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Notes

Nonmonotonic Behavior of Sodium-Based Complex Initiators in Butadiene Polymerization

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It is frequently observed in Ziegler−Natta polymerization that the dependence of the overall polymerization rate on the catalyst/cocatalyst ratio has a more or less marked maximum (see, e.g., Porri and Giarusso[1]). However, in lithium-initiated anionic polymerization, the addition of organometallic modifiers usually monotonically decreases the overall rate. As early as 1960, it was shown[2] that the addition of $AlEt_3$ or $ZnEt_2$ to *n*-BuLi gradually decreases the rate of styrene polymerization in benzene to full inactivity at $Al/Li \approx 1$ and $Zn/Li \approx 10$, respectively. This was easily explained by the formation of $LiAlR_4$ and $LiZnR_3$ “ate” complexes which are known to be inactive in polymerization of nonpolar monomers.[2,3] A similar monotonic dependence was observed later for butadiene polymerization in cyclohexane with the *sec*-BuLi−Bu_2Mg initiator.[4] All of these findings did not encourage a search for new bimetallic anionic initiators for polymerization of nonpolar monomers.

However, in the case of heavier alkali metals the situation seems to be different. True, a few earlier attempts to use a preformed stoichiometric $NaMgR_3$ complex in diene polymerization also were unsuccessful. From the data reported,[5] one can estimate that the first-order rate constant $[k' = -(1/M)(dM/dt)]$ for isoprene polymerization in cyclohexane at 20 °C is on the order of 10^{-6} s^{-1}, and at 50 °C, it is on the order of 10^{-5} s^{-1} in comparison to 3×10^{-4} (30 °C) for the uncomplexed organosodium initiator[6] (the initiator concentration was ca. 5×10^{-3} M in all cases). According to a later publication,[7] only 16% yield of polybutadiene was achieved after “1 day or more” with the same initiator in hexane at 50 °C.

Much more interesting results were obtained with substoichiometric mixtures. It was observed recently that the addition of small amounts of various aluminum alkyls such as $AlEt_3$, $Al(i\text{-}Bu)_3$, $HAl(i\text{-}Bu)_2$, and so on to the common disodium tetra-α-methylstyrene initiator greatly increased the rate of butadiene polymerization in hydrocarbon solvents up to a certain maximum value.[8] The Al/Na ratio at the maximum depended on the particular aluminum compound. The addition of an aluminum compound above the optimum ratio decreased the overall rate to the full cessation of the process.

In all of these cases, small amounts of a polar solvent were introduced with the organosodium component; hence, the role of solvation effects and the solvation/complexation competition could not be excluded. However, as was reported in the preliminary communication,[9] at least for one particular model system, namely, 1,1,3-triphenylpropylsodium−$AlPh_3$, the dependence of the polymerization rate on the Al/Na ratio passed through a maximum even in a pure hydrocarbon medium (toluene) without any polar additives.

Here, we reported the results of the investigation of butadiene polymerization with a RNa−R_2Mg system in toluene. In this study the same R = 2-ethylhexyl was used for both sodium and magnesium components. Because of the solubility of 2-ethylhexylsodium in hydrocarbons, such combinations allow polymerization to be performed under homogeneous conditions and avoid the precipitation of sodium alkyls that could be expected with other combinations, for example, with commercially available Bu_2Mg. To prevent the metalation of toluene, the components were introduced into the reaction vessel in the following order: toluene, $(2\text{-}EtHex)_2Mg$, butadiene, and 2-EtHexNa; i.e., the interaction between organometallic compounds took place in the presence of monomer.

The dependence of k' on the composition of the Mg−Na complex initiator is shown in Figure 1; for comparison, the results obtained with the model Al−Na system are also included.

As can be seen from Figure 1, in both systems the addition of even very small quantities of organometallic modifier to organosodium initiator results in a drastic increase in the polymerization rate that unambiguously indicates the formation of new highly reactive centers. By comparing the maximum polymerization rate with the rate observed with uncomplexed organosodium and taking into account that the fraction of complex active centers cannot exceed the fraction of modifier added, one can estimate that the reactivity of complex Na−Al centers is ca. 20 times, and of Na−Mg centers is ca. 80 times, as much as the reactivity of uncomplexed polybutadienylsodium growing chains. For both Mg−Na and Al−Na systems, the overall rate decreases as Mt/Na molar ratio approaches unity, corroborating the low reactivity of stoichiometric ate complexes.

The difference in the behavior of lithium and sodium-based complex initiators can be explained by the difference in the structure of intermediate complexes, as was suggested earlier.[10] However, the precise structure of highly reactive intermediate Na−Mg and Na−Al complexes still remains unclear. As the components were mixed in the presence of monomer, the participation of the latter in the complexes also is possible.

