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Polymerization of Diethyl Vinylphosphonate Mediated by Rare-Earth Tris(amide) Compounds

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Introduction. Phosphorus-containing polymers, particularly copolymers, are of interest because of potential flame-retarding properties,[1] also because of their ability to adhere to metal surfaces[2] and bind to metal ions.[3] Practical preparative routes for the synthesis of vinylphosphonate monomers were reported starting in the late 1940s.[4] A few reports have been published investigating the free radical polymerization of vinylphosphonates. In 1948, Lindsey reported that "α,β-ethylenically unsaturated phosphonic acid compounds including the acids, their esters and their amides have been found to be essentially unpolymerizable by themselves in spite of numerous attempts".[5] About the same time Kosolapoff observed that diethyl vinylphosphonate "decolorized permanganate instantly in the cold and possessed mildly expressed polymerizability".[4b] In 1960, Pike and Cohen published the di-*tert*-butyl peroxide-initiated polymerization of vinylphosphonates (R = Et, iPr) yielding clear, light-yellow, viscous liquid oligomers with molecular weights up to slightly above 1000 g/mol, depending on the initiator concentration used.[4c] In 1967, Muray also observed that vinylphosphonates polymerize with difficulty, yielding oligomers with only relatively low molecular weights.[6] In 2008, Hirano et al. reported quantitative polymerization of dialkyl vinylphosphonates (R = Me, Et) with dicumyl peroxide at 130 °C yielding low molecular weight polymers (M_n = (3.4−3.5) × 10^3 g/mol),[7] and Wegner et al. reported the characterization of oligo(vinylphosphonates) (R = Me, Et, iPr) by high-resolution electrospray ionization mass spectrometry. These oligomers were obtained in low yield by free radical polymerization using AIBN or 4,4-azobis(4-cyanovaleric acid) at 60 °C.[8] All studies independently found that electron-poor vinylphosphonate monomers fail to homopolymerize to high molecular weight products. In the same year Komber et al. presented a study of the microstructure of poly(phosphonic acid) and its dimethyl ester by analyzing their ^{1}H, ^{13}C, and ^{31}P NMR spectra.[9]

Since lanthanide compounds are known to be excellent catalysts for a variety of transformations, we were interested in investigating the polymerization of vinylphosphonates mediated by rare-earth compounds. Our work was motivated by an earlier report from Yasuda demonstrating that MMA can effectively be polymerized by organolanthanide(III) derivatives yielding high weight polymers with narrow polydispersities via group transfer catalysis.[10]

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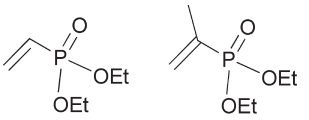
Results and Discussion. We attempted polymerization of diethyl vinylphosphonate (DEVP)[4] as well as the α-methyl-substituted diethyl 1-methylvinylphosphonate (DEMVP)[11] using several different known trivalent lanthanide complexes.



DEVP DEMVP

We started our investigations using a readily available tris(alkyl) compound of yttrium, $Y[CH_2SiMe_3]_3(THF)_2$,[12] as an initiator. Reactions were carried out in toluene solutions at −25 °C. However, only viscous, oily materials were obtained, indicating that formation of low weight oligomers had occurred. Additionally, only incomplete conversion of the monomer was observed. Similar observations were made when employing tris(phosphanide) compounds of general composition $Ln[P(SiMe_3)_2]_3(THF)_2$ (Ln = Nd,[13a] Tm[13b]). Tris(amide) compounds of general composition $Ln[N(SiMe_3)_2]_3$ (Ln = La, Nd, Sm)[14] were found to yield solid, colorless materials, in fairly low yield though, exhibiting only one broad signal in the ^{31}P NMR spectra (at 33.1 ppm in $CDCl_3$).

