Kinetic Investigations of Polymerization of Methyl Methacrylate with Zirconocenes

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Dedicated to Prof. Dr. Dr. h.c. Hj. Sinn on the occasion of his 70th birthday

SUMMARY: The polymerization of methyl methacrylate (MMA) in toluene with Cp_2ZrMe_2 (**1**) – $Ph_3C^+B(C_6F_5)_4^-$ (**4**) as initiating system was kinetically investigated. This system can be regarded as a combination of the systems described by Collins and Soga. Only if the ratio of **1/4** was larger than 1, monomer conversions of more than 99 % and polymers with number-average molecular weights higher than 200 000 and polydispersities 1.5 - 1.6 were obtained. From a kinetic analysis of time-conversion curves using the software package Predici, it can be deduced that the mechanism is consistent with that proposed by Collins et al. However, the mechanism has to be extended by incorporating a first-order termination reaction of the active species. Rate coefficients of all elementary reactions were determined from time-conversion curves. The kinetic investigations were accompanied by ab initio calculations, which support the assumed kinetic model.

Introduction

Neither the group transfer polymerization (GTP) nor the metal-free anionic polymerization could solve the problem of polymerizing methyl methacrylate (MMA) to stereospecific polymers[1-5]. Due to the good experience with metallocene catalysts in the stereospecific polymerization of propene, such systems were employed as catalysts in the polymerization of MMA[6-14]. Collins et al.[9-11] reported that in the presence of neutral $Cp_2Zr(CH_3)_2$ (**1**), the cationic zirconocene compound $Cp_2Zr(CH_3)(THF)^+BPh_4^-$ (**2**) predominantly promotes syndiospecific polymerization of MMA (80% *r*-diads at 0 °C) in dichloromethane as solvent at room temperature. Japanese authors[12,13] initiated the polymerization of MMA with the precursor of the borate **2** of Collins, which was substituted by pentafluorophenyl ligands. When an equimolar mixture of $B(C_6F_5)_3$ (**3**) or $Ph_3C^+B(C_6F_5)_4^-$ (**4**) and **1** was added to a solution of MMA in toluene, only $Cp_2ZrMe^+B(C_6F_5)_4^-$ (**5**) was formed in a high yield. However, when **3** was added to a solution of MMA and $Zn(C_2H_5)_2$ in toluene and aged for 1 h, followed by addition of **1**, PMMA was formed in high yield. A syndio-rich atactic polymer was obtained.

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There are some differences and some common features in the systems of Collins et al. and those of Soga's group. In this contribution, we propose that both systems can be described by the same mechanism.

Results and discussion

The systems of Collins and of Soga were combined using **4** and **1** as catalyst components and toluene as solvent and used in the polymerization of MMA. The ratio of **4** to **1** was varied. Table 1 summarizes the results, Figs. 1a and 1b show time – conversion curves.

Table 1. Times t_e for 100 % conversion, experimental and calculated number-average molecular weights $\overline{M}_n$ and dispersion index D in the polymerization of MMA in toluene at 0 °C with $Ph_3C^+B(C_6F_5)_4^-$ (**4**) - $Cp_2Zr(CH_3)_2$ (**1**) as initiating system. $[MMA]_0 = 1.04$ mol/L.

PMMA	$[\mathbf{1}]_0$ mmol/L	$[\mathbf{4}]_0$ mmol/L	t_e min	$\overline{M}_{n,exp} \times 10^{-5}$	D_{exp}	$\overline{M}_{n,calc} \times 10^{-5}$	D_{calc}
1	6.00	1.00	95	2.16	1.54	1.85	1.62
2	4.00	1.00	95	1.86	1.69	1.85	1.62
3	2.00	1.00	105	2.06	1.62	1.85	1.62
4	1.60	1.00	165	2.13	1.61	1.85	1.62
5	3.50	0.50	190	2.32	1.46	2.20	1.53
6	3.40	0.40	235	2.29	1.50	2.25	1.51
7	3.25	0.25	355	2.28	1.52	2.20	1.55

