Determination of *E*/*Z* and Meso/Racemic End-Group Stereochemistry in the Anionic Polymerization of Methyl Methacrylate in Tetrahydrofuran

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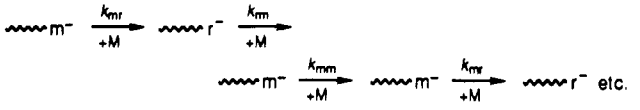
ABSTRACT: Methyl methacrylate (MMA) was polymerized anionically in THF at -70 °C in the presence of Li^+, Na^+, K^+, Cs^+, and cryptated K^+ cations. The living enolates were converted to silylketene acetals through addition of $ClSi(CH_3)_3$. The ^{13}C NMR signals of the end groups show a split with respect to *E*/*Z* stereochemistry. A further split into triads of meso/racemic (m/r) stereochemistry is observed. The peaks are assigned and the corresponding fractions of stereoisomers calculated. The fraction of *E* end groups increases from 0.3% for Li^+ to 95% for Cs^+ on a sigmoidal curve, which has its inflection for K^+. For the same cation the meso fraction of the main chain and the deviation from Bernoullian statistics show a maximum too. This coincidence is consistent with the following assumptions: (1) transition-state monomer approach to the living end is s-cis for Li^+ and Na^+ (leading to *Z* chain ends) due to coordination with the counterion and s-trans for Cs^+ and cryptated K^+ (leading to *E* chain ends) due to steric reasons; (2) tacticity is determined by the *E*/*Z* stereoisomerism of the chain end and possibly also by the stereochemistry of the preceding diad; (3) with increasing radius of the counterion, addition of monomer to *E* isomers results in an increasing fraction of racemic diads, while the *Z* isomers give a decreasing amount of racemic diads.

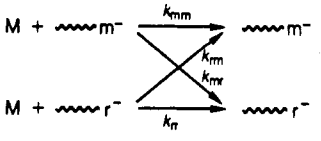
Introduction

Anionic polymerization of vinyl monomers frequently leads to a distribution of stereosequences, which is inconsistent with simple Bernoullian statistics.[1,2] This is especially true for methacrylates. Here, distributions are generally consistent with first-order Markov statistics.[3,4] However, it is important to state that Markov *statistics* just *describe* the distribution of stereosequences but that several *mechanisms* may *generate* such a distribution.

A "penultimate" mechanism frequently has been used in order to account for the non-Bernoullian statistics.[5-7] This mechanism assumes that the probability of a given placement depends on whether the preceding diad of monomer units is meso or racemic:



It is summarized by the following kinetic scheme:



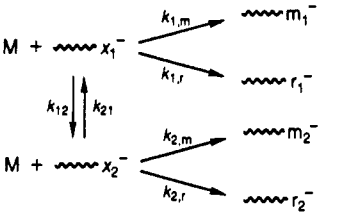
The four rate constants, due to normalization, are reduced to two independent parameters, i.e., the conditional probabilities of a first-order Markov chain

$$P_{mr} = 1 - P_{mm} = (mr)/2(m) \quad (1a)$$

and

$$P_{rm} = 1 - P_{rr} = (mr)/2(r) \quad (1b)$$

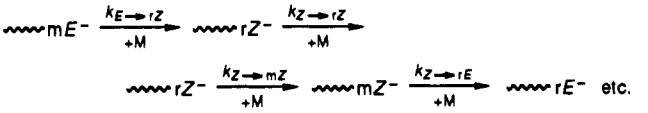
A multistate mechanism was proposed by Coleman and Fox[8] in which the active chain end may exist in two (or more) states being able to interconvert (x = m or r):



This model consists of six rate constants (plus monomer concentration) and generally is inconsistent with Markov statistics. Only if interconversion is much faster than propagation, i.e., k_{12} and $k_{21} \gg k_{i,x}[M]$, are Bernoullian statistics expected.

However, NMR studies of living oligomers of vinyl pyridine[9,10] have shown that the propagating ion pair is a mixture of *E* and *Z* stereoisomers, which do *not* interconvert on the polymerization time scale *but may interconvert upon monomer addition*. Thus, s-trans presentation of monomer leads to *E* chain ends and vice versa. Similar studies of dimers of methyl methacrylate (MMA)[11] showed the existence of two isomers, which can be attributed to *E* and *Z*. Recently, the existence of *E* and *Z* stereoisomers was reported for the silylketene acetal ended dimer of MMA.[12]

Khan and Hogen-Esch[13] have proposed that stereocontrol is only given by the *E*/*Z* stereoisomerism of the chain end:



This model consists of eight rate constants (which due to normalization reduce to six independent parameters) and

