Effect of minor additives of arenes on chain termination in low-temperature cationic polymerization of isobutylene in aliphatic solvents

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The influence of small concentrations (1—8 mmol L^{-1}) of arenes (*viz.*, hexafluorobenzene, chlorobenzene, benzene, toluene, and mesitylene) on the molecular weight, molecular weight distribution, and degree of functionalization by terminal olefin groups was studied for polymers prepared by low-temperature (−78 °C) isobutylene polymerization in *n*-hexane initiated by the MeOH—$AlBr_3$ and Bu^tCl—$AlBr_3$ systems. The criteria "extent of livingness" k_{el}/k_p were calculated, where k_{el} and k_p are the rate constants of proton elimination and chain propagation, respectively. It was established that arenes can be involved in proton elimination from the growing carbocation, and their activity in this process increases with an increase in the basicity. Arenonium ions formed by the interaction of arenes with the components of the initiating system or with the growing ionic active centers can form complexes with counteranions, thus retarding proton elimination with the transfer to the counterion.

Key words: isobutylene, methanol, *tert*-butyl chloride, aluminum bromide, cationic polymerization.

We have shown previously[1] that in low-temperature (−78 °C) isobutylene cationic polymerization in *n*-hexane initiated by the MeOH—$AlBr_3$ and Bu^tCl—$AlBr_3$ systems, preliminary mixing of solutions of the Lewis acid and arene (*viz.*, benzene, chlorobenzene) (variant I) considerably increases the overall polymerization rate and efficiency of initiation (E_{in}). However, when aluminum bromide is added to a solution of the monomer containing an initiator (*viz.*, methanol or *tert*-butyl chloride) and a minor amount (~8 mmol) of arene (variant II), an accelerating effect of arenes is absent. In order to explain this effect, we supposed that the preparation of mixtures according to variant I favors the formation of arenonium complexes, which, as shown previously, can exist in σ- and π-forms.

The purpose of this study is to elucidate the mechanism of effect of minor arene amounts on chain termination in low-temperature isobutylene cationic polymerization and on the molecular weight of the polymers.

Experimental

Procedures for preparation of reactants and solvents, isolation and analysis of polymers have been described earlier.[1—3] Solutions under study were prepared in *n*-hexane to allow determination of aromatic groups in polymers. Optical spectra of the solutions in a region of 200—300 nm were recorded on a Specord UV-VIS spectrophotometer in 1-cm quartz cells.

Formulas for calculation of the maximal and minimal initiation efficiencies E_{in} are presented in Ref. 1: $E_{in}{}^{max}$ is calculated under assumption of the complete absence of chain transfer and, on the contrary, $E_{in}{}^{min}$ is calculated assuming that the chain transfer occurs completely, *i.e.*, all protons eliminated during polymerization enter into reinitiation. The intervals $(E_{in}{}^{max} - E_{in}{}^{min}) \equiv E_{in}$ are presented in Table 1.

Results and Discussion

The characteristics of the polymers obtained by low-temperature isobutylene polymerization in hexane initiated by the MeOH—$AlBr_3$ and Bu^tCl—$AlBr_3$ systems are presented in Table 1. A decrease in the molecular weight of the polymer is clear evidence for the involvement of additives in chain termination. However, to compare different samples, it is important that all other conditions, including the initiator concentration, the initial concentration of the monomer, and its conversion, be approximately the same, which is not always attainable. In addition, in processes where the chain transfer is not the main factor for determination of the degree of polymerization (including the conditions of living polymerization), the molecular weight should depend on E_{in}. The latter, as seen from the data in Table 1, can noticeably change

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Table 1. Characteristics of polymers obtained by isobutylene polymerization in the presence of the MeOH—AlBr$_3$ and Bu^{t}Cl—AlBr$_3$ systems (–78 °C, [AlBr$_3$] = [MeOH]) with ~99% conversion of the monomer