In all experiments, the conversion of MMA was 100 %. The polymer contained about 66 % syndiotactic structures. The microtacticity distribution obeyed Bernoullian statistics. It is remarkable that the polymer has the same pentad structure as Soga found in PMMA formed with **1**, **4** and $Zn(C_2H_5)_2$ as initiating system. This indicates that the propagation step is identical in both systems. The time conversion curves in Figs. 1a and 1b show induction periods. Their length increases with decreasing concentration of **1**. Therefore, it has to be assumed that the reaction system is characterized by a slow initiation reaction due to the addition of a first monomer molecule to an initiator species.

The reaction between **1** and **4** is very fast. The deep red color of **4** in toluene vanishes immediately when **1** is added in equimolar or higher amounts. The initial initiator solution should contain **5** in a concentration corresponding to the initial concentration of tritylium borate **4**, and remaining **1**, corresponding to its excess in comparison with **4** (Scheme 1).

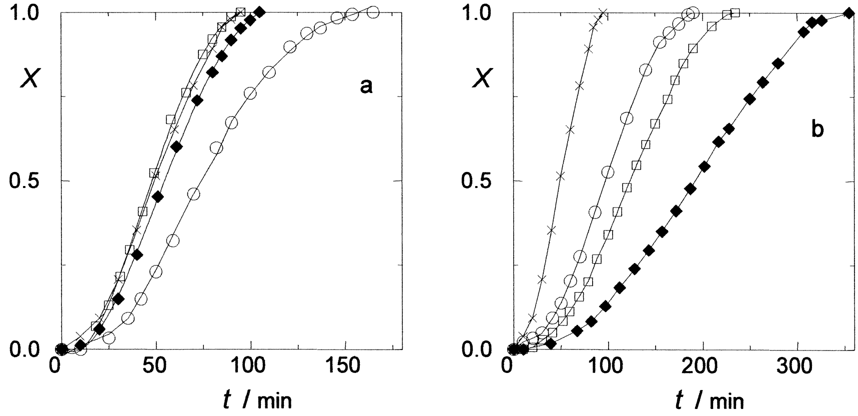
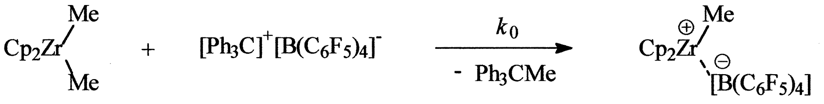


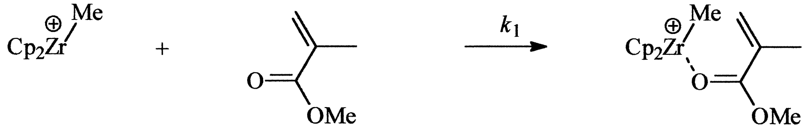
Fig. 1. Time – conversion curves in the polymerization of MMA with **4** and **1** in toluene at 0 °C in dependence on (a) $[\mathbf{1}]_0$ and (b) $[\mathbf{1}]_0$ and $[\mathbf{4}]_0$. $[\mathrm{MMA}]_0 = 1.04$ mol/L.
(a) $[\mathbf{4}]_0 = 1$ mmol/L; $[\mathbf{1}]_0 = 6$ (□), 4 (×), 2 (◆) and 1.6 (○) mmol/L; (b) $[\mathbf{1}]_0 + [\mathbf{4}]_0 = 3$ mmol/L; $[\mathbf{4}]_0 = 1$ (×), 0.5 (○), 0.4 (□) and 0.25 (◆) mmol/L.



