the EGDMA–styrene copolymer (Table 2). The value of E_1 for the EGDMA–styrene copolymer is practically 10 times greater than that for the EGDMA–DDMA copolymer. Styrene incorporated in a polymer chain as an alternating unit, neither forms the network junctions or reduces the concentration of intermolecular cross-links.[8] As a result, the EGDMA–styrene copolymer exhibits high physico-mechanical properties. Bulky alkyl substituents of DDMA prevent the formation of chemical cross-links leading to a decrease of the density of chemical network and to a change of the mechanical properties.

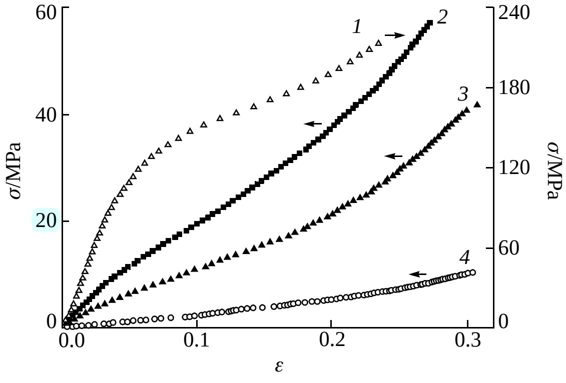

Figure 4 Stress–strain curves for EGDMA–styrene copolymers (1:1) and EGDMA–DDMA copolymers. The conversion of C=C bonds of the EGDMA–styrene copolymer is ~90%. The rate of deformation is $\dot{\varepsilon} = 1\times10^{-4}\,s^{-1}$. $T = 20$ °C. The curve numbers correspond to the polymer sample numbers presented in Table 2.

Table 2 Physico-mechanical characteristics of EGDMA–styrene and EGDMA–DDMA copolymers obtained in the absence or presence of $Co^{II}P$.

Sample	Polymer	$[Co^{II}P]$/ mol dm^{-3}	$E_1/10^{-2}$ MPa	$E_2/10^{-2}$ MPa
1	EGDMA–styrene	—	27.4	4.0
2	EGDMA–DDMA	—	2.5	1.6
3	EGDMA–DDMA	4.8×10^{-4}	1.8	0.9
4	EGDMA–DDMA	3.9×10^{-3}	—	0.24

The addition of $Co^{II}P$ leads to the further change of mechanical properties of the EGDMA–DDMA copolymer. Its origins are the appearance of a great deal of ‘free ends’ due to CCTR and the formation of a polymer network consisting of short polymeric methacrylate chains cross-linked by oligomer units. Dramatic changes in the network structure were found in the EGDMA–DDMA copolymer obtained by bulk polymerization in the presence of $Co^{II}P$ (3.9×10^{-3} mol dm^{-3}). The $Co^{II}P$ addition leads to a change of the physical state of copolymers from glass to high elasticity.

The results of this study suggest that network structure formation in the cross-linking copolymerization of EGDMA can be effectively regulated using a catalytic chain-transfer agent that limits the growth of polymeric chains and addition of comonomer with bulky alkyl substituents.

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