Rate Constants of the Tactic Monomer Addition in the Anionic Polymerization of Methyl Methacrylate in THF with Cesium as Counterion†

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ABSTRACT: Tacticity measurements of PMMA samples prepared anionically in THF with Cs^+ as counterion show that tactic monomer addition in this system does not obey Bernoullian statistics, the average sequence lengths being shorter than to be expected. It is shown that the Coleman–Fox model is not applicable; the results rather can be fitted by Markovian statistics. In conjunction with the overall rate constant known from kinetic measurements the rate constants for the four different ways of monomer addition are calculated, assuming a first-order Markov process. The Arrhenius plots of these constants show that syndiotactic addition is favored energetically but has to meet higher steric requirements regarding the transition state.

During the last 20 years a number of investigations have been published concerning the stereospecific polymerization of methyl methacrylate and possible mechanisms involved.[1] The aim was to elucidate a model suitable to account for the effects observed in different systems.

Concerning the anionic polymerization of methyl methacrylate two solvent systems must be clearly distinguished, i.e., polar and nonpolar ones. Polymerization in nonpolar solvents, such as toluene, is characterized by complex kinetics, the products showing broad molecular weight distributions and strong isotacticity. The tactic addition of the monomer does not obey Bernoullian statistics, the average sequence lengths being longer than to be expected according to Bernoullian statistics. This system has been investigated quite throughly regarding kinetics and tacticities, but owing to its complexity without final results.

Polymerization in polar solvents, such as THF or DME, is characterized by much simpler kinetics, narrow MWD's, and rather syndiotactic products.[2,3] The investigations published regarding tacticities mostly dealt with polymers prepared with Li^+ and Na^+ as counterions,[4–6] sometimes using strong solvating agents such as cryptands or crown ethers.[5,7] Tactic monomer addition in this system shows Bernoullian behavior, tacticities being quite similar to those of polymers produced by radical polymerization. Concerning polymers prepared with Cs^+ as counterion, the tacticity of only one sample of poly(ethyl methacrylate) has been reported,[8] showing a strong deviation from Bernoullian statistics, the average sequence lengths being shorter than to be expected. No attempt was made, however, to explain this behavior. Our results concerning the kinetics with Cs^+ as well as with Na^+ as counterions are published elsewhere;[2,3,9,10] some of the conclusions are given in the following discussion.

In this paper we want to report and discuss the results of tacticity measurements obtained with polymers which were produced under kinetically well-defined conditions in the system $PMMA^-Cs^+$/THF. Due to common ion salt addition, causing a suppression of free anions, all active centers were present in the form of ion pairs and no triple ion formation was possible.

Experimental Section

(a) Preparation of Polymers. Polymers were prepared in kinetic runs either in a flow tube reactor or in a stirred discontinuous tank reactor with an automatic sample outlet. Details concerning the techniques are given elsewhere.[3,11,12]

The initiator used was cumyl cesium. Cesium triphenylcyanoborate[13] was added as a common ion salt to suppress the dissociation into free anions. The purification of solvent and monomer, the preparation of the initiator, and the performance of the experiments have been reported earlier.[3,11]

The reaction obeys first order with respect to the monomer concentration, and the degree of polymerization is a linear function of conversion. The detailed kinetic results are given in ref 10.

The molecular weights of the polymers were measured by GPC using six Waters Styragel columns (5×10^6 Å; 6.5×10^4 Å; 1.5×10^4–5×10^4 Å; 5×10^3–1.5×10^4 Å; 2×10^3–5×10^3 Å; 7×10^2–2×10^3 Å). The apparatus was calibrated by means of fractionated anionic PMMA samples, which were characterized by ultracentrifugue, light scattering, and viscometry.

The molecular weight distributions of the polymers (by GPC) are very narrow; $\overline{M}_w/\overline{M}_n$ is between 1.01 and 1.1.

(b) Measurement of Tacticities. Tacticities were measured by the ^{1}H-NMR method established by Bovey.[14] The first series of measurements was performed by means of a 220-MHz Varian HR 220 spectrometer, the solvent was *o*-dichlorobenzene, and the temperature was 120 °C. For the second series a Bruker 90-MHz Fourier impulse spectrometer was used, the solvent was tetradeuterio-*p*-dibromobenzene, and the temperature was 130 °C. The spectra were accumulated ten times. The concentrations ranged from 5 to 10% (w/v).

The methyl proton peak areas (corresponding to triads) were analyzed by means of a Du Pont 320 curve resolver.

