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Cross-linking radical polymerization of di(meth)acrylates in the presence of cobalt(II) porphyrin

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The influence of small additives of cobalt(II) porphyrin ($Co^{II}Pn$) on cross-linking radical polymerization of butane-1,4-diol dimethacrylate and its structural analog butane-1,4-diol diacrylate was studied. The kinetics of cross-linking radical polymerization of di(meth)acrylates in the absence and presence of $Co^{II}Pn$ and the diffusional sorption and physical mechanical properties of the resulting polymers were studied. Cobalt(II) porphyrin decreases substantially the polymerization rate and partially suppresses the gel effect. Diacrylate polymerization in the presence of $Co^{II}Pn$ proceeds with an induction period, whose value is determined by the content of $Co^{II}Pn$. Cobalt(II) porphyrin modifies the structure and properties of the formed cross-linked polymers. In the case of dimethacrylate, this is caused by the catalytic chain transfer reaction, whereas for diacrylate the reason is the reversible inhibition reaction.

Key words: di(meth)acrylates, cobalt(II) porphyrin, chain transfer catalysis, reversible inhibition, kinetics, structure, sorption, mechanical properties.

In cross-linking radical polymerization of polyfunctional monomers, the growth of linear chains bearing "pendant" double bonds is accompanied by intramolecular cyclization and intermolecular and intramolecular cross-linking in branched macromolecules, microgel particles, and macrogel.[1,2] As a result, special topological (small cycles) and morphological (microgel particles, grains) structures are formed in the polymer, and the cross-linked polymer formed is characterized by a high degree of structural heterogeneity.[1,2] The process of structure formation of cross-linked polymers can be controlled successfully by inhibitors of radical polymerization (nitro and nitroso compounds),[3] standard (thiols)[4,5] and catalytic (cobalt(II) macrocycles)[6—9] chain transfer agents, and agents of living radical polymerization (alkoxyamines, transition metal complexes, iniferters).[10—12] The use of them makes it possible to control the contribution of reactions of polymer chain propagation, cyclization, and cross-linking to the total conversion of C=C bonds.

Cobalt(II) macrocycles based on porphyrin, phthalocyanine, and cobaloxime demonstrate high efficiency as controlling additives. These compounds are widely used in radical polymerization of monofunctional monomers to prepare oligomers or polymers with low degree of polymerization.[13,14] The main regularities of catalytic reactions that occur in the presence of the cobalt(II) macrocycles were established for vinyl monomers of different structure.[14] The radical polymerization of vinyl monomers with addition of cobalt(II) macrocycles, in particular, $Co^{II}Pn$, is accompanied by the following reactions:

$$R_n^{\bullet} + Co^{II}Pn \rightarrow Z_n^{=} + HCo^{III}Pn, \qquad (1)$$

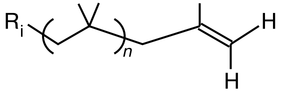
$$HCo^{III}Pn + M \rightarrow Co^{II}Pn + R_1^{\bullet}, \qquad (2)$$

$$HCo^{III}Pn + R_m^{\bullet} \rightarrow Pn_m + Co^{II}Pn, \qquad (3)$$

$$R_n^{\bullet} + Co^{II}Pn \rightleftharpoons R_n—Co^{III}Pn, \qquad (4)$$

where $R_n^{\bullet}$, $R_m^{\bullet}$, and $R_1^{\bullet}$ are radicals with degrees of polymerization of *n*, *m*, and 1, respectively; M is monomer, $HCo^{III}Pn$ is hydride, $Z_n^{=}$ is oligomer or polymer with the terminal double bond, and $R_n—Co^{III}Pn$ is an active intermediate with the C—Co bond formed due to the reaction of the $R_n^{\bullet}$ radical with $Co^{II}Pn$. Reactions (1)—(2) are known as catalytic chain transfer, and reactions (3) and (4) are catalytic and reversible inhibitions, respectively. The probability of these catalytic reactions to occur is determined by the nature of the polymeric radical interacting with the Co^{II} macrocycles.[14]

Catalytic chain transfer reaction was discovered[13] for the bulk radical polymerization of methyl methacrylate in the presence of $Co^{II}Pn$. As a result of H atom abstraction from the Me group, chain transfer to the monomer occurs, and unsaturated oligomer with different degrees of



R_i is AIBN initiator radical

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polymerization containing the terminal C=C bond is formed.

This newly formed bond differs by reactivity from the C=C bond in the initial monomer, which is indicated by the difference in frequencies of stretching vibrations of the latter in the IR spectra of methyl methacrylate and its oligomer.[15]

Chain transfer catalysis is accompanied by catalytic inhibition reaction (3). In this case, the H atom is transferred from radical to radical terminating the chain. Reaction (3) occurs during methyl methacrylate polymerization at high concentrations of cobaloximes or cobalt phthalocyanines and porphyrins. Its efficiency is substantially enhanced when the reaction is carried out in aprotic solvents (DMF, DMSO, quinoline).[14] The contribution of the catalytic inhibition reaction increases with an increase in the solvent concentration and, finally, reactions (1)—(2) are completely suppressed.

Reversible inhibition reaction (4) was discovered for the polymerization of butyl acrylate[16] and styrene.[17] The reaction of the secondary carbon-centered radical $R_n^{\bullet}$ with $Co^{II}Pn$ affords an intermediate R_n—$Co^{III}Pn$, which reversibly decomposes to regenerate polymeric radicals and $Co^{II}Pn$ in the reaction system. The Co—C bond formed by the reaction of the acrylate radical with $Co^{II}Pn$ in the R_n—$Co^{III}Pn$ intermediate is stronger than in styrene and, therefore, reaction (4) competes successfully with reactions (1)—(3).[14]

The $Co^{II}Pn$ complex turned out to be very efficient for controlling cross-linking radical (co)polymerization of dimethacrylates of different structure and formation of the network structure of (co)polymers formed.[6—9] Small additives of $Co^{II}Pn$ (10^{-4}—10^{-3} mol L^{-1}) change fundamentally the kinetics of polymerization of dimethacrylates and modify substantially the structure and properties of polymers that formed.

