Stereochemistry of Living Poly(methyl methacrylate) Anions As Determined by ^{13}C NMR Analysis of Carbon-13-Labeled Methyl End Groups

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ABSTRACT: The stereochemistry of polymerization of living poly(methyl methacrylate) (PMMA) anions in THF in the presence of Li and Cs ions at various temperatures was investigated by ^{13}C NMR analysis of a ^{13}C-labeled chain-end methyl group formed by reaction of living PMMA with carbon-13-enriched CH_3I and of the chain itself. This detailed approach allowed an evaluation of the relative rates of propagation of enolates having meso or racemic stereochemistry of the two asymmetric centers adjoining the carbanion. For both the Li/THF and Cs/THF cases, it was found that the overall $r(m)$ diad content of the chain matches the fraction of r^- or m^- chain ends. This was especially surprising for the Cs enolate since, in this case, the chain is non-Bernoullian as judged from the chain triads. The stereochemistry of methylation was also investigated and was shown to be quite similar to that of monomer addition, i.e., syndiotactic-like. Perhaps most surprising was the finding that the m^- anions undergo Claisen-type side reactions much faster than the corresponding r^- anions. This was explained in terms of the conformations of the two types of chain-end anions.

Introduction

Comparison of the stereochemistry of the chain end and that of the main chain has been shown to be of considerable value in the determination of plausible mechanisms of stereoregulation.[1-5]

For instance, from a knowledge of the fractions of triads adjacent to the chain-end anion (rr^-, mr^-, rm^-, mm^-) the conditional probabilities for first-order Markoff statistics, P^-_{rm} and P^-_{mr}, may be determined:[4]

$$P^-_{rm} = mr^-/r^- \quad \text{and} \quad P^-_{mr} = rm^-/m^- \tag{1}$$

where the fractions of meso and racemic diads (m^- and r^-) adjoining the chain end are given by $m^- = mm^- + rm^-$ and $r^- = rr^- + mr^-$.

Comparison with the corresponding parameters obtained from the main-chain stereochemistry then allows a test of first-order Markoff chain without information from higher n-ads than triads (eq 2).

$$P_{rm} = mr/2r \quad \text{and} \quad P_{mr} = mr/2m \tag{2}$$

A "penultimate mechanism" in which the relative stereochemistry of the last two asymmetric centers influences the stereochemistry of monomer addition has frequently benn invoked to account for first-order Markoff statistics. In the corresponding kinetic model, it may be shown that the rate constants of tactic monomer addition may be calculated from the stereochemistry of the main chain, that of the chain end, and the overall propagation rate constant.[6] The differential equations

$$dm/dt = [M][P^*](r^-k_{rm} + m^-k_{mm}) \tag{3a}$$

$$dr/dt = [M][P^*](r^-k_{rr} + m^-k_{mr}) \tag{3b}$$

relate statistical with kinetic quantities. Here, the concentration of meso and racemic end-group anions is given by their fractions and the total living end-group concentration:

$$[m^-] = m^-[P^*] \quad \text{and} \quad [r^-] = r^-[P^*]$$

From the stationarity principle ($d[m^-]/dt = -d[r^-]/dt = 0$) follows

$$r^-k_{rm} = m^-k_{mr} \tag{4}$$

Insertion into eq 3 leads to

$$dm/dt = [M][P^*]m^-(k_{mr} + k_{mm}) \tag{5a}$$

$$dr/dt = [M][P^*]r^-(k_{rr} + k_{rm}) \tag{5b}$$

The probability to find a meso or racemic diad is given by

$$m = \frac{dm/dt}{d[M]/dt} \quad \text{and} \quad r = \frac{dr/dt}{d[M]/dt} \tag{6}$$

Insertion of eq 5 into eq 6 leads to

$$m = m^-\frac{k_{mr} + k_{mm}}{k_p} \quad \text{and} \quad r = r^-\frac{k_{rr} + k_{rm}}{k_p} \tag{7}$$

The special case that $m = m^-$ (and thus $r = r^-$) leads to the relation

$$k_{mr} + k_{mm} = k_{rr} + k_{rm} \tag{8}$$

This relation is usually fulfilled for a Bernoullian process; however, it is not a prerequisite. *Thus, even for Bernoullian statistics, the determination of the stereochemistry of the chain end provides additional information*

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about the kinetics of the tactic monomer addition which is not available from main-chain statistics alone.

The fractions of triads are related to the rate constants of a "penultimate mechanism" by

$$mm = \frac{[m^-]k_{mm}}{[P^*]k_p} = m^-k_{mm}/k_p, \text{ etc.} \quad (9)$$

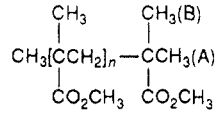
This leads to the relative rate constants

$$\frac{k_{mm}}{k_p} = \frac{mm}{m^-} \quad \frac{k_{rr}}{k_p} = \frac{rr}{r^-} \quad (10a)$$

$$\frac{k_{mr}}{k_p} = \frac{mr}{2m^-} \quad \frac{k_{rm}}{k_p} = \frac{mr}{2r^-} \quad (10b)$$

The absolute rate constants may be calculated on the basis of previous kinetic studies.[6] ^{13}C NMR analysis of living polymer anions terminated with ^{13}C-enriched methyl iodide was shown to be a suitable method to determine the stereochemistry of the chain end in the anionic polymerization of 2-vinylpyridine,[7] 4-vinylpyridine,[7] and 2-isopropenylpyridine.[5]