Entry	[AlBr$_3$] /mmol L^{-1}	Arene (c*/mmol L^{-1})	Variant of arene introduction	[M]$_0$ /mol L^{-1}	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_w/\bar{M}_n$	$f_{C=C}$	E_{in}
							(%)	
			System MeOH—AlBr$_3$					
1	0.80	—	—	1.83	358	4.6	45	36—20
2	1.05	C_6F_6 (8.4)	I	1.92	—	—	—	—
3	0.88	C_6H_5Cl (7.0)	I	1.83	121	4.0	40	96—58
4	0.82	C_6H_6 (6.5)	I	1.62	175	3.4	35	63—41
5	0.80	C_6H_5Me (6.4)	I	1.69	256	5.2	48	46—24
6	0.81	$C_6H_3Me_3$ (6.5)	I	1.69	169	7.6	72	69—19
7	1.05	C_6F_6(1.0)	II	1.92	486	3.9	24	21—16
8	0.87	C_6H_6 (8.0)	II	1.62	137	5.2	79	76—16
9	0.81	C_6H_5Me (8.0)	II	1.62	125	6.8	85	90—14
10	0.80	$C_6H_3Me_3$ (8.0)	II	1.62	53	12.0	90	214—21
			System Bu^{t}Cl—AlBr$_3$					
11	0.80	—	—	1.81	109	4.2	31	93—64
12	0.96	C_6F_6 (7.6)	I	1.81	—	—	—	—
13	0.97	C_6H_5Cl (7.7)	I	1.83	89	5.0	22	111—87
14	0.95	C_6H_6 (7.6)	I	1.83	106	4.1	18	102—84
15	0.95	C_6H_5Me (7.6)	I	1.58	107	4.3	49	87—44
16	0.95	$C_6H_3Me_3$ (7.6)	I	1.58	105	4.9	56	89—39
17	0.96	C_6F_6 (1.0)	II	1.81	230	2.0	14	46—40
18	0.95	C_6H_6 (8.0)	II	1.81	96	3.4	55	111—50

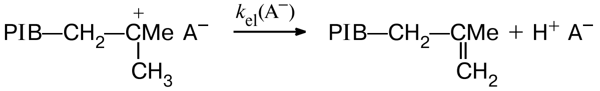
* Concentration.

depending on the type of the initiating system and polymerization conditions. In particular, in the systems with methanol (see Table 1, entries *3* and *4*) the E_{in} interval exceeds 40%, while in entries *1* and *7* it is lower than 36 and even 21%, respectively, indicating that the initiator has not been exhausted completely. For the system with *tert*-butyl chloride (see Table 1), the same pronounced distinction is observed in entries *13* and *14* (E_{in} > 80%), on the one hand, and in entry *17* (E_{in} < 50%), on the other hand. Although in the most experiments E_{in} does not exceed 100%, it achieved 214% in entry *10*, indicating the chain transfer reaction.

In order to explain more correctly the relative contribution of proton elimination with transfer to the counterion, which is the only chain termination for initiation by acyl halide complexes with the Lewis acids in an aliphatic solvent or its mixture with CH_2Cl_2 (Scheme 1, PIB is the polyisobutylene chain, and A$^-$ is the counteranion), we proposed[4] to use the criteria "extent of livingness" and presented formulas for calculation of these criteria. The criterion, being the ratio of the rate constants of proton elimination and chain growth, k_{el}/k_p, turned out to be especially useful.

$$k_{el}/k_p = \frac{f_{C=C}}{\overline{DP}_n} \cdot \frac{[M]_0}{10^4} \cdot \frac{Q}{\ln[100/(100-Q)]}.$$

Scheme 1



$$\text{PIB—CH}_2\text{—}\overset{+}{\underset{\text{CH}_3}{\text{C}}}\text{Me A}^- \xrightarrow{k_{el}(\text{A}^-)} \text{PIB—CH}_2\text{—}\underset{\text{CH}_2}{\overset{\|}{\text{C}}}\text{Me + H}^+\text{ A}^-$$

Calculation of this criterion needs the conversion of monomer Q (%), its initial concentration [M]$_0$, number-average degree of polymerization of the formed polymer $\overline{DP}_n$ (or number-average molecular weight of the polymer $\bar{M}_n$ and molecular weight of the monomer M), and degree of functionalization by the terminal C=C olefin groups appeared due to chain termination ($f_{C=C}$). The polymers prepared in the presence of the acyl complexes at the ends of chains contained only the C=C and C—X bonds, where X is halogen ($f_{C=C} + f_{C-X} \approx 100\%$). However, in most cases, the latter corresponds to the presence of not decayed but "sleeping" growth centers equilibrated with active ion pairs, and the equilibrium is very strongly shifted toward the "sleeping" centers.[5—9] Only for the initiation of polymerization by the equimolar acetyl bromide complex with AlBr$_3$, we found[10] that the C—Br groups at the ends of polymeric chains cannot participate in further steps of growth, probably, due to an insufficient amount of free Lewis acid.