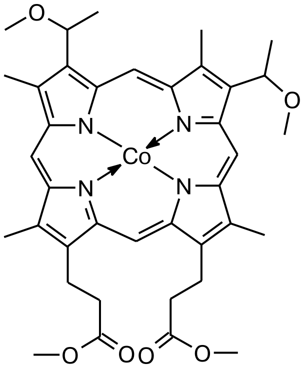
We found no literature data on an ability of $Co^{II}Pn$ to control the cross-linking radical polymerization of polyfunctional monomers of the acrylic series, which are close to dimethacrylates in reactivity but substantially differ from them by specific features of interaction of the polymeric radicals with $Co^{II}Pn$. The purpose of the present work is to study in comparison the influence of $Co^{II}Pn$ on the kinetics of cross-linking radical polymerization of polyfunctional monomers of the acrylic and methacrylic series and on the structure and properties of the cross-linked polymers formed. Butane-1,4-diol dimethacrylate (**1**) and its structural analog, *viz*., butane-1,4-diol diacrylate (**2**), were chosen as objects of the study.

$H_2C=C(Me)C(O)OCH_2CH_2CH_2CH_2O(O)C(Me)C=CH_2$ (**1**)
$H_2C=CHC(O)OCH_2CH_2CH_2CH_2O(O)CHC=CH_2$ (**2**)

Both monomers have the same length of the oligomeric block linking the reacting C=C groups. This made it possible to study specific features of cross-linking radical polymerization in the presence of $Co^{II}Pn$ caused by differences in reactivity only of the reacting methacrylate and acrylate groups.

Experimental

Monomers **1** and **2** (Aldrich) were used without additional purification. Cobalt(II) tetramethylhematoporphyrin ($Co^{II}Pn$) was used as the regulator of chain growth, whose concentration was varied in a range of 10^{-4}—10^{-3} mol L^{-1}.



Polymerization was conducted in glass ampules sealed *in vacuo* after multiple freezing and evacuation of the reaction mixture. The bulk polymerization kinetics in the absence and presence of $Co^{II}Pn$ was studied by precision isothermal calorimetry at 60 °C. The methods for calculation of the conversion of C=C bonds and reduced copolymerization rate w/[M] have been described earlier.[18] For these calculations, we used the values of specific heats of polymerization equal to 58.82 and 77.87 kJ mol^{-1} for monomers **1** and **2**, respectively. The initiator was azobis(isobutyronitrile) (AIBN, 0.1 wt.%).

The structural physical properties of polymers **1** and **2** prepared under the conditions of standard polymerization and in the presence of different $Co^{II}Pn$ additives were studied by the method of sorption of benzene and water vapors at atmospheric pressure and T = 20 °C. For sorption measurements we used cylindrical samples of polymers 5 mm in height and 3 mm in diameter with similar levels of residual unsaturation, which was achieved by annealing for additional polymerization in the stepwise regime of temperature increase from 70 to 120 °C.

The conversion of the C=C bonds in polymers **1** and **2** after annealing for additional polymerization was determined by IR spectroscopy. The bands of stretching vibrations of the C=C bond (ν = 1638 cm^{-1}) or bending vibrations of the hydrogen atoms in the $—C=CH_2$ group (ν = 812 cm^{-1}) were used as analytical bands. The band of stretching vibrations of the C=O bond (ν = 1725 cm^{-1}) was used as the internal standard. The conversion (C) of the C=C bonds in polymers **1** and **2** was calculated by the formula

$$C = 1 - (A_{C=C}/A_{C=O})_p/(A_{C=C}/A_{C=O})_m,$$

where $(A_{C=C}/A_{C=O})_p$ is the ratio of the absorbance (A) of the analytical absorption band to the absorbance of the absorption band of the C=O bond in the polymer; $(A_{C=C}/A_{C=O})_m$ is the same value measured in the initial monomers. IR spectra of polymers were recorded on a Specord IR-75 spectrophotometer (suspensions in Nujol).

Physicomechanical properties of polymers were studied under the uniaxial compression conditions using a precise lever-type dynamometer designed for studies of mini-samples (~0.1 g).

Results and Discussion

Effect of $Co^{II}Pn$ on cross-linking radical polymerization of 1. The kinetic curves of polymerization of **1** under standard conditions and in the presence of $Co^{II}Pn$ additives are shown in Fig. 1. Unlike monofunctional methacrylate, compound **1** is polymerized in the autoacceleration regime (gel effect) from the very beginning of the reaction. At $C = 22\%$ the reduced polymerization rate $w/[M]$ reaches a maximum value, and the reaction transits to the autoretardation regime. This is caused, as in the case of linear polymerization, by a decrease in the apparent rate constant of polymer chain termination (k_t) and rate constant of chain propagation (k_p) due to diffusion restrictions.[1] However, the mechanism of decreasing the diffusional mobility of the reaction medium for the polymerization of **1** differs from that in the case of vinyl monomers. The presence of the second C=C bond in monomer **1** results in the situation when the polymerization first produces polymeric chains bearing one unreacted ("pendant") C=C bond in each unit, whose further polymerization results in branched macromolecules, microgel particles, and spatially cross-linked macrogel.[1,2] The early beginning of the gel effect in cross-linking polymerization of polyfunctional monomers is caused by microheterogeneity of the reaction medium, because the reaction mixture becomes heterogeneous almost from the very beginning of its occurrence and consists of microgel particles acting as autonomous microreactors in which the polymerization occurs.[1]

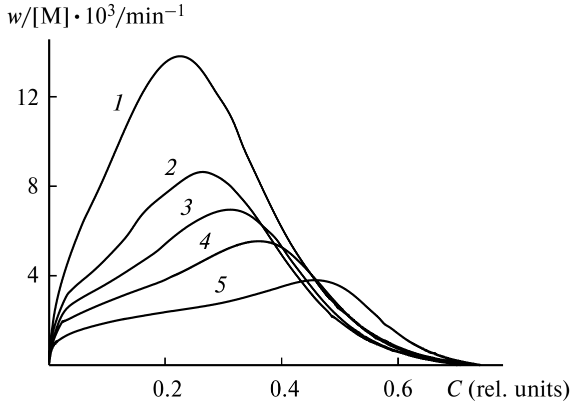


Fig. 1. Polymerization kinetics of compound **1** in the absence (*1*) and presence of $1 \cdot 10^{-4}$ (*2*), $3 \cdot 10^{-4}$ (*3*), $1 \cdot 10^{-3}$ (*4*), and $3 \cdot 10^{-3}$ *M* $Co^{II}Pn$ (*5*); $[AIBN] = 6.4 \cdot 10^{-3}$ mol L^{-1}, $T = 60$ °C.

