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Poly(vinylphosphonate)s Synthesized by Trivalent Cyclopentadienyl Lanthanide-Induced Group Transfer Polymerization

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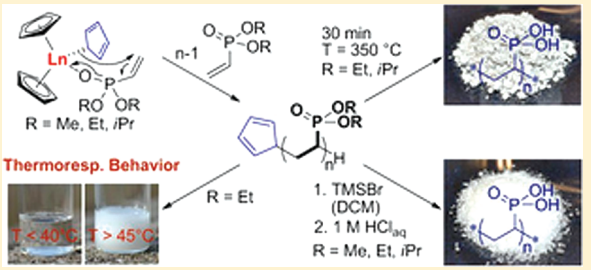
Supporting Information

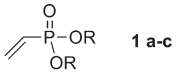
ABSTRACT: Recent studies have shown that diethyl vinylphosphonate can be converted into high-molecular-weight polymers by rare earth metal-initiated group transfer polymerization. Here we report on the use of tris(cyclopentadienyl)lanthanide complexes (Cp_3Ln, Ln = Gd to Lu) for the polymerization of dialkyl vinylphosphonates (alkyl: methyl, ethyl, isopropyl) yielding polymers with precise molecular weight and low polydispersity. Additionally, the thermosensitive behavior of poly(diethyl vinylphosphonate) was characterized, and methods for a conversion of the obtained high-molecular-weight poly(vinylphosphonate)s (M_n > 250 kg mol^{-1}) to poly(vinylphosphonic acid) by both thermal treatment and a mild hydrolysis were established. A series of independently performed reactions showed high activities and initiator efficiencies for the Cp_3Ln complexes for the homopolymerization of the applied monomers. Poly(vinylphosphonate)s of high molecular weight with a previously unknown low polydispersity index (PDI < 1.05) have been determined by GPC-MALS (multiangle light scattering) methods. The reaction shows a linear M_w vs consumption plot, thus proving a living type polymerization. The initiation of the reaction has been investigated by end-group analysis with MALDI-ToF and ESI mass spectrometric analysis. A new and interesting chain-end functionalization of the achieved polymers has been detected over the course of the MS analytical studies. The so far unreported LCST (lower critical solution temperature) of poly(diethyl vinylphosphonate) in water has been evaluated, and the correlation between the molecular weight of the material with this temperature has been determined.



INTRODUCTION

Poly(vinylphosphonate)s, as well as their derivatives, may be used as binders in dental or bone concrete, in new energy technologies as proton conducting membranes, as halogen-free flame retardants or as antifouling agents on metal surfaces.[1] Polymerization reactions of this type of monomer have first been studied in the 1960s and 1970s, with reports of low molecular weights and yields, mostly achieved by radical and anionic approaches.[2] Only few publications over the last years report on high-molecular-weight poly(vinylphosphonate)s, with even fewer reports on the free acid.[3] A few years ago we reported on successfully performed catalytic polymerizations using rare-earth metal complexes comprising σ-donor ligands.[3c] Later on, initial investigations on the microstructure of poly(diethyl vinylphosphonate) (PDEVP) were published using the same type of catalytic compounds.[3e] Nevertheless, mechanistic details as well as an absolute characterization of the molecular weight of the PDEVPs were missing. Recently, we reported on the first use of bis(cyclopentadienyl)ytterbium complexes (Cp_2YbCl and Cp_2YbMe) for the polymerization of diethyl vinylphosphonate (DEVP, **1b**).[4] This work has demonstrated the first instance of block copolymer production with methyl methacrylate (MMA). The reaction proceeds in a living fashion and appears to be a group transfer polymerization (GTP), which is already well-known for acrylic monomers.[5]

Nevertheless, the molecular weight of the resulting homopolymers was not consistent with the initial monomer to catalyst ratio, indicating low initiator efficiencies and the use of dialkyl vinylphosphonates other than the diethyl species are still not known. Herein we describe the first use of tris(cyclopentadienyl)lanthanide complexes for the polymerization of dimethyl vinylphosphonate (DMVP, **1a**), diethyl vinylphosphonate (DEVP, **1b**), and diisopropyl vinylphosphonate (DIVP, **1c**), and we provide pathways for the conversion of high-molecular-weight poly(vinylphosphonate)s to the corresponding poly(vinylphosphonic acid) by both thermal treatment and hydrolysis under mild conditions.



1 a-c

R: Me (**a**), Et (**b**), *i*Pr (**c**).

Figure 1. Dimethyl vinylphosphonate (DMVP, **1a**), diethyl vinylphosphonate (DEVP, **1b**), and diisopropyl vinylphosphonate (DIVP, **1c**).

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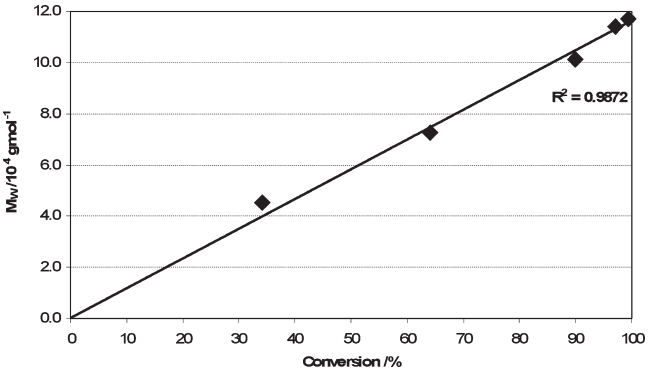
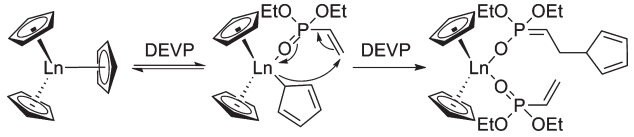


Figure 2. Linear growth of PDEVP molecular weight with conversion (Cp_3Lu, toluene, −10 °C).

