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

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ABTRACT: A transition energy scale was established on the basis of dimethyl indoaniline as organic dye for 23 mono- and bidentate polar additives. From polymerization experiments of isoprene with *s*-butyllithium in mixtures of *n*-hexane and the selected bases, the microstructure of polyisoprenes was determined by ^{1}H-NMR spectroscopy. The vinyl contents of these polymers could be satisfactorily correlated with the transition energy measurements. However, it turned out that especially bidentate bases do not fit into this scheme. Obviously, besides their influence on the polarity of the reaction solution, they exhibit special interactions with the growing centers. The developed correlations allow the prediction of 1,2- and 3,4-linkages in polyisoprenes from anionic polymerization of isoprene with butyllithium in polar solvents in the presence of low concentrations, also of bases hitherto not investigated. The temperature dependence of the microstructure can likewise be estimated. As in the case of butadiene, at least for weak bases, it was found that the vinyl contents depend primarily on the polarity of the reaction mixture determined by the base concentration and not on the molar ratio of base to initiator. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1533–1547, 1999

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

INTRODUCTION

In a recent paper, we described a method to estimate the microstructure of polybutadiene from anionic polymerization with *n*-butyllithium in dependence of the concentrations of polar additives from measurements of transition energies.[1] In this paper, we would like to extend this method to the anionic polymerization of isoprene with *s*-butyllithium.

RESULTS

Influence of the Concentration of Polar Additives on the Vinyl Content of Polyisoprene

We selected the polar compounds listed in Table I. On the one hand, monofunctional bases like open chain ethers and amines with different substituents or cyclic compounds were selected. For the latter ones, five- or six-membered heterocycles are recommended for stability reasons. Tetrahydrothiophene was chosen for a comparison with the corresponding oxygen base tetrahydrofuran (THF). On the other hand, bifunctional bases ex-

Table I   Influence of Polar Additives on the Microstructure of Polyisoprene in Anionic Polymerizations of Isoprene with *s*-Butyllithium (BuLi) in *n*-Hexane at 50°C

Additive	[Additive]/ [BuLi]	Microstructure (mol %)			
		1,2	3,4	*cis*-1,4	*trans*-1,4
—	—		6	69	25
Tetrahydrothiophene	20		6.5	66	27.5
	100		8	63.5	28.5
	300		12	59	29
Dimethoxy methane	5		6.5	68	25.5
	20		7.5	68	24.5
	100		11	65	24
	250		24.5	52	23.5
Triethylamine	5		7	69	24
	20		9	66.5	24.5
	100		18.5	57	24.5
	250		27	48	25
Diisopropyl ether	5		7	69	24
	20		8.5	68	23.5
	100		17	58	24.5
	300		27	46	27
Diethyl ether	5		7.5	66	26.5
	20		10	63.5	26.5
	100		22	52	26
	250		31	42.5	26.5
t-Butylmethyl ether	5		7	66.5	26.5
	20		11	62	27
	100		23	50	27
	250		32	42.5	25.5
N-Methyl piperidine	5		8.5	66	25.5
	20		16	58	26
	100		32	46	21.5
	250		40	39	20
1,3-Dipiperidino ethane	1		7	68.5	24.5
	5		9.5	65.5	26
	20		16.5	53	30.5
	100	0.5	33	36.5	30
TMMDA	1		7	67	26
	5		10	64.5	25.5
	20		17.5	55.5	27
	100	1	37.5	35.5	26
1,4-Dioxane	1		7	66	27
	5		11	64.5	24.5
	20		20.5	52	27.5
	100	2	41.5	34	22.5
1,3-Dioxolane	1		8.5	63	28.5
	5		12	61.5	27.5
	20		20	53	27
	100	2	42	32	24
TMBuDA	1		8	66	26
	5		12.5	60	27.5
	20		25.5	44.5	30
	100	3	43	31	23
Tetrahydropyran	1		8	68	24
	5		12	63	25
	20		25	48.5	26.5

