Dependence of the Propagation Rate Constants on the Degree of Polymerization in the Initial Stage of the Anionic Polymerization of Methyl Methacrylate in Tetrahydrofuran†

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ABSTRACT: Oligomers of methyl methacrylate (MMA) were prepared in a flow-tube reactor using metalloesters as initiators in THF at −46 °C. No side products were formed. The rate constants for the formation of the individual i-mers, k_{i-1}, were calculated by integrating the corresponding differential equations and using optimization procedures to give a best fit to the experimentally determined conversion and molecular weight distribution (MWD). For Li^+ as the counterion, k_1 is larger than the rate constant for polymerization, k_p, where k_2, k_3, and k_4 are smaller than k_p. This can be explained in terms of interaction of the penultimate ester group in the polymer chain with the counterion ("intramolecular solvation") or in terms of association of ion pairs. For Na^+ as the counterion, the dependence of k_i on i is less pronounced, except for k_2 being larger than k_p. However, a strong dependence of k_p on the concentration of living ends is observed, indicating the coexistence of associated and nonassociated ion pairs. The equilibrium constant for association is estimated.

Introduction

Polymers having a narrow molecular weight distribution (MWD)—in the limiting case of the Poisson type—are formed under the following four conditions:

1. The process is free of termination and transfer reactions. Whereas this holds true for the anionic polymerization of hydrocarbon monomers[1] and some methacrylic esters,[2] the conditions is not fulfilled for methyl methacrylate (MMA), especially at temperatures above −75 °C. Several types of termination reactions have been discussed.[3,4] It will be shown below that the use of metalloesters as initiators in polar solvents, e.g., tetrahydrofuran (THF), virtually can overcome termination, as was proposed recently.[4]

2. Only one type of propagating species exists or the rate of interconversion of different species is much faster than the rate of polymerization. This condition holds true for the polymerization of hydrocarbon monomers in hydrocarbon solvents[1a,c] and of polar monomers in polar solvents in the presence of a common-ion salt.[5] In the case of styrene in polar solvents, the coexistence of three species (contact and solvent-separated ion pairs and free anions) was shown[6] and the effect on the MWD was calculated.[7] For the polymerization of alkyl methacrylates various coexisting species have been proposed, including ion-pair associates.[8,9,29]

3. The rate of initiation is higher or equal to the rate of propagation. This condition holds true for a great number of initiators. It is perfectly fulfilled, when a model of the end group of the living polymer is used as the initiator, e.g., metalloesters for the initiation of MMA,[10] given that condition 4 holds true.

4. The rate constant of propagation k_p is independent of the degree of polymerization. This is generally assumed to hold true for higher degrees of polymerization i. The dependence of the individual rate constants k_i on i is of special interest in the interpretation of penultimate effects in the anionic copolymerization.[11] The rather short terminal sequences of monomers A and B in the living copolymer can be considered to behave simularly to living oligomers. Thus, nonequal homopropagation constants have to be taken into account (e.g., $k_{ABB} \neq k_{BBB}$; corresponding to $k_1 \neq k_2$ in our nomenclature) and may be calculated on the basis of the results given below.

Based on kinetic experiments, first estimations of individual rate constants were published by Lee et al. on 2-vinylpyridine[11] and by Zilkha et al. on methacrylonitrile[12] and MMA.[13] In the present work we used a combination of kinetics and of the analysis of the MWD of the oligomers produced in the initial stage of the polymerization, in order to elucidate the individual k_i values in the system MMA/THF/Li^+ or Na^+, respectively.

The dependence of k_i on i is difficult to predict in this system, because steric, inductive, as well as ion-pairing and association effects may contribute to the reactivity of the oligomers. The greatest difference is to be expected between the first and the second addition step, because the first step introduces a penultimate ester group. Beside steric constaints, this group may exert a negative inductive effect. Moreover, interaction with the counterion becomes possible. This interaction, often called "intramolecular solvation", has been proposed by several authors on the basis of kinetic,[14] tacticity,[15] and spectroscopic[16] measurements. More recent kinetic experiments[17,18] as well as ^{13}C NMR[19] and conductivity[20] measurements did not corroborate this, especially in polar solvents. Bernoullian statistics in the tacticities of the polymers prepared with certain counterions and solvents[17,18] further seem to contradict intramolecular solvation.