Scheme 1. Initiation of the Cp_3Ln-Induced Polymerization of Vinylphosphonates with the Example Monomer DEVP



RESULTS AND DISCUSSION

Cp_3Ln Complexes for Vinylphosphonate Polymerization. The here-presented work is focused on the use of trivalent cyclopentadienyl lanthanide complexes (Cp_3Ln) for the homopolymerization of various dialkyl vinylphosphonates, allowing a precise control of molecular weight and molecular weight distribution of the polymer product. In addition, these complexes are structurally characterized for most of the rare-earth metals (Ln: Ce−Lu),[6] and their synthesis is easier than the previously applied monochloro- or monomethyl complexes (Cp_2YbX, X = Cl, Me),[4] affording even better yields. Initial kinetic studies using Cp_3Lu and DEVP have been performed at −10 °C by taking aliquots during the reaction. A linear growth of the molecular weight with conversion, as detected by ^{31}P NMR spectroscopy, can be observed which proves the living character of the polymerization reaction supporting further our hypothesis of a GTP mechanism[4] (Figure 2).

In order to understand the initiation process, oligomers have been produced by using a 5 to 1 ratio of DEVP to catalyst in toluene solution and were subsequently analyzed by ESI MS. For all peaks, the molar mass of the corresponding oligomers was found to be $n \times M_{DEVP} + 66$ g mol^{-1} (Figure S1 and Table S1). The remaining 66 g mol^{-1} corresponds to a cyclopentadienyl group, which initiated chain growth and a proton from the termination reaction during methanolic work-up. Thus, a transfer of the coordinated ligand to a monomer in the initial step is evident. This type of initiation could also be observed for the polymerization of DMVP and DIVP and was further confirmed by MALDI-ToF MS (exemplarily shown in Figure S2 and Table S2).

Because of the small ionic radii of late trivalent rare earth metals and the steric demand of the ligands, it is therefore unlikely that all three Cp ligands are bound to the metal center in a η^5 fashion. This is underlined by previous X-ray diffraction studies which have shown that Cp_3Lu is a polymeric material in the solid state.[7] In this structure single Cp rings form bridges between the individual Cp_2Lu moieties by η^1-metal−Cp bonding.

By using phosphonates, which are known to be strongly coordinating, two electron-donating species, the η^1-(σ)-character of the metal−Cp bond is strengthened, thus allowing a nucleophilic transfer to a coordinated monomer. An additional phosphonate is now able to bind to the vacant coordination site (Scheme 1). The polymerization reaction then proceeds via repeated conjugate addition of a coordinated monomer to the growing chain end.

The investigations of Evans et al. on sterically crowded tris(pentamethylcyclopentadienyl)lanthanide complexes (Cp^*_3Ln, Ln = La, Ce, Pr, Nd, Sm) and the therein described equilibrium between η^5-and η^1-Cp* metal bonding further support the assumption of an initiation by nucleophilic transfer of a cyclopentadienyl ligand.[8]

The larger metal radii of lighter rare earth metals result in sterically less crowded trivalent cyclopentadienyl complexes. This leads to a higher η^5 character of the metal−Cp bond and should lower the nucleophilicity of the Cp anion, therefore disfavoring its transfer to a monomer. This is confirmed by the use of metal centers with different ionic radii. At 30 °C the polymerization of DEVP in toluene is possible when complexes of the heavier rare earth metals are used, showing high polymer yields and low PDI (below 1.4) for all centers between Lu and Dy (Table 1). With Tb and the corresponding lighter metals it was not possible to isolate polymeric material under these conditions.

With decreasing ionic radius the expected molecular weight (M_{exp}) fits better to the determined values. This dependence on the radius is a further evidence for the transfer theory as the lower nucleophilicity of the Cp ligand for early lanthanides leads to lower initiator efficiencies I^* (higher M_n/M_{exp}, observed decrease of I^* from Lu to Dy: 58−77% (entries 1−3) to 8−24% (entries

Table 1. Polymerization of DEVP (Cp_3Ln, Toluene, 30 °C)

entry	Cp_3Ln	monomer[a]	reaction time/h	M_w/ kDa	M_n/ kDa	PDI	I^{*b}/ %	yield[c]/ %
1	Lu	200	1	60	57	1.05	58	88
2	Lu	400	1	110	100	1.10	66	99
3	Lu	800	1	210	170	1.26	77	99
4	Yb	200	1	93	83	1.12	39	94
5	Yb	400	1	140	120	1.16	55	93
6	Yb	800	1	230	200	1.15	66	97
7	Tm	200	1	120	100	1.22	33	89
8	Tm	400	1	200	170	1.20	38	93
9	Tm	800	1	230	190	1.16	69	96
10	Er	200	1	180	135	1.36	24	86
11	Er	400	1	260	210	1.25	31	95
12	Er	800	1	380	290	1.34	45	97
13	Ho	200	3	310	240	1.31	14	85
14	Ho	400	3	450	335	1.34	19	85
15	Ho	800	3	640	480	1.34	27	87
16	Dy	200	5	490	400	1.24	8	94
17	Dy	400	5	570	430	1.33	15	96
18	Dy	800	5	710	550	1.31	24	95

[a] Monomer-to-catalyst ratio. [b] $I^* = M_{exp}/M_n$, I^* = initiator efficiency, M_{exp} = expected molecular weight, based on living polymerization calculation. [c] Determined by weighing of the components.

