the questionable condition $[\text{all } P_1]^{1/2} + [\text{all } P_2]^{1/2} =$ constant but is based on the proper condition $[\text{all } P_1] + [\text{all } P_2] =$ constant.

Finally, the lack of consideration of the highly probable mixed dimerization casts doubt on the calculations of O'Driscoll and Kuntz[7] pertaining to copolymerization of styrene and butadiene initiated in benzene by alkyllithium. It would be advisable to reconsider this kinetics with proper consideration of the mixed dimerization.

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On the Structure of the Propagating Species in the Anionic Polymerization of Methyl Methacrylate. Kinetic Investigations in Tetrahydrofuran Using Monofunctional Initiators

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ABSTRACT: The kinetics of the propagation step in the anionic polymerization of methyl methacrylate in THF were investigated over the temperature range of +20 to −100 °C with cumylcesium and at −25 °C with monofunctional oligomeric α-methylstyrylsodium as initiators. A flow tube reactor and a stirred tank reactor were used. At low temperatures the termination is nearly avoided, but it gains in importance at higher temperatures especially when sodium is used as a counterion. The Arrhenius plots of the rate constants for the monomer addition to ion pairs of PMMA–Cs and PMMA–Na are linear; presumably the reacting ion pairs exist in one form only. The Arrhenius parameters for both counterions are identical within experimental errors: Cs$^+$, A = 7.7, E_a = 4.9 kcal/mol = 21 kJ/mol; Na$^+$, A = 7.4, E_a = 4.7 kcal/mol = 20 kJ/mol. These results are in strong contrast to the kinetics of the polymerization of styrene. They can be explained by the assumption of an "intramolecular solvation" of the counterion by the penultimate or antepenultimate ester group of its own polymer chain.

The nature of the active species in the anionic polymerization of styrene has been disclosed to a high degree. The picture revealed, however, has proven not to be transferable to polar monomers such as methyl methacrylate. Here, in addition, termination reactions complicate the kinetics and broaden the molecular weight distributions of the polymers. Although these side reactions are less pronounced in polar solvents than in nonpolar ones only very few investigations dealt with the kinetics of the anionic polymerization of methyl methacrylate (MMA) in polar solvents. According to Löhr and Schulz[2,3] and to Mita et al.[4] little or no termination is observed when the reaction proceeds in THF at $T \le -75$ °C, whether Na$^+$ or Cs$^+$ is used as a counterion. The rate of propagation is first order with respect to the monomer and the number average degree of polymerization is a linear function of conversion. Moreover, the molecular weight distributions are narrow. At higher temperatures termination reactions gain in importance as indicated by deviations from the first-order kinetics, by broadening of the molecular weight distribution,[5] and by the generation of alkali methoxide.[4]

Conductance studies of Löhr and Schulz[2,3] and of Figueruelo[6] show that the dissociation constants of PMMA–alkali metal ion pairs are low as compared with ion pairs involving polystyryl or fluorenyl anions. Mita et al.[4] attributed this fact to the exclusive existence of contact ion pairs. The kinetic results of Löhr and Schulz[2,3] prove that at least two different kinds of species are involved in the propagation, i.e., free anions and ion pairs. Their experiments, however, give no evidence on the nature of the ion pairs.

It is known that two kinds of ion pairs, i.e., contact and solvent separated ion pairs, participate in the anionic polymerization of styrene with Na$^+$[7] or Cs$^+$[8] as counterions. They are in equilibrium with each other and propagate with different rates. The Arrhenius plot of the ion pair rate constants taken over a wide temperature range exhibits a distinct curvature.

The kinetic data reported for the polymerization of MMA with Na$^+$ as a counterion are questionable because they were obtained with bifunctional initiators, i.e., naphthalenesodium[4] or oligomers of α-methylstyrylsodium.[3] According to Warzelhan and Schultz,[9] when bifunctional initiators are employed intramolecular association of the chain ends occurs. This results in a deviation from first-order kinetics. The analogous intermolecular association has not been observed within the investigated range of concentrations of living ends ($10^{-4} \le c^* \le 10^{-3}$ mol/L).

