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COMPENSATORY METHOD FOR THE SYNTHESIS OF CHELATING POLYMERIC LIGANDS BASED ON STYRENE AND 5-METHYL-5-HEXENE-2,4-DIONE AS A WAY TO INCREASE THE EFFICIENCY OF MACROINITIATORS OF THE β-DIKETONATE TYPE

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Polymeric chelating ligands based on styrene and unsaturated β-diketone 5-methyl-5-hexene-2,4-dione (MHD) were prepared by radical copolymerization initiated by benzoyl peroxide in benzene solution at the volume ratios of monomers styrene:MHD=1:30 and 1:10. In this case, β-diketone was added to the system by conventional (simultaneous) and compensatory (equal portions at conversions of 0, 5, and 10%) methods. The resulting products were studied by IR and ^{1}H NMR spectroscopies. It has been shown that macrochelates obtained on the basis of such ligands differ in their structure and as a consequence in their macroinitiating ability in the grafting of vinyl monomers. Polymeric ligands synthesized at the ratio of 1:10, regardless of the preparation method, form mixed-ligand complexes in the subsequent complexation reaction with cobalt(II) acetate, which exhibit weak activity in styrene grafting and are not effective in the case of methyl methacrylate. The use of a small amount of MHD (1:30) in combination with the compensatory synthesis method leads to the predominant formation of intramolecular complexes of the β-diketonate type, which are more active macroinitiators in the graft polymerization of styrene and methyl methacrylate than those obtained by the traditional simultaneous method of adding MHD.

Keywords: styrene, unsaturated β-diketone, copolymerization, chelation, polymeric β-diketonate, macroinitiator.

Introduction

Macroinitiators (MIs) are widely used for the modification of polymeric materials to obtain graft block copolymers or homopolymers with a branched structure [1]. An indisputable advantage of their use in comparison with other methods of grafting is the ability to control the number of initiating centers, which allows regulating the frequency and number of grafted chains. This factor directly affects the physical, chemical, and mechanical properties of polymeric materials.

It was shown in our previous studies [2−4] that polymers containing covalently bound β-diketonates of some metals in the chain are effective MIs, which allows preparing grafted homo- and copolymers with a branched structure and a number of useful physicochemical characteristics. The initiating role

in this case belongs to the β-diketonate cycle. Obtaining such MIs is possible in two ways. The first method consists in the copolymerization of vinyl monomers (styrene, methyl methacrylate (MMA)) with unsaturated β-diketonates having a double bond in the ligand. Moreover, the latter participate in polymerization as monomers and initiators simultaneously (inimers). The most promising inimer is cobalt(II) 5-methyl-5-hexene-2,4-dionate (MHD−Co), whose double bond is conjugated with the chelate ring [3,4] (Scheme 1).
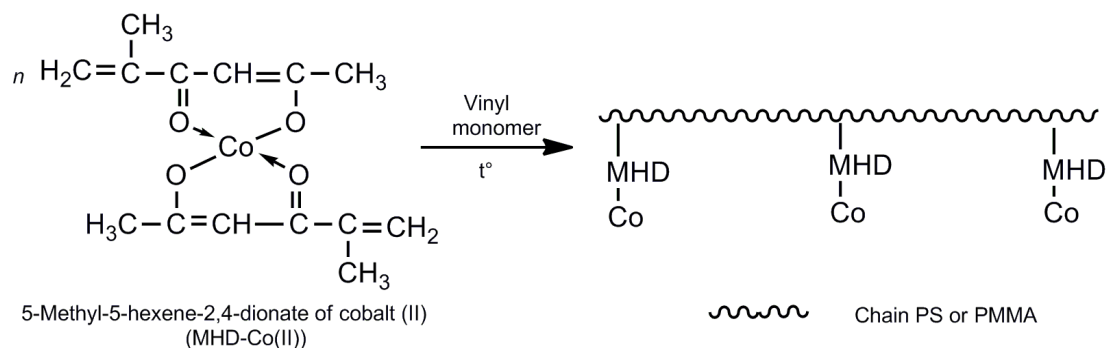
A detailed study of this synthesis method revealed a number of process features that lead to a decrease in the efficiency of MIs. Firstly, it is impossible to use inimer concentrations greater than $1 \cdot 10^{-2}$ mol/l, since a strong inhibitory effect is observed at large amounts. It is associated with the

5-Methyl-5-hexene-2,4-dionate of cobalt (II)
(MHD-Co(II))

Chain PS or PMMA

Scheme 1. Synthesis of β-diketonate-type MIs by copolymerization of a chelate monomer

formation of irreversible complexes between the growing radicals and the metal atom. This leads to a limitation of the amount of β-diketonate groups in MIs (less than 1%). Second, the β-diketonate groups are unevenly distributed along the polymer chain. It has been shown that the amount of MHD-Co incorporated into the polymer reaches 60% with respect to the initial value at a conversion of 5−10% and then does not change with an increase in conversion up to 25% [4]. In addition, it is not possible to keep all chelate groups active, because some of them can graft side chains already at the stage of MIs synthesis and not participate in the subsequent grafting.