As can be seen from the data in Fig. 1, the $Co^{II}Pn$ additives decrease the reduced polymerization rate $w/[M]$ and substantially transform the shape of the kinetic curves. An increase in the $Co^{II}Pn$ concentration results in the shift of the beginning of the gel effect to the region of high conversions, and its scales decrease substantially. In the presence of $3 \cdot 10^{-3}$ *M* $Co^{II}Pn$, the polymerization of **1** proceeds as a weakly pronounced autoacceleration followed by transition (at deep stages, $C > 45\%$) to autoretardation. The kinetics of polymerization of **1** changes in the presence of $Co^{II}Pn$ due to catalytic chain transfer reaction, which restricts the propagation of polymeric chains.

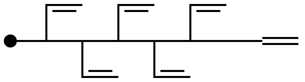
The gel effect, which takes place at $C > 30\%$ for the polymerization of **1** in the presence of $3 \cdot 10^{-3}$ *M* $Co^{II}Pn$ (see Fig. 1, curve *5*), is caused, probably, by diffusion control of the catalytic chain transfer reaction. As the conversion of the C=C bonds increases with the accumulation of the cross-linked polymer and glass transition of the reaction medium, its efficiency decreases due to a decrease in the molecular mobility of the bulky $Co^{II}Pn$ complexes. The influence of the viscosity of the reaction medium on the catalytic chain transfer constant $C_s = k_{tr}/k_p$ (k_{tr} and k_p are the rate constants of the chain transfer and propagation reactions) is indicated by the dependence[19]

$$C_s k_p \eta^{\alpha} \approx \text{const},$$

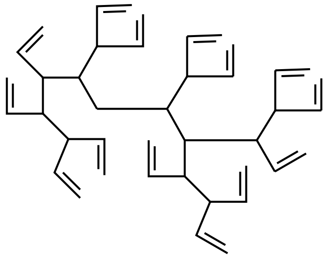
where η is viscosity, and $\alpha = 0.5—1$. According to this equation, the C_s value decreases with an increase in the viscosity of the reaction medium. For the cross-linking radical polymerization of polyfunctional monomers, the dependence of C_s on the viscosity is more pronounced, most likely, because chain transfer catalysis occurs in a highly structured reaction medium.

The gel effect during polymerization of dimethacrylates can be suppressed completely if the reaction is carried out in the presence of $\sim 10^{-2}$ *M* $Co^{II}Pn$ in aprotic solvents, for instance, in DMF.[15] The polymerization in the whole interval of conversions proceeds in the autoretardation regime when the polymer chain termination stops to be diffusion-controlled. In this case, the products of dimethacrylate polymerization are low-molecular oligomers **3** with different architecture (linear (**3a**), branched and hyperbranched macromolecules (**3b**)) and degree of polymerization *n*.

Hyperbranched macromolecules **3b** with a dendrimer-like structure and properties similar to those of dendrimers are of special scientific and practical interest. These polymers are valuable objects of investigation due to their high solubility in different organic media, high thermodynamic compatibility with polymers of different chemical nature, high sorption capacity in combination with the ability to transport low-molecular-



3a



3b

weight compounds, and low viscosity compared to that of linear polymers with the same molecular weight.[20] Thus, the reaction medium for dimethacrylate polymerization in the presence of $Co^{II}Pn$ is a solution of oligomers **3** of different architecture (linear, branched, and hyperbranched) in the initial monomer. This is a principal distinction between the structure of the reaction medium and that formed during standard cross-linking radical polymerization where microgel particles act as intermediates.

Due to the pendant C=C bonds of high reactivity, oligomers **3** are further involved in the cross-linking radical polymerization of monomer **1**. It is shown[15] that bulky macromolecular structures **3** are polymerized in the autoretardation regime with a rate lower than that of the initial monomer due, probably, to a decrease in the viscosity of the reaction medium and high mobility of short polymer chains. The high reactivity of the pendant C=C bond in oligomers **3** allows one to use them as macromonomers for design of polymer networks of a new generation.[15]

Due to the formation *in situ* of oligomers **3** with the terminal C=C bond, which was formed in reactions (1)—(2), the cross-linking radical polymerization of dimethacrylate is supplemented by an additional reaction. Radicals formed by the attack of the terminal C=C bond in oligomer **3** are characterized by the low propagation rate because of steric hindrance. The adducts formed by the interaction of the $R^{\bullet}$ radicals with the terminal C=C bond of oligomer **3** can undergo β-cleavage (elimination of the terminal unit).[14] In this case, oligomers **3** act as chain transfer agents. This reaction makes a certain contribution, most likely, to the polymerization kinetics and play an important role in restriction of processes of cross-linked structure formation.

Thus, using the catalytic chain transfer reaction, the polymerization of dimethacrylates can be ceased at the step of formation of oligomers **3**, and this can prevent the appearance and growth of microgel particles. However, for the bulk polymerization of dimethacrylates, the formation of a cross-linked structure cannot be eliminated completely because of the diffusion-controlled catalytic chain transfer reaction and a decrease in the effective C_s value. At the same time, as it is indicated by the results of studies of the polymerization kinetics of compound **1** (see Fig. 1), the development of this process can substantially be restricted. This is proved by the partial suppression of the gel effect, which is directly related to cross-linked structure formation in the cross-linking polymerization of polyfunctional monomers.