We continued our investigations, trying to optimize the reaction conditions, by varying the substituents on the amide ligand. Tris(amide) compounds of general composition $Ln[N(SiHMe_2)_2]_3(THF)_2$ (Ln = La, Nd,[15a] Sm[15b]) featuring a sterically less demanding amide ligand are readily accessible. Using these particular rare-earth tris(amides), we found that for Ln = Nd and Sm the olefinic precursor is converted to solid poly(diethyl vinylphosphonate) (poly(DEVP)) in 80% yield, while the lanthanum derivative produces somewhat lower yield of homopolymer (60%). The materials obtained exhibit a broadened ^{31}P NMR signal at 33.1 ppm in $CDCl_3$, and the ^{1}H NMR spectra confirm the absence of vinylic protons.

In a typical experiment, a monomer/initiator ratio of 500:1 was used (Table 1). In a glovebox, a toluene solution (10 mL) of the corresponding lanthanide tris(amide) compound was prepared and cooled to −35 °C (glovebox refrigerator). 1.0 g (6.1 mmol) of diethyl vinylphosphonate (DEVP), which was previously dried over CaH_2, destilled under reduced pressure, and degassed, was also cooled to this temperature (in a syringe). The DEVP was then added at once to the catalyst containing solution, and the mixture was warmed up upon vigorous stirring to glovebox temperature. After 14 h the homogeneous mixture was taken out of the glovebox and poured upon stirring into excess hexanes, resulting in precipitation of the homopolymer, which was washed repeatedly with hexanes and then dried under vacuum. The homopolymers obtained are colorless solids and show no visible sign of degradation/decomposition up to 200 °C (Table 1). They are soluble in methanol, chloroform, and arene solvents. These solvents were used in the NMR study to find the best signal separation for stereochemical structure characterization, and finally, measurements in C_6D_6 at 70 °C has proved to be the best choice.[16] Measurements at higher

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Table 1. Comparison of Polymerization Results ([M]/[I] = 500:1), Tacticities, Temperature Maxima of Derivative Weight (T_{DTG}), Corresponding Weight Loss, and Residue after the Second Decomposition Step

Ln	M_w (g/mol)	M_n (g/mol)	PDI	yield (%)	*mm* (%)	*rm* (%)	*rr* (%)	T_{DTG} (°C) (1st step)	weight loss (%)	T_{DTG} (°C) (2nd step)	weight loss (%)	residue (%) (after 2nd step)
La	213 000	65 000	3.26	60	66	30	4	314	40.4	467	35.0	19.7
Sm	261 000	84 000	3.11	80	79	20	1	313	42.9	466	34.2	22.9
Nd	280 000	79 000	3.56	80	79	20	1	311	40.9	473	33.2	21.6

temperatures in aromatic solvents only result in a marginal line narrowing. Whereas the NMR spectra of poly(DEVP) prepared from the Nd and Sm catalyst are identical, the La catalyst results in a polymer with different tacticity (Figure S1). The analysis of the NMR spectra follows mainly the procedure outlined in detail for poly(dimethyl vinylphosphonate) (poly(DMVP)) wherein some special spectral features are described in more detail.[9] Figure 1 shows a comparison of the ^{13}C (region of backbone carbons) and ^{31}P NMR spectra of the polymers obtained employing the Sm (Figure 1a,b) and the La catalyst (Figure 1c,d). In spite of a long measuring time, the signal-to-noise ratio of the ^{13}C NMR spectra is rather poor for this region, and the spectra are complicated due to scalar $^{13}C-^{31}P$ couplings. Based on DEPT measurements and the HMQC spectrum (Figure 2a), the methine and methylene signal regions can be assigned. It can be concluded from these spectra that the signals of methylene carbons cover the full 27−35 ppm range and the methine carbon signals appear between 31 and 35 ppm, thus preventing any quantification. However, the oxymethylene carbon results in three signals at 61.8 (*mm*), 61.5 (*mr*), and 61.2 ppm (*rr*) (Figure S2), which were assigned to triads in accordance with the results from the ^1H NMR spectra. The ^{31}P spectra (Figure 1b,d) are characterized by broadened low-field signals appearing as shoulder of a sharp signal at 34.1 ppm. The content of structures represented by the sharp signal is lower for the La-catalyzed sample, and based on interpretation of the ^1H NMR spectra this signal is assigned to longer *isotactic* sequences whereas the broadened shoulder is caused by *heterotactic* ones.