Table I *Continued*

Additive	[Additive]/[BuLi]	Microstructure (mol %)			
		1,2	3,4	*cis*-1,4	*trans*-1,4
	100	3	45.5	31.5	20
Dipiperidino methane	1		8	67	25
	5		15	61	24
	20		30	45	25
	100	1	52	25	22
Tetrahydrofuran	1		8.5	64.5	27
	5		19	54	27
	20	2	35	36.5	26.5
	50	4	52	22	22
	150	8.5	57	17	17.5
1,4-Dimethoxy butane	0.5		8	67	25
	1		11	64	25
	5		24	50	26
	20	1	44	31.5	23.5
DABCO	1		13	63	24
	5		30	46.5	23.5
	20	3.5	41	31	24.5
	100	6	47.5	26	20.5
1,3-Dimethoxy propane	0.5		13	61	26
	1		35	39.5	25.5
	5	4	53.5	22	20.5
	20	9	64	9	18
TMPrDA	0.2		7.5	67	25.5
	0.5		19	54	27
	1		33	39	27
	5	4	52	22	22
	20	10	57	11	22
1,2-Dipiperidino ethane	0.2		10	62	28
	0.5		17	54.5	28.5
	1	1	33	38	28
	5	7	55	19	19
	20	12	58.5	10.5	19
1,2-Dimethoxy ethane	0.2		8	67	25
	0.5		21	53	26
	1	0.5	40	35.5	24
	5	4	56.5	19.5	20
	20	7	67	10	16
Diglyme	0.2		8.5	67	24.5
	0.5		18	56	26
	1	1	46.5	30	22.5
	5	8	67	11	14
	20	10	69	9	12
TMEDA	0.2		7.5	65.5	27
	0.5	1.5	36	38.5	24
	1	7.5	53	23.5	16
	5	10	60	15	15
	20	13	60	13	14

[BuLi] = $1 \cdot 10^{-3}$ mol/L. TMMDA: *N,N,N′N′*-tetramethylmethylene diamine; TMBuDA: *N,N,N′,N′*-tetramethyl-1,4-diamino butane; DABCO: diazabicyclooctane; TMPrDA: *N,N,N′,N′*-tetramethyl-1,3-diamino propane; diglyme: diethylene glycol dimethyl ether; TMEDA: *N,N,N′N′*-tetramethylethylene diamine.

Figure 1 E_T(DMIA) values for binary mixtures of polar additives with n-hexane at 20°C from UV–vis measurements in dependence of the logarithm of the additive concentration ln c_p.

ert strong influences on lithium organyls due to their molecular geometry.

The polymerizations were performed at a constant initial initiator concentration [BuLi] of $1 \cdot 10^{-3}$ mol/L at 50°C. We used s-butyllithium as initiator to reduce the length of the induction period at the beginning of the reaction, as it is known for n-butyllithium due to a slow initiation reaction. The high temperature is comfortable since the interaction of polar compounds with the Li—C bond is now reduced. Therefore, their effect on the microstructure can be observed over a larger concentration range up to

the maximal vinyl group content. The microstructure of the polyisoprenes was determined by ^{1}H-NMR spectroscopy. Table I summarizes the results.

From this table it can be deduced that in general the increase of additive concentration causes an increase of the 3,4-structure and a decrease of the 1,4-*cis* structure. The amount of the 1,4-*trans* structure remains constant in a first approximation. In polyisoprenes with more than 35% 3,4-structure 1,2-structure also is observed.

Changing from linear to cyclic additives causes a higher increase in vinyl groups, as a comparison

Figure 1 (*Continued from the previous page*)

between diethyl ether and dioxane or triethyl-amine and DABCO shows.

The effect of bifunctional bases, where the functional groups are bound by alkyl groups of different lengths, also depends on the geometry of the molecule. Basic groups connected by ethylene or propylene groups cause high vinyl group contents already under stoichiometric conditions. The influence of basic groups connected by methyl or butyl groups is appreciably lower. Within one class of compounds more or less large alkyl substituents at the hetero atom shift the effectivity to those with shorter alkyl bridges: In the group of dimethoxy substituted compounds, 1,2-dimethoxy ethane (DME) and 1,3-dimethoxy propane (DMPr) show comparable effectivity. Comparing the bis-(dimethylamino) bases, N,N,N',N'-tetramethylethylene diamine (TMEDA) gives significantly higher vinyl contents than N,N,N',N'-tetramethyl-1,3-propane diamine (TMPrDA), and in the group of piperidyl bases even dipiperidino methane (DPM) is more effective than 1,3-dipiperidino propane (DPPr).

The results can be summarized to the following classification:

Diethyl ether	<	Dioxane		
Triethylamine	<	NMP	≪	DABCO
DMM	<	DMBu	<	DMPr	≈	DME
TMMDA	≈	TMBuDA	<	TMPrDA	<	TMEDA
DPPr	<	DPM	<	DPE		

(NMP: N-methyl piperidine; DMM: dimethoxy methane, DMBu: 1,4-dimethoxy butane, TMMDA: N,N,N',N'-tetramethylmethylene diamine, TMBuDA: N,N,N',N'-tetramethyl-1,4-diamino butane, DPE: 1,2-dipiperidino ethane).