The kinetic effect caused by a $Co^{II}Pn$ additive has a general character for polymerization of polyfunctional methacrylates. This is shown by the results of studies of the polymerization kinetics of dimethacrylates of different structure in the presence of $Co^{II}Pn$.[8] However, its character and scales are determined by the structure of the initial dimethacrylate, including the conformational mobility of the oligomeric block connecting the reacting C=C groups, and physical properties of the reaction medium. In the series of dimethacrylates, ethylene glycol dimethacrylate (**4**) is closest in structure to compound **1**. Dimethacrylate **4** has the shortest oligomeric block ($—OCH_2CH_2O—$) and forms a densely cross-linked polymer with weak relaxation properties. We have shown[8] that in the presence of $3 \cdot 10^{-3}$ *M* $Co^{II}Pn$ the most part of double bonds in compound **4** are polymerized with a virtually constant rate $w/[M]$ and the maximum polymerization rate decreases by ~4 times. A similar effect caused by the same additive of $Co^{II}Pn$ is observed for the polymerization of compound **1**, *i.e.*, an elongation of the oligomeric block by two $—CH_2—$ groups exerts almost no effect on the efficiency of chain transfer catalysis. At the same time, on going to diethylene glycol dimethacrylate (**5**) when the length and flexibility of the oligomeric block change substantially, the efficiency of chain transfer catalysis increases, which is indicated by a decrease in the maximum polymerization rate in the presence of $3 \cdot 10^{-3}$ *M* $Co^{II}Pn$ more than by 8 times.[8] Unusual manifestation of chain transfer catalysis during polymerization of compound **5** is the presence of two maxima at $C = 6$ and 53% in the kinetic curves $w/[M] = f(C)$. The high efficiency of chain transfer catalysis for the polymerization of compound **5** compared to that of compounds **4** and **1** is caused, most likely, by an increase in the probability of intramolecular chain transfer to the pendant double bonds due to the high mobility of long side chains.

For the polymerization of methyl methacrylate, *viz.*, linear analog of compound **1**, in the presence of $1 \cdot 10^{-3}$ or $3 \cdot 10^{-3}$ *M* $Co^{II}Pn$, the average length of the primary polymer chains n is ~2—4 units. The n value was calculated by the formula

$$n^{-1} = w_i/w + C_s \cdot [\mathrm{Co^{II}Pn}]/[\mathrm{M}],$$

where w_i is the initiation rate* equal to $0.8 \cdot 10^{-7}$ mol L^{-1} s^{-1}, w is the polymerization rate, C_s = 2400,[14] and M is monomer. In the case of monomer **1**, the length of primary chains considerably exceeds, most likely, the calculated value because of a decrease in the apparent C_s value. For example, the numerical mean value of molecular weight M_n of oligomers **4** obtained in a DMF solution (20 wt.%) in the presence of $1 \cdot 10^{-2}$ *M* Co^{II}Pn is 4000, *i.e.*, $n \approx 20$ units.[8] This means that the bulk polymerization of compound **1** in the presence of Co^{II}Pn also produces *in situ* short-chain oligomers **3**, whose presence decreases considerably the viscosity of the reaction medium. As a consequence, the diffusion control of bimolecular chain termination and propagation decreases. This is indicated by the results of kinetic studies (see Fig. 1). Another important consequence of the formation of short polymer chains is the restriction of the primary cyclization reaction and a decrease in the probability of formation of small cycles, as well as the suppression of intra- and intermolecular cross-linking reactions leading to the nucleation and growth and microgel particles.[6,7] Thus, the catalytic chain transfer reaction restricts substantially the development of microheterogeneity of the reaction medium.

In the cross-linking radical polymerization of polyfunctional monomers, the reaction kinetics is tightly related to processes of structure formation.[1] Therefore, the change in the shape of the kinetic curves (see Fig. 1) caused by an additive of Co^{II}Pn indirectly indicates the modification of the structure of the formed cross-linked polymer. Direct proofs were obtained by the study of the structural physical properties of the cross-linked polymers synthesized under the conditions of standard radical polymerization and in the presence of Co^{II}Pn additives by diffusion sorption probing using molecules of different size and thermodynamic affinity, such as benzene (solvent) and water (not solvent).

It is known[21] that the sorption kinetics of water and benzene characterizes the structure of cross-linked polymers. In the case of water, the diffusion sorption properties of a polymer are determined by the presence of structural defects of the type of microcracks, which appear due to internal strains. Thus, water sorption can serve as a test for defectness of the formed polymer network.

The kinetic curves of water sorption by polymers **1** prepared under standard polymerization conditions and in the presence of Co^{II}Pn are shown in Fig. 2, *a*. According to the data of IR spectroscopy, all polymers **1** under study have close values of conversion of C=C bonds (*C* ~80%). This was achieved in the process of annealing for additional polymerization due to the freezing out of the molecular mobility of the pendant C=C bonds attached to the polymer framework and residual monomer. As can be seen from the data in Fig. 2, *a* (curves *2* and *3*), the Co^{II}Pn additives (~10^{-4} mol L^{-1}) insignificantly affect the diffusion rate of water molecules and the limiting levels of sorption. Polymers **1** prepared in the absence and presence of ~10^{-4} *M* Co^{II}Pn have close values of the limiting sorption levels *S* ~2%. However, an increase in the Co^{II}Pn content to $(1—3) \cdot 10^{-3}$ mol L^{-1} decreases the diffusion rate of water molecules and the limiting sorption levels (curves *4* and *5*). This results indicates, most likely, a decrease in the number of structural defects of the microcrack type in the formed cross-linked polymers. This is possible due to the alignment of the rates of chemical shrinkage and polymerization reactions, which favors a decrease in the level of internal strains.[22] Similar regulari-

