

## NMR Studies on the Propagation Mechanisms of Methyl Methacrylate Polymerization with Alkyl-Iron and Cobalt Complexes

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**ABSTRACT:** Stereochemical configurations of poly(methyl methacrylate)s prepared with alkylbis(dipyridyl)cobalt and dialkylbis(dipyridyl)iron were studied by NMR spectroscopy. From the dyad, triad, and tetrad information of poly(methyl methacrylate)s prepared with the alkyl-transition metal catalysts, the propagation mechanisms giving acetone-soluble and acetone-insoluble polymers were studied. The process forming the acetone-soluble polymer was found to follow the Bernoulli trial statistics. The acetone-insoluble polymer which was prepared with  $\text{FeEt}_2(\text{dipy})_2$  in solvents of weak coordinating ability was found to be a stereoblock type and to obey the first-order Markovian statistics. The penultimate and pen-penultimate effects were estimated for the two types of polymerization processes, and the role of solvents in the propagation mechanisms is discussed. The results are consistent with the coordinated anionic mechanism and a possible model for the propagating species to satisfy these results is proposed.

**KEY WORDS** NMR / Propagation / Methyl Methacrylate / Dialkylbis(dipyridyl)iron / Alkylbis(dipyridyl)cobalt / Stereoblock / First-order Markov Statistics / Penultimate Effect / Coordinated Anion / Polymerization /

Previously we reported the isolation of diethylbis(dipyridyl)iron<sup>1</sup> and ethylbis(dipyridyl)cobalt<sup>2</sup> from the mixed systems containing iron and cobalt acetylacetonates, diethylaluminum monoethoxide and dipyridyl. These complexes having alkyl-transition metal bonds show unique properties of catalyzing the oligomerization of butadiene<sup>1,2</sup> and the polymerization of various vinyl monomers<sup>3,4</sup>. Among these monomers, methyl methacrylate (MMA) was found to give stereoblock polymers with diethylbis(dipyridyl)iron under certain conditions. In this paper we report the results of NMR studies on the stereochemical configuration of the poly(methyl methacrylate)s obtained with the alkyl-iron and cobalt complexes and on the propagation mechanisms of MMA polymerization with these complexes.

### EXPERIMENTAL

#### *Reagents*

Methyl methacrylate was purified by washing with a saturated aqueous solution of sodium hydrogen sulfite, a 5-% solution of sodium hy-

droxide and water, and then dried over calcium chloride and Drierite. The monomer was distilled twice under nitrogen before use.

Diethylbis(dipyridyl)iron<sup>1</sup> and ethylbis(dipyridyl)cobalt<sup>2</sup> were prepared as previously described. The corresponding methyl derivatives were prepared by using dimethylaluminum monoethoxide in place of diethylaluminum monoethoxide. The purity of the alkyl complexes was checked by chemical analysis, and volumetric measurements of the alkanes evolved on hydrolysis and alcoholysis.

#### *Polymerization*

The polymerization was carried out in a sealed ampoule in which the catalyst, monomer, and solvent were transferred in an atmosphere of nitrogen or by trap-to-trap distillation *in vacuo*. After the set time of polymerization, the ampoule was opened, and the content poured into acidic methanol. The precipitate was filtered, washed with methanol and dried. The polymer was extracted in a Soxhlet extractor with acetone for 1 week and separated into acetone-soluble and insoluble fractions.

*NMR Spectra*

Proton magnetic resonance spectra of poly-(methyl methacrylate) were obtained with a Japan Electron Optics Lab. Model JNM-4H-100 high-resolution spectrometer. Nitromethane and *o*-dichlorobenzene were used as solvents and tetramethylsilane was used as an internal standard.

*IR Spectra*

Infrared spectra of the polymers were observed with a Hitachi Model EPI-G3 Grating Infrared Spectrophotometer.

*Molecular Weight and Molecular Weight Distribution*

The relative viscosity of acetone-soluble polymer was determined at 25°C with a modified Ubbelohde viscometer in benzene solution and the molecular weight was calculated by using the following equation<sup>5</sup>:  $[\eta] = 3.80 \times 10^{-5} M^{0.79}$

The molecular weight distribution was observed by a Gel-Permeation Chromatograph of Waters Associates, Model 200 using 0.25-% tetrahydrofuran solutions of polymers.

## RESULTS AND DISCUSSION

In Table I are summarized the results of polymerization of MMA with  $\text{FeR}_2(\text{dipy})_2$  and  $\text{CoEt}(\text{dipy})_2$

( $\text{dipy})_2$  in various solvents. The catalysts are soluble in benzene, toluene, tetrahydrofuran (THF), acetonitrile, dimethyl formamide (DMF), and acetone. The polymerization proceeded very slowly in these solvents and the blue color of the solutions did not change throughout the polymerization. The catalysts are not soluble in hexane and no polymer was obtained in this solvent. The reason why no polymer was obtained in acetone is not clear at the moment.

