Macromol. Symp. ***174,*** *247–253 (2001)*

Polymerization of Methyl Methacrylate with the Neutral Zirconocene Enolate $Cp_2ZrMe[OC(Me)=CMe_2]$

Friedhelm Bandermann[a], Michael Ferenz[a], Reiner Sustmann[b] and Willi Sicking[b]*

[a] Institut für Technische Chemie, [b] Institut für Organische Chemie,
Universität Essen, Universitätsstrasse 5, D-45117 Essen, Germany

SUMMARY: The polymerization of methyl methacrylate (MMA) with the neutral enolate $Cp_2ZrMe[OC(OMe)=CMe_2]$ in the absence and in the presence of zirconocene cations Cp_2ZrMe^+ to bypass the rate- limited initiation of the system was investigated. Only by itself the enolate is not active in polymerization, but as soon as the reaction system contains the cation MMA is quantitatively converted into syndiotactic-rich PMMA with high molecular weight (M_n > 100 000 g mol^{-1}) and very narrow molecular weight distribution ($M_w/M_n < 1.05$). The rate of polymerization was found to be first order reffering to the neutral enolate and also reffering to the cation. Rate coefficents of all elementary reactions were determined and compared to those received by the kinetic investigation of the polymerization using the initiator system $Cp_2ZrMe_2/Ph_3CB(C_6F_5)_4$. The agreement of both sets of calculated coefficients is satisfying. These results confirm that the mechanism of Collins et al. is suitable to describe the properties of the polymerization process.

Introduction

Some time ago, we reported on the results obtained by investigating polymerization of methyl methacrylate (MMA) with the neutral zirconocene $Cp_2Zr(CH_3)_2$ (**1**) and triphenylmethyl-tetrakis(pentafluorphenyl) borate $Ph_3C^+B(C_6F_5)_4^-$ (**2**).1) Modelling of the reaction showed that the mechanism according to Collins et al.2-4) can both describe the kinetics of this reaction as well as calculate the molecular weights and the dispersion index of the polymers which are being formed. The reaction scheme used by us, however, includes many variables so that the question was justified whether this system might possibly be ambiguous. Therefore, our next goal was to simplify the reaction system by trying to circumvent initiation of polymerization. For that purpose we investigated polymerisation of MMA with the neutral zirconocene enolate $Cp_2ZrMe[OC(Me)=CMe_2]$ (**3**), which according to the postulated mechanism is responsible for chain propagation.

Results and Discussion

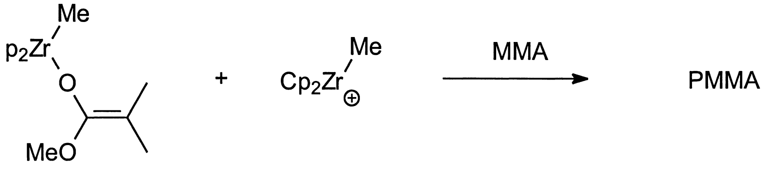
1. Polymerization Experiments

When investigating the polymerization characteristics of enolate **3**, we have initially checked whether this can polymerize MMA without further components being present. However, neither at 0°C nor at 40°C, and with an initiator concentration of 5 mM as well as a monomer content of 1.04 M, neither in toluene nor methylene chloride, PMMA was formed. This result was to be expected since investigations on the dimethyl zirconocene / tritylborate system also

CCC 1022-1360/00/$ 17.50+.50/0

gave reason to assume that the enolate does not promote growth by itself. Collins et al. came to an analogous result when investigating similarly neutral enolates.[4)]

However, in the presence of zirconocene cations (**4**) in the reaction mixture, a rapid polymerisation of MMA could be observed (Scheme 1).



3 **4**

Scheme 1

All experiments were carried out as follows: First dimethyl zirconocene was mixed with toluene as a basis and then converted to the corresponding methylzirconocene cation **4** by adding an equimolar quantity of tritylborate; reaction temperature was 0 °C and reaction period 15 min. A solution of the enolate in toluene was then added, stirred for five minutes and the monomer finally added. By this method it should be ensured that the tritylborate could exclusively react with the dimethylzirconocene but not with the enolate.The results of the polymerization experiments are summarized in Table 1. In the case of experiments 1 to 4, concentration of the enolate was varied and that of the zirconocene cations kept constant, whereas in the case of experiments 1, 5 and 6 we operated with equal enolate and varying cation concentrations.