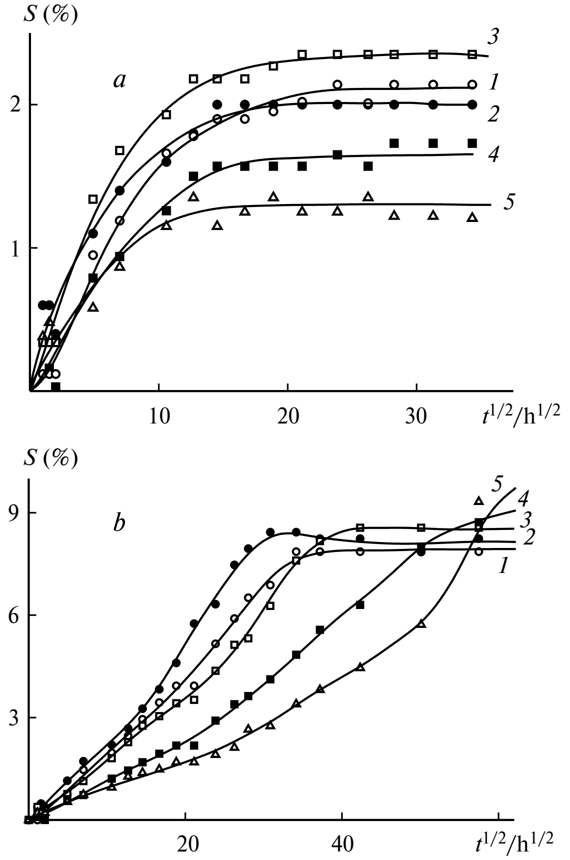


Fig. 2. Sorption kinetics of water (*a*) and benzene (*b*) vapors by polymers **1** prepared in the absence (*1*) and presence of $1 \cdot 10^{-4}$ (*2*), $3 \cdot 10^{-4}$ (*3*), $1 \cdot 10^{-3}$ (*4*), and $3 \cdot 10^{-3}$ *M* Co^{II}Pn (*5*); *T* = 20 °C; *S* is sorption. Conversion of the C=C bonds: 77.5 (*1*), 82.4 (*2*), 78.3 (*3*), 83.4 (*4*), and 80.6% (*5*).

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* The calculation of w_i was performed by the formula $w_i = 2fk_d[\mathrm{I}]$, where f is the efficiency of initiation equal to 0.5, k_d is the rate constant of initiator decomposition equal to $12 \cdot 10^{-6}$ s^{-1} at 60 °C, and [I] is the AIBN concentration.

ties were observed for water sorption by polymers **4** and **5** prepared in the presence of $Co^{II}Pn$.[8]

The kinetic curves of benzene sorption by polymers **1** are presented in Fig. 2, *b*. It is seen that the sorption curves can be classified as the pseudo-normal type. This implies that the sorption rate is determined by the diffusion rate of benzene molecules in the polymeric matrix and the sorption process itself obeys Fick´s law, *i.e.*, the polymers behave as isotropic media toward benzene diffusion and the diffusion coefficient is independent of the diffusant concentration. The diffusion coefficients D of benzene were calculated from the linear regions of the $S(t^{1/2})$ plots. According to the calculations, the polymers prepared in the absence and presence of $Co^{II}Pn$ have similar diffusion coefficients lying in the interval $(0.7—1) \cdot 10^{-9}$ cm^2 s^{-1}. These values agree with the known data on the diffusion coefficients of benzene in polymers of triethylene glycol dimethacrylate.[21]

As in the case of water sorption, the $Co^{II}Pn$ additives (~10^{-4} mol L^{-1}) exert a weak effect on the kinetics of benzene sorption by polymers **1**. The data in Fig. 2, *b* (curves *1—3*) show that polymers **1** synthesized in the absence of $Co^{II}Pn$ and in the presence of its small additives have similar diffusion rates of benzene and almost simultaneously reach the equilibrium degree of swelling, which is ~8%. In polymers **1** prepared in the presence of $(1—3) \cdot 10^{-3}$ *M* $Co^{II}Pn$ (curves *4* and *5*), the benzene diffusion rates decrease. This decrease can be caused by a more compact molecular packing of the polymer chains compared to polymer **1** synthesized under standard conditions.

Although these polymers reach sorption equilibrium much more slowly, they demonstrate a higher level of sorption. According to the Flory—Renner theory, the swelling ability of polymers **1** synthesized in the presence of high concentrations of $Co^{II}Pn$ increases due to a decrease in the effective density of the polymer network because of the formation of many defects of the type of "free ends" (C=C bonds appeared due to chain transfer catalysis) in the polymer. These regularities are also observed during benzene sorption by polymers **4** and **5** synthesized in the presence of ~$3 \cdot 10^{-3}$ *M* $Co^{II}Pn$.[8] Both polymers demonstrate an increase in the limiting sorption of the polymer as compared to the polymers prepared under standard polymerization conditions, despite differences in the kinetics of benzene sorption caused by specific features of the chemical and physical networks.

The strain—deformation diagram of polymers **1** synthesized in the absence and presence of $3 \cdot 10^{-3}$ *M* $Co^{II}Pn$ are shown in Fig. 3 (curves *1* and *2*). The deformation of the samples under study is summated by two components: elastic and forced elastic. The effective elasticity moduli E_1 were determined from the slopes of the initial regions of the strain—deformation diagrams, and the effective forced elasticity moduli E_2 were calculated from the linear regions of the diagrams in the region of deformation 10—15%. The E_1 value reflects the contribution to the properties of polymers of two networks, namely, physical and chemical. Since for $\sigma > \sigma_1$ the transition to the forced elastic state occurs by the destruction of nodes of the physical network (more exactly, due to the shortening of the lifetime of physical nodes), the E_2 value reflects the contribution of the chemical network to a considerably greater extent than E_1 does.[1]

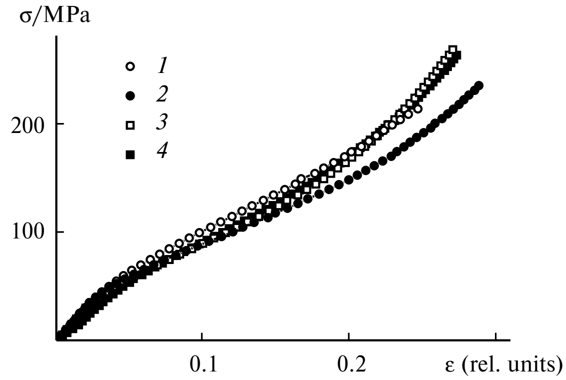

Fig. 3. Strain—deformation diagrams for polymers **1** (*1*, *2*) and **2** (*3*, *4*) prepared in the absence (*1*, *3*) and presence of $3 \cdot 10^{-3}$ *M* $Co^{II}Pn$ (*2*, *4*).