When the polymerization was carried out in the absence of solvent with alkyl-iron or cobalt complexes the polymers obtained were soluble in acetone. The effect of the alkyl groups attached to the iron complex on the properties of polymers was observed in solution polymerizations. Whereas the methyl-iron complex gave acetone-soluble polymers regardless of the solvent employed, the ethyl-iron complex afforded acetone-insoluble polymers in less polar solvents such as benzene, toluene, and tetrahydrofuran. The solution containing the iron complex and MMA was homogeneous at the outset of polymerization and the polymer was gradually formed and precipitated as the polymerization proceeded. The polymer recovered from the solution was soluble in acetone, and the polymer obtained from the precipitate was insoluble in acetone.

**Table I.** Polymerization of methyl methacrylate with  $\text{FeEt}_2(\text{dipy})_2$  and  $\text{CoEt}(\text{dipy})_2$

Expt. No.	Catalyst <sup>a</sup> (mg)	Monomer (ml)	Solvent (ml)	Time (days)	Yield (%)	Acetone-insoluble fraction (%)
1	Co-Et 240	15	—	2	39	0
2	Fe-Et 200	10	—	12	76	0
3	Fe-Et 810	10	Benzene 20	3	24	13
4	Fe-Et 1050	35	Benzene 70	2	10	48
5	Fe-Et 400	10	Toluene 20	3	7	26
6	Fe-Et 520	10	THF 20	7	9	12
7	Fe-Et 410	10	$\text{CH}_3\text{CN}$ 20	3	9	0
8	Fe-Et 550	10	DMF 20	2hrs	88	0
9	Fe-Et 410	10	Hexane 20	3	0	—
10	Fe-Et 550	10	Acetone 20	3	0	—
11	Fe-Et 340	10	Acetone 20	3	0	—
12	Fe-Me 40	10	—	6	16	0
13	Fe-Me 100	10	Toluene 20	6	6	0
14	Fe-Me 460	10	DMF 20	6	6	0
15	Fe-Me 330	10	THF 20	6	3	0

<sup>a</sup> Co-Et, Fe-Et, and Fe-Me mean  $\text{CoEt}(\text{dipy})_2$ ,  $\text{FeEt}_2(\text{dipy})_2$ , and  $\text{FeMe}_2(\text{dipy})_2$  complexes respectively.

**Table II.** Assignments of tetrad methylene signals of poly(methyl methacrylate)<sup>a</sup>

<i>mmm</i>		<i>mnr</i>		<i>rmr</i>		<i>mr</i> <i>m</i>	<i>mrr</i> <sup>b</sup>	<i>rrr</i>
Threo	Erythro	Threo	Erythro	Threo	Erythro			
8.38	7.79	8.46	7.86	8.51	7.90	7.92	7.99	8.06
8.23	7.64	8.31	7.71	8.36	7.76			

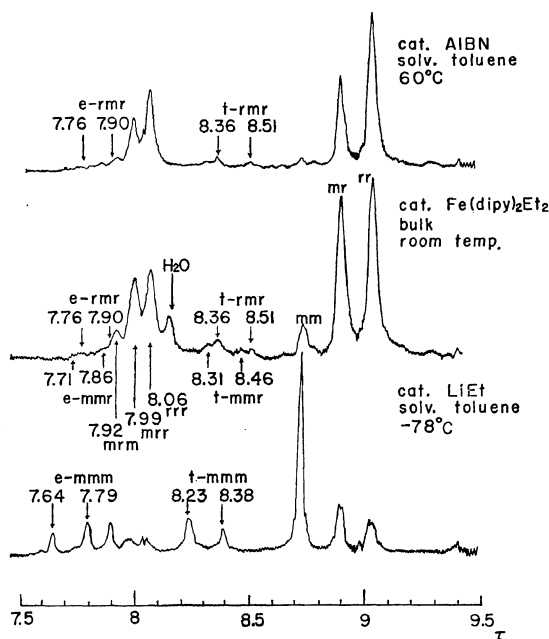
<sup>a</sup> The spectra were taken in  $\text{CH}_3\text{NO}_2$  at  $120^\circ\text{C}$ .

<sup>b</sup> The *mrr* tetrad is in principle heterosteric and should exhibit an AB quartet. In the observed spectrum the peak at  $\tau$ , 7.99 is regarded as the center of the unresolved *mrr* quartet with too weak outer lines for observation.

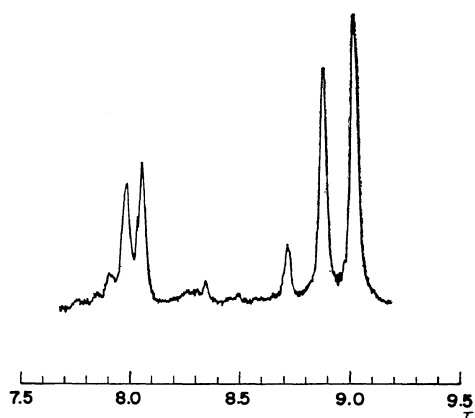
In more polar solvents such as acetonitrile and dimethylformamide, the solution remained homogeneous throughout the polymerization and the polymer obtained was soluble in acetone.