Since in this work polymerization was performed at the same temperature that was used for the development of this criterion,[4] hereafter we use the k_{el}/k_p value to evaluate the relative role of chain termination reactions in the systems with arene additives. Samples for analysis were prepared at ~100% conversion (dilatometric data), and in calculations the conversion was taken equal to 99% (for substantiation, see Ref. 4).

When arenes are present in the reaction system, polymers with terminal aromatic groups ("alkylates") are not formed under these conditions. Our attempts to determine by UV spectroscopy the content of aromatic fragments in some synthesized and reprecipitated samples were unsuccessful. We cannot either exclude that the polymers contained traces of the aromatic groups because a very weak increase in the absorption was observed at 250—270 nm. Analysis of the published data showed that the yield of alkylate depends strongly on the catalyst (initiator) used. However, to obtain the ~100% yield, the process was carried out in an aromatic solvent (toluene).[11] The relative fraction of the alkylate decreases considerably with the temperature decrease. Calculation based on these data showed that we can hardly expect for our conditions (concentration of arene is three orders of magnitude lower than that when the arene is used as a solvent) that the degree of functionalization of polyisobutylene by the aromatic groups (f_{Ar}) could exceed 0.1%. For this reason, we ignore below the participation of arenes in the chain termination steps due to alkylate formation in the Friedel—Crafts reaction.

Let us analyze the data on the effect of arene additives and the method of their introduction on the indices of relative contribution of chain termination reactions (Table 2). This first point, significant in the context of the data in Table 2, is a much easier proton elimination when the system is prepared by variant II. For example, for the methanol system at close concentrations of the corresponding arenes, the $k_{\mathrm{el}}/k_{\mathrm{p}}$ values are 3—4 times higher than those for the systems prepared according to method I. This criterion increases approximately in the same way in experiments with benzene in the system with *tert*-butyl chloride.

The increase in the $k_{\mathrm{el}}/k_{\mathrm{p}}$ value, when rather basic arenes (see Table 2, *cf.* entries *1*, *8—10*, *11*, and *18*) and especially mesitylene are used, indicates, most likely, that these compounds are involved in proton elimination (chain termination). However, the strong influence of the order of introduction of the arene additives cannot be explained by bonding of some amount of the arenes to form onium complexes in the systems prepared by variant I. In fact, in all experiments (except those with hexafluorobenzene (HFB)) the arene concentrations exceed by almost an order of magnitude the concentrations of the initiator or Lewis acid. Therefore, even at the maximal possible arene bonding to form a complex, the amount of the remaining, unbound arene should be at least 80—90% of the initial amount. It is most probably that the lower value of the $k_{\mathrm{el}}/k_{\mathrm{p}}$ criterion in the systems of type I compared to those of type II is caused by an elevated

Table 2. Calculated criterion "extent of livingness" and constants of elementary steps for low-temperature (–78 °C) isobutylene polymerization in hexane[a]

Entry	Arene (c^b/mmol L^{-1})	Variant of mixing	$(k_{\mathrm{el}}/k_{\mathrm{p}})\cdot10^4$ /mol L^{-1}	$k_{\mathrm{el}}\cdot10^{-4}$ /s^{-1}	$k_{\mathrm{el}}(\mathrm{Ar})\cdot10^{-7}$ /L mol^{-1} s^{-1}
			Initiator MeOH		
1	—	—	0.28	1.40	—
2	C_6F_6 (8.4)	I	[c]	—	—
3	C_6H_5Cl (7.0)	I	0.74	3.70	—
4	C_6H_6 (6.5)	I	0.39	1.95	—
5	C_6H_5Me (6.5)	I	0.39	1.95	—
6	$C_6H_3Me_3$ (6.4)	I	0.87	4.35	—
7	C_6F_6 (1.0)	II	0.12	0.60	—
8	C_6H_6 (8.0)	II	1.14	5.70	0.54
9	C_6H_5Me (8.0)	II	1.34	6.70	0.66
10	$C_6H_3Me_3$ (8.0)	II	3.34	16.7	1.92
			Initiator Bu^{t}Cl		
11	—	—	0.63	3.15	—
12	C_6F_6 (8.4)	I	[c]	—	—
13	C_6H_5Cl (7.0)	I	0.55	2.75	—
14	C_6H_6 (6.5)	I	0.38	1.90	—
15	C_6H_5Me (6.5)	I	0.88	4.40	—
16	$C_6H_3Me_3$ (6.4)	I	1.02	5.10	—
17	C_6F_6 (1.0)	II	0.13	0.65	—
18	C_6H_6 (8.0)	II	1.26	6.30	0.39

[a] It was accepted in calculations that $k_{\mathrm{p}} \approx 5\cdot10^8$ L mol^{-1} s^{-1} (see text).