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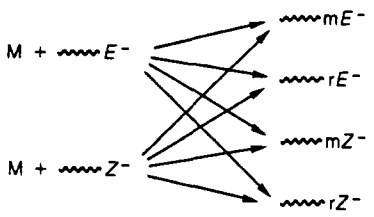
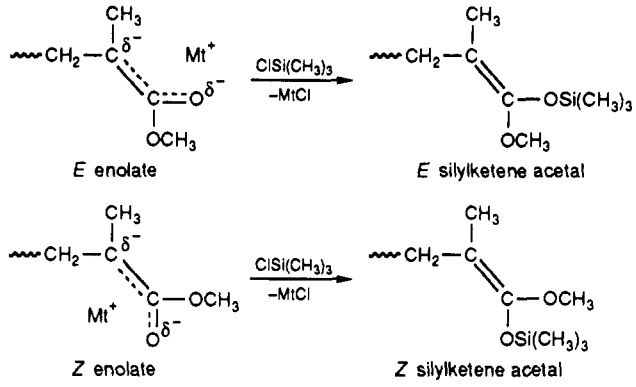
can be represented by the following kinetic scheme:



This two-state model generally is inconsistent with Markov statistics.[13] Yet, in most cases the deviations from first-order Markov statistics are too small to be detected experimentally.

Thus, it is of interest to find out whether the tacticity of PMMA is determined by E/Z or by m/r stereoisomerism of the chain end (or possibly by both). Since both E/Z and penultimate mechanisms are consistent with Markov statistics, they cannot be differentiated by main-chain statistics alone.

In order to determine the ratio of E/Z chain ends, the anionic polymerization of MMA in THF at −70 °C in the presence of various counterions was terminated by $ClSi(CH_3)_3$. The ^{13}C NMR spectra of the silylketene acetals formed were measured and analyzed in order to determine the fractions of E and Z chain ends as well as the adjacent m and r diads:



In order to assign E and Z configurations to the above isomers all metal ions are given the same seniority as silicon in the corresponding silylketene acetals.

Experimental Section

Methyl methacrylate (Röhm GmbH, Darmstadt, FRG) was stirred over calcium hydride for 12 h and distilled into break-seal ampules in vacuo where it was diluted with THF. The initiators (diphenylmethyl salts of Li^+, Na^+, K^+, and Cs^+) were prepared in THF by metalation of diphenylmethane[14] and stored in ampules equipped with Teflon valves. In some experiments they were replaced by lithiated or sodiated methyl isobutyrate, which was supplied as a crystalline powder by Dr. L. Lochmann, Prague. The experiments were performed in the presence of common ion salts (tetraphenyl borates and cesium triphenylcyanoborate) in order to suppress the dissociation into free ions. The cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; Merck "Kryptofix 222") was used in a 3-fold excess without purification. Chlorotrimethylsilane (Merck) was stirred for 1 h over cross-linked poly(4-vinylpyridine) (Merck) and distilled into an ampule equipped with a Teflon valve where it was diluted with THF (1:10). THF (BASF) was fractionally distilled over potassium, dried over a Na/K alloy, distilled in vacuo into the reaction vessel, and mixed with initiator ($[I]_0$ = 0.003 mol/L). The monomer ($[M]_0$ = 0.1 mol/L) was then rapidly injected from the break-seal ampule. After 0.5–30 min (depending on the counterion), the living polymers were reacted with a 10-fold excess of $ClSi(CH_3)_3$. Termination is faster than 2 s. THF was then removed by distillation at −20 °C, and the paraffinlike powder was dissolved in $CDCl_3$ (from an ampule containing molecular sieves of 4 Å) and transferred into an NMR tube, which was directly connected to the reactor. The tube was sealed off in vacuo and centrifuged in order to move residual solids to the top of the tube. The number-average degree of polymerization was determined by GPC to be ca. 30.

