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Controlled radical polymerization of vinyl monomers in the presence of organometallic compounds of Group III—V elements as active additives

Summary — A review with 35 refs. covering the specific features of homo and copolymerization of vinyl monomers with allyl compounds and olefins, initiated by organometallic compounds of non-transition metals. When coordinated to the growing macroradicals, the organometallic compounds modify the reactivity and thus directly affect the formation of macromolecules at the chain growth step.

Key words: vinyl monomers, controlled radical polymerization, organometallic compounds as active additives.

Development of new unique initiators that are not only capable of effectively generating radicals under energetically favorable conditions, but also can directly affect the formation of macromolecules at the stage of chain growth, is an urgent problem in polymer chemistry. Organometallic compounds used in combination with traditional radical initiators (azo compounds, peroxides) are promising. The initiators based on organometallic compounds are usually divided into two groups: redox systems containing an organometallic compound of a non-transition metal and an oxidizer (oxygen, peroxides), and Ziegler—Natta catalysts. The latter are mainly used for the synthesis of olefin and diene (co)polymers, but are less useful for (co)polymerization of vinyl monomers, particularly acrylates, because these monomers are highly reactive toward organometallic compounds of nontransition metals [1].

On the contrary, binary initiator systems containing organometallic compounds of Group II—III metals and oxidizers, including organoelement peroxides (OEP), effectively initiate homo- and copolymerization of (meth)acrylates [2—4]. In addition, the components of an organoelement initiator have vacant *p*- and *d*-orbitals; therefore, they are capable of forming complexes with the growing macroradicals and monomers, thus changing their reactivity [4] [see scheme (1), p. 682]. Therefore, organoelement initiators can directly affect the composition and structure of copolymers, as well as the kinetic regularities of (co)polymerization.

For a number of monomer pairs, a trialkylboron-peroxide redox composition has been found to effectively generate radicals under energetically favorable conditions [3] and to initiate readily homo- and copolymerization of vinyl monomers [4]. Moreover, the copolymer composition and copolymerization rate as a function of monomer feed composition have been directly affected [4—6]. The controlling effect of organometallic compounds is most pronounced in the copolymerization of (meth)acrytales with electron-donating monomers.

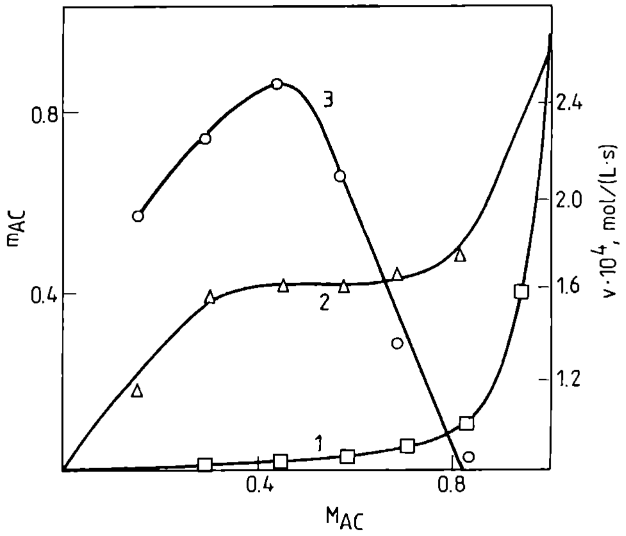

Fig. 1. MMA—AC (1, 2) copolymer composition vs. monomer feed and (3) copolymerization rate vs. monomer feed. Initiators: (1) AIBN, (2, 3) TIBB + DBPSb (0.1 mol %); T = 293 K

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*) Presented at the 7th International Seminar on Organometallic Complexes as Catalysts of Vinyl Compounds Polymerization [1—4], Turawa n/Opole, 12—17 September 1999.