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Table 2. Polymerizations of DIVP (Cp_3Ln, Toluene, 30 °C, Monomer-to-Catalyst Ratio: 200)

Cp_3Ln	reaction time/h	M_w/kDa	M_n/kDa	PDI	I^{*a}/%	yield[b]/%
Lu	1	39	38	1.03	100	52
Yb	1	57	56	1.02	69	53
Tm	1	79	76	1.04	51	58
Er	3	83	79	1.05	48	28
Ho	5	92	86	1.07	44	37

[a] $I^* = M_{exp}/M_n$, I^* = initiator efficiency, M_{exp} = expected molecular weight, based on living polymerization calculation. [b] Determined by weighing of the components.

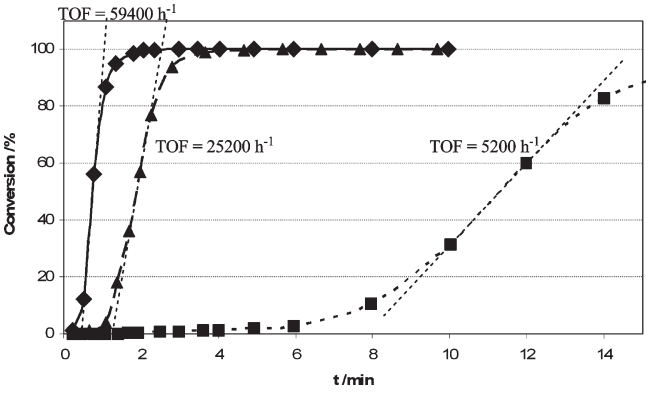


Figure 3. Determination of the catalytic activity of Cp_3Yb (diamond, plain, TOF = 59 400 h^{-1}), Cp_3Tm (triangles, long dashed, TOF = 25 200 h^{-1}), and Cp_3Er (squares, short dashed, TOF = 5200 h^{-1}) for the polymerization of DEVP (monomer-to-catalyst ratio: 600).

16−18)). An increase of the monomer-to-catalyst ratio generally improves the efficiency of this starting process (e.g., from 39% to 66% for Yb (entries 4−6)). This is in good agreement with the expectation as longer reaction times are necessary for full monomer conversion, thus allowing more catalyst molecules to initiate the polymerization.

By increasing the reaction temperature to 70 °C, it was possible to initiate the polymerization also with earlier lanthanides (Tb, Gd), but with low yields (Table S3). In addition, the resulting molecular weights (M_n) for the lighter lanthanides correspond slightly better to the calculated values (M_{exp}) for living polymerizations (higher I^*).

Besides DEVP, there are other simple dialkyl vinylphosphonate monomers available, e.g., dimethyl vinylphosphonate (DMVP) and diisopropyl vinylphosphonate (DIVP). Both can be polymerized using Cp_3Ln complexes as initiators. Specifically, DMVP showed high reactivity; however, the limiting factor is the low solubility of the resulting polymer in solvents suitable for this polymerization. Formed PDMVP precipitates almost immediately from toluene (or THF[3d]) solution with a molecular weight (M_w) below 50 kDa (determined by static light scattering, using Zimm plots). Because of adsorption on the column material, GPC separation, in order to gather information about PDI and M_n, was not possible.

On the other hand, the polymerization of DIVP proceeds slower than with DMVP or DEVP but produces materials with high molecular weight which corresponds better to the initial monomer-to-catalyst ratio. The higher initiator efficiency can be

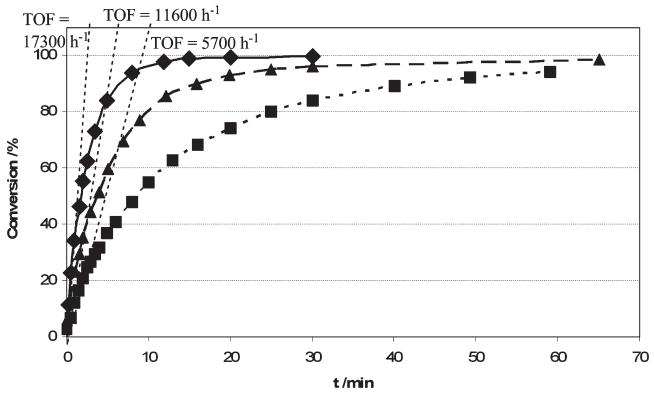


Figure 4. Determination of the catalytic activity of Cp_3Lu (diamond, plain, TOF = 17 300 h^{-1}), Cp_3Yb (triangles, long dashed, TOF = 11 600 h^{-1}), and Cp_3Tm (squares, short dashed, TOF = 5700 h^{-1}) for the polymerization of DIVP (monomer-to-catalyst ratio: 600).