It is of interest that dipiperidino ethane, causing the highest vinyl group content in the polymerization of butadiene, exerts a smaller influence than TMEDA in the polymerization of isoprene. One explanation could be the large repulsive interaction of the additional methyl group in the active center with the big substituents of DPE. This effect should not be so large in the case of the smaller base TMEDA.

According to the procedure described in ref. 1, we did not relate our transition energy measurements to the commonly used pyridinium-N-phenoxide betaine, proposed by Dimroth et al.,[2] but to N,N-dimethyl indoaniline (DMIA), which is commercially available and soluble in n-hexane. We determined E_T(DMIA) values of mixtures with 1.25, 2.5, 5, 12.5, 25, 50, and 70 vol % of the selected polar compound in n-hexane and in pure polar solvents by UV–visible (vis) spectroscopy (Fig. 1).

Table II E_T(DMIA) Values for Pure Substances, Parameters E_D(DMIA) and c^*(DMIA) and the Ratio E_D(DMIA)/c^*(DMIA) Determined from the Curves in Figures 1(a)–1(f) According to Eq. (1) for Binary Mixtures of Polar Additives in *n*-Hexane at 20°C

Substance	E_T(DMIA) (kJ/mol)	E_D(DMIA) (kJ/mol)	c^*(DMIA) (mol/L)	E_D(DMIA)/c^*(DMIA) (kJ/L)
Hexane	219.98			
Tetrahydrothiophene[b]	204.99	−10.22	3.40	−3.01
Dimethoxy methane	214.36	−8.08	11.23	−0.72
Triethylamine	216.63	−4.02	5.89	−0.68
Diisopropyl ether	214.57	−6.87	6.04	−1.14
Diethyl ether	214.11	−4.81	4.28	−1.13
t-Butylmethyl ether	213.48	−6.11	4.70	−1.30
N-methyl piperidine	214.32	−5.65	4.86	−1.16
1,3-Dipiperidino propane	212.82	−14.11	6.87	−2.05
TMMDA[b]	215.37	−7.87	9.37	−0.84
1,4-Dioxane	210.93	−6.07	3.55	−1.71
TMBuDA	206.83	−10.09	6.31	−1.60
1,3-Dioxolane	213.53	−7.08	2.83	−2.43
Tetrahydropyran	209.38	−7.83	3.69	−2.12
Dipiperidino methane[b]	213.74	−17.75	12.85	−1.50
Tetrahydrofuran	208.13	−6.99	2.83	−2.47
1,4-Dimethoxy butane	209.76	−8.54	3.17	−2.69
DABCO[a]		−4.89	1.14	−3.47
1,3-Dimethoxy propane[b]	210.39	−7.70	3.60	−2.14
TMPrDA[b]	213.95	−11.43	9.06	−1.26
1,2-Dipiperidino ethane[b]	212.27	−14.82	6.91	−2.14
1,2-Dimethoxy ethane[b]	208.71	−7.24	2.62	−2.76
Diglyme	207.75	−7.45	1.70	−4.38
TMEDA[b]	213.36	−8.54	5.53	−1.54

[a] At 60°C.
[b] Additives that do not fit into a classification on the basis of the ratio E_D(DMIA)/c^*(DMIA).

According to eq. (1), derived from a procedure proposed by Langhals,[3]

$$E_T(\text{DMIA}) = E_T(\text{DMIA})_o$$
$$+ E_D(\text{DMIA}) \cdot \ln(c_p/c^*(\text{DMIA}) + 1) \quad (1)$$

with $E_T(\text{DMIA})_o \equiv$ transition energy in *n*-hexane, we determined the coefficients E_D(DMIA) and c^*(DMIA) by regression analysis. All results are summarized in Table II. They are listed with increasing effectivity of the polar additives to create vinyl structures in polyisoprene. Since DABCO

Table III   Parameters E_D(DMIA) and c^*(DMIA) and Their Ratio for Ternary Mixtures of *n*-Hexane/Additive/Isoprene Compared to the Same Values for Binary Systems

	Ternary			Binary
Additive	E_D(DMIA) (kJ/mol)	c^*(DMIA) (mol/L)	E_D(DMIA)/c^*(DMIA) [kJ/L]	E_D(DMIA)/c^*(DMIA) (kJ/L)
Triethylamine	−12.02	19.41	−0.61	−0.68
Diisopropyl ether	−9.76	9.60	−1.02	−1.14
1,3-Dipiperidino propane	−19.90	9.86	−2.02	−2.05
Tetrahydrofuran	−7.24	3.16	−2.29	−2.47
1,2-Dimethoxy ethane	−7.37	2.77	−2.66	−2.76

has only a low solubility in *n*-hexane at room temperature (approximately 0.2 mol/L), these experiments were performed at 60°C (solubility 1.4 mol/L). The consequence is, of course, that in this case $E_T(DMIA)_o$ is higher for pure hexane.

