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Reactivity of 1,1-diphenylalkyl and triphenylmethyl compounds as initiators of anionic polymerization of nonpolar monomers. Some considerations connected with the use of low basicity initiators

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Abstract

The kinetics of initiation of styrene and butadiene polymerizations by bis(triphenylmethyl)barium (Tr_2Ba) and 1,1-diphenylalkylbarium and -sodium were studied. It was found that the initiation efficiency of Tr_2Ba is very low in THF but greatly increases when THF is replaced by benzene. The dependencies of initiator efficiency and the MWD of the polymers formed on k_i/k_p and M_0/I_0 were investigated theoretically. According to the results obtained, at certain conditions the initiators studied can be considered as suitable for controlled polymerization despite the fact that the basicity of 1,1-diphenylalkyl and, especially, triphenylmethyl carbanions is much lower than that of benzyl and allyl carbanions. The general aspects related to initiation with low basicity carbanions are discussed. In particular, attention was paid to the fact that, besides triphenylmethyl anion, some other low basicity carbanions such as poly(*N*,*N*-dimethylacrylamide) and poly(4-vinylpyridine) living chain ends are also capable of initiating polymerization of nonpolar monomers. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Anionic polymerization; Initiation kinetics; Low basicity carbanions

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1. Introduction

A considerable interest is observed in recent years to the use of 1,1-diphenylalkyl compounds as initiators of anionic polymerization. Different aspects of 1,1-diphenylethylene (DPE) chemistry in connection with controlled anionic polymerization have been comprehensively considered by Quirk et al. [1]. It was demonstrated, in particular, that 1,1-diphenylalkyl lithium compounds are very promising initiators for polymerization not only of polar monomers like alkyl(meth)acrylates, but of butadiene and styrene as well.

Besides lithium, some other counterions are also of interest for polymer synthesis, for example, for controlling microstructure and, consequently, properties of diene polymers [2]. In particular, organosodium initiators are promising for the synthesis of high vinyl butadiene polymers and copolymers [3–5], barium initiators provide polybutadienes with high content of *cis*-1,4 or, what is more unusual, *trans*-1,4-structure [6], etc. However, the proper choice of the initiator in the case of heavier alkali metals and, especially, of alkaline earth metals is much more difficult than in the case of lithium. In fact, until recently, very little information concerning nonlithium initiators has been published [2,7].

The solubility in hydrocarbons was indicated in the first place among the criteria for the successful choice of initiator [1,8]. Having in mind nonlithium initiators, one should add the criterion of thermal stability which is a major obstacle in the present case. With regard to both these criteria, the triphenylmethyl and 1,1-diphenylalkyl derivatives have marked advantages over simple alkyl compounds of the metals under consideration.

To our knowledge, 2-ethylhexylsodium still remains the only hydrocarbon-soluble and relatively stable alkyl compound of heavier alkali and alkaline earth metals [3,4] (organomagnesium compounds are beyond the scope of this paper because of their inactivity in nonpolar monomer polymerization). However, even its stability (ca. 1 week at room temperature and several months in a refrigerator [4]) is much less than, e.g. that of *n*-butyllithium [9]. 2-Ethylhexylpotassium, which can also be easily synthesized similar to 2-ethylhexylsodium, decomposes in a few minutes at room

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temperature [10,11]. At the same time, after DPE addition, both compounds are stable for at least a year in aromatic solvents where they are slightly soluble [4,11].

Bis(1,1-diphenylalkyl)barium and bis(triphenylmethyl)-barium, Tr_2Ba, are soluble and stable in aromatic solvents for several years [6]. Moreover, Tr_2Ba, along with Tr_2Sr, represent the only type of alkaline earth metal compounds which can be obtained in the complete absence of any electron donor additives which is essential for some catalytic applications [12]. This is the reason why during our study on barium-initiated butadiene and styrene polymerization we widely used initiators with di- and tri-α-phenylated carbanions. The kinetics of chain propagation with these initiators was recently discussed elsewhere [13]. However, the initiation step, as is the general case with all counterions other than lithium [2,7], was almost unstudied.

In this paper, we present the results of experimental study on the kinetics of styrene and butadiene polymerizations with α-di- and -triphenylsubstituted organobarium and, to a lesser extent, organosodium initiators. Besides, as was pointed out some time ago [1,2], the basicity of such carbanions is considerably less than that of benzyl and allyl carbanions. The pK_a values for the conjugated acids corresponding to di- and triphenyl methyl anions and to anions of typical nonpolar monomers differ by more than 10 units (Ph_3CH, pK_a 30.6; Ph_2CH_2, pK_a 32.2; $PhCH_3$, pK_a 43; CH_2=$CHCH_3$, pK_a 44 [2]) so that the ability of these carbanions to initiate styrene and butadiene polymerization might seem strange. This apparent contradiction recently was discussed in detail in connection with 1,1-diphenylalkyl-lithium initiators [1]. Nevertheless, due to general importance of the problem some additional considerations along with the most recent results related to the cross-reactions of relatively low basicity carbanions are also included.