The choice of toluene as a solvent gives an additional opportunity to prove the formation of active centers of a new type (Table 1). It is well-known that uncomplexed polybutadienylsodium growing chain ends are highly

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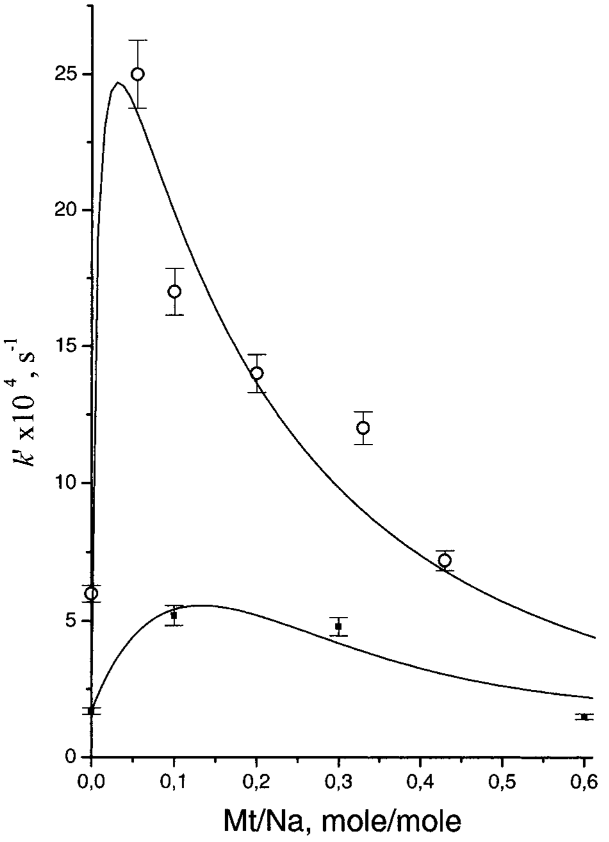

Figure 1. Dependence of the first-order rate constant for butadiene polymerization with complex sodium-based initiators in toluene at 30 °C. ○ = initiator, 2-EtHexNa + (2-EtHex)$_2$Mg; $C_{Na} = 7 \times 10^{-3}$ M. ■ = initiator, 1,1,3-triphenylpropylsodium + AlPh$_3$; $C_{Na} = 3 \times 10^{-3}$ M. Mt = Mg for (○) and Mt = Al for (◆).

inclined to chain-transfer reactions. At room temperature, the chain-transfer constant of toluene is unusually high, $C_s = 0.037$;[11] accordingly, only low-molecular-weight polymer is formed when polymerization is performed in toluene (Table 1, line 1).

However, even at Mg/Na = 0.05 mol/mol the number-average molecular weight is close to the value calculated for living polymerization, indicating the decrease in C_s by several orders of magnitude. A similar effect was observed with RNa−Ph$_3$Al complex initiator.[9] Because C_s does not depend on the *number* of active centers, its drastic decrease can be explained only by the change of the *nature* of the centers. Of course, uncomplexed growing chains also participate in the process, but their contribution is fairly small because of low reactivity. The polydispersity index of the polymer is relatively low for the multistate process (Table 1). This fact as well as the unimodal shape of GPC-traces corresponds well to polymerization predominantly via highly reactive quasiliving growing chains accompanied with a very fast exchange between different active centers.[11]

Table 1. Butadiene Polymerization in the Presence of 2-EtHexNa−(2-EtHex)$_2$Mg Complex Initiator[a,b]

Mg/Na, mol/mol	$k' \times 10^4$, s^{-1}	$M_n \times 10^{-3}$	M_w/M_n
0	6.0	0.3	2.5
0.05	25	16.7	1.5
0.1	17	18.5	1.4
0.2	14		
0.33	12	19	1.3
0.43	7.2	17	1.9
0.6		19	1.4

[a] Polymerization in toluene at 30 °C; $C_{Na} = 7 \times 10^{-3}$ M; $M_{theor} = 20 \times 10^3$. [b] The possible error in the determination of k' does not exceed 5%; for number-average molecular weights, the possible error is within 20% for low-molecular-weight polymers and within 5% for other polymers.

In conclusion, the nonmonotonic kinetics was observed for butadiene polymerization with R$_3$Al−RNa and R$_2$Mg−RNa mixtures, in which the overall polymerization rate greatly increased in the presence of small amounts of modifier and then decreased as the molar ratio modifier/initiator approached unity.

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References and Notes

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