Eur. Polym. J. Vol. 20, No. 4, pp. 349–355, 1984
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0014-3057/84 $3.00 + 0.00

ON THE TERMINATION REACTION IN THE ANIONIC POLYMERIZATION OF METHYL METHACRYLATE IN POLAR SOLVENTS—I

KINETIC STUDIES†

F. J. Gerner, H. Höcker,* A. H. E. Müller and G. V. Schulz
Institut für Physikalische Chemie der Universität Mainz, D-6500 Mainz, FRG and
Sonderforschungsbereich 41, "Chemie und Physik der Makromoleküle", Sektion Mainz, FRG

(*Received* 14 *July* 1983)

Abstract—The kinetics of the termination reaction in the anionic polymerization of methyl methacrylate, using monofunctional initiators with sodium as the counterion in the presence of excess $NaB(C_6H_5)_4$ have been studied. For monitoring the living-end concentration, a labelling technique was used. Tetrahydrofuran (THF) and tetrahydropyran (THP) were used as solvents. The rate constants for the propagation reaction in THF are smaller than those in THP by a factor of two. The kinetic investigation of the termination shows that only a fraction of chains becomes terminated. This fraction, as well as the rate of termination, is dependent on the initial monomer concentration. None of the reaction mechanisms discussed in the literature (i.e. termination by ester groups of the polymer or of the monomer) is able to explain these results. A new mechanism for the termination is proposed and verified; it is based on the assumption that a deactivating species is formed in the initial step of the polymerization. This species reacts with the living polymers during polymerization, leading to termination in a second-order reaction. The Arrhenius plot of the termination rate constant is linear (activation energy $E_a = 48$ kJ/mol; frequency exponent $A = 13$) in both solvents. The initial concentration of the deactivating species shows a linear dependence on the initial concentration of both the monomer and the living ends.

INTRODUCTION

In the anionic polymerization of polar monomers, e.g. methyl methacrylate (MMA), the polar side-group of both the monomer and the polymer may give rise to numerous side-effects. The ester group plays an important role not only in the solvation of the counterion, it also may be attacked in a nucleophilic way by the initiator as well as by the living-chain ends, resulting in termination. However, it has been shown that, in polar solvents using monofunctional initiators at low temperatures ($T \leqslant -75$°C), the polymerization of MMA proceeds in an almost unperturbed way. Linear first-order plots for the conversion of monomer vs time are obtained [1–5]:

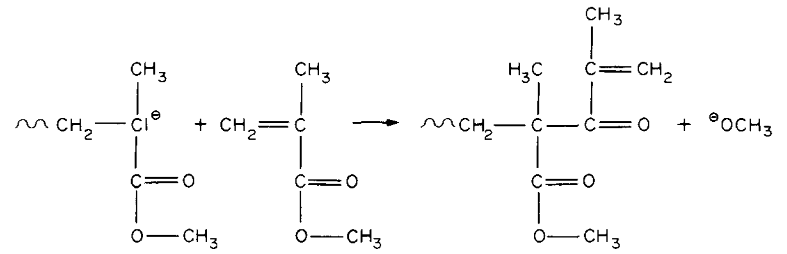
$$\ln\frac{[M]_0}{[M]} = k_p \cdot c^* \cdot t \qquad (1)$$

k_p = propagation rate constant; c^* = concentration of living ends.

The resulting polymers show narrow molecular weight distributions (MWD) [2–5]. At elevated temperatures, or in non-polar solvents, the polymerization deviates from the behaviour of a typical living anionic polymerization [6–12]. A downward curvature of the linear first-order plot (equation 1) is observed, indicating a decrease of the living-end concentration c^* during polymerization. The MWD's are broadened and exhibit a tailing towards the low molecular weight range. Especially in non-polar solvents, considerable oligomeric side-products are observed.