Table 1. Apparent reactivity ratios of comonomers in copolymerization

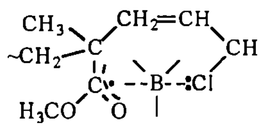
Pair of monomers:		r_1	r_2	Initiator*)	Reference
AN	BA	4.05	0.06	AIBN	[37]
		0.97	0.20	TIBB + TBP	[14]
		0.90	0.04	TIBB + TBPSN	[14]
		0.85	0.05	TIBB + TBPGE	[14]
		0.40	0.03	TIBB + TBPSB	[14]
		0.35	0.42	TIBB + DBPSB	[14]
	AC	3.05	0.05	AIBN	[37]
		3.78	0.15	TIBB + DBPSB	[7]
	MMA	0.15	1.35	BP	[37]
		0.04	1.53	TIBB + TBP	[14]
		0.15	0.75	TIBB + TBPSN	[14]
		0.26	0.67	TIBB + TBPGE	[14]
		0.10	0.64	TIBB + DBPSB	[14]
	VC	2.80	0.04	AIBN	[37]
		0.86	0.05	TIBB + DBPSB	[36]
		0.74	0.05	TIBB + TBPSB	[36]
	VDC	0.91	0.37	AIBN	[37]
		0.12	0.14	TIBB + DBPSB	[6]
	MMA	0.15	5.50	AIBN	[37]
		0.15	0.43	TIBB + DBPSB	[15]
MMA	MMA	0.58	1.40	BP	[37]
		0.95	0.99	AIBN + TIBB	[15]
		1.07	0.62	AIBN + DBPSB	[15]
		0.45	0.28	TIBB + DBPSB	[15]
		1.10	0.85	AIBN + TBPSI	[15]
	AC	48.10	0.03	AIBN	[37]
		0.57	0.03	TIBB + DBPSB	[7]
	ST	0.46	0.52	AIBN	[37]
		0.37	0.57	TIBB + DBPSB	[10]
		0.32	0.33	AIBN + DBPSB	[10]
	VDC	2.50	0.50	AIBN	[37]
		1.04	0.06	TIBB + DBPSB	[6]
	VC	15.00	0.02	AIBN	[37]
		6.70	0.02	TIBB + TBPSB	[5]
	AC	1.03	0.03	TIBB + TBPSI	[15]
VA	VDC	0.03	3.60	AIBN	[8]
		0.12	0.20	TIBB + DBPSB	[6]
	VP	0.20	3.02	AIBN	[37]
		0.32	0.19	TIBB + TBP	[21]
		0.17	0.15	TIBB + TBPGE	[21]
VP	ST	0.05	5.20	AIBN	[37]
		0.29	0.94	TIBB + TBPGE	[21]
Ethylene	VA	1.00	1.30	AIBN	[37]
		0.95	1.10	TIBB + TBPSI	[17]
	VC	0.24	3.60	AIBN	[37]
		0.22	0.50	TIBB + DBPSB	[17]
		0.20	2.00	Ziegler—Natta	[17]
Propylene	VC	0.28	0.39	TIBB + DBPSB	[17]
Hexene	VC	0.05	0.65	TIBB + DBPSB	[17]
		0.13	0.94	TIBB + TBPSI	[17]
	AN	0.00	12.20	AIBN	[37]
		0.10	4.60	TIBB + DBPSB	[17]

Footnote: TBP — *tert*-butyl peroxide; TBPSI — *tert*-butylperoxytrimethylsilicon; TBPSN — *tert*-butylperoxytriethyltin; TBPGE — *tert*-butylperoxytriethylgermanium; TBPSB — *tert*-butylperoxytetraphenylantimony; BP — benzoyl peroxide; AA — acrylic acid; VDC — vinylidene chloride; VP — vinylpyrrolidone.