2. Experimental

All operations were carried out under high vacuum conditions in an all-glass apparatus using break-seal techniques as described earlier [3,14]. Solvents and monomers were purified by standard procedures [15] finally being treated with liquid K–Na alloy (tetrahydrofuran, THF) or BuLi (toluene, styrene, butadiene, and DPE).

Tr_2Ba was prepared via the reaction of hexaphenylethane (HPE) with a mirror of barium metal in THF at room temperature [16] or in toluene at 50 °C [12]. In a typical experiment, 0.03 M solution of HPE, which was obtained by the action of Hg on triphenylmethyl chloride in acetone and recrystallized from the latter, was contacted with barium mirror for 3–4 h. The yield of Tr_2Ba determined by UV-spectrometry ($\lambda_{max} = 450$ nm) was quantitative. Triphenylmethylsodium (TrNa) was synthesized similarly in toluene solution.

Barium initiator with one living end, bis(1,1,3-triphenylpropyl) barium (TPP_2Ba) was obtained by the addition of DPE to dibenzylbarium in THF [17]. This initiator could be obtained in the toluene-soluble unsolvated form by complete removal of THF in vacuum [18]. The two-ended barium salt of dimeric DPE dianion (DPE-Ba) was prepared via the usual reaction of barium metal with DPE solution in THF [19–21].

1,1-Diphenyl-4-ethyloctyl sodium (DEOS) was obtained by DPE addition to 2-ethylhexylsodium in toluene.

Polymerization kinetics was measured by dilatometry [3, 22]. Unless otherwise indicated, the typical initial concentration of initiator, I_0, was 2.5×10^{-3} g equiv./l and that of monomer, M_0, 2.5 mol/l (styrene) or 3 mol/l (butadiene).

Kinetics of initiation was followed by spectrometry with UV–vis Shimadzu 360 apparatus using all-sealed high-vacuum quartz cylindrical cells (optical path-length from 0.3 to 1 mm) which simultaneously played a role of the lower part of a dilatometer. The whole construction was kept at the temperature needed. The following λ_{max} values (nm) were used: Tr_2Ba, 455 in THF [16] and 450 in toluene [12]; bis(1,1-diphenylalkyl) barium compounds (TPP_2Ba and DPE-Ba), 445 both in toluene and THF [23].

The conventional second-order rate constants k_i and k_p are defined according to usual equations for the rates of initiation, R_i, and propagation, R_p

$$R_i = k_i IM, \qquad R_p = k_p P^* M$$

where $P^* = I_0 - I$ is the total concentration of growing chains.

3. Results and discussion

3.1. Initiation kinetics

3.1.1. Bis(triphenylmethyl)barium

Triphenylmethyl sodium (TrNa) apparently, was used for the first time as a homogeneous anionic initiator in a classical series of Ziegler's works [24] which Szwarc named among the predecessors of his discovery of living polymers [15]. However, the subsequent work showed the low efficiency of triphenylmethylalkali initiators in polymerization of nonpolar monomers. For example, the polystyrene yield in homogeneous polymerization with TrK (8 h in boiling benzene) was as low as 52% [25]. Our observation confirmed a low reactivity of TrNa in butadiene polymerization in toluene (the polymer yield ca. 20% was obtained after two days at room temperature) [26]. In THF, styrene polymerization with TrLi and TrNa at room temperature proceeds very fast, however, only 2–5% of the initiator was consumed, as one can judge from the molecular weight of the polymers [26,27]. Since then, apparently no further attempts to use triphenylmethyl-alkali compounds as polymerization initiators have been undertaken.