To eliminate these drawbacks, another method was developed for the synthesis of β-diketonate-type MIs, which includes two stages [5]. At the first stage, a chelating ligand was prepared by copolymerization of 5-methyl-5-hexene-2,4-dione (MHD) with styrene (Scheme 2, stage 1). At the second stage, a macrochelate was obtained by the complex formation reaction of the polymer ligand with a metal salt (Scheme 2, stage 2). This method made it possible to increase the number of initiating groups in the

polymer and completely eliminate the participation of β-diketonate groups in the grafting of side chains at the stage of MIs synthesis.

However, studies of the grafting process with the participation of such MIs showed that despite the different amount of metal in the MI, they initiated grafting at similar rates. This indicated that chelate centers were formed in limited amounts, and the rest of the metal was in the composition of metal complexes of the non-chelate type, which are not capable of initiating grafting. We assumed that this is due to the uneven distribution of chelating groups along the chain: the resulting macroligand is enriched in β-diketone, which is quickly exhausted from the system, and its units are located mainly at the beginning of the chain. These considerations are based on a large difference in the values of the copolymerization constants of styrene and MHD ($r_{St}=0.09$; and $r_{MGD}=1.70$) [6].

To solve this problem, a compensation method is used in macromolecular chemistry [7], the essence of which is the steady batch dosing of a more active comonomer (MHD in our case) during copolymerization. The activity of any MI, based on

Stage I - obtaining of polymer ligand

5-Methyl-5-hexene-2,4-dion (MHD)
enol form
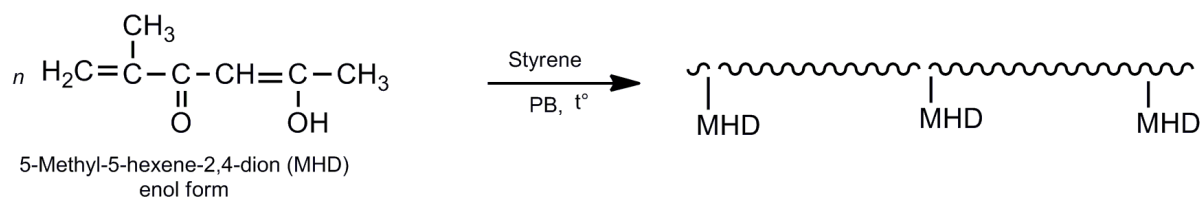
Stage II - complexation
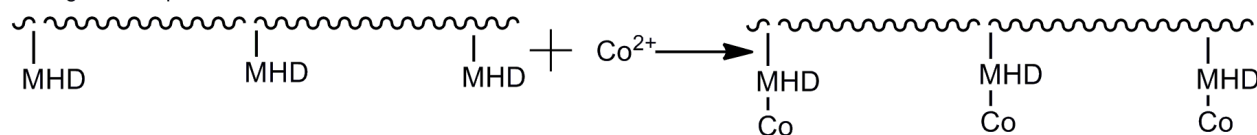
Scheme 2. Two-stage synthesis of β-diketonate-type MIs by complexation

general concepts, is determined by the number of initiating centers and the uniformity of their distribution in the polymer chain. In the case of MI of the β-diketonate type, this can be realized in two following ways: by increasing the concentration of β-diketone in the initial mixture with styrene, and by the dosed addition of a more active comonomer (MHD) during the copolymerization process. The combination of these two approaches can eventually lead to a higher metal content in the polymer and as a consequence to a higher initiating activity of such MI.

In connection with the above, the aim of this work was to optimize the procedure for the synthesis of β-diketonate MIs obtained by the method of complexation by increasing the concentration of β-diketonate comonomer in the initial mixture and using a compensation approach to obtain a chelating ligand.

Experimental

Reagents and research methods

5-Methyl-5-hexene-2,4-dione was synthesized according to the method described elsewhere [6]. Monomers (styrene and MMA) manufactured by Sigma-Aldrich with a purity of ≥99% were used after preliminary purification from the inhibitor and double distillation in vacuum. Solvents (benzene, 1,4-dioxane, and ethanol) were purified according to standard procedures.

The kinetics of the process was studied by dilatometric and gravimetric methods. The polymerization rate (V_p) was calculated from the kinetic curves of the conversion (S, %) versus time. The content of cobalt in metal polymers was determined on a Saturn atomic absorption spectrophotometer with an accuracy of ±0.002. Intrinsic viscosity was determined using an Ubbelohde viscometer in benzene solution at 25°C. The IR spectra of the polymers were recorded on a Perkin Elmer Frontier FT-IR IR spectrometer in the range of 400−4000 cm^{-1} in films deposited from toluene solutions (3%) onto the KBr glass surface. The ^{1}H NMR spectra of the copolymers were recorded on a BRUKER WM 400 MHz spectrometer. Deuterated carbon tetrachloride was used as a solvent with tetramethylsilane as an internal standard. Composition of copolymers was measured from the integrated area of the phenyl peak to the integrated total proton peak [8].

Synthesis of chelating ligands by a compensatory method (compensation addition)

Radical copolymerization of MHD and styrene was carried out at a temperature of 80°C in a benzene solution at the volume ratios of monomers of 1:30

and 1:10. As an initiator, benzoyl peroxide (BPO) was used at a concentration of 0.03 mol/l. Air was removed from the polymerizing solutions by evacuation. The control of the process kinetics was carried out in a dilatometer in parallel with the main synthesis in the flask. MHD was added in the course of the reaction in three equal portions at conversions of 0, 5, and 10% with constant stirring of the polymerizing system. The polymer was isolated at 15% conversion by precipitation into ethanol. Subsequently, it was purified three times by reprecipitation in the benzene−ethanol system.