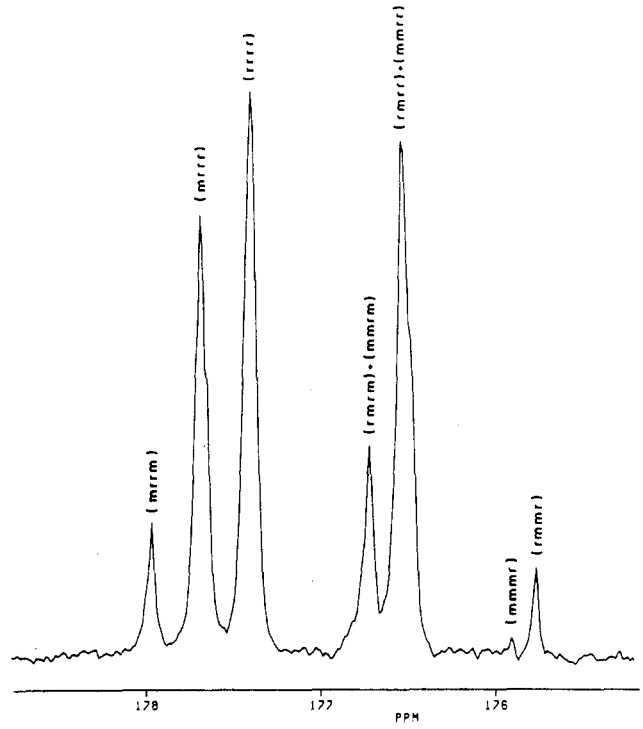


Figure 1. Carbonyl region of the 100-MHz ^{13}C NMR spectrum of PMMA prepared by anionic polymerization in THF in the presence of Na^+ counterion. Solvent: $CDCl_3$.

^{13}C and ^{29}Si FT NMR measurements were performed at 20 °C in a Bruker WM 400 spectrometer (60 000–100 000 scans, ca. 10–20 h of sampling). Nonresolved peaks were submitted to line-shape analysis using Lorentz curves. The absolute experimental error for the end-group fractions is ca. 0.01–0.02 and results from noise, from deviation between Lorentz and true signal shapes, and perhaps from differences between the unknown T_1 relaxation times.

In order to examine whether the E/Z ratios of the silylketene acetals really reflect the true E/Z ratios of the enolates, the following experiment was performed: a solution of living oligomers was prepared with Cs^+ as the counterion. After complete monomer conversion, lithium tetraphenylborate was added in 3-fold excess. Li^+ binds much stronger to the chain ends, leading to a replacement of Cs^+ by Li^+. Then this solution was silylated. The E/Z ratio found was identical with the one without exchange of counterion. An analogous experiment was performed by starting with Li^+ counterion and adding a 10-fold excess of cesium triphenylcyanoborate. Again, no change of the E/Z ratio was found. A quantitative analysis of this experiment shows that the reversal of E enolates to Z silylketene acetals and vice versa by silylation has a probability of <5% for Cs^+ and <1% for Li^+.

Results

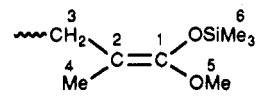
Main-Chain Pentads. The ester carbonyl signals of the main chain are located at 176–178 ppm (cf. Figure 1). They are split into pentads. The assignments of Peat and Reynolds[15] were used in order to determine their fractions. They are shown in Table I, and a fit to first-order Markov statistics is given. The assignments of Ferguson and Ovenall[16] do not lead to a satisfactory fit for some heterotactic pentads.

The fraction of racemic diads as well as the persistence ratio, ρ, pass through a minimum for K^+. This is in

Table I
Percentages of the Main-Chain Pentads, Triads, and Diads of PMMA Prepared in THF at −70 °C in the Presence of Various Counterions and Fit of Pentads to First-Order Markov Statistics

	Li^+		Na^+		K^+		Cs^+		K^+ (222)[a]
	exptl	calc	exptl	calc	exptl	calc	exptl	calc	exptl
(mmmm)	0	0	0	0	<0.6	0.2	0	0	
(mmmr)	0	0	0.7	0.5	1.7	1.7	0.8	0.6	
(rmmr)	0.5	0.4	1.9	2.0	3.6	4.1	2.2	2.4	
(rmrm) + (mmrm)	1.7	1.5	9.1	9.5	21.7	21.0	16.8	17.4	
(rmrr) + (mmrr)	16.4	15.0	29.5	29.1	34.7	34.5	33.2	32.6	
(mrrm)	0.8	0.7	4.7	3.6	6.6	6.6	5.3	5.7	
(mrrr)	14.3	13.7	21.2	21.9	17.5	17.9	21.6	21.3	
(rrrr)	66.3	68.8	32.8	33.2	13.6	12.5	20.1	20.0	
(mm)	0.5		2.6		5.3		3.0		2.0
(mr)	18.1		38.7		56.4		50.0		31.0
(rr)	81.4		58.7		38.3		47.0		67.0
(m)	9.3		21.9		34.0		28.0		17.5
(r)	91.7		78.1		66.0		72.0		82.5
P_{mr}	0.951		0.881		0.822		0.893		0.89
P_{rm}	0.090		0.248		0.426		0.347		0.18
ρ[b]	0.96		0.89		0.78		0.80		0.93

[a] K^+ cryptated by the cryptand 222 (cf. the Experimental Section). Resolution not sufficient for the determination of pentads. [b] $\rho = 2(m)(r)/(mr) = 1/(P_{mr} + P_{rm})$ is the persistence ratio.[6]