Table 1. Results of polymerization experiments of MMA with compounds **3** und **4**. [a]

Exper.	[**3**]/mM	[**4**]/mM	X/% [b]	M_n/(g mol^{-1})	M_w/M_n	A/% [c]
1	1.50	0.40	> 99	107 000	1.03	65
2	1.25	0.40	> 99	133 000	1.04	62
3	1.00	0.40	> 99	174 000	1.06	60
4	0.75	0.40	> 99	233 000	1.18	60
5	1.50	0.70	> 99	102 000	1.05	68
6	1.50	1.00	> 99	106 000	1.03	65

[a] Reaction temperature 0 °C, [MMA] = 1.04 M, reaction time 5 h, solvent toluene.

[b] conversion X = g polymer / initial g monomer. [c] activity = amount polymer / amount enolate.

In all experiments MMA was completely converted within five hours. On account of the selected reaction conditions, PMMA was formed with a high molecular weight ($M_n > 100\,000$ g mol^{-1}) and a low dispersion index (M_w / $M_n < 1.18$). It also proved that the degree of polymerization depends on the enolate content but not on the cation concentration. This result can be easily explained by the mechanism of Collins since here both an enolate particle as well as a cation participate in the propagation step, however, at the end of this step a cation is being released which does not differ from the original one. Also the dispersion index is solely dependent on the enolate concentration under the reaction conditions selected by us. In the case of experiments 1 to 4 it increases from 1.04 to 1.18. The increase in polydispersity can be put down to the fact that with a decreasing enolate concentration a prolongation occurs in the reaction time by which a complete conversion of the monomer is attained, so that the relatively slow termination reaction becomes more and more important. In the case of the experiments at constant enolate concentration, however, the conditions were such that complete conversion of MMA took place in such a short period of time that this effect was of no importance.

2. Microtacticity of the Formed Polymers

The ^{13}C-NMR-spectroscopic analysis of the formed polymer shows that its structure is mainly syndiotactic, whereby the observed pentade distribution is identical to that which can also be found in PMMA formed with the aid of the system dimethylzirconocene / tritylborate.$^{1)}$

3. Reaction Kinetics

Kinetics of the enolate system was thoroughly investigated by determining dilatometrically conversion of the monomer. Fig. 1 and 2 show the monomer concentration in dependence of time for experiments 1 to 6 in Tab. 1.

First of all it showed that monomer conversion is relatively rapid compared with the system that used dimethylzirconocene and tritylborate for initiating polymerization$^{1)}$. Now, an induction period is no longer observed. It is further worth to be pointed out that the reaction rate depends both on the enolate and also on the cation concentration.

These results show that there is no slow preceding initiation reaction in this system so that chain propagation alone is the rate determining step of monomer conversion.

The measured time / conversion behavior was modelled with the aid of the PREDICI software package. We proceeded in the same way as described for the dimethylzirconocene / tritylborate system.$^{1)}$ As it turned out, the Collins model can very well be used also in this case for

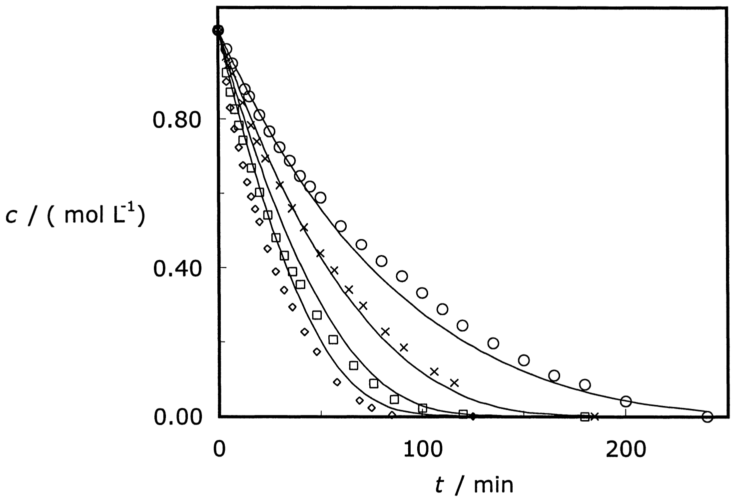


Figure 1: Time-conversion curves of the polymerization of MMA with compounds **3** and **4** at different enolate (**3**) concentrations (experiments 1 - 4 in Tab. 1). Reaction temperature 0 °C, solvent toluene, [MMA] = 1.04 M, [**4**] = 0.40 mM, [**3**]: ◊: 1.50 mM, □: 1.25 mM, **x** 1.00 mM, ○: 0.75 mM.