To assess the role of the compensatory synthesis method, the copolymerization was carried out under similar conditions. However, β-diketone was added to the initial reaction mixture not in portions, but all at once (simultaneous addition).

Synthesis of macromolecular chelates of cobalt(II) and graft polymerization of styrene and MMA with their participation were carried out according to the methods described elsewhere [5].

Results and discussion

Synthesis of chelating macroligands based on styrene and MHD

In the work [5], the preparation of a macroligand (ML) based on styrene and MHD was carried out by block copolymerization of monomers using a 30-fold excess of styrene. This ratio was calculated based on the literature data on the copolymerization constants [6] of the initial monomers in such a way that the β-diketone groups in the copolymer were separated by ~10 methylene fragments. This composition of the copolymer leads to the most favorable steric conditions for polymer chelation. On the other hand, a small amount of β-diketone monomer will obviously lead to a small amount of chelating groups in the polymer, which can also subsequently result in low graft polymerization rates when used as MIs.

Based on these considerations, the ratios of styrene:MHD=1:10 (C-1:10) and 1:30 (C-1:30) were used in the synthesis of MLs by the compensation method. Since the synthesis was carried out in the work [5] by radical copolymerization in a block, and the compensation method requires the use of a solvent, we also carried out the corresponding synthesis of polymer ligands in a solvent, but by the simultaneous addition of (S-1:10, S-1:30) for a more correct comparison of the objects obtained by the simultaneous and compensation methods. The results of the experiment are shown in Table 1.

It follows from the data given in Table 1 that the method of adding MHD does not significantly affect either the process rate (V_p) or the intrinsic

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Kinetic parameters of copolymerization of styrene and 5-methyl-5-hexene-2,4-dione in benzene solution at different volume ratios of monomers. Initiator BPO. [PBO]=3·10^{-2} mol/l. Temperature 80^{0}C

Macroligand	Volume ratio MHD:styrene	$V_p \cdot 10^5$, mol (l s)$^{-1}$	S_d, %	S_g, %	$[\eta]_{ML}$, dl/g	Composition of the copolymer poly(MHD:styrene)
S-1:30	1:30	15.0	19.6	18.0	0.36	1:9
S-1:10	1:10	10.9	15.5	7.8	0.18	1:2.5
C-1:30	1:30	12.5	15.1	15.0	0.35	1:9
C-1:10	1:10	10.5	15.5	13.0	0.20	1:2.3

viscosity of the macroligand ($[\eta]_{ML}$) at the same comonomer ratio. An increase in the proportion of MHD in a mixture with styrene, along with a decrease in the polymerization rate, leads to a discrepancy between the yields calculated based on dilatometry (S_d) and gravimetry (S_g) data. This indicates the presence of the polymerization inhibition effect by unsaturated β-diketone, which we also observed during block polymerization and which is not associated with chain transfer to the solvent. The reasons for this phenomenon were analyzed in ref. [9]. It should be noted that the compensatory route of administration reduces inhibition. The difference between S_d and S_g for this method of introducing MHD for a ratio of 1:10 (C-1:10) is only 16%, while with the simultaneous addition of monomers (S-1:10) almost half of the product cannot be precipitated into ethanol because of its low molecular weight.

The resulting copolymers were studied by using IR and ^{1}H NMR spectroscopies. All ^{1}H NMR spectra have the same position of proton signals and differ only in area values. As an example, Fig. 1 shows the ^{1}H NMR spectrum of macroligand C-1:10.

Along with the signals of the protons of the hydrocarbon part of the polymer chain in the region of 0−2 ppm, the ^{1}H NMR spectra contain signals of aromatic protons (6.99 and 6.61 ppm), as well as methylene (=CH) protons (5.13 and 4.61 ppm) and hydroxyl (−OH) groups (15.81 and 15.44 ppm) of the enol form of the diketone, which indicates that it is predominantly in the enol form in the polymer chain. These protons are split into doublets due to enol-enol tautomerism in unsymmetrical β-diketones [6]. The polymeric state sterically hinders both keto-enol and enol-enol proton transitions. The composition of the copolymer, calculated on the basis of ^{1}H NMR spectra, shows that the polymers are significantly enriched in MHD units compared to the monomer mixture.

Figure 2 shows the IR spectra of ML obtained by the compensation method (spectra 2 and 3). For clarity, the same figure shows the spectrum of polystyrene that does not contain an MHD group
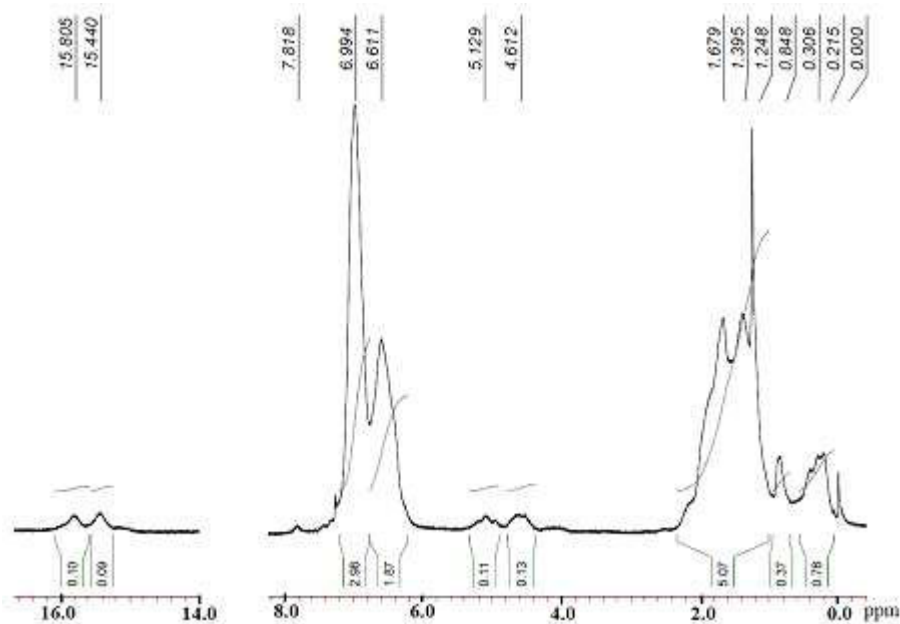