From the MWD, it was seen qualitatively that the relative amount of termination depends on the solvating power of the solvent: least termination is found in dimethoxyethane (DME) [5], more in tetrahydrofuran (THF) and even more in tetrahydropyran (THP). For a given solvent, the polydispersity decreases with increasing size of the counter-ion [2–4]. In 1960 Schreiber [6] proposed the following mechanisms for the termination of the living ends during polymerization:

(i) reaction of the living end with a carbonyl group of the monomer resulting a vinyl ketone ("monomer termination"):



$$\sim CH_2-\underset{\underset{\displaystyle OCH_3}{|}}{\overset{CH_3}{C^{\ominus}}}\!\!\!\!\!\!\!\!\!\!\!\!\!\!\!\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;(C{=}O) + CH_2{=}C(CH_3)(C{=}O)OCH_3 \longrightarrow \sim CH_2-C(CH_3)(COOCH_3)-C(=O)-C(CH_3){=}CH_2 + {}^{\ominus}OCH_3 \qquad (2)$$

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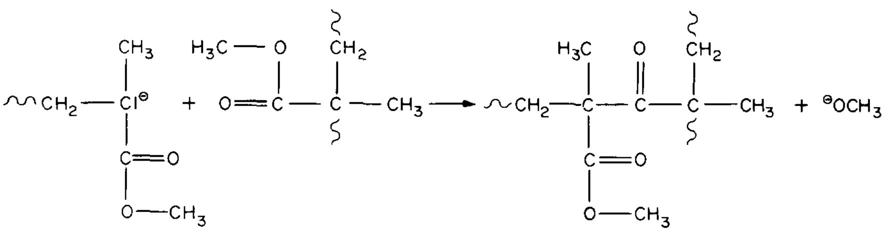
*Present address: Lehrstuhl für Makromolekulare Chemie, Universität Bayreuth, D-8580 Bayreuth, FRG.

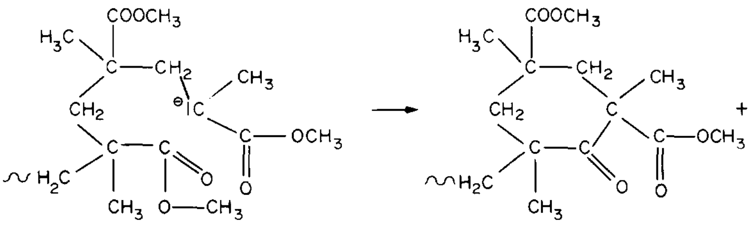
†Dedicated to Professor Dr H. J. Cantow on the occasion of his 60th birthday.

(ii) reaction of the living end with a carbonyl group of another polymer chain leading to chain coupling ("intermolecular polymer termination"):



(3)

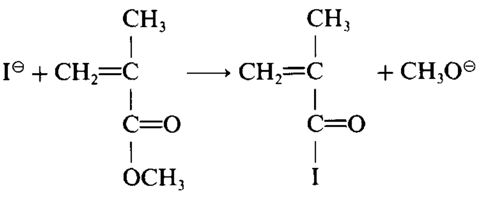
(iii) reaction of the living end with a carbonyl group of its own chain resulting in the formation of a cyclic β-ketoester ("intramolecular polymer termination"; "backbiting reaction"):



(4)

Methoxide is formed in all these reactions and may participate further acting as an initiator or as a complexing agent.

Only a few investigations have been reported concerning the side products during the polymerization in polar solvents, but some findings in non-polar solvents may also be of interest for the reaction mechanism in polar solvents. It was shown [1, 13, 14] that most of the methoxide is formed during the initial step of the polymerization. This might be explained by attack of the initiator on the carbonyl group of the monomer forming a vinyl ketone:



$$\begin{array}{c} \\ \\ I^{\ominus} + \\ \\ \\ \end{array}\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH_2{=}C} \\ \quad | \\ \quad \mathrm{C{=}O} \\ \quad | \\ \quad \mathrm{OCH_3} \end{array} \longrightarrow \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH_2{=}C} \\ \quad | \\ \quad \mathrm{C{=}O} \\ \quad | \\ \quad \mathrm{I} \end{array} + \mathrm{CH_3O^{\ominus}} \qquad (5)$$

I = initiator

Furthermore, a cyclic β-ketoester trimer resulting from an intramolecular termination could be identified [15, 16].

To differentiate between the possible mechanisms mentioned above, direct observation of the concentration of living ends as a function of time is necessary. In the experiments reported here, a method introduced by Glusker [17] was used. Samples of the polymerization solution drawn at different times were reacted with tritiated acetic acid (CH_3COOT). Thus only the living ends were labelled with tritium and subsequent activity measurements gave the dependence of c^* on time. By using this method, first kinetic studies [4] showed first-order kinetics for the decrease of c^*, indicating that termination is predominantly caused by intramolecular polymer termination (equation 4). Monomer termination (equation 2) was shown to play a subordinate role only. As these results were obtained during polymerization only (monomer conversion $< 90\%$), it seemed necessary to investigate the kinetics over a longer period of time, i.e. even after complete monomer conversion. In the case of intramolecular polymer termination, first-order decrease of c^* was expected to continue, independent of the monomer concentration. Results of the experiments shown below will illustrate, that none of the mechanisms given in the literature can explain the termination kinetics.

