Classification of Polar Additives with Respect to Their Influence on the Microstructure in Anionic Polymerization of Butadiene with Butyllithium by Transition Energy Measurements

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ABSTRACT: On the basis of so-called linear free enthalpy correlations, a method is developed to predict vinyl contents of polybutadienes from anionic polymerizations with butyllithium in nonpolar solvents in the presence of bases. According to Reichardt with an extension by Langhals, a transition energy scale for the solvatochromic dye N,N-dimethyl indoaniline in dependence of concentrations of some bases is established. The bases were taken from polymerizations of butadiene of Antkowiak et al. and of Jin et al. It could be shown that vinyl contents determined by these authors correlate well with measured transition energies over the whole concentration range of the bases. Also, temperature dependences of vinyl contents can be predicted satisfactorily. Furthermore, it was found that vinyl contents in polybutadienes depend for weak bases primarily on the polarity of the solution mixture determined by the base concentration and not on the molar ratio of base to initiator. The results are extensively discussed in comparison with earlier attempts in the literature to predict the microstructure in polybutadienes in dependence of polar modifiers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1521–1532, 1999

Key words: anionic polymerization; polar additives; butadiene; microstructure; transition energy measurements

INTRODUCTION

In anionic polymerization of dienes like butadiene and isoprene with butyllithium as initiator, the addition of polar substances increases the number of vinyl side groups in the polymers. Additives differ in concentrations necessary for a shift in the vinyl content and in the maximum vinyl content available. In general, this influence levels off at higher additive/initiator ratios. Table I gives a survey of the effect of some selected polar additives on the vinyl content of poly(butadiene) and poly(isoprene). $^{1-12}$

We tried to arrange the polar substances due to their effectiveness. Of course, this order can only have qualitative character, since the experimental conditions reported in the literature differ in concentrations and reaction temperatures. The additives may be separated into three groups. Linear ethers or tertiary amines exhibit only weak interactions. They cause an increase in the vinyl content when used in high excess with respect to the initiator. Their effect is diminished by large substituents, as the case of diphenyl ether shows. Here even an excess of 120 with respect to the initiator does not remarkably change the microstructure. Cyclic ethers like THF and amines

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Addition	[Additive]/	T (°C)	Vinyl Content	Dof
Additive	[DULI]	$I(\mathbf{C})$	(11101 %)	Rel.
Polybutadiene				
_	_	20	8	1
Diphenyl ether	120	50	10.5	2
Triethylamine	30	30	21.4	2
Diethyl ether ^a	20	30	31	3
1,4-Dioxane ^a	10	35	36.2	4
THF	5	30	44	2
DABCO	3	30	41	2
HMPTA ^a	2	30	60.5	3
t-BuOK ^a	1	30	48	5
1,2-Dimethoxyethane ^a	1	30	68.5	6
TMEDA ^a	1	30	73.3	3
Diglyme ^a	1	30	83	3
1,2-Dipiperidinoethane	1	30	98.7	7
DIDIOX	0.6	5	96	8
Polyisoprene				
a	_	30	5	1
Diphenyl ether ^b	115	30	8	9
Triethylamine ^b	30	30	20	9
Diethyl ether ^b	20	30	21	9
THF ^a	15	30	31	1
1- <i>t</i> -Butoxy-2-ethoxyethane	1	30	55	10
TMEDA	1	15	70	11
1,2-Dipiperidinoethane ^a	1	5	62	12

Table I Influence of Polar Additives on the Microstructure of Poly(butadiene) (1,2 content) and Poly(isoprene) (3,4 and 1,2 content) in Anionic Polymerizations of Butadiene with *n*-Butyllithium (BuLi) in *n*-Hexane

THF: tetrahydrofuran; DABCO: diazabicyclooctane; HMPTA: hexamethylphosphoric acid triamide; *t*-BuOK: potassium *t*-butylate; TMEDA: N,N,N',N'-tetramethylethylene diamine; diglyme: diethylene glycol dimethyl ether; DIDIOX: 2,2'-bis-(4,4,6-trimethyl-1,3-dioxane).

^a In cyclohexane. ^b In *n*-heptane.

like DABCO exhibit medium interaction forces. Even in small excess to the initiator, the content of vinyl groups highly increases. Obviously, the solvation of the Li—C bond by two cyclic molecules is more favorable than by two linear ones. The third group is represented by bidentate complex ligands like TMEDA or diglyme. They appreciably change the microstructure of the polydienes even at stoichiometric ratios to the initiator. Interestingly, but not surprisingly, higher reaction temperatures diminish the influence of all additives, the effect being largest for strong additives.

The question arises whether it is possible to correlate the influence of polar additives on the microstructure of polydienes with one of their physicochemical parameters. In Table II, $^{13-19}$

some polar additives and some of these parameters are listed in the order corresponding to that in Table I.