Fig. 1. ^{1}H NMR spectrum of macroligand C-1:10. Solvent CCl$_4$

Compensatory method for the synthesis of chelating polymeric ligands based on styrene and 5-methyl-5-hexene-2,4-dione as a way to increase the efficiency of macroinitiators of the β-diketonate type
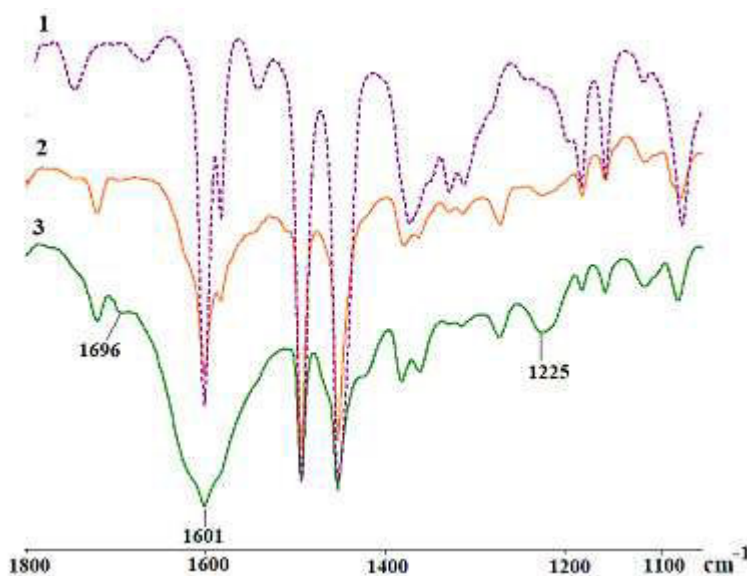
Fig. 2. IR spectra: 1 − polystyrene; 2 − C-1:30; and 3 − C-1:10

(spectrum 1).

The IR spectra confirm the presence of MHD in the copolymer. The band at 1720 cm⁻¹ cannot be unambiguously interpreted in favor of the diketone form, since it can also be assigned to the ν(C=O) end groups of the BPO. The presence of a shoulder in the region of 1696 cm⁻¹ is attributed by some authors to ν(C=O) trans-enol [10]. Its shift to the short-wavelength region is due to conjugation with C=C-bond of the enol ring. We are also inclined to a similar interpretation, since this band is also present in the IR spectrum of the MHD homopolymer. The band with a maximum at 1601 cm⁻¹, which corresponds to the stretching vibrations of the aromatic ring in the case of ML, is significantly expanded compared to ordinary polystyrene (Fig. 2, spectrum 1), since it includes the stretching vibrations of the enol ring: ν(C=O)+ν(C=C). This is especially clearly seen for sample S-1:10 (Fig. 2, spectrum 3), in which the amount of MHD is quite large. A wide band with a maximum at 1225 cm⁻¹ directly indicates the presence of enol, since it refers to the stretching vibrations ν(C−OH) and takes place for any diketones in the enol form [11].

Thus, the IR and ¹H NMR spectra confirm the presence of β-diketone groups in the copolymers, with the overwhelming majority of them being in the enol form.

Synthesis of macroinitiators of the β-diketonate type by complexation of macroligands with a metal salt

The interaction of the obtained MLs with different amounts of cobalt(II) acetate in aqueous dioxane solutions followed by precipitation into ethanol gave polymeric metal complexes. For all synthesized macrochelates, the metal content ($\omega_{Co(II)}$, %) was determined and the intrinsic viscosity ($[\eta]_{MCH}$) was measured. The results are summarized in Table 2.