Therefore, we decided to reinvestigate the kinetics of the polymerization of MMA with monofunctional initiators, such as benzyloligo(α-methylstyryl)sodium[23] and cumyl cesium, over a wide temperature range. Cs$^+$ was chosen as a counterion since termination reactions seem

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to be less pronounced in the Cs^+ system than with Na^+.[2]

Experimental Section

Reagents. Unstabilized methyl methacrylate[24] was refluxed over calcium hydride at 100–200 torr and distilled over a 1-m column. Next it was stirred with a magnetic stirrer for 24 h over calcium hydride and distilled off in vacuo. This operation was repeated once. The pure MMA was stored under nitrogen at −78 °C.

Tetrahydrofuran[25] and nitrogen were purified by the methods described elsewhere.[12]

Cumyl cesium used as the initiator was prepared from cumyl methyl ether and cesium metal.[14] Monofunctional oligomeric α-methylstyrylsodium was prepared in THF from benzylsodium (ICN Pharmaceuticals Inc., K&K Labs Div.) and α-methylstyrene.[13]

Sodium tetraphenylborate ($NaB(C_6H_5)_4$) and cesium triphenylcyanoborate ($Cs(C_6H_5)_3BCN$)[2,15] respectively were added to suppress the dissociation of ion pairs into free ions and to reduce the probability of triple ion formation.

Kinetic Measurements. At higher temperature ($+20\ °C \geq T \geq -60\ °C$) the kinetic experiments were performed in a flow tube reactor described elsewhere.[3,12] By varying the tube length ($0.33\ m \leq l \leq 3.16\ m$) and the flow rate, reaction times could be varied from 0.1 to 3 s. Lower flow rates required at lower temperatures, in conjunction with increasing solvent viscosity, lead to Reynolds numbers below 3000; thus a turbulent flow of the reaction solution could not be attained then.[16]

Therefore, at lower temperatures ($-50\ °C \geq T \geq -100\ °C$) the experiments were performed in a stirred tank reactor with an automatically controlled sample outlet which allowed kinetic studies of slower reactions with half-lives of 2 s or longer.[11]

The minimum accuracy of the results in both the flow tube and the stirred reactor is observed when approaching their lower and upper limits with respect to the half-life of the reaction, i.e., when investigating reactions with half-lives of 2–3 s. In the system studied this corresponds to a temperature range from −60 to −40 °C (cf. Figure 4a).

The degree of conversion was determined gravimetrically and, using the flow tube, additionally from the reaction enthalpy by measuring the temperature difference between the mixing and the quenching jet. This is sufficiently accurate since the heat transfer from the flow tube to the constant temperature bath is negligible during short reaction times.

Characterization of the Polymers. Molecular weights were measured by gel permeation chromatography (GPC) using 6 Waters Styragel columns (5×10^5 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) and THF as the solvent. The GPC apparatus was calibrated by means of fractionated PMMA samples which were characterized by ultracentrifugation, light scattering, and viscometry. The nonuniformity U of the polymers was estimated from the GPC eluograms by the 4σ method according to Wesslau:[17]

$$U = (M_w/M_n) - 1 = e^{(B\sigma)^2} - 1 \tag{1}$$

σ is the standard deviation of the GPC elution curve and B is the slope of the GPC calibration curve plot of ln M vs. elution volume.

A broadening of the distribution due to axial dispersion was taken into account by subtracting an excess nonuniformity U_{ex} according to the method of Berger and Schulz:[18]

$$U_{polymer} = (1 + U_{app})/(1 + U_{ex}) \approx U_{app} - U_{ex} \tag{2}$$

for $U << 1$. U_{ex} was determined from very narrowly distributed PMMA and polystyrene samples to be 0.035 ± 0.010.