Additionally, the order and/or the degree of intermolecular association of ion pairs may be dependent on the degree of polymerization, given the existence of associates is possible under the conditions used. The aim of this work therefore was to determine the k_i values of the living oligomers of MMA. It was of additional interest to estimate the degree of polymerization, beyond which k_i becomes independent of i. In order to avoid initiation effects which complicate the system when hydrocarbon initiators are used,[4,21] methyl α-lithio- and methyl α-sodioisobutyrate (MIB-Li and MIB-Na, cf. Scheme I) were employed, which model the end group of the living polymers.[10] Thus, only the propagation reaction (starting from $i = 1$) has to be considered.

Formal Relations and Mathematical Procedure

The differential equations for the formation and disappearance of the living i-mers P^*_1, P^*_2, ..., P^*_i, as well as for the consumption of monomer, are given in the following:

† Dedicated to Prof. B. L. Erussalimsky on the occasion of his 70th birthday.

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$$d[P^*_1]/dt = -k_1[M][P^*_1] \quad (1a)$$

$$d[P^*_2]/dt = [M](k_1[P^*_1] - k_2[P^*_2]) \quad (1b)$$

$$\vdots$$

$$d[P^*_i]/dt = [M](k_{i-1}[P^*_{i-1}] - k_i[P^*_i]) \quad (1c)$$

$$d[M]/dt = -[M]\sum_{i=1}^{\infty} k_i[P^*_i] \quad (2)$$

For this scheme it is presumed that condition 2 is fulfilled; i.e., there is only one type of propagating species. For coexisting active species (i.e., ion pairs and associates), the k_i are to be regarded as averaged rate constants (cf. eq 17 and 18).

For given rate constants k_i these equations are integrated numerically by using the Runge–Kutta method,[22] resulting in the molar concentrations of all i-mers and of the monomer at time t.

The relative weight concentration of the living i-mer P^*_i is given by

$$\{P^*_i\} = i[P^*_i] \quad (3)$$

The weight fraction (corresponding to the MWD) thus is

$$w(i) = \{P^*_i\}/\sum_{i=1}^{\infty}\{P^*_i\} \quad (4)$$

The calculated MWD and monomer conversion are compared with the experimentally determined values and the sum of squared differences is calculated.

In order to obtain the best set of rate constants, all k_i values first are assumed to be equal to the average rate constant of polymerization, $\bar{k}_p$ (cf. eq 9). Now, k_1–k_4 as well as k_p are varied in an iterative procedure by using Marquardt's optimization algorithm[23] until the best fit of calculated and experimental data is obtained for all conversions (cf. Figures 3b and 5b). To ensure that the solution is unique (problem of "false minima"), different initial values for k_i were tested, too. They all led to the same results. The errors of the method (cf. Figure 4) are mainly given by uncertainties in the determination of $w(i)$.

From the experimentally determined MWD, two different number averages of the degree of polymerization were calculated:

$$\bar{P}_n^{(1)} = \sum_{i=1}^{\infty} w(i)/\sum_{i=1}^{\infty} w(i)/i \quad (5a)$$

$$\bar{P}_n^{(2)} = \sum_{i=2}^{\infty} w(i)/\sum_{i=2}^{\infty} w(i)/i \quad (5b)$$

The former includes the initiator ($i = 1$); the latter only counts the oligomers formed ($i \geq 2$). Subsequently, from $\bar{P}_n$ and the conversion of monomer

$$x_p = ([M]_0 - [M]_t)/[M]_0 \quad (6)$$

two different concentrations can be calculated:

$$[I]_{eff} = [M]_0 x_p/(\bar{P}_n^{(1)} - 1) \quad (7a)$$

$$c^* = [M]_0 x_p/(\bar{P}_n^{(2)} - 1) \quad (7b)$$

$[I]_{eff}$ is the effective initiator concentration; its difference from the initial concentration $[I]_0$ is equal to the amount of side products formed. c^* is the concentration of living oligomers formed by addition of monomer to the initiator:

$$c^* = \sum_{i=2}^{\infty}[P^*_i] \quad (8)$$

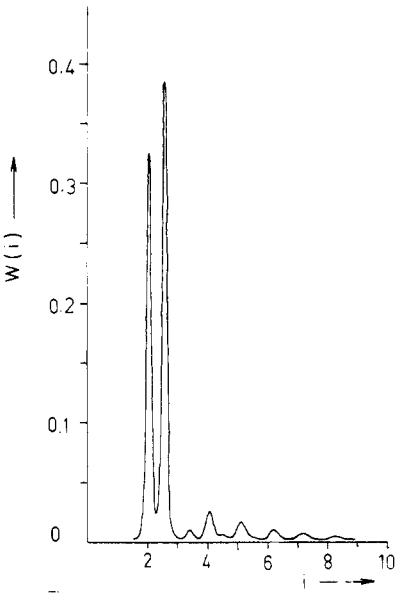


Figure 1. MWD of an oligo-MMA prepared by condensation of monomer (high-vacuum technique) using MIB-Li as the initiator in THF at −78 °C. The peak at $i = 2.5$ corresponds to cyclic trimer.

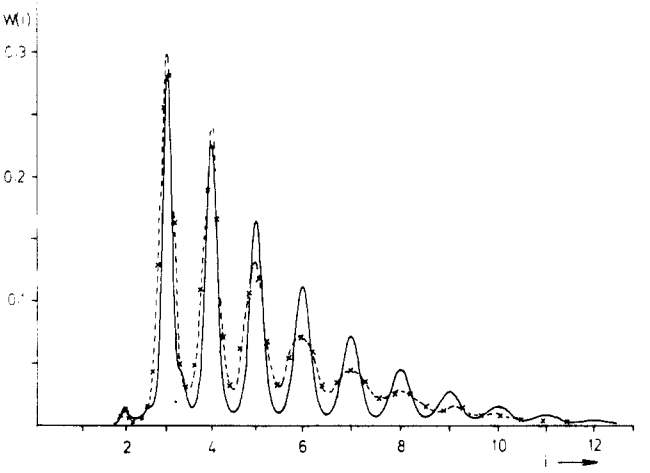


Figure 2. MWD of an oligo-MMA prepared in the flow-tube reactor using MIB-Li as the initiator in THF at −46 °C: (—) RI detector; (--×--) ^3H activity of fractions taken every 0.5 mL (cf. text).

The "averaged" rate constant $\bar{k}_p$ follows from integration of eq 2, assuming $k_1 = k_2 = \ldots = k_p \equiv \bar{k}_p$:

$$\ln([M]_0/[M]_t) = \bar{k}_p c^* t \quad (9)$$

With this assumption, Poisson distributions are calculated; they are compared to the experimental MWD's in Figures 3a and 5a.

Polymerization Technique

Two different techniques were used: (1) slow condensation of monomer to a stirred solution of "initiator" under high vacuum at −78 °C ($t \approx 1$ h) and (2) mixing of initiator and monomer solutions in a jet-type mixing chamber, followed by a short reaction in a flow-tube reactor at −46 °C ($t \leq 0.6$ s) and termination in a quenching jet.[24]

Figures 1 and 2 show the different MWD's resulting from the two methods. The condensation technique (Figure 1) mainly produces living dimer and cyclic trimer (viz., peak at $i = 2.5$), which was confirmed to be the product of an attack of the anion of the living trimer onto the antepenultimate ester group, resulting in a cyclic β-keto ester and methoxide.[10] Although the polymerization tem-

Table I
Experimental Conditions and Results for the Anionic Oligomerization of MMA in THF at −46 °C Using Methyl α-Lithioisobutyrate as the Initiator

run no.	$[M]_0$[a]/(mol/L)	$10^3[I]_0$[b]/(mol/L)	t[c]/s	x_p[d]	$10^3[I]_{eff}$[e]/(mol/L)	10^3c^*[f]/(mol/L)	$\bar{k}_p$[g]	k_1[h]	k_2[h]	k_3[h]	k_4[h]	k_p[i]
RL 22/23	0.117	35.7	0.22	0.23	23.7	18.1	55	60	32	27	40	60
			0.42	0.38	31.8	27.2	55	60	32	27	40	60
RL 24-26	0.118	12.4	0.42	0.23	12.4	12.4	58	110	32	40	50	70
			0.28	0.20	12.8	12.8	58	110	32	40	50	70
			0.21	0.14	11.4	10.0	58	110	32	40	50	70
RL 27-29	0.49	3.36	0.20	0.04	3.0	3.0	70					70
			0.29	0.05	2.9	2.9	70					70
			0.44	0.08	4.0	4.0	70					70
ref 18[j]	0.29	0.9			0.78	0.78	70					70