The decrease in the viscosity of the obtained

Table 2

Characteristics of cobalt(II) macrochelates synthesized from macroligands. Solvent − 1,4-dioxane. V_{solv}=20 ml; m_{ML}=0.2 g. V_{H2O}=1.0 ml. Temperature 25⁰C

Macrochelate	Yield, %	$\omega_{Co(II)}$, %	$[\eta]_{MCH}$, dl/g	$\Delta[\eta]$ [7], %	$\Delta[\bar{\eta}]$
S-(1:10)-1[1]	86	1.80	0.14	22	22
C-(1:10)-1[1]	65	3.50	0.18	10	
C-(1:10)-2[2]	75	1.60	0.16	20	
C-(1:10)-3[3]	72	1.14	0.15	25	28
C-(1:10)-4[4]	74	0.50	0.14	30	
C-(1:10)-5[5]	50	0.25	0.12	40	
C-(1:10)-6[6]	55	0.15	0.11	45	
S-(1:30)-1[1]	93	2.40	0.26	28	
S-(1:30)-2[2]	85	1.40	0.25	31	31
S-(1:30)-3[3]	82	0.74	0.24	33	
C-(1:30)-1[1]	89	2.17	0.18	49	
C-(1:30)-2[2]	82	1.20	0.17	51	
C-(1:30)-3[3]	86	0.81	0.12	65	56
C-(1:30)-4[4]	97	0.35	0.12	65	
C-(1:30)-5[5]	92	0.25	0.18	49	
C-(1:30)-6[6]	93	0.11	0.15	57	

Notes: [1] − $m_{Co(II)\ acetate} \cdot 10^{-2}$=3.11 g; [2] − $m_{Co(II)\ acetate} \cdot 10^{-2}$=1.56 g; [3] − $m_{Co(II)\ acetate} \cdot 10^{-2}$=0.78 g; [4] − $m_{Co(II)\ acetate} \cdot 10^{-2}$=0.39 g; [5] − $m_{Co(II)\ acetate} \cdot 10^{-2}$=0.19 g; [6] − $m_{Co(II)\ acetate} \cdot 10^{-2}$=0.10 g; [7] − D$[\eta]$=(($[\eta]_{ML}$−$[\eta]_{MCH}$)/$[\eta]_{ML}$)·100%.

macrochelates compared to the initial polymeric ligands ($[\eta]_{ML}$, Table 1) indicates the formation of intramolecular complexes (Scheme 3, structure a). In this case, the amount of metal in the polymer chain will not strictly correspond to the amount of cobalt(II) 5-methyl-5-hexene-2,4-dionate fragments. This is due to the fact that, along with chelate structures, mixed-ligand complexes can also be formed, in which one ligand will be β-diketonate, and the second ligand will be acetate (Scheme 3, structure b). In the case of the formation of complexes (b), the viscosity will not change significantly, since the formation of such structures does not lead to folding of the polymer chain.
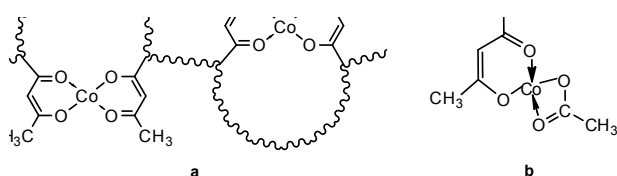
Scheme 3. Fragment of a macrochelate chain:
a − intramolecular complex of β-diketonate type;
b − mixed-ligand complex

Based on this, it can be assumed that the predominant formation of one or another type of complexes will be indicated not by the value of their intrinsic viscosity itself, but by the difference in the intrinsic viscosities of the initial macroligand and the polymer chelate obtained from it, expressed as a percentage ($\Delta[\eta]$). It can be seen from Table 2 that the average value of this value is the smallest (28% and 22%) for the complexes obtained from the C-1:10 and S-1:10 macroligands, respectively. As shown by the composition of the copolymer, the complexing groups in their chains are located too densely, so steric stresses will probably contribute to the formation of a large number of mixed-ligand objects (Scheme 3, structure b). The highest content of cobalt(II) 5-methyl-5-hexene-2,4-dionate fragments (Scheme 3, structure a) and hence the maximum macroinitiating activity should be expected in polymers obtained from the C-1:30 macroligand.

It can be seen from ^{1}H NMR spectroscopy data that a part of the enol groups in the C-1:10 macroligand after complexation remains unreacted (~20%) with the addition of the same amount of cobalt salt, due to steric hindrance (Fig. 3,a). Most likely, they are in the form of trans-enol. At the same time, in the chelating polymeric ligand C-1:30 (Fig. 3,b), only traces of the enol group are observed after complexation, which indicates a more complete reaction. However, it should also be taken into

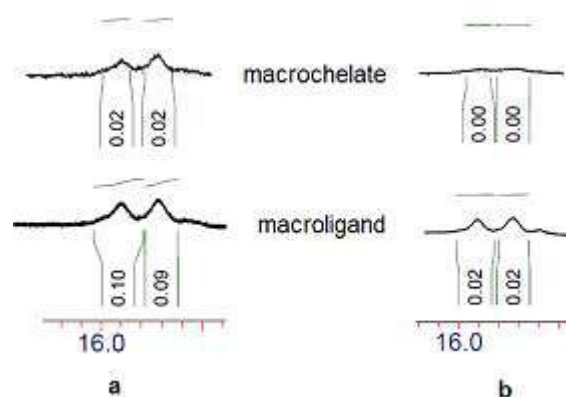account here that enol is initially contained in this macroligand in a rather small amount.

Fig. 3. Fragments of ^{1}H NMR spectrum in the region of enol proton signals in macroligands: a − C-1:10; and b − C-1:30 and macrochelates based on them: a − C-1:10-3; and b − C-1:30-3. Solvent CCl_4

Some information about the structure of macromolecular chelates can be obtained from IR spectra. For samples of metal polymers obtained by the compensation method, C-1:30-1 and C-1:10-1, which contain the maximum amount of metal, IR spectra were studied (Fig. 4).