Table 3. Catalytic Activity of Cp_3Ln Complexes for the Polymerization of DEVP (Monomer-to-Catalyst Ratio: 600)

Cp_3Ln	reaction time	conv[a]/ %	init per[b]	M_n/ kDa	I^{*c}/ %	TOF[a]/ h^{-1}	TOF/ I^*/h^{-1}
Lu	5 min	100		210	47	>125000	>265000
Yb	10 min	100	20 s	310	32	59400	185000
Tm	10 min	100	60 s	280	35	25200	72000
Er	32 min	100	6 min	530	19	5200	28000
Ho	2 h	99.5	30 min	670	15	1200	8000
Dy	5 h	85	100 min	710	12	270	2300

[a] Determined by ^{31}P NMR spectroscopic measurement. [b] Init per: initiation period, reaction time until 3% conversion is reached. [c] $I^* = M_{exp}/(M_n \times conv)$, I^* = initiator efficiency, M_{exp} = expected molecular weight, based on living polymerization calculation.

attributed to both the slower chain growth (due to the stronger steric hindrance for the coordination of a DIVP monomer) and a shortening/absence of an initiation period which is observable for DEVP (see determination of catalytic activity). Therefore, the rate of the initiation is faster than for the chain growth, affording remarkably narrow PDIs (below 1.1) for all experiments (Table 2). A quantitative precipitation of the polymer with hexane was not possible due to the increased solubility of PDIVP in nonpolar solvents leading to the observed low yields, generally between 30% and 60%.

Determination of the Catalytic Activity. The above results indicate clearly that the initiator efficiency is strongly affected by the radius (and therefore also the Lewis acidity) of the metal center. In order to investigate the influence of these parameters on the catalytic activity of the different Cp_3Ln complexes, further polymerizations at 30 °C were carried out with both DEVP and DIVP. The activity was thereby determined by taking aliquots which are quenched with deuterated methanol and subsequently analyzed by ^{31}P NMR spectroscopy.

The turnover frequency (TOF) was defined as the maximum slope of the conversion vs reaction time plot (Figures 3 and 4). In order to determine whether the varying catalytic activities could only originate from different initiator efficiencies, the polymer contained in the remaining reaction mixture (after taking aliquots) was isolated and the molecular weight

Table 4. Catalytic Activity of Cp_3Ln Complexes for the Polymerization of DIVP (Monomer-to-Catalyst Ratio: 600)

Cp_3Ln	reaction time	conv[a]/%	M_n/kDa	I^*[b]/%	TOF[a]/h^{-1}	TOF/I^*/h^{-1}
Lu	30 min	100	128	89	17300	19400
Yb	65 min	99	153	75	11600	15400
Tm	60 min	94	179	60	5700	9500
Er	3 h	92	188	56	2000	3600
Ho	5 h	49	336	17	500	2900

[a] Determined by ^{31}P NMR spectroscopic measurement. [b] $I^* = M_{exp}/(M_n \times \text{conv})$, I^* = initiator efficiency, M_{exp} = expected molecular weight, based on living polymerization calculation.

analyzed by GPC-MALS in order to determine the initiator efficiency I^*. By dividing the TOF by I^*, a normalized catalytic activity can be calculated which only considers active complexes (Tables 3 and 4).

For the polymerization of DEVP an initiation period is observed (Figure 3 and Figure S3), which is considerably lengthened through the series Lu to Dy and results also in decreasing initiator efficiencies. This decrease is in good agreement with the results detailed above. Different absolute values for I^* can be attributed to different catalyst and monomer concentrations (see Experimental Section).

The measurements clearly show that not only the initiator efficiency but also the (normalized) catalytic activity strongly decreases for earlier lanthanides (Table 3). The normalized catalytic activity therefore changes by an approximate factor of 2.5−3.5 moving from one metal to its lighter homologue.

For DIVP an initiation period as it is observed for DEVP does not occur (Figure 4 and Figure S4). This can be attributed to the stronger steric demand of DIVP facilitating the nucleophilic transfer of a cyclopentadienyl ligand by destabilizing the intermediate shown in Scheme 1. The stronger steric hindrance also leads to a strong decrease (by approximately a factor of 10) in catalytic activity in comparison to DEVP (Table 4). Both facts explain the observed higher initiator efficiency and lower PDI for the polymerization of DIVP.

Moving from one metal to its lighter homologue, the normalized catalytic activity decreases by a factor 1.5−2, showing that the influence of the metal radii on the catalytic activity is smaller for DIVP than it is for DEVP. Taking into consideration that the steric hindrance influencing the rate of chain propagation, in comparison to DEVP, is stronger for the late (small) lanthanides, this observation is in good agreement with the expectation.

As the normalized turnover frequency is independent of the initiator efficiency and initiation mechanism, these results clearly show that in case of all lanthanide metallocenes (Cp_2LnX) coordinative anionic polymerization of vinylphosphonates with high catalytic activity can only be achieved by using late lanthanides. Even if a more uniform start of polymerization can be established by a different initiation, the catalytic activity of earlier lanthanides would still be very limited.

Solubility and Thermoresponsive Behavior of Poly(vinylphosphonate)s. Poly(vinylphosphonate)s show a differing solubility behavior depending on the nature of the ester side chain. While PDMVP is soluble in water, it displays very limited solubility in common organic solvents, thus affording precipitation of the material soon after starting polymerization. This inhibits the formation of high-molecular-weight polymers. PDIVP, on the other hand, shows high solubility in many solvents leading to a more challenging purification by precipitation of the product (and is only possible for molecular weights above ca. 30 kg mol^{-1}).

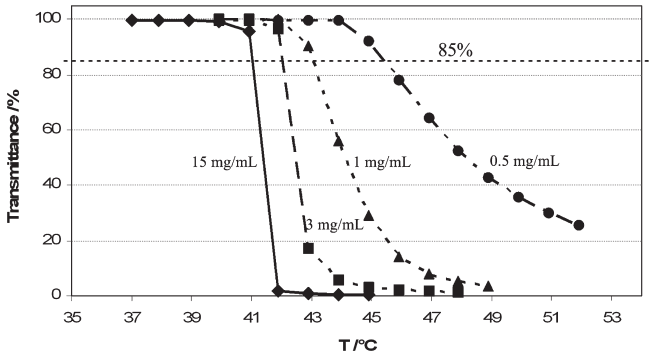


Figure 5. Change of transmittance at λ = 550 nm for PDEVP with 160 kg mol^{-1} at different concentrations: 15 mg mL^{-1} (diamonds, plain), 3 mg mL^{-1} (squares, long dashed), 1 mg mL^{-1} (triangles, short dashed), and 0.5 mg mL^{-1} (circles, broken).