A typical NMR spectrum of acetone-soluble poly(methyl methacrylate) prepared by bulk polymerization with  $\text{FeEt}_2(\text{dipy})_2$  at room temperature is shown in Figure 1, together with the spectra of polymers obtained with azobisisobutyronitrile and ethyl lithium as initiators. The spectra were observed in nitromethane<sup>6</sup>, which is known as a good solvent for observing the triad

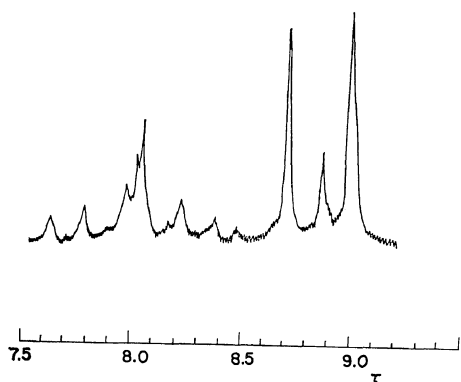
methyl signals of poly(methyl methacrylate), and we found that tetrad methylene signals can be clearly observed as well. (The signal at  $\tau$  8.15 is due to the water present as an impurity contained in the polymer and is omitted from the following discussions.) In Table II are summarized the assignments of the tetrad methylene signals. The tetrad assignments were made by comparing the relative intensity of each peak with triad signals, taking into account the reported tetrad assignments obtained by a 220 MHz-spectrometer<sup>7</sup>. The observation of racemic methylene signals of poly(methyl methacrylate) in chloroform with a 100 MHz spectrometer was reported by Hatada, Ota, and Yuki<sup>8</sup> but the tetrad meso methylene signals were not observed. The recent development of the 220 MHz-spectrometer has made the observation of all the tetrad signals possible. However the 220 MHz-spectrometer is not easily accessible. Consequently the feasibility of



**Figure 1.** NMR Spectra of poly(methyl methacrylate)s obtained with azobisisobutyronitrile,  $\text{FeEt}_2(\text{dipy})_2$  and ethyllithium as initiators (from the top to the bottom). Spectra were taken in  $\text{CH}_3\text{NO}_2$  at  $120^\circ\text{C}$  with a 100 Mc spectrometer.



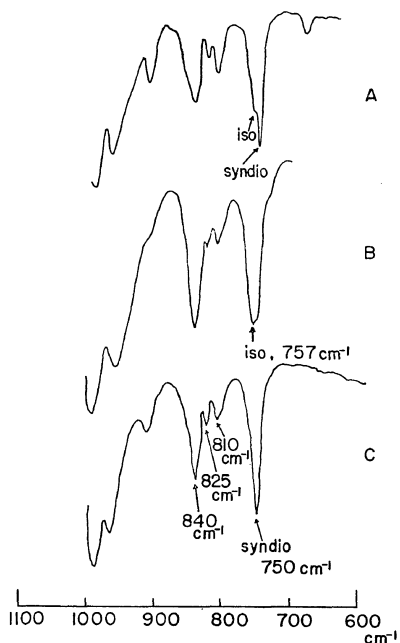
**Figure 2.** NMR Spectrum of acetone-soluble fraction of poly(methyl methacrylate) prepared with  $\text{FeEt}_2(\text{dipy})_2$  in benzene.



**Figure 3.** NMR Spectrum of acetone-insoluble fraction of poly(methyl methacrylate) prepared with  $\text{FeEt}_2(\text{dipy})_2$  in benzene; observed in nitromethane at  $120^\circ\text{C}$ .

the observation of racemic and meso methylene tetrad signals in nitromethane with a 100 MHz spectrometer may be of some value.

In Figures 2 and 3 are shown the typical spectra



**Figure 4.** Infrared spectra of polymers of methyl methacrylate.

A: Prepared with  $\text{FeEt}_2(\text{dipy})_2$  in benzene (acetone-insoluble stereoblock fraction).

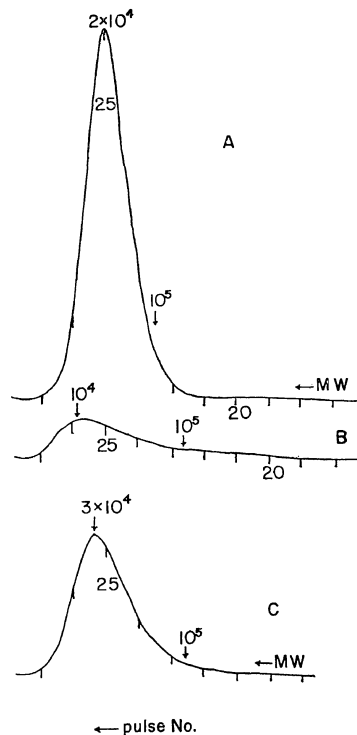
B: Prepared with  $\text{LiEt}$  in toluene (isotactic polymer).