Results

The results of the tacticity measurements as well as the polymerization conditions are given in Table I. I, H, and S represent placement triads, p_i and p_s are placement dyads, and $\bar{l}_i$ and $\bar{l}_s$ are the average sequence lengths of isotactic or syndiotactic placements, given by

$$\bar{l}_i = 2p_i/H \tag{1a}$$

$$\bar{l}_s = 2p_s/H \tag{1b}$$

ρ is the persistence ratio defined by

$$\rho = 2p_ip_s/H \tag{2}$$

giving the average sequence lengths relative to the sequence lengths to be expected according to Bernoullian statistics.

In Figure 1 the results are plotted within a ternary diagram;[15] the loci of equal persistence ratio are represented by single lines, thus directly showing deviations from Bernoullian statistics.

The results can be summarized as follows: (a) syndiotacticity and the average sequence length of syndiotactic placements decrease with increasing temperature; (b) tacticities are independent of monomer and living end concentrations, conversion, and molecular weight within the limits of experimental error; (c) Bernoullian statistics are not fulfilled, the average sequence lengths are shorter than to be expected ($\rho \approx 0.85$)

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† Dedicated to Professor M. L. Huggins on the occasion of his 80th birthday.

Table I
Conditions and Degrees of Polymerization,[a] Tacticities, Average Sequence Lengths, and Persistence Ratios for PMMA Samples Prepared Anionically in THF (Initiator = cumyl cesium)

Sample No.	T, °C	$[M]_0$, mol/L	10^3c^*, mol/L	x_p	P_{max}	I	H	S	p_i	p_s	$\bar{l}_i$	$\bar{l}_s$	ρ
85/1B	+20	0.25	0.20	0.19	238	0.10	0.555	0.345	0.38	0.62	1.36	2.24	0.85
81/1B	+3	0.26	0.36	0.40	285	0.065	0.57	0.365	0.35	0.65	1.23	2.28	0.80
72/2B	−9	0.34	1.08	0.80	250	0.075	0.525	0.40	0.34	0.66	1.29	2.52	0.85
73/2B	−11	0.19	0.61	0.70	217	0.08	0.52	0.40	0.34	0.66	1.31	2.54	0.86
71/4B	−13	0.50	0.61	0.57	463	0.075	0.515	0.42	0.325	0.675	1.29	2.63	0.87
51/1B	−53	0.49	1.23	0.74	293	0.053	0.524	0.423	0.315	0.685	1.20	2.61	0.82
30/5B	−54	0.50	0.38	0.19	254	0.035	0.475	0.49	0.27	0.73	1.15	3.06	0.83
30/5R	−54	0.50	0.38	1.00	1290	0.055	0.503	0.442	0.31	0.69	1.22	2.76	0.85
50/5B	−66	0.49	0.45	0.22	244	0.05	0.53	0.42	0.315	0.685	1.19	2.58	0.81
50/5R	−66	0.49	0.45	1.00	983	0.04	0.535	0.425	0.31	0.69	1.15	2.59	0.80
130/6	−80	0.23	0.72	1.00	310	0.005	0.52	0.475	0.265	0.735	1.02	2.83	0.75
132/6	−97	0.18	0.53	1.00	306	0	0.435	0.565	0.22	0.78	1.0	3.6	0.78
127/2	−100	0.23	0.08	0.08	225	0	0.40	0.60	0.20	0.80	1.0	4.0	0.80
127/7	−100	0.23	0.08	0.93	2550	0.005	0.43	0.565	0.22	0.78	1.02	3.6	0.80
PEMA[b]	−78	0.75	21	1?		0.05	0.47	0.48	0.28	0.72	1.2	3.0	0.84

[a] $[M]_0$ = initial monomer concentration, c^* = concentration of active centers, x_p = conversion, P_{max} = degree of polymerization corresponding to the maximum of the GPC eluogram. For other symbols see text. [b] PEMA = poly(ethyl methacrylate). Values from ref 8; initiator = fluorenyl cesium.