1 **4** **5**

Scheme 1

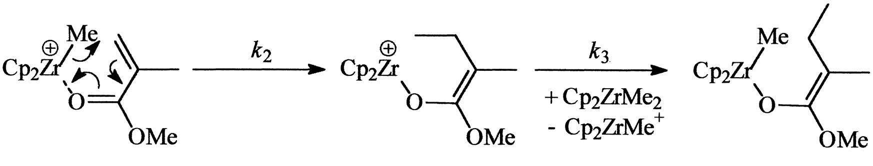
Collins et al.[9] reported the formation of a complex between $\mathrm{Cp_2Zr(CH_3)(THF)^+BPh_4^-}$ (**2**) and MMA with release of THF. In our system without THF, this reaction should proceed as shown in Scheme 2 with formation of **5·MMA** . Due to the results of ab initio calculations[15], it has to be assumed that this reaction is completely shifted to the right-hand side because of the high gain in energy. Furthermore, such enolate complexes with **5** and methyl isobutyrate as reference molecule are characterized not only by a covalent zirconium-oxygen bond but also by additional electrostatic interactions.



5 **MMA** **5·MMA**

Scheme 2

The addition of one MMA molecule to the complex **5·MMA** should lead to a zirconium enolate cation (**6**) (Scheme 3) with transfer of the methyl group from the zirconium atom to the *β*-carbon atom of the MMA double bond.

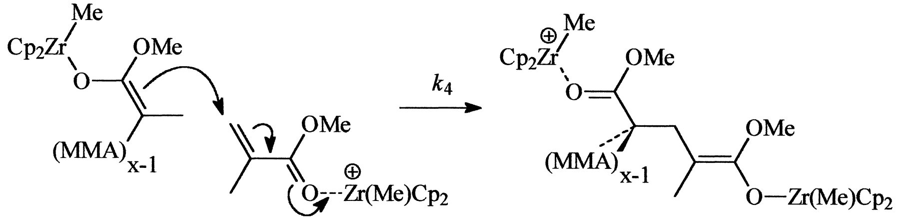


5·MMA **6** **7**

Scheme 3

Clearly, species **6** could be active in the addition of another MMA in the propagation reaction. However, when the ratio of zirconocene **1** to tritylium borate **4** is lower than unity, no polymerization of MMA is observed. Therefore, species **6** cannot be active in polymerization of MMA. This is confirmed by ab initio calculations using acrylic acid as substrate15). Since a polymerization of MMA was only observed when **1** was used in excess to **4**, the neutral enolate **7** could be the active species, too. This compound can be formed by a reaction of **6** with zirconocene **1** via transfer of methyl group. In this reaction, zirconocene cation **5** is released. This zirconium cation **5** can again undergo complexation with MMA and thereby start a new cycle leading to the formation of neutral enolate **7**. Such a mechanism could explain why the number of polymer chains after polymerization of PMMA 6 and 7 (Table 1) exceeds that of zirconocene cations which are present in the beginning.

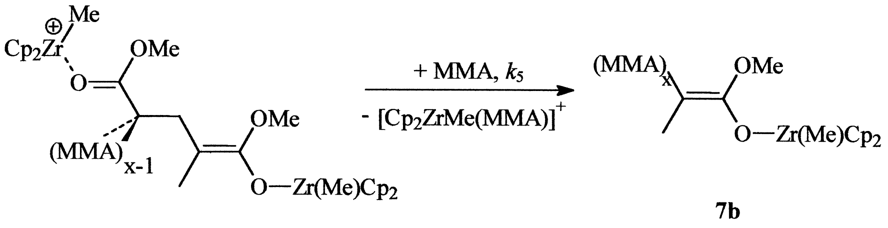
The question arises whether the neutral zirconocene - enolate complex **7** could act as a single active species in MMA polymerization. In separate experiments, the findings of Collins et al.11) could be confirmed, i.e., that the neutral enolate **7** is nearly ineffective in the absence of zirconocene **1**. Collins et al. propose a propagation step assuming the reaction of **7** with an activated MMA, complex **5·MMA** in our notation, leading to the intermediate **8** (Scheme 4).