Whereas the vibrations of the free β-dicarbonyl group are masked by polystyrene bands, these groups can be detected on the spectra of chelated polymers, as two bands corresponding to the metal chelate cycle are found because of complex formation, instead of one wide band of the enol form, and these bands are shifted to a shorter wavelength region. The spectrum of the sample C-(1:30)-1 (Fig. 4, spectrum 1) shows two separate bands at 1552 and 1509 cm^{-1}, which can be attributed to stretching vibrations of the β-diketonate metallocycle [12]. In the region of 1218 cm^{-1}, there is a band ν(C−O), and it is also shifted compared to the vibration band of the same group in the macroligand (1225 cm^{-1}, Fig. 2, spectra 2 and 3) due to the formation bonds with a metal atom. In the region of 700−400 cm^{-1}, there are bands corresponded to stretching vibrations of the Co−O bond (438 cm^{-1}) and bending vibrations of the metal chelate cycle (667 cm^{-1}) [12]. The IR spectrum of the sample C-(1:10)-1 (Fig. 4, spectrum 2), which contains a much larger amount of chelating fragments in the initial copolymer, somewhat differs from the IR spectrum of C-(1:30)-1, which proves their different structures. The main difference is observed in the broadening of the band in the region of 1600−1550 cm^{-1}, while its splitting into several arms can
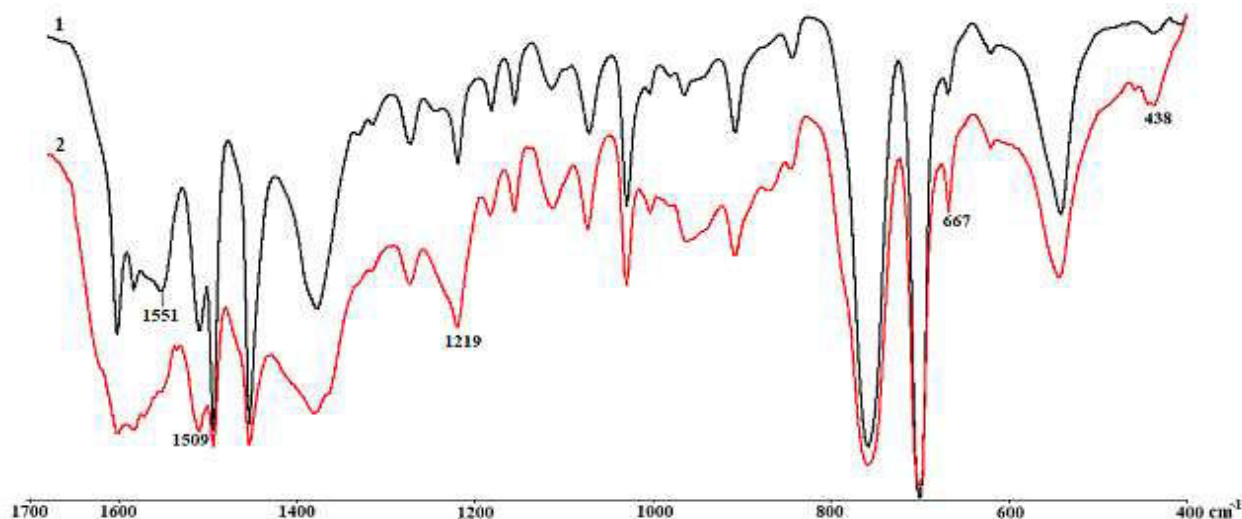
Fig. 4. IR spectrum of polymeric metal complexes: 1 − C-(1:30)-1; and 2 − C-(1:10)-1

be seen. This fact may indicate that mixed-ligand complexes are formed along with "pure" β-diketonate cycles, in which the role of the second ligand is played by the acetate ion, whose stretching vibrations are observed in the region of 1580−1560 cm^{-1} [12].

It should be noted that only groups formed according to the chelate type will participate in the process of macroinitiation (Scheme 3, structure a), and it is their number in the polymer molecule that will determine the rate of graft polymerization. Mixed-ligand metal complexes (Scheme 3, structure b) do not take part in initiation, but can have an inhibitory effect on radical processes, since they are capable of irreversibly binding growing radicals.

Grafted radical polymerization of styrene and MMA on β-diketonate-type MIs obtained by different methods

The resulting macromolecular chelates were used as MIs for the graft polymerization of styrene and MMA. As a result, branched polystyrene was obtained. The kinetic parameters of the processes are summarized in Table 3.

Analysis of data given in Table 3 shows that, despite the different metal content in MIs obtained with a simultaneous addition, the styrene grafting rates are close in their values and are similar to the data obtained in the work [5], in which MI was synthesized by block polymerization also by a one-stage addition of MHD. This indicates that the determining factor is the structure of MI macromolecules, which depends on the method of adding MHD, will be similar in all these cases. The strong folding of the initial sections of the chain (conversion up to 5%) leads to the fact that only

chelate groups that appear on the surface of the coil will take part in macroinitiation. The initiating centers inside the coil will be inaccessible to the monomer molecules. It should be noted that the coordination

Table 3

Parameters of graft polymerization of styrene and MMA on MI of β-diketonate type. [MI]=0.2%. Temperature 85⁰C

