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Phosphorus-Containing Polymers

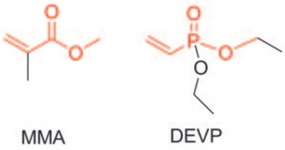
High-Molecular-Weight Poly(vinylphosphonate)s by Single-Component Living Polymerization Initiated by Rare-Earth-Metal Complexes[**]

*Uwe B. Seemann, Joachim E. Dengler, and Bernhard Rieger**

Polymeric materials containing covalently bound heteroatoms are interesting for a wide field of science and applications. Specifically, phosphorus-containing polymers have become prominent in recent research, for instance, poly(vinylphosphonic acid) has found commercial application as a binder in bone and dental concrete.[1] Other prospective uses for this material are as membranes in fuel cells or flame retardants in commodity polymers.[2–6]

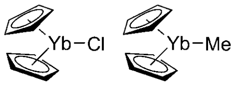
To date, attempts employing radical and ionic approaches to form poly(vinylphosphonate) homo- and copolymers mostly resulted in low yields and degrees of polymerization.[7–10] A first example of high-molecular-weight poly(vinylphosphonic acid), which was produced by anionic polymerization of diisopropyl vinylphosphonate and subsequent saponification, and characterized by aqueous GPC, was recently reported.[7] Work carried out by our research group, as well as recently published results, have shown that diethyl vinylphosphonate (DEVP) can be polymerized by rare-earth-metal complexes that employ monodentate ligands such as trimethylsilane or different amides. However, no mechanistic results that concern this type of reaction have been presented to date.[11,12]

DEVP is one of the simplest phosphorus-containing vinyl monomers. Its structural and electronic similarity to acrylates mean that, as with many other electron-acceptor-substituted compounds, it undergoes Michael addition reactions (Scheme 1).[13,14] Methylmethacrylate (MMA), which is the commercially most important and scientifically interesting commodity acrylic monomer, is polymerized by radical and anionic methods in the majority of cases. It may also be polymerized by the group-transfer polymerization (GTP) mechanism, which is initiated by different rare-earth-metal and other metal complexes.[15–19]



Scheme 1. Structural comparison of MMA and DEVP as examples of Michael acceptors.

Copolymerization reactions of vinylphosphonates with other commodity monomers (styrene in the majority of cases) were predominantly conducted by applying radical polymerization techniques or by an anionic pathway, in order to produce block copolymers.[7,10,20–23] No block copolymer of DEVP and MMA has been reported to date.



1 **2**

Scheme 2. Bis(cyclopentadienyl)ytterbium chloride (**1**) and bis(cyclopentadienyl)methyl ytterbium (**2**).

Herein, we describe the first metallocene-catalyzed polymerization with simple ytterbium complexes. The polymerization leads to high-molecular-weight DEVP homopolymers as well as MMA/DEVP block copolymers (Scheme 2). This polymerization shows fast and complete conversion and produces polymeric material with a weight-averaged molecular weight (M_W) between 10^5 and 10^6 g mol^{-1}. The resulting polymers were characterized by NMR spectroscopy as well as GPC analysis using conventional calibration methods and light-scattering detection. The insolubility of the resulting high-molecular-weight homopolymers in common organic solvents precluded the usage of standard GPC measurements for analysis. Instead the molecular weight of these polymers was determined from Zimm plots of static light scattering results from aqueous solutions.[24] Therefore it was not possible to determine the corresponding polydispersity indices. The achieved molecular weights indicate a M_w value of up to 10^6 g mol^{-1} (Table 1).

The polymerization reactions with [Cp_2YbCl] (**1**) in toluene were conducted at different temperatures and catalyst/monomer ratios, and show a strong dependence of the degree of polymerization on the reaction temperature. As the reaction temperature increased, products with significantly lower M_w were obtained. On the other hand, reactions carried out at 30 °C with different catalyst/monomer ratios all showed M_w values of the same magnitude (Table 1).