[b] Concentration.

[c] No polymerization.

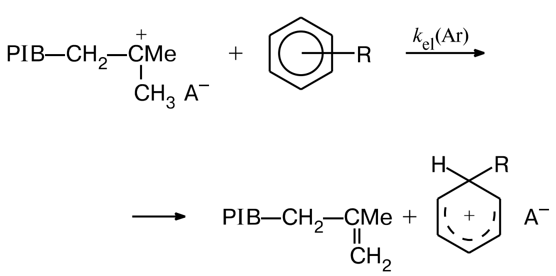
concentration of the arenonium ions formed in the very beginning of the process in the first case. Rather close values of the criteria in entries *1* (the system unmodified with arenes), *4*, and *5* (see Table 2) can be related to the compensation of two factors. The arenonium ions suppress the chain termination (proton elimination) reaction, while molecules of the free π-donor (arene), by contrast, favor this reaction.

To elucidate the nature of the compensation effect, one should consider in more detail possible mechanisms of the influence of the arenonium ions and free arenes on the elimination of protons from growing carbocations. In earlier studies of isobutylene polymerization in the presence of the 1 : 2 benzoyl chloride—aluminum bromide complex[12] and mixed complexes of acetyl bromide and benzoyl chloride with aluminum bromide,[13] we have also found a significant suppression of proton elimination compared to experiments performed in the presence of complexes of aliphatic haloanhydrides $AcBr \cdot 2AlBr_3$ or $AcCl \cdot 2AlBr_3$. Taking into account the second order found for the polymerization rate with respect to $[BzCl \cdot 2AlBr_3]$, we assumed that the counteranion in the active center (ion pair) contains an additional molecule of the aromatic haloanhydride complex.[12,13] Evidently, the change in the characteristics of the counterion (size, basicity, nucleophilicity, *etc.*) should affect the rate of the chain growth and termination. Modification of a counterion is widely used for the creation of living cationic polymerization systems.[14] In our case, it can be assumed that the formation of a complex is caused by the interaction of the electron-deficient cycle of the arenonium ion with an excess electron density of the counterion resulting in a decrease in the basicity of the latter.

It is of interest to consider one more possible mechanism of the influence of the arenonium ions on the rate of proton elimination. It is known that in several cases, electrolyte additives can be used to go from non-living cationic polymerization to living polymerization. For example, such a change was achieved in the work[15] for styrene polymerization due to the addition of tetra-*n*-butylammonium chloride to the 1-phenethyl chloride—$SnCl_4$ initiating system. The $HI—R_4N^+ClO_4^-$ system produces the living polymer of isobutyl vinyl ether,[16] although in the absence of this or similar salt the additive of hydrogen iodide produces only a low-molecular adduct. Since the arenonium complexes are also ionic species, they probably act in our systems as salt additives. Nevertheless, these mechanisms do not basically differ: in the first case, the components are bound due to the donor-acceptor interaction, and in the second case, bonding occurs due to the electrostatic interaction.

Free arenes, being π-bases, can react with the carbocation to eliminate a proton (Scheme 2).

Scheme 2

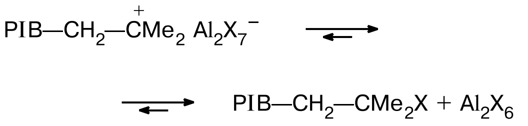


Another way of chain termination (*viz.*, arene alkylation) is improbable under our conditions. Therefore, this reaction performs the chain transfer, although the step of repeated protonation can have no time to occur completely in the case of formation of highly stable complexes.[1] The reactivity of various arenes in the reaction (see Scheme 2) is determined by their basicity, increasing with an increase in the number of alkyl or other electron-donating substituents in the ring (see, *e.g.*, Ref. 17); among the arenes under study mesitylene is the most basic.

Thus, the increase in basicity of arenes in the series hexafluorobenzene < chlorobenzene < benzene < toluene < mesitylene should favor an increase in their activity in proton elimination, *i.e.*, an increase in the k_{el}/k_p criterion. However, when the systems are formed by variant I, the concentration of the arenonium complexes formed in the very beginning of the process increases in the same series, and they retard the proton transfer to the counterion, thus decreasing this criterion. As a result of the opposite direction of these two tendencies, the compensation effect observed in entries *4* and *5* (see Table 2) arises. The compensation can be incomplete, which is especially pronounced in experiments with mesitylene (see Table 2, entries *6* and *16*). Here the compensation is only partial, probably, due, to a great extent, to steric hindrances for the formation of a complex between the arenonium ion and counterion. The formation of the systems in variant II does not favor the formation of the arenonium complexes, due to which the compensation effect is substantially weakened, and the k_{el}/k_p values are higher under other similar conditions.