7a **5·MMA** **8**

Scheme 4

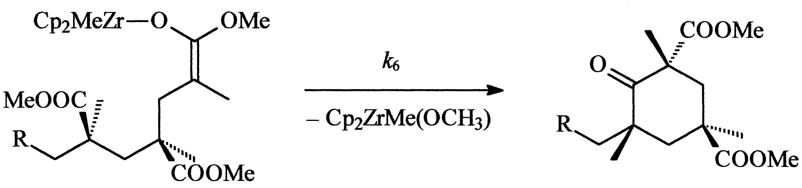
The separation of **5** from **8** is energetically not feasible. Moreover, an assistance in the separation can be expected[15)] by a new monomer molecule approaching from the rear side of **8**. This would correspond to the dinuclear substitution process already favored by Collins. In our case, the reaction of MMA according to Scheme 5 would yield a neutral zirconium enolate complex prolonged by one monomer unit and a zirconium enolate complex **5·MMA**, which can start a new propagation step.



Scheme 5

In all experiments, complete conversions of MMA are obtained under the chosen reaction conditions. At constant tritylium borate concentration (experiments 1-4 in Table 1), the overall reaction rate and the reaction times corresponding to 100 % conversion are only slightly dependent on the zirconocene concentration as long as the ratio of **1** and **4** is equal or higher than 2 (Fig. 1a). The reaction rates decrease and the reaction times increase more and more when, at a constant difference of $[\mathbf{1}]_0$ and $[\mathbf{4}]_0$ (3 mmol/L in experiments 2, 5-7 in Table 1), the concentration of tritylium borate **4** is lowered (Fig. 1b). This dependence can be understood under the assumption that zirconocene **5** participates in the propagation step.

The complete conversion of MMA means that termination does not play a dominant role during our polymerization experiments. However, of course, it cannot be excluded. The number-average degrees of polymerization (column 5 in Table 1) change only slightly and without real trend in dependence on the concentrations of the initiator components. Furthermore, the values of polydispersity (column 6 in Table 1) are higher than in living polymerizations without termination. Therefore, side reactions which influence the degree of polymerization have to be taken into account. Hence in one experiment, the number-average degree of polymerization in dependence on time was measured (Fig. 2). A slight decrease in $\overline{M}_n$ with time is observed, a hint to termination or to chain transfer reactions. It is tempting to assume that termination in this system is also possible by a backbiting reaction as it is known in anionic polymerizations of MMA (Scheme 6).



7b Scheme 6 **9**

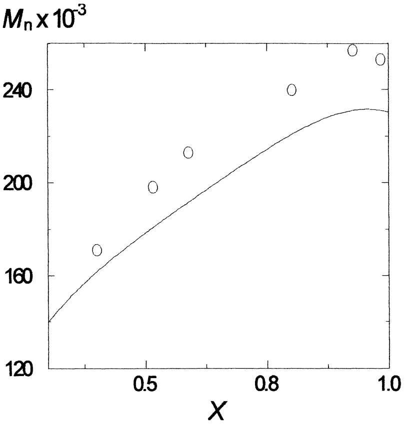


Fig. 2. Dependence of the number-average molecular weight $\overline{M}_n$ on conversion in the polymerization of MMA with $Ph_3C^+B(C_6F_5)_4^-$ (**4**) – $Cp_2Zr(CH_3)_2$ (**1**) in toluene at 0 °C. $[MMA]_0 = 1.04$ mol/L, $[\mathbf{1}]_0 = 3.45$ mmol/L, $[\mathbf{4}]_0 = 0.45$ mmol/L. The line was calculated from the rate coefficients discussed below.

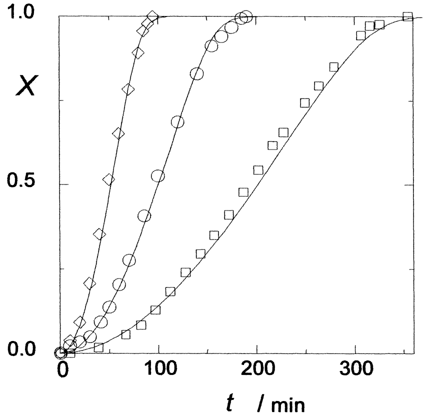


Fig. 3. Experimental and calculated time conversion curves in the polymerization of MMA with **1** – **4** in toluene at 0 °C. $[MMA]_0 = 1.04$ mol/L; $[\mathbf{1}]_0 - [\mathbf{4}]_0 = 3$ mmol/L, $[\mathbf{4}]_0 = 1$ (◇), 0.5 (○) and 0.25 (□) mmol/L.