Thus, in the AIBN-initiated copolymerization of methyl methacrylate (MMA) with allyl chloride, the copolymer is enriched in MMA as a more active monomer (r_1 = 3.05, r_2 = 0.05) over the entire range of monomer feed compositions. The rate of copolymerization decreases as the content of allyl chloride in the monomer feed is increased. With the binary triisobutylboron (TIBB)-di-*tert*-butylperoxytriphenylantimony (DBPSb) initiator, the copolymer composition *versus* monomer feed composition follows an S-shaped curve (Fig. 1) [7]. This curve has a pronounced portion, where the copolymer composition is dependent from the monomer feed composition and the monomer units tend to alternate. The reactivity ratios of the monomers tend to become considerably closer to each other and become less than unity (Table 1). The product of the reactivity ratios, $r_1 \cdot r_2$, tends to zero [8].

Organoelement initiators control the composition and structure of MMA—allyl chloride (AC) copolymers at initiator contents of 0.01—0.1 mol %. This strong effect at such low concentrations of the initiator results from coordination of the growing macroradical with the components of the initiating system. Study on the effects of individual initiator components on the relationship of copolymer composition *vs.* monomer feed composition in MMA—AC copolymerization indicates that TIBB, which contains the boron atom with a vacant *p*-orbital, plays the most active role in complex formation with the macroradical. Coordination of boron to the growing poly(methyl methacrylate) radical leads to redistribution of the electron density on the radical, which enhances its electrophilicity and increases its reactivity toward the π-bond of allyl chloride as an electron-donating monomer [9, 10].

The plot of the copolymerization rate of allyl chloride with MMA *vs.* monomer feed composition shows a clearly defined maximum (Fig. 1) at the nearly equimolar monomer content. This confirms the coordination-radical nature of the copolymerization and also allows us to suggest that chain growth proceeds *via* formation, by the monomers and macroradicals, of the cyclic reaction complex



(I)

The cyclic mechanism of chain propagation precludes a degradative chain transfer to the allylic monomer. This allows to account for the high conversion in copolymerization of allyl chloride with MMA and acrylonitrile (AN) [7].

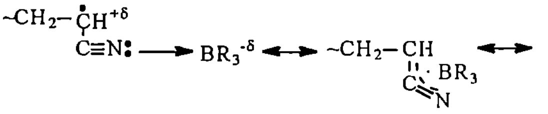
In the case of AN and AC, when the cyclic reaction complex is impossible to form because of steric hindrance, the effect of the organoelement initiator on the relationship of copolymer composition and copolymerization rate *vs.* monomer feed composition is less strong

(Table 1). At any point of the composition curve, the copolymer is enriched in AN as the more active monomer ($r_1 > 1$, $r_2 < 1$), although, for AIBN and OEP, the reactivity ratios are somewhat different. When the TIBB + DBPSb system is used as an organoelement initiator, the rate of copolymerization of AC with AN is markedly higher than that with a classical radical initiator.

On the contrary, the relationships of copolymerization of MMA with styrene as an electron-donating monomer are similar to those observed in the copolymerization of MMA with AC [10—12]: the copolymerization rate *vs.* monomer feed composition curve shows a maximum. This also allows us to suggest that chain growth proceeds *via* the formation of a reaction complex; the reactivity ratios of the two monomers are significantly less than unity (Table 1). The controlling effect of organoboron compounds in the copolymerization of MMA with styrene has been first established by Hirooka *et al.* [13] for alkyl boron halides. Addition of these compounds at a level of 0.5—3.0 mol % led to the formation of the alternating copolymer. In the case of alkyl boron halides, their effect on the copolymer composition was stronger than that of trialkylborates.

