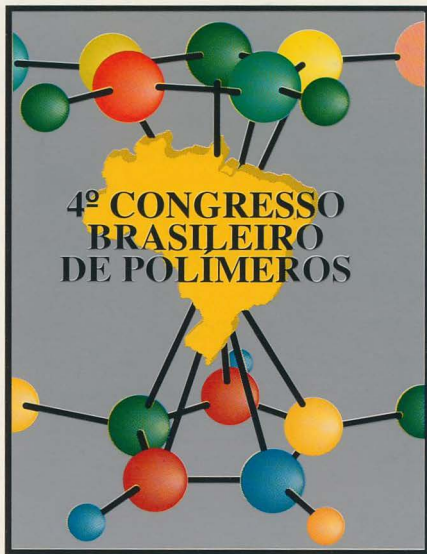


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Promoção:



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Mechanistic Studies of the Anionic Polymerization of Aminofunctionalized Dienes

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Introduction

The anionic polymerization of conjugated 1,3-dienes like 1,3-butadiene and isoprene has been studied since the early days of anionic polymerization. *N,N*-dialkyl-2-methylene-3-buten-1-amines (trivial name: 5-(*N,N*-dialkylamino)isoprenes) are a new class of 1,3-dienes and their anionic polymerization behavior is far from being understood. The first reports on the anionic polymerization of 5-(*N,N*-dialkylamino)isoprenes^{1,2,3} suffered from difficulties in the monomer preparation and monomer purity. This prohibited a detailed investigation on the polymerization mechanism, which was attributed mainly to monomer impurities. These impurities, introduced during Frauenrath synthesis⁴, were ruled out due to the development of an efficient monomer synthesis⁵. Highly pure 5-(*N,N*-dialkylamino)isoprenes have now become accessible in large quantities.

In our previous work we have already shown, that the type of the dialkyl substituent has a profound effect on the polymer microstructure. While polymers have been obtained in solvents of low polarity, polymerization appeared to slow down in polar solvents like THF. This was especially surprising, as the use of THF generally accelerates the anionic polymerization of 1,3-dienes due to the enhanced charge separation via solution of the cation. Another peculiar observation was that conversion was never quantitative, which was attributed to nonpolymerizable impurities in the monomer.

The present paper summarizes some recent kinetic studies on the homopolymerization behavior of 5-(*N,N*-dimethylamino)isoprene, 5-(*N,N*-diethylamino)isoprene and 5-(*N,N*-di-n-propylamino)isoprene in various solvents.

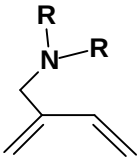
Results and Discussion

Preliminary experiments have been carried out in n-hexane and benzene to investigate the influence of solvent polarity. In these experiments monomer concentrations were kept around 0.1 - 0.3 mole/l at initiator concentrations around 0.4 - 1,5*10⁻³ mole/l. The attempted molecular weights ($[M]_o/[I]_o * M_{\text{monomer}}$) were above 20000 g/mole. The temperature was varied between 4°C and 40°C. In these experiments the monomer conversion was not quantitative. Conversion decreased with increasing temperature. In all these experiments it has been observed that the reacting solution turned slightly opaque during polymerization after a few minutes. This turbidity disappeared immediately after termination with methanol. These results can be interpreted as the result of a poor solubility of the poly-dialkylaminoisoprenes in nonpolar solvent in combination with aggregation of the living chain ends in the nonpolar solvent. As will be demonstrated below, the complexation of the Li⁺ counter ion with amino groups of the monomer but also with amino groups of the polymer chain - both intra- and intermolecular - play an important role in the polymerization

behaviour. In recent experiments carried out in a slightly more polar solvent high molecular weight polymers have been prepared at quantitative monomer conversion without precipitation⁶.

All of the following kinetic experiments were carried out in n-hexane with attempted number-average molecular weights not exceeding 7.000 g/mole to avoid precipitation. In these experiments monomer conversions were quantitative. Temperature were kept around 5°C. Table 1 summarizes the reaction conditions of these kinetic experiments.