C: Prepared with azobisisobutyronitrile in toluene (syndiotactic polymer).

of the acetone-soluble and insoluble polymers prepared with  $\text{FeEt}_2(\text{dipy})_2$  in benzene. The acetone-soluble polymer is similar to the polymer obtained by bulk polymerization and is rich in syndiotactic sequences whereas the acetone-insoluble polymer is different from acetone-soluble polymer and is a stereoblock type.

The differences in the stereoregularities of the polymers are also reflected in the infrared spectra. In Figure 4 are shown the infrared spectra of stereoblock, isotactic and syndiotactic poly(methyl methacrylate)s. The figure shows that the isotactic polymer has a band at  $757\text{ cm}^{-1}$ ; the syndiotactic polymer at  $750\text{ cm}^{-1}$  and the stereoblock polymer has both bands<sup>9</sup>.

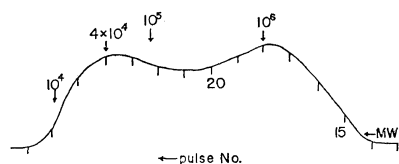
The molecular weight distributions of both acetone-soluble and insoluble polymers were measured by gel-permeation chromatography.



**Figure 5.** Molecular weight distribution of poly(methyl methacrylate) prepared with  $\text{FeEt}_2(\text{dipy})_2$ . A: Acetone-soluble fraction (the polymer was prepared in acetonitrile).

B: Acetone-insoluble fraction of polymer prepared in benzene.

C: Acetone-soluble fraction of polymer prepared under the same conditions as B.



**Figure 6.** Molecular weight distribution of poly (methyl methacrylate) prepared with  $\text{FeEt}_2(\text{dipy})_2$  in the absence of solvent.

There was no remarkable difference in molecular weight distribution between the acetone-soluble and insoluble polymers prepared with  $\text{FeEt}_2(\text{dipy})_2$  in benzene (Figure 5). On the other hand, the polymer prepared with  $\text{FeEt}_2(\text{dipy})_2$  in the absence of solvent had two peaks in the molecular weight distribution curve (Figure 6). The molecular weights determined by viscosity measurement were  $7.59 \times 10^5$  for the polymer obtained by bulk polymerization,  $0.88 \times 10^5$  for the polymer prepared in benzene solution and  $0.32 \times 10^5$  for the polymer prepared in acetonitrile solution. The employment of polar solvents appears to decrease the molecular weight of the polymer.

The assignments of the racemic methylene

tetrad signals were supported by comparing the relative intensities of the observed triad signals with the calculated values derived from the observed tetrad signals with following relations<sup>9</sup>.

$$(mm) = (mmm) + \frac{1}{2}(mmr)$$

$$(mr) = (mmr) + 2(rmr) = (mrr) + 2(mrm)$$

$$(rr) = (rrr) + \frac{1}{2}(mrr)$$

In this paper we use the notations proposed by Bovey<sup>10</sup>. In Tables III and IV are shown the comparisons of observed and calculated tacticities of acetone-soluble and acetone-insoluble polymers. In these Tables are also given the observed intensities of dyad signals and the calculated dyad values derived from triad signals according to the following equations.

$$(m) = (mm) + \frac{1}{2}(mr)$$

$$(r) = (rr) + \frac{1}{2}(mr)$$

$$(m) + (r) = 1$$

Good agreement between the observed and

**Table III.** Stereoregularity of poly(methyl methacrylate) (Acetone-soluble fraction)

No. <sup>a</sup>	Catalyst	Solvent	Dyads				Triads						Tetrads			$Pf_m$
			Obsd.		Calcd. <sup>d</sup>		Obsd.			Calcd. <sup>e</sup>			Obsd.			
			<i>m</i>	<i>r</i>	<i>m</i>	<i>r</i>	<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>mrm</i>	<i>mrr</i>	<i>rrr</i>	
R-1 <sup>b</sup>	AIBN	Toluene	20	80	21	79	6	31	63	6	31	63	3	25	51	0.21
R-2 <sup>c</sup>	LiEt	Toluene	71	29	75	25	63	24	13	61	28	11	10	8	7	—
1	Co-Et	—	13	87	18	82	2	33	65	1	34	65	6	22	54	0.19
2	Fe-Et	—	29	71	29	71	8	43	49	4	50	46	10	30	31	0.30
3-1	Fe-Et	Benzene	30	70	33	67	12	43	45	13	40	47	8	24	35	0.33
4-1	Fe-Et	Benzene	26	74	30	70	9	43	48	10	40	50	6	28	36	0.31
5-1	Fe-Et	Toluene	30	70	31	69	13	37	50	9	41	50	8	25	37	0.29
6-1	Fe-Et	THF	27	73	27	73	8	39	53	6	42	52	8	26	39	0.27
7	Fe-Et	$\text{CH}_3\text{CN}$	19	81	24	76	5	38	57	3	41	56	7	27	42	0.25
8	Fe-Et	DMF	30	70	31	69	11	41	48	10	43	47	9	25	34	0.31
12	Fe-Me	—	25	75	24	76	5	38	57	1	46	53	8	30	38	0.25
13	Fe-Me	Toluene	23	77	22	78	3	38	59	1	42	57	8	26	44	0.24

<sup>a</sup> The numbers correspond with those in Table I. Acetone-soluble fractions are designated by the numbers with -1 (as 3-1), and acetone-insoluble fractions with -2 (cf., Table IV).