MI	$V_p \cdot 10^5$, mol (l s)$^{-1}$	S_d, %	S_g, %	τ, min
Monomer − styrene				
S-(1:30)-1	5.4	10.8	8.8	275
S-(1:30)-2	5.0	10.2	8.2	286
S-(1:30)-3	5.0	10.4	7.0	300
S-(1:10)-1	5.2	9.9	8.6	266
C-(1:30)-1	13.6	10.0	9.3	118
C-(1:30)-2	13.1	9.8	9.3	116
C-(1:30)-3	10.9	9.8	8.9	135
C-(1:30)-4	8.1	9.8	9.3	178
C-(1:30)-5	7.7	9.8	9.4	190
C-(1:30)-6	6.3	10.4	9.7	248
C-(1:10)-1	9.7	9.9	9.0	142
C-(1:10)-2	7.7	9.8	8.4	175
C-(1:10)-3	6.6	9.9	8.0	230
C-(1:10)-4	6.6	10.2	8.8	204
C-(1:10)-5	6.8	10.5	8.1	220
C-(1:10)-6	6.8	10.5	8.7	219
Monomer − MMA				
C-(1:30)-2	23.4	10.7	7.5	69
C-(1:30)-3	18.0	10.3	5.1	85
C-(1:10)-2	0.5	1.1	−	360
C-(1:10)-3	0.4	1.8	−	720

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of the monomer with the chelate cycle is the first step of initiation by metal-containing initiators, and it is the rate-determining one [13]. On the contrary, machrochelates synthesized from the C-1:30 and C-1:10 ligands exhibit a high initiating activity. They provide rates 2−2.5 times higher than the corresponding values for their counterparts obtained with the simultaneous addition of MHD. Chelate groups in this case are more evenly distributed along the chain, which makes them sterically more accessible to monomer molecules and, as a result, increases the grafting rate.

The presence of a direct dependence of the grafting rate on the metal content in MIs (Fig. 5) confirms the validity of the above statements. It also follows from Fig. 5 that, despite the fact that the macrocomplexes obtained from the C-1:10 ligand contain significantly more metal in polymers than their analogs obtained from C-1:30, their activity as MIs turned out to be much lower. Thus, the kinetic studies confirm the conclusions made on the basis of viscosity measurements and IR spectroscopy data that, along with β-diketonate fragments (Scheme 3, a), the C-1:10 macroligand is also characterized by the formation of a significant number of mixed-ligand structures (Scheme 3, b) that increase the metal content but are not capable of macroinitiation.
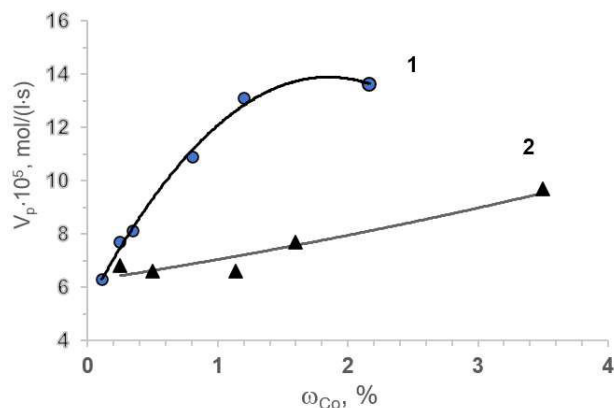
of complexes with metal-containing initiators due to the presence of a carbonyl group [13]. On the one hand, this circumstance can promote initiation by activating it as a monomer. However, on the other hand, if the formation of complexes occurs between the metal atom and the growing MMA radical, this will slow down or stop the polymerization process. Previously, we have shown that the participation of MHD or its chelates in the radical process leads to a stronger inhibition of MMA polymerization compared to styrene [9].

Figure 6 shows ^{1}H NMR of a copolymer poly(styrene-graft-methyl methacrylate) prepared from MI C-(1:30)-3. It shows that the grafted chains are atactic polymethyl methacrylate (PMMA) with the predominant formation of syndiotactic units. The ratio of syndio-, hetero- and isotactic triads is 5:3:1, that is, polymeric initiators of the β-diketonate type do not have a noticeable stereospecific effect on the MMA grafting process. The signal of phenyl protons in the region of ~6.9 ppm has a small area (0.01), since the mass of grafted PMMA chains significantly exceeds the mass of MI. The influence of MI can be observed in the shift of all PMMA signals by 0.1 ppm to the region of a strong field, which occurs due to the presence of the "ring current" effect of benzene rings in MI.
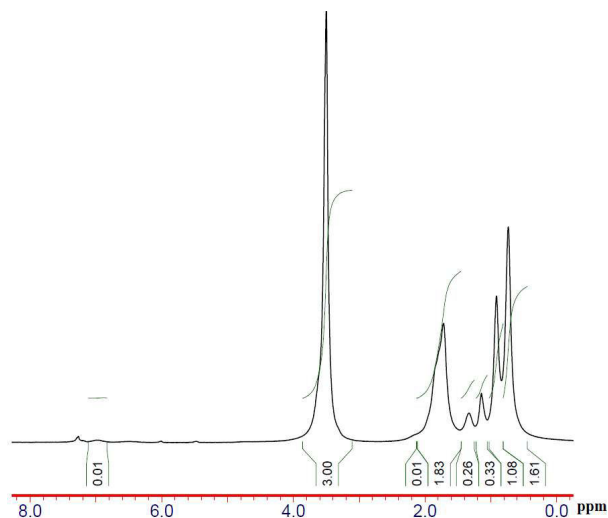