Valuable structural information can be deduced from the ^1H NMR spectra (Figure S1 and Figure 3). The regions of the methine and methylene backbone proton signals are well separated (Figure 2a), showing the expected 1:2 intensity ratio. In the methylene protons region one can distinguish a less-structured signal of *racemic*-centered sequences at ~2.2 ppm and signal pairs of the nonequivalent geminal methylene protons in the three *meso*-centered tetrads (Figure 2b). The lowest chemical shift difference is observed for the two signals of the dominating *mmm* tetrad. In the methine protons region the high-field part represents the *mm*-triad with a splitting in the pentads *mmmm*, *mmmr*, and *rmmr*. It is followed by a less structured signal region from the *rm*-triad. Finally, the broadened signal of low intensity at ~3.35 ppm is caused by the *rr*-triad. All together, the sequence of tacticity-dependend signals corresponds to those found for poly(DMVP) and poly(vinylphosphonic acid).[9] The *mm*-, *rm*-, and *rr*-triad fractions were determined from the methine protons region and from the oxymethylene carbon signals by line-fitting. The homopolymer (Ln = La) gives 66% (67% from ^{13}C), 30% (31%), and 4% (2%), respectively, whereas 79% (80%), 20% (17%), and 1% (3%), respectively, were determined for the other homopolymers (Ln = Nd, Sm; for Nd ^1H only). Calculating the parameters for first-order Markov statistics[17] gives $P_{m/r} = 0.185 \pm 0.005$ (Ln = La) and 0.105 ± 0.01 (Ln = Sm and Nd). $P_{r/m}$ could not be calculated with a satisfying accuracy because the error in determining the content of the *rr* triad is too large. If stereoregulation follows a Bernoullian pathway, the fraction

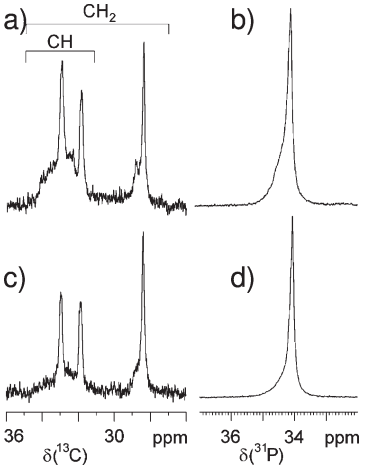

Figure 1. ^{13}C NMR spectra (a, c) and ^{31}P NMR spectra (b, d) of poly(DEVP) obtained from La catalyst (a, b) and Sm catalyst (c, d), measured in C_6D_6 at 70 °C. Only the region of the CH and the CH_2 backbone carbons is shown. The signals of the ethyl ester groups appear at 16.8 (CH_3), 61.8 (*mm*), 61.5 (*mr*), and 61.2 ppm (*rr*, OCH_2), respectively (see Figure S2).

of *meso*-dyads, P_m, should be $1 - P_{m/r}$, that is ~81.5% (Ln = La) and ~89.5% (Ln = Sm and Nd). The experimental values determined from the intensity ratio of the low-field signal region of methylene protons to the methine protons are found to be $87 \pm 2\%$ (Ln = La) and $95 \pm 2\%$ (Ln = Nd and Sm) (see Figure S1). The calculated and experimentally determined values are substantially different beyond experimental error, indicating that the polymerizations are of first-order Markovian rather than Bernoullian sequence distribution.

Finally, the samples investigated are *isotactic*-rich polymers with a content of *m*-dyads significantly higher than reported for poly(DMVP) obtained by radical polymerization ($59 \pm 2\%$).[9]

The thermal behavior of the obtained poly(DEVP) homopolymers was investigated by both TGA/FT-IR and DSC techniques.[18] Independent of the rare-earth compound used for the polymerization, all samples show a two-step decomposition according to TGA analysis (Figure 4 and Table 1). Besides a small content of moisture at lower temperatures during the first degradation step, ethene and ethanol were identified as volatiles from the FT-IR spectra (Figures S3 and S4). The second degradation step is presumably caused by the main-chain scission, with small differences in the maximum temperature of the derivative curves, possibly due to varying molecular weights and/or tacticities.[19] DSC measurements of all three homopolymers are shown in Figure S5. The glass transition temperatures were determined from the reversing heat capacity signal of the second heating run. T_g was found at −28 °C (Ln = Nd) and at −30 °C (Ln = Sm). For Ln = La the glass transition is outside the lower limit of the instrument (−80 °C).[18]