The values of elasticity E_1 and forced elasticity E_2 moduli in polymer **1** (Table 1) indicate a high rigidity of the polymer network. Polymer **1** is similar to polymer **4** by mechanical properties. During measurements of the physical mechanical properties, the annealed samples of polymers **1** are cracked and decomposed similarly to polymers **4**, indicating a high level of internal shrinkage strains, which cannot relax through volume shrinkage of the formed polymer because of high rigidity of the network. The elasticity E_1 and forced elasticity E_2 moduli in polymers **1** (see Table 1) and **4*** have close values. However, the σ_1 value, at which violations from Hooke´s law begin to occur, for polymer **1** is higher than that for polymer **4****. For the glassy densely cross-linked polymers, the σ_1 value coincides with the tensile strength.[23] In other words, polymer **1** is characterized by a higher strength than polymer **4**. This is caused, probably, by the difference in conversions of the C=C bonds. According to the data of IR spectroscopy, the conversion of the C=C bonds in polymers **1** and **4** is 77.5 and 56%, respectively.

For polymer **1** synthesized in the presence of $3 \cdot 10^{-3}$ *M* $Co^{II}Pn$, the elasticity modulus E_1 remains almost unchanged (see Table 1), *i.e.*, the level of intermolecular interactions (physical network) in the polymer remains the same as in the polymer synthesized by standard polymerization. However, it is noteworthy that the forced elasticity modulus E_2 decreases. This indicates a decrease

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* In polymer **4** $E_1 = 14.4 \cdot 10^2$ MPa, $E_2 = 6.8 \cdot 10^2$ MPa.[7]

** In polymer **4** $\sigma_1 = 32.5$ MPa.[7]

Table 1. Physical mechanical properties of polymers **1** and **2** prepared in the absence and presence of Co^{II}Pn

Polymer	Sample	Co^{II}Pn /mol L^{-1}	$E_1 \cdot 10^{-2}$	$E_2 \cdot 10^{-2}$	E_1/E_2	σ_1	σ_2	$\Delta\sigma$	ε_1	ε_2
			MPa			MPa			rel. units	
1	**I**	0	15.4	7.0	2.2	40.5	70.3	29.8	0.028	0.058
	II	$3 \cdot 10^{-3}$	15.1	5.8	2.6	43.5	61.3	17.8	0.032	0.054
2	**III**	0	15.6	6.4	2.4	34.0	49.9	15.9	0.026	0.039
	IV	$3 \cdot 10^{-3}$	11.6	7.1	1.65	44.7	59.6	14.9	0.043	0.064

in the effective value of the volume concentration of nodes in the stable network ν_{eff}, which contains not only chemical but also physical nodes with enhanced stability remained after the transition. In this case, the width of transition $\Delta\sigma$ from the glassy to forced elastic state decreases by ~1.7 times (see Table 1). The decrease in the forced elasticity modulus E_2 indicates an increase in the molecular mobility and elasticity of the polymer network formed under the chain transfer catalysis conditions. This result agrees with the data on measurements of diffusion sorption. Thus, the polymerization of compound **1** in the presence of $3 \cdot 10^{-3}$ *M* Co^{II}Pn generates a polymer network characterized by a high molecular mobility compared to that of the polymer prepared under standard polymerization conditions. This is caused by the reaction of catalytic chain transfer, which results in the fragmentation of polymer chains and formation of a special type of the polymer network consisting of short polymethacrylate chains cross-linked by oligomeric blocks.

The results of the studies suggest that, unlike the linear polymerization of methyl methacrylate in which the Co^{II}Pn additives affect only the degree of polymerization of the formed polymer, in the cross-linking radical polymerization of dimethacrylates the catalytic chain transfer reaction substantially changes the topology and morphology of the polymer network. On the one hand, shortening of the primary polymer chains decreases the probability of formation of small cycles and decreases the contribution of primary cyclization to the total conversion of the C=C bonds.[8] The latter favors a decrease in microheterogeneity at the topological level due to a decrease in the number of small cycles. On the other hand, the catalytic chain transfer reaction prevents the formation of microgel particles and development of the gel effect in processes of cross-linking radical polymerization of dimethacrylates and, as a consequence, favors the modification of the morphological structure of the cross-linked polymer.

Effect Co^{II}Pn on cross-linking radical polymerization of 2. The kinetic curves of polymerization of monomer **2** in the absence and presence of Co^{II}Pn are presented in Fig. 4. It is seen that the polymerization kinetics of **2** (curve *1*) obeys the same regularities as **1**. The polymerization of **2** proceeds in the autoacceleration—autoretardation regime due to microheterogeneity of the reaction medium.[1] A comparison of Figs 1 and 4 (curves *1*) shows that monomer **2** is polymerized with a higher rate than **1**. As a result, the conversion of the C=C bonds in polymer **2** is higher than that in polymer **1**. In fact, according to the data of calorimetry, the conversion of the C=C bonds in polymer **2** is 78%, *i.e.*, by almost 7% higher than that for the polymerization of **1**. This is caused by the fact that the volume relaxation rate is slower than the polymerization rate.[24] As a result, the free volume increases in the reaction system and, as a consequence, the mobility of polymer chains and the conversion of the C=C bonds in polymer **2** increase.

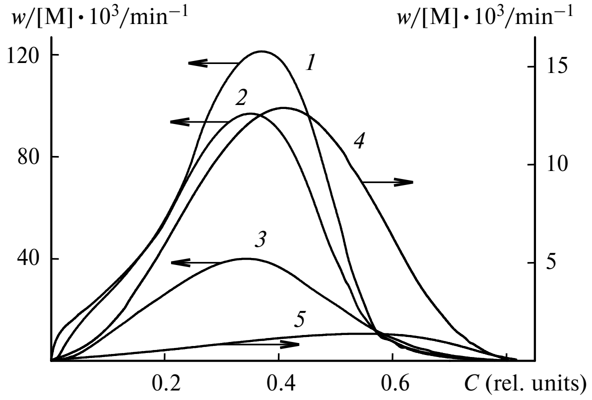

Fig. 4. Polymerization kinetics of **2** in the absence (*1*) and presence of $1 \cdot 10^{-4}$ (*2*), $3 \cdot 10^{-4}$ (*3*), $1 \cdot 10^{-3}$ (*4*), and $3 \cdot 10^{-3}$ *M* Co^{II}Pn (*5*); [AIBN] = $6.4 \cdot 10^{-3}$ mol L^{-1}; $T = 60$°C.