(*Z*)-silylketene acetal

Table II
Assignment of the ^{13}C Signals of the Silylketene Acetal of PMMA in $CDCl_3$ and Comparison with Lithiated Dimer[11]

	position (δ), ppm				Li enolate of dimer[11]	
no.	*Z*	*E*	DEPT	ref 19	α	β
1	153	151.8		151.99	162.4	161.5
2	90.4	89.7		89.78	72.8	74.8?
3	30	29	g	54.28(?)	45.4	44.9
4	14.7	15.8	u	29.56(?)	18.3	17.8
5	57.2	55.3	u	55.42		
6	0.0	−0.2	u	−0.11		

Table III
^{29}Si NMR Positions of (*E*)- and (*Z*)-Silylketene Acetals of PMMA in $CDCl_3$

	δ, ppm	
	Brittain[12]	this work
Z	18.9	19.5
E	20.5	21.5

accordance with literature data.[3,4] In the case of Li^+, it may be argued that the deviation from Bernoullian statistics is rather small and even within limits of experimental error. However, this small deviation has been repeatedly observed.[17,18]

***E*/*Z* End-Group Signals.** The silylketene acetal ^{13}C NMR signals disappear after hydrolysis and are thus easily identified. For each carbon atom, two well-resolved signal groups are found, which are separated by ca. 0.2–1.5 ppm (cf. Figure 2). The fine splitting within each signal group is due to the tacticity next to the chain end. The division into groups is due to *E*/*Z* isomerism. Table II shows the assignments and DEPT measurements, which decide between carbon atoms with even (g) and odd (u) hydrogen numbers. Data of Sogah et al.,[19] which are not differentiated for *E* and *Z*, are given as a reference. These authors report different shifts for C_3 (methylene) and C_4 (α-methyl). Our assignments, however, are corroborated by the DEPT measurements. They are also in good agreement with data of Vancea and Bywater on the metalated dimer of MMA.[11] The absolute assignments of *E* and *Z* signals are based on the ^{29}Si NMR assignments of the silylketene acetal of the dimer of MMA given by Brittain.[12] These, in turn, were determined from the coupling constants in proton NMR.

A comparison consistent with our results is shown in Table III. As can be seen from Table IV, the *E*/*Z* splitting in ^{29}Si NMR is reflected in ^{13}C NMR. The area ratios of the groups are identical with those of ^{29}Si measurements for all four ketene acetal carbon atoms. Table IV gives the *Z* fractions for all counterions used. This 5-fold coincidence provides strong evidence for our assignments. It should be noted that the values for cryptated K^+ result from both cryptated ion pairs and free anions because dissociation cannot be completely suppressed.

Vancea and Bywater[11] reported ^{13}C NMR spectra of the metalated dimer of MMA. A splitting of the signals into α and β peaks was observed but not identified. Table IV shows a reasonable correlation between the fractions of *Z* and α end groups.

Some differences are seen that may be due to the following:

(1) Bywater's samples were prepared by direct metalation instead of monomer addition.

(2) At −20 °C equilibration is comparable to the time needed for the ^{13}C NMR measurement;[11] thus, the measured *E*/*Z* ratios did not result from kinetic but from thermodynamic control.

(3) Using the dimer instead of higher oligomers and high concentrations also favors the formation of aggregates, which may lead to different shifts.

Signals Due to m/r End-Group Diads and Triads. Within the *E* and *Z* groups of signals, further splitting into up to four signals can be seen and quantified by using line-shape analysis. This splitting is due to the tacticity of the penultimate and antepenultimate monomer units.

The assignments are based on two arguments:

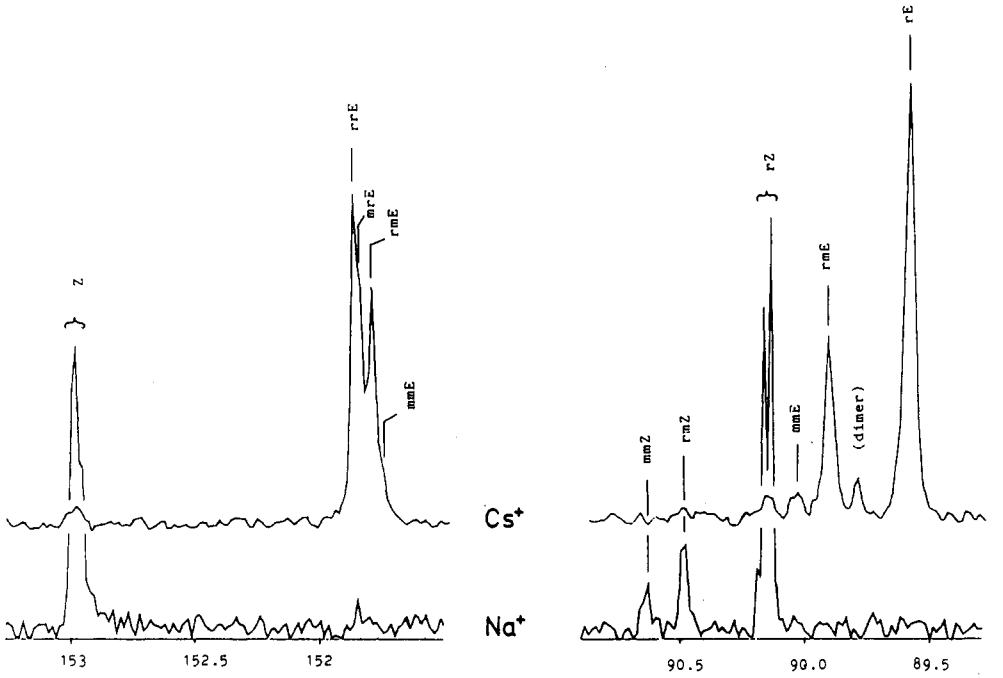


Figure 2. 100-MHz ^{13}C NMR spectrum of PMMA silylketene acetal prepared by anionic polymerization in THF in the presence of Na^+ and Cs^+ counterions. Solvent: $CDCl_3$.

Table IV
Percentages of *Z* Enolates (at −70 °C) and Assignment of ^{13}C Signals by Area Comparison to ^{29}Si Measurements and Comparison to NMR Values of Metalated Dimers[11]

	carbon no.						ref 11
	6	5	1	2	^{29}Si	wtd ave *Z*	α
Li^+	99.7	>99.5	>99.5	>99.5	>99.5	99.7	>80, 65[a]
Na^+	97	96	96.5	95	97	97	55–60[a]
K^+	60	61	60	61		60	20[a]
Cs^+	6.1	6.2	5.0	4.9	5.3	5	
K^+ (222)[b]	10	10	8.5	9		10	

[a] At −20 °C. [b] K^+ cryptated by the cryptand 222 (cf. the Experimental Section).

Table V
Fine Splitting of ^{13}C End-Group Signals of PMMA Silylketene Acetals in $CDCl_3$ According to Tacticity

carbon no.	assignt	position (δ), ppm	assignt	position (δ), ppm
1	*Z*⁻	153.05	mm*E*⁻	151.81
			rm*E*⁻	151.83
			mr*E*⁻	151.87
			rr*E*⁻	151.89
2	mm*Z*⁻	90.65	mm*E*⁻	90.05
	rm*Z*⁻	90.5	rm*E*⁻	89.93
	r*Z*⁻	90.15	r*E*⁻	89.43
4	m*Z*⁻	14.5	m*E*⁻	15.7
	mr*Z*⁻	14.92	r*E*⁻	15.9
	rr*Z*⁻	14.86		
5	m*Z*⁻	57.2	m*E*⁻	55.4
	r*Z*⁻	57.13	r*E*⁻	55.32
6	*Z*⁻	0.0	*E*⁻	−0.2

(1) Chemical shift differences decrease with an increasing number of bonds. Therefore, mm^- and rm^- end-group signals should have closely similar chemical shifts and should be separated from mr^- and rr^- end-group signals.

(2) In the presence of Li^+, Na^+, and Cs^+, the chain ends almost exclusively exist as one of the *E* or *Z* isomers. In this case end-group statistics can be treated by using the penultimate model according to which the end-group fractions are given by[7,20]

$$mm^- = m^- \cdot P_{mm} \qquad rm^- = m^- \cdot P_{mr} \tag{2a}$$

$$mr^- = r^- \cdot P_{rm} \qquad rr^- = r^- \cdot P_{rr} \tag{2b}$$

One starts by assigning the m^- and r^- peak groups, assuming that their fractions roughly correspond to the main-chain diads (m) and (r), respectively. By using the conditional probabilities obtained from eq 1, one now can compute mm^-, etc., and assign peaks of corresponding area (taking into account argument 1).

Performing the assignments based on these arguments for any given counterion results in a good fit for the other ones too. A complete assignment of all end-group signals of mm*Z*⁻, rm*Z*⁻, mr*Z*⁻, rr*Z*⁻, mm*E*⁻, rm*E*⁻, mr*E*⁻, and rr*E*⁻ is given in Table V. The absolute positions may vary by ca. ±0.15 ppm, depending on concentration, temperature, etc. Thus the information on Table V mainly pertains to the relative distances and order within one signal group for a given carbon atom.

Table VI shows the fractions of all chain ends and compares them with the predictions of eq 2. The conditional probabilities, P_{mm}, etc., can be calculated independently from main-chain (eq 1) and end-group statistics (eq 2). In Table VI these values are compared.