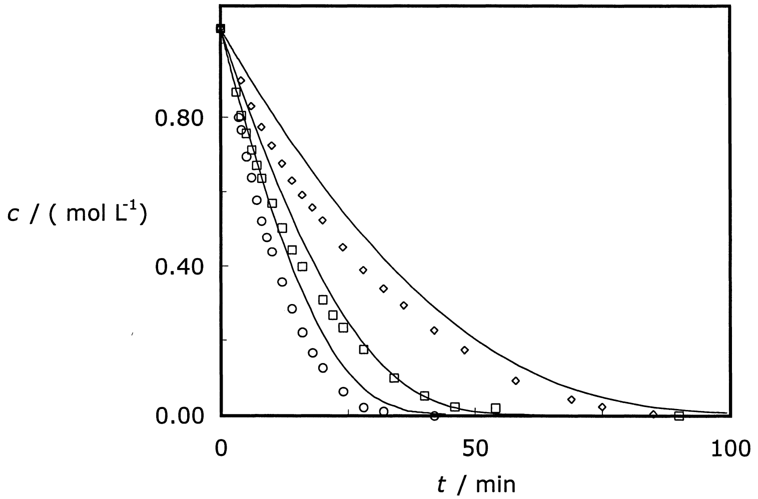


Figure 2: Time-conversion curves of the polymerization of MMA with compounds **3** and **4** at different enolate (**3**) concentrations (experiments 1, 5 and 6 in Tab. 1). Reaction temperature 0 °C, solvent toluene, [MMA] = 1.04 M, [**3**] = 1.50 mM. [**4**]: ◊: 0.40 mM, □: 0.70 mM, ○: 1.00 mM.

describing the reaction and / or its characteristics. As against the initiator system dimethylzirconocene / tritylborate with six rate coefficients, only four coefficients must now be adapted, since two elementary reactions of initiation no longer occur. The numerical values for the individual rate coefficients determined by adaption of the theoretical function to the experimental data are shown in Table 2. For comparison, the results of the PREDICI simulation of the dimethylzirconocene/tritylborate system1) are also shown here.

Table 2. Comparison of rate coefficients of elementary reactions in the polymerization of MMA with $Cp_2ZrMe_2/Ph_3CB(C_6F_5)_4$1) and $Cp_2ZrMe[enolate]/Ph_3CB(C_6F_5)_4$ as initiating systems.

	Initiating system	
Coefficient	$Cp_2ZrMe_2/Ph_3CB(C_6F_5)_4$1)	$Cp_2ZrMe[enolate]/Ph_3CB(C_6F_5)_4$
k_1	$1.00 \cdot 10^4$ L mol^{-1} min^{-1}	---
k_2	$6.30 \cdot 10^3$ min^{-1}	$6.95 \cdot 10^3$ min^{-1}
k_3	$1.00 \cdot 10^4$ L mol^{-1} min^{-1}	---
k_4	$8.89 \cdot 10^4$ L mol^{-1} min^{-1}	$8.36 \cdot 10^4$ L mol^{-1} min^{-1}
k_5	$3.59 \cdot 10^2$ L mol^{-1} min^{-1}	$3.03 \cdot 10^2$ L mol^{-1} min^{-1}
k_6	$2.64 \cdot 10^{-3}$ min^{-1}	$2.94 \cdot 10^{-3}$ min^{-1}

Table 3. Comparison of experimental and calculated values of the number average molecular weight M_n and of the dispersion index M_w/M_n in the polymerization of MMA with $Cp_2ZrMe[enolate]/Ph_3CB(C_6F_5)_4$. Experimental conditions c.f. Table 1.

Exper.	[3]/mM	[4]/mM	M_n/(g mol^{-1}) experimental	M_n/(g mol^{-1}) calculated	M_w/M_n experimental	M_w/M_n calculated
1	1.50	0.40	107 000	106 000	1.03	1.06
2	1.25	0.40	133 000	132 000	1.04	1.07
3	1.00	0.40	174 000	174 000	1.06	1.09
4	0.75	0.40	233 000	230 000	1.18	1.13
5	1.50	0.70	102 000	102 000	1.05	1.03
6	1.50	1.00	106 000	106 000	1.03	1.03

In addition, the theoretical functions of monomer concentration and the experimental data are plotted in dependence of reaction time in Fig. 1 and 2. With the aid of this model, also the numerical values for the molecular weights of the forming polymers as well as their dispersion index were calculated, which are shown in Tab. 3 together with the experimental results.