The molecular weight distributions turn out to be very narrow ($0.01 \leq U \leq 0.1$) although a slight tailing of the elution curve toward the low molecular weight side is observed. Figure 1 shows the GPC elution curve of a PMMA sample in comparison with that of a standard polystyrene sample (Pressure Chemical Co.). Thus for the calculation of the concentration of living ends c^* (eq 3) the number average degree of polymerization $\bar{P}_n$ can be substituted by the degree of polymerization corresponding to the maximum of the GPC elution curve P_{max}.

$$c^* = [M]_0 x_p/\bar{P}_n \approx [M]_0 x_p/P_{max} \tag{3}$$

$[M]_0$ is the initial monomer concentration and x_p is the conversion.

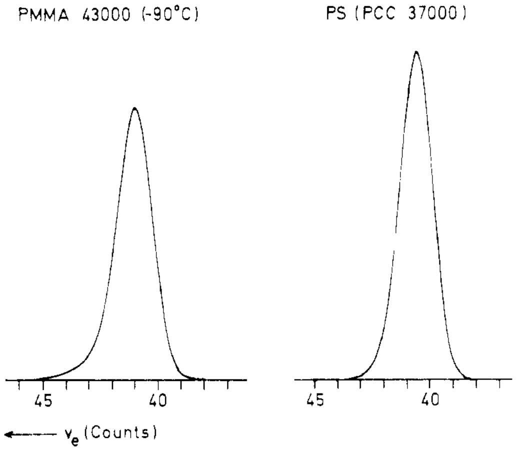

Figure 1. GPC eluogram of a PMMA sample prepared at −90 °C in comparison with a standard polystyrene sample (Pressure Chemical Co.) of similar molecular weight.

Results

It was confirmed that for Cs^+ as a counterion at temperatures up to ca. −10 °C the propagation reaction obeys first-order kinetics with respect to the monomer:

$$\ln [M]_0/[M]_\tau = k_p\, c^* \tau \tag{4}$$

Since a common ion salt was added the rate constant k_p is to be regarded as that of the ion pairs, $k_{(\pm)}$. In Figure 2 the time/conversion curves are plotted according to eq 4. At higher temperatures deviations resulting from termination reactions become evident. The first-order plots exhibit a downward curvature (Figure 2b) due to a decrease of c^*; the GPC eluograms show a marked low molecular weight tailing making $\bar{P}_n$ different from P_{max} ($\bar{P}_n < P_{max}$). For the evaluation of k_p, however, the effect of the termination reactions can be eliminated by taking the initial slope of the first-order plot and by calculating $\bar{P}_n$ from the GPC eluogram using the "stripes method".[26] Thus, rate constants for the polymerization with Cs^+ as a counterion were determined up to ca. +20 °C, whereas with Na^+ as a counterion reliable results could only be achieved up to ca. −25 °C. The observed linear relationship between $\bar{P}_n$ (P_{max}) and the conversion (Figure 3) demonstrates the absence of transfer reactions. The results of the kinetic experiments are given in Tables I and II.

The rate constants for PMMA–Cs differ from those of Löhr and Schulz by about a factor of 2. The differences may result from an improved technique of the flow tube reactor (automatic flow rate measurement, precise measurement of the temperature rise, more perfect thermal control of burets, and flow tube) as well as from an improved GPC column set and calibration curve.

The Arrhenius plots of the rate constants for Cs^+ and Na^+ as counterions are shown in Figure 4a. The plots are linear and yield the following parameters: PMMA–Cs, $A = 7.7$, $E_a = 4.9$ kcal/mol = 21 kJ/mol; PMMA–Na, $A = 7.4$, $E_a = 4.7$ kcal/mol = 20 kJ/mol.[27] This Arrhenius plot reveals two striking features: First, the plot is linear within the limits of experimental error; thus there is no evidence for the existence of two kinds of ion pairs (such as contact and solvent-separated ion pairs) reacting at significantly different rates. Second, the Arrhenius parameters found for Na^+ and Cs^+ salts are identical within the limits of experimental errors.

These results are in strong contrast to the kinetics of the polymerization of styrene (Figure 4b),[7c,8] where curved Arrhenius plots are observed. The curvature indicates the presence of two differently active ion pairs, generally referred to as the contact and the solvent-separated ion

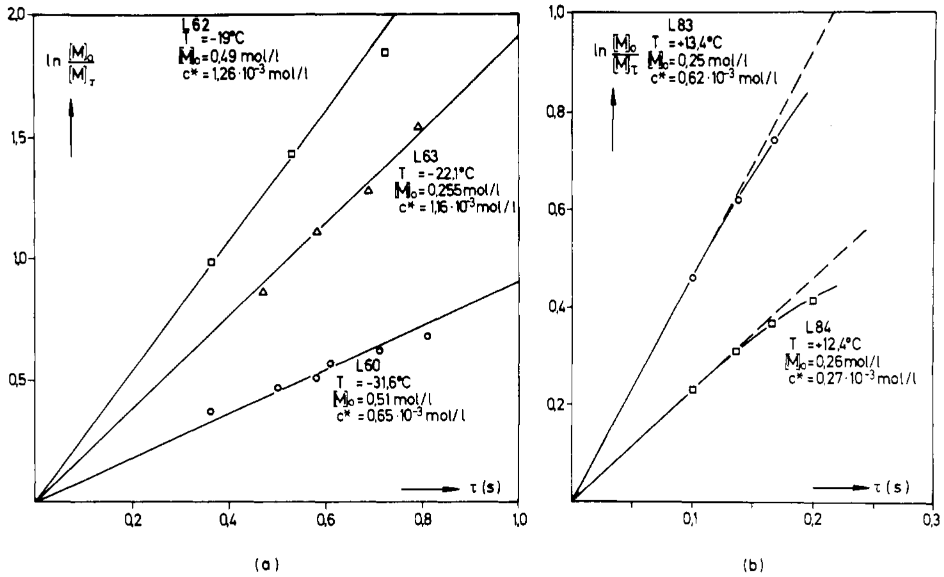

Figure 2. First-order time/conversion plot for the anionic polymerization of MMA in THF: (a) ideal behavior; (b) simultaneous termination reactions.

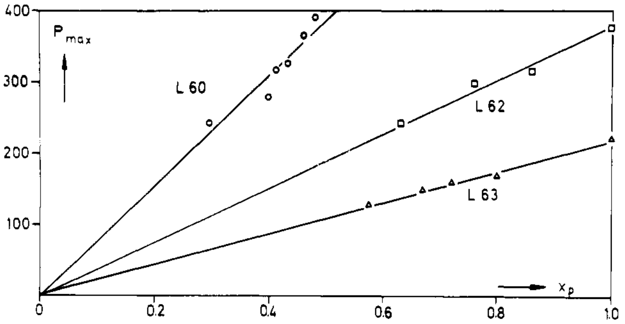

Figure 3. Plot of the degree of polymerization (as evaluated from the maximum of the GPC elution curve) vs. conversion for PMMA prepared by anionic polymerization in THF with Cs^+ as a counterion.

pair. The contact ion pair rate constants $k_{(\pm)c}$ for PS–Na are lower than those for PS–Cs by a factor of about 4, while the rate constants for the solvent separated ion pairs can be regarded to a first approximation to be independent of the counterion.

The lack of dependence of the rate constants in the anionic polymerization of MMA on the nature of counterions (Na^+ or Cs^+) suggests that they are not of the contact ion pair type. The rate constants of contact ion pairs are expected to be affected by a change of counterion.

On the other hand, the ion pairs cannot be considered to be solvent separated since Cs^+ is poorly solvated by THF, much less than Na^+. Moreover, the dissociation constants measured for PMMA-Na and PMMA-Cs in THF are extremely low ($K_{diss} \approx 10^{-9}$mol/L at −78 °C).[2,3]

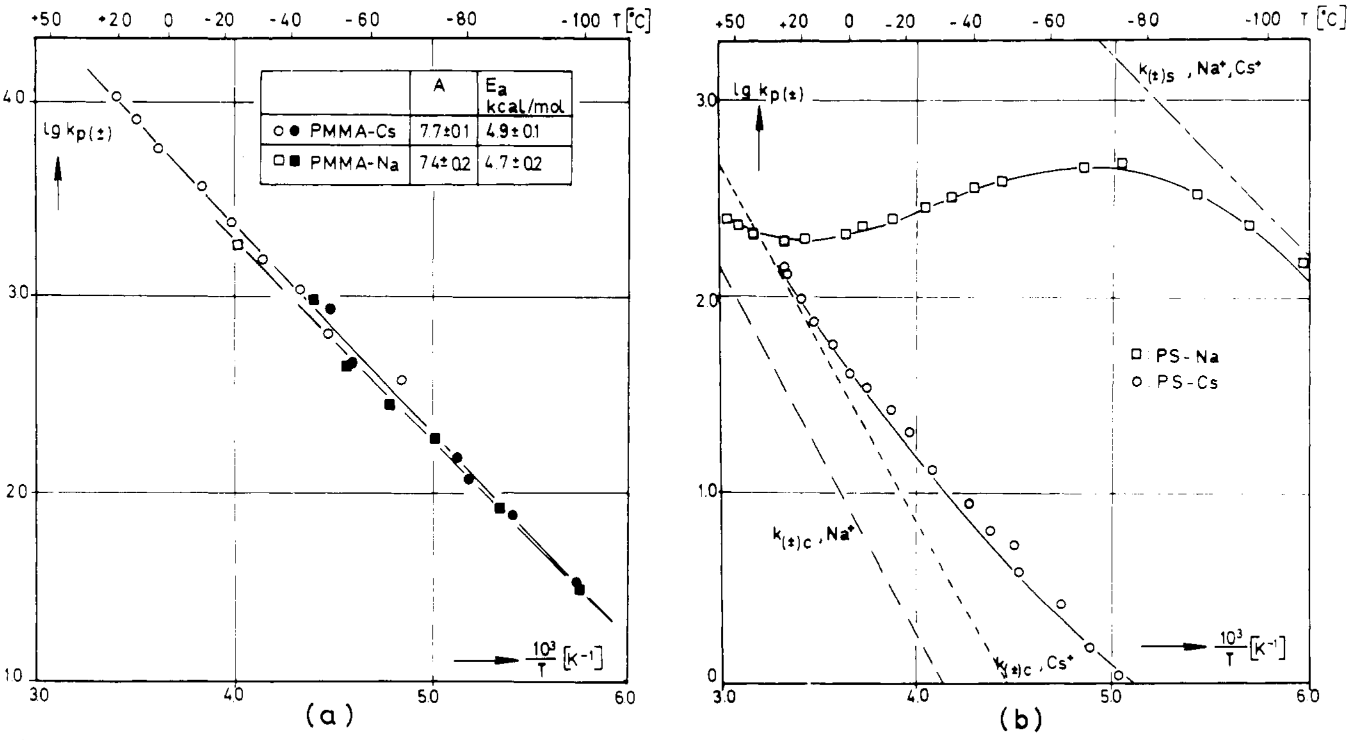

Figure 4. Arrhenius plots of the rate constants of the anionic polymerization of vinyl monomers in THF as the solvent and with Na^+ or Cs^+ as the counterion. (a) MMA: (●, ○, □) this work, (□) ref 13. Results from measurements in the flow tube (open symbols) and in the automatically controlled stirred reactor (filled symbols), averaged values from Table I and II. (b) Styrene: (○) Cs^+ as the counterion (ref 8); (□) Na^+ as the counterion (ref 7).

Table I
Rate Constants for the Anionic Polymerization of MMA Obtained in the Flow Tube

$\bar{T}_{\text{eff}}$, °C	$[M]_0$, mol/L	10^3c^*,[a] mol/L	$k_\pm$, L/mol·s
Initiator:	monofunctional α-methylstyrylsodium		
−24.5	0.32	0.73	1820
	Initiator:	cumyl cesium	
+20.5	0.25	0.20	10200
+13.4	0.25	0.63–0.59	7310
+12.4	0.26	0.27–0.26	8230
+3.9	0.26	0.74–0.70	5590
−9.7	0.33	1.11–1.02	2650
−10.1	0.26	0.59–0.37	3950
−11.5	0.19	0.39–0.37	4040
−11.6	0.19	0.69–0.56	3340
−12.4	0.51	0.76–0.54	2690
−12.8	0.24	0.20	3310
−19.0	0.49	1.35–1.29	2100
−21.8	0.52	0.44–0.34	2350
−21.8	0.24	0.23	2440
−22.1	0.26	1.21–1.15	1660
−29.7	0.48	0.45–0.43	1440
−30.7	0.24	0.24	1730
−31.6	0.51	0.70–0.50	1380
−39.2	0.49	0.53–0.33	1020
−39.8	0.24	0.26	1160
−46.3	0.50	0.36–0.33	666
−46.5	0.50	0.94–0.82	607
−46.6	0.52	0.88–0.47	521
−50.2	0.51	0.32–0.08	745
−52.4	0.50	1.23–1.16	340
−53.6	0.50	0.56–0.35	421
−53.8	0.48	0.31–0.25	665
−58.5	0.50	0.58–0.54	282

[a] The decrease of c^* is due to initiator decomposition between the single runs to obtain the time–conversion curve. The decomposition products, however, do not seem to affect the polymerization.

Table II
Rate Constants for the Anionic Polymerization of MMA with Cumylcesium as an Initiator Obtained in the Stirred Reactor[a]

T_{eff}, °C	$[M]_0$, mol/L	10^3c^*, mol/L	$k_\pm$, L/mol·s
−51.0	0.25	0.17	860
−55.4	0.23	0.09	441
−67.4	0.19	0.15	374
−77.6	0.26	0.14	150
−78.6	0.23	0.10	149
−80.2	0.23	0.72	114
−87.5	0.18	0.64	70.5
−89.2	0.24	0.06	78.9
−97.3	0.18	0.53	32.7
−99.8	0.24	0.08	35.3

[a] For experimental results with Na^+ as a counterion, cf. ref 13.

These results can be explained by the high solvating power of the ester group of the polymer chain. Consequently, we assume that the counterions of the carbanionic species are solvated intramolecularly by the penultimate or the antepenultimate ester group of the polymer chain as suggested earlier.[10]

Additional solvation by solvent molecules (THF) and an equilibrium between both structures is admitted. Differences in the propagation rate constants of both complexes have to be within the limits of experimental error.

If the counterion is fixed to the chain end in a chelate-like solvation complex the very low dissociation constants observed are plausible. On the other hand, the solvation of the counterion by an ester group of the same polymer chain weakens the electrostatic interaction between carbanion and counterion; thus the active species resembles a solvent-separated ion pair rather than a contact ion pair. Consequently, the counterion is of negligible influence on the rate constants.

The results of tacticity measurements are in accord with these considerations. They are discussed in detail elsewhere.[10]

It should be mentioned that Bovey et al.[19] postulated a similar model for the system PMMA–Li/THF on the basis of NMR measurements. According to Szwarc et al.[20] and Sigwalt et al.[21] also in the anionic polymerization of 2-vinyl pyridine, intramolecular solvation of the counterion by the nitrogen atoms of the pyridyl rings is very likely to occur.

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(23) Detailed kinetic results obtained at low temperatures with this initiator are given elsewhere.[13]
(24) Supplied by Röhm GmbH, Darmstadt.
(25) Supplied by BASF AG, Ludwigshafen.
(26) The linear relationship between $\bar{P}_n$ (in contrast to $P_{\max}$) and conversion is not affected by termination reactions, as long as the number of chains remains constant.
(27) Calculated from the results of the present work in conjunction with the values given in ref 13.