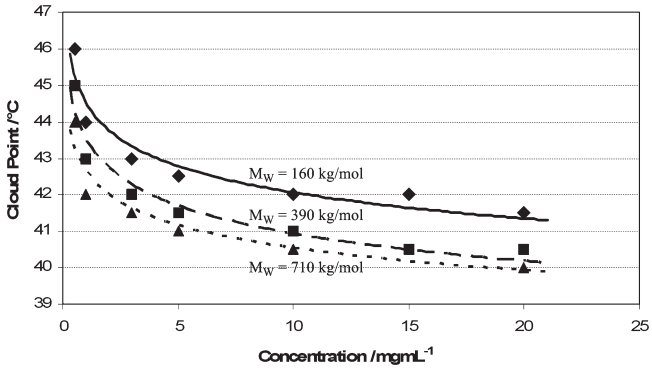


Figure 6. Cloud point vs concentration for aqueous PDEVP solutions with different molecular weight: 160 kg mol^{-1} (diamonds, plain), 390 kg mol^{-1} (squares, long dashed), and 710 kg mol^{-1} (triangles, short dashed).

Being between the two solubility extremes showed by the hydrophilic PDMVP and the rather hydrophobic PDIVP, respectively, it is not surprising that PDEVP shows amphiphilic behavior. It is highly soluble in both water and lighter alcohols, whereas the solubility in other solvents is strongly dependent on the molecular weight: after a distinct swelling (between 10 and 25 mg of solvent per mg of polymer) polymers with a molecular weight below ~1000 kg mol^{-1} start to dissolve while ultrahigh-molecular-weight polymers stay in the swollen state. Only in hydrophobic solvents such as hexane or pentane no significant solubility or polymer swelling could be observed.

The amphiphilicity of PDEVP is further underlined by the existence of a lower critical solution temperature (LCST) of aqueous PDEVP solutions. Hereby the LCST is close to the physiological range (Figure 5). For further LCST studies this polymer is interesting due to the living character of the polymerization. Thus, narrow molecular weight distributions (sharp LCST) can be achieved, and block copolymer structures are easily accessible.

Previous studies on thermoresponsive PNIPAM and poly(2-oxazoline)s have shown that the cloud point of these systems exhibits a significant dependence on both concentration and molecular weight of the polymer[9] thus enabling the design of materials with a specific LCST. In the case of PDEVP, we found

that a decrease of the concentration leads to a broadening of the transition and to higher cloud points. Both effects are stronger with reduced concentration (Figures 5 and 6).

To determine the influence of the molecular weight on the LCST of PDEVP, aqueous solutions with a polymer concentration of 5 mg mL^{-1} (M_w range of 39−1200 kg mol^{-1}) were used. Higher concentrations lead to very viscous solutions for high-molecular-weight polymers, and lower concentrations result in broad transitions. As well as for the concentration the cloud point shows a strong dependence on the molecular weight of the polymers. Lower degrees of polymerization result in polymer solutions with a higher LCST, again with an increasing effect the smaller the molecular weight is (Figure 7).

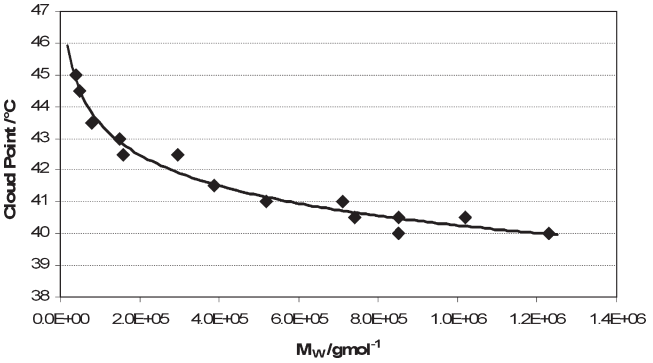
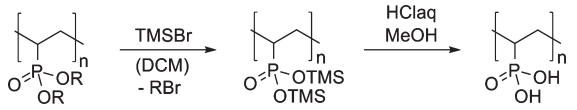


Figure 7. Cloud point vs weight-average M_w of PDEVP.

Scheme 2. Transesterification of Poly(dialkyl vinylphosphonate)s to Poly(bis(trimethylsilyl)-vinylphosphonate) and Subsequent Mild Hydrolysis to Poly(vinylphosphonic acid)



Polymer Analogous Hydrolysis to Poly(vinylphosphonic acid). In order to hydrolyze the here-presented esters to their respective acids, a mild method to cleave the alkyl groups is needed in order to avoid polymer degradation. Recently, Wagner et al. presented a hydrolysis of lower molecular weight poly(vinylphosphonate)s (M_n < 40 kDa) under mild conditions by treatment with trimethylsilyl bromide in refluxing dichloromethane.[3d] We found that this reaction proceeds in a two-step fashion by transesterification and subsequent hydrolysis, similar to the previously described hydrolysis of monomeric phosphonic esters with trimethylsilyl chloride (Scheme 2).[10] The intermediate poly(bis(trimethylsilyl)vinylphosphonate) can be isolated (Figure 8) but proved to be very sensitive to hydrolysis. A direct transformation of this intermediate to other ester functionalities (e.g., poly(dibenzyl vinylphosphonate)) by treatment with TBAF and the corresponding bromide (e.g., benzyl bromide) was possible; however, complete separation of *tert*-butylammonium from the product could not be achieved.