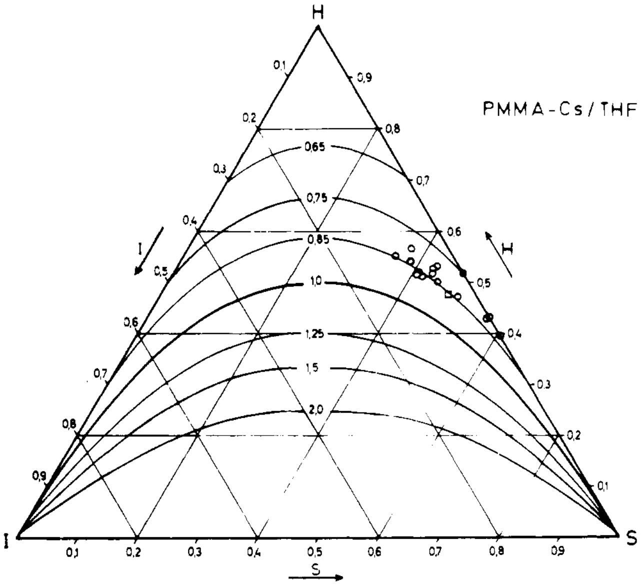


Figure 1. Tacticity diagram of the PMMA samples from Table I (○). (□) Poly(ethyl methacrylate). Loci of equal persistence ratio are represented by curved lines (ρ = 1: Bernoullian statistics).

Discussion

Non-Bernoullian behavior in general can be explained by two different models, namely by the Coleman–Fox mechanism or by Markovian statistics.

The model proposed by Coleman and Fox[16,17] implies that the active center exists in two different states which are in a dynamic equilibrium, both being able to add the monomer, however, with different tacticity. In the present case, these species could be the contact ion pair and the solvent separated ion pair (due to common ion salt addition there are no free anions in the system). The results of the kinetic experiments,[10] however, did not render any evidence for the existence of two differently active species in the anionic polymerization of MMA in THF with Cs^+ as counterion as well as with Na^+.[10a]

For both counterions we find the same *linear* Arrhenius plot in the temperature range from +20 to −100 °C. This fact is in strong contrast to the case of styrene[18] where curved Arrhenius plots were observed, the rate constant for PS–Na being higher than that of PS–Cs by a factor of about 500 at −78 °C.

From these results we conclude that the propagating species in MMA polymerization has the same structure for both counterions. As it is very improbable from spectroscopic and conducitivity data that ion pairs containing Na^+ or Cs^+ are in the same solvation state (contact ion pair or solvent separated ion pair) the results can best be explained under the assumption that the counterion is not solvated by THF molecules but by the ester groups of the chain. In this concept, the active center (with both counterions) is a contact ion pair solvated by the penultimate or antepenultimate ester group of its own polymer chain. The remaining coordination sites of the counterion may be occupied by THF molecules. A similar model was proposed by Bovey et al.[8] for the system PMMA–Li/THF from NMR data and by Sigwalt et al.[19] for the system poly(2-vinylpyridyl)–Na/THF from kinetic and conductivity data.

In addition, the Coleman–Fox mechanism predicts that the average sequence lengths decrease with decreasing monomer concentration (or increasing conversion); when the monomer concentration approaches zero Bernoulian statistics should be fulfilled. These requiriments are not matched by our results (cf. Table I) as well as by the results of Amerik et al.[4] using Li^+ as counterion.

Thus the Coleman–Fox mechanism can be excluded for the system with a high degree of probability.

We assume therefore that the tactic monomer addition is governed by Markovian statistics. Since the resolution of the spectrometers used did not allow us to determine placement pentads the results can only be fitted by first order Markovian statistics. Defining, e.g., p_{is} as the conditional probability that an isotactic placement is followed by an syndiotactic placement, the triad probabilities result as follows:

$$I = p_i \cdot p_{ii} \tag{3a}$$

$$H = p_i \cdot p_{is} + p_s \cdot p_{si} \tag{3b}$$

$$S = p_s \cdot p_{ss} \tag{3c}$$

with

$$p_{ii} + p_{is} = 1 \tag{4a}$$

$$p_{ss} + p_{si} = 1 \tag{4b}$$

Table II
Conditional Probabilities and Single Rate Constants for the Different Kinds of Monomer Addition to Ion Pairs of PMMA–Cs Assuming First-Order Markov Statistics

Sample No.	T, °C	p_{ii}	p_{is}	p_{ss}	p_{si}	$\bar{k}_p$[a]	k_{ii}	k_{is}	k_{ss}	k_{si}
85/1B	+20	0.26	0.74	0.55	0.45	10000	2600	7400	5500	4500
81/1B	+3	0.19	0.81	0.56	0.44	6000	1140	4860	3360	2640
72/2B	−9	0.22	0.78	0.60	0.40	3900	860	3040	2340	1560
73/2B	−11	0.24	0.76	0.61	0.39	3700	890	2810	2260	1440
71/4B	−13	0.23	0.77	0.62	0.38	3500	810	2700	2170	1330
51/1B	−53	0.17	0.83	0.62	0.38	610	104	506	378	230
30/5B	−54	0.13	0.87	0.67	0.33	580	75	505	390	190
30/5R	−54	0.18	0.82	0.64	0.36	580	104	476	371	209
50/5B	−66	0.16	0.84	0.61	0.39	300	48	252	183	117
50/5R	−66	0.13	0.87	0.61	0.39	300	39	261	183	117
130/6	−80	0.02	0.98	0.65	0.35	125	3	122	81	44
132/6	−97	0	1.0	0.72	0.28	36	0	36	26	10
127/2	−100	0	1.0	0.75	0.25	29	0	29	22	7.3
127/7	−100	0.02	0.98	0.72	0.28	29	1	28.5	21	8.1