Within experimental error, the correspondence of the calculated values to the experimental ones is very good for all counterions except K^+. In contrast to the distribution of main-chain stereosequences, the end-group distribution is not consistent with first-order Markov statistics. The significant deviations for K^+ will be dealt with in a subsequent paper based on a more general model, which combines the penultimate and *E*/*Z* models.[21]

Earlier we reported on an independent determination of the chain-end tacticities of poly(vinylpyridine)[20,22] and

Table VI
Experimental End-Group Compositions and Calculated Values According to Equation 2[a]

	Li^+		Na^+		K^+		Cs^+		K^+ (222)	
	exptl	calc	exptl	calc	exptl	calc	exptl	calc	exptl	calc
mmZ^-	<0.01	0.004	0.04	0.03	<0.01	0.03				
rmZ^-	0.08	0.086	0.17	0.18	0.19	0.17	≈0.3			
mrZ^-	0.07	0.09	0.20	0.21	0.30	0.36				
rrZ^-	0.84	0.82	0.58	0.57	0.50	0.44	≈0.7			
mmE^-					0.02	0.07	0.05	0.06	0.14	0.19
rmE^-					0.39	0.34	0.28	0.27		
mrE^-					0.15	0.27	0.24	0.23	0.86	0.81
rrE^-					0.45	0.33	0.43	0.43		

[a] The fractions for *E* and *Z* chain ends are each normalized to 1.

Table VII
First-Order Markov Conditional Probabilities As Calculated from Main-Chain (Equation 1, cf. Table I) and End-Group Statistics (Equation 2)

	Li^+		Na^+		K^+		Cs^+	
	eq 1	eq 2	eq 1	eq 2	eq 1	eq 2	eq 1	eq 2
P_{rm}	0.09	0.08	0.25	0.26	0.43	0.33	0.35	0.36
P_{mr}	0.95	>0.9	0.88	0.81	0.82	0.96	0.89	0.85

Table VIII
Comparison of End-Group Tacticities for PMMA Terminated by a Silylketene Acetal (a) and $^{13}CH_3$ End Group[23,24] (b)

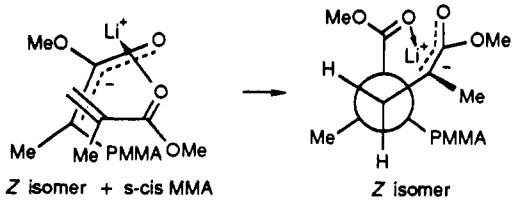
	Li^+		Na^+	K^+	Cs^+	
	(a)	(b)	(a)	(a)	(a)	(b)
mm$^-$	<0.01		0.04	0.01	0.05	
rm$^-$	0.08	0.08	0.17	0.27	0.28	0.28
mr$^-$	0.07	0.10	0.20	0.24	0.24	0.26
rr$^-$	0.84	0.82	0.58	0.48	0.43	0.46

PMMA[23,24] by terminating the polymerization with $^{13}CH_3I$. When model oligomers were used the ^{13}C NMR splitting due to the end-group tacticity was assigned absolutely. The comparison given in Table VII clearly confirms the above assignments for silylketene acetals.

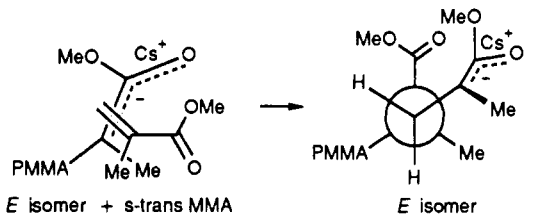
It can be noted that determination of end-group stereochemistry by silylation has two advantages over methylation: silylation is much faster and it renders information on the *E*/*Z* ratio at the same time. On the other hand, methylation renders information on some end-group tetrads, and the products are stable toward moisture. Due to the ^{13}C label, the signal/noise ratio is much enhanced, leading to shorter measurement times.

Discussion

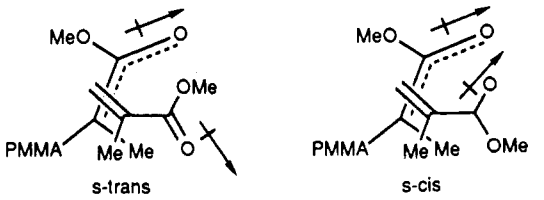
In order to understand the dependence of the *E*/*Z* ratio on the counterion radius, one has to take into account that *E*/*Z* ratios are determined by the s-cis/s-trans monomer approach. For Li^+ and Na^+ the s-cis approach may be favored due to coordination of the monomer carbonyl group to the counterion in the transition state:



For Cs^+ this coordination is not feasible sterically because of its large size. In this case the s-trans monomer approach is favored since it allows positioning of Cs^+ in such a way as to minimize repulsive interactions:



Similar arguments may pertain to cryptated K^+. Alternatively, especially for the free anion, this effect may be due to an intrinsic preference for the s-trans monomer approach as a result of less unfavorable dipole–dipole interaction in the s-trans approach.