SEC investigations on a commonly used GPC setup utilizing THF[20] as an eluent yielded no convenient results. We assume that the polar polymers have a strong tendency to

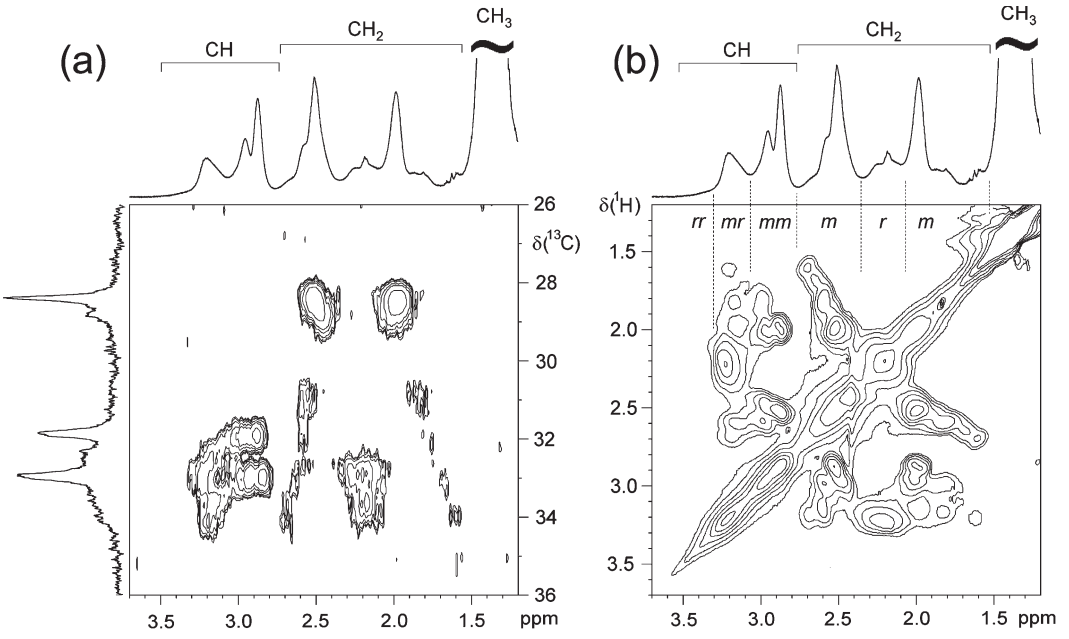

Figure 2. Regions of the $^{1}H-^{13}C$ HMQC spectrum (a) and $^{1}H-^{1}H$ TOCSY spectrum (b, mixing time 20 ms) of poly(DEVP) obtained from La catalyst (solvent: C_6D_6; T = 70 °C).

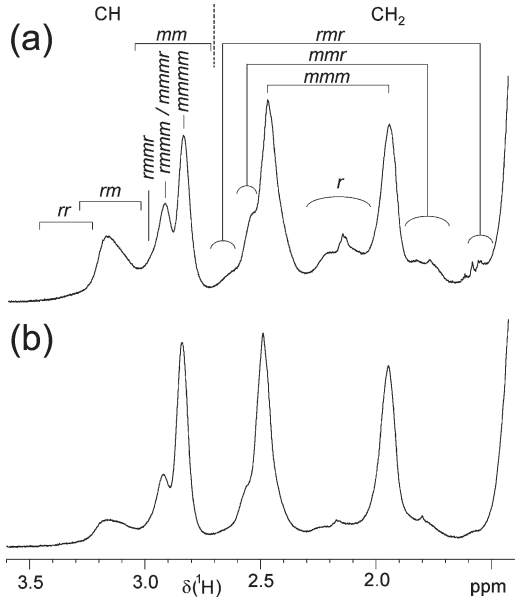

Figure 3. ^{1}H NMR spectra of poly(DEVP) obtained from La catalyst (a) and Sm catalyst (b) measured in C_6D_6 at 70 °C. Only the region of CH and CH_2 backbone protons is shown. The less-structured signals of the ethylester groups appear at 1.36 ppm (CH_3) and 4.29 ppm (OCH_2), respectively (see Figure S1).