In a recent publication,[8] we showed that the ^{13}C NMR spectra of methylated model oligomers of methyl methacrylate (MMA; **2–6**) in particular were useful for the



1, $n = 0$; **2**, $n = 1$; **3**, $n = 2$; **4**, $n = 3$; **5**, $n = 4$; **6**, $n = 5$

elucidation of the relative stereochemistry of the four adjacent asymmetric centers as illustrated in Figure 1. The A and B methyl groups absorb at 29.4–30.0 and 22.0–22.8 ppm, respectively. The fine structure could be assigned on the basis of the ^1H and ^{13}C NMR spectra of the model oligomers **3–6** and that of analogous model oligomers of 2- and 4-isopropenylpyridine.[5] The above assignments are expected to provide a reliable basis for the stereochemical assignments of the diads adjacent to the propagating centers of the corresponding polymers prepared by anionic polymerization of MMA and terminated with ^{13}C-enriched methyl iodide.[9]

Alternatively, the stereochemistry of the chain end for living poly(meth)acrylates can be determined by termination with chlorotrimethylsilane and ^{13}C NMR spectroscopy of the resulting silyl ketene acetal.[8] In addition to the information on the E/Z ratio (see below) these measurements also give information on the chain-end triads. In order to compare the information resulting from the two methods, a study was undertaken to determine the chain-end stereochemistry of living PMMA using ^{13}C-labeled CH_3I. Li and Cs^+ ions were chosen as the counterions at temperatures ranging from −30 to −100 °C.

This study was carried out by both the Gainesville and the Mainz groups, however, using different experimental procedures. Polymerizations in Mainz were conducted in a stirred tank reactor where monomer and initiator solutions were mixed instantaneously, whereas in Gainesville, the monomer was added in vacuo by vapor-phase distillation of the monomer. Some preliminary results were published earlier.[10]

Experimental Section

Diphenylmethyllithium (DPMLi) and -cesium (DPMCs) were prepared by reaction of recrystallized diphenylmethane with *n*-BuLi and oligo(α-methylstyryl)cesium, respectively, in THF at −78 °C.

Methyl methacrylate was purified by repeated distillation in vacuo from CaH_2 and by distillation from a sodium mirror.

The procedures for polymerization and methylation carried out in Gainesville are essentially the same as those reported previously in a similar study on the stereochemistry of polymerization of 2-vinylpyridine.[3,7] Polymerizations were carried out by slow (ca. 1 h) distillation of MMA (1–2 g) into a solution of the initiator in THF at various temperatures under rapid stirring. After polymerization, a 2× molar excess of ^{13}C-labeled CH_3I (New England Nuclear, 90% enriched) was distilled into the reaction vessel. At that temperature and after 2 h, an additional 5 equiv of ordinary CH_3I was added in order to ensure complete reaction. After 5 h, the vessel was warmed to 25 °C and the contents of the flask was slowly added to hexane. After washing the precipitated polymer with hexane, it was dried in vacuo at 40 °C for 24 h.

^{13}C NMR spectra were obtained in tetrachloroethane-d_2 (15% by weight) at 90 °C at 50 MHz. The spectra were acquired using a 5.0-s pulse delay and an acquisition time of 1.5 s using 5000–8000 transients.

Polymerizations in Mainz were performed in a discontinuous stirred tank reactor similar to that in former kinetic experiments.[11] Precooled initiator and monomer solutions were rapidly mixed and filled into the reactor within 0.4 s. An excess of common ion salt ($LiBPh_4$ and $CsBPh_3CN$, respectively) was added to the initiator in order to suppress the possible dissociation into free ions. After the completion of the reaction (10–15 half-lives) the reaction solution was transferred to a flask containing a 2-fold excess of $^{13}CH_3I$ (Ventron, 90% enriched) and stirred for 15–30 min without further cooling in order to increase the rate of methylation. Thus, the average temperature of methylation was considerably higher than that of polymerization.

Then the solvent was evaporated on a rotary evaporator, and the residue was dissolved in benzene, filtered, and freeze-dried. The number-average degree of polymerization, as determined by GPC, was 15 ± 5.

^1H NMR measurements (400 MHz) were performed in bromobenzene-d_5 (5% by weight) at 110 °C and ^{13}C NMR measurements (100 MHz) were taken in 10% $CDCl_3$ solution at room temperature.

Results and Discussion

Assignment of Peaks. An example of the $^{13}CH_3$-end-labeled PMMA prepared by initiation of MMA by RLi/THF at −45 °C and terminated by $^{13}CH_3I$ is shown in Figure 2. It is clear that the stereochemical resolution permits unambiguous assignment of the relative stereochemistry of up to three diads adjoining the propagation center. The information obtained from the down- and upfield signals is clearly redundant, as is the case with the oligomers.[8] The ^{13}C chemical shifts of the end-group tetrads of the downfield (B) signal are arranged in the order of decreasing magnetic field $mr^- > rrr^- > mrr^- > mrm^- > rrm^-$, and the reverse is the case for the upfield (A) absorption.