Table II shows that the $E_T(DMIA)$ values of the pure substances (second column) decrease from the top to the bottom of the table. However, the change is not uniform. This may be a consequence of the fact that due to different densities and molecular weights the molar concentrations of the pure polar additives differ appreciably (4.4 mol/L for pure dipiperidino propane and 14.3 mol/L for pure dioxolane). Also, the single parameters $E_D(DMIA)$ and $c*(DMIA)$ are not suited for a classification; however, their ratio $E_D(DMIA)/c*(DMIA)$ can be used for this purpose. These values increase with the effect of the additives on the vinyl group content from the top to the bottom of the table.

However, there are some additives that do not fit into this classification; these are marked by a cross (x). To this group belong tetrahydrothiophene with a very low influence on the polymerization but with a strong interaction with DMIA, and the bifunctional bases dimethoxy ethane, dimethoxy propane, TMMDA, TMEDA, TMPrDA, dipiperidino methane, and dipiperidino ethane. The behavior of tetrahydrothiophene can be explained by the concept of hard and soft acids and bases (HSAB). Organic sulfides can be easily polarized. Therefore, as soft bases they can strongly interact with the delocalized π-electron system of the organic dye and influence the transition energy. With the lithium cation as hard acid no stronger interactions are possible.

Bidentate bases like dimethoxy compounds with alkyl bridges $(CH_2)_n$ and $n = 2$ and 3, bis-(dimethylamino) compounds with $n = 1$, 2 and 3, and dipiperidino compounds with $n = 1$ and 2 can strongly interact with lithium organyls forming chelate complexes due to their molecular geometry. With the large dye molecule, no similarly strong interaction is possible. Therefore, their influence on the vinyl structure cannot be explained by parameters of solvent polarity. For compounds with other alkyl bridging groups, i.e., dimethoxy methane, TMBuDA, and dipiperidino propane, the interactions with lithium organyls are not very intensive. Therefore, their influence on the microstructure may be described on the basis of the solvent polarity.

The question arises whether the $E_T(DMIA)$ values measured from additive/hexane mixtures can be used to estimate the microstructure of polyisoprene, since in a real polymerization system the monomer isoprene is present, too. Therefore, we performed some measurements with a ternary system, containing also isoprene. The results are summarized in Table III.

In comparison to the binary system, the $E_D(DMIA)$ and $c*(DMIA)$ values are unambiguously changed but the order of their ratio for the several additives is not varied. The absolute values of $E_D(DMIA)/c*(DMIA)$ for the ternary system are slightly smaller than for the binary system. We can therefore assume that also the polarity parameter, determined for the binary systems, can be used in a first approximation to estimate microstructures formed in a ternary polymerizing system.

As in ref. 1, for polybutadiene, we tried to describe the correlation between the polyisoprene microstructure and the additive concentration again by the two-parameter equation:

$$PI = PI_o + E_D(PI) \cdot \ln((c_p/c_I)/(c*(PI)/c_I) + 1) \quad (2)$$

with

$$PI = \lg \frac{\% \ 3,4\text{-polyisoprene} + \% \ 1,2\text{-polyisoprene}}{\% \ 1,4\text{-polyisoprene}} \quad (3)$$

PI_o corresponds to the PI value in pure *n*-hexane. The c_p and $c*(PI)$ are scaled as in ref. 1 to the initial initiator concentration c_I. The results are shown in Figure 2.

It can be seen that the influence of the bidentate additives DME, DMPr, TMEDA, TMPrDA, and DPE cannot be represented by eq. (2), since the regression curve does not fit very well with the measured values, which seem to level off at additive concentrations above $c_p/c_I = 1$. As a general phenomenon observed for all additives at high concentrations, a maximum content of vinyl side groups is reached that is nearly similar to the content obtained in pure polar solvents. In this concentration range, the regression function does not fit with the experimental values. However, for other additives than TMEDA, etc., this leveling off is observed at very high additive concentrations (e.g., for THF at $c_p/c_i > 300$). Table IV lists the parameters $E_D(PI)$ and $c*(PI)/c_I$ in eq. (2) from the curves in Figure 2 in the order of effectivity of the additives. Since $c*(PI)$ is scaled by c_I, the

Figure 2   Ratio PI of 3,4- and 1,2- to 1,4-polyisoprene structures according to eq. (3) in the polymerization of isoprene with s-butyllithium in n-hexane at 50°C in dependence of the logarithm of the ratio of the concentration of polar additive c_p and of the concentration of initiator c_I deduced from Table I. $c_I = 1 \cdot 10^{-3}$ mol/L.

values in Table IV have to be multiplied by $1 \cdot 10^{-3}$ mol/L to obtain the real value of $c^*(\mathrm{PI})$.