Nevertheless, some time ago we have found that Tr_2Ba is

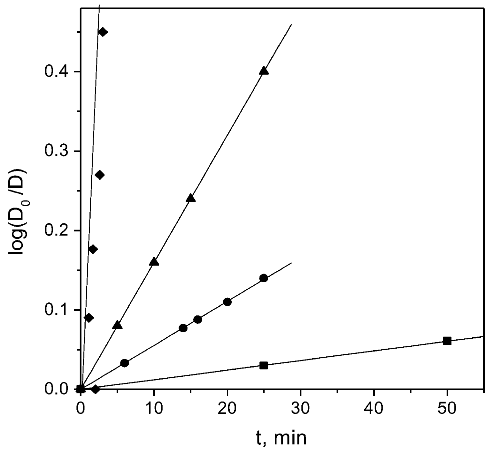


Fig. 1. Kinetics of the initiation of styrene polymerization with Tr_2Ba at 70 °C in various media. (■) THF; (●) 30/70; (▲) 10/90 THF/benzene mixtures; (◆) benzene. $I_0 = 2.5 \times 10^{-3}$ g equiv./l; $M_0 = 2.5$ mol/l.

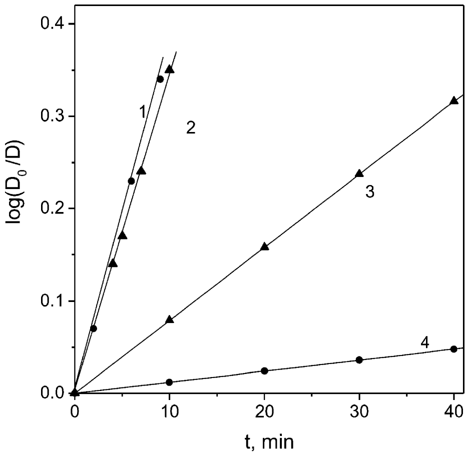


Fig. 2. Kinetics of the initiation of butadiene (▲) and styrene (●) polymerizations in THF with DPE-Ba at 30 °C (lines 1 and 2) and Tr_2Ba at 70 °C (lines 3 and 4). $I_0 = 2.5 \times 10^{-3}$ g equiv./l. $M_0 = 3$ mol/l for butadiene and 2.5 mol/l for styrene.

a useful initiator for butadiene and styrene–butadiene polymerizations [28]. In this connection, its behavior was studied in more detail. Typical kinetic curves for the initiation step are presented in Figs. 1 and 2 (lines 3 and 4). In all cases, the reaction followed the first-order law in initiator that enabled to calculate the initiation rate constants, k_i, which are presented in Table 1. From the point of view of polymer synthesis, the intrinsic reactivity of the initiator expressed in terms of k_i is not so important as its relative reactivity with respect to chain propagation which can be characterized by k_i/k_p ratio, where k_p is the propagation rate constant. The corresponding data are also included in Table 1.

One can see that the behavior of Tr_2Ba in reactions with butadiene and styrene is just opposite to that of the corresponding compounds of alkali metals. As was mentioned earlier, the reactivity of the latters in hydrocarbon solvents is very low and greatly increases in THF. At the same time, for Tr_2Ba, both the initiation rate and k_i/k_p ratio in THF are very low and greatly increase on passing from THF to benzene. The comparison with triphenylmethyl-alkali compounds suggests that this 'inverse' behavior is a specific feature of alkaline earth counterion rather than of triphenylmethyl species.

Due to the very low initiation rate of styrene polymerization in THF, only a small fraction of initiator is consumed in the process so that the main propagating species is asymmetric ion pair Tr–Ba–St where the dissociation constant of the –Ba–St bond and, thus, the concentration of free St^- anions are greatly reduced in comparison with previously studied polymerization with St–Ba–St active centers [29,30]. Various consequences of this specific mechanism of chain propagation were discussed elsewhere [6,13]. It should be pointed out that a similar inverse effect of the medium polarity is also characteristic of chain propagation in styrene and butadiene polymerizations with barium counterion [13].

3.1.2. 1,1-diphenylalkylsodium and -barium

The data on initiation kinetics with 1,1-diphenylalkylsodium and -barium compounds for styrene and butadiene polymerizations are presented in Table 2.

In an early work by Szwarc et al., the incomplete consumption of DPE-Na initiator in the course of styrene polymerization in THF have been reported [31]. Our recent experience also confirmed the incomplete initiation in butadiene polymerization with 1,1-diphenylalkyl-type sodium and potassium compounds in THF [32]. However, some time ago it was observed that 1,1-diphenyl-4-ethyloctylsodium (DEOS) is a reactive initiator when nonpolar solvents are used [33]. In butadiene polymerization in toluene, the initial period is very short so that the kinetic curves obtained with DEOS and 2-ethylhexylsodium are almost identical (Fig. 3). Another 1,1-diphenylalkylsodium initiator, TPP-Na, was applied in the study of chain transfer reactions [34] and as a component of a complex sodium–aluminum initiator in polybutadiene synthesis [35]. However, in most recent investigations more simple 2-ethylhexylsodium was used [3,4,22].