EXPERIMENTAL

Reagents

The purifications of solvents (THF, THP), common ion salt ($NaB(C_6H_5)_4$, sodium tetraphenylborate) and inert gas (N_2) were described elsewhere [4]. Common ion salt was added in order to suppress the dissociation into free ions.

Monomer

MMA (Röhm GmbH, Darmstadt) was refluxed over CaH_2 at reduced pressure and distilled over a 1 m column. After degassing, the distillate was stirred twice over CaH_2 and distilled under high vacuum. Then it was stored under purified N_2 at $-40°C$. The level of impurities in the monomer solution was less than 0.01% (by gas chromatography).

Initiators

Benzyl-oligo-α-methylstyrylsodium [4] and diphenylmethylsodium [18] were synthesized according to literature.

Termination solution

Tritium-labelled acetic acid (CH_3COOT) was prepared by reacting acetic anhydride and tritiated water in equimolar amounts. It was dissolved in pure THF and stored under dry N_2.

Scintillation cocktail

1,4-Di-(2-(4-methyl-5-phenyloxazoyl))-benzene puriss. (0.5 g/l) and 5.0 g/l 2,5-diphenyloxazole puriss. in toluene p.a.

Kinetic experiments

Depending on the reaction rate, the experiments were performed in an automatically controlled stirred tank reactor [19] or a flow tube reactor [2b, 20]. Monomer conversion was determined by gravimetric and gas chromatographic methods. With respect to the temperature rise caused by the heat of polymerization, the rate constants were determined in the following way. The initial conditions of polymerization (c_0^*, $[M]_0$, temperature, etc.) and the experimental data (X_P, c^*, $\bar{P}_n$) of the polymer samples obtained, as well as the differential equations of the mechanism to be examined, were submitted to a Fortran program. The integration was done by using a Runge–Kutta method. Estimated values of the unknown parameters were changed until approximation of experimental and calculated data was received. From the temperature dependence of the "zeroth approximation" rate constants, the activation parameters were calculated and entered into the program in order to correct for temperature effects. The procedure was repeated until consistent.

Characterization of the polymers

Molecular weights were measured by gel permeation chromatography with Polymer-Laboratory columns (10μ; 10^3 and 10^5 Å) and THF as the solvent. The apparatus was calibrated by means of polystyrene and poly(methyl methacrylate) samples of narrow MWD, characterized by light scattering.

Activity measurements

By termination with tritiated acetic acid, only those polymers bearing living ends were labelled. Thus, the concentration of living ends during the reaction can be monitored by measuring the activity of the various polymer samples in a liquid scintillation counter (Packard Tricarb 3225). For the measurements, two methods were applied:

(i) Part of the solution drawn from the reactor was evaporated to remove excess CH_3COOT; scintillator cocktail was added and tritium decays were measured in the scintillation counter. Counting efficiency, background and quenching effects were calculated using external standards [21–23]. The molar activity A_{mol}, directly proportional to the concentration of living ends, was calculated from the volume activity (A_{vol} = dpm/l) by

$$A_{mol} = f \cdot c^* = A_{vol}/c_0^* \tag{6}$$

The initial concentration of living ends (c_0^*) was determined from the number-average degree of polymerization as determined by GPC (equation 8).

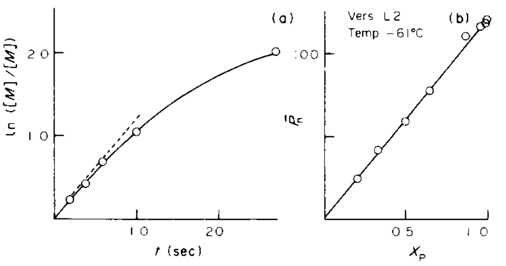


Fig. 1. Propagation in the anionic polymerization of MMA in THF with Na^+ as counterion at −60°C. (a) First-order plot of monomer conversion vs time. (b) Plot of $\bar{P}_n$ vs monomer conversion X_P. For reaction conditions cf. Table 1; exp. L2.

