^{1}H, ^{13}C, and ^{31}P