Table IV shows that the $E_D(\mathrm{PI})$ values increase and the $c^*(\mathrm{PI})/c_I$ values decrease with increasing effectivity of the additives. However, as for polybutadiene, the product $E_D(\mathrm{PI}) \cdot \ln(c^*(\mathrm{PI})/c_I)$ is the better term for classifying the additives.

We used the same procedure as in ref. 1 to correlate PI and $E_T(\mathrm{DMIA})$ values.

The concentrations c_p are much lower than the values $c^*(\mathrm{DMIA})$ in the UV measurements with DMIA. Therefore, here holds the equation

$$E_T(\mathrm{DMIA}) = E_T(\mathrm{DMIA})_0$$
$$+ E_D(\mathrm{DMIA}) \cdot c_p/c^*(\mathrm{DMIA}) \quad (4)$$

On the other hand, the ratio c_p/c_I used in polymerization experiments is much higher than the $c^*(\mathrm{PI})/c_I$ values. Thus, in this case we have

$$\mathrm{PI} = \mathrm{PI}_0 + E_D(\mathrm{PI}) \cdot \ln((c_p/c_I)/(c^*(\mathrm{PI})/c_I)) \quad (5)$$

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

(e)

(f)

(g)

Figure 2   (*Continued from the previous page*)

$$E_T(\text{DMIA}) - E_T(\text{DMIA})_o$$
$$= E_D(\text{DMIA}) \cdot 1 \cdot 10^{-3}/c^*(\text{DMIA}) \quad (6)$$

$$\text{PI} - \text{PI}_o = -E_D(\text{PI}) \cdot \ln(c^*(\text{PI})/1 \cdot 10^{-3}) \quad (7)$$

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

$$E_T(\text{DMIA}) - E_T(\text{DMIA})_o$$
$$= E_D(\text{DMIA}) \cdot 1 \cdot 10^{-3} \cdot e/c^*(\text{DMIA}) \quad (8)$$

$$\text{PI} - \text{PI}_o = E_D(\text{PI}) - E_D(\text{PI})$$
$$\cdot \ln(c^*(\text{PI})/1 \cdot 10^{-3}) \quad (9)$$

For both cases, Figures 3(a)–3(d) show the dependence of the parameters at the right-hand sides of eqs. (6)–(9).

For all monofunctional and a part of bifunctional bases, Figures 3(a) and 3(c) show a linear correlation between $-E_D(\text{PI}) \cdot \ln(c^*(\text{PI})/c_I)$ and $E_D(\text{DMIA})/c^*(\text{DMIA})$. It is due to a correlation between the difference of activation energies for 3,4- + 1,2 and 1,4-propagation reactions of the isoprene monomer molecule and the transition energy of DMIA. Both processes are influenced by the polarity of the reaction mixture caused by dipole–dipole interactions. Also from these plots it can be deduced [Figs. 3(b) and 3(d)] that the interaction with some of the bidentate bases can-

Table IV $E_D(\text{PI})$, $c*(\text{PI})/c_I$, and $E_D(\text{PI}) \cdot \ln(c*(\text{PI})/c_I)$ Values from the Polymerization of Isoprene with s-Butyllithium in n-Hexane at 20°C in the Presence of Polar Additives, Derived from the Curves in Figure 2 According to Eq. (2) ($c_I = 1 \cdot 10^{-3}$ mol/L)