We applied the method described by Wagner et al.[3d] to the obtained high-molecular-weight poly(vinylphosphonate)s (M_n > 250 kDa for both PDEVP and PDIVP, as detailed above PDMVP with M_w > 50 kDa was not accessible) and observed high conversion rates for both PDEVP and PDMVP, as demonstrated by ^{1}H NMR spectroscopy (Figure 8 and Figure S5). Using this hydrolysis procedure, it was not possible to achieve a complete cleavage of the ester bonds for high-molecular-weight PDIVP (Figure S6), probably due to a stronger steric hindrance for cleavage of the isopropyl group and to a higher boiling point of the side product 2-bromopropane, which therefore cannot be removed from equilibrium.

In order to verify if the end groups are retained during hydrolysis, we applied the described procedure to oligomeric vinylphosphonates and analyzed the obtained oligomeric vinylphosphonic acids by both ESI and MALDI-ToF MS as well as by ^{1}H NMR spectroscopy. In the resulting ^{1}H NMR spectrum signals in the region between 5 and 7 ppm were not observed indicating an absence of the expected cyclopentadienyl end group. In MALDI-ToF MS different oligomeric distributions with $\Delta(m/z) = 108$ (molar mass of vinylphosphonic acid) could be observed in the negative mode, but the corresponding end

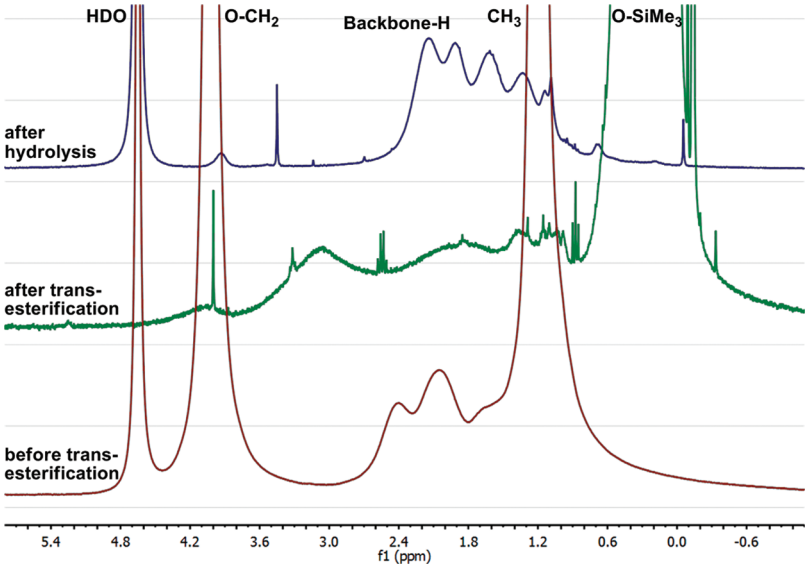


Figure 8. ^{1}H NMR spectra of PDEVP before (in D_2O, red) and after (in C_6D_6, green, for easier comparison this spectrum was shifted 0.20 ppm to higher field) transesterification with TMSBr and after hydrolysis (in D_2O, blue).

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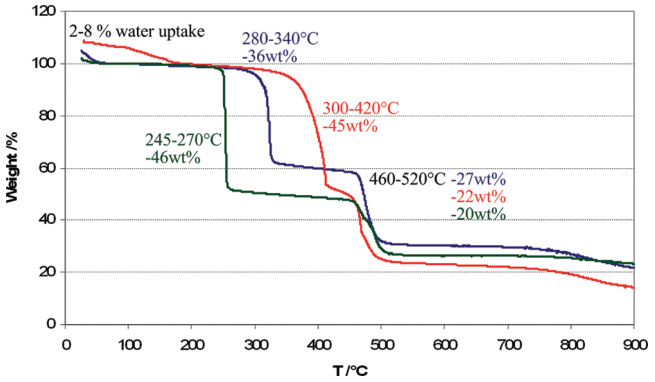
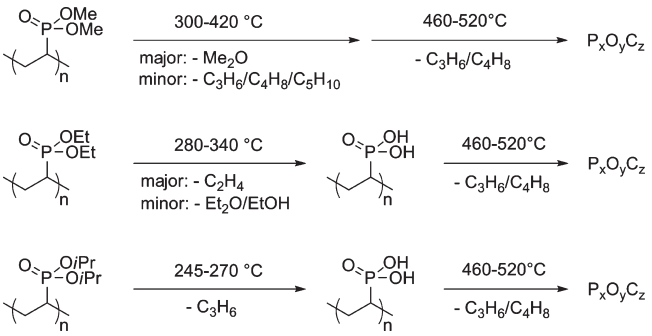


Figure 9. TGA measurements for PDMVP (red), PDEVP (blue), and PDIVP (green); mass losses reported in weight percent (wt %).

Scheme 3. Proposed Decomposition Processes for Poly(vinylphosphonate)s According to TGA MS



groups could not be identified. Ionization of the oligomers by ESI MS was not possible.