On the other hand, bis(1,1-diphenylalkyl)barium initiators proved to be the reactive ones in butadiene and styrene polymerizations both in polar and nonpolar solvents. As can be seen from Fig. 2, in THF, initiation rate with DPE-Ba (lines 1 and 2) is much higher than with Tr_2Ba (lines 3 and 4). It is of interest to note that in THF, the former compound initiates butadiene and styrene polymerization at about the same rate whereas the latter is much more reactive in butadiene polymerization than in styrene polymerization. At the same time, in benzene, styrene is more reactive than butadiene with both initiators. All this suggests that the decreased reactivity of Tr_2Ba is not only due to a noticeable loss of a conjugation energy, as will be discussed later, but also steric hindrances play role, which in

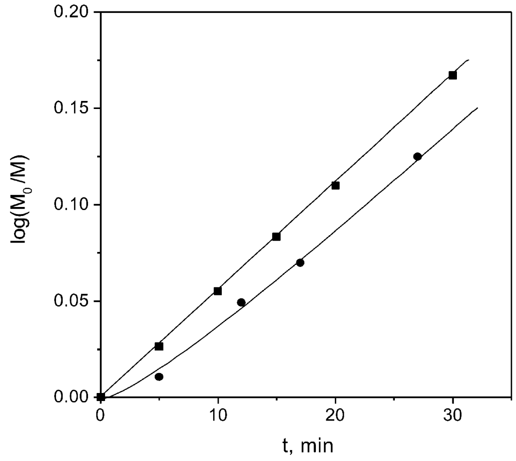


Fig. 3. Initial kinetics of butadiene polymerization in toluene at 30 °C with 2-ethylhexylsodium (■) and 1,1-diphenyl-4-ethyloctylsodium (•). $I_0 = 4 \times 10^{-3}$ g equiv./l; $M_0 = 3$ mol/l.

the case of a bulky styrene molecule is greater than in the case of more compact butadiene molecule.

The initial period in butadiene and styrene polymerizations in benzene with TPP_2Ba is completed at monomer conversions less than 10% (Fig. 4) which is characteristic of fast initiation. From Fig. 4 one can also see that, in benzene, the kinetic curves of Tr_2Ba-initiated polymerizations are close to those obtained with TPP_2Ba; the difference between the two initiators is lower at higher temperatures. Therefore, in nonpolar medium Tr_2Ba can also be considered as a fast initiator.

3.2. Kinetic evaluation of the efficiency of di- and triphenylmethylbarium initiators and of polydispersity of the polymers obtained

One of the most important characteristics of polymerization initiators is their initiation efficiency, that is, the fraction of the initiator converted into growing chains. In practice, it is usual to determine this parameter as the ratio of the experimental molecular weight of the polymer to its theoretically predicted value, $f = M_{n,exp}/M_{n,theor}$ [36]. This method of estimation, which can be considered an a posteriori one, gives an essentially integral value, which takes into account both the incomplete initiation and the losses of initiator in side reactions, e.g. in reactions with the pendant groups of polar monomer. However, knowing the kinetic ratio k_i/k_p, one is able to calculate the a priori value, $f = (I_0 - I)/I_0$, where I is the concentration of unreacted initiator [15,37]. In the generalized form, the relationship between f and the kinetic parameters can be written as

$$\alpha\gamma x = -\ln(1 - f) - (1 - \alpha)f \qquad (1)$$

where α is k_i/k_p, γ is M_0/I_0 and $x = (M_0 - M)/M_0$ is the monomer conversion. The kinetic f values for the initiators

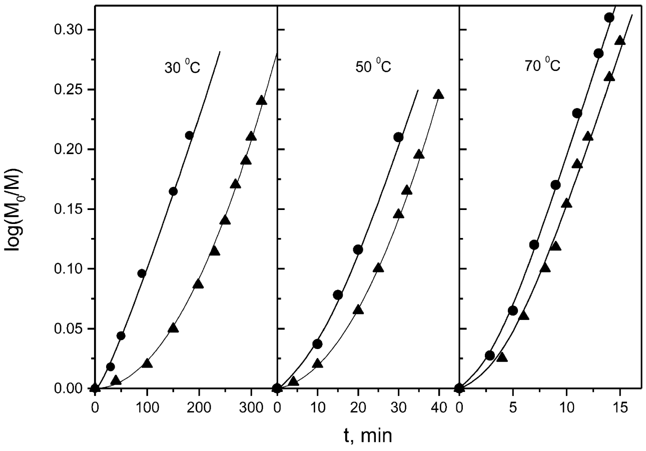


Fig. 4. Kinetics of butadiene polymerization in benzene with TPP_2Ba (•) and Tr_2Ba (▲). $I_0 = 2.5 \times 10^{-3}$ g equiv./l; $M_0 = 3$ mol/l.

studied were calculated with the use of Eq. (1) and are included in Table 1.