<sup>b</sup> R-1, the polymer was prepared with azobisisobutyronitrile at 60°C.

<sup>c</sup> R-2, the polymer was prepared with EtLi at -78°C.

<sup>d</sup> Calculated from observed triad values.

<sup>e</sup> Calculated from observed tetrad values.

<sup>f</sup> Average values calculated from observed triad values.

**Table IV.** Stereoregularity of poly (methyl methacrylate) (Acetone-insoluble fractions)

No. <sup>a</sup>	Polymerization conditions		Dyads				Triads			Tetrads			$\bar{n}^b$	$\rho^b$			
			Obsd.		Calcd.		Obsd.			Calcd.							
	Catalyst	Solvent	<i>m</i>	<i>r</i>	<i>m</i>	<i>r</i>	<i>mm</i>	<i>mr</i>	<i>rr</i>	<i>mm</i>	<i>mr</i>	<i>rr</i>			<i>mrm</i>	<i>mrr</i>	<i>rrr</i>
3-2	Fe-Et	Benzene	42	58	42	58	32	21	47	36	21	43	4	23	31	4.8	2.3
4-2	Fe-Et	Benzene	41	59	45	55	35	20	45	32	26	42	4	18	33	5.0	2.5
5-2	Fe-Et	Toluene	41	59	49	51	41	16	43	40	18	42	1	16	34	6.2	3.1
6-2	Fe-Et	THF	46	54	43	57	35	16	49	35	16	49	2	12	43	6.2	3.0

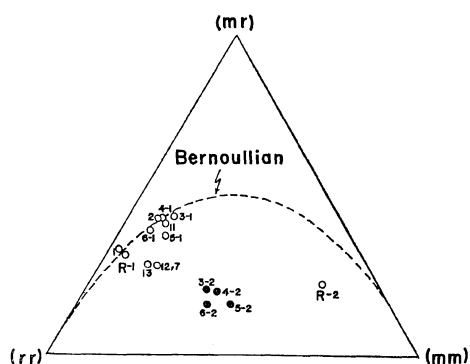
<sup>a</sup> *cf.*, Tables I and III.<sup>b</sup>  $\bar{n}$  and  $\rho$ , see the text.

calculated values indicates the validity of the assignments.

The propagation mechanisms can be studied by examining the dyad, triad, and tetrad information about the polymers obtained. If the propagation steps obey the Bernoullian statistics the following equations should hold<sup>10,11</sup>

$$\begin{aligned} \text{dyad:} \quad & (m) = P_m, \quad (r) = 1 - P_m \\ \text{triad:} \quad & (mm) = P_m^2, \\ & (mr) = 2P_m(1 - P_m) \quad (rr) = (1 - P_m)^2 \\ \text{tetrad:} \quad & (mrm) = P_m^2(1 - P_m) \\ & (mrr) = 2P_m(1 - P_m)^2 \\ & (rrr) = (1 - P_m)^3 \end{aligned}$$

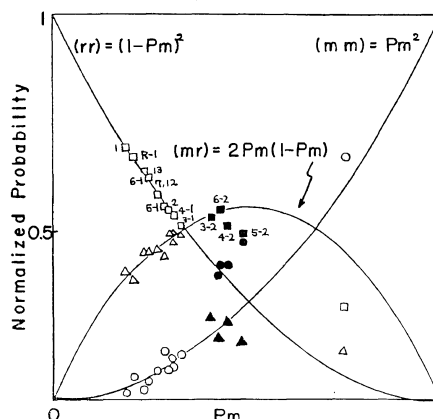
where  $P_m (= \sigma)$  represents the probability of a meso (isotactic) placement during propagation. As Figures 7, 8, and 9 show, the propagation steps to yield the acetone-soluble polymers follow the Bernoullian statistics, whereas the acetone-

**Figure 7.** Stereoregularity of poly(methyl methacrylate) represented by a triangular coordinate.

○: Acetone-soluble polymers.

●: Acetone-insoluble polymers.

For figures in the triangle refer to Table I.

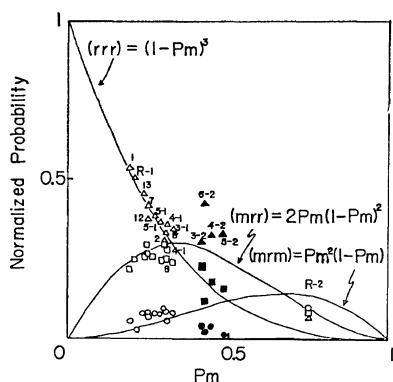
**Figure 8.** Stereoregularity of poly(methyl methacrylate) expressed as a function of  $P_m$  (triad).□, ■: *rr*.△, ▲: *mr*.○, ●: *mm*.