[a] Taken from the Arrhenius equation $\log \bar{k}_p/\mathrm{L\ mol^{-1}\ s^{-1}} = 7.66 - (4900\ \mathrm{cal\ mol^{-1}}/2.303\,RT)$ (see ref 10d).

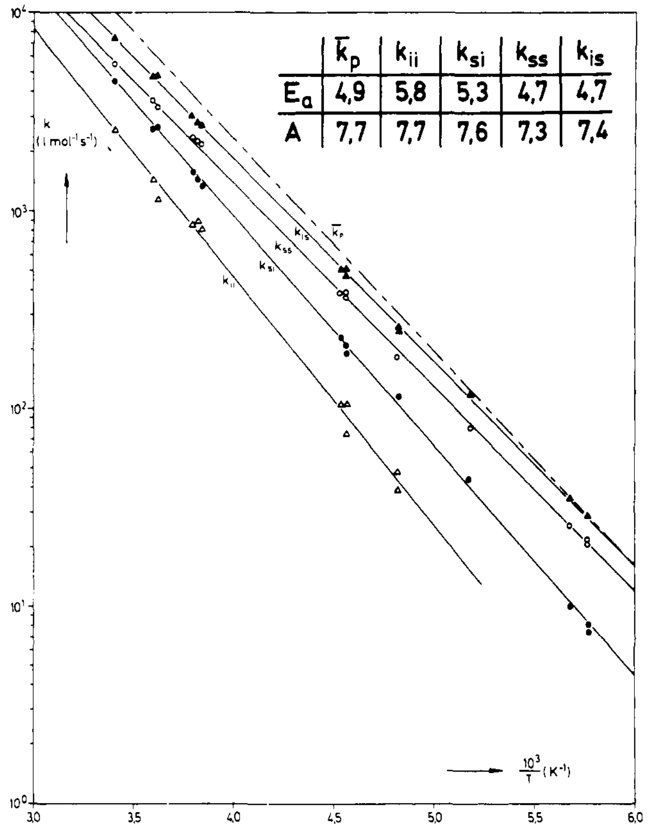


Figure 2. Arrhenius plot of the single rate constants for the different kinds of monomer addition to ion pairs of PMMA–Cs.

From stationarity considerations it follows:

$$p_s \cdot p_{si} = p_i \cdot p_{is} = H/2 \tag{5}$$

Hence the four placement probabilities can be calculated from the following set of equations

$$p_{ii} = I/p_i \tag{6a}$$

$$p_{is} = H/2p_i \tag{6b}$$

$$p_{si} = H/2p_s \tag{6c}$$

$$p_{ss} = S/p_s \tag{6d}$$

The related rate constants for the different addition reactions result from the differential equation of monomer consumption:

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = \bar{k}_p c^*[\mathrm{M}] = (k_{ii}c_i + k_{is}c_i + k_{si}c_s + k_{ss}c_s)[\mathrm{M}] \tag{7}$$

$$1 = \frac{k_{ii}}{\bar{k}_p}\frac{c_i}{c^*} + \frac{k_{is}}{\bar{k}_p}\frac{c_i}{c^*}\mathrm{r} + \frac{k_{si}}{\bar{k}_p}\frac{c_s}{c^*} + \frac{k_{ss}}{\bar{k}_p}\frac{c_s}{c^*} \tag{8}$$

$$1 = p_{ii} \cdot p_i + p_{is} \cdot p_i + p_{si} \cdot p_s + p_{ss} \cdot p_s \tag{9}$$

$$1 = I + H + S \tag{10}$$

with $c^* = c_i + c_s$. $\bar{k}_p$ = overall rate constant for propagation, and, e.g., k_{is} = rate constant for syndiotactic addition to an isotactic chain end.