It can be seen that neither the dielectric constant ε nor the dipole moment μ are appropriate parameters for classification. The strong additive diglyme has a relatively low ε value in comparison to THF, but yields a much higher vinyl content. On the other hand, its μ value is not so much higher than that of THF to explain the same effect. Also, the so-called donor number (DN) is not useful, since for example triethylamine has a relatively high donor number but one of the lowest effects on the microstructure. The interaction enthalpies ΔH , measured for solutions of *n*-butyllithium and poly(styryl)lithium, seem to show the right order. However, the value for *n*-butyllithium is lower with diglyme than with THF or TMEDA.

⁷Li-, ¹H-, and ¹³C-NMR measurements with isoprenyllithium oligomers allowed, in a number of cases, the qualitative estimate of the vinyl contents of polydienes in dependence of the polar additive used.^{10,19} However, we were interested in finding a simpler and more powerful method.

In this paper, we would like to present a method based on so-called linear free enthalpy correlations (LFE), using a procedure described by Reichardt¹⁴ with an extension developed by Langhals.²⁰ We will use the anionic polymerization of butadiene with butyllithium as example. We began these investigations in 1988.¹⁰ Simultaneously but independently, Jin and Yao¹⁸ started partially comparable investigations. Their results also will be discussed below.

RESULTS

Influence of the Concentration of Polar Additives on the Vinyl Content in Polybutadienes

The interaction between Li—C bonds and polar compounds is very complicated. Besides Coulomb, dipole, and induced dipole interactions, specific electron pair donator and acceptor interactions also can play an important role. Therefore, it is not surprising that such a complex interaction behavior cannot be described as in anionic polymerizations of dienes with butyllithium in the presence of bases with only one parameter like the dipole moment of the solvent or other variables. Dimroth et al.²¹ have proposed a so-called $E_T(30)$ solvent parameter to estimate the effect of solvents on chemical reactions. E_T values refer to solvatochromism of dyes, i.e., the change in position and sometimes intensity of an UV-visible (vis) absorption band accompanying a change in the polarity of a solution.¹⁴ $E_T(30)$ values are based on the transition energy for the longestwavelength solvatochromic absorption band of the pyridinium-N-phenoxide betaine (No. 30 in ref. 21). They are measured in kcal/mol. Usually, normalized E_T^N values are used with water and tetramethyl silane (TMS) as reference solvents:

$$E_T^N = \frac{E_T(30)(\text{solvent}) - E_T(30)(\text{TMS})}{E_T(30)(\text{water}) - E_T(30)(\text{TMS})}$$
(1)

This definition corresponds to a E_T^N and thus polarity scale from 0.000 for TMS as the least polar solvent to 1.000 for water as the most polar solvent.

According to Langhals,²⁰ the $E_T(30)$ values of binary solvent mixtures can be quantitatively described by the two-parameter equation:

$$E_T(30) = E_T(30)_o + E_D \cdot \ln(c_p/c^* + 1) \qquad (2)$$

In this equation, $E_T(30)_o$ is the $E_T(30)$ value of the pure component with lower polarity, c_p is the molar concentration of the more polar component, and E_D ("Energiedurchgriff") and c^* ("Erscheinungskonzentration") are adjustable parameters, specific for the binary solvent system under study. The c^* can be interpreted as threshold value defining a transition between two regions.

Table II Dielectric Constants ε , Dipole Moments μ , Donor Numbers (DN), Interaction Enthalpies ΔH with *n*-Butyllithium and with Poly(styryl)lithium (PSLi) in *n*-Hexane, and Transition Energies $E_T(30)$ for Some Polar Additives in Table I¹³⁻¹⁸

Additive	(10^{-30} cm)	μ [kJ/mol]	DN [kJ/mol]	$\Delta H_{ m n-BuLi}$ [kJ/mol]	$\Delta H_{ m PSLi}$ [kJ/mol]	$E_{T}(30)$
<i>n</i> -Hexane	1.88	0		_	_	129.4
Triethylamine	2.42	2.9	255.4	5	1.3	139.4
Diethyl ether	4.2	3.8	80.4	7.5	1.3	144.9
1,4-Dioxane	2.21	0	62	_	6.3	150.7
THF	7.58	5.8	83.7	31.8	18.8	156.6
1,2-Dimethoxyethane	7.2	5.7	100.5	_	41	159.9
TMEDA	_	_	230.3^{a}	43.1	55.7	148^{b}
Diglyme	5.8	6.6	_	27.2		161.6

^a For ethylenediamine.

^b Extrapolated from a $E_T(N,N$ -dimethyl indoaniline)/ $E_T(30)$ plot.¹⁹



Figure 1 Plot of E_T (DMIA) values vs E_T (30) values according to Table III.