Main-Chain Stereochemistry. The stereochemistry of the main chain as determined by ^{13}C NMR of the C=O groups as well as by ^1H NMR of the α-methyl groups and that of the methyl end group of PMMA prepared in THF between +30 and −100 °C in the presence of Li^+ and Cs^+ as the counterion is shown in Tables I and II. The data for the main chain (Li^+: Table I) indicate that the preference for a syndiotactic (*rr*) placement increases at lower temperature in accordance with the results of numerous other workers. The increase in the *rr* content at lower temperatures comes mainly at the expense of the *mr* sequences that decline from 0.28 to 0.16 in the −37 to −100 °C interval. The stereochemistry appears to be consistent with Bernoullian statistics since the persistence ratio ($\rho = 2mr/(mr)$) is close to unity, again consistent with the results of most other workers for this system. This is not the case for the Cs/THF system where the

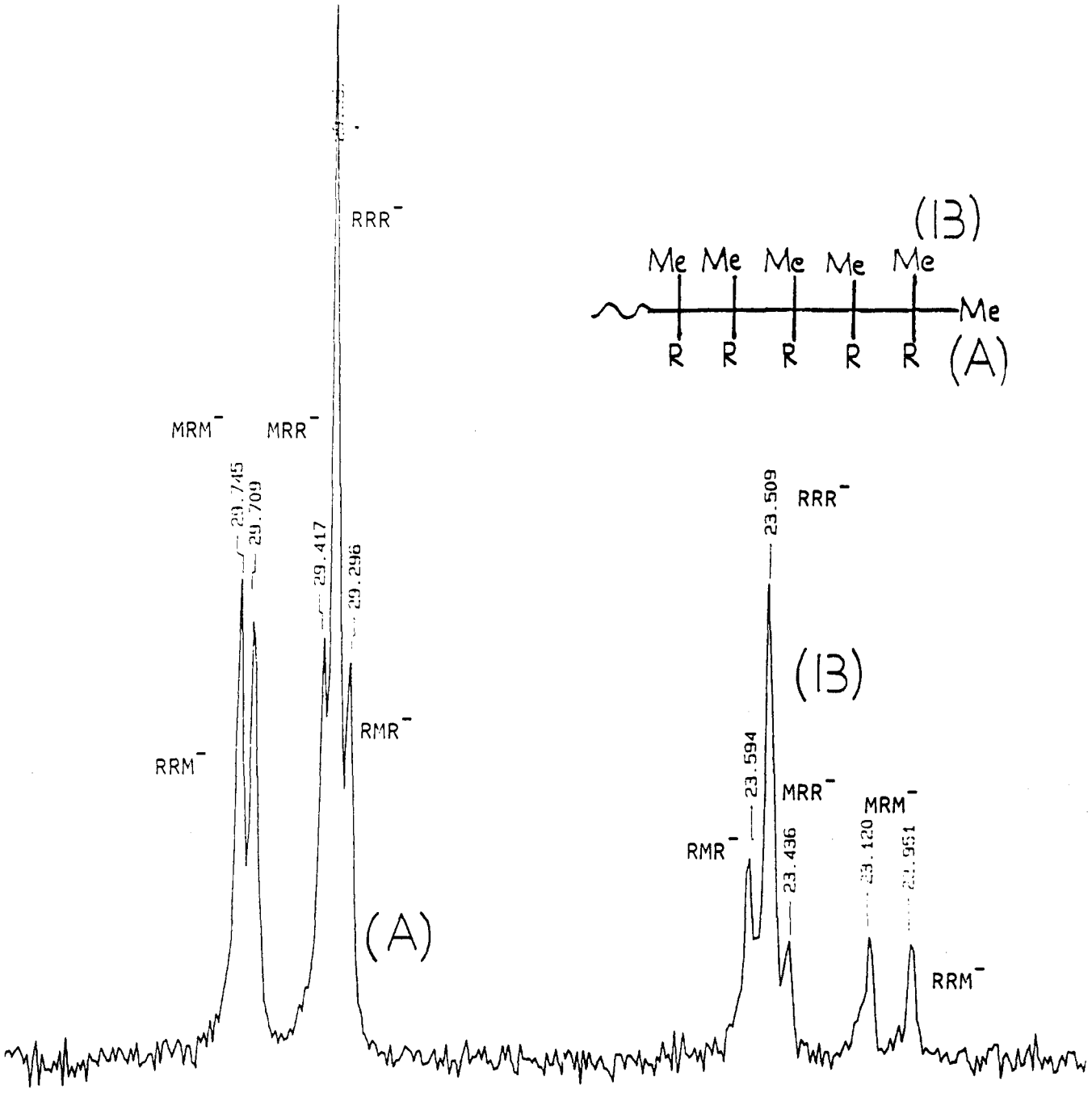


Figure 1. Carbon-13 NMR spectrum of carbon-13-labeled methyl end groups of PMMA.

value of ρ is clearly lower than 1. Furthermore, in this system, the increase in the syndiotactic content at lower temperature is less pronounced.

The right-hand side of Tables I–II gives the fractions of the diads, triads, and tetrads adjacent to the end group and compares the racemic diads, r^-, to those of the main chain, r. These results will be discussed in detail below.

Stereochemistry of Side Reactions. The results of the first experiments conducted in Mainz showed a peculiar temperature dependence of the end-group statistics. For both Li^+ and Cs^+ as the counterions the values of r^- are rather similar at temperatures above −52 °C and much higher than those at lower temperatures. It was concluded that side reactions might occur at elevated temperatures, especially since the temperature of methylation was even higher than that of polymerization. A preferential depletion of the meso chain ends could not be excluded.