The recently published[18—20] results of studying low-temperature cationic isobutylene polymerization showed that the rate of polyisobutylene chain growth under these conditions was determined by the diffusion factors, and the rate constant was $k_p \approx 0.7 \cdot 10^9$ L mol^{-1} s^{-1}. This value is average for the $(0.3—1.0) \cdot 10^9$ L mol^{-1} s^{-1} interval containing the data found by two methods of diffusion clock.[18] In our experiments, due to a higher (by ~1.6 times[18]) viscosity of hexane compared to its mixture with CH_2Cl_2, k_p can taken as $\sim 5 \cdot 10^8$ L mol^{-1} s^{-1}. It should be kept in mind that the active center implies, in this case, some ionized form of the growing $PIB—CH_2—C^+Me_2A^-$ chain. The current concentration of this active form is very small under standard conditions of cationic alkene polymerization. The main portion (>>99.999%) of the growing chains exists in an inactive, "sleeping" form,[5—9] but two states of the terminal groups are permanently transformed into each other (Scheme 3).

Scheme 3



$$\mathrm{PIB{-}CH_2{-}\overset{+}{C}Me_2\ Al_2X_7^-} \rightleftarrows \mathrm{PIB{-}CH_2{-}CMe_2X + Al_2X_6}$$

This equilibrium is simplified because it ignores a possibility of different types of ion pairs and free ions.

Based on $k_p \simeq 5 \cdot 10^8$ L mol^{-1} s^{-1} and the k_{el}/k_p criterion presented in Table 2, we can estimate k_{el} for polymerization in the presence of various arenes. In the case when arene is involved in the deprotonation of carbocations, k_{el} is determined by the parallel proton transfer both to the counterion (monomolecular reaction with the $k_{el}(A^-)$ constant, see Scheme 1) and to the arene (bimolecular reaction with the $k_{el}(Ar)$ constant, see Scheme 2)

$$k_{el} = k_{el}(A^-) + k_{el}(Ar)[Ar].$$

Assuming that $k_{el}(A^-)$ is independent of the presence of arene, this equation can give $k_{el}(Ar)$, which is an index more clearly demonstrating the ability of the arene to deprotonate the growing chain. Such an assumption with some reservations (see below) can be accepted only for the systems prepared by variant II, because in the systems with mixing by variant I a considerable concentration of the initially formed arenonium complexes noticeably suppresses proton elimination. In calculations we accepted that $[Ar] \simeq [Ar]_0$. Since the initial k_p values for each system are approximate, then the $k_{el}(A^-)$ and $k_{el}(Ar)$ constants should be considered only as estimate, effective values. This is even more so that elimination by an aromatic compound produces arenonium complexes preventing elimination. Nevertheless, the constants found can be used for the semiquantitative characterization of arene involvement in chain termination.

These data demonstrate the tendency for increasing the relative rate of proton elimination with an increase in the arene basicity (see Table 2, entries *8—10* and *18*). The reactivity of mesitylene in carbocation deprotonation is only ~25-fold lower than the reactivity of isobutylene in chain growth. This fact demonstrates the very high efficiency of this hydrocarbon as a regulator of the molecular weight in cationic polymerization. In entries *3—7* and *13—17* (see Table 2), the concentration of arenonium complexes should be higher and, therefore, here we cannot estimate even approximately the $k_{el}(Ar)$ values. However, the k_{el}/k_p (and k_{el}) values still change in parallel with an increase in the basicity of the aromatic additive. Some deviations of the results obtained with chlorobenzene can be caused by the known specific feature of halide substituents in the aromatic cycle.[21] Although they are more electronegative than hydrogen, these substituents are *ortho-para*-orientants in monohalide-substituted arenes due to the participation of unshared electron pairs in conjugation with electrons of the aromatic ring.

For the systems unmodified by arenes and involving various initiators, the k_{el}/k_p indices differ by ~2 times (*cf.* entries *1* and *11* in Table 1). It is highly probable that in the methanol system $AlBr_3$ is partially alcoholyzed to form alkoxides of the $MeOAlBr_2$ type. These metal compounds containing a heteroatom (electron donors *in situ*), which are formed by the reaction of the components of the reaction system are known to provide the "living" character for isobutylene polymerization[22,23] under the corresponding conditions, including the systems containing alcohols as initiators.[24,25] It seems that in our case such oxygen-containing products or methanol also act as additional stabilizers of the carbocation preventing its deprotonation.