For low concentrations of the more polar solvent $(c^* \ge c_p)$, eq. (2) may be approximated by

$$E_T(30) = E_T(30)_o + E_D(c_p/c^*)$$
(3)

and the $E_T(30)$ values increase linearly with the molar concentration of the more polar component, c_p . For high concentrations of the more polar solvent ($c^* \ll c_p$), eq. (2) can be written as

$$E_T(30) = E_T(30)_o + E_D \ln(c_p/c^*)$$
(4)

and values of $E_T(30)$ correlate linearly with the logarithm of the molar concentration of the more polar component, ln c_p .

The standard betaine dye of Dimroth et al.²¹ has been commercially available since 1991.²² It is only soluble in slightly polar solvents. Measurements in nonpolar solvents like *n*-hexane have been carried out using the dye in its penta-*tert*-butyl substituted form. Its synthesis is very laborious. Therefore, in our experiments we used the organic dye *N*,*N*-dimethyl indoaniline (DMIA), which is commercially available. It is easily soluble in nonpolar solvents. Since it shows positive solvatochromism, the molar transition energy is decreased with increasing polarity of the solvent according to

$$E_T(\text{kJ/mol}) = 119621/\lambda_{\text{max}}$$
(5)

For this dye $\lambda_{\rm max}$ values range between 552 nm in cyclohexane and 668 nm in water.

Thus, this dye is not as sensitive as the betaine dye of Dimroth et al. However, according to our experience, it is sensitive enough to allow measurements of shifts of the longest wavelength also at concentrations of DMIA as low as 10^{-6} to 10^{-5} mol/L by UV–vis spectroscopy. Figure 1 shows the correlation between E_T (DMIA) and E_T (30) values for different solvents.

Table III lists the corresponding values. They are ordered with respect to their effectivity creating vinyl structures in polybutadiene.

A linear relationship exists between both scales with a slope of less than one, showing that the shift of the longest wavelength is higher for the betaine than for the DMIA, as expected. Comparing the E_T (DMIA) values for the pure polar additives with their influence on the polymerization of butadiene, it can be seen that the additive with the biggest influence on the microstructure exhibits the lowest E_T (DMIA) value, since the E_T (DMIA) values decrease from the top to the bottom of Table III.

We applied the combined procedure of Reichardt and Langhals to polymerization experiments of Antkowiak et al.² They polymerized butadiene with *n*-BuLi in *n*-hexane with different amounts of the polar additives triethylamine, diethyl ether, THF, and diethylene glycol dimethyl ether (diglyme). Table IV shows their results.

We measured the $E_T(\text{DMIA})$ values for solutions of the four polar additives used by Antkowiak et al. in *n*-hexane in dependence of the additive concentration (Fig. 2), and calculated the constants $E_D(\text{DMIA})$ and $c^*(\text{DMIA})$ according to eq. (2), using nonlinear regression analysis (Table V). For $E_T(\text{DMIA})_o$ we used the molar transition energy of hexane of 220.0 kJ/mol.

The $E_D(DMIA)$ values increase with increasing effect of the additives on the vinyl contents of

Table III E_T (DMIA)¹⁰ and E_T (30)¹⁴ Values for Several Pure Substances

Solvent	<i>E</i> _T (DMIA) (kJ/mol)	<i>E</i> _T (30) (kJ/mol)
<i>n</i> -Hexane	220.0	129.4
Triethylamine	216.6	139.4
Diethyl ether	214.1	144.9
Dioxane	210.9	150.7
THF	208.1	156.6
1,2-DME	208.7	159.9
Diglyme	207.8	161.6

1,2-DME: 1,2-dimethoxy ethane, diglyme: diethylene glycol dimethyl ether.

		Vinyl Content (mol %)			
Additive	[Additive] : [BuLi]	30°C	50°C	70°C	
Triethylamine	30	21.4	17.6	14.2	
Triethylamine	270	37.1	32.9	24.7	
Triethylamine	510	39.6			
Diethyl ether	12	22.0	16.2	14.1	
Diethyl ether	96	35.7	26.0	23.5	
Diethyl ether	180	38.5	29.1	26.9	
THF	5	44.0	25.4	20.4	
THF	45	68.9	41.2	39.2	
THF	85	73.1	49.4	46.0	
Diglyme	0.10	51.0	23.8	14.4	
Diglyme	0.45	77.3	56.2	27.9	
Diglyme	0.80	77.7	63.7	39.5	

Table IVVinyl Content of Polybutadienefrom the Polymerization of Butadienewith *n*-Butyllithium in *n*-Hexane withDifferent Amounts of Polar Additives

Initial concentration of $n\text{-butyllithium}~[\text{BuLi}] = 1.3\cdot 10^{-3}~\text{mol/L}^{\bullet 2}$

polybutadiene; the $c^*(DMIA)$ values decrease in the same direction.

We tried to postulate a correlation equivalent to eq. (2) between the vinyl contents of the polymer (PB) and the additive concentration c_p . The amount of 1,2- and 1,4-structures in polybutadiene is proportional to the rate coefficients of 1,2-



Figure 2 E_T (DMIA) values for binary mixtures of polar additives and *n*-hexane from UV-vis measurements in dependence of the logarithm of the additive concentrations c_p .