This was checked in Gainesville by a series of experiments in which the polymerization (Li/THF) was carried out at −78 °C but in which the polymerization mixture was methylated under a set of different conditions (runs 2–4, Table I). When the methylation was carried out at −78 °C during monomer addition, the rm^- content was 8% but aging for 40 min at −78 and −45 °C gave lower fractions of rm^- (6 and 2%, respectively). This apparent preferential depletion of the rm^- anions is illustrated in Figure 2, clearly showing the virtual disappearance of this anion relative to the anions with an r^- terminal group. These lower values of m^- were quite consistent with those found by the Mainz group. Thus, at −82 °C, the temperatures during methylation were apparently low enough to prevent complete destruction of rm^- anions (run M5, Table I).

Polymerization and methylation at −45 °C gave about 12% rm^- content (run 1), whereas ambient methylation conditions at higher temperatures (runs M1 and M3, Table I) gave no visible rm^- peaks at all. Similar results were obtained for the Cs system (runs 7–9, Table II). Aging the polymerization mixture obtained at −78 °C for 40 min at −45 °C followed by cooling to −78 °C and methylation at that temperature gave 12% rm^- (run 8), whereas meth-

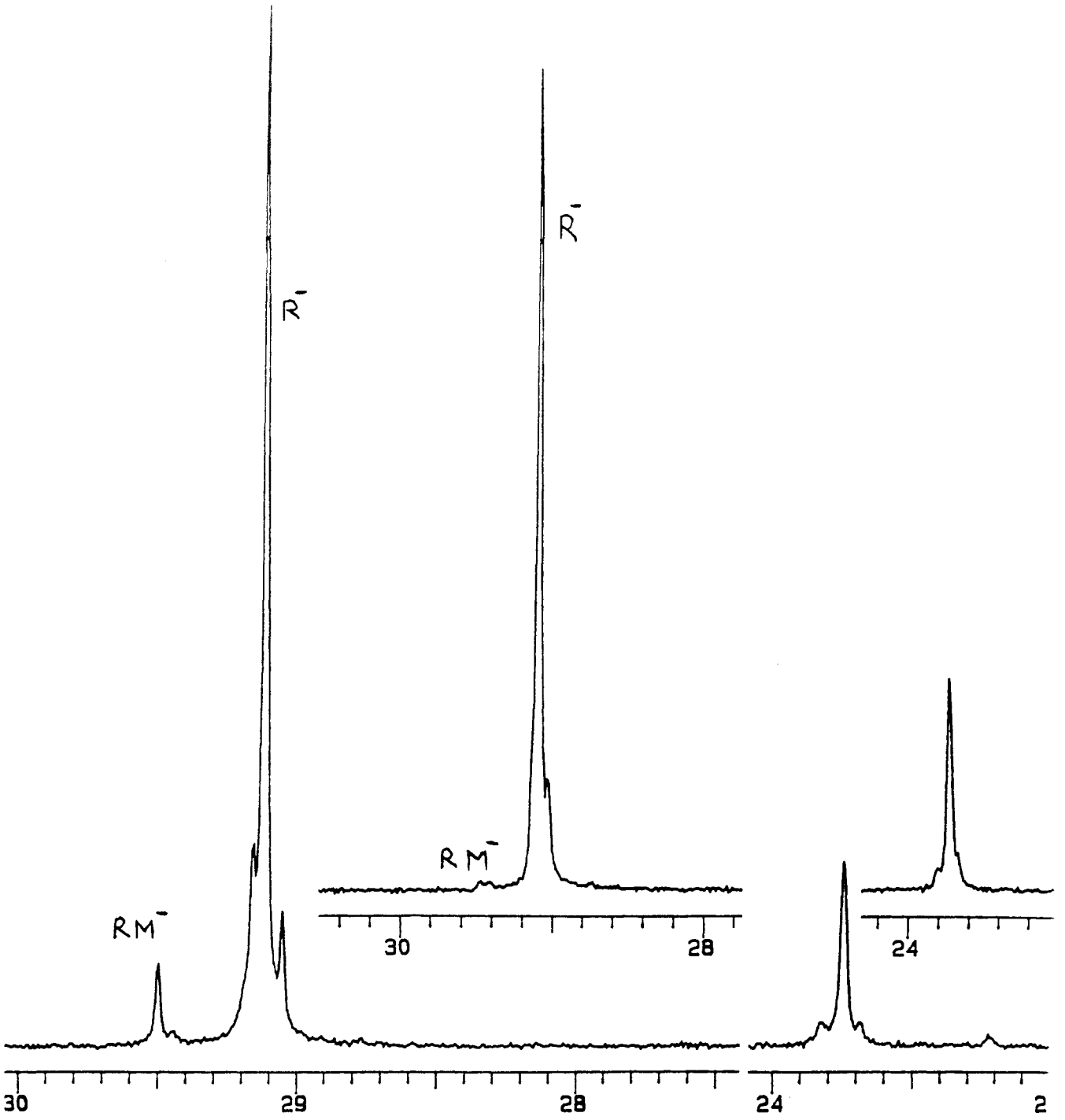


Figure 2. Demonstration of preferential side reactions of m^- anions of PMMA.

ylation at −78 °C without aging gave 28% rm^- (run 9). Aging 15 min at −78 °C did not appear to affect the methylation stereochemistry (run 7). Polymerization at −45 °C followed by cooling to −78 °C and methylation at that temperature gave an rm^- content of 28% (run 6) in contrast with the 3% rm^- content obtained under ambient methylation conditions (runs M7 and M8). Again it is clear that the preferential depletion of the rm^- anions at higher temperatures adds to the relative intensity of the rr^- sequences (runs 8 and 9). Below about −70 °C, the end-group stereochemistry results obtained by the two groups are in very good agreement. Apparently at −70 °C or below, the methylation under ambient conditions occurs at a low enough temperature so as not to distort the relative proportion of the stereoisomeric anions.