Eq. (1) was derived assuming first-order with respect to each reagent for both initiation and chain propagation [37]. Luckily, for all reactions involved in Table 1, this assumption was verified experimentally; the only exception is chain propagation in butadiene polymerization in benzene where, due to aggregation of active centers, the order in initiator is 1/3 [6].

Eq. (1) is useful for the analysis of the factors which determine the intrinsic initiation efficiency which depends only on the kinetics of the process and is free of different secondary effects such as side reactions, incomplete mixing of reagents, etc. In particular, it is of interest to estimate the conditions required for the complete initiator consumption which is essential for obtaining polymers with predictable molecular weight. As follows from Eq. (1), for $\alpha \ll 1$, the value of f depends only on the product $\alpha\gamma$; the case when α is of the order of unity is of no interest for the analysis because it automatically leads to $f \approx 1$. The theoretical dependence of initiator consumption vs. monomer conversion for different $\alpha\gamma$ is plotted in Fig. 5. It was shown that the low limit for obtaining $f \approx 1$ at the end of the process lies near $\alpha\gamma = 4$ [36].

Furthermore, the initiator suitable for controlled polymerization must provide a narrow molecular weight distribution (MWD) of the polymers [1,2]. It is usually indicated that low polydispersity can be achieved if the initiation rate constant is comparable or higher than that of propagation ($k_i \geq k_p$) [1,15,38,39]. This requirement is apparently obvious, but a more detailed analysis demonstrates that it is, of course, sufficient, but not necessary. In fact, as early as 1958 Gold had shown for the first time that polymers with $P_w/P_n < 1.1$ can be obtained at rather low k_i/k_p if only all initiator is consumed before the end of polymerization [40]. As implicitly follows from Gold's calculations and is clearly seen from Fig. 5, to satisfy the latter condition, M_0/I_0 should be higher for the smaller k_i/k_p. Unfortunately, Gold's calculation was made regardless of

Table 1
Reactivity and initiation efficiency of bis(triphenylmethyl)barium at styrene and butadiene polymerizations at 70 °C

Monomer	Solvent	k_i[a] (l/(mol s))	k_p (l/(mol s))	k_i/k_p	f[b]
Styrene	THF	1.8×10^{-5}	0.22	7×10^{-5}	0.33
	THF/benzene; 30/70, v/v	5×10^{-5}	0.41	12×10^{-5}	0.41
	THF/benzene; 10/90, v/v	23.5×10^{-5}	0.9	26×10^{-5}	0.56
	Benzene	0.016[c]	1.1	0.015	≈1
Butadiene	THF	12×10^{-5}	0.2	60×10^{-5}	0.74
	Benzene	≈0.001[c]	–	≈0.01	≈1

$I_0 = 2.5 \times 10^{-3}$ g equiv./l; $M_0 = 2.5$ mol/l for styrene and 3 mol/l for butadiene.

[a] Determined by spectrometry.

[b] $f = (I_0 - I)/I_0$, fraction of initiator consumed to the end of the process, calculated for $M_0/I_0 = 10^3$.

[c] Estimated from the initial shape of the kinetic curve.

any particular process so that some cases looked unrealistic. For example, a narrow MWD ($P_w/P_n \leq 1.05$) can be obtained even at k_i/k_p as low as 10^{-4}, however, in this case M_0/I_0 should be of the order of 10^5 [40]. Moreover, the form of presentation of the results in Ref. [40] is inconvenient for practical use. That is why it seems reasonable to explicitly demonstrate the dependence of polydispersity on conversion at different $\alpha\gamma$ (Fig. 6). The polydispersity index was calculated numerically from the obvious equation for the chain-length distribution of growing chains P_i^*

$$\frac{dP_i^*}{dt} = k_p M(P_{i-1}^* - P_i^*) + k_i M I \delta_{i1}$$

where the first term in the right-hand side describes the increase in chain length due to propagation, and the second term means the formation of chains with one monomer unit due to initiation ($\delta_{i,j}$ is the usual Kroenecker's symbol; $\delta_{i,j} = 1$ if $i = j$ and 0 else).

Although the calculations were made for $\gamma = 100$, the results for $\gamma = 1000$ are almost identical except for the interval of very low conversions.