(ii) Polymers were precipitated; a weighed amount was dissolved in scintillator cocktail and the specific activity (A_{sp} = dpm/g) of the polymer was measured. The molar activity was calculated by

$$A_{mol} = f \cdot c^* = A_{sp} \bar{M}_n \tag{7}$$

Within the limits of experimental error, both methods lead to the same results. Thus it was verified that no unreacted initiator or living oligomers were left in the reaction solution at the time of termination with CH_3COOT. The labelled polymers were tested for isotope exchange by treatment with water at higher temperatures. No evidence for tritium exchange was found.

The distribution of labelled chains in a polymer sample was determined by fractionating the sample in a GPC apparatus and measuring the activity of each fraction.

RESULTS AND DISCUSSION

Kinetics of propagation

Kinetic data on the anionic polymerization of MMA in THF have been published [1–4], therefore only some details of interest for the termination reaction will be presented. The conditions for the experiments and the rate constants for the propagation reaction are given in Table 1. Figure 1a shows that, at temperatures above −70°C, the first-order plots of the monomer conversion vs time are curved downward, indicating that c^* is decreasing during

Table 1. Conditions and results for the anionic polymerization of methyl methacrylate using Na^+ as counterion

Experiment No.	Solvent	Initiator	T (°C)	$[M]_0$ (mol/l)	$c_0^* \cdot 10^4$ (mol/l)	k_p (l mol^{-1} sec^{-1})	X_p (max)	$[S]_0 \cdot 10^4$ (mol/l)	k_t (l mol^{-1} sec^{-1})
71/72	THF	BαMS	−41	0.26	13.0	580	1	13.0	500
03	THF	BαMS	−41	0.26	6.8	580	1	6.2	650
06/07	THF	BαMS	−58	0.26	5.0	270	1	1.9	30
A4/A5	THF	BαMS	−63	0.56	4.6	270	1	4.6	35
A6	THF	BαMS	−62	0.38	4.7	270	1	3.6	30
A7/A8	THF	BαMS	−63	0.15	4.8	270	1	2.3	35
A9	THF	BαMS	−62	0.06	4.4	270	1	0.9	30
71/72	THF	BαMS	−81	0.27	12.0	95	1	5.0	2
81	THF	BαMS	−81	0.69	10.0	110	1	4.7	3
L1	THF	DPM	−40	0.07	5.8	580	1	3.0	580
L2	THF	DPM	−60	0.07	6.0	200	1	2.0	35
E2	THP	BαMS	−15	0.23	2.7	—	0.26	2.7	8000
E1	THP	BαMS	−25	0.46	2.7	(560)	0.32	2.6	3500
D8/D9	THP	BαMS	−36	0.46	3.8	(530)	0.65	3.5	600
E3	THP	BαMS	−45	0.37	3.3	360	1	3.0	400
D7	THP	BαMS	−47	0.47	3.9	320	1	3.6	300
D6	THP	BαMS	−49	0.68	7.7	280	1	6.5	200

BαMS = benzyl-α-methylstyrylsodium; DPM = diphenylmethylsodium; X_p(max) = maximum conversion of monomer.

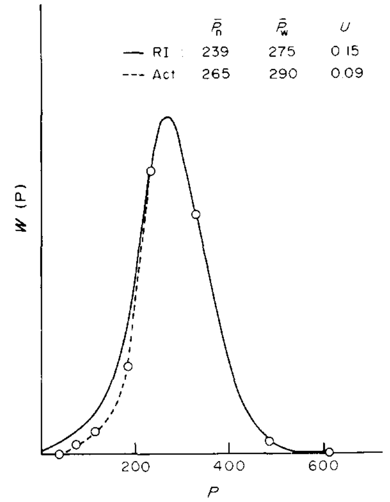


Fig. 2. Molecular weight distribution including distribution of labelled chains of a PMMA sample prepared at −60°C in THF; for reaction conditions cf. Table 1; exp. A7.