□, △, ○: Acetone-soluble fractions.

■, ▲, ●: Acetone-insoluble fractions.

Dyad intensity (*m*) was used instead of  $P_m$  for acetone-insoluble fractions.

insoluble polymers deviate from the Bernoullian. In these figures are also included the tacticities of a polymer prepared with ethyllithium as an initiator (R-2). In Table III are included  $P_m$  values for acetone-soluble polymers.  $P_m$  values for the polymerization of methyl methacrylate with  $\text{FeEt}_2(\text{dipy})_2$  are higher compared with the  $P_m$  value (0.18) for radical polymerization at the same temperature. It is also noted that the  $P_m$  values in the polymerizations with  $\text{FeMe}_2(\text{dipy})_2$  are slightly lower compared with those with  $\text{FeEt}_2(\text{dipy})_2$ . The difference in  $P_m$  values for polymerizations with the methyl- and ethyl-iron initiators may be explained by assuming that one of



**Figure 9.** Stereoregularity of poly(methyl methacrylate) as a function of  $P_m$  (tetrad).

△, ▲:  $rrr$ .

□, ■:  $mrr$ .

○, ●:  $mrm$ .

△, □, ○: Acetone-soluble fractions.

▲, ■, ●: Acetone-insoluble fractions.

Dyad intensity ( $m$ ) was used instead of  $P_m$  for acetone-insoluble fractions.

the two alkyl groups is still attached to the iron complex during the propagation steps and exerts some stereochemical effect on the polymerization. The effect of the alkyl group is more marked in the polymerization in benzene, toluene, and THF, where the ethyl complex gives acetone-insoluble stereoblock polymers and the methyl complex affords only acetone-soluble polymers.

The deviation of the polymerization process leading to acetone-insoluble polymers from Bernoulli statistics leaves the possibilities of several propagation mechanisms to be tested.<sup>10-12, 14, 15</sup> The enantiomorphic mechanism<sup>12</sup> can be excluded from consideration because the stereoblock polymer obtained is rich in isotactic and syndiotactic sequences and poor in heterotactic sequences.

With the information on dyad, triad, and tetrad

fractions we can test if the acetone-insoluble polymers are the first-order Markovian. In the first-order Markov process, the propagation steps can be described by two independent probabilities,  $P_{mr}$  or  $u$  and  $P_{rm}$  or  $w$ . The designation  $P_{mr}$  means the probability that the monomer adds in  $r$ -fashion to an  $m$ -chain end, and  $P_{rm}$  vice versa.  $P_{mr}$  and  $P_{rm}$  are related to  $P_{mm}$  and  $P_{rr}$  by the following equations.

$$u = P_{mr} = 1 - P_{mm}, \quad w = P_{rm} = 1 - P_{rr}$$

If the polymer chains obtained are the first-order Markovian, the dyad, triad, and tetrad intensities can be expressed by the following equations<sup>14</sup>.

$$\text{dyad:} \quad (m) = w/(u + w) \quad (r) = u/(u + w)$$

$$\text{triad:} \quad (mm) = (1 - u)w/(u + w)$$

$$(mr) = 2uw/(u + w)$$

$$(rr) = u(1 - w)/(u + w)$$

$$\text{tetrad:} \quad (mrm) = uw^2/(u + w) = (mr)^2/4(r)$$

$$(mrr) = 2uw(1 - w)/(u + w) =$$

$$(mr)(rr)/(r)$$

$$(rrr) = u(1 - w)^2/(u + w) = (rr)^2/(r)$$

The  $u$  and  $w$  values can be obtained from triad data by using the following equations.<sup>10</sup>

$$u = P_{mr} = \frac{(mr)}{2(mm) + (mr)}$$

$$w = P_{rm} = \frac{(mr)}{2(rr) + (mr)}$$

In Table V are shown the  $u$  and  $w$  values thus calculated from triad data of acetone-insoluble polymers and the calculated dyad, triad, and tetrad intensities with these  $u$  and  $w$  values. These calculated values in Table V are in agreement with experimental ones in Table IV. The propagation steps to yield the acetone-insoluble polymers

**Table V.** Stereoregularity of acetone-insoluble polymers calculated on the assumption of first-order Markovian process

Expt. No. <sup>a</sup>	$u$	$w$	Dyad		Triad			Tetrad		
			$m$	$r$	$mm$	$mr$	$rr$	$mrm$	$mrr$	$rrr$
3-2	0.25	0.18	42	58	31	21	48	2	17	39
4-2	0.22	0.18	45	55	35	20	45	2	16	37
5-2	0.16	0.16	50	50	42	16	42	1	13	33
6-2	0.19	0.14	42	58	34	16	50	1	14	43

<sup>a</sup> cf., Tables I, III, and IV.