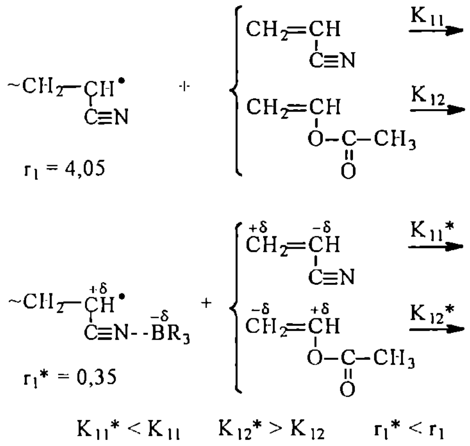
When a conventional radical initiator AIBN is used, the AN—vinyl acetate copolymer is enriched with AN as the more reactive monomer (r_1 = 4.05, r_2 = 0.06) at any monomer feed composition. The curve of copolymer composition *vs.* monomer feed composition, obtained with the organoelement initiator TIBB + OEP, follows an S-shaped course [14] with a portion where the copolymer composition is essentially independent of the monomer feed composition. The suggests that monomer units tend to alternate in the copolymer and indicates to the complex-radical character of copolymerization. This is also supported by the fact that the magnitudes of the reactivity ratios of the monomers tend to become closer: r_1 = 0.35, r_2 = 0.42 (for comparison, r_1 = 4.27, r_2 = 0.06, respectively, as calculated according to the Q—e scheme) and by the deviation from linearity of the plot used in the calculation of reactivity ratios according to Kelen-Tudos [8].

Such a strong effect of the initiator at low concentrations (0.01—1.0 mol %) seems to be the result of coordination of the growing macroradical to the components of the initiating system. In this case, TIBB should play and active role; TIBB has the boron atom with a vacant *p*-orbital and the element in EOP with a low-lying vacant *d*-orbital. The coordination of an organoelement compound to a growing AN macroradical leads to redistribution of the electron density on the reactive species



$$\longleftrightarrow \sim CH_2{-}CH{=}C{=}\dot{N}\!: \longrightarrow BR_3 \qquad (1)$$

The increase in the reactivity ratio of AN in the presence of organoelement compounds may be associated both with a decrease in k_{11} and an increase in k_{12} or with simultaneous variation of both constants in these directions. As shown above, these changes are due to an increase in the electron-accepting properties (electrophilicity) of the poly(acrylonitrile) radical coordinated to an organometallic compound. It is evident that, as the electrophilicity increases, the reactivity of the growing macroradical toward the π-bonds, as of a monomer with a strong electron-accepting group, decreases, whereas that with respect to vinyl acetate as an electron-donating monomer increases



(2)

As a result, the reactivity ratio of AN considerably decreases (r_1*< r_1).

The rate constant for the addition of the poly(vinyl acetate) radical coordinated to organometallic compound to vinyl acetate increases (k_{22}* > k_{22}), whereas, in the case of AN as an electron-accepting monomer, it decreases (k_{21}* > k_{21}). The overall effect leads to some variation in the reactivity ratio of vinyl acetate.

Similar regularities were found in the copolymerization of AN with MMA and AA [15] and also with MMA [5].

In the case of the MMA-MAA monomer pair, the organoelement initiator also strongly affects the relationship of copolymer composition *vs.* monomer feed composition [10]. When these monomers are copolymerized in the absence of organoelement compounds, the copolymer is enriched in MAA units as the more active monomer at any monomer feed composition. In the case of the binary organoelement initiator TIBB-DBPSb, the copolymer composition curve follows an S-shaped course, the reactivity ratios of both monomers being markedly less than unity (Table 1), and the product of reactivity ratios $r_1 \cdot r_2 \rightarrow 0$. This suggests alternation of monomer units in the copolymer [16].

Studies on the individual effects associated with each component of the binary organoelement initiator of the chain growth showed that, at AIBN content of 0.2 mol/l, addition of 0.1 mol % of TIBB makes the magnitudes of the reactivity ratios of the monomers approach to each other (Table 1). Adding organosilicon peroxide to AIBN also significantly changes the reactivities of the monomers and growing radicals; at any point on the copolymer composition curve, the copolymer is enriched in MMA. A similar effect on the apparent reactivity ratios of MMA and MAA is also observed with DBPSb, which is widely used as an effective coinitiator with trialkylborates [3, 6]. In the case of organosilicon and organoantimony peroxides, the absolute reactivity ratios are virtually identical (Table 1).