[a] Initial concentration of monomer. [b] Initial concentration of initiator. [c] Reaction time. [d] Monomer conversion. [e] Effective concentration of initiator (cf. eq 7a). [f] Concentration of oligomers formed (eq 7b). [g] "Averaged" propagation rate constant. [h] Individual rate constant in L/(mol·s). [i] Rate constant for higher degrees of polymerization in L/(mol·s). [j] Initiator: (diphenylmethyl)lithium; 10^{-3} mol/L $LiBPh_4$ added.

Table II
Experimental Conditions and Results for the Anionic Oligomerization of MMA in THF at −46 °C Using Methyl α-Sodioisobutyrate as the Initiator

run no.	$[M]_0$/(mol/L)	$[I]_0$/(mol/L)	$[NaBPh_4]$/(mol/L)	t/s	x_p	$10^3[I]_{eff}$/(mol/L)	10^3c^*/(mol/L)	$\bar{k}_p$	k_1	k_2	k_p
RN 21/23	0.058	25.8		0.21	0.46	25.8	13.5	140	110	310	100
				0.45	0.79	25.8	20.8	140	110	310	100
RN 22/24	0.058	25.8	1.35	0.22	0.48	25.8	14.7	140	110	310	100
				0.45	0.82	25.8	20.0	140	110	310	100
RN 25	0.059	9.75	3.2	0.35	0.69	10.0	10.0	270	330	500	235
RN 27/28	0.265	9.1		0.22	0.45	12.0	12.0	210			210
				0.40	0.62	12.0	12.0	210			210
RN 29/30	0.255	4.8		0.57	0.67	6.0	6.0	260			260
				0.21	0.25	6.0	6.0	260			260
RN 31	0.47	1.65		0.19	0.12	1.7	1.7	400			400
ref 25[a]	0.24	0.5	1.0			0.4	0.4	500			500

[a] Initiator: benzyloligo(α-methylstyryl)sodium.

perature was 30 K higher than in the former experiment, only linear oligomers are formed in the flow-tube reactor. As the polymerization was terminated with tritiated acetic acid (CH_3COOT), scintillation measurements on the GPC fractions prove that these oligomers had been living up to the time of quenching. [Cf. Figure 2. The low content of dimer is due to the workup procedure (removal of solvent and monomer under high vacuum). For the kinetic calculations, the content of dimer and trimer was calculated from GC measurements. The relative broadness of the scintillation "peaks" is due to the finite volume of the fractions samples in a semipreparative run. The relative areas of the corresponding RI and scintillation peaks equal each other, however.] This result is easily understood on the basis of two competing reactions of the living trimer:

$$P^*_3 + M \xrightarrow{k_3} P^*_4 \qquad \text{(propagation)}$$

$$P^*_3 \xrightarrow{k_c} P^c_3 + CH_3OMt \qquad \text{(cyclization)}$$

P^*_3 and P^*_4 represent living trimer (tetramer), P^c_3 represents cyclic trimer, and Mt represents metal ion.

It is easily shown that the relative amount of cyclic trimer is inversely proportional to the monomer concentration [M]:

$$\frac{[P^c_3]}{[P^*_4]} = \frac{k_c}{k_3}\frac{1}{[M]} \tag{10}$$

As [M] → 0 in the condensation technique, mainly cyclic trimer is produced. Thus, in further experiments, only the flow-tube technique was used.

In a recent publication, we concluded that a termination reaction different from cyclization occurs when hydrocarbon initiators are used,[4] this being due to a side reaction between the initiator and the monomer leading to a deactivating species. It was proposed that the use of initiators of lower reactivity would eliminate this side reaction. The present results confirm this prediction.

Results and Discussion

The experimental results as well as the calculated rate constants k_i and k_p are given in Table I for Li^+ and in Table II for Na^+ as the counterion. In the bottom line, experimental conditions and propagation rate constants of the corresponding polymerization experiments are given. These experiments were conducted in a stirred tank reactor using hydrocarbon initiators.[18,25] The difference in the behavior of the two counterions is remarkable, both quantitatively and qualitatively.