Table V Parameters E_D (DMIA) and c^* (DMIA)
Determined from the Curves in Figure 2
According to Eq. (2) for Binary Mixtures
of Polar Additives and <i>n</i> -Hexane

Additive	$E_D({ m DMIA})$ (kJ/mol)	c*(DMIA) (mol/L)
Triethylamine Diethyl ether	-4.40 -5.15	4.65 4.14
THF Diglyme	$\begin{array}{c} -7.16 \\ -7.39 \end{array}$	$2.75 \\ 1.45$

and 1,4-additions in the propagation step. However, to be able to compare these values with those from E_T scales, we have to logarithm the rate coefficients. Their ratio is proportional to the difference of free activation enthalpies:

 $PB = lg rac{\% 1,2-polybutadiene}{\% 1,4-polybutadiene}$

$$= -\frac{\Delta G_{1,2}^{\#} - \Delta G_{1,4}^{\#}}{2.303 \cdot RT} \quad (6)$$

We assumed that the vinyl contents in polybutadiene will not depend on the absolute concentration of the additive but on its ratio to the initiator concentration. Therefore, we used the ratio [additive]/[initiator], (c_p/c_I) , as independent variable. Of course, due to this definition, we have to scale $c^*(PB)$, too:

$$PB = PB_0 + E_D(PB)\ln((c_p/c_I)/(c^*(PB)/c_I) + 1)$$
(7)

For the calculation of PB_o we used a vinyl content of 10%, obtained in pure hexane. This amount is relatively independent of the reaction temperature. Figure 3 shows curves for 30°C, and Table VI the calculated values of $E_D(PB)$ and $c^*(PB)/c_I$, for 30, 50, and 70°C, obtained by nonlinear regression from the values of Antkowiak et al. Since all $c^*(PB)$ values are normalized to the initial initiator concentration, the real $c^*(PB)$ values have to be calculated by multiplying the $c^*(PB)/c_I$ values in Table VI by the initial initiator concentration of $1.3 \cdot 10^{-3}$ mol/L, used in all experiments of Antkowiak et al.

Figure 3 shows that all PB values change in the same order in dependence of $\ln(c_p/c_I)$ as the E_T (DMIA) values in dependence of $\ln c_p$ (Fig. 2),



Figure 3 Ratio PB of 1,2- and 1,4-polybutadiene structures in the polymerization of butadiene with *n*-butyllithium in *n*-hexane according to eq. (7) in dependence of the logarithm of the ratio of the concentration of a polar additive c_p and the concentration of the initiator c_I at 30°C, deduced from the values in Table IV. $c_I = 1.3 \cdot 10^{-3}$ mol/L.

however with an inverse sign. In the concentration range investigated the linear relationship between $\ln(c_p/c_I)$ and PB according to eq. (7) is fulfilled. It does not hold for lower base concentrations. This is due to the fact that in pure nheptane about 10 % vinyl groups are formed already, and especially for weak bases higher concentrations are necessary to exhibit a significant influence on the microstructure. On the other hand, we have to consider that the vinyl contents in polybutadiene only increase to a maximum level, e.g., 85% at 39°C in pure THF, which corresponds to a PB value of 0.75. A comparable value of PB, however, is already obtained in a mixture of THF and hexane at $c_p/c_I = 100$ (99.3) vol hexane, 0.7 vol THF). That means that for

very high c_p/c_I values, where there is no further influence of the additive concentration on the vinyl contents, the regression function (7) cannot explain the experimental results. Therefore, we drew dotted lines in Figure 3 in this range.

The next step was the attempt to derive a correlation between $E_T(\text{DMIA})$ and PB values. Comparing the absolute additive concentrations in the experiments of Antkowiak et al. $(0.039 \le c_p \le 0.66 \text{ mol/L}$ for triethylamine, $0.00013 \le c_p \le 0.0010 \text{ mol/L}$ for diglyme) with $c^*(\text{DMIA})$ values in Table V, the $E_T(\text{DMIA})$ values can be approximated by the linear equation

$$E_T(\text{DMIA}) = E_T(\text{DMIA})_o + E_D(\text{DMIA}) \cdot c_n/c^*(\text{DMIA}) \quad (8)$$

On the other hand, the absolute c_p values in the polymerization experiments of Antkowiak et al. are much higher than the real $c^*(PB)$ values in Table VI. Therefore PB can only be approximated by the nonlinear equation

$$PB = PB_o + E_D(PB) \cdot \ln((c_p/c_l)/(c^*(PB)/c_l)) \quad (9)$$

Due to these results, a simple mathematical correlation between PB and $E_T(\text{DMIA})$ cannot be established. However, the slopes of both functions, $E_D(\text{DMIA})/c^*(\text{DMIA})$ and $-E_D(\text{PB})\ln(c^*(\text{PB})/c_I)$ can be correlated. This is shown for two arbitrarily selected concentrations of the bases.