propagation. Simultaneously the molecular weight distributions become broader, the GPC eluograms showing low molecular weight tailing. The distribution of labelled chains (Fig. 2) clearly shows that the low molecular weight tailing consists of unlabelled chains, i.e. that these chains had been terminated before the addition of tritiated acetic acid. Therefore, initiation caused by methoxide formed *in situ* can be ignored. The lack of a high molecular weight tailing indicates that an intermolecular polymer termination is not very probable. This is in congruence with the results of Rempp *et al.* [7] that even the more reactive polystyrylsodium anion only attacks PMMA ester groups at longer reaction times and higher temperatures. As the number-average degree of polymerization $\bar{P}_n$ is given by

$$\bar{P}_n = \frac{\text{number of monomer units}}{\text{total number of chains}} = \frac{X_P[M]_0}{c_{tot}} \quad (8)$$

X_p = conversion of monomer; c_{tot} = concentration of all chains.

The linearity of a plot of $\bar{P}_n$ vs X_P (Fig. 1b) indicates that the total number of chains remains constant. Thus transfer, chain coupling, or re-initiation can be excluded.

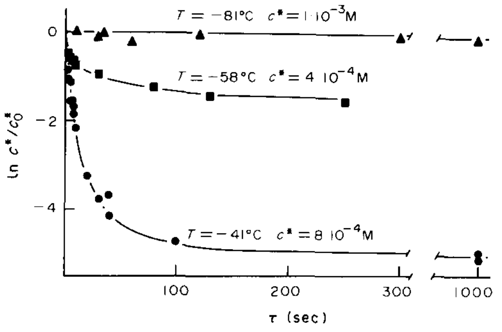


Fig. 3. First-order plot of the decrease of the living-end concentration c^* vs time in the anionic polymerization of MMA in THF with Na as the counterion. For reaction conditions cf. Table 1; exps 81 (▲); 06/07(■); 01/02 (●).

The investigation of the kinetics of propagation in THP (cf. Table 1) shows qualitatively that the polymerization is more perturbed by termination as compared with THF. At temperatures above −35°C, monomer conversion does not reach 100% and the MWD's of the polymers are broader than those obtained in THF, although $\bar{P}_n$ is still a linear function of X_P. The rate constants for the propagation are smaller by a factor of 2 as compared with THF.

Kinetics of termination

From earlier experiments it was concluded that termination is caused by the backbiting reaction (equation 4). In this case the decrease of c^* has to obey a first-order law irrespective of the monomer concentration:

$$-\frac{dc^*}{dt} = k_t \cdot c^* \quad (9)$$

k_t = termination rate constant

$$\ln \frac{c_0^*}{c^*} = k_t \cdot t \quad (10)$$

A first-order plot of c^* vs time at different temperatures gave straight lines during polymerization ($0.1 < X_P < 0.9$), indicating no influence of the actual monomer concentration on the termination [4].

Our kinetic investigations over a longer period of time (even after complete monomer conversion) show that the decrease of c^* slows down and in some cases seems to stop, i.e. only a fraction of living chains becomes terminated (cf. Fig. 3). As this fraction is temperature dependent, deactivation of the living chains by impurities in the monomer solution can be excluded.

In another series of experiments, the initial monomer concentration was varied. Again, we obtain a first-order decrease of c^* during polymerization (Fig. 4) but the slopes of the curves show a distinct dependence on the initial monomer concentration. The investigation up to longer reaction times (Fig. 5) shows that the fraction of terminated chains also depends on the initial monomer concentration. In THP, as the solvent, similar results were obtained.

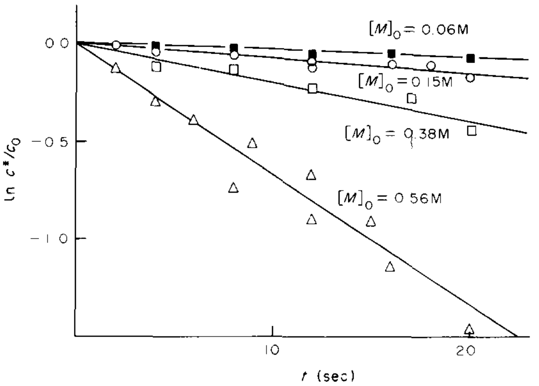


Fig. 4. First-order plot of the decrease of the living-end concentration c^* vs time during the propagation stage of the anionic polymerization of MMA in THF with Na as counterion at −60°C with different initial monomer concentrations $[M]_0$. For reaction conditions cf. Table 1; exps A4–A9.