**Table VI.** Penultimate and pen-penultimate effects in MMA polymerization to acetone-soluble polymers

No. <sup>a</sup>	Catalyst	Solvent	Penultimate effect					Pen-penultimate effect					$\rho$		
			$P_{mm}$	$P_{mr}$	$P_{rm}$	$P_{rr}$	$P_{rr}/P_{mr}$	$P_{mm}/P_{rm}$	$P_{rrr}$	$P_{rrm}$	$P_{mrm}$	$P_{mrr}$		$P_{rrr}/P_{mrr}$	$P_{mrm}/P_{rrm}$
R-1	AIBN	Toluene	0.29	0.71	0.20	0.80	1.1	1.5	0.81	0.19	0.17	0.83	0.98	0.89	1.01
R-2	LiEt	Toluene	0.84	0.16	0.48	0.52	3.3	1.8	0.54	0.46	0.83	0.17	3.2	1.8	1.44
1	Co-Et	—	0.11	0.89	0.21	0.79	0.89	0.52	0.83	0.17	0.34	0.66	1.3	2.0	0.91
2	Fe-Et	—	0.28	0.72	0.31	0.69	0.96	0.90	0.63	0.37	0.45	0.55	1.1	1.2	0.97
3-1	Fe-Et	Benzene	0.36	0.64	0.33	0.67	1.0	1.1	0.78	0.22	0.36	0.64	1.2	1.6	1.03
4-1	Fe-Et	Benzene	0.30	0.70	0.31	0.69	0.99	0.97	0.75	0.25	0.27	0.73	1.0	1.1	0.99
5-1	Fe-Et	Toluene	0.42	0.58	0.27	0.73	1.3	1.6	0.74	0.26	0.39	0.61	1.2	1.5	1.18
6-1	Fe-Et	THF	0.30	0.70	0.27	0.73	1.0	1.1	0.74	0.26	0.39	0.61	1.2	1.5	1.03
7	Fe-Et	CH <sub>3</sub> CN	0.21	0.79	0.25	0.75	0.95	0.84	0.74	0.26	0.37	0.63	1.2	1.4	0.96
8	Fe-Et	DMF	0.35	0.65	0.30	0.70	1.1	1.2	0.71	0.29	0.45	0.55	1.3	1.6	1.05
12	Fe-Me	—	0.21	0.79	0.25	0.73	0.95	0.84	0.67	0.33	0.42	0.58	1.2	1.3	0.96
13	Fe-Me	Toluene	0.14	0.86	0.24	0.76	0.88	0.58	0.75	0.25	0.42	0.58	1.3	1.7	0.91

<sup>a</sup> cf., Tables I and III.**Table VII.** Penultimate and pen-penultimate effects in MMA polymerization yielding acetone-insoluble polymers

No. <sup>a</sup>	Catalyst	Solvent	Penultimate effect		Pen-penultimate effect	
			$P_{rr}/P_{mr}$	$P_{mm}/P_{rm}$	$P_{rrr}/P_{mrr}$	$P_{mrm}/P_{rrm}$
3-2	Fe-Et	Benzene	3.4	4.0	1.0	1.0
4-2	Fe-Et	Benzene	3.7	4.3	1.2	1.5
5-2	Fe-Et	Toluene	5.3	5.3	0.90	0.57
6-2	Fe-Et	THF	4.5	5.8	1.2	2.1

<sup>a</sup> cf., Tables I, III, IV, and V.

thus obey the first-order Markov statistics. In Table IV are also included<sup>15</sup>  $\bar{n}$ , the number-average block sequence length, calculated as  $\bar{n} = 1/(mr)$  and  $\rho$ , the persistence ratio defined as  $\rho = 2(m)(r)/(mr) = 1/(P_{mr} + P_{rm})$ .

From the comparison of dyad, triad, and tetrad data, we can estimate the penultimate and pen-penultimate effects in propagation steps.  $P_{rrr}$ ,  $P_{mrr}$  and  $P_{mrm}$  ( $P_{mrr}$  means the probability of  $r$ -addition to an  $mr$ -growing chain) can be expressed by the following equations.

$$(rrr) = (rr) \times P_{rrr}$$

$$(mrr) = (mr)/2 \times P_{mrr} + (rr) \times P_{rrm}$$

$$(mrm) = (mr) \times P_{mrm}/2$$

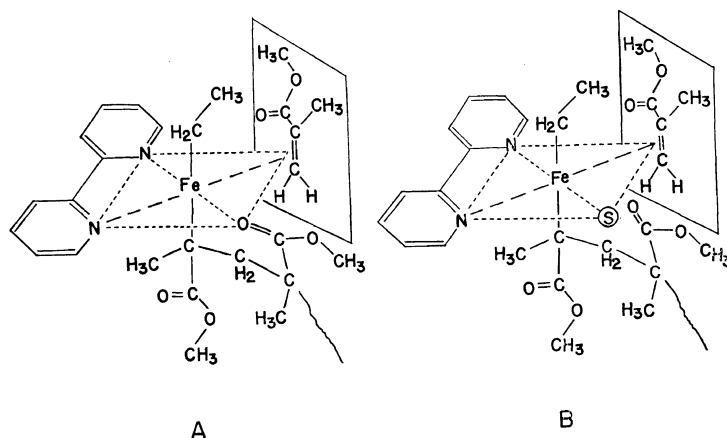
$$P_{rrr} + P_{rrm} = 1, P_{mrr} + P_{mrm} = 1$$