Assuming $c_p = c_I = 1.3 \cdot 10^{-3}$ mol/L, i.e., $c_p/c_I = 1$, we get

$$E_T(\text{DMIA}) - E_T(\text{DMIA})_o = E_D(\text{DMIA})$$

 $\cdot 1.3 \cdot 10^{-3}/c^*(\text{DMIA})$ (10)

$$PB - PB_{o} = -E_{D}(PB)$$
$$\cdot \ln(c^{*}(PB)/1.3 \cdot 10^{-3}) \quad (11)$$

Table VI $E_D(PB)$ and $c^*(PB)/c_I$ Values in the Polymerization of Butadiene with *n*-Butyllithium in *n*-Hexane in the Presence of Polar Additives, Derived from the Curves in Figure 3 According to Eq. (7) for 30, 50, and 70°C ($c_I = 1.3 \cdot 10^{-3}$ mol/L)

	30°C		5	0°C	70°C	
Additive	$\overline{E_D(\mathrm{PB})}$	c*(PB)/c _I	$\overline{E_D(\mathrm{PB})}$	c*(PB)/c _I	$\overline{E_D(\mathrm{PB})}$	$c^{*}(PB)/c_{I}$
Triethylamine	0.14	1.90	0.16	5.33	0.14	8.35
Diethyl ether	0.14	0.64	0.13	2.17	0.15	5.57
THF	0.19	0.062	0.16	0.26	0.20	0.92
Diglyme	0.25	0.0015	0.43	0.048	0.55	0.27

Assuming $c_p = 1.3 \cdot 10^{-3} \cdot e \text{ mol/L}$ and $c_I = 1.3 \cdot 10^{-3} \text{ mol/L}$, i.e., $c_p/c_I = e$, we have

$$E_T(\text{DMIA}) - E_T(\text{DMIA})_o$$

= $E_D(\text{DMIA}) \cdot 1.3 \cdot 10^{-3} \cdot e/c^*(\text{DMIA})$ (12)

$$PB - PB_{o} = E_{D}(PB) - E_{D}(PB)$$
$$\cdot \ln(c^{*}(PB)/1.3 \cdot 10^{-3}) \quad (13)$$

When plotting the parameters of the righthand sides of eqs. (11) and (13) vs the parameters of the right-hand sides of eqs. (10) and (12), respectively, we obtained Figures 4(a) and 4(b).

Linear relationships were obtained between both terms at different temperatures, which can be described by the equations

$$-E_D(PB) \cdot \ln(c^*(PB)/c_I)$$

= $AE_D(DMIA)/c^*(DMIA) + B$ (14)

$$E_D(PB) - E_D(PB) \cdot \ln(c^*(PB)/c_i)$$

= $C \cdot e \cdot E_D(DMIA)/c^*(DMIA) + D$ (15)

$$T = 30^{\circ}C \quad A = -0.41 \quad B = 0.48$$

$$T = 50^{\circ}C \quad A = -0.37 \quad B = 0.62$$

$$T = 70^{\circ}C \quad A = -0.25 \quad B = 0.56$$

$$C = -0.16 \quad D = -0.37$$

$$C = -0.16 \quad D = -0.59 \\ C = -0.13 \quad D = -0.56$$

These equations allow the estimation of the amount of the 1,2-microstructure in polybutadiene in dependence of the concentration of other polar additives not investigated before. At first, UV-vis absorption measurements have to be performed with DMIA in *n*-hexane and with different amounts of the new polar additive. Subsequently, $E_D(DMIA)$ and $c^*(DMIA)$ values are obtained using nonlinear regression analysis according to eq. (2). For $c_p/c_I = 1$ and $c_p/c_I = e$, the parameters $E_D(PB)$ and $c^*(PB)/c_I$ can be extrapolated from the linear plots in Figures 4a and 4b using eqs. (14) and (15). For example, $E_{\rm D}(\rm PB)$ results from subtracting eq. (14) from eq. (15). Then, $c^{*}(PB)/c_{I}$ can be determined, e.g., from eq. (14). Subsequently, eq. (9) allows us to calculate the vinyl content of the polymer.

The developed procedure is simpler and more powerful than all other methods proposed in the literature to predict the vinyl contents of poly-



Figure 4 Correlation between $E_D(PB) \cdot \ln(c^*(PB)/c_I)$ values (a) and $E_D(PB) - E_D(PB) \cdot \ln(c^*(PB)/c_i)$ values (b) from the vinyl contents in polybutadiene in the presence of polar additives (Table VI) and $E_D(DMIA)/c^*(DMIA)$ values (Table V) for $c_p/c_I = 1$ (a) and $c_p/c_I = e$ (b) according to eqs. (14) and (15), respectively. $c_I = 1.3 \cdot 10^{-3}$ mol/L.

but adiene in anionic polymerizations of butadiene with *n*-butyllithium.^{2,18,23–28}

Influence of the Reaction Temperature on the Vinyl Content in Polybutadiene

The results of Antkowiak et al. can also be used to investigate the temperature dependence of the vinyl contents on the presence of polar additives. According to eq. (6), PB is equal to the logarithm



Figure 5 Plot of $-E_D(PB) \cdot \ln (c^*(PB)/c_I)$ from Table VI vs 1/T. $c_I = 1.3 \cdot 10^{-3}$ mol/L.

of the ratio of two rate coefficients, which usually obey the Arrhenius law. Therefore, we plotted the slope from eq. (9), $-E_D(\text{PB}) \cdot \ln(c^*(\text{PB})/c_I)$, vs. 1/T, from the values in Table VI. We obtained the results illustrated in Figure 5.