It is further very remarkable that there is a strong correlation of the *E*/*Z* ratio to main-chain tacticity. On a sharp sigmoidal curve, the predominant population of the chain ends changes from *Z* to *E* exactly at the point where the meso fraction and the persistence ratio of the main chain pass through their maxima (cf. Figure 3). This suggests that the *E*/*Z* isomerism has an effect on tacticity and vice versa.

The general behavior of the system can be expressed as follows:

(1) For the smaller counterions predominantly *Z* end groups are present. With an increasing radius of counterion, r_c, the fraction of meso placements *increases for Z end groups.*

(2) For the larger counterions, predominantly *E* ends are present. With increasing r_c the fraction of meso placements *decreases for E end groups.*

It seems reasonable to extrapolate this behavior of the *E* and *Z* ends as monotonous functions of r_c. This leads to a simple model that qualitatively explains all of the observed results:

(1) For *E* and *Z* ends the probabilities of producing meso placements are monotonous functions of the radius of counterion.

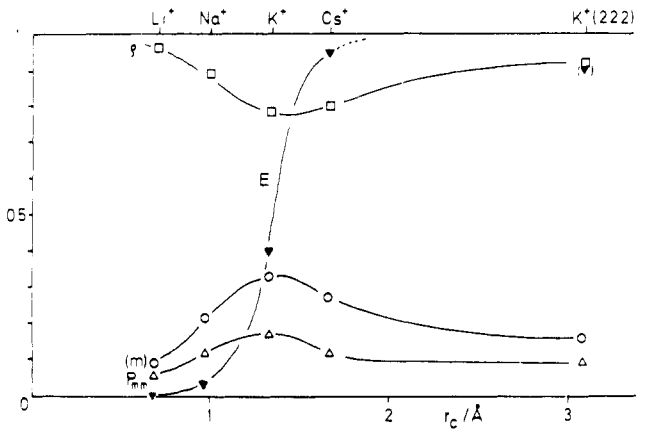


Figure 3. Dependence of fractions of E chain ends: E main chain meso placements, (m), conditional probability P_{mm}, and persistence ratio ρ, on the counterion radius, r_c. For better visulization the data points are connected by lines.

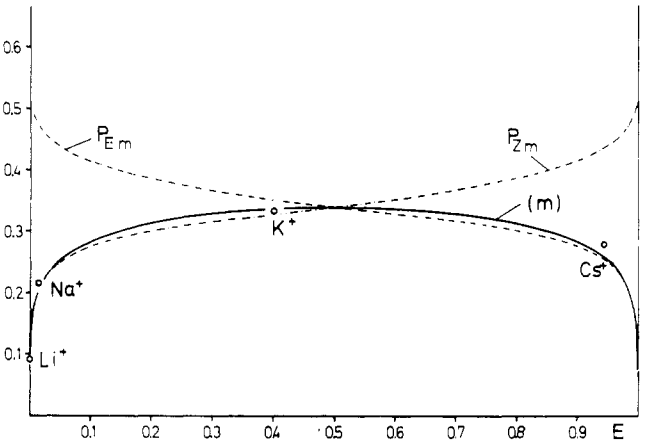
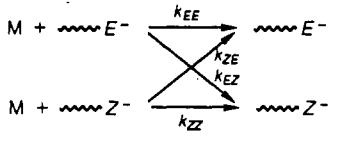


Figure 4. Dependence of main-chain meso placements, (m), and conditional probabilities of E and Z chain ends to generate meso placements, P_{Em} and P_{Zm}, on the radius of the counterion (transformed into the fraction of E chain ends); cf. eqs 9 and 10: (O) experimental data; (—) fit using $b = 0.34$ and $a = 6.5 \times 10^3$.

(2) Presumably due to steric interactions, the system tries to avoid the formation of those E or Z isomers that form meso end groups.

On the basis of these two assumptions, the change from E to Z can be understood as well as the maximum of meso groups at the position of this change: the higher the probability that a Z end produces meso, the higher the free activation energy to produce Z and analogous for E. In this way the system selects the isomer that produces less meso. At the point where the probabilities of Z and E for forming meso placements cross each other, Z and E are selected in equal amounts (this is approximately the case for K^+, where the E/Z ratio is 40/60). At this point the fraction of meso placements reaches its maximum because here none of the two isomers is able to produce only small amounts of meso.