In all experiments, the efficiency of the initiators is very high, as can be seen by comparing $[I]_0$ and $[I]_{eff}$. This indicates that almost no side products are formed. In some experiments, the concentration of living oligomers c^* is lower than $[I]_{eff}$, reflecting the fact that initiation was not completed at the time of quenching.

Whereas $\bar{k}_p$ is the "averaged" rate constant (cf. eq 9), k_p is the result of the optimization procedure:

$$k_p = \lim_{i\to\infty} k_i \tag{11}$$

When no values of k_i are given, the degrees of polymerization of the oligomers were too high to allow for the calculation of individual rate constants. In these cases, k_p was assumed to be equal to $\bar{k}_p$.

Lithium Counterion. Figure 3 shows the experimental and calculated MWD's for two different monomer conversions. A Poisson distribution (Figure 3a,c) obviously does not fit the data. The results of the optimization

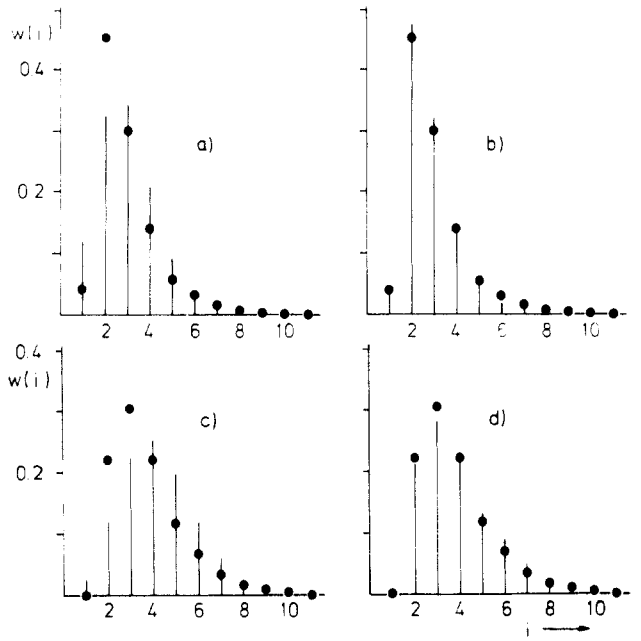


Figure 3. Experimental (●) and calculated (—) MWD for the anionic oligomerization of MMA using MIB-Li as the initiator in THF at −46 °C: (a, c) $k_1 = k_2 = ... = k_p = 58$ L/(mol·s); (b, d) $k_1 = 110$, $k_2 = 32$, $k_3 = 40$, $k_4 = 50$, $k_5 = k_6 = ... = k_p = 70$ L/(mol·s); (a, b) monomer conversion $x_p = 14\%$ (run RL 26); (c, d) $x_p = 23\%$ (run RL 24).

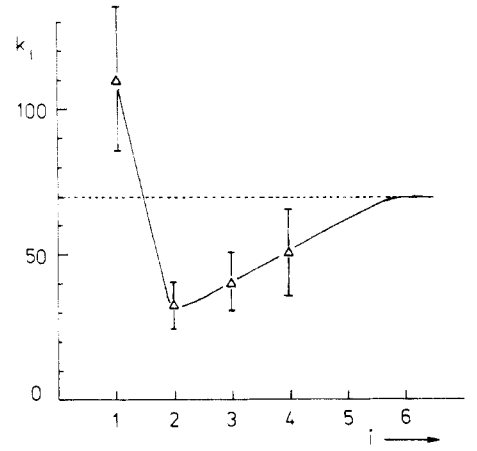


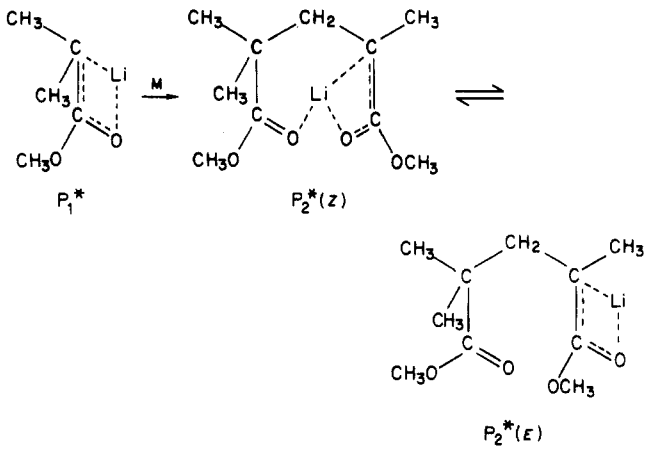
Figure 4. Dependence of the propagation rate constant k_i on the degree of polymerization i in the anionic oligomerization of MMA using MIB-Li as the initiator.