Kinetic studies (Figure 1) performed by GC and in situ NMR spectroscopy during the reaction of DEVP with **1**, demonstrated that the polymerization shows a high reaction velocity after a short latency time, and reaches completion within less than half an hour at 30 °C. The initial monomer

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[*] U. B. Seemann, J. E. Dengler, Prof. B. Rieger
Technische Universität München
WACKER-Lehrstuhl für Makromolekulare Chemie
Lichtenbergstrasse 4, 85747 Garching bei München (Germany)
Fax: (+49) 89-289-13562
E-mail: rieger@tum.de
Homepage: http://www.makro.ch.tum.de/

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Table 1: Homopolymers of poly(DEVP) formed by polymerization at different temperatures and catalyst/monomer ratios.[a]

Entry	[DEVP]/[Cat.]	T [°C]	M_w [$\times 10^5$ g mol^{-1}]	Conv. [%][b]
1	200	90	2.01	58
2	200	70	3.64	75
3	200	50	5.45	91
4	200	30	9.83	94
5	200	0	12.3	98
6	200	−18	–	0
7	400	30	12.8	97
8	100	30	8.65	99
9	50	30	10.1	98

[a] Reactions carried out with 20 mg of **1** in 15 mL toluene. [b] Determined by weighing the components.

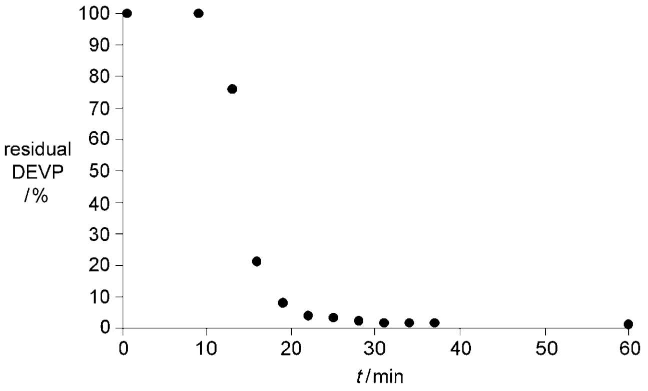


Figure 1. Kinetic studies performed on **1** by ^{1}H NMR spectroscopy, showing consumption of monomer during polymerization at 30 °C in [D$_6$]benzene. Initial concentration of DEVP 0.2 g mL^{-1}, catalyst 0.2 mg mL^{-1}.

consumption is very fast, until the inherent viscosity of the polymerization mixture slows the reaction, presumably as a result of diffusion limitations.

The combination of the observed latency time, which comprises a time lapse of several minutes with low reaction velocity, and the strong temperature dependence of the resulting degree of polymerization leads to following conclusion: this activation period occurs because of the high strength of the metal–chloride bond. At higher temperatures, a faster activation takes place and the higher concentration of activated species in solution mean that a lower molecular weight is achieved. In our opinion, a simultaneous activation of all [Cp$_2$YbCl] molecules at moderate temperatures seems to be unlikely, as this would result in a low concentration of active species that polymerize in a high monomer excess, thereby producing polymers with very high molecular weights. Therefore the initial metal complex/monomer ratio does not affect the M_w value at 30 °C. Kinetic studies could not be reliably performed on compound **1** in order to provide a mechanistic suggestion because of this disfavored starting reaction as well as the rapid polymerization process

In order to provide support the polymerization mechanism by kinetic studies, a catalytic system with a faster and simultaneous activation process is required. Therefore polymerization of DEVP was performed using [Cp$_2$YbMe] (**2**) as polymerization catalyst at −10 °C, as these conditions satisfy the above requirements. This alternative catalytic system produced shorter-chain polymers that were soluble in organic solvents. The relative peak molecular weight M_p of these chains showed a linear chain growth upon monomer conversion, as determined by GPC retention time and ^{31}P NMR spectroscopy (Figure 2).

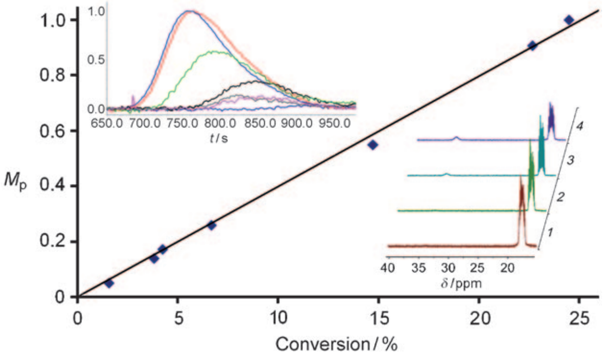


Figure 2. Linear growth of the relative peak molecular weight (M_p) upon DEVP consumption, as detected by ^{31}P NMR spectroscopy and GPC retention time. NMR spectrum: 1 = no conversion, 2 = 1.5 %, 3 = 14.7 %, 4 = 24.5 % conversion. GPC traces: smallest peak = 1.5 %, largest peak = 24.5 % conversion.