The activation energies of this reaction and those of chain transfer reactions should be higher than that of the propagation reaction. In that case, higher number-average degrees of polymerization should be obtained at lower temperatures. Table 2 shows the results of two experiments at -25 °C and, for comparison, the data from two comparable experiments in Table 1. At lower temperatures, the number-average degrees of polymerization are appreciably higher. Obviously deactivation and/or chain transfer is reduced with decreasing temperatures.

In attempts to model the whole polymerization, we checked the validity of three mechanistic models. First we combined Schemes 1, 2, and 6 and assumed that in Scheme 3, only the enolate cation **6** was formed, representing the active species in the propagation reaction. Second, we assumed in Scheme 3 the neutral enolate **7** to be the active species. Third, we checked a mechanism combining Schemes 1 to 6, which corresponds to the proposals of Collins et al.. Only the mechanism of Collins et al. allowed a satisfactory simulation of time –

concentration curves (Fig. 3). For this mechanism, the system of differential equations shown in Scheme 7 was applied. We determined the unknown rate coefficients of the elementary reactions in each system, including only termination by backbiting and no chain transfer, by a parameter optimization technique, provided by the software package Predici[16)].

Table 2. Number-average molecular weights $\overline{M}_n$ and polydispersity D in the polymerization of MMA in toluene at 0 °C and -25 °C with $Ph_3C^+B(C_6F_5)_4^-$ (**4**) – $Cp_2Zr(CH_3)_2$ (**1**) as initiating system. $[MMA]_0 = 1.04$ mol/L.

PMMA	$[\mathbf{1}]_0$ mmol/L	$[\mathbf{4}]_0$ mmol/L	T °C	$\overline{M}_n \times 10^{-5}$	D
1	4.00	1.00	-25	6.34	1.38
2	4.00	1.00	0	1.86	1.69
3	3.50	0.50	-25	7.44	1.29
4	3.50	0.50	0	2.32	1.46

We assumed the reaction in Scheme 1 to be very fast and did not take into account any terms of the components of this step in the differential equations. The result of the optimization procedure is shown in Fig. 3 for experiments 2, 5 and 7 in Table 1. The curves were calculated using the differential equations in Scheme 7 and the following optimized values of rate constants: $k_1 = 1\cdot10^4$ L/(mol·min), $k_2 = 6.30\cdot10^{-3}$ L/min, $k_3 = 1\cdot10^4$ L/(mol·min), $k_4 = 8.89\cdot10^4$ L/(mol·min), $k_5 = 3.59\cdot10^2$ L/min, $k_6 = 2.64\cdot10^{-3}$ L/min.

$$d[\mathbf{1}]/dt = -k_0[\mathbf{1}][\mathbf{4}] - k_3[\mathbf{1}][\mathbf{6}]$$
$$d[\mathbf{4}]/dt = -k_0[\mathbf{1}][\mathbf{4}]$$
$$d[\mathbf{5}]/dt = k_0[\mathbf{1}][\mathbf{4}] - k_1[\mathbf{5}][MMA] + k_3[\mathbf{1}][\mathbf{6}]$$
$$d[\mathbf{5{\cdot}MMA}]/dt = k_1[\mathbf{5}][MMA] - k_2[\mathbf{5{\cdot}MMA}] - k_4[7][\mathbf{5{\cdot}MMA}] + k_5[\mathbf{8}][MMA]$$
$$d[\mathbf{6}]/dt = k_2[\mathbf{5{\cdot}MMA}] - k_3[\mathbf{1}][\mathbf{6}]$$
$$d[\mathbf{8}]/dt = k_4[7][\mathbf{5{\cdot}MMA}] - k_5[\mathbf{8}][MMA]$$
$$d[7]/dt = k_3[\mathbf{1}][\mathbf{6}] - k_4[7][\mathbf{5{\cdot}MMA}] + k_5[\mathbf{8}][MMA] - k_6[7]$$
$$d[MMA]/dt = -k_1[\mathbf{5}][MMA] - k_5[\mathbf{8}][MMA]$$