procedure are given in Figures 3b,d and 4. They show that k_i is highly dependent on the degree of polymerization i, k_1 being higher than k_p, whereas k_2, k_3, and k_4 are lower. For $i \geq 5$, k_i is not distinguishable from k_p, which in turn is identical with the value given by Jeuck and Müller.[18]

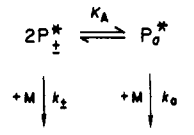
This dependence may have several causes: (a) steric effects (the addition of the monomer may be sterically hindered by the preceding monomer units in the chain), (b) inductive effects (a penultimate ester group may decrease the charge at the anion or ion pair and thus the reactivity of the living end), and (c) structural changes of the living end with chain length, especially solvation and association effects. "Intramolecular solvation" of the counterion by the penultimate ester group is only possible for $i \geq 2$ (see Scheme I).

This interaction may occur with the antepenultimate unit, i.e., for $i \geq 3$, also. Although the interaction of ester groups with the counterion was proposed by some authors,[14-16] this was not corroborated by all experiments cited in the Introduction. However, this model also can

Scheme I



Scheme II



explain the increase from k_2 to k_p from entropic causes: the formation of an intramolecular solvation complex is increasingly hindered by the motions of the preceding monomer units. The same trend was observed in the rate of cyclization, which drastically decreases from the trimer to the higher oligomers.[16,21]

On the other hand, it is known from vapor pressure measurements that MIB-Li is associated in THF.[29] Thus, the dependence of k_i on i could be due to changes of the degree of association with i or to changes in the reactivity of the associated species with i. In contrast to sodium counterion (cf. below) our kinetic results, however, do not show a pronounced effect of initiator concentration on k_p, indicating either the nonexistence of associates or a very high association constant, i.e., the sole existence of associates as active species. In the latter case, the different k_i values could be explained by changes in the reactivity of the associates with i. However, the minimum at $i = 2$ is hard to understand by using this model. We therefore believe that "intramolecular solvation" is the most probable explanation for the effects observed.

High ratios of k_1/k_2 were also found in the oligomerization of 2-vinylpyridine (2VP) initiated by polystyrylsodium in THF[11] ($k_1/k_2 = 4.3$). The formation of intramolecular complexes of poly(2VP) ion pairs in THF has been discussed by many authors[26] because of the higher solvating power of the pyridyl nitrogen as compared to the ester group. Results of Freireich and Zilkha[13] even indicate $k_1/k_2 = 5$ for the oligomerization of MMA initiated with CH_3ONa in methanol at +78 °C. However, the system used is not quite comparable to the present one and the method of calculation is not unambiguous.

Sodium Counterion. In contrast to Li^+ as the counterion, the dependence of k_i on i for Na^+ is less marked, except that $k_2 > k_p$ (cf. Table II and Figure 5). A tentative explanation for this is given farther below.

A very distinct dependence of k_p on the initiator concentration is observed, however, which is not influenced by the addition of common ion salt (cf. runs RN 21 and 23 vs. RN 22 and 24).

Thus, dissociation as well as triple-ion formation cannot explain this result. Association of ion pairs offers the most reasonable explanation. Taking into account dimeric associates only, Scheme II results.

