KINETICS AND MECHANISMS OF ANIONIC POLYMERIZATION OF (METH)ACRYLATES IN THE PRESENCE OF LITHIUM 2-METHOXYETHOXIDE

Andreas Maurer , Xavier Marcarian, Axel H.E. Müller

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

Bruno Vuillemin, Christophe Navarro

Elf-Atochem S.A., GRL, F-64170 Artix, France

Introduction

It has been shown by Wiles and Bywater[1] that the anionic polymerization of methyl methacrylate, MMA, initiated by 1,1 diphenylhexyllithium, DPH-Li, in pure toluene is a very slow reaction (at temperatures from -78 °C to -31 °C half-lives $0,1 \, h < t_{1/2} < 3 \, h$) leading to broad, multimodal molecular weight distributions ($20 \quad M_w/M_n \quad 80$) in the absence of any additive. The polymerization deviates from a linear first-order time-conversion plot, however a linear relationship between degree of polymerization and monomer conversion indicates the absence of transfer reactions.

Alkali alkoxides (Lochmann and Vlcek[2]) and aluminum alkyls (Hatada[3], Ballard[4] and Müller[5]) have been used as μ-type ligands in order to improve this behaviour in pure toluene. Recently, alkoxy alkoxides (**1**) were discovered by Teyssié et al.[6] as a new class of ligands. They comprise the advantages of alkoxides and Lewis bases (σ-type ligands) in one molecule. These additives allow a fast and controled anionic polymerization of methacrylates and even primary acrylates in non-polar solvents, like toluene. ^{13}C NMR measurements of mixtures of **1** (n=2, R =Me) with models of the chain end in THF and toluene indicate the formation of a 2:1 adduct.

$$n = 1, 2, \quad \quad (1)$$
$$R = Me,$$
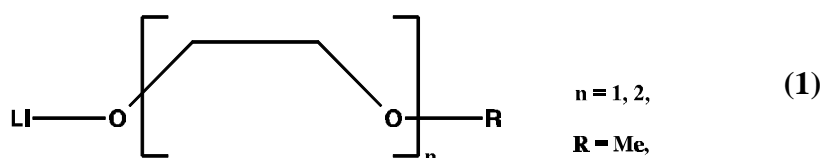
In order to gain more insight into the mechanism of polymerization with these ligands we performed kinetic experiments using DPH-Li and lithium-2-methoxy ethoxide, LiOEM, (**1;** n=1, R=Me) as a ligand in toluene at temperatures between -40 and +90 °C. Since the reactions are very fast (half-lives $t_{1/2} < 10 \, s$) they were conducted in a flow-tube reactor which allows a mixing time of less than 1 ms.

Experimental:

MMA (Röhm) is first dried over calcium hydride (CaH_2) and destilled under reduced pressure (45 mbar) in the presence of Irganox 1010 (Ciba Geigy) as non-volatile polymerization inhibitor. After degassing, it was stirred at least one night on calcium hydride cooled by an ice bath, degassed again and kept refrigerated. Then, it was destilled from CaH_2 just before use.

DPH-Li was prepared by the reaction of diphenylethylene and n-butyllithium in hexane. After stirring for two days at room temperature a

red salt precipitated. The precipitate was filtered, washed with hexane and dried at the vacuum line. ^{13}C-NMR measurements show the absence of residual 1.1-diphenylethylene.

LiOEM was prepared by the reaction of 2-methoxyethanol (Aldrich, anhydrous) and n-butyllithium (Aldrich, 1,6 molar in hexan) in toluene, under pure nitrogen , at 0°C, using diphenylethylene as colour indicator.