Living polymerization mechanisms are characterized by linear chain growth, as shown by the experiment in which **2** was applied as a catalyst. It is assumed that [Cp$_2$YbCl] demonstrates the same catalytic reactivity behavior as [Cp$_2$YbMe], but involves a slower activation. The increased latency period of [Cp$_2$YbCl] (in comparison with that of [Cp$_2$YbMe]) combined with its rapid rate of polymerization made it difficult to provide a final proof that a living polymerization mechanism occurs with this complex.

To provide a supplementary demonstration for a living-type mechanism, and in order to find a verification for the similarity to the already well-known MMA group transfer polymerization (GTP) system, further reactions that use MMA as a comonomer were performed with **2**. In previous studies, all sequential GTP reactions with vinylphosphonates, in which MMA was used as the starting monomer, resulted in end-capping of the MMA chain with a single phosphonic ester group.[25] We investigated block copolymers formed by sequential copolymerization with MMA as the starting monomer (Table 2). The formation of polymer blocks was verified by GPC and GPC light-scattering studies. Both methods show low polydispersity indices for the starting MMA block as well as for the resulting polymer. Furthermore, the increasing molecular weight of the growing chains is clear. In combination with the congruent light-scattering data, an accidental overlap of separately formed homopolymers at different monomer proportions seems to be unlikely. Solubility studies in water performed with both copolymers show a slight solubility in the case of PMMA$_{100}$DEVP$_{100}$. The

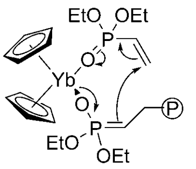
Table 2: Catalytically synthesized copolymers of DEVP and MMA at different monomer proportions[a].

Sample	MMA[b]	DEVP[b]	Calculated M_w [$\times10^4$ g mol^{-1}]	GPC conventional M_w [$\times10^4$ g mol^{-1}]	GPC conventional PDI	GPC light scattering M_w [$\times10^4$ g mol^{-1}]	GPC light scattering PDI	MMA/DEVP[c]	Conv.[d]
$MMA_{100}DEVP_{100}$	100	100	2.6	2.9	1.3	2.4	1.2	1.15:1	94%
$MMA_{200}DEVP_{100}$	200	100	3.6	4.6	1.2	5.3	1.1	2.1:1	95%

[a] Conducted at 30°C. [b] Equivalents per mole of catalyst. [c] Ratio of monomer units present in the polymer. Calculated from ^{1}H NMR spectra. [d] Determined by weighing the components.

^{1}H NMR spectra of the aqueous fraction, the residue, and the initial material showed that these three samples had the same composition. $PMMA_{200}DEVP_{100}$ has no appreciable solubility in water.

Related studies on the polymerization of MMA and other polar monomers with (rare-earth) metal complexes exposed a GTP that is now well-established.[17–19,26,27] On the basis of the living homopolymerization, as well as the resulting block copolymer, a GTP mechanism is also a reasonable proposal for the (co)polymerization of DEVP. A possible intermediate is shown in Scheme 3; chain growth occurs by transfer of the coordinated monomeric species to the covalently bound chain end.



Scheme 3. Postulated DEVP intermediate in the group-transfer mechanism.

In summary, poly(DEVP) with an M_w value of up to 10^6 g mol^{-1} as well as the first block copolymer of MMA and DEVP have been synthesized. Use of rare-earth-metal complexes in the polymerization resulted in complete monomer consumption and high reaction rates. Kinetic studies indicate a living polymerization behavior. When combined with the potential to perform sequential copolymerization reactions, GTP is the preferred mechanistic assumption for this type of reaction. The present work provides a new approach toward phosphorus-containing (co)polymers with high molecular weights. Extensions of this work, including the development of related catalytic systems, the incorporation of additional functionalities, and the use of other monomers, are currently underway.

Experimental Section

Polymers were prepared under an inert atmosphere in dry and degassed toluene. After dissolving the complex in toluene and thermostating to the desired temperature, the appropriate amount of neat monomer was added in one injection. The resulting mixture was allowed to stir at constant temperature until the reaction was complete. In the case of copolymerization reactions, DEVP (the second monomer) was added after a reaction time of 1 h. An excess of methanol was added in order to terminate the reaction. The mixture was poured into hexane to induce precipitation of the polymeric material, which was dried at 80°C under vacuum.

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