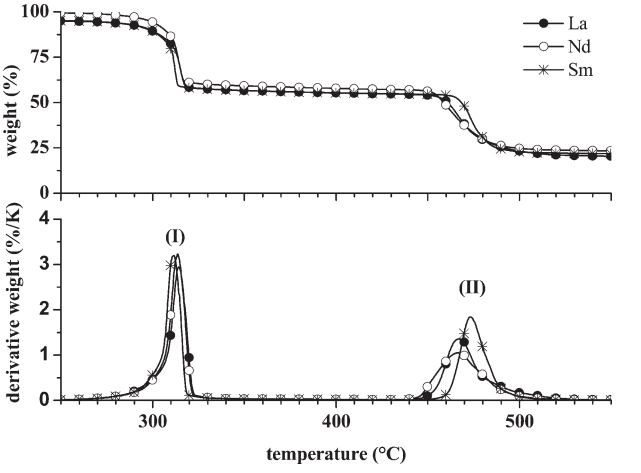

Figure 4. TGA of poly(DEVP) obtained from Ln tris(amide) catalysts (Ln = La, Nd, Sm).

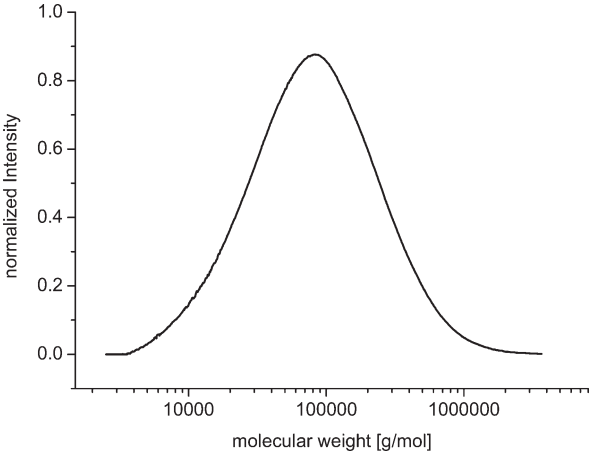

Figure 5. SEC trace of poly(diethyl vinylphosphonate) via Nd-catalyzed polymerization; RI detection; with THF at a flow rate of 0.5 mL/min; molecular weight is given with respect to narrowly distributed PS standards.

interact with the column material. However, addition of 0.25 wt % of an electrolyte (tetrabutylammonium bromide) to the eluent effectively managed to suppress such adsorption phenomena, and Gaussian type curves were obtained corresponding to molecular weights (M_n) in the range of 65−85 000 g/mol and polydispersity indices (PDIs) between 3 and 4, referenced to polystyrene standards (Figure 5). The observation of fairly broad PDIs might be attributed to the presence of more than one initiating group. A comparison or the influence of different [M]/[I] ratios (Ln = Nd) on the molecular weight distributions showed very similar results for [M]/[I] of 500:1 and 250:1, but somewhat lower molecular weights for [M]/[I] of 100 (Figure S6). We also investigated how, after

quantitative conversion of the monomer, the addition of more monomer would affect the molecular weight distributions. We found that more polymer is obtained with virtually identical GPC curves, indicating that the polymerization is not "living", but the catalyst still being active.

Interestingly, we found that the yttrium tris(amide) derivative $Y[N(SiHMe_2)_2]_3(THF)_2$ does not initiate polymerization of DEVP. So it appears that a certain minimum size of metal cation is required for the polymerization to actually occur. Under the same reaction conditions, quantitative formation of a colorless 1:2 adduct $Y[N(SiHMe_2)_2]_3(DEVP)_2$ is observed, based on ^{31}P and ^{1}H NMR spectroscopic data.[21] The signals of the coordinated THF protons of the tris(amide) precursor (1.32 and 3.77 ppm in C_6D_6) are replaced by resonances of two coordinated DEVP molecules. We failed to obtain single crystalline material from this compound which is well soluble in hexanes.