A semiquantitative insight to this can be given by the following rough model. Imagine a set of four kinetic constants k_{EE}, k_{EZ}, k_{ZE}, and k_{ZZ}, which are given by the scheme



This generates a steady-state equilibrium ratio of $E/Z = k_{ZE}/k_{EZ}$, where E and Z denote the fractions of E and Z isomers.

Now let the probability of forming meso placements from E be P_{Em} and the probability of forming meso placements from Z be P_{Zm}. Then the tacticity of the main chain is given by

$$(m) = E \cdot P_{Em} + Z \cdot P_{Zm}, \quad \text{where } E + Z = 1 \tag{3}$$

We can now write the kinetic constants in the form

$$k_{ZE} = (kT/h) \exp(-\Delta G^{\ddagger}_{ZE}/RT) \tag{4a}$$

$$k_{EZ} = (kT/h) \exp(-\Delta G^{\ddagger}_{EZ}/RT) \tag{4b}$$

$$E/Z = k_{ZE}/k_{EZ} = \exp[-(\Delta G^{\ddagger}_{ZE} - \Delta G^{\ddagger}_{EZ})/RT] \tag{5a}$$

$$E/Z = k_{ZE}/k_{EZ} = \exp(-\Delta\Delta G^{\ddagger}/RT) \tag{5b}$$

In order to force the system to avoid those E/Z isomers that generate meso placements, we set the free energy of activation for their formation to be proportional to the difference of probabilities that they do form meso placements, $\Delta P = P_{Em} - P_{Zm}$

$$\Delta\Delta G^{\ddagger} = a\Delta P \tag{6}$$

Then

$$E/Z = k_{ZE}/k_{EZ} = \exp(-a\Delta P/RT) \tag{7}$$

The system will now select the isomer that forms less meso placements. Rearrangement of eq 7 results in

$$\Delta P = -RT \ln (E/Z)/a \tag{8}$$

In order to obtain absolute probabilities we set

$$P_{Em} = b + 0.5\Delta P \text{ and } P_{Zm} = b - 0.5\Delta P \tag{9}$$

The functions of eqs 6 and 9 are chosen arbitrarily because they are simple and monotonous. However, for a qualitative description they are sufficient. The fraction of meso diads, (m), can now be calculated by using only two arbitrary parameters, a and b, which are common for all counterions:

$$\begin{aligned}(m) &= b + (E - Z)RT \ln (E/Z)/(2a) \\ &= b + (2E - 1)RT \ln [E/(1 - E)]/(2a)\end{aligned} \tag{10a}$$

The result of a fit of a and b to the experimental data is shown in Figure 4.

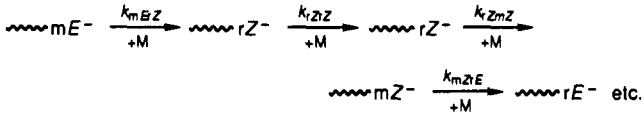
Conclusions

Our experimental results strongly suggest that E/Z isomerism plays an important role in the control of polymer tacticity. The fraction of meso diads as well as the deviation from Bernoullian statistics is not a monotonous function of the counterion. Both have maxima at K^+, and exactly at this point the system switches from producing Z end groups to producing E end groups. Obviously, tacticity and E/Z isomerism correlate with each other. In contrast to earlier mechanisms (penultimate and Coleman–Fox models), the E/Z mechanism is based on experimental observations, not assumptions.

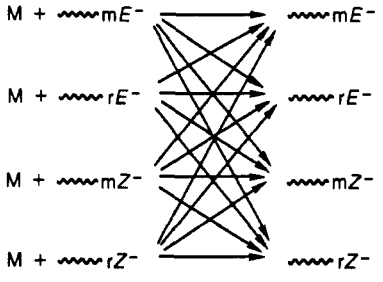
However, if tacticity is controlled by E/Z isomerism exclusively *and* only one of the two isomers is formed, Bernoullian statistics are expected. For Li^+, Na^+, and Cs^+, one of the E/Z isomers is present in only negligible amounts. The observation of non-Bernoullian statistics (especially for Na^+ and Cs^+) has to be explained either by

the additional existence of the penultimate mechanism or by a very high reactivity of the less abundant E/Z isomers.

Presently, tacticity of the end group cannot be completely ruled out as an additional factor determining tacticity. A realistic model for the generation of tacticity may be described by the following kinetic chain:



The complete kinetic scheme is of the form



This scheme consists of 16 rate constants (which due to normalization reduce to 12 independent parameters). A theoretical evaluation of this problem will be presented in a subsequent article.[21]

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Registry No. Li diphenylmethyl, 881-42-5; Na diphenylmethyl, 5152-68-1; K diphenylmethyl, 10060-17-0; Cs diphenylmethyl, 712-49-2; methyl methacrylate, 80-62-6.