When acrylates are copolymerized with alkenes, the regulating action of organoelement compounds is not so marked as shown above [17]. The rates of copolymerization of AN with cyclohexene and hexene-1, MMA with ethylene, and vinyl acetate with ethylene, decrease in a linear fashion as the olefin content in the monomer feed is increased. The reactivity ratios are somewhat different from the similar values for common radical initiators, although to a lesser extent than in the copolymerization of two vinyl monomers. This is probably due to the fact that olefins, particularly their growing radicals, are less prone to complex formation than are monomers containing functional groups or atoms with unshared electron pairs. At the same time, analysis of patent disclosures suggests that it is possible to use catalytic amounts of alkylhalides of boron, zinc, aluminum, and mercury in combination with halides or alkylhalides of Group IV elements for the synthesis of alternating copolymers of olefins with (meth)acrylates and other vinyl monomers [18] including vinyl chloride (VC) [19, 20].

The effective controlling action of organoelement initiators is also disclosed when both copolymerizing monomers are electron donors, although they contain functional groups capable of coordinating with Lewis acids, for example, vinyl pyrrolidone (VP) and vinyl acetate. The kinetic relationship and the composition and structure of copolymers unambiguously indicate to the complex-radical character of copolymerization [21]. The monomers form a reaction complex with the components of the initiator at the stage of chain growth: the copolymerization rate *vs.* monomer feed composition plot shows a maximum at a nearly equimolar monomer feed composition.

The organoelement initiator also significantly affects the copolymerization of VP with vinylidene chloride (VDC). These comonomers are naturally alternating. When di-*tert*-butylperoxalate (DCPC) is used as initiator, the copolymer composition curve follows an S-shaped course. If the copolymerization of this pair is initiated by the binary system TIBB + EOP, the copolymer is enriched in VDC (Table 1).

For the pairs of monomers MMA—AC [9] and VC—olefin [6, 17], alkyl derivatives of antimony, aluminum, and bismuth, as well as organoboron compounds have been shown to effectively control the composition of the copolymers.

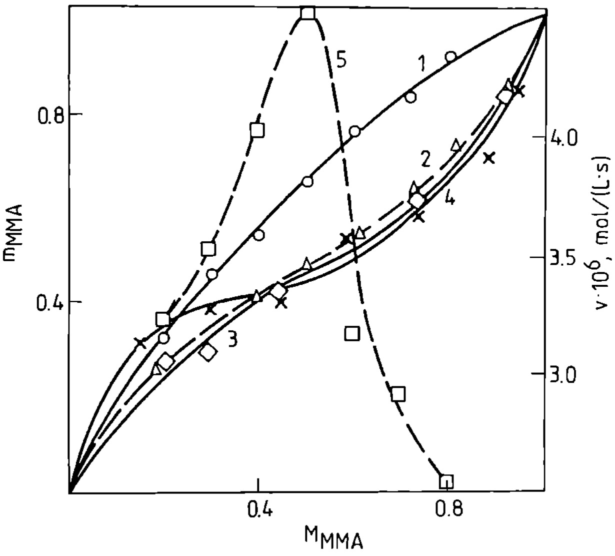


Fig. 2. The effect of organoelement compounds on (1—4) MMA-styrene copolymer composition and (5) of copolymerization rate on monomer feed. Initiators: (1) DCPC + TIBB, (2) DCPC, (3, 5) TIBB + DBPSb, (4) DCPC + DBPSb; T = 313 K

Some variations in the controlling action of the organoelement compounds mentioned are probably due to the different coordination abilities of their hetero-atoms.

It is clear that the modifying action of catalytic amounts of organoelement initiators can be explained by the coordination of organoelement compounds to the growing macroradicals.