Additive	$E_D(\text{PI})$	$c*(\text{PI})/c_I$	$E_D(\text{PI}) \cdot \ln(c*(\text{PI})/c_I)$
Tetrahydrothiophene	0.48	305.8	2.75
Dimethoxy methane	0.34	14.4	0.91
Triethylamine	0.29	19.7	0.88
Diisopropyl ether	0.28	19.9	0.83
Diethyl ether	0.29	13.3	0.74
t-Butylmethyl ether	0.28	11.5	0.69
N-methyl piperidine	0.31	5.9	0.55
1,3-Dipiperidino propane	0.28	4.0	0.42
TMMDA	0.30	3.8	0.40
1,4-Dioxane	0.32	3.4	0.40
TMBuDA	0.33	2.6	0.31
1,3-Dioxolane	0.29	3.0	0.32
Tetrahydropyran	0.31	2.3	0.26
Dipiperidino methane	0.31	1.7	0.16
Tetrahydrofuran	0.37	1.5	0.14
1,4-Dimethoxy butane	0.34	0.80	−0.07
DABCO	0.26	0.27	−0.34
1,3-Dimethoxy propane	0.51	0.36	−0.52
TMPrDA	0.52	0.30	−0.63
1,2-Dipiperidino ethane	0.48	0.25	−0.67
1,2-Dimethoxy ethane	0.45	0.21	−0.70
Diglyme	0.60	0.30	−0.72
TMEDA	0.49	0.14	−0.96

not be described by polarity parameters. The reason for this behavior has already been discussed above.

From Figures 3(a) and 3(c), $E_D(\text{PI})$ and $c*(\text{PI})/c_I$ values can be calculated for all other additives:

$$E_D(\text{PI}) = y' - y \qquad (10)$$

$$c*(\text{PI})/c_I = \exp(y/(y - y')) \qquad (11)$$

with

$$y = -0.44 \cdot E_D(\text{DMIA})/c*(\text{DMIA}) - 1.20 \qquad (12)$$

$$y' = -0.18 \cdot e \cdot E_D(\text{DMIA})/c*(\text{DMIA}) - 0.96 \qquad (13)$$

Therefore, only from UV–vis measurements of appropriate polar substances with DMIA we have the opportunity to estimate the microstructure of polyisoprene in dependence of the additive concentration.

These equations allow us to estimate the amount of the 1,2- and 3,4-microstructure in polyisoprene 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, $E_D(\text{DMIA})$ and $c*(\text{DMIA})$ values are obtained using nonlinear regression analysis. For $c_p/c_I = 1$ and $c_p/c_I = e$, the parameters $E_D(\text{PI})$ and $c*(\text{PI})/c_I$ can be extrapolated from the linear plots in Figures 3(a) and 3(c) using eqs. (10)–(13). Subsequently, eq. (5) allows us to calculate the vinyl content of the polymer.

In a first approximation, due to their derivation, eqs. (10)–(13) are only valid for an initial initiator concentration of $1 \cdot 10^{-3}$ mol/L and for a reaction temperature of 50°C. It has to be tested whether this equation can also be used to predict the microstructure at other initiator concentrations and reaction temperatures.

Figure 3 Correlation between $E_D(PI) \cdot \ln(c^*(PI)/c_I)$ values (a and b) and E_D (PI) $- E_D(PI)\ln(c^*(PI)/c_I)$ (c and d) from the 3,4 and 1,2 contents in polyisoprene in the presence of polar additives (Table IV) and $E_D(DMIA)/c^*(DMIA)$ values (Table II) for $c_p/c_I = 1$ (a and b) and $c_p/c_I = e$ (c and d). $c_I = 1 \cdot 10^{-3}$ mol/L.

Table V   1,2- + 3,4-Structures in Polyisoprenes in the Polymerization of Isoprene with *s*-Butyllithium in *n*-Hexane–Polar Additive Mixtures at 50°C at Different Initial Initiator Concentrations but Equal Molar Ratios of Additive and Initiator

Additive	c_p/c_I	$c_I = 3 \cdot 10^{-4}$ mol/L (% Vinyl)	$c_I = 1 \cdot 10^{-3}$ mol/L (% Vinyl)	$c_I = 3 \cdot 10^{-3}$ mol/L (% Vinyl)
THF	1	7.5	8.5	12
	5	10	19	31.5
	20	20.5	37	53
	50	33	56	66
TMEDA	0.2	7	37.5	13
	0.5	33	37.5	42
	1	58	60.5	62
	5	69	70	72

c_I[mol/L]	E_D(PI)	c^*(PI)/c_I
0.0003	0.34	0.51
0.001	0.37	1.5
0.003	0.37	5.0

(a)

E_D(PI)	c^*(PI) [mol/L]
0.36	0.0015

(b)

Figure 4 PI values from polymerizations of isoprene with s-butyllithium in n-hexane at 50°C with THF as polar additive in dependence of $\ln(c_p/c_I)$ (a), and of $\ln c_p$ (b). The numbers at the curves denote the initial initiator concentrations in mol/L.

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

To determine the effect of the initial initiator concentration on the microstructure of polyisoprene we performed polymerizations using constant additive/initiator ratios. As representative additive, we chose THF and TMEDA. The results are summarized in Table V and Figures 4 and 5.