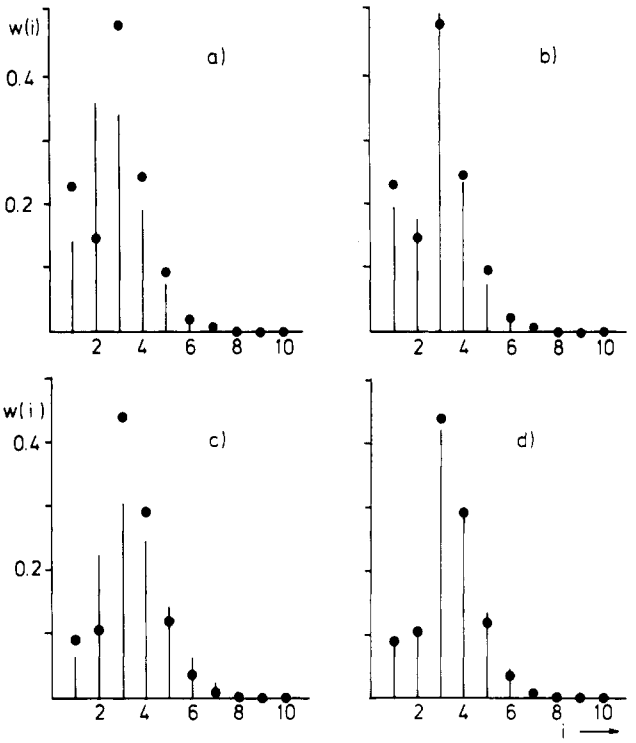


Figure 5. Experimental (●) and calculated (—) MWD for the anionic oligomerization of MMA using MIB-Na as the initiator in THF at −46 °C: (a, c) $k_1 = k_2 = ... = k_p = 140$ L/(mol·s); (b, d) $k_1 = 110$, $k_2 = 310$, $k_3 = k_4 = ... = k_p = 100$ L/(mol·s); (a, b) monomer conversion $x_p = 46\%$ (run RN 21); (c, d) $x_p = 79\%$ (run RN 23).

The ion pairs $P^*_{\pm}$ may add monomer with the rate constant $k_{\pm}$, whereas the associates P^*_a may add monomer with the rate constant k_a. The equilibrium constant of association K_A is given by

$$K_A = [P^*_a]/[P^*_{\pm}]^2 \tag{12}$$

By use of the relations

$$c^* = [P^*_{\pm}] + 2[P^*_a] \tag{13}$$

$$\alpha = [P^*_{\pm}]/c^* \tag{14}$$

the fraction of ion pairs α is calculated:

$$\alpha = (-1 + (1 + 8K_a c^*)^{1/2})/4K_A c^* \tag{15}$$

For $K_A c^* \gg 1$

$$\alpha = 1/(2K_A c^*)^{1/2} \tag{16a}$$

and for $K_A c^* \ll 1$

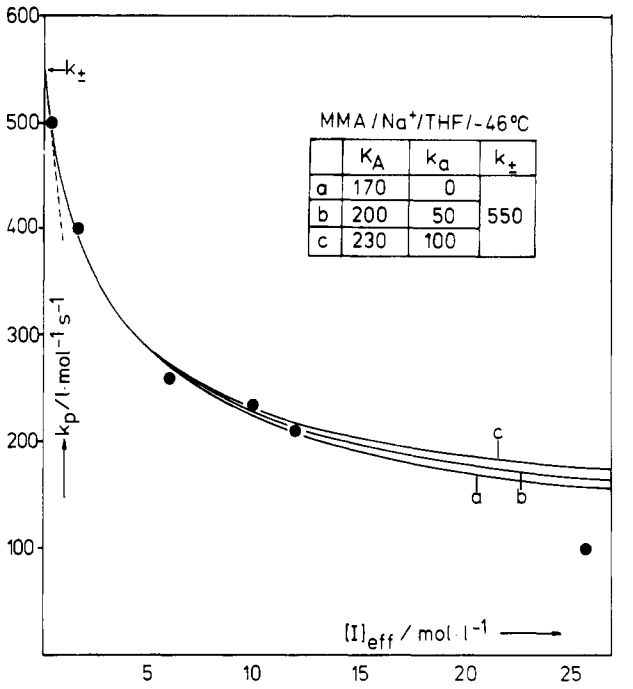
$$\alpha = 1 - 2K_A c^* \tag{16b}$$

The apparent rate constant k_p is given by

$$k_p = \alpha k_{\pm} + [(1 - \alpha)/2]k_a = \tfrac{1}{2}k_a + (k_{\pm} - \tfrac{1}{2}k_a)\alpha \tag{17}$$

The possibility of K_A being dependent on the degree of polymerization was not taken into account. Moreover, the rate constants for the association equilibrium may be comparable to the propagation rate constants, resulting in further complications in the kinetic scheme. A broadening which was observed in the MWD's of PMMA[28] and which is not caused by termination may be the result of this effect.