The expected linear relationships were obtained. They can be described by the following equations:

Triethylamine:

$$E_D(PB) \cdot \ln(c^*(PB)/c_I) = -545/T + 1.91$$
 (16)

Diethyl ether:

$$E_D(\text{PB}) \cdot \ln(c^*(\text{PB})/c_I) = -831/T + 2.68$$
 (17)

THF:

$$E_D(PB) \cdot \ln(c^*(PB)/c_I) = -1333/T + 3.88$$
 (18)

Diglyme:

$$E_D(PB) \cdot \ln(c^*(PB)/c_I) = -2336/T + 6.03$$
 (19)

With these equations it is possible to predict the vinyl content of polybutadiene not only over a broad concentration range of polar additives but also over a broad temperature range. For diglyme, it has to be taken into account that both values $E_D(PB)$ and $c^*(PB)/c_I$ depend on the reaction temperature. This result can be understood if we assume that the influence of diglyme on the microstructure not only depends on the polarity of

the solvent but also on specific chelate interactions. The vinyl content is relatively high already at stoichiometric diglyme concentrations. A further increase causes only small further increases in the vinyl content. There, also the influence of reaction temperature is diminished.

The results of Jin et al.²⁴ show the same behavior. We used their values from the polymerization of butadiene with *n*-butyllithium in mixtures of cyclohexane with THF, dioxane, or diethyl ether, listed in Table VII, to calculate PB values. These are plotted in Figure 6 vs $\ln(c_p/c_I)$ for THF.

The similarity to our curves in Figure 3 is striking. Plots for diethyl ether and dioxane exhibit the same pattern. With increasing temperature, higher amounts of the polar additive are necessary to get the same vinyl contents as at lower temperatures. We applied our procedure on all results of Jin et al. in Ref. 24 and evaluated $E_D(PB)$ and $c^*(PB)/c_I$ values according to eq. (9). Since Jin et al. had worked with more polar solvents, we assumed that in that case the PB_o values would only change slightly and used our PB_o values for all temperatures. Table VIII summarizes the results.

It is obvious that in a first approximation $E_D(PB)$ values are independent of the temperature, while the $c^*(PB)/c_I$ values increase with increasing temperature. As stated above, the terms $-E_D(PB) \cdot \ln(c^*(PB)/c_I)$ are linearly dependent on 1/T. For the correlations in the three solvents used by Jin et al., we obtained the following:

Diethyl ether:

$$E_D(PB) \cdot \ln(c^*(PB)/c_I) = -392/T + 1.01$$
 (20)

Dioxane:

$$E_D(PB) \cdot \ln(c^*(PB)/c_I) = -1154/T + 3.58$$
 (21)

THF:

$$E_D(PB) \cdot \ln(c^*(PB)/c_I) = -1363/T + 3.91$$
 (22)

The results of Antkowiak et al. and Jin et al. deliver nearly the same values for THF, though the initiator concentration differs. However, for diethyl ether different values are obtained, probably due to the different temperature ranges $(10-30^{\circ}C \text{ in polymerizations of Jin et al. and } 30-70^{\circ}C \text{ in polymerizations of Antkowiak et al.}).$

			% Vinyl						
Additive	[Additive]/[BuLi]	10°C	20°C	25°C	30°C	35°C	40°C	50°C	65°C
Diethyl ether	10	30.0	28.0		25.8				
Diethyl ether	20	34.4	31.8		29.0				
Diethyl ether	40	38.8	35.7		32.4				
Diethyl ether	80	43.2	39.6		35.8				
Diethyl ether	150	46.9	43.0		39.0				
Diethyl ether	300	50.6	46.6		42.3				
Dioxane	10		47.3			36.2		27.6	23.4
Dioxane	20		57.8			46.3		35.8	29.8
Dioxane	40		66.4			56.0		44.9	37.6
Dioxane	80		72.7			63.9		53.6	45.8
Dioxane	150		76.1			69.3		60.2	52.9
Dioxane	300		78.5			73.3		65.9	59.4
THF	10		60.1		54.7		46.5	39.4	
THF	20		65.7		59.3		50.4	42.8	
THF	40		72.6		66.3		56.8	48.8	
THF	80		79.5		74.5		65.5	57.5	
THF	150		83.1		80.0		70.0	66.3	
THF	7^{a}			29.5					
THF	23^{a}			40.5					
THF	67^{a}			52.9					
THF	180^{a}			63.0					
THF	448^{a}			69.8					
THF	785^{a}			71.5					
THF	1670^{a}			75.8					