Tab. 1: Reaction conditions for anionic polymerization

Monomer	T °C	[M] ₀ mole*l ⁻¹	[I] ₀ mole*l ⁻¹	k _{app} l*mole ⁻¹ *s ⁻¹	k _p l ² *mole ⁻² *s ⁻¹	
	dimethyl-	4	0.09	1.8*10 ⁻³	0.143 (± 13*10 ⁻³)	80 (± 13)
	diethyl-	6	0.10	2.8*10 ⁻³	0.309 (± 11*10 ⁻³)	110 (± 12)
	di-n-propyl-	4	0.08	1.9*10 ⁻³	0.188 (± 12*10 ⁻³)	99 (± 9)

The polymerization of the alkylaminoisoprenes is quite fast (compared to butadiene and isoprene under identical conditions). Under the conditions given above 50 % conversions are reached after around 2 - 3 minutes and the reaction is quantitative after around 20 minutes.

Figure 1 shows a typical „1st order plot“ of the reaction of 5-N,N-dimethylaminoisoprene. Already at very low conversion a considerable deviation from the behavior expected for a polymerization which is in first order with respect to the monomer concentration is observed. The same holds for the other aminoisoprenes. This is in contrast to the behaviour of all non-polar diene monomers in hydrocarbon solvents^{7,8,9}.

Surprisingly the kinetic behavior can be described perfectly if a second order reaction with respect to the monomer concentration is assumed. This is shown in Figure 2 for the three different 5-N,N-dialkylaminoisoprenes where the reciprocal value of the monomer concentration is plotted as a linear function of the reaction time.

The same behavior is observed in all polymerizations as long as the polymer does not precipitate. The apparent rate constants (k_p*[I]₀) derived from these 2nd order kinetic plots as well as the „true“ rate constants k_p are also given in Table 1. Within the experimental uncertainty of these experiments there is no strong influence of the alkyl substituents on the homopolymerization rate constants. The surprising second order kinetic behavior has to be attributed to the specific properties of the aminoisoprene monomers, more specifically to the possibility of the tertiary amino group to form a complex with the Li⁺ counter ion. A detailed mechanistic proposal based on the structure of aminofunctional lithium organic compounds will be given.

Acknowledgments

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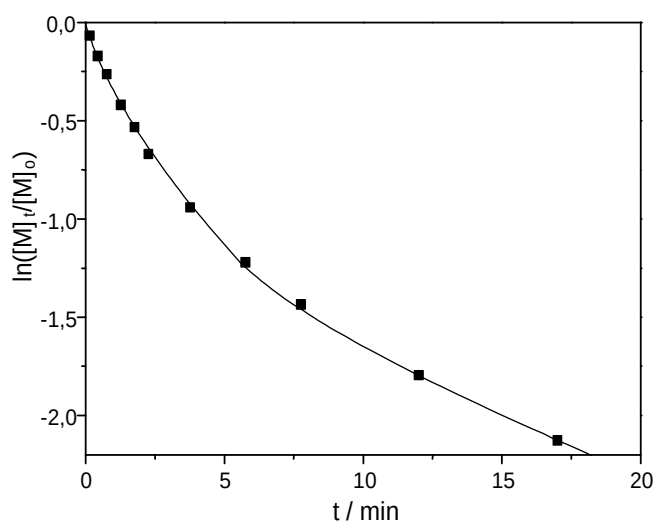


Fig. 1: Semilogarithmic plot of the monomer conversion in the polymerization of 5-(N,N-dimethylamino)isoprene (I_o : M_o)

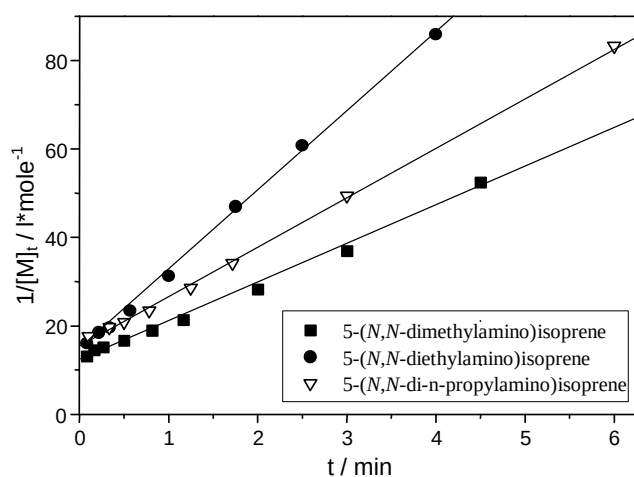


Fig.2: Analysis of the kinetic data of the polymerization of 5-(N,N-dialkylamino)isoprenes in hexane according to a second order kinetic behaviour with respect to the monomer concentration.

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