Kinetic Experiments:

The kinetic experiments were carried out in a specially designed flow-tube reactor. Monomer and initiator solution were mixed efficiently within less than 1 ms in a mixing jet and allowed to pass through a capillary tube (1mm inner diameter). The particular residence time ($5 \ ms \leq \tau \leq 5 \ s$) of the polymerization solution was achieved by changing the flow rate and the capillary tube length ($4 \ cm \leq l \leq 6 \ m$). Then 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 flow rate was carefully chosen in order to maintain turbulent flow during the polymerization with a characteristic Reynolds number, Re > 3000, at polymerization temperature. Monomer conversion was determined by GC using n-octane as an internal standard. Molecular weights and MWD were determined using SEC equipped with two UV detectors with variable wavelength, an RI detector, and two 60 cm PSS-SDV gel columns: 1 x 5 μ/100 Å, 1 x 5μ/linear: 10^2-10^5 Å with THF as eluent at room temperature. The calibration was performed using PMMA standards.

Results and discussion

When LiOEM is added as an additive, to the anionic polymerization of MMA, the rate of polymerization increases strongly with the ratio of additive over initiator concentration, r = [LiOEM]/[DPH-Li]$_0$. At ratios r   5, a linear first-order time-conversion plot is observed and a unimodal polymer with a narrow molecular weight distribution is obtained. No further beneficial effect was observed when r was increased to a ten fold excess. Small amounts of THF ($\leq 5\%$) did not affect the rates
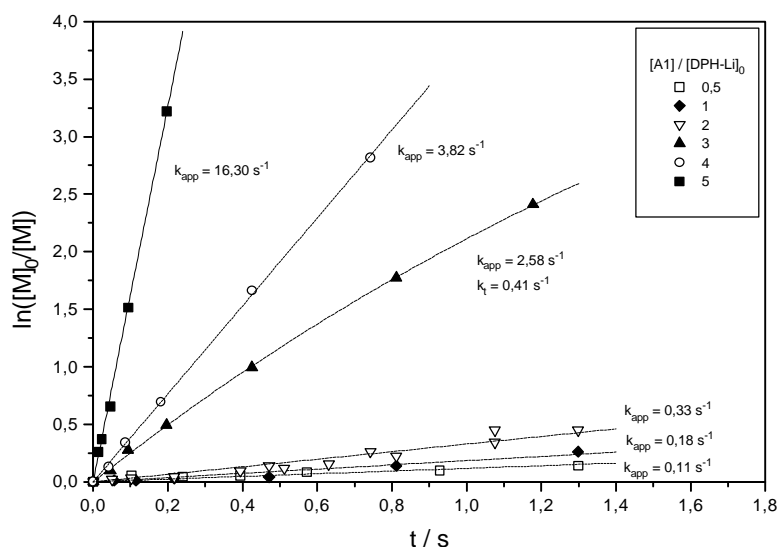
Fig.1: First-order time-conversion plot for the anionic polymerization of MMA ($[M]_0 = 0{,}2$ mol/l) initiated by DPH-Li ($[I]_0 = 10^{-3}$ mol/l) in pure toluene at 0°C in the presence of different amounts of LiOEM.

The MWD is narrow (M_w/M_n 1.1 at -40 °C $\leq$ T $\leq$ 0 °C) with a unimodal, symmetrical distribution for an almost quantitative monomer conversion.
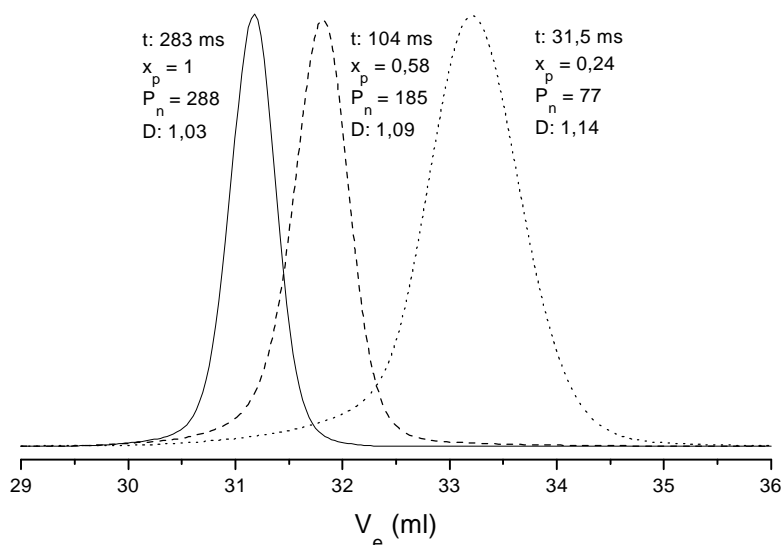