Scheme 7

The fit of the experimental points by the simulated curves is very good. The rate-determining steps in the overall reaction are the first reaction in Scheme 3 and the deactivation step in Scheme 6. All other reactions are very fast. With the set of rate coefficients, we calculated the number-average molecular weights and polydispersities of our polymers and compared them with experimental values. The agreement of both sets of data is satisfactory, as Table 1 shows. Figure 3 also shows the calculated function of $\overline{M}_n$ versus monomer conversion. It can be seen that the experimental values are in relatively good agreement with the calculated ones.

Conclusion

The presented results indicate that the polymerizations of MMA with the catalytic systems of both Collins and Soga can be described by the reaction mechanism, which was developed by Collins. The role of $Zn(C_2H_5)_2$ in the initiation reaction, as discussed by Soga, can be taken over by $Cp_2Zr(CH_3)_2$. Its reaction with a zirconium enolate cation, formed from $Cp_2ZrMe^+B(C_6F_5)_4^-$ and MMA, is the rate-determining step in the whole reaction sequence, as kinetic and modeling studies show. According to the pentad structure of the formed PMMA, the propagation step in both systems seems to be the same. In addition to the mechanistic proposal of Collins, chain transfer and termination reactions also have to be taken into account in order to describe the course of time conversion curves. The results of ab initio calculations of several reaction steps, not discussed in detail in this paper, make the mechanism of Collins highly probable.

References

1. O.W. Webster, W.R. Hertler, D.Y. Sogah, W.B. Farnham, T.V. Rajanbabu, *J. Am. Chem. Soc.* **105**, 5706 (1983)
2. M.T. Reetz, R. Ostarek, *J. Chem. Soc., Chem. Commun.* 213 (1988)
3. R.P. Quirk, G. Bidinger, *Polym. Bull. (Berlin)* **22**, 63 (1989)
4. A.H.E. Müller, *Makromol. Chem. Macromol. Symp.* **32**, 87 (1990)
5. A.P. Zagala, T.E. Hougen-Esch, *Macromolecules* **29**, 3038 (1996)
6. M.T. Reetz, *Pure Appl. Chem.* **57**, 1781 (1985)
7. W.B. Farnham, W.R. Hertler (E.I. DuPont de Nemours and Co.), U.S. 4728706 (1988); *Chem. Abstr.* **98**, P 144031 (1983)
8. T. Yong, A.B. Holmes, P.L. Taylor, J.N. Roninson, J.A. Segal, *Chem. Commun.* 863 (1996)
9. S. Collins, D.G. Ward, *J. Am. Chem. Soc.* **114**, 5460 (1992)
10. S. Collins, D.G. Ward, K.H. Suddaby, *Macromolecules* **27**, 7222 (1994)
11. Y. Li, D.G. Ward, S.S. Reddy, S. Collins, *Macromolecules* **30**, 1875 (1997)
12. K. Soga, H. Deng, T. Yano, T. Shiono, *Macromolecules* **27**, 7938 (1994)
13. H. Deng, T. Shiono, K. Soga, *Macromol. Chem. Phys.* **196**, 1971 (1995)
14. H. Deng, K. Soga, T. Shiono, *Polym.Bull. (Berlin)* **36**, 667 (1996)
15. R. Sustmann, W. Sicking, F. Bandermann, M. Ferenz, *Macromolecules* **32**, 4204 (1999)
16. Software package Predici “Simulation of Macromolecular Processes”, Dr. M. Wulkow, CiT GmbH, Rastede (Germany)