These results, particularly the preferential depletion of the m^- anions, appear to be unprecedented and provide striking evidence for the influence of the stereochemistry of the penultimate diad of living PMMA in side reactions. The observation that the m^- anions are more prone to these side reactions is of interest and appears to be the first report of its kind. The effect of stereochemistry of the diad adjoining the chain end strongly supports an intramolecular reaction between the enolate and the antepenultimate ester group. The greater reactivity of the m^- anion in this case is intriguing and should be related to the predominant conformation of the chain adjoining the enolate end. The r^- anion is expected to be largely in the tt conformation, and this appears consistent with the much greater shielding of the pro-meso methyl group compared to the pro-racemic methyl group.[5,8] In this conformation, the enolate is well removed from the chain end (Scheme I).

Table I
End-Group and Main-Chain Stereochemistry for the Polymerization of MMA Initiated by DPMLi in THF

		main chain					chain end					
run no.	T, °C	*mm*	*mr*	*rr*	*r*	ρ	rrm^-	rrr^-	mrr^-	rmr^-	r^-	r^-/r
M1[d]	−37	0.03	0.28	0.69	0.83	1.02	<0.003	0.70	0.17	0.13	1.00	1.20
M2[d]	−40	0.04	0.26	0.69	0.83	1.08	<0.003	0.73	0.16	0.11	1.00	1.20
M3[d]	−45	0.03	0.25	0.71	0.84	1.07	<0.003	0.78	0.13	0.09	1.00	1.19
1[a]	−45	0.01	0.25	0.74	0.87	0.93	0.12	0.67	0.10	0.11	0.88	1.01
M4[d]	−67	0.02	0.20	0.78	0.88	1.09	0.035	0.75	0.11	0.10	0.96	1.09
2[a]	−78	0.01	0.18	0.81	0.90	1.00	0.08	0.69	0.13	0.10	0.92	1.02
3[b]	−78	0.01	0.21	0.78	0.88[5]	0.97	0.06	0.75	0.11	0.08	0.94	1.06
4[c]	−78	0.01	0.21	0.78	0.88[5]	0.99	0.02	0.84	0.06	0.08	0.98	1.11
M5[d]	−82	0.01	0.15	0.84	0.91[5]	1.06	0.041	0.77	0.09	0.09	0.95	1.04
5[a]	−100	0.01	0.16	0.83	0.91	1.02	0.08	0.75	0.12	0.07	0.94	1.03

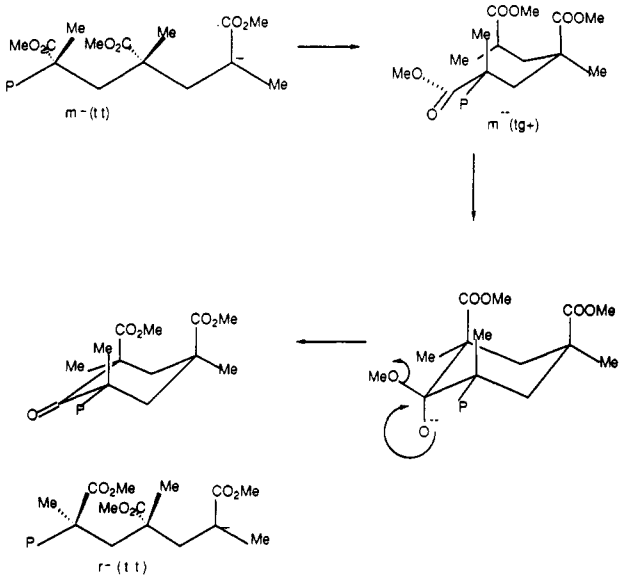
[a] Methylation during polymerization. [b] Aged 40 min at −78 °C and then methylated at −78 °C. [c] See footnote *b* but aged 40 min at −45 °C, 15 min at −78 °C, and methylated at −78 °C. [d] Monomer added in one batch; methylation after polymerization; the solution was allowed to reach room temperature after addition of CH_3I.