Thermal Decomposition of Poly(vinylphosphonate)s. TGA measurements of poly(vinyphosphonate)s revealed a two-step thermal decomposition process for the three evaluated ester side groups (methyl, ethyl, isopropyl). Additionally, water uptake (confirmed by TGA MS) could be observed, which differs according to the hydrophilicity of the polymers (2−8 wt %). In all cases the second decomposition step occurs at the same temperature range (460−520 °C), thus confirming the previous assumption of backbone degradation.[3e] The three polymers differ in the first decomposition step: while for PDIVP a sharp transition is observed at lower temperatures (245−270 °C) relative to PDEVP (280−340 °C), for PDMVP a broader transition at higher temperatures (300−420 °C) is observed (Figure 9). Hereby the mass losses for PDEVP and PDIVP correspond well to cleavage of the ester side chains by elimination: 34 wt % for ethylene cleavage in case of PDEVP (observed: 36 wt %), 44 wt % for propylene cleavage in case of PDIVP (observed: 46 wt %).

In order to understand the decomposition process for PDMVP and to confirm the side-chain cleavage for PDEVP and PDIVP, TGA MS measurements were carried out. For the latter, only propylene (m/z = 41/42) could be found as a volatile during the first decomposition step, proving side-group cleavage by elimination. In contrast to the results of Rabe et al.,[3e] for PDEVP not only ethylene (m/z = 26/27/28, major decomposition compound) and ethanol (m/z = 45/46, very small amount) could be identified as volatiles, but also diethyl ether (m/z = 74/59/45, very small amount) (Scheme 3).

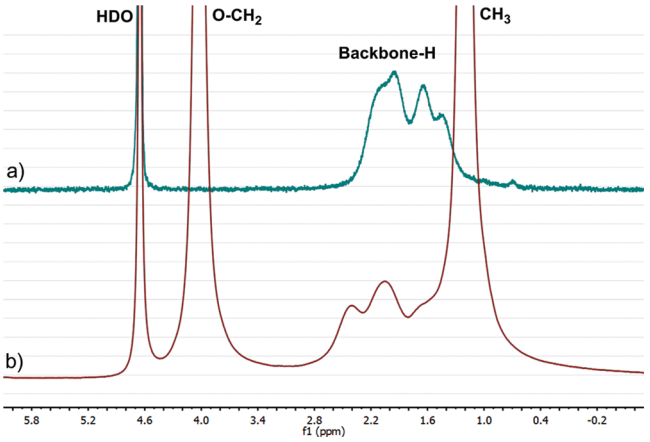


Figure 10. ^{1}H NMR spectra in D_2O of (a) poly(vinylphosphonic acid) (PVPA) synthesized by thermal treatment (green) of the (b) corresponding poly(diethyl vinylphosphonate) PDEVP (red).

As for PDMVP an elimination reaction as side group cleavage is not possible; only the cleavage of dimethyl ether is observed (m/z = 45/46). During this decomposition also partial degradation of the polymer backbone occurs, which can be supported by both the detection of alkenes (propylene m/z = 41/42, butene m/z = 55/56, pentene m/z = 69/70) as volatile decomposition products as well as by the weight loss (34 wt % for dimethyl ether cleavage, observed: 45 wt %) (Figure 9 and Scheme 3).

For all three polymers during the second degradation step only small amounts of propylene and butene can be observed, indicating main-chain scission. The observed weight loss shows that some volatile phosphorus compounds must be evolving (mass of P_2O_5 is much higher than the residual mass), which could though not be observed by MS.

According to these results, poly(vinylphosphonic acid) (PVPA) should be easily accessible by thermal treatment of both PDEVP and PDIVP. This could be confirmed by tempering the corresponding poly(vinylphosphonate)s for 30 min at 350 °C in a nitrogen atmosphere, yielding poly(vinylphosphonic acid) as a gray solid. Full cleavage of the ester side chains was determined by ^{1}H NMR spectroscopy (see Figure 10 and Figure S7) and further confirmed by elemental analysis. The molecular weight of the resulting polymer was determined by static light scattering methods in batch, producing Zimm plots. Within the limits of the experimental accuracy, degradation of the polymer backbone could not be observed. Similarly as for the hydrolysis with TMSBr, the end groups of obtained oligomeric vinylphoshonic acids could not be identified.

CONCLUSIONS

Trivalent cyclopentadienyl lanthanide complexes are easily accessible in a one-step reaction and proved to be, in the case of late lanthanides, efficient initiators and highly active catalysts for the group transfer polymerization of various dialkyl vinylphosphonates. For DEVP and DIVP, this living polymerization leads to well-defined polymers with low PDI and a molecular weight close to the initial monomer to catalyst ratio even at elevated temperatures (30−70 °C). The initiation proceeds via nucleophilic transfer of a cyclopentadienyl ligand as shown by mass spectrometric studies. The smaller the metal center (i.e., the higher the Lewis acidity), the higher the initiator efficiency and the normalized catalytic

activity TOF/I^*. Therefore, Cp_2LnX-initiated coordinative anionic polymerization of vinylphosphonates with high catalytic activity can only be achieved by using late lanthanide complexes.

Because of the low solubility of PDMVP in suitable solvents, a well-controlled lanthanide-mediated group transfer polymerization of DMVP is not thus far possible. By contrast, due to its high solubility in most common organic solvents, purification of PDIVP by precipitation does not give satisfactory results. Combined with high polymerization activity and easy conversion by both mild hydrolysis or thermal treatment, this makes PDEVP the ideal basis for well-defined high-molecular weight poly(vinylphosphonic acid) with narrow chain length distribution. Furthermore, aqueous PDEVP solutions exhibit a lower critical solution temperature (LCST) close to the physiological range, which is strongly dependent on both concentration and molecular weight of the polymer (40−46 °C).