 Table VII
 Vinyl Contents of Polybutadiene from the Polymerization of Butadiene with

 n-Butyllithium in Cyclohexane with Different Amounts of Polar Additives

Initial concentration of *n*-butyllithium [BuLi] = $4 \cdot 10^{-3}$ mol/L.²⁴ ^a [BuLi] = $1 \cdot 10^{-4}$ mol/L.²³

Influence of the Initial Initiator Concentration on the Vinyl Content of Polybutadiene

Antkowiak et al. performed their polymerization experiments only at one initial initiator concentration of $1.3 \cdot 10^{-3}$ mol/L. At higher initial initiator concentrations the vinyl contents usually increase in the presence of polar additives though the ratio c_p/c_I is the same as for low initial initiator concentrations. This can be deduced from the results of Jin et al.^{23,24,28} They performed polymerizations of butadiene in THF using an initial initiator concentration of $1 \cdot 10^{-4}$ mol/L at $25^{\circ}C^{23}$ and of $4 \cdot 10^{-3}$ mol/L at $20^{\circ}C.^{24,28}$

Using their results, and applying our method, we obtained the curves in Figure 7(a). For both

initial initiator concentrations the same $E_D(PB)$ values are obtained (Table IX).

The values for $c^*(PB)/c_I$ increase with increasing initial initiator concentration. This effect can be explained by the fact that $c^*(PB)$ is scaled on the initial initiator concentration. Multiplying the $c^*(PB)/c_I$ values with the corresponding initial initiator concentration, we got nearly the same values (Table IX). Therefore, we plotted the PB values also vs $\ln c_p$ [Fig. 7(b)]. The two curves in Figure 7(a) merged to only one curve. Applying our method to this curve again, we got the same value with 0.18 for $E_D(PB)$ as for the two single curves, and with $4.1 \cdot 10^{-5}$ mol/L for $c^*(PB)$, a value that is the



Figure 6 PB values according to eq. (7) in dependence of the logarithm of the molar ratio of polar additives and initiator at different temperatures for THF from Ref. 24. $c_I = 4 \cdot 10^{-3}$ mol/L.

average of the $c^*(PB)$ values for the corresponding initial initiator concentrations.

Also, the results of Antkowiak et al. may be incorporated into these considerations. In Table VI a value of $E_D(PB) = 0.19$ and of $c^*(PB)/c_I =$ 0.062 is given for the system *n*-hexane/*n*-butyllithium $(1.3 \cdot 10^{-3} \text{ mol/L}, 30^{\circ}\text{C})$ and THF. When multiplying the last value with the initial initiator concentration, we obtain a value of $8.1 \cdot 10^{-5}$ mol/L for $c^*(PB)$, which is slightly higher than those in Table IX, presumably due to the higher reaction temperature.

These results lead to the assumption that the vinyl content in polybutadiene in anionic polymerizations of butadiene with butyllithium may mainly be dominated by the concentration of the polar additive and therefore by the polarity of the reaction medium and not by the molar ratio of the additive to the initiator, at least for weak, mono-



Figure 7 PB values according to eq. (7) from the polymerization of butadiene with *n*-butyllithium in cyclohexane with THF as polar additive in dependence (a) of the logarithm of the ratio c_p/c_I of the concentrations of THF and initiator, and (b) of the logarithm of the THF concentration c_p : \Box at 25°C with $c_I = 1 \cdot 10^{-4}$ mol/L²³ and \bullet at 20°C with $c_I = 4 \cdot 10^{-3}$ mol/L.^{24,28}

Table VIII $E_D(PB)$ and $c^*(PB)/c_I$ Values in the Polymerization of Butadiene with *n*-Butyllithium in Cyclohexane, Calculated According to Eq. (9) from Results of Jin et al.²⁴

	Т	HF	Dioxane				Dieth	yl Ether
°C	$E_D(PB)$	$c^{*}(\text{PB})/c_{I}$	°C	$E_D(PB)$	$c^{*}(PB)/c_{I}$	°C	$E_D(PB)$	$c^{*}(PB)/c_{I}$
20	0.18	0.017	20	0.23	0.18	10	0.11	0.035
30	0.18	0.035	35	0.24	0.55	20	0.10	0.040
40	0.18	0.088	50	0.24	1.23	30	0.094	0.050
50	0.18	0.18	65	0.23	1.68			