For THF, the vinyl content increases with increasing initial initiator concentration when the ratio additive/initiator is held constant. The

course of the curves in Figure 4(a) is nearly parallel. The values of E_D(PI) are nearly constant; those of c^*(PI)/c_I increase with decreasing initial initiator concentration. This behavior may be explained by the fact that c^*(PI)/c_I is scaled by the initial initiator concentration. Multiplying this term with the corresponding initial initiator concentration yields a constant value with c^*(PI) = 0.0015 mol/L. This shows that as in butadiene polymerization[1] the microstructure depends primarily on the absolute additive concentration and therefore on the solvent polarity and not on the

(a)

(b)

Figure 5 PI values from polymerizations of isoprene with s-butyllithium in n-hexane at 50°C with TMEDA as polar additive in dependence of $\ln(c_p/c_I)$ (a), and of $\ln c_p$ (b). The numbers at the signs denote the initial initiator concentrations in mol/L.

Table VI   Experimental (50°C) and Estimated (60 and 70°C) Parameters E_D(PI) and c^*(PI)/c_I Used to Describe the Temperature Dependence of the 1,2- and 3,4-Structure in Polyisoprene Formed in the Presence of Some Polar Additives in the Anionic Polymerization of Isoprene with Butyllithium ($c_I = 1 \cdot 10^{-3}$ mol/L)

Additive	30°C		50°C		70°C	
	E_D(PI)	c^*(PI)/c_I	E_D(PI)	c^*(PI)/c_I	E_D(PI)	c^*(PI)/c_I
Triethylamine	0.29	14	0.29	20	0.29	29
Diethyl ether	0.29	7.1	0.29	13	0.20	21
Dioxane	0.32	1.6	0.32	3.5	0.32	6.7
THF	0.37	0.70	0.37	1.5	0.37	2.8

molar ratio c_p/c_I, at least for weak bases. In mixtures with equal additive concentrations but different initial initiator concentrations, equal microstructures can be expected. This is shown in Figure 4(b). The results of all three experiments can be described by one curve with E_D(PI) = 0.36 and c^*(PI) = 0.0015 mol/L, when PI is plotted vs ln c_p.

In the case of TMEDA [Fig. 5(a) and 5(b)], the slopes of the curves differ appreciably from those in Figure 4(a) and 4(b). The inverse behavior is observed. In a first approximation, the curves for all initiator concentrations seem to converge to one curve, when PI is plotted vs ln c_p/c_I. On the other hand, the curves in the plot of PI vs ln c_p are clearly separated. This can be understood when we consider that the interaction between active centers and TMDEA is nearly like a stoichiometric chemical reaction, the equilibrium lying on the right side:

$$(RLi)_n + n \cdot TMEDA = n \, RLi \cdot TMEDA$$

Obviously, the influence on the microstructure depends here actually on the ratio additive/initiator.

Influence of the Reaction Temperature on the Vinyl Content of Polyisoprene

The polymerization experiments described above were performed at 50°C. The activation energies of the anionic polymerization of butadiene and isoprene in pure solvents are comparable (e.g., 83, 56, and 29 kJ/mol for butadiene polymerizations in n-hexane, diethyl ether, and THF compared with 95, 66, and 28 kJ/mol for corresponding isoprene polymerizations[4]). Therefore, we tried to extend the temperature range for isoprene poly-

merization in solvent mixtures. From the values of E_D(PI) and c^*(PI)/c_I for 50°C in this work and the corresponding values E_D(PB) and c^*(PB)/c_I from the polymerization of butadiene at 30, 50, and 70°C,[1] we estimated the values missing here for E_D(PI) and c^*(PI)/c_I at 30 and 70°C. All values are summarized in Table VI.

As expected from the results of butadiene polymerizations, the E_D(PI) values are independent of reaction temperature, while the scaled c^* values increase with increasing reaction temperature. In Figure 6, the term $-E_D$(PI) $\cdot$ ln (c^*(PI)/c_I) is plotted vs E_D(DMIA)/c^*(DMIA) from the transition energy measurements for 30, 50, and 70°C. The bold line corresponds to the measured values, the broken line to the simulated values under the above-mentioned assumptions.

Figure 6   Correlation between E_D(PI) $\cdot$ ln(c^*(PI)/c_I) values from measurements of the microstructure of polyisoprene and E_D(DMIA)/c^* values from UV–vis measurements of DMIA in the presence of several polar additives at different temperatures. Experimental data at 50°C, estimated data for 30 and 70°C.