Table II
End-Group and Main-Chain Stereochemistry for the DPMCs-Initiated Polymerization of the MMA Main Chain

		main chain					chain end					
run no.	T, °C	*mm*	*mr*	*rr*	*r*	ρ	rm^-	rrr^-	mrr^-	$(r)mr^-$	r^-	r^-/r
M6[e]	−30	0.04	0.51	0.45	0.70	0.82	0.03	0.48	0.24	0.24	0.97	1.39
M7[e]	−40	0.05	0.50	0.46	0.71	0.84	0.03	0.48	0.22	0.26	0.97	1.37
6[b]	−45	0.04	0.56	0.40	0.68	0.78	0.28	0.29	0.26	0.17	0.72	1.06
M8[e]	−52	0.04	0.45	0.51	0.73	0.88	0.03	0.46	0.20	0.30	0.97	1.33
M9[e]	−70	0.03	0.48	0.49	0.73	0.83	0.26	0.35	0.17	0.23	0.74	1.01
7[c]	−78	0.04	0.58	0.39	0.69	0.74	0.28	0.39	0.17	0.16	0.72	1.04
8[d]	−78	0.02	0.54	0.44	0.71	0.76	0.12	0.46	0.22	0.20	0.88	1.24
9[a]	−78	0.02	0.58	0.40	0.69	0.74	0.28	0.31	0.15	0.26	0.73	1.06
M10[e]	−80	0.03	0.42	0.55	0.76	0.86	0.27	0.37	0.16	0.20	0.73	0.96
10[a]	−100	0.03	0.54	0.43	0.69	0.79	0.26	0.32	0.13	0.28	0.73	1.06
M11[e]	−102	0.02	0.42[5]	0.56	0.77	0.83	0.28	0.37	0.15	0.20	0.72	0.94

[a] Methylation during polymerization. [b] Methylated at −78 °C. [c] Aged 15 min at −78 °C methylated at −78 °C. [d] See footnote *c* but aged at −45 °C for 40 min and then methylated at −78 °C. [e] See Table I, footnote *d*.

Scheme I
Stereochemistry of Intramolecular Attack of the m^- Enolate on an Antepenultimate Ester



Because of the large bulk of the ester group, the tt conformation of the m^- diad is expected to be destabilized with respect to the more compact tg^- or tg^+ conformation. In either conformation, the enolate would be quite close to the antepenultimate ester, thus increasing the entropy of activation and increasing the rate of intramolecular reaction (Scheme I).

The stereochemistry of the cyclic trimer is also of interest since only two stereoisomers have been isolated that differ only in the cis/trans placement of the two ester groups.[12] This is consistent with Scheme I since the nucleophilic attack of the enolate on the antepenultimate ester group is not expected to be stereoselective. Thus, the enolate ester group occupies an equatorial or axial position (as shown) in the transition state, giving rise to a trans or cis position of the two ester groups. The stereochemistry of the penultimate and antepenultimate asymmetric carbons remains fixed (meso stereochemistry only), and this is consistent with the greater reactivity of the m^- enolate.

Stereochemistry of the Chain End. Monomer Addition. From Table I, it is clear that the *r* and r^- contents of the chains for the Li/THF systems obtained using low methylation temperatures are essentially the same within experimental error. Even at −45 °C, the *r* and r^- values are identical (0.87 and 0.88 respectively, Table I, run 1). For the Li/THF system, the polymerization thus appears to be consistent with a Bernoullian mechanism since the persistence ratio, ρ, is equal to 1 as well.

For the Cs/THF systems, the stereochemistry of polymerization is inconsistent with a Bernoullian process since the persistence ratio, ρ, is much lower than 1 (Table II). Interestingly for this system, $r \approx r^-$ at least under conditions conducive to a correct evaluation of chain-end stereochemistry (see above). Of course the equality, $r \approx r^-$, is still consistent with a Markoff or some other process and does not mean that the chain is Bernoullian since $\rho < 1$.

From the data on the chain stereochemistry, further valuable information may be extracted concerning the viability of Markoff processes. From eqs 1 and 2, the Markoff parameters for the chain end and for the main chain are readily obtained. Hence, the viability of a first-order Markoff chain may be tested. The results for the Li^+ and Cs^+ systems are shown in Tables III and IV, respectively. It appears that for the Li system, the first-

Table III
Relevant First-Order Markoff Parameters Calculated for the Polymerization of MMA in THF in the Presence of Li

		main chain					chain end	
run no.	T, °C	r	ρ	P_{rm}	P_{mr}	ΣP	r^-	P^*_{rm}
1[a]	−45	0.87	0.93	0.14	0.92	1.06	0.88	0.12
M4	−67	0.88	1.09	0.11	0.83	0.94	0.96	0.10
2[a]	−78	0.90	1.00	0.10	0.90	1.00	0.92	0.11
3[b]	−78	0.88	0.97	0.12	0.91	1.03	0.94	0.08
M5[d]	−82	0.91	1.06	0.08	0.88	0.96	0.95	0.09
5[a]	−100	0.91	1.02	0.09	0.89	0.98	0.94	0.08

[a-d] See Table I.

Table IV
Relevant First-Order Markoff Parameters Calculated for the Polymerization of MMA in THF in the Presence of Cs

		main chain				chain end	
run no.	T, °C	r	ρ	P_{rm}	P_{mr}	r^-	P^*_{rm}
6[b]	−45	0.68	0.78	0.41	0.87	0.72	0.24
M9	−70	0.73	0.83	0.33	0.89	0.75	0.31
7[c]	−78	0.69	0.74	0.42	0.93	0.72	0.22
9[a]	−78	0.69	0.74	0.42	0.93	0.73	0.35
M10	−100	0.76	0.86	0.28	0.87	0.73	0.27
10[a]	−100	0.69	0.79	0.39	0.87	0.73	0.38
M11	−102	0.77	0.83	0.28	0.92	0.72	0.28

[a-c] See Table II.