Both external and *in situ* electron donors modify the growing carbocation and thus suppress the tendency of the latter to chain termination and, moreover, decrease its reactivity in the growth acts decreasing k_p.[14] In fact, the decrease in reactivity is due to the higher stability. This is another reason for which the k_{el} values calculated from the values found for the k_{el}/k_p criterion and specified constant k_p should be considered only as approximates. They can be used to compare the influence of this or another factor varied with retention of other conditions. However, comparing the relative role of termination reactions in different systems, it is more correct to use the criteria "extent of livingness."

Extrapolation of the tendencies found for a decrease in the electron-donating abilities of the arene additives to the region of more electron-withdrawing arenes suggests that polymers with the higher molecular weight and lower $f_{C=C}$ and k_{el}/k_p indices can be formed under the same conditions with the use of HFB. These changes are due to a decrease in the counteranion basicity through the formation of a complex with the electron acceptor. The low basicity of these arenes much impedes the formation of the arenonium cations under polymerization conditions, due to which the polymerization activity and the efficiency of initiation in their presence should barely change much. For the same reason, these additives should not be involved in the chain transfer to arene. At a low HFB concentration (1 mmol L^{-1}), the real situation (see Table 2, entries *7* and *17*) corresponds to the expected one, but at the standard concentration of this additive (~8 mmol L^{-1}) we unexpectedly faced the complete inhibition of polymerization instead of the strengthening of these effects. As mentioned in the work[1] devoted to the influence of arenes on the polymerization kinetics, reasons for polymerization inhibition at high HFB concentration are presently unclear and require additional studies. We can assume as a preliminary working hypothesis that HFB reversibly binds $AlBr_3$.

The polydispersity index of polymers is often used as an indicator of the "living" polymerization. When the irreversible chain transfer and chain termination are absent and initiation is fast (initiation constant $k_i > k_p$), the $\bar{M}_w/\bar{M}_n$ value should be close to 1.0.[24] The authors of several works on the living anionic,[26—28] cationic,[29,30] and (in recent years) radical[31,32] polymerization showed that this index, indeed, is close to unity. However, already at inhibited initiation but with retaining the "living" character of the system, the polydispersity index can considerably increase, losing its information value. It was of interest to reveal how the polydispersity of polymers and the livingness criterion correlate in our experiments. A comparison of the corresponding data in Tables 1 and 2 shows that, indeed, the minimal polydispersity index (entry *17*) corresponds to the minimal k_{el}/k_p value, and the broadest MWD was found for the product with the maximal k_{el}/k_p index (entry *10*). The very high polydispersity index with the use of mesitylene ($\bar{M}_w/\bar{M}_n = 14.4$) is determined by the slow initiation during polymerization process, efficient chain transfer to arene, chain termination by the counterions, and reinitiation involving the arenonium complexes formed already in polymerization involving mesitylene. Nevertheless, we failed to reveal a correlation between these two values for the most part of other experiments. It is not surprising because the processes are complicated, in the general case, by prolonged initiation, various chain termination and reinitiation reactions, involvement of products, which can accumulate during polymerization, in these reactions, *etc*. The application of the polydispersity index to similar systems provides much less information than does the data from the k_{el}/k_p quantitative criteria.

Analysis of the effect of arene additives on the molecular weight of polymers shows that the maximal $\bar{M}_n$ value is achieved in the presence of HFB (entry *7*), and the minimal $\bar{M}_n$ is attained in the presence of mesitylene (see Table 2, entry *10*). However, as in the case with the polydispersity index, an attempt to reveal any certain influence of the arene basicity on this index was unsuccessful because for at least ~99% conversion (which is of the greatest practical interest) the molecular weight depends on both the relative role of chain termination and the method of introduction of components of the initiating system, the efficiency of initiation, and other factors.

The obtained results show a variety of factors to act in the systems under study. Some of them favor chain transfer reactions and other, on the contrary, decrease the contribution of these reactions. The "extent of livingness" criterion makes it possible to estimate, at least semiquantitatively, the role of this or another factor and to determine conditions for the preparation of polymers with required properties. In addition, the proposed approach allows one to make the quantitative estimation of the contribution and outlooks of different methods for suppression or promotion of chain termination.

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