A plot according to eq 15 + 17 is shown in Figure 6 for three different sets of k_a and K_A. From our data it is not possible to conclude whether the associated species are able to propagate or not. Especially the k_p value at the highest



	K_A	k_a	$k_{\pm}$
a	170	0	550
b	200	50	
c	230	100	

Figure 6. Dependence of the propagation rate constant k_p on the effective initiator concentration (cf. eq 7a) in the anionic polymerization of MMA using MIB-Na as the initiator (according to eq 15 and 17). The limiting slope according to eq 16b is shown by a dashed line.

initiator concentration significantly deviates from the calculated lines. This may be due to higher aggregates formed at this concentration.[27c]

The existence of associated *un*reactive ion pairs is well-known in nonpolar or low-polar media.[1a,27] The existence of reactive associates was postulated for the polymerization of MMA by using bifunctional hydrocarbon initiators with Na^+ as the counterion in THF.[8] From the experimental data given in that paper, one can conclude that the rates of dissociation and association are smaller than the rate of polymerization.

The strange dependence of k_i on i for Na^+ (cf. Table II) is not easily understood. A tentative explanation is given in the following: If we assume α to be dependent on the degree of polymerization as well as $k_{\pm}$

$$k_i = \alpha_i k_{\pm,i} \qquad (k_a \ll k_{\pm}) \tag{18}$$

the maximum of k_i for $i = 2$ could be explained as the superposition of two effects: a decrease of $k_{\pm,i}$ (as for Li^+) and an increase of α_i. More kinetic data as well as direct evidence are necessary to clarify this point, especially the question of the magnitude of the rate constants of association and dissociation.

Experimental Part

Reagents. Metalloesters were prepared from slight excess ester and the corresponding substituted amide (see below) in toluene at −78 °C according to Lochmann et al.[30] High-vacuum break-seal techniques were used throughout. Toluene, excess ester, and amine were removed by distillation. The product was washed with cold diethyl ether and stored at −78 °C for no longer than a few hours. The purity (absence of autocondensation products) was checked by GC. Lithium diisopropylamide was prepared from 5% excess amine and *n*-butyllithium in hexane at −78 °C and then allowed to reach room temperature and stirred for $^1/_2$ h. The white precipitate was filtered and washed with cool hexane. Solvent and excess amine were removed by distillation at 10^{-4} mbar. Sodium bis(trimethylsilyl)amide (sodium hexamethyldisilazane) was prepared from the silazane and sodium amide in refluxing benzene. After dissolution of the amide, the mixture was filtered,

solvent and unreacted silazane were removed by distillation, and the residue was distilled at 10^{-4} mbar, forming a white powder.

The purification of the other reagents (monomer, $NaB(C_6H_5)_4$, N_2, THF, ...) followed standard procedures used in this laboratory.[1b,14,25]

Polymerization. See Polymerization Technique (above).

Analysis of Oligomers. Conversion was determined gravimetrically after evaporation of solvent, residual monomer, and MIB. The weight of initiator incorporated into the oligomers was subtracted.

The relative concentrations of the oligomers P_1–P_3 were determined from the reaction solution by GC using a 3-m column packed with Carbowax 20M on Chromosorb WAW ($70 \leq T \leq 210$ °C). The concentrations of P_2–P_4 were determined by using a column WCOT OV-101 (2 m, $60 \leq T \leq 325$ °C). The concentrations of P_3–P_{20} were determined by GPC from the redissolved product. Three columns 5μ-PL-gel (60 cm each; 2 × 100 Å, 500 Å) and THF as eluent at 0.5 mL/min were used. The MWD's given in Figures 1 and 2 were calculated from the eluograms by means of the "stripes" method.

The trimer peak was used as an internal standard to construct the MWD from the results of the different methods. The response factors (peak area/sample weight) were determined by injecting the pure oligomers.

Scintillation measurements were performed on GPC fractions (0.5 mL) of some samples in order to measure the ^3H content of the oligomers. In these cases tritiated acetic acid (CH_3COOT) was used as the terminating agent instead of methanol. The procedure is described elsewhere.[4,21] Due to the very high column load in these fractionations as well as to the finite fraction size, the peaks are broadened.

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