Figure 7 PI in dependence of $\ln c_p$ according to values presented by Worsfold and Bywater[5] in the polymerization of isoprene with n-butyllithium in THF.

c_p/c_I	c_p (mol/L)	% Vinyl
2	$6 \cdot 10^{-4}$	13
15	$4.5 \cdot 10^{-3}$	31
4114	1.23	75

To test the reliability of these calculations, we used the published data of Worsfold and Bywater for the polymerization of isoprene in cyclohexane with n-butyllithium at 30°C in the presence of THF.[5] In Table VI the corresponding values for this temperature are $E_D(\text{PI}) = 0.37$ and $c^*(\text{PI})/c_I = 0.7$. For a plot of PI vs $\ln c_p$, $c^*(\text{PI})/c_I$ has to be multiplied by the initiator concentration $1 \cdot 10^{-3}$ mol/L. The curve in Figure 7 results.

A good agreement is obtained with experimental results at relatively low additive concentrations $c_p/c_I = 2$ and 15. The microstructure for a 10 mol % THF solution in cyclohexane does not fit with the curve. However, at this high THF concentration, the vinyl content is already as high as in pure THF. Therefore, the deviation of this point in Figure 7 is not surprising.

CONCLUSIONS

The vinyl contents of polyisoprenes from anionic polymerization with butyllithium in the presence of polar additives can be satisfactorily predicted from a correlation between the vinyl microstructure and transition energies, measured with *N,N*-dimethyl indoaniline. This result corresponds to that obtained for butadiene.[1] It offers the possibility to estimate the effect of bases, not investigated in this study, on the vinyl microstructure of polyisoprenes.

Comparing the butadiene and the isoprene polymerization, it turns out that the vinyl content at lower base concentration is lower for polyisoprene than for polybutadiene. The c^* values are lower for the latter one. That means that at first higher base concentrations are necessary to cause the formation of vinyl structures in polyisoprenes. On the other hand, with increasing additive concentration, the vinyl content increases stronger for polyisoprene than for polybutadiene. The maximal vinyl contents for both monomers in the same solvent are comparable (Table VII).

However, for polyisoprene they are reached at lower base concentrations. Different effects on the aggregation and on the solvation of the growing centers may be the reason for these observations.

Obviously, the developed method is especially suited to describe the influences of ethers and tertiary amines on the polyisoprene microstructure. Sulfur compounds and aromatics seem to interact more strongly with the dye than with the growing centers. Bidentate bases like TMEDA may form stable stoichiometric complexes by specific chelate interactions.

Furthermore, the vinyl contents depend primarily on the polarity of the reaction solution determined by the base concentration and not on the molar ratio of base to initiator, at least for weak bases.

EXPERIMENTAL

The preparation and purification of chemicals as well as the UV measurements are described elsewhere.[1] Polymerizations were carried out under

Table VII Vinyl Contents of Polybutadienes and Polyisoprenes from Anionic Polymerizations of Butadiene and Isoprene in Polar Solvents

Solvent	% 1,2-Polybutadiene[6]	Solvent	% 1,2-/3,4-Polyisoprene[7]
THF, 30°C	85.4	THF, 30°C	88
Dioxane, 20°C	81.8	Dioxane, 15°C	86
Ether, 20°C	64.8	Ether, 20°C	65

argon in glassware previously dried at 80°C under vacuum. The initial monomer concentration was 1 mol/L, the initial concentration of the initiator s-BuLi was $1 \cdot 10^{-3}$ mol/L. The microstructures of the polyisoprenes were determined in $CDCl_3$ by ^{1}H-NMR spectroscopy according to Tanaka et al.,[8] using a 200 MHz spectrometer Gemini 200.

REFERENCES

1. Hesterwerth, D.; Beckelmann, D.; Bandermann, F. J Appl Polym Sci 1999, 73, 1521.
2. Dimroth, K.; Reichardt, C.; Siepmann, T.; Bohlmann, F. Liebigs Ann Chem 1963, 661, 1.
3. Langhals, H. Angew Chem 1982, 94, 739.
4. Jin, G.; Yao, W. J Polym Mater 1989, 6, 187.
5. Worsfold, D. J.; Bywater, S. Can J Chem 1964, 42, 2884.
6. Jin, G.; Fan, L.; Yao, W. J Polym Mater 1987, 4, 215.
7. Morton, M. Anionic Polymerization: Principles and Practice; Academic Press: New York, 1983.
8. Tanaka, Y.; Takeuchi, Y.; Kobayahi, M.; Tadokoro, H. J Polym Sci A-2 1971, 9, 43.