Table IX $E_D(PB)$, $c^*(PB)/c_I$ and $c^*(PB)$ Values in the Polymerization of Butadiene with *n*-Butyllithium in Mixtures of Cyclohexane and THF,^{23,24,28} Calculated from the Curves in Figures 7(a) and 7(b)

c_I (mol/L)	$E_D(\mathrm{PB})$	$c^{*}(\text{PB})/c_{I}$	<i>c</i> *(PB) (mol/L)
$4 \cdot 10^{-3} \\ 1 \cdot 10^{-4}$	0.18 0.18	$\begin{array}{c} 0.017\\ 0.31\end{array}$	$\begin{array}{c} 5.1{\cdot}10^{-5} \\ 3.1{\cdot}10^{-5} \end{array}$

dentate Lewis bases. In mixtures with equal additive concentrations but different initiator concentrations, the same amount of vinyl groups in polybutadiene should be obtained. This seems to be inconsistent with results published in literature allegedly showing that the vinyl content in polydienes increases with the ratio of [base]/[Li]. However, the only papers presenting such results for weak bases are those of Antkowiak et al. and Jin et al., and their experiments can be interpreted in the way discussed above. Another support for our interpretation could be the fact that large amounts of weak bases relative to lithium must be present to obtain significant amounts of vinyl microstructure. Of course, the situation dramatically changes using bases that interact very strongly with lithium. With strongly coordinating bases like TMEDA, dipiperidinoethane, bismorpholinoethane, 2,2'-bis(4,4,6-trimethyl-1,3-dioxane (DIDIOX) and cis-N,N,N',N'-tetramethyl-1,2-diaminocyclopentane, high vinyl microstructure is produced at base to lithium ratios as low as 1–2.²⁹ In this case, the interaction between active centers and strong coordinating bases is nearly like a stoichiometric chemical reaction, the equilibrium lying on the right side. Therefore it can be understood that the microstructure here actually depends on the molar ratio additive/initiator.

CONCLUSIONS

The dependence of the vinyl contents of polybutadienes in anionic polymerizations of butadiene with n-butyl lithium in mixtures of nonpolar solvents and polar additives can be advantageously predicted from linear free enthalpy correlations. At first, the dependence between the shift of the longest wavelength of an organic dye in UV-vis measurements and the vinyl contents in polybutadienes from different amounts of a variety of polar additives has to be established. From these correlations, which should also include the temperature dependence, vinyl contents in polybutadienes obtained in the presence of polar additives hitherto not investigated can be estimated.

The procedure is not applicable to all bases. Especially bidentate bases may show appreciable deviations from the developed LFE correlations. Besides their effect on the polarity of the solution mixture, this behavior has to be attributed to specific interactions of these compounds with growing centers.

EXPERIMENTAL

All experiments were performed under argon, purified by Sicapent (from Merck, Germany) and Oxisorb (from Messer-Griesheim, Germany).

n-Hexane (Baker, Germany) was refluxed for two days over sodium wire and distilled at atmospheric pressure. Before use, it was condensed from *n*-butyl lithium in high vacuum. The d⁶benzene (Aldrich, Germany) was also condensed from *n*-butyl lithium in high vacuum.

The oxygen-containing polar additives diethyl ether, diisopropyl ether, *t*-butylmethyl ether, dioxane, dioxolane, THF, tetrahydropyran, dimethoxymethane, dimethoxyethane, and diethylene glycol dimethyl ether were purchased (pro synthesis) from Fluka, Aldrich, and Merck, all in Germany. Dimethoxypropane and dimethoxybutane were synthesized according to ref. 30 with yields of 60 and 65% [gas chromatography (GC): 97 and 98%], respectively. All ethers were refluxed over sodium wire and distilled. Before use, they were condensed from LiAlH₄.

The nitrogen-containing additives triethylamine, DABCO, TMMDA, TMEDA, TMPrDA, TMBuDA, *N*-methylpiperidine, dipiperidinomethane, and 1,2dipiperidinoethane were purchased (pro synthesis) from Fluka and Janssen, both in Germany. 1,3-Dipiperidinopropane was synthesized according to ref. 31, yield 80% (GC: 98%). DABCO was sublimed in high vacuum and stored under argon. All other amines were stirred for three days over CaH₂ and distilled. TMPrDA, TMBuDA, dipiperidinomethane, dipiperidinoethane, and dipiperidinopropane were distilled from LiAlH₄ before use; all other compounds were condensed from LiAlH₄ in high vacuum. Tetrahydrothiophene (Aldrich, Germany, pro synthesis) was stirred over sodium wire for two days and then distilled.

UV-vis measurements were performed with a spectrometer Pye Unicam, type SP 8-500 (Philips, Germany). For that purpose, DMIA (Aldrich, Germany) was dissolved in the polar additive and in *n*-hexane in concentrations, such that the extinction in the maximum of absorbance of each solution was 1. From these stock solutions, appropriate mixtures were measured in a quartz cuvette of 1 cm in length. The wavelength of maximal absorption, λ_{max} was determined using the Mathias rule³² with an accuracy of ±0.2 nm, according to a transition energy accuracy of ±0.08 kJ/mol.

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