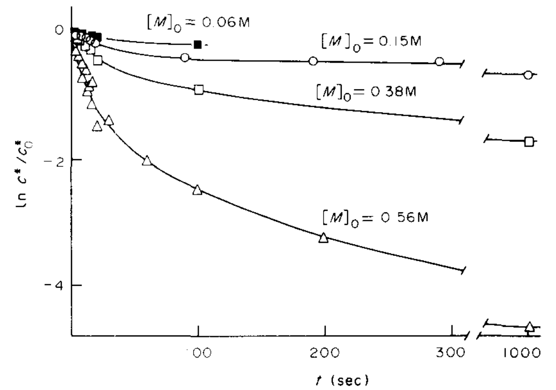


Fig. 5. First-order plot of the decrease of the living-end concentration c^* vs time during the polymerization stage and after complete conversion of the monomer. Same experiments as in Fig. 4.

The results shown above cannot be explained by any of the mechanisms previously discussed. It should be mentioned that the assumption of a combined mechanism (monomer and intramolecular polymer termination simultaneously) does not lead to a satisfactory approximation of these data. The dependence of the termination rate as well as of the extent of terminated chains on the initial monomer concentration points to the fact that termination is caused by events in the initial stage of the polymerization when $[M]$ equals $[M]_0$. This agrees with the findings of Bywater *et al.* [13, 14] that most of the methoxide is produced in the initial stage.

We therefore propose a new mechanism, starting from the assumption that, in the initial stage of the polymerization, i.e. when mixing the monomer and initiator solutions, a deactivating species S is formed. This species is supposed to lead to termination during polymerization, reacting with the living ends in a second-order reaction:

$$P_i^* + S \xrightarrow{k_t} P_i' \qquad (11)$$

P_i = polymer with degree of polymerization i; (*) = living; (′) = terminated; k_t = rate constant of termination.

Termination occurs as long as either deactivating species or living ends are present in the reaction mixture.

Integration of the differential equations

$$-\frac{dc^*}{dt} = k_t[S]c^* \qquad (12)$$

$$-\frac{d[S]}{dt} = k_t[S]c^* \qquad (13)$$

leads to the following expression:

$$\frac{1}{c_0^* - [S]_0} \ln \frac{c^* \cdot [S]_0}{[S] \cdot c_0^*} = k_t \cdot t \qquad (14)$$

$[S]_0$ is approximately equal to the difference between the concentrations of living ends at the beginning and the end of the reaction. The actual concentration of S is then given by

$$[S] = [S]_0 - (c_0^* - c^*) \qquad (15)$$

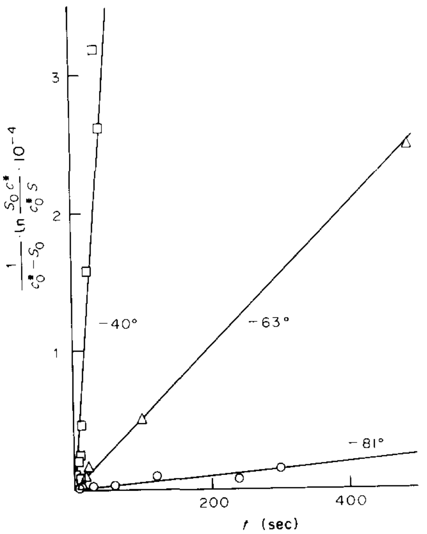


Fig. 6. Second-order plot according to equation 14 for the termination in the anionic polymerization of MMA in THF with Na as counterion. For reaction conditions cf. Table 1; exps 71/72 (○); A7/A8 (△); 01/02 (□).

In a plot according to equation 14, $[S]_0$ and k_t are then varied to obtain the best fit of the experimental data. Linear plots are obtained for all experiments in both solvents (cf. Figs 6 and 7). The termination rate constants obtained from the slopes give straight lines in an Arrhenius plot (Fig. 8); in both solvents nearly identical values for activation energy and frequency exponent are obtained ($E_a = 48$ kJ/mol; $A = 13$). The first-order decrease of c^* during polymerization can be explained by a pseudo-unimolecular reaction, for the change in $[S]$ is rather small at the beginning of the reaction.