As can be seen, the time / conversion behavior of the reaction can be very well described and the number average molecular weight as well as the dispersion index of the forming PMMA calculated. The effect that with a prolonging duration of reaction the polydispersity of the polymers increases can likewise be explained with the underlying mechanism. It is further worth to be emphasized that the results for the rate coefficients from both test series were almost identical. This confirms our assumption that the mechanism according to Collins is applicable to the polymer systems investigated up to now.

3. Dependency of Polymerization Degree upon Monomer Conversion

The kinetic investigations of the enolate system show that the termination reaction plays only a subordinate role in this system so that under certain reaction conditions, „quasi-live“ systems are obtained. These are featured by a degree of polymerization being directly linear to conversion. In order to take up the said correlation and to confirm the results so far obtained, experiments were carried out in the course of which polymerization was stopped before the MMA had been completely converted. The results of this test series are listed in Tab. 4 and the dependency of the number average molecular weight upon monomer conversion is shown in Fig. 3.

Table 4. Dependence of the number average molecular weight M_n and of the dispersion index M_w/M_n of monomer conversion X in the polymerization of MMA with $Cp_2ZrMe[enolate]/Ph_3CB(C_6F_5)_4$.

Experiment	t/min	X/%	M_n/(g mol^{-1})	M_w/M_n
1	10	15	41 000	1.04
2	25	32	71 500	1.03
3	40	48	99 000	1.04
4	60	62	124 500	1.05
5	80	75	151 000	1.08
6	160	99	194 000	1.08

As had been expected, a linear correlation prevails between the values in question. Furthermore, it should be noted that the dispersion index of the polymer increases only

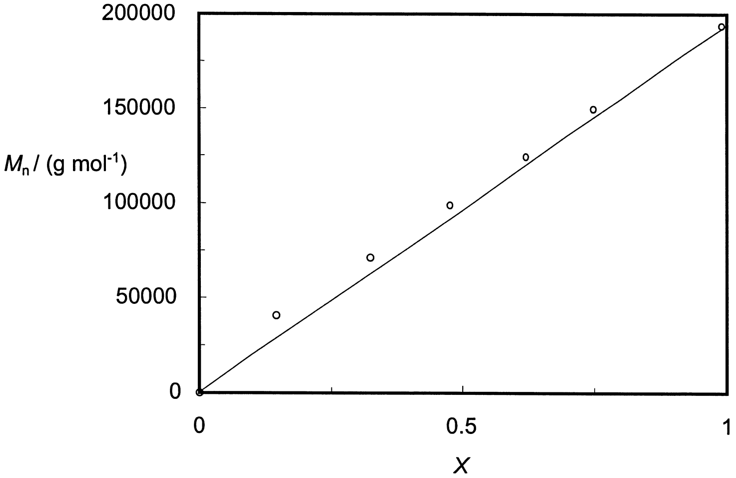


Figure 3: Dependence of the number average molecular weight M_n of the monomer conversion X in the polymerization of MMA with $Cp_2ZrMe[enolate]/Ph_3CB(C_6F_5)_4$.

insignificantly with increasing monomer conversion, which are both criteria which testify to a quasi-live character of the system.

Conclusion

The neutral enolate $Cp_2ZrMe[OC(OMe)=CMe_2]$ (**3**), an intermediate in the reaction sequence in the polymerization of MMA with Cp_2ZrMe_2 / $Ph_3CB(C_6F_5)_4$, cannot initiate the polymerization by itself. Only in the presence of further zirconocene cations Cp_2ZrMe^+ the polymerization is started. The rate of polymerization is first order reffering to the neutral enolate and also reffering to the cation. The agreement of sets of corresponding rate coefficients indicates that the enolate / Cp_2ZrMe^+ initiated system is part of the full system with Cp_2ZrMe_2 / $Ph_3CB(C_6F_5)_4$ as initiators. The modelling of the kinetic, using the software package PREDICI, indicates that the mechanism of Collins et al. is suitable to describe the properties of the polymerization process.

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