Table V
First-Order Markoff Rate Constants for the Anionic Polymerization of MMA in the Presence of Li^+/THF

		stereochemistry							
run no.	T, °C	rr	mr	mm	r^-	k_{rr}/k_p	k_{mr}/k_p	k_{rm}/k_p	k_{mm}/k_p
1[a]	−45	0.74	0.25	0.01	0.88	0.84	1.04	0.14	0.08
M4[d]	−67	0.78	0.20	0.02	0.96[5]	0.81	(2.86)	0.10	(0.57)
2[a]	−78	0.81	0.18	0.01	0.92	0.88	1.12	0.10	0.12[5]
3[b]	−78	0.78	0.21	0.01	0.94	0.83	(1.75)	0.11	(0.16)
M5[d]	−82	0.84	0.15	0.01	0.95	0.88	(1.88)	0.08	(0.25)
5[a]	−100	0.83	0.16	0.01	0.94	0.88	1.33	0.08	0.12[5]

[a-d] See Table I.

Table VI
First-Order Markoff Rate Constants for the Anionic Polymerization of MMA in THF in the Presence of Cs^+

		stereochemistry							
run no.	T, °C	rr	mr	mm	r^-	k_{rr}/k_p	k_{mr}/k_p	k_{rm}/k_p	k_{mm}/k_p
6[b]	−45	0.40	0.56	0.04	0.72	0.56	1.00	0.39	0.14
M9[e]	−70	0.49	0.48	0.03	0.74	0.66	0.92	0.32	0.12
7[c]	−78	0.39	0.58	0.04	0.72	0.54	1.03	0.40	0.14
9[a]	−78	0.40	0.58	0.02	0.73	0.55	1.07	0.40	0.07
M10[e]	−80	0.55	0.42	0.03	0.73	0.75	0.78	0.29	0.11
10[a]	−100	0.43	0.54	0.03	0.73	0.59	1.04	0.37	0.11
M11[e]	−102	0.56	0.42[5]	0.02	0.72	0.78	0.76	0.30	0.07

[a-e] See Table II.

order Markoff parameters P_{rm} obtained from the NMR data of the chain and the chain end are the same within experimental error. For the Cs system, this does not appear to be the case for the cases in which methylation occurred under controlled conditions (Table IV, runs 6, 7, and 9). In the other cases (runs M9, M10, M11, and 10), however, there are some discrepancies in the data gathered by the two groups, with regard to both the main chain and chain end. It is plausible that this is due to differences in the polymerization methods. These include the use of ionizing salts in order to prevent ionization of the enolates by the Mainz group. In view of these uncertainties, a firm conclusion with regard to compliance with a first-order Markoff process does not appear to be warranted. Clearly, the polymerization is non-Bernoullian for the data obtained by both research groups.

The rate constants for those cases in which the methylation was carried out under conditions in which substantial spontaneous termination can be excluded are tabulated in Tables V and VI for the Li and Cs, respectively. As expected, the data for the Li/THF system shows reasonable compliance with Bernoullian statistics, the pairs k_{rr} and k_{rm} and k_{mr} and k_{mm} being very close although first Markoff statistics could not be excluded. For the Cs system, the differences in rate constants are somewhat greater. For both systems, the values of k_{rm} and k_{mm} are the lowest and that for k_{mr} is the highest. The effects of temperature are quite small. This is not surprising since variations with temperature in the ratio of rate constants are expected to be small. The determination of the relative values k_{mr}/k_p and k_{mm}/k_p is expected to be the least accurate since both depend on the value of m^- which is both small and subject to underestimation because of preferential side reactions involving m^-. Thus, for runs M4, M5, and 3, especially the values of k_{mr}/k_p but also those of k_{mm}/k_p are consistently high, giving unreasonably large values.

Scheme II
Stereochemistry of Monomer Addition

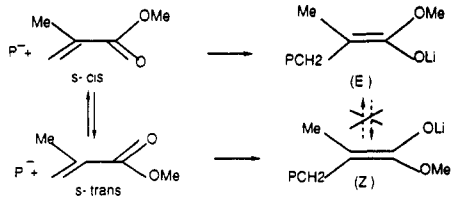


Table VII
Stereochemistry of Methylation of Living PMMA in THF in the Presence of Li Ion at Various Temperatures

run no.	T, °C	rr	rm	mr	mm	$rr/(rr + rm)$
M1[d]	−37	0.66	0.34			0.66
M2[d]	−40	0.69	0.31			0.69
M3[d]	−45	0.71	0.29			0.71
M4[d]	−67	0.66	0.31	0.03		0.68
M5[d]	−82	0.78	0.16	0.05	0.01	0.72
2[a]	−78	0.72	0.20	0.06	0.02	0.78
3[b]	−78	0.78	0.16	0.05	0.01	0.79

[a-d] See Table I.

The values for k_{mr}/k_p tend to increase and that of k_{rm}/k_p tends to decrease with temperatures. The ratio k_{rr}/k_p remains remarkably constant over the −45 to −100 °C range.

For the results in the Cs system, it is interesting to note that, in that case, the agreement in the values of r^- (m^-) is excellent for both sets of values, whereas the main-chain values differ somewhat (Tables II and VI). This results in different values, especially for k_{mr}/k_p, depending on the method of polymerization. The values for k_{mm}/k_p are the least accurate because of the low values for both mm and m^-. As was the case for the Li/THF system, the values of k_{mr}/k_p are the highest, followed by k_{rr}/k_p.