The ESR spectra of methyl methacrylate radicals obtained with di-*tert*-butylperoxalate, a common organic initiator, differ significantly from those obtained with the TIBB—DBPSb organoelement binary system [5, 15, 22]. If the complex-radical initiator TIBB + EOP is used, the ESR spectrum, which is the superposition of the quartet and quintet attributed to the terminal methyl methacrylates radicals, shows an increase in the intensity of five central peaks. This transformation of the spectrum may be associated with coordination of the components of the initiator to the macroradicals. The absence of splitting due to boron and the element in peroxide in the ESR spectrum allows us to suggest that the acceptor interacts with the functional group of the macroradical.

Similar complexes of macroradicals with the halides of Group II metals have been described [23].

Such coordination interaction favors the enhancement of the electron-donating properties (electrophilicity) of the growing macroradical and an increase in its reactivity toward the multiple bond of the monomer. This leads to an increase in the propagation rate constant. In addition, it is clear that, for the coordinated poly(methyl methacrylate) radical, the rate constant of chain termination is significantly less than that in the absence of the complexing agent because of steric factors and increased electrophilicity of the radical. These factors together are responsible for the increase in the rate of (meth)acrylate polymerization.

Thus, the rate of homo- and copolymerization of MMA in the presence of AIBN and DCPC increases significantly when TIBB is introduced in amounts that are comparable to the concentration of the initiator (0.1 mol % of DCPC) [24, 25]:

V·10 000 mol/(L·s)	0.74	1.08	1.48
[TIBB], mol % (T = 298 K)	0	0.2	0.4

The AIBN-initiated polymerization of AN is also accelerated by TIBB, the rate of polymerization increasing simultaneously with an increase in the content of organoboron compound in the mixture. Similar results were obtained in copolymerization of MMA with styrene and allylic monomers using organoelement initiators [7, 10].

Other organoelement compounds of Group III metals, in particular dibutylbutoxyboron and triethylaluminum, also accelerate MMA polymerization [25]. Dibutylbutoxyboron, which is a stronger Lewis acid than trialkylborate, shows an increased coordination ability; therefore, the effect on the polymerization rate is markedly stronger than that of TIBB [25].

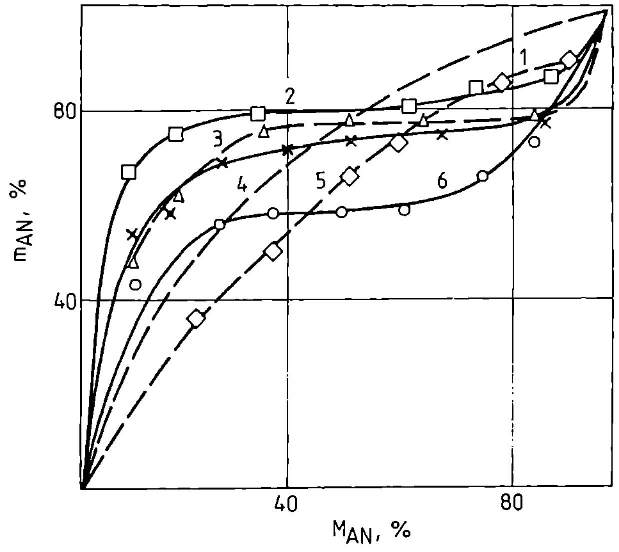


Fig. 3. The effect of Group IV—V elements in peroxide on AN—vinyl acetate copolymer composition. Initiators: (1) AIBN, (2) TIBB + TBPSi, (3) TIBB + TBPSn, (4) TIBB + TBPSb, (5) TIBB + TBP, (6) TIBB + DBPSb

In the presence of small amounts of tributylbismuth (TBB), the rate of vinyl acetate polymerization increases by more than one order of magnitude. TBB and triethylantimony (TEA) affect the polymerization of butyl acrylate in a similar fashion. The TEA additives accelerate appreciably the acrylate polymerization not only in the bulk, but also in the ethyl acetate solution [26].