The polymerization of monomer **2** can be accompanied by the abstraction of hydrogen atoms from the tertiary carbon atom due to high reactivity of the growing acrylate radicals.[14] During the reaction, the newly formed polymer radicals can undergo fragmentation to form oligomers containing C=C bonds. This reaction can make some contribution, most likely, to the formation of the cross-linked structure during diacrylate polymerization.

As can be seen from the data in Fig. 4, the introduction of Co^{II}Pn substantially decreases the reduced polymerization rate w/[M] (curves *2*—*5*). To compare the polymerization processes of **1** and **2**, we used identical additives of Co^{II}Pn. A distinctive feature of the polymerization of **2** in the presence of Co^{II}Pn is the induction period, whose value is determined by the content of Co^{II}Pn. For instance, with an increase in the Co^{II}Pn concentration from $1 \cdot 10^{-3}$ to $3 \cdot 10^{-3}$ mol L^{-1}, the induction period τ increases from 40 to 97 min. The kinetic data were used to calculate the inhibition parameter γ, which represents the ratio of the initial reduced polymerization rates of **2** in the absence and presence of Co^{II}Pn. It turned out that an increase in the Co^{II}Pn concentration from $1 \cdot 10^{-3}$ to $3 \cdot 10^{-3}$ mol L^{-1} induces an increase in γ from 22 to 220, *i.e.*, by 10 times.

The induction period appears during the polymerization of **2** in the presence of Co^{II}Pn due to the reversible inhibition reaction.[14,25] The R$_n$—Co^{III}Pn intermediate formed during the induction period by the interaction of the acrylate radical with Co^{II}Pn is sufficiently stable and decomposes *via* the dissociation mechanism, which makes it possible to regenerate Co^{II}Pn along with the material and kinetic chain and, as a consequence, to enhance the degree of polymerization during the process. Unlike reversible inhibition, the chain transfer catalysis results in the polymer chain termination and the formation of "dead" polymer.

The effective concentrations of Co^{II}Pn involved in reversible inhibition were calculated from the experimental values of induction periods τ using the formula

$$\tau = [\mathrm{Co^{II}Pn}]/w_\mathrm{i}$$

(w_i is the initiation rate equal to $0.8 \cdot 10^{-7}$ mol L^{-1} s^{-1}). It turned out that they are $1.9 \cdot 10^{-4}$ and $4.4 \cdot 10^{-4}$ mol L^{-1} (19 and 15% of the initial Co^{II}Pn concentrations, respectively). However, for the polymerization of **2** in the presence of Co^{II}Pn, a powerful kinetic effect is observed, which appears as a considerable decrease in the reaction rate. For instance, for the polymerization of **2** in the presence of $3 \cdot 10^{-3}$ *M* Co^{II}Pn, the $(w/[\mathrm{M}])_\mathrm{max}$ value decreases by ~80 times, whereas for the polymerization of **1** in the presence of the same Co^{II}Pn additive this decrease is 4 times, *i.e.*, Co^{II}Pn is a more efficient regulator of polymer chain propagation for the polymerization of **2** as compared to the polymerization of **1**.

For the reversible dissociation of the cobalt—carbon bond between the terminal acrylate radical of the polymer and Co^{II}Pn, the reaction transits, probably, to the regime of living polymerization. This assumption is based on published data,[25] according to which the polymerization of acrylates in the presence of Co^{II}Pn is partially living. This is assumed to be caused by side catalytic reactions (1)—(3), which can be suppressed by the introduction of additional axial ligands into Co^{II}Pn.[26] A monodispersed sample of poly(methyl acrylate) with $M_\mathrm{w}/M_\mathrm{n} \approx 1.1$ was thus prepared.

In the case of cross-linking polymerization of polyfunctional acrylates, the main criteria of the living chain regime,[25] namely, linear plot of the numerical mean molecular weight M_n *vs.* conversion and a narrow dispersity distribution of the polymer that formed, are inappropriate because of the formation of an insoluble cross-linked polymer. The living chain regime can be concluded from other properties, for example, by a change in the kinetics of cross-linking polymerization and structural physical properties of cross-linked polymers synthesized in the presence of agents of living radical polymerization (alkoxyamines, transition metal complexes, cobalt macrocycles, and others).[25]

In the cross-linking radical polymerization of **2**, reversible inhibition reaction (4), as catalytic chain transfer reactions (1)—(2), is diffusion-controlled, *i.e.*, the molecular mobility of the bulky Co^{II}Pn complexes decreases along with the efficiency of this catalytic reaction with an increase in the conversion of the C=C bonds and viscosity of the reaction medium. As a result, at deep steps monomer **2** is polymerized, probably, in the regime of standard cross-linking polymerization.

The kinetic curves of water sorption by polymers **2** synthesized in the absence and presence of the Co^{II}Pn additives are presented in Fig. 5, *a*. According to the data