The initial concentration of the deactivating species, $[S]_0$, obtained from the fit of the experimental data, shows a linear dependence on the initial concentrations of monomer and initiator (Fig. 9).

$$[S]_0 = \text{const.}\ c_0^*\,[M]_0 \qquad (16)$$

It should be noted that this result follows from the fitting procedure and was not used as a prior condi-

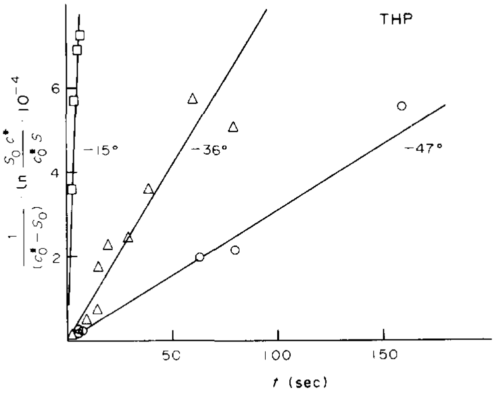


Fig. 7. Second-order plot according to equation 14 for the termination in the anionic polymerization of MMA in THP with Na as counterion. For reaction conditions cf. Table 1; exps D7 (○); D8/D9 (△); E2 (□).

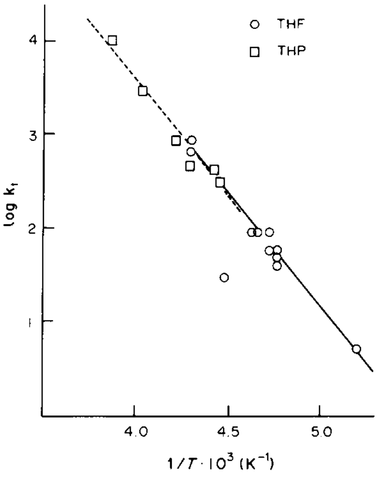


Fig. 8. Arrhenius plot of the rate constants for a second-order termination reaction in the anionic polymerization of MMA with Na as counterion in THF and THP.

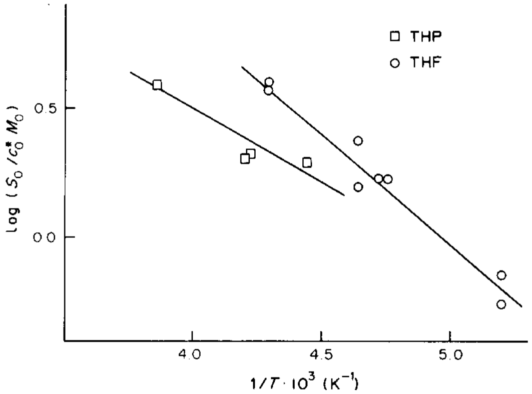


Fig. 10. Temperature dependence of the formation of the deactivating species S and the living ends c^* in the initial step of the anionic polymerization of MMA with Na^+ as counterion in THF and THP.

tion for the calculation. This correlation points to the fact that the deactivating species is formed from the initiator and the monomer during the initial stage of the polymerization. A hypothetical scheme, which is able to explain the observed dependence on both $[M]_0$ and c_0^*, is given below:

$$\begin{tikzcd} I + M \arrow[r, "k_x"] & {[X]} \arrow[r, "k_1"] \arrow[d, "k_2", "+M"'] & P^* \\ & S & \end{tikzcd} \qquad (17)$$

[X] = intermediate product; P* = living oligomer. This scheme leads to the expression

$$[S]_0 = \frac{k_2}{k_1} c_0^* [M]_0 \qquad (18)$$

A plot of $\log\{[S]_0/c_0^*[M]_0\}$ vs $1/T$ should give the temperature dependence of the ratio of the rate constants for the formation of the deactivating species and the living ends (Fig. 10). The fact that, in THP the polymerization is increasingly perturbed by termination as compared to THF as the solvent, can be explained by the different ratios of k_p/k_t. From the results presented above, it can be concluded that termination possibly can be prevented if the formation of the deactivating species in the initiation step is suppressed. This can be done by initiating the reaction with an initiator having the same reactivity as the living ends, since the living end preferably adds to the vinyl double bond of the monomer.