In Tables VI and VII are summarized the penultimate and pen-penultimate effects in the polymerization of methyl methacrylate to yield acetone-soluble and acetone-insoluble polymers.

The polymerization forming the acetone-soluble polymers showed neither penultimate nor pen-penultimate effects, whereas the polymerization forming the acetone-insoluble stereoblock polymers had significant penultimate effects and negligible pen-penultimate effects. For a more rigorous test of the penultimate effects the temperature dependence of tacticities should be checked<sup>13</sup>. However, because the present initiator systems are unstable at higher temperatures and polymerization activities at low temperatures are small, such testing was not feasible.

In the preceding communication<sup>4</sup> we proposed a coordinated anionic mechanism involving the partial dissociation of dipyrilidyl ligand from  $\text{FeR}_2(\text{dipy})_2$ , coordination of the monomer to the iron complex  $\text{FeR}_2(\text{dipy})$  and insertion of the monomer between the metal-alkyl bond. We have also observed that the coordinating ability of solvents with  $\text{NiR}_2(\text{dipy})$  is in the order  $\text{CH}_3\text{CN} >$





**Figure 10.** Possible models for propagating species in the polymerization of methyl methacrylate with  $\text{FeEt}_2(\text{dipy})_2$ .

A: in a solvent of weaker coordinating ability.

B: in a solvent of stronger coordinating ability.

DMF > acetone > MMA > THF > toluene > benzene > hexane<sup>16</sup>. The presence of the penultimate effect in the MMA polymerization by  $\text{FeEt}_2(\text{dipy})_2$  in benzene, toluene, and THF, *i.e.*, solvents of weaker coordinating ability, and the absence of the effect in solvents of stronger coordinating ability, DMF and acetonitrile, may be explained by the competitive coordination of the solvent and the penultimate ester group with a vacant coordination site of the iron complex. It may be premature to figure out the detailed propagation mechanism at the present stage, but the following propagation species appear to explain the experimental results. From a molecular model examination, the formation of a six-membered chelate ring involving the interaction of a carbonyl group of the penultimate unit with the iron atom as shown in Figure 10-A is feasible. Solvents of stronger coordinating ability, such as acetonitrile and DMF, may interfere with the chelate formation by displacing the ester group of the penultimate unit with the resultant coordination of the solvent molecule as shown in Figure 10-B. In this case, the penultimate effect is absent and the tacticity of the polymer will be determined mainly by the mutual steric and electronic interactions between the approaching monomer and the ester group of the chain end, thus giving syndio-rich polymers following the Bernoulli statistics. In bulk polymerization also

the acetone-soluble polymer is obtained and the monomer molecule appears to be playing a similar role as a polar solvent. However, the presence of two maxima in the molecular weight distribution curve for the bulk polymerization suggests a polymerization mechanism without solvent may not be a simple one. In solvents of weaker coordinating ability the chelate formation may be taking place, thus leaving free only one coordination site of the octahedral iron complex to be coordinated by a monomer molecule. The dipyriddy ligand, alkyl group, and the growing polymer chain may exert some stereochemical effect on the incoming MMA molecule. The exact configuration around the iron complex will not be discussed for the present. In Figure 10-A is depicted one model of several possible configurations. The configurational change around the iron complex with a possible participation of the solvent molecule results in the change of stereochemical effect on the approaching monomer. In a solvent of weaker coordinating ability, the solvent molecule may interact with the iron complex for only a short period, breaking the chelate and thus intercepting the foregoing configurational sequence. The life-time of the solvent-coordinated propagation species (Figure 10 B) may be short in less polar solvents and the chelate formation may be restored again. A repetition of the process may lead to a stereoblock polymer.

If this should be true, the relatively small values of the persistence ratios may be an indication that a frequent configurational change is taking place.

Recently the resolutions of a so-called stereoblock polymer into isotactic and syndiotactic polymers were reported<sup>17,18</sup> and the present stereoblock polymers obtained with  $\text{FeEt}_2(\text{dipy})_2$  were considered to be in fact the stereo-complex. However no separation was observed when our stereoblock polymers were eluted on a thin layer chromatograph of silica gel with acetone and ethyl acetate. These polymers are considered homogeneous as far as one can judge from a thin layer chromatographic technique recently developed by Inagaki and his co-workers<sup>18</sup>.

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