The non-Bernoullian character in the Cs/THF polymerization is reflected by the rather different values of k_{mr}/k_p and k_{rr}/k_p in most cases and of k_{rm}/k_p and k_{mm}/k_p. From the data of Table V, it would seem that for the Li/THF case $k_{mr} > k_{rr}$. This would seem to suggest that this is consistent with an influence of the relative stereochemistry of the last two chiral centers on the polymerization as well. In this case, however, the case for a non-Bernoullian polymerization is not as strong as for the Cs/THF case.

There are, however, other mechanisms that could give rise to non-Bernoullian chains. One of these mechanisms is based on the presence of E and Z geometric isomers of the propagating anion.[13] The E and Z anions are generated upon addition of the monomer in the s-trans and s-cis forms in the transition state (Scheme II). This mechanism generally was shown to lead to non-Bernoullian and even non-Markoffian statistics for the general case in which the E and Z structures do not interconvert on the reaction time scale and in which the stereochemistry of monomer addition is dependent upon the structure (E or Z) of the isomers. There is some support for this based upon the fact that E and Z enolates have been shown to discriminate stereochemically in aldol condensation reactions.[14,15] In the present case, we[9] and others[16,17] have shown the presence of E and Z enolates of alkali metals by reaction with trimethylsilyl chloride and ^{13}C NMR analysis of the resulting silyl ketene acetals. Thus, at −70 °C in THF, the lithium enolate was shown to exist almost exclusively as the Z isomer (99.7%), whereas the cesium enolate exists predominantly in the E form (95%). Since the model is one in which the exclusive participation of either E or Z anions leads to Bernoullian statistics, the Li/THF system seems to fit such a model quite well. For the Cs system, the minor (Z) form (5%) may well be more reactive than the E form and this would then lead to substantial Z participation, thus giving rise to non-Bernoullian chains. Therefore, we believe that a mechanism based on the presence of E and Z enolates is more likely. However, the present systems that tend to heavily favor one isomer or the other are probably not well suited to resolve this question. The study of the stereochemistry of other systems (Na, K, Rb) in THF where substantial fractions of both isomers coexist should be of considerable interest in this regard.

Stereochemistry of Methylation. The stereochemistry of methylation is tabulated in Tables VII and VIII for the Li/THF and Cs/THF systems, respectively. It is important to note that the ratio $rr/(rr + rm)$ reflects the stereochemistry of methylation of the anion adjacent to an r diad (r^-) and this preference for **r** methylation slightly increases at lower temperatures. Because of the rapid degradation of the m^- anions under the conditions of methylation (except run 2) and also because of the very low values of both mr and mm, the stereochemistry of methylation of m^- could not be determined reliably. From the model compounds, the larger downfield methyl signal is attributable to the pro-racemic position in the product. Thus, the stereochemistry of methylation is qualitatively similar to that of monomer addition. For the Li/THF system, the preference for the **r** methylation is moderate, increasing slightly at lower temperature. In evaluating methylation stereochemistry, the preferential depletion of the m^- anions at the higher temperatures should be taken into consideration.

For the Cs/THF system, similar data are obtained. The stereochemistry of methylation of the r^- anion is essentially temperature independent. The stereochemistry of methylation of m^- is only evaluated from runs M9 and M11 since, at −50 °C temperatures and higher, the m^- anion undergoes extensive reactions (see above). Again, there appears to be little dependence of the methylation stereochemistry of the m^- anion on temperature, but the preference of m^- for **r** methylation is somewhat higher than for r^- (Table VIII). The lack of stringent temperature control in some cases (see above) allows only a semiquantitative evaluation of methylation stereochemistry.

However, from the assignments it is clear that the stereochemistry of methylation and vinyl addition are similar. This is in sharp contrast with the corresponding reaction

Table VIII
Stereochemistry of Methylation of Living PMMA in THF at Various Temperatures in the Presence of Cs Ion

run no.	T, °C	rr	rm	mr	mm	$rr/(rr + rm)$	$mr/(mr + mm)$
M6[e]	−30	0.75	0.22	0.07		0.77	
M7[e]	−40	0.73	0.23	0.03		0.77	
M8[e]	−50	0.74	0.22	0.04		0.77	
M9[e]	−70	0.58	0.17	0.22	0.04	0.77	0.85
M10[e]	−80	0.59	0.14	0.23	0.03	0.81	0.88
M11[e]	−102	0.58	0.14	0.25	0.03	0.81	0.89

[e] See Table II.

of living poly(2-vinylpyridine) lithium in THF where methylation is highly meso stereoselective (>96%), in contrast to monomer addition that is only slightly meso selective (~60%).[3,4] The methylation stereoselectivity was shown to be related to intramolecular coordination of a Li ion by penultimate pyridine nitrogen. The Cs salt of this polymer anion shows very little methylation stereoselectivity (~60% meso).

Once again, this suggests the absence of occurrence of intramolecular cation coordination by the ester group(s) in the case of the Li or Cs salts of living PMMA in THF.

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Registry No. PMMA (homopolymer), 9011-14-7; Li, 7439-93-2; Cs, 7440-46-2.