The comparison of Figs. 5 and 6 shows that, if M_0/I_0 is sufficiently high, the conditions necessary for obtaining high initiation efficiency and a narrow MWD of the final polymer are almost identical. If all initiator is consumed prior to the end of the process, which happened, as was mentioned earlier, at $\alpha\gamma \geq 4$, the final polymer will possess a narrow MWD with $P_w/P_n \leq 1.1$. Therefore, for $M_0/I_0 = 1000$, the boundary value of k_i/k_p for controlled polymerization lies near 4×10^{-3}. As is seen from Tables 1 and 2, Tr_2Ba in benzene and almost all DPE-based initiators satisfy this condition. However, the boundary condition $\alpha\gamma \approx 4$ is valid only for one-step synthesis. The requirements for the multistep synthesis of compositionally uniform block copolymers are more strict. In this case, the major part of initiator should be consumed at the early stage of the process which is possible if $\alpha\gamma$ value is not less than 10 (Fig. 5).

3.3. Some notes on the use of low basicity initiators

In the case under consideration, the initiation step, similar to chain propagation, is essentially a nucleophilic addition of a carbanionic species to a monomer double bond. In early work by Wooding and Higginson, the general qualitative correlation between the basicity of the anions and their initiation ability was established [41]. In spite of some limitations [42,43], this correlation is useful as a working tool for a proper choice of initiator for the particular monomer. In quantitative terms, the common rule is that the pK_a values of the conjugated acids corresponding to anions of initiator and monomer should be of the same order of magnitude [1,2,39]. If the basicity of the initiating species is much lower than that of the anion formed from the monomer, the initiation does not occur. For example, as has been shown many years ago, the inability of methyl methacrylate (MMA) to copolymerize with styrene and

Table 2
Reactivity of 1,1-diphenylalkylsodium and barium initiators in butadiene and styrene polymerizations at 30 °C

Monomer	Initiator	Solvent	k_i (l/(mol s))	Method of estimation[a]	k_p (l/(mol s))	k_i/k_p
Butadiene	DEOS[b]	Toluene	≈0.01	A	≈0.1	≈0.1
Styrene	DPE-Na[c]	THF	0.5–0.7	B	–	0.0018
	DPE-Ba	THF	6×10^{-4}	C	–	(0.015)
	TPP_2Ba	Benzene	8×10^{-3}	A	0.4	0.02
Butadiene	DPE-Ba	THF	5.5×10^{-4}	C	0.008	0.07
	TPP_2Ba	Benzene	3×10^{-4}	A	–	(0.04)

$I_0 = 2.5 \times 10^{-3}$ g equiv./l; $M_0 = 2.5$ mol/l for styrene and 3 mol/l for butadiene.

[a] A, analysis of the initial part of the kinetic curve; B, spectrometric determination of the residual initiator; C, spectrometric study of the initiation kinetics.

[b] 1,1-Diphenyl-4-ethyloctylsodium, $I_0 = 4 \times 10^{-3}$ mol/l.

[c] According to Ref. [31].

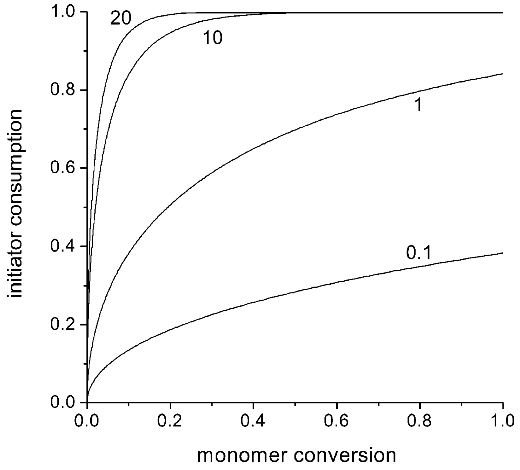


Fig. 5. Initiator consumption in the course of polymerization calculated according to Eq. (1). The numbers on the lines denote the $\alpha\gamma$ values.

other nonpolar monomers is due to the low basicity of PMMA anion [44,45]. To make the subsequent discussion more clear, the pK_a values of several key substances are presented in Table 3. Indeed, one can see that pK_a for ethyl acetate which can be regarded as a model of a conjugated acid for the PMMA growing anion, is more than 10 units lower than pK_a's of conjugate acids corresponding to propagating anions of typical nonpolar monomers like styrene or butadiene.