Unlike metal halides as Lewis acids [16], organometallic additives accelerate chain growth when added in amounts comparable to the concentration of the initiator (0.01—0.1 mol % with respect to monomer). This unambiguously indicates that it is the complex formation of the organometallic compound with the macroradical, and not with the monomer, that is responsible for the increase in the rate of copolymerization. This is the more so as the stabilities of the complexes of the electron acceptors with the growing radicals are somewhat higher than those with the monomers [23].

Taking into account the aforesaid, it is suggested that one molecule of organometallic compound as a complexing agent can be involved is several consecutive chain growth reactions, permanently keeping the growing macroradical in the coordination sphere. Chain growth occurs *via* a cyclic reaction complex including a growing macroradical, a monomer and a complexing agent.

The metal atom, which keeps the growing macroradical in the coordination sphere, orients the monomer molecule and produces the conditions that are energetically and sterically most favorable to chain growth.

With this mechanism of chain growth, the complexing agent stays, for the most part, at the terminus of the growing chain and migrates as the reaction center propagates. Therefore, catalytic amounts of the modifier are sufficient to vary the reactivity of macroradicals as active centers.

A similar cyclic mechanism involving the formation of an eight-membered reaction complex was suggested by Kabanov [27] and Zubov [28] to account for the increase in the propagation rate constant during the polymerization of MMA in the presence of metal halides and, also, by Semchikov *et al.* [29] for AN-vinyl acetate copolymerization in the presence of germanium salts.

Chain growth *via* a cyclic reaction complex can also be regarded [27] as a pericyclic 1,4-addition reaction for which the Hückel principle of orbital symmetry with a total number of electrons equal to $(4n + 2)$ holds true. The transition state involves a growing allylic radical, an organoboron compound, and a monomer.

The complex-radical character of chain in the presence of an organometallic compound allows to explain the kinetic regularities of acrylate polymerization initiated by organoelement compounds in the presence of phenolic inhibitors.

In the presence of trialkylborates, diphenylolpropane and hydroquinone do not inhibit the radical polymerization of acrylates but, on the contrary, accelerate it. Thus, the rates of MMA and AN polymerizations increase significantly in the presence of an organometallic compound of a Group III metal and grow simultaneously with an increase in the content of the organometallic compound and the inhibitor [19, 23].

Such an uncommon behavior of phenols is, in part, attributed to the reaction of chain transfer to the organometallic compound [24, 25, 30—34].

The polymerization of MMA on the "living" mechanism in the presence of the additive C-phenyl-*N-tert*-butylnitrone about (PBN) is of significant interest. In this case the gel effect disappears when PBN content is comparable to the AIBN concentration at 50—75°C and the uniform growth of polymer molecular weight is observed. However, the period of induction is 5—10 minutes long [35]. It disappears when TIBB is introduced into the system at the ratio of TIBB:PBN equal to 1:1. It is necessary to note that all the features of "living" polymerization continue to be preserved also in the presence of the organometallic additive.

The data obtained allow us to believe that it is promising to use catalytic amounts of organometallic compounds as modifiers of homo- and copolymerization of vinyl monomers. Addition of small amounts of organoelement compounds that behave like Lewis acids, affect the reactivity of macroradicals and thus allow to control the kinetic parameters of the process at the stages of initiation, chain growth, and termination, as well as composition, structure, and properties of the (co)polymers.

Using the catalytic amounts of a modifier eliminates the steps of purification of the end product to remove the modifier and opens certain prospects for industrial application of this approach to the synthesis of (co)polymers with predetermined properties, without preliminary purification of the monomers from stabilizers.

This work was supported by the Russian Foundation for Basic Research (Grant N 99003-33346).

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Organizator: Instituto Alvaro Alonso Barba, Universidad Carlos III de Madrid.

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16—20 czerwca 2002 r. Guimăraes, Portugalia. Eighteenth Annual Meeting — PPS-18.

Organizator: The Polymer Processing Society + University of Minho, Guimnraes, Portugalia.

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