EXPERIMENTAL SECTION

General. All reactions were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. All glassware was heat dried under vacuum prior to use. Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich or Acros Organics and used as received. Toluene was dried using a MBraun SPS-800 solvent purification system. Tetrahydrofuran (THF) was distilled over potassium prior to use. All metal complexes, DEVP, and DIVP were prepared according to literature procedures.[4c,6] DMVP was purchased from Alpha Aesar. Monomers were dried over calcium hydride and destilled prior to polymerization.

NMR spectra were recorded on a Bruker ARX-300 spectrometer. ^{1}H NMR spectroscopic chemical shifts δ are reported in ppm relative to tetramethylsilane and calibrated to the residual proton signal of the deuterated solvent. ^{31}P NMR spectroscopic chemical shifts are reported in ppm relative to and calibrated to 85% H_3PO_4. Deuterated solvents were obtained from Deutero Deutschland GmbH and used as received. Elemental analyses were measured at the Laboratory for Microanalytics at the Institute of Inorganic Chemistry at the Technische Universität München. ESI MS analytical measurements were performed with isopropanol solutions on a Varian 500-MS spectrometer, using 70 keV in the positive ionization mode. MALDI-ToF MS measurements were performed on a Bruker Ultraflex ToF/ToF mass spectrometer. All samples were prepared and run in THF solution dithranol doped with sodium trifluoroacetate. TGA was carried out on a Texas Instruments TGA-Q5000 with a heating rate of 10 K min^{-1}. TGA MS measurements were performed on the same instrument using a heating rate of 25 K min^{-1}.

Polymerizations. Polymerizations were performed in 16 mL of toluene, using a catalyst concentration of 0.625 mg mL^{-1} (10 mg of catalyst). After dissolving the catalyst in the solvent and thermostatting to the desired temperature, the calculated amount of monomer was added. The reaction was stirred at the given temperature for the stated reaction time and then quenched with MeOH (0.5 mL). The polymer was precipitated by addition of the reaction mixture to hexane (150 mL) and decanted from solution. Residual solvents were removed by drying under vacuum at 70 °C overnight.

Activity Measurements. For activity measurements 21.7 μmol (1 equiv) of the catalyst was dissolved in 20 mL of toluene, and the reaction mixture was thermostated to 30 °C. Then 2.00 mL (2.14 g, 600 equiv) of DEVP or 2.50 g (600 equiv) of DIVP was added. During the course of the measurement aliquots (0.5 mL) are taken and quenched by adding to deuterated methanol (0.2 mL). The conversion was determined by ^{31}P NMR spectroscopy. After the stated reaction time a last aliquot was taken, and the reaction was quenched by addition of MeOH (0.5 mL). Work-up of the polymer was carried out according to the regular polymerizations.

Molecular Weight Determination. GPC was carried out on a Varian LC-920 equipped with two PL Polargel columns. As eluent a mixture of 50% THF, 50% water, and 9 g L^{-1} tetrabutylammonium bromide (TBAB) was used in the case of PDEVP; for PDIVP analysis the eluent was THF with 6 g L^{-1} TBAB. Absolute molecular weights have been determined online by multiangle light scattering (MALS) analysis using a Wyatt Dawn Heleos II in combination with a Wyatt Optilab rEX or the integrated RI detector (356-LC) as concentration source.

Determination of the LCST. Turbidity measurements for the determination of the cloud point were carried out with a Cary 50-UV/vis spectrometer from Varian with 4 mL glass cuvettes and aqueous polymer solutions of different concentrations (0.5−20 mg mL^{-1}). Using a Peltier thermostat, the samples were heated at a rate of 1 K min^{-1} followed by a 3 min waiting period to ensure thermal equilibrium. The cloud point was determined by repeated spectrophotometric detection of the changes in transmittance at a wavelength of 550 nm. It was defined as the temperature corresponding to a 15% decrease in optical transmittance. For further evaluation the results of the single experiments are averaged and rounded to 0.5 °C.

Polymer Analogous Hydrolysis to Poly(vinylphosphonic acid). Poly(dialkyl vinylphosphonate) was dissolved in dry dichloromethane (10 g L^{-1}), 3 equiv of trimethylsilyl bromide (respective to the ester functionalities) was added, and the resulting reaction mixture was refluxed for 24 h. Then the volatiles were removed in vacuo, and the residue was dissolved in a small amount of methanol (∼5 equiv) and aqueous HCl (1 M, 4 equiv). After 2 h the reaction mixture was dried in vacuo and purified by aqueous dialysis (100 kDa MWCO).

Thermal Treatment of Poly(vinylphosphonate)s. Poly(diethyl vinylphosphonate) (PDEVP) or poly(diisopropyl vinylphosphonate) (PDIVP) was heated at a rate of 20 °C min^{-1} to 350 °C and tempered for 30 min at this temperature. After cooling the corresponding poly(vinylphosphonic acid) was obtained as a gray solid.

Elemental analysis: PVPA: calculated (disregarding end groups): C 22.2%, H 4.66%, P 28.7%; found: from PDEVP: C 24.5%, H 4.66%, P 29.0%; from PDIVP: C 24.0%, H 4.28%, P 29.9%).

ASSOCIATED CONTENT

Supporting Information. ESI and MALDI-ToF MS data of oligomer analysis, DEVP polymerization results at 70 °C, conversion vs reaction time diagrams for catalysts with low activity, further ^{1}H NMR spectra for polymer analogous hydrolysis and thermal treatment. This material is available free of charge via the Internet at http://pubs.acs.org.

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