Following this principle strictly, one should expect that 1,1-diphenylalkyl and, particularly, less basic triphenylmethyl carbanions are incapable of initiating styrene and butadiene polymerizations. However, the experimental data presented in Refs. [1,2] and in the preceding sections firmly disprove such assumptions. Quirk et al. demonstrated that the explanation of this apparent contradiction consists of an account of the exothermicity of the addition of the first monomer molecule [1]. Once again, one has to note that, with respect to thermodynamics, the ionic initiation is also much less studied than the chain propagation. Therefore, it seems useful to give some more quantitative estimations.

According to Table 3, the difference in pK_a's of diphenylmethane and toluene in DMSO is equal to 10.8 units which corresponds to the loss of about 15 kcal/mol when 1,1-diphenylalkyl carbanion is transformed into a benzyl one [1]; in the case of triphenylmethane (TrH), the loss is ca. 17.1 kcal/mol (in DMSO). For the reactions in solvents of moderate polarity, it seems more appropriate to use the pK_a values obtained with a cesium ion pair in cyclohexylamine (Table 3); as was shown recently, they are close to the values obtained in THF, which is actually used in our work [47]. As is seen from Table 3, the energy loss in these solvents is markedly lower than in DMSO and is equal to ca. 11 kcal/mol for a DPE–toluene pair and ca. 13.5 kcal/mol for a TrH–toluene pair.

On the other hand, during the act of initiation, similar to the chain propagation, a π-bond of the monomer converts into a new-forming σ carbon–carbon bond of the adduct [1] (Scheme 1). The standard energy gain on such transformation is approximately equal to the heat of ethylene polymerization, i.e. to 22.3 kcal/mol [48]. For other monomers, the energy gain is somewhat less due to the loss of conjugation energy in monomer molecule and some other factors. Taking into account the similarity in the structures of 1:1 DPE–styrene adduct (Scheme 1) and of polystyrene chain (Scheme 2), one may assume the energy gain in styrene addition to the initiator to be approximately equal to the styrene polymerization heat, i.e. to 16.7 kcal/mol [48] which is sufficient to compensate for the loss in the thermodynamic stability of the carbanion. At the same time, the overall exothermicity of initiation is rather small that can explain both the rather sharp borderline between the initiation-reactive (triphenylmethyl) and inactive (ester enolate, hexamethylsilazanate [49]) anions and a great sensibility of Tr-based initiators to reaction conditions such as the nature of counterion and the solvent polarity.

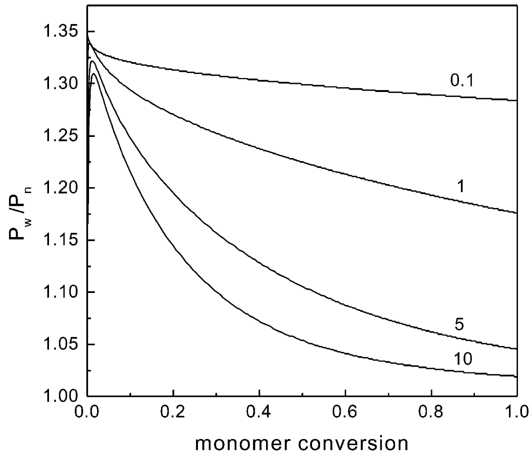


Fig. 6. The evolution of polymer polydispersity in the course of polymerization calculated for $\gamma = 100$. The numbers on the lines denote the $\alpha\gamma$ values.

Taking into account these considerations, it is reasonable to examine more thoroughly the pK_a data in order to search for other relatively low basicity carbanions which could be capable of adding to nonpolar monomers. When one looks through Table 3 with this in mind, two substances become the focus of attention, namely, 4-methylpyridine (pK_a 35) and *N*,*N*-dimethylacetamide (pK_a 34–35), which can be regarded as model conjugated acids for 4-vinylpyridine (4VP) and *N*,*N*-dimethylacrylamide (DMAA) growing anions, respectively.

Indeed, in a recent publication, it was reported that PDMAA growing anion initiates the polymerization of styrene and butadiene and adds DPE [49]. The IR-spectra of the thoroughly purified polymerization products demonstrated the presence of nonpolar fragments (aromatic ring in the case of styrene and a vinyl group in the butadiene case) along with a DMAA carbonyl group. As an additional proof, it was shown that α-potassio-*N*,*N*-dimethylaminopropionamide, which is a model of PDMAA active center, also initiates styrene and butadiene polymerization in THF [49].