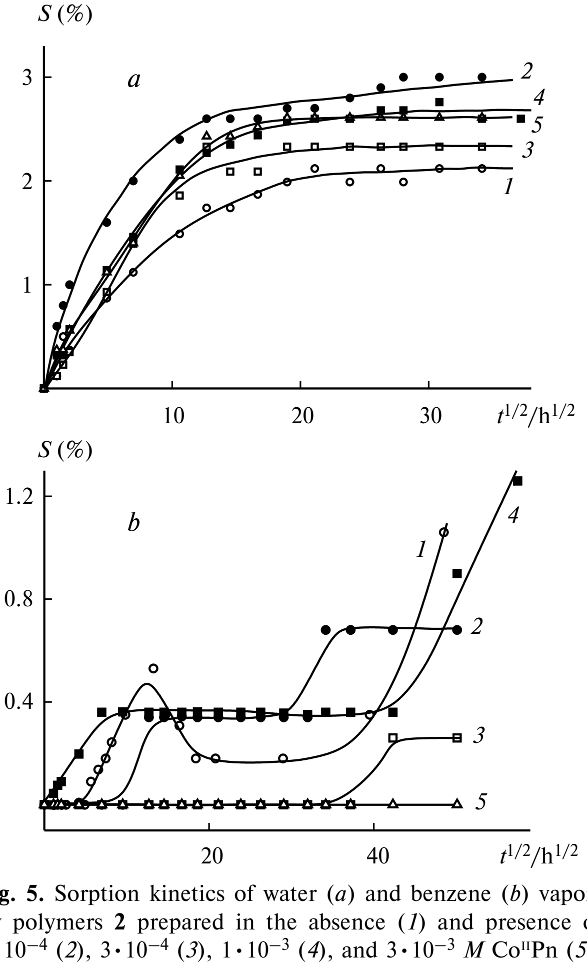

Fig. 5. Sorption kinetics of water (*a*) and benzene (*b*) vapors by polymers **2** prepared in the absence (*1*) and presence of $1 \cdot 10^{-4}$ (*2*), $3 \cdot 10^{-4}$ (*3*), $1 \cdot 10^{-3}$ (*4*), and $3 \cdot 10^{-3}$ *M* Co^{II}Pn (*5*); $T = 20$ °C; *S* is sorption. Conversion of the C=C bonds: 85.2 (*1*), 88.7 (*2*), 90.4 (*3*), 90.5 (*4*), and 90.8% (*5*).

of IR spectroscopy, the conversion of the C=C bonds in polymers **2** is ~85—90%. As can be seen from a comparison of the data in Figs 2, *a* and 5, *a* (curves *1*), polymers **1** and **2** synthesized in the absence of $\mathrm{Co^{II}Pn}$ are characterized by close values of the limiting sorption levels (S ~2%) in spite of differences in conversions of the C=C bonds. This indicates the close level of defectness determined by the number of microcracks in these polymers. However, $\mathrm{Co^{II}Pn}$ exerts a different effect on the kinetics of water sorption by polymers **2**. As follows from the data in Fig. 5, *a*, the limiting sorption of polymers **2** synthesized in the presence of $\mathrm{Co^{II}Pn}$ achieves ~2.5%, *i.e.*, defectness of the formed polymer network changes insignificantly. Thus, $\mathrm{Co^{II}Pn}$ exerts virtually no effect on the diffusional sorption properties of polymer **2**, which are caused by structural defects of the microcrack type.

The curves of benzene sorption by polymers **2** synthesized under standard polymerization conditions and in the presence of $\mathrm{Co^{II}Pn}$ additives are presented in Fig. 5, *b*. A comparison of the data in Figs 2, *b* and 5, *b* shows that polymers **2**, which were prepared in both the absence and presence of $\mathrm{Co^{II}Pn}$, sorb benzene much less efficiently than polymers **1** do. For instance, the limiting sorption values in polymers **2** range from 0 to 1.2%. Meanwhile, the limiting sorption in polymers **1** reaches ~9%. This can be caused by the difference in values of the limiting conversions of the C=C bonds in polymers **1** and **2**. It is known[1] that the properties of the cross-linked copolymers depend on the conversion of the C=C bonds.

As can be seen from the data in Fig. 5, *b*, benzene sorption by polymers **2** synthesized in the presence of $\mathrm{Co^{II}P}$ has a stepped character, which indicates the fast and slow steps of sorption. The sorption capacity of polymers **2** decreases (curves *3* and *5*) with an increase in the $\mathrm{Co^{II}Pn}$ concentration.* A prolong induction period is observed before the polymers begin to sorb benzene. It is noteworthy that polymer **2** synthesized in the presence of $3 \cdot 10^{-3}$ *M* $\mathrm{Co^{II}Pn}$ does not virtually sorb benzene (curve *5*). Under these conditions, most likely, a polymer with a high density of molecular packing is formed, which results in the sharp restriction of diffusion of benzene molecules.

The deformation curves of polymers **2** prepared in the absence and presence of $3 \cdot 10^{-3}$ *M* $\mathrm{Co^{II}Pn}$ are shown in Fig. 3 (curves *3* and *4*). The polymer network of **2**, as in the case of **1**, is characterized by high rigidity, which is indicated by the low value of the E_1 modulus and high E_2 value (see Table 1). Note that polymers **1** and **2** have similar values of the elasticity and forced elasticity moduli (see Table 1, samples **I** and **III**), despite differences in structures of the initial monomers and conversions of the C=C bonds. The $\mathrm{Co^{II}Pn}$ additives decrease the E_1 elasticity modulus and insignificantly increase the E_2 modulus for polymer **2**. Since the transition from the glassy to forced elastic state occurs by the destruction of nodes of the physical network, it can be assumed that in these polymers the lifetime of nodes of the physical network is shorter than that in standard polymer **2**. This means that the physical network in polymer **2** prepared in the presence of $\mathrm{Co^{II}Pn}$ is less stable. It is most likely that the $\mathrm{Co^{II}Pn}$ additives to the polymerization of **2** favor the formation of such a structure that provides a decrease in the level of intermolecular interactions and favorable conditions for the formation of the chemical network and an increase in the concentration of chemical nodes. The σ_1 value is higher in polymer **2** synthesized in the presence of $\mathrm{Co^{II}Pn}$, and the transition from Hooke´s region is observed at a greater deformation (see Table 1). In this case, the width $\Delta\sigma$ for the transition from the glassy to forced elastic state changes insignificantly. Therefore, $\mathrm{Co^{II}Pn}$ affects the physical mechanical and diffusional sorption properties of polymer **2**. The modifying effect is determined by the $\mathrm{Co^{II}Pn}$ content in the reaction system.

Thus, $\mathrm{Co^{II}Pn}$ is an efficient tool for controlling the cross-linking radical polymerization of polyfunctional monomers of different chemical nature and for macromolecular design of the structure of formed polymers. Small $\mathrm{Co^{II}Pn}$ additives (10^{-4}—10^{-3} mol L^{-1}) make it possible to vary the polymerization rate of these monomers in wide limits and modify the structure of formed cross-linked polymers and their properties, which are related, first of all, to the molecular mobility. This provides new challenges for preparation of polymeric materials with enhanced molecular mobility and relaxation ability.

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* The exception is polymer **2** synthesized in the presence of $1 \cdot 10^{-3}$ *M* $\mathrm{Co^{II}Pn}$.

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