For reasons of comparison we also investigated the reactivity of the α-methyl-substituted derivative DEMVP.[11] However, in our hands this vinylphosphonate compound was found to be unpolymerizable, even at elevated temperatures, in contrast to the unsubstituted diethyl vinylphosphonate (DEVP). This observation suggests that steric hindrance, particularly in the propagation step, might play an important role in the polymerization, but other effects can be involved also.

Conclusions. While we are unable at this point to come up with a detailed discussion of a possible mechanism of the polymerization reaction, it is still somewhat likely to assume that, as a very first step, two vinylphosphonate molecules will coordinate to a lanthanide atom, as was observed in the case of the yttrium derivative.

Using the combination of (a) the right size rare-earth cation on one hand and (b) a suitable ligand system on the other, we have been able to demonstrate that the homopolymerization of diethyl vinylphosphonate to relatively high molecular weight polymers is in principle feasible under mild conditions. The reluctance of some vinyl phosphorus systems to homopolymerize had earlier been attributed to steric effects retarding the chain propagation reaction.[22] This assumption may now be questioned, based on the findings from this work. At this point one might think about what other metal/ligand combinations are suitable for initiating the polymerization of diethyl vinylphosphonate and perhaps yield even higher molecular weights and lower polydispersity values.

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Supporting Information Available: Various NMR spectra as well as FT-IR spectra, DSC curves and SEC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) ^{1}H (500.13 MHz), ^{31}P (202.46 MHz), and ^{13}C (125.74 MHz) NMR spectra were recorded on a Bruker DRX 500 spectrometer using a 5 mm $^{1}H/^{13}C/^{19}F/^{31}P$ gradient probe using C_6D_6 as solvent at 70 °C. The solvent peak was used as reference: $\delta(^{1}H) = 7.16$ ppm; $\delta(^{13}C) = 128.7$ ppm. The ^{31}P NMR spectra were referenced on external H_3PO_4 ($\delta(^{31}P) = 0$ ppm). The $^{1}H-^{1}H$ correlation spectra (gs-COSY, TOCSY), $^{1}H-^{13}C$ gs-HMQC spectra, and DEPT135 spectra were recorded using the pulse sequences in the Bruker software package.
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(18) TGA measurements were carried out on a TGA Q 5000 apparatus (TA Instruments) coupled with an FT-IR spectrometer Nicolet 380 from Thermo Electron. Modulated DSC measurements were performed using a DSC Q 1000 apparatus (TA Instruments) under a N_2 atmosphere. The heat capacity was calibrated in the modulated mode with sapphire. Samples of about 10 mg were encapsulated in a standard aluminium pan and measured in the temperature range between −80 and 150 °C. The heating−cooling−heating cycle was monitored at an averaged heating rate of 2 K/min with the amplitude of ±0.31 K and a period of 40 s.
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(20) GPC sample preparation: all samples were prepared using a concentration of 2 mg/mL and passing the polymer solution trough 0.2 μm Teflon filters. SEC setup: measurements were performed utilizing a Waters 510 HPLC pump equipped with a Waters 486 tunable UV detector and a Waters 410 differential RI detector at a flow rate of 0.5 mL/min (THF with 0.25 wt % TBAB). The column setup consists of a guard column (PSS; SDV-Gel; 5 × 0.8 cm; particle size 5 μm; pore size: 100 Å) and three analytical colums (PL; PL-Gel; 30 × 0.8 cm, particle size: 5 μm; pore sizes: 100, 10^3, and 10^4 Å, respectively); molecular weights are given with respect to polystyrene standards.
(21) ^{31}P NMR (C_6D_6) δ: 13.9 (br, ν = ca. 100 Hz). ^{1}H NMR (C_6D_6) δ: 0.45 (36H, d, Me_2Si), 1.09 (12H, br, CH_3), 4.12 (8H, v br, CH_2O), 5.17 (6H, sept, SiH), plus several broad vinylic resonances from 5.6 to 6.4 ppm (6H, m).
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