Two different experiments were performed in order to investigate the polymerization under unperturbed conditions. In the first experiment, monomer and initiator were mixed, the conversion of monomer and the decrease of c^* were observed and, after complete conversion of monomer and cessation of the termination reaction, a second batch of monomer was added. This time, no termination was observed (Table 2 and Fig. 11; exp. L3). This can be explained by the fact that S was almost consumed and no deactivating species was formed after the second monomer addition. (The dotted line shows the expected result if the deactivating species had been formed newly.) Moreover, the plot of monomer conversion vs time (Fig. 12) clearly shows that, for

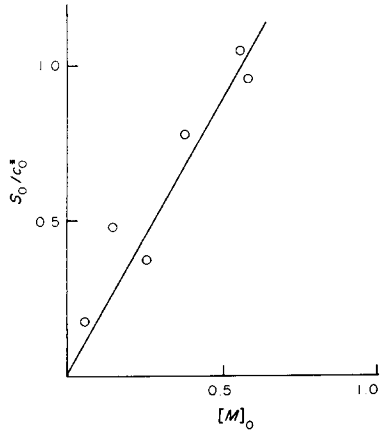


Fig. 9. Dependence of the initial concentration of the deactivating species S on the initial monomer concentration $[M]_0$ and the initial living-end concentration c_0^* at −60°C in THF.

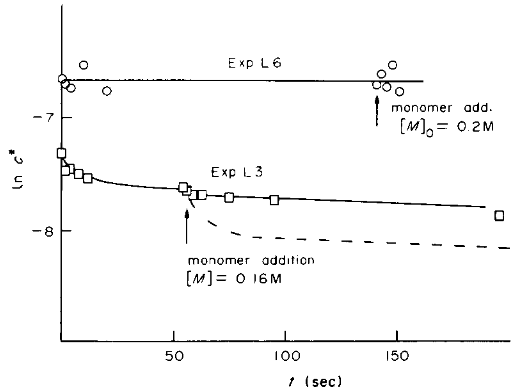


Fig. 11. First-order plot of the concentration of the living ends c^* vs time for the experiments. (a) With living MMA oligomers as the initiator (exp. L6). (b) With a second monomer addition (exp. L3); the dotted line shows the expected decrease of c^* if the deactivating species S had been formed newly during the second monomer addition. For reaction conditions cf. Table 2.

Table 2. Conditions and results for control experiments in THF at −60°C

Experiment No.		$[M]_0$ (mol/l)	$c_0^* \cdot 10^4$ (mol/l)	k_p ($l\,mol^{-1}sec^{-1}$)
L3	1st monomer addition	0.07	6.7	210
	2nd monomer addition	0.16	4.8	160
L6	after distillation	~0	12.0	—
	monomer addition	0.20	12.0	150

Initiator: diphenylmethylsodium.

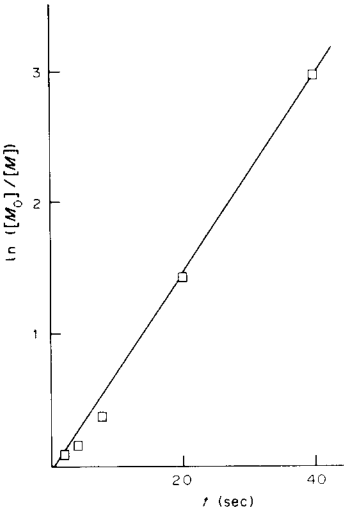


Fig. 12. Unperturbed propagation reaction during the anionic polymerization of MMA in THF with Na^+ as counterion. Exp. L3, second monomer addition. For conditions cf. Table 2.

the second monomer addition, the propagation proceeds in an ideal manner without any termination (for a "normal" perturbed propagation reaction with comparable conditions, cf. Fig. 1a). The lack of termination upon the second monomer addition proves that termination is not due to impurities in the monomer.

In a second experiment, monomer was slowly distilled to a solution of the initiator to produce living MMA oligomers. In this case, during distillation of the monomer, $[M]_0$ should be near to zero and no deactivating species should be formed (cf. equation 16). No termination was observed in this solution and, even after addition of the monomer solution to these oligomers, c^* remained constant (Fig. 11; exp. L6). These experiments verify the newly proposed mechanism. Nevertheless from kinetic investigations, it is not possible to draw conclusions on the structure of the deactivating species postulated. Results from analytical investigations of side-products will be given in a subsequent publication [24].

Acknowledgement—This work is supported by the Deutsche Forschungsgemeinschaft within the Sonderforschungsbereich 41 "Chemie und Physik der Makromoleküle".

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