Table 3
Acidities of some weak acids and the initiation ability of conjugated anions

Substance	pK_a in DMSO	pK_a, CsCHA[a]	Ability of the conjugated anion to initiate styrene polymerization
CH_2=CH–CH_3	44		+
$PhCH_3$	43	41.2	+
4-Methylpyridine	35		+
$CH_3CON(CH_3)_2$	34–35		+
Ph_2CH_2	32.2	33.38	+
Ph_3CH	30.6	31.45	+
$CH_3COOC_2H_5$	30–31		−
$[(CH_3)_2Si]_2NH$	29.5[b]		−

pK_a values are cited according to [Ref. 2, Table 2.3].

[a] Ion-pair acidity in cyclohexylamine.

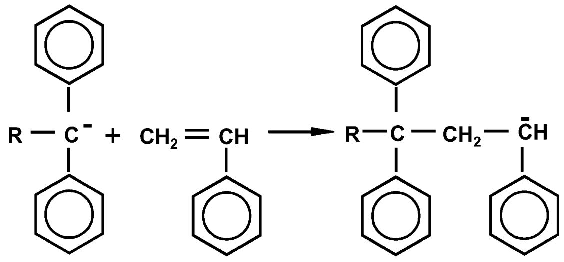
[b] From Ref. [46].

In a more recent experiment, the ability of living poly(4-vinylpyridinyl)lithium to initiate styrene polymerization in THF–toluene mixture was observed [50]. Although the process was complicated by the insolubility of 4VP polymer, the styrene addition was proved by IR- and NMR-spectra of the resulting polymer. In a separate experiment, the use of living butadiene-*block*-4VP pre-polymer provided the homogeneity of the reaction mixture. Here too, the presence of all three monomers (butadiene, 4VP and styrene) in the final product was confirmed [50].

The exact chemistry of the processes seems to be rather complex. Due to the simultaneous presence of highly nucleophilic nonpolar anions and reactive polar functional groups, a number of side reactions are probable; for PDMAA case, they are discussed in some details in Ref. [49]. However, the ability of living PDMAA and P4VP anions to initiate the polymerization of nonpolar monomers seems to be beyond question.

4. Conclusions

The main object of the paper was the study of the kinetics of initiation of styrene and butadiene polymerizations by Tr_2Ba and bis(1,1-diphenylalkyl)barium. Some data on initiation with the participation of 1,1-diphenylalkylsodium were also obtained. In spite of the very low basicity of 1,1-diphenylalkyl and, especially, of triphenylmethyl carbanions in comparison with that of benzyl and allyl anions, the organometallic compounds studied were found to be capable of adding the above-mentioned monomers. The initiation efficiency of Tr_2Ba is very low in THF but greatly increases when THF is replaced by benzene. The comparison with triphenylmethylalkali compounds suggests that this inverse pattern is a specific feature of alkaline earth counterion. The reason of this effect is not clear yet and, apparently, is worthy of a special quantum-chemical investigation.

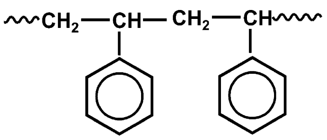


Scheme 1. The addition of styrene to 1,1-diphenylalkyl carbanion.

The general behavior of the system including three pairs of variables, namely, monomers (styrene and butadiene), carbanions (1,1-diphenylalkyl and triphenylmethyl), and solvents (THF and benzene) is difficult to describe by simple rules. For example, with Tr_2Ba in benzene, styrene is more reactive than butadiene whereas in THF the reverse order, butadiene > styrene, was observed; bis(1,1-diphenylalkyl)barium in THF is much more reactive than Tr_2Ba while in benzene both initiators are of similar reactivity, etc. Therefore, one can suppose that several factors such as loss of conjugation energy when passing from more stable to less stable carbanion, the steric hindrances and, possibly, some others affect the reaction rates in the system.

The dependences of initiator efficiency and the MWD of the polymers formed on the polymerization conditions such as M_0/I_0 and the relative reactivity of initiator expressed in terms of k_i/k_p were theoretically studied. The results obtained demonstrate that at sufficiently high M_0/I_0 some of the initiators studied can be used for initiating controlled polymerization.

The general aspects related to the reactivity of low basicity carbanions and the correlation between the pK_a values of some weak acids and initiation ability of conjugated carbanions were discussed. The special attention was drawn to the fact that, besides triphenylmethyl and 1,1-diphenylalkyl anions, some other low basicity carbanions such as poly(*N*,*N*-dimethylacrylamide) and



Scheme 2. Polystyrene chain.

poly(4-vinylpyridine) living chain ends are also capable of initiating polymerization of nonpolar monomers.

The experimental and theoretical results obtained demonstrate that the low basicity carbanions are of interest for controlled polymer synthesis which makes further investigations in this field very promising.

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