From eq 4, 8, and 9 it follows:

$$k_{ii} = p_{ii} \cdot \bar{k}_p \text{ etc.} \tag{11}$$

As the overall rate constant is known from kinetics,[10] it is possible to calculate the individual rate constants. The placement probabilities and the individual rate constants for the samples investigated are given in Table II. Figure 2 shows an Arrhenius plot of the rate constants together with the resulting activation energies and frequency exponents.

From the Arrhenius parameters it follows that syndiotactic addition is favored energetically, whereas isotactic addition shows a dependence on the preceding placement, i.e., a change of configuration is favored over its retention. This shows up in the small average sequence lengths of isotactic placements $\bar{l}_i$ (cf. Table I). The relatively small values of the frequency exponents A_{ss} and A_{is} indicate that the syndiotactic addition has to meet higher steric requirements regarding the transition state.

Assuming that with Cs+ as well as with Na+ as counterion the same general kind of active center is the propagating one, the question arises why different statistics are observed concerning the tacticity. In the case of Na+ as counterion using *monofunctional initiators Bernoullian statistics were observed*.[5,10a]

With bifunctional initiators intramolecular association of the chain ends occurs leading to different tacticities.[9] This association has not yet been observed using monofunctional initiators, because the concentrations of living ends are too small ($10^{-4} \leq c^* \leq 10^{-3}$ mol/L). Tacticities of bifunctionally initiated polymers therefore cannot be considered within this frame.

The different statistics observed with Na+ and Cs+ as

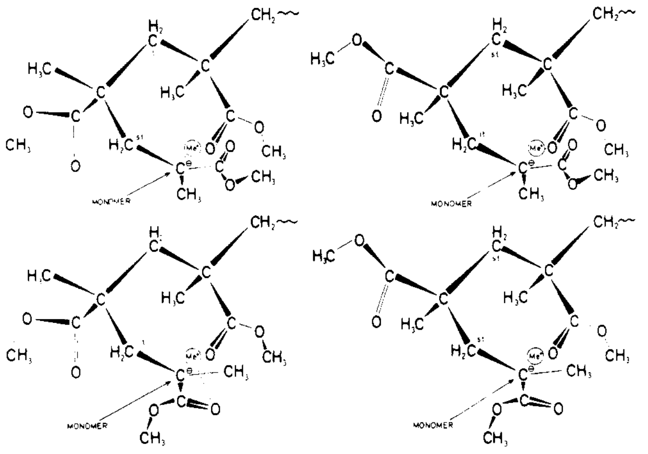
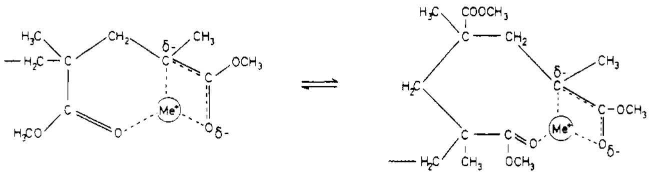


Figure 3. Possibilities of tactic monomer addition resulting from the combination of isotactic and syndiotactic conformation of the chain end and configuration of the penultimate placement in the case of solvation by the antepenultimate ester group of the chain.

counterions may be explained under the assumption of two different cyclic complexes as propagating species, which may be in equilibrium, i.e., in complex I the counterion is solvated by the penultimate and in complex II by the antepenultimate ester group of the chain:



I II

The relative amount of species I and II which are considered to propagate with the same rate constant should depend on the size of the cation; there might be an influence on the rate of exchange between these species, too, caused by a different degree of external solvation by THF molecules.

Markovian statistics are to be expected when the counterion is solvated by the antepenultimate ester group and when the rate of exchange is slow compared with the rate of propagation. In this case, regarding the configuration of the cyclic structure, it means a difference whether the configuration of the penultimate or the antepenultimate monomer unit is syndio- or isotactic, because the spacial requirements of the methyl group and the ester group are different.

The cyclic complexes corresponding to the four placement combinations are shown in Figure 3.

When the counterion is solvated by the penultimate ester group the kind of linkage between the penultimate and antepenultimate ester group is of far less importance, because the latter is placed outside the cyclic complex. Thus Bernoullian statistics are favored. Bernoullian statistics should apply as well when the rate of the exchange reaction is greater than the rate of propagation.

To decide which influence is dominant, information gathered from the kinetics of the termination reactions is useful. As termination by the reaction of the carbanion with the antepenultimate ester carbonyl group under formation of a cyclic β-ketoester ("intramolecular polymer termination")[10c,20] is greatly facilitated by the cyclic complex II, the dependence of the rate of this termination reaction on the counterion could possibly give information about the relative amount of this complex, although one has to consider that the different cation size in complex II has an influence on the rate constant of termination, too.

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