Fig. 5. Dependence of the rate of grafting of styrene on MIs of β-diketonate type on the percentage of cobalt in them. Macrochelates synthesized on the basis of chelating ligands: 1 − C-1:30; and 2 − C-1:10

Fig. 6. ^{1}H NMR spectrum of the PMMA graft product on MI C-(1:30)-3. Solvent CDCl$_3$

Conclusions

It was shown in this work that the compensatory method for the synthesis of β-diketone chelating ligands based on polystyrene and 5-methyl-5-hexene-2,4-dione significantly affects the structure of

Another confirmation that the polymeric metal complexes obtained from the C-1:30 and C-1:10 ligands are very different is their different behavior during MMA grafting (Table 3). The C-(1:30)-2,3 macrochelates graft MMA at high rates, while their C-(1:10)-2,3 analogs inhibit polymerization. It should be noted that MMA is more prone to the formation

macrochelates, which are obtained from them, in comparison with the conventional method of radical polymerization when two comonomers are simultaneously mixed at the beginning of the reaction. The compensation method leads to a more uniform distribution of chelating groups along the polymer chain.

In the case of using small amounts of β-diketone comonomer (1:30) with respect to styrene, the macroligands bind cobalt ions predominantly through the formation of intramolecular complexes of the β-diketonate type, which show themselves as active macroinitiators for the graft polymerization of styrene and methyl methacrylate. An increase in the amount of unsaturated β-diketone in the initial mixture to 1:10 leads to a more frequent arrangement of chelating groups in the chain, which sterically prevents the formation of macrochelates and leads to the predominance of structures of the mixed-ligand type, incapable of macroinitiation. This reduces the activity of β-diketonate MIs. However, such polymeric ligands can be extremely useful in the processes of sorption and concentration of metal ions, since they are capable of binding a large amount of metal.

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КОМПЕНСАЦІЙНИЙ МЕТОД СИНТЕЗУ ХЕЛАТУЮЧИХ ПОЛІМЕРНИХ ЛІГАНДІВ НА ОСНОВІ СТИРОЛУ І 5-МЕТИЛ-5-ГЕКСЕН-2,4-ДІОНУ ЯК СПОСІБ ЗБІЛЬШЕННЯ ЕФЕКТИВНОСТІ МАКРОІНІЦІАТОРІВ β-ДИКЕТОНАТНОГО ТИПУ
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Полімерні хелатуючі ліганди на основі стиролу та ненасиченого β-дикетону 5-метил-5-гексен-2,4-діону (МГД) були одержані радикальною кополімеризацією, ініційованою пероксидом бензоїлу в розчині бензену при об'ємному співвідношенні мономерів стирол:МГД=1:30 та 1:10. При цьому β-дикетон додавали в систему звичайним (одночасним) та компенсаційним (рівними порціями при конверсіях 0, 5, 10%) способами. Одержані продукти вивчені методами ІЧ- та ¹H ЯМР спектроскопії. Показано, що макрохелати, одержані на основі таких лігандів, відрізняються за структурою і, як наслідок, макроініціюючою здатністю до прищеплення вінілових мономерів. Полімерні ліганди, синтезовані при співвідношенні 1:10, незалежно від способу отримання, в подальшій реакції комплексоутворення з кобальт(ІІ) ацетатом утворюють змішанолігандні комплекси, які проявляють слабку активність у прищепленні стиролу і зовсім не ефективні у разі метилметакрилату. Використання невеликої кількості МГД (1:30) у поєднанні з компенсаційним способом синтезу приводить до утворення переважно внутрішньомолекулярних комплексів β-дикетонатного типу, які є більш активними макроініціаторами прищепленої полімеризації стиролу та метилметакрилату порівняно з одержаними традиційним одночасним способом додавання МГД.

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COMPENSATORY METHOD FOR THE SYNTHESIS OF CHELATING POLYMERIC LIGANDS BASED ON STYRENE AND 5-METHYL-5-HEXENE-2,4-DIONE AS A WAY TO INCREASE THE EFFICIENCY OF MACROINITIATORS OF THE β-DIKETONATE TYPE

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Polymeric chelating ligands based on styrene and unsaturated β-diketone 5-methyl-5-hexene-2,4-dione (MHD) were prepared by radical copolymerization initiated by benzoyl peroxide in benzene solution at the volume ratios of monomers styrene:MHD=1:30 and 1:10. In this case, β-diketone was added to the system by conventional (simultaneous) and compensatory (equal portions at conversions of 0, 5, and 10%) methods. The resulting products were studied by IR and ^{1}H NMR spectroscopies. It has been shown that macrochelates obtained on the basis of such ligands differ in their structure and as a consequence in their macroinitiating ability in the grafting of vinyl monomers. Polymeric ligands synthesized at the ratio of 1:10, regardless of the preparation method, form mixed-ligand complexes in the subsequent complexation reaction with cobalt(II) acetate, which exhibit weak activity in styrene grafting and are not effective in the case of methyl methacrylate. The use of a small amount of MHD (1:30) in combination with the compensatory synthesis method leads to the predominant formation of intramolecular complexes of the β-diketonate type, which are more active macroinitiators in the graft polymerization of styrene and methyl methacrylate than those obtained by the traditional simultaneous method of adding MHD.

Keywords: styrene; unsaturated β-diketone; copolymerization; chelation; polymeric β-diketonate; macroinitiator.

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