Macromolecules **1997,** *30,* 1869−1874

Kinetic Investigation on Metal Free Anionic Polymerization of Methyl Methacrylate Using Tetraphenylphosphonium as the Counterion in Tetrahydrofuran

D. Baskaran[†] and Axel H. E. Müller*

Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany

Received September 26, 1996; Revised Manuscript Received January 29, 1997[⊗]

ABSTRACT: The anionic polymerization of methyl methacrylate using tetraphenylphosphonium triphenylmethanide as an initiator proceeds in a living manner even at room temperature. The rate constants of propagation were measured between −20 and +20 °C using a flow tube reactor. At 0 °C the reaction half-lives range from 0.3 to 1 s. The polymerization follows first-order kinetics with respect to monomer conversion (with a short induction period) and shows a linear dependence of the number-average degree of polymerization on conversion with high initiator efficiencies and narrow molecular weight distributions ($M_w/M_n < 1.1$). The dependence of the measured rate constants on the active center concentration is consistent with the coexistence of ion pairs and free ions. The Arrhenius parameters obtained in the temperature range from −20 °C to +20 °C (activation energy, $E_a = 28$ kJ mol^{-1} and frequency exponent, $\log A = 7.9$) are similar to those for the Li$^+$ cation. The determined rate constants for the ion pairs are 1−2 orders of magnitude smaller than those expected for such a large cation, indicating a large fraction of dormant species. NMR and quantum-mechanical studies of a model compound confirm the presence of a dormant ylide in equilibrium with a small amount of enolate ion pairs.

Introduction

In recent years considerable efforts have been made to polymerize alkyl (meth)acrylates at a relatively high temperature keeping all advantages of a living polymerization. The basic problem associated with alkyl (meth)acrylates is the presence of the polar ester group that plays a significant role in propagation and also in side reactions during the polymerization. Numerous kinetic and mechanistic studies revealed the optimum conditions for the polymerization of methyl methacrylate that generally include the use of bulky initiators in order to prevent the initiator destruction by reaction with the carbonyl group of monomer, polar solvent, and low temperature (<−60 °C).

The effect of cation in the anionic polymerization of methacrylates and other monomers is well-documented.[1] It was shown that both free anions and ion pairs contribute to propagation. The fraction as well as the propagation rate constants of ion pairs decrease with decreasing ionic radius, indicating that these ion pairs are (peripherally solvated) contact ion pairs. The degree of termination (as measured by the ratio of rate constants of termination and propagation, k_t/k_p) decreases from Li$^+$ to Cs$^+$.[2] Another problem is the tendency of ester enolates to aggregate to dimers or tetramers. In some cases the slow exchange between aggregated and nonaggregated ion pairs causes a considerable broadening of the molecular weight distribution (MWD).[3]

Two routes have been followed in order to overcome termination and aggregation. Various σ- and μ-type ligands, such as crown ethers,[4] cryptands,[5] pyridine,[6] alkali metal alkoxides,[7,8] halides,[9] and alkoxyalkoxides,[10] as well as aluminum alkyls,[11,12] have been used in order to stabilize the active centers. On the other hand, the chemical nature of the cation itself was varied by the use of metal-free initiators.

Using silyl ketene acetal end groups (which formally can be seen as trimethylsilyl enolates), group transfer polymerization (GTP) provides the unique technique to prepare methacrylates at ambient or even at higher temperatures without losing the living character.[13] However, GTP fails to polymerize nonpolar monomers. Thus, the synthesis of corresponding block copolymers via sequential monomer addition is impossible. Moreover, polymerizations of acrylates and methacrylates need strongly different solvent/catalyst systems, preventing the facile synthesis of acrylate−methacrylate block copolymers.

Reetz et al.[14,15] used tetrabutylammonium thiolates and malonates as initiators for the polymerization of *n*-butyl acrylate. Subsequently, Sivaram et al.[16] have used functional metal-free initiators for the polymerization of acrylonitrile and alkyl acrylates. Although the preliminary results published by these authors were promising, the difficulties associated with the preparation of ammonium salts at a good level of purity still exist. Preliminary kinetic results in our laboratory showed that these polymerizations have considerable induction periods, nonlinear time−conversion plots, and broader molecular weight distributions than reported before.[17] Results obtained in various laboratories indicate that ammonium salts are less suitable for the polymerization of methacrylates, partially due to Hoffmann elimination between the ester enolate anion and the NBu$_4$ cation.[18,19] Bidinger and Quirk[20] used the Bu$_4$N$^+$ salt of 9-methylfluorene as an initiator for the polymerization of MMA in THF at ambient temperatures. At very low initiator concentrations they obtained a low yield (24%) of PMMA with a broad MWD ($M_w/M_n = 2.16$). Recent studies of MMA polymerization using the *n*-Bu$_4$N$^+$ salt of fluorenyl and 9-ethylfluorenyl as an initiator show that a large fraction of the initiator does not take part in the polymerization.[21,22]

Recently, Zagala and Hogen-Esch[23] have reported the synthesis of PMMA with a narrow molecular weight distribution at ambient temperatures initiated by tetraphenylphosphonium triphenylmethanide in THF at ambient temperature. We now present the results of a kinetic investigation on the anionic polymerization of

---

[†] Permanent address: National Chemical Laboratory, Division of Polymer Chemistry, Pune 411008, India.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

S0024-9297(96)01430-1 CCC: $14.00

Table 1. Kinetic Results of MMA Polymerization Initiated by Tetraphenylphosphonium Salts in THF Using a Flow-Tube Reactor, $[MMA]_0 = 0.2$ mol/L

run	$10^3[I]_0$, mol/L	T_{eff}, °C	t_{max},[a] s	$x_{p,max}$[b]	$P_{n,GPC}$ at $x_{p,max}$[c]	M_w/M_n at $x_{p,max}$	f[d]	$[P^*]$[e], mol/L	k_{app}, s^{-1}	$\bar{k}_p$, L mol^{-1} s^{-1}
					Initiator Ph_3CPPh_4					
1	9.95	0	1.40	1	24.4	1.04	0.90	8.96	2.20	246
2	5.30	0	1.85	1	43.4	1.04	0.96	5.09	1.46	287
3	2.37	0	1.98	0.78	76.5	1.07	0.75	1.78	0.608	342
4	1.42	0	2.40	0.80	168.0	1.06	0.76	1.08	0.516	478
5	5.20	−20	2.90	1	32.6	1.08	1	5.20	0.642	123
6	5.20	+20	1.00	1	37.6	1.05	0.93	4.84	3.75	775
					Initiator $(MIB)PPh_4$					
7	5.10	+20	3.42	0.19	36.5	2.1	0.20[f]	1.0	0.059	59

[a] Longest reaction time. [b] Conversion obtained at t_{max}. [c] $P_{n,GPC} = (M_{n,GPC} - M_{Init})/M_{Mon}$ where M_{Init} and M_{Mon} are the molecular weights of the initator fragment (Ph_3CH or (MIB)H) and of the monomer, respectively. [d] Initiator efficiency, $f = P_{n,th}/P_{n,GPC}$ from the ratio of $[M]_0/[I]_0$ and slope of the plot of $P_{n,GPC}$ vs conversion. [e] $[P^*] = f[I]_0$. [f] Determined as $P_{n,th}/P_{n,GPC}$ at $x_{p,max}$.

MMA using the tetraphenylphosphonium cation in THF between −20 and +20 °C.

Experimental Section

Materials. Methyl methacrylate (MMA, Röhm GmbH, Darmstadt) was first stirred over CaH_2 for 12 h and then fractionated in the presence of stabilizer Irganox 1010 (Ciba-Geigy) under reduced pressure over a 1 m column filled with Sulzer packing. The distillate was collected over fresh CaH_2, degassed and stirred for 12 h at 0 °C, and stored at −20 °C. This prepurified MMA was redistilled just before polymerization. No impurities were detectable by GC.

Triphenylmethane (Aldrich) was dried under high vacuum for 2 days at room temperature (RT). The precursor initiator (triphenylmethyl)potassium ($Ph_3C^-K^+$) was prepared under vacuum in THF using potassium mirrors and triphenylmethane at room temperature. The excess metal was filtered off, and the concentration of the resulting (triphenylmethyl)potassium solution was determined using Gilman double titration.[24] Methyl sodio- or lithioisobutyrate was obtained from Dr. L. Lochmann (Prague). Tetraphenylphosphonium chloride (Ph_4PCl, Fluka) was dried under dynamic high vacuum at 90 °C for 15 h. Tetraphenylphosphonium triphenylmethanide ($Ph_3C^-P^+Ph_4$) and α-tetraphenylphosphonium methylisobutyrate ($(MIB)PPh_4$) were prepared *in situ* in THF at −78 °C by cation exchange reaction of the corresponding metal precursor with tetraphenylphosphonium chloride. The formation of $Ph_3C^-P^+Ph_4$ and $(MIB)PPh_4$ are characterized by the change of the red color of the $Ph_3C^-K^+$ salt solution ($\lambda_{max} = 502$ nm) into a deep maroon color ($\lambda_{max} = 510$ nm) and by the change of the colorless solution of MIB−Na or MIB−Li into the orange-red ($\lambda_{max} = 415$ nm) of the phosphonium salt, respectively. *n*-Octane was distilled over Na−K alloy and used as an internal standard for GC. Fractionated THF was purified by refluxing over K metal and stored over fresh Na−K alloy in a vacuum line.

Batch Experiments. The anionic polymerization of MMA initiated by $(MIB)PPh_4$ was carried out in a flamed glass reactor under an argon atmosphere. To the orange-red tetraphenylphosphonium methylisobutyrate initiator solution was transferred the desired amount of THF. The initiator solution was brought to the particular reaction temperature, and then the required amount of MMA (50% v/v THF solution) was added within 2−5 s with pure N_2 pressure. The color of the polymerization solution remained unchanged. Polymerization was continued for a few minutes and terminated with methanol containing a small amount of dilute HCl.

Kinetic Experiments. All the experiments were carried out in a specially designed flow-tube reactor. The monomer and initiator solution were precooled and mixed efficiently within less than 1 ms in a mixing jet and allowed to pass through a capillary tube (1 mm inner diameter). The reaction mixture was terminated in a quenching jet at the end of the capillary tube with methanol containing a small amount of acetic acid. The temperatures of the mixing jet, T_m, and quenching jet, T_q, were determined using thermocouples. The particular residence time ($5 \text{ ms} \le \tau \le 5 \text{ s}$) of the polymerization solution was achieved by changing the flow rate and the capillary tube length ($4 \text{ cm} \le l \le 6 \text{ m}$). In all runs the flow rate was carefully chosen in order to maintain turbulent flow during the polymerization with a characteristic Reynolds number, Re >3000, at polymerization temperature.

Experiments were carried out at mixing jet temperatures, $T_m = -20, -10, 0,$ and 20 °C. Since the polymerizations are very fast, heat transfer through the walls of the tube is negligible, leading to a nearly adiabatic behavior. This leads to a temperature rise, ΔT, between 2 and 10 K. Thus, the effective temperature was determined using the equation[25]

$$T_{eff} \approx T_m + 0.55\Delta T$$

For all reaction times, t, conversions corresponding to T_{eff} were recalculated to T_m using the equation

$$\left(\frac{\ln([M]_0/[M]_t)}{t}\right)_{T_m} = \left(\frac{\ln([M]_0/[M]_t)}{t}\right)_{T_{eff}} + \frac{E_a}{R}\left(\frac{1}{T_{eff}} - \frac{1}{T_m}\right)$$

In a first approximation, the activation energy, E_a, was obtained from an Arrhenius plot of the uncorrected data. In further cycles, new values of E_a were determined until self-consistency was reached.

The slope of the first-order time−conversion plot obtained from the corrected conversions was taken as the apparent rate constant, k_{app}, as shown in Table 1.

Monomer conversion was determined by GC using *n*-octane as an internal standard. PMMA was recovered by stripping off the solvent, and the residue was dissolved in CH_2Cl_2. This was washed twice with little distilled water in order to remove tetraphenylphosphonium chloride, once with $NaHCO_2$ solution and once with NaCl solution. The organic layer was dried over anhydrous $MgSO_4$ and filtered. After evaporation of the solvent, the polymer was dissolved in benzene and freeze-dried. Molecular weights and MWD were determined using GPC equipped with two UV detectors with variable wavelength, an RI detector, and two 60 cm 5 μ PSS-SDV gel columns (1 × 100 Å, 1 × linear: 10^2−10^5 Å) with THF as eluent at room temperature. The calibration was performed using PMMA standards.

Results and Discussion

The results of kinetic experiments of the anionic polymerization of MMA using $Ph_3C^-P^+Ph_4$ as an initiator at different temperatures, and at different initial initiator concentrations, $[I]_0$, are summarized in Table 1.

First, a series of experiments was performed at 0 °C with a variation of initiator concentration in the range $1.42 \times 10^{-3} \le [I]_0/(\text{mol/L}) \le 9.95 \times 10^{-3}$. The first-order time−conversion plots (Figure 1) are approximately linear; however, a slight upward curvature cannot be

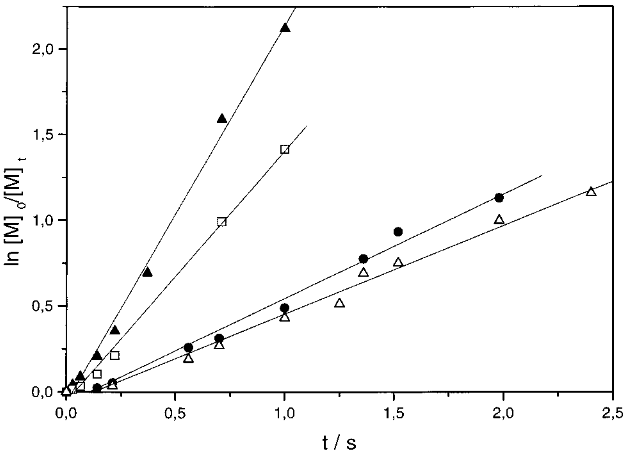


Figure 1. First-order time–conversion plots of the anionic polymerization of MMA using the P^+Ph_4 counterion at various initiator concentrations in THF at 0 °C. $[M]_0 = 0.2$ mol/L. $[I]_0$: (▲) 9.95×10^{-3}, (□) 5.3×10^{-3}, (●) 2.37×10^{-3}, and (△)1.42×10^{-3} mol/L.

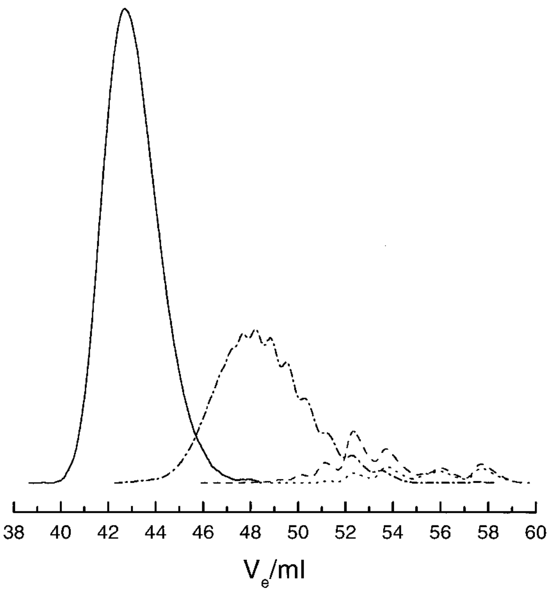


Figure 2. GPC eluograms (RI) at different conversions of the polymerization of MMA using the P^+Ph_4 counterion in THF (Table 1, run 1): (···) conversion, $x_p = 0.04$, $P_n = 1.4$; (- - -) $x_p = 0.085$, $P_n = 2.3$; (– · –) $x_p = 0.32$, $P_n = 8.3$; (—) $x_p = 1$, $P_n = 24.4$). The signals of the oligomers are not corrected for refractive index differences.

excluded. A short induction period (0.03–0.1 s, depending on initiator concentration) is always observed. The induction periods might indicate a slow initiation step compared to propagation or a change in the structure of the active chain end in the initial stage. The reaction is very fast with half-lives ranging from 0.3 to 1 s. The lack of a downward curvature in the first-order time–conversion plots indicates the absence of termination reactions. The slope of the first-order time–conversion plot was taken as the apparent rate constant, k_{app}.

The obtained polymers exhibit narrow molecular weight distributions, indicating that the observed induction periods are not due to slow initiation ($M_w/M_n < 1.1$) (Table 1). The GPC eluograms of PMMA obtained at various times during the polymerization (Figure 2) show that the molecular weight increases with conversion and no oligomers are detected at higher conversion. The linearity of the plot of the number-average degree of polymerization, P_n, versus conversion, x_p (Figure 3), does not give any indication of slow initiation or of transfer reactions. However, at low concentrations of initiator, $[I]_0 \leq 2.3 \times 10^{-3}$ mol/L, $P_{n,GPC}$ deviates from the theoretical line, indicating a decrease of initiator efficiency, *f*, from unity to 0.75. This may be due to slow decomposition of initiator between the experiments. It was confirmed by UV absorption measurements that the initiator decomposes with a half-life of ≈10 min at room temperature. Thus slow decomposition at the storage temperature of −78 °C is not improbable. The active center concentration, $[P^*] = f[I]_0$, was determined using the initiator efficiencies, *f*, calculated from the slope of the plot of P_n versus conversion and the ratios of initial monomer to initiator concentrations. The polydispersity index decreases with conversion in all experiments (Figure 4). Thus, if an equilibrium between species of different activity exists, the rate of exchange must be large compared to the rate of propagation.[26]

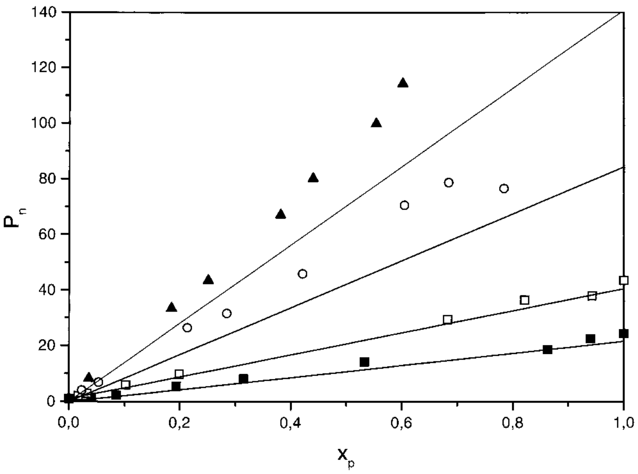


Figure 3. Dependence of the number-average degree of polymerization, P_n, on conversion, x_p, at 0 °C for the anionic polymerization of MMA in THF using P^+Ph_4 as the counterion. $[M]_0 = 0.2$ mol/L. $[I]_0$: (■) 9.95×10^{-3}, (□) 5.3×10^{-3}, (○) 2.37×10^{-3}, and (▲)1.42×10^{-3} mol/L.

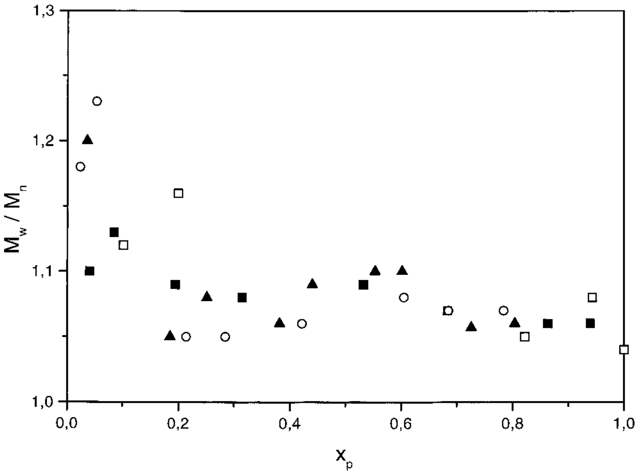


Figure 4. Dependence of the polydispersity index on conversion for the anionic polymerization of MMA using P^+Ph_4 as the counterion in THF at 0 °C. Symbols: see Figure 3.

A bilogarithamic plot of k_{app} versus the active center concentration, $[P^*]$, results in linearity with a slope of 0.72 ± 0.06 (Figure 5). The fractional order of the reaction with respect to active center concentration indicates that the active species may be involved in a dynamic equilibrium with different kinds of reactive species. Similar fractional reaction orders were observed in the anionic polymerization of MMA and nonpolar monomers using alkali counterions. They can

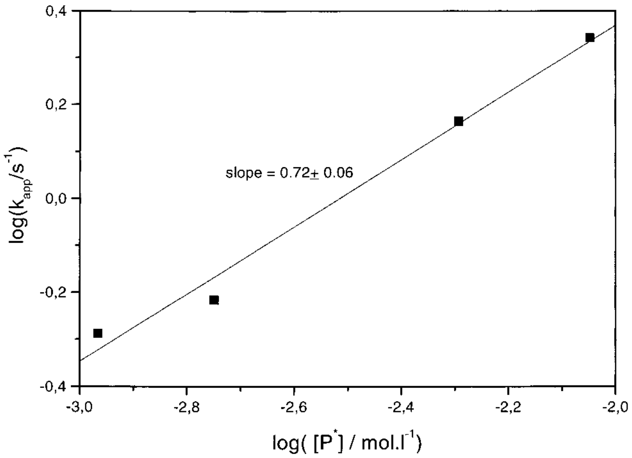


Figure 5. Bilogarithamic plot of the active center concentration, [P*], versus the apparent rate constant, k_{app}.

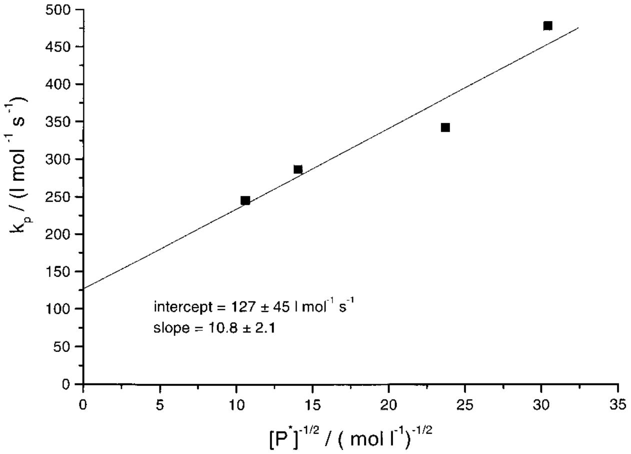


Figure 6. Dependence of the rate constants of polymerization on the concentration of active centers at 0 °C.

be either attributed to the formation of aggregated ion pairs or to dissociation into free ions. Aggregation is very unlikely for the bulky tetraphenylphosphonium counterion. Thus, the concentration dependence of the rate constants of polymerization is attributed to the coexistence of ion pairs and free ions propagating with different rate constants, $k_\pm$ and k_-, respectively. For the equilibrium between free ions and ion pairs, the overall rate constant of polymerization, $\bar{k}_p = k_{app}/[P^*]$, is given by

$$\bar{k}_p = \alpha k_- + (1 - \alpha)k_\pm = k_\pm + (k_- - k_\pm)\alpha \qquad (1)$$

where $\alpha \approx (K_D/[P^*])^{1/2}$ is the degree of dissociation and K_D is the dissociation constant. The rate constant for the polymerization via ion pairs, $k_\pm = 127 \pm 45$ L mol^{-1} s^{-1} is determined as the intercept of Figure 6. From the slope, the product $(k_- - k_\pm)K_D^{1/2} = 10.8 \pm 2.1$ is obtained.

Experiments carried out at −20 and +20 °C also have linear first-order time−conversion plots with an indication of a slight upward curvature (Figure 7). This indicates the absence of termination reactions even at +20 °C. A considerable induction period (<0.2 s) is noticed at −20 °C. A linear dependence of P_n versus conversion is again observed with initiator efficiency f = 1. The effect of temperature on the overall rate constants of propagation is seen in Table 1 (runs 2, 5, and 6). The Arrhenius plot obtained using the overall values, $\bar{k}_p$, at three temperatures results in linearity with an activation energy, $E_a = 28.3 \pm 2.5$ kJ mol^{-1}, and a frequency exponent, log $A = 7.9 \pm 0.5$ (Figure 8). Surprisingly, the rate constants and activation parameters are comparable to the ones reported for the considerably smaller Li$^+$ counterion in THF[27] ($E_a = 24$ kJ mol^{-1} and log A = 7.4). Quantum-mechanical calculations[28] indicate that the interionic distance, a, between the enolate anion and the P$^+$Ph$_4$ counterion is 4.1 Å, which is between that with cryptated sodium (Na$^+$,222; a = 6.1 Å) and with Cs$^+$ counterion (a = 3.3 Å). However, the obtained rate constants with the P$^+$-Ph$_4$ counterion are about 2 orders of magnitude lower than expected for such a bulky cation, especially if we use $k_\pm$ instead of $\bar{k}_p$ for the comparison. This indicates that only a fraction of the chain ends takes part in the polymerization whereas the majority is in a dormant state. The high initiator efficiencies and the narrow MWD of the polymers show that the active species must be in a fast dynamic equilibrium with dormant species.

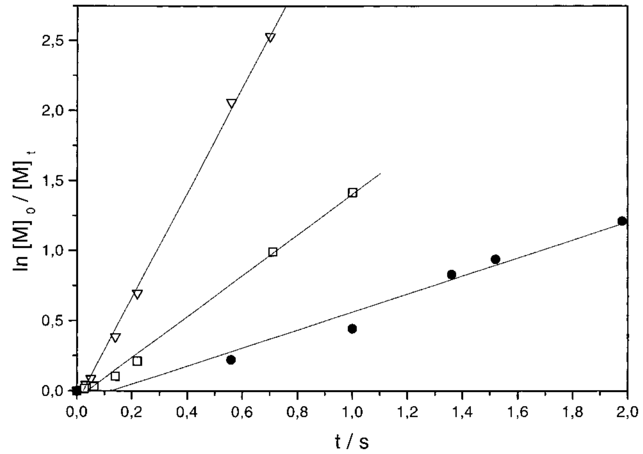


Figure 7. First-order time−conversion plots at −20, 0, and +20 °C for the anionic polymerization of MMA in THF using P$^+$Ph$_4$ as the counterion (Table 1, runs 2, 5, and 6): (▽) T = +20 °C; (□) T = 0 °C; (●) T = −20 °C.

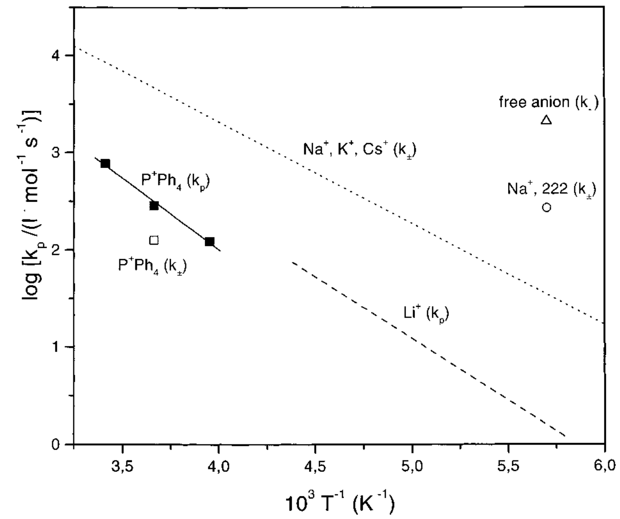
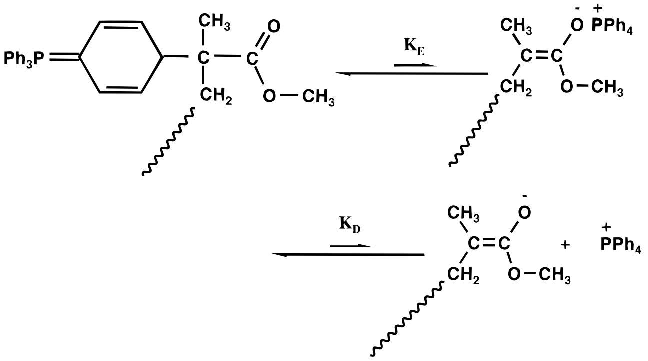


Figure 8. Arrhenius plot of the propagation rate constants in the anionic polymerization of MMA in THF with the P$^+$Ph$_4$ counterion and the reported values[5,27,33] for other counterions and the free anion.

The THF solution of the model compound of the growing PMMA chain end, i.e., α-tetraphenylphosphonium methylisobutyrate ((MIB)PPh$_4$), shows the same orange-red color as the PMMA chain end with the PPh$_4$ counterion, indicating a similar structure. It has a UV/vis absorption at $\lambda_{max} = 415$ nm ($\epsilon \approx 1.7$ L mol^{-1} cm^{-1}),

Scheme 1. Dynamic Equilibrium between Ylide, Enolate Ion Pair, and Enolate Anion



which is much higher than that of normal ester enolates ($\lambda_{max} \approx 230$ nm). Detailed NMR, IR, and quantum-mechanical studies of this model compound[28,29] revealed the existence of a phosphor ylide as the major (dormant) species in equilibrium with (active) phosphonium enolate (Scheme 1).

As a consequence of the existence of a large fraction of dormant species, we must correct eq 1 for the fraction of enolate ion pairs and anions,

$$\alpha_E = \frac{[P_\pm] + [P_-]}{[P^*]}$$

leading to

$$\bar{k}_p = k_\pm\alpha_E + (k_- - k_\pm)\alpha\alpha_E = \alpha_E k_\pm + (k_- - k_\pm)\left(\frac{\alpha_E K_D}{[P^*]}\right)^{1/2} \quad (2)$$

where the degree of dissociation is $\alpha \approx (K_D/\alpha_E[P^*])^{1/2}$ for $\alpha << 1$. Thus, we obtain for the slope of the plot of $\bar{k}_p$ versus $[P^*]^{-1/2}$:

$$\text{slope} = (k_- - k_\pm)\sqrt{\alpha_E K_D} \quad (3)$$

The dissociation constant can be estimated using the Fuoss equation:[30]

$$K_D = \frac{3000}{4\pi N_A a^3}\exp\left(\frac{e_0^2}{aDkT}\right) \approx 10^{-7}\ \text{L mol}^{-1} \quad (4)$$

with the dielectric constant of THF $D = 8.24$, temperature $T = 273$ K, and the interionic distance obtained from quantum-mechanical calculations[28] $a = 4.1$ Å. A rough estimate of $k_\pm \approx 10^4$ L mol^{-1} s^{-1} (between Cs$^+$ and the extrapolated value for Na$^+$,222) leads to a fraction of enolate, $\alpha_E \approx 10^{-2}$. From eq 3, with a slope of 10.8 and $K_D \approx 10^{-7}$ L mol^{-1} we obtain $k_- \approx 6 \times 10^5$ L mol^{-1} s^{-1}, which is in the order of magnitude of the value extrapolated for the anion from Figure 8, assuming similar activation energies for all counterions and the free anion. However, for $[I]_0 = 10^{-3}$ we obtain $\alpha \approx 0.1$. Thus the approximation $\alpha << 1$ is no longer fulfilled. In that case α_E also becomes concentration-dependent, which explains why the reaction order is higher than the expected value of 0.5. The mathematical treatment of a similar three-state system (cationic polymerization with covalent species, ions, and ion pairs) including MWD has been given elsewhere.[31]

A kinetic experiment of MMA polymerization performed at +20 °C using (MIB)PPh$_4$ as an initiator in the flow-tube reactor (Figure 9) shows a large induction period (0.5 s) compared to the one obtained using the triphenylmethyl anion (0.01 s). The obtained polymer has a broad molecular weight distribution, $M_w/M_n = 2.1$. A plot of the number-average degree of polymerization, P_n, versus conversion (Figure 10) shows a strong downward curvature, indicating slow initiation. The initiator efficiency, as determined from the last point of that plot, is low ($f = 20\%$). These results may be explained by a slower isomerization of ylides to ion pairs in the initiator as compared to the living polymers. This is confirmed by NOE kinetic experiments.[32]

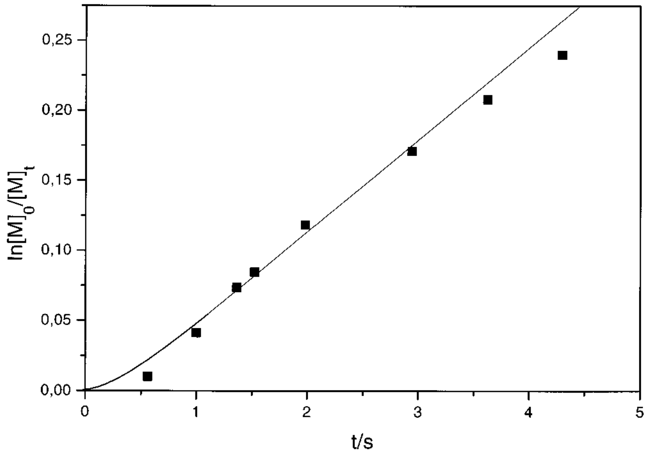


Figure 9. First-order time–conversion plot for the anionic polymerization of MMA using α-tetraphenylphosphonium methylisobutyrate as the initiator in THF at +20 °C.

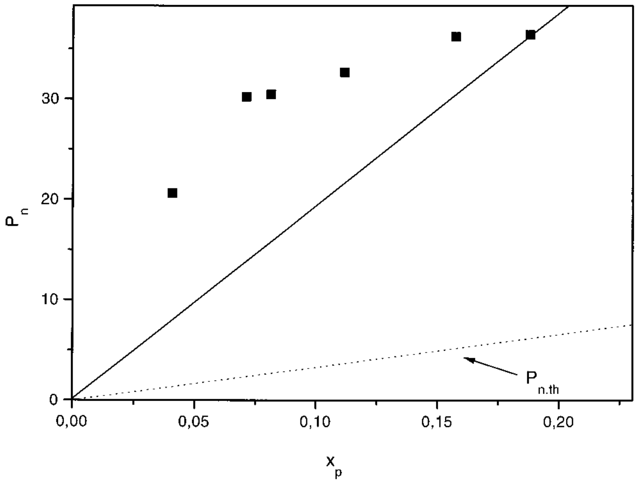


Figure 10. Dependence of the number-average degree of polymerization, P_n, on conversion, x_p, using α-tetraphenylphosphonium methylisobutyrate as the initiator in THF at +20 °C.

Table 2. Polymerization of MMA in a Batch Reactor Using α-Tetraphenylphosphonium Methylisobutyrate as an Initiator in THF (Conversions ≥95% in All Cases)

run	$10^3[I]_0$, mol/L	$[M]_0$, mol/L	T, °C	$P_{n,th}$	$P_{n,GPC}$	M_w/M_n	f
1	1.30	0.48	0	370	722	1.77	0.51
2	0.97	0.33	0	344	620	2.10	0.55
3	1.53	0.42	−78	275	1118	1.22	0.24
4	1.50	0.31	−78	206	941	1.20	0.21

The results of batch experiments carried out using (MIB)PPh$_4$ as initiator at 0 and −78 °C are shown in Table 2. The polymers obtained exhibit broad molecular weight distributions at 0 °C which narrow at −78 °C (M_w/M_n < 1.2). The initiator efficiencies are <50% at 0 °C and only <20 % at −78 °C. It was also noticed at −78 °C that the red color of the living polymerization solution did not disappear upon addition of methanol, indicating a very slow isomerization of dormant ylide species to ion pairs at that temperature.

Acknowledgment. This work is supported by the German *Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie* and *BASF AG*, Ludwigshafen. D.B. acknowledges a grant from the *German Academic Exchange Service (DAAD).*

References and Notes

(1) Müller, A. H. E. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon: Oxford, U.K., 1988; p 387.
(2) Warmkessel, J.; Kim, J.; Quirk, R.; Brittain, W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 589.
(3) Kunkel, D.; Müller, A. H. E.; Lochmann, L.; Janata, M. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 315.
(4) Varshney, S. K.; Jérôme, R.; Bayard, P.; Jacobs, C.; Fayt, R.; Teyssié, P. *Macromolecules* **1992**, *25*, 4457.
(5) Johann, C.; Müller, A. H. E. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 687.
(6) Gia, H.-B.; McGrath, J. E. In *Recent Advances in Anionic Polymerization*; Hogen-Esch, T., Smid, J., Eds.; Elsevier: New York, 1987; p 173.
(7) Lochmann, L.; Kolarik, J.; Doskocilova, D.; Vozka, S.; Trekoval, J. *J. Polym. Sci., Polym. Chem. Ed.* **1979**; *17*, 1727.
(8) Lochmann, L.; Müller, A. H. E. *Prepr., IUPAC Intl. Symp. on Macromol., Merseburg* **1987**, *1*, 78.
(9) Varshney, S. K.; Hautekeer, J. P.; Fayt, R.; Jérôme, R.; Teyssié, P. *Macromolecules* **1990**, *23*, 2618.
(10) Wang, J.-S.; Jérôme, R.; Bayard, P.; Patin, M.; Teyssié, P. *Macromolecules* **1994**, *27*, 4635.
(11) Kitayama, T.; Shinozaki, T.; Sakamoto, T.; Yamamoto, M.; Hatada, K. *Makromol. Chem., Suppl.* **1989**, *15*, 167.
(12) Haddleton, D. M.; Muir, A. V. G.; O'Donnell, J. P.; Richards, S. N.; Twose, D. L. *Macromol. Symp.* **1995**, *91*, 91.
(13) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.
(14) Reetz, M. T.; Ostarek, R. *J. Chem. Soc., Chem. Commun.* **1988**, 213.
(15) Reetz, M. T. *Angew. Chem.* **1988**, *100*, 1026.
(16) Raj, D. J. A.; Wadgaonkar, P. P.; Sivaram, S. *Macromolecules* **1992**, *25*, 2774.
(17) Janata, M.; Müller, A. H. E. Unpublished results.
(18) Bandermann, F. Private communication.
(19) Brittain, W. B. Private communication.
(20) Quirk, R. P.; Bidinger, G. P. *Polym. Bull. (Berlin)* **1989**, *22*, 63.
(21) Baskaran, D.; Sivaram, S. Unpublished results.
(22) Zagala, A. P.; Hogen-Esch, T. E. Unpublished results.
(23) Zagala, A. P.; Hogen-Esch, T. E. *Macromolecules* **1996**, *29*, 3038.
(24) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447.
(25) Löhr, G.; Schmitt, B. J.; Schulz, G. V. *Z. Phys. Chem. (Frankfurt am Main)* **1972**, *78*, 177.
(26) Müller, A. H. E.; Zhuang, R.; Yan, D. Y.; Litvinenko, G. *Macromolecules* **1995**, *28*, 4326.
(27) Jeuck, H.; Müller, A. H. E. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 121.
(28) Yakimanski, A.; Müller, A. H. E.; Weiss, H. Manuscript in preparation.
(29) Baskaran, D.; Müller, A. H. E.; Kolshorn, H.; Zagala, A. P.; Hogen-Esch, T. E. *Angew. Chem.*, submitted for publication.
(30) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059.
(31) Yan, D.; Dong, H.; Ye, P.; Müller, A. H. E. *Macromolecules* **1996**, *29*, 8057.
(32) Baskaran, D.; Müller, A. H. E.; Kolshorn, H.; Zagala, A. P.; Hogen-Esch, T. E. Manuscript in preparation.
(33) Kraft, R.; Müller, A. H. E.; Warzelhan, V.; Höcker, H.; Schulz, G. V. *Macromolecules* **1978**, *11*, 1095.

MA9614306