t: 283 ms
$x_p = 1$
$P_n = 288$
D: 1,03

t: 104 ms
$x_p = 0{,}58$
$P_n = 185$
D: 1,09

t: 31,5 ms
$x_p = 0{,}24$
$P_n = 77$
D: 1,14

V_e (ml)

Fig.2: SEC of obtained polymer. Experimental conditions: T = -20 °C; $[I]_0 = 10^{-3}$ mol/l ; $[M]_0 = 0{,}2$ mol/l, [LiOEM]/$[I]_0 = 5$ in a 95/5 toluene/THF solution.
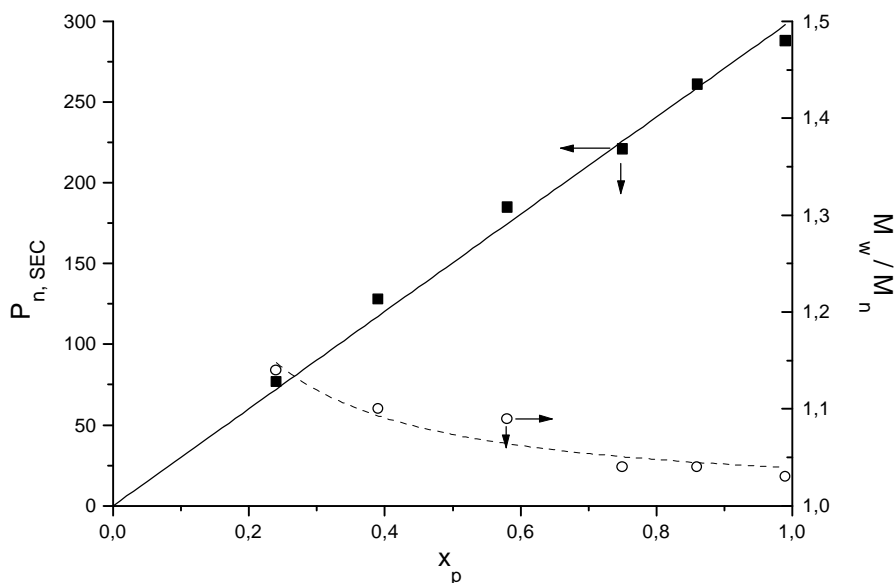

Fig.3: Degree of polymerization versus conversion for the anionic polymerization of MMA initiated by DPH-Li in the presence of [LiOEM]/$[I]_0 = 5$ in toluene/THF 95/5 mixture at -20 °C

Plots of DP_n versus conversion are linear and initiator efficiencies are high. The reaction order with respect to the active center concentration, [P*], was determined by a bi-logarithmic plot of k_{app} versus [P*] to be 1,2 at 0 °C and 1,1 at +50 °C indicating non-aggregated active centers.

While the first-order time-conversion plots are linear at lower temperatures a slight downward curvature is observed above 0 °C. MALDI-TOF-MS measurements show that this is due to „back-biting". For temperatures above 50 °C the first-order time-conversion plot can not be

fitted exactly by the kinetic equation for unimolecular termination. Therefore a two-state mechanism is assumed. The model is based on two living species $P^{(1)}$ and $P^{(2)}$ which are in equilibrium and a deactivation by unimolecular termination. Possibly, one of the two species is dormant; then the obtained $k_p^{(2)}$ has to be taken as αk_p where α is the fraction of active chain ends.
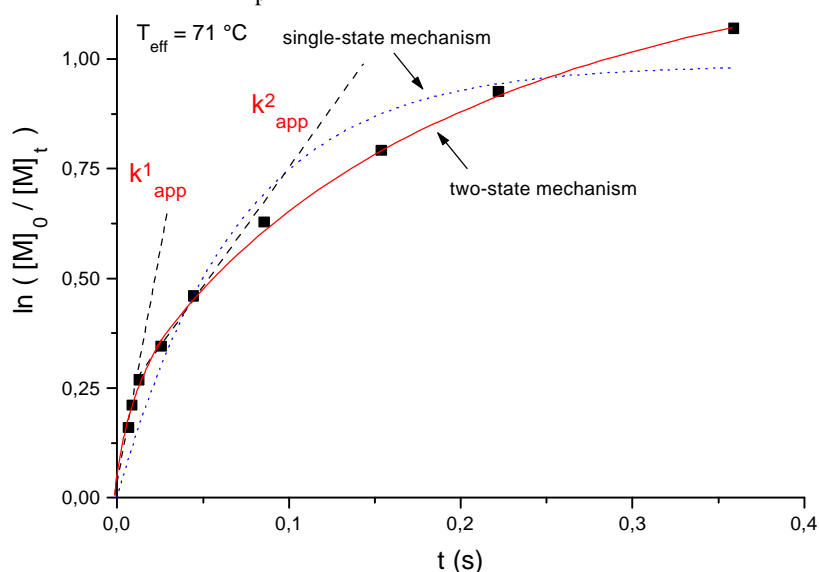

Fig.4: First-order time-conversion plot for the anionic polymerization of MMA ($[M]_0 = 0,2$ mol/l) initiated by DPH-Li ($[I]_0 = 10^{-3}$ mol/l) in the presence of $[LiOEM]/[I]_0 = 5$ in pure toluene at $T_{eff} = 71\ °C$.
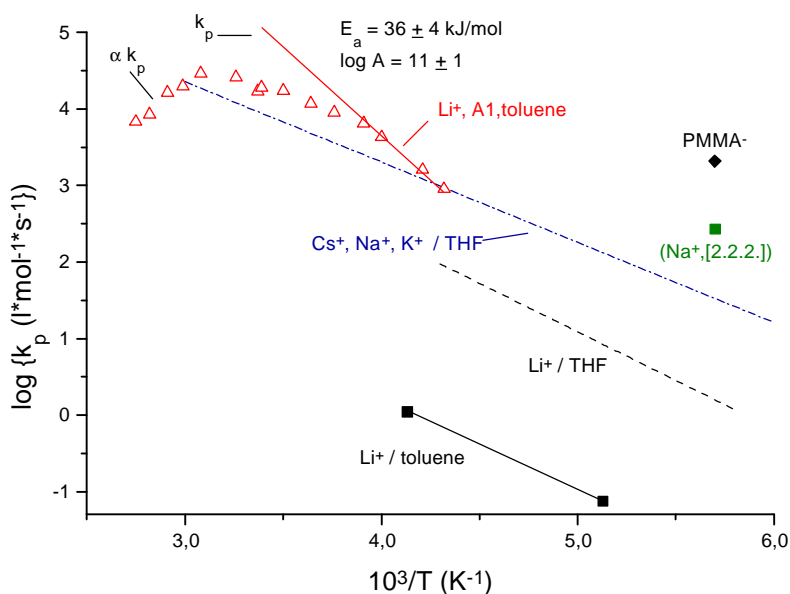

Fig.5: Arrhenius plot for rate constant of polymerization of MMA in THF and toluene using various counterions.

The rate constants of polymerization are very high ($k_p > 10^4$ l mol^{-1} s^{-1} at $0\ °$ C), corresponding to those obtained with cryptated counterions in THF. They are higher than those of lithium in toluene without additive by three orders of magnitude. This may indicate the analogous formation of "ligand-separated" ion pairs in this system. The curved Arrhenius plot is also consistent with the coexistence of different active species. The activation energy is determined to be $E_a = 36\ )\ 4$ kJ mol^{-1} and the frequency exponent, $\log A = 11$. This value is significantly higher than those obtained in THF.

Block Copolymerization of Methyl Methacrylate and n-Butyl Acrylate

In previous works it was necessary to polymerize at T   -78 °C in order to obtain a living polymerization of acrylates. Preliminary kinetic results at T = -20 °C indicate that the reaction is extremely fast ($t_{1/2}$ < 0.01 s) but can be easily controled by using the flow tube technology. Living PMMA anions, prepared as described were accordingly used to initiate n-BuA in a second mixing jet of the flow tube apparatus. The SEC results (Fig.6) show that we obtain > 95% coupling efficiency and narrow MWD of block copolymer. The effort to initiate MMA by a living n-BuA block was not successful under flow-tube reactor conditions.
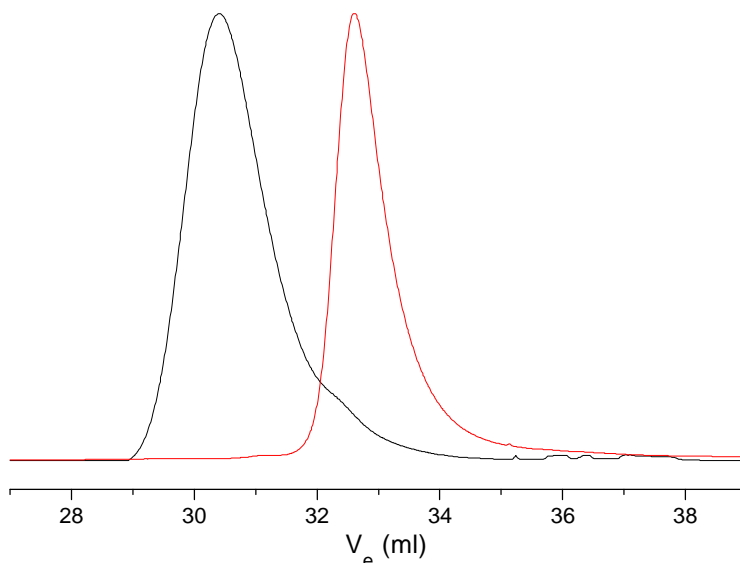

Fig.6: SEC of obtained polymer. Experimental conditions: T_{eff} = -10 °C, $[I]_0 = 10^{-3}$ mol/l [LiOEM]/$[I]_0$ = 10 in toluene (A) PMMA block $[I]_0 = 10^{-3}$ mol/l, $[MMA]_0$ = 0,05 mol/l, x_p = 1; M_n = 7500 M_w/M_n = 1,25, (B) PMMA-*b*-n-BuA $[I]0 = 6,7 \cdot 10^{-4}$, $[n\text{-BuA}]_0$ = 0,067 mol/l, M_n = 27000 M_w/M_n = 1,35;

References

1) D.M. Wiles and S. Bywater, *Trans Faraday Soc.*; **61**, 150 (1965).

2) P. Vlcek, L. Lochmann, J. Trekoval, *Collect. Czech. Chem.* **42**, 1355 (1977).

3) T. Kitayama, T. Shinozaki, T. Sakamoto, M. Yamamoto, K. Hatada, *Makromol. Chem., Supplement* **15**, 167 (1989).

4) D.G.H. Ballard, R.J. Bowles, D.M. Haddleton, S.N. Richards, R. Sellens, D.L. Twose, *Macromolecules* **20**, 1442 (1987).

5) H. Schlaad, A.H.E. Müller, *Macromol. Symp.* **107**, 163 (1996)

6) J.-S. Wang, R. Jerome, Ph. Bayard, M. Patin, Ph. Teyssié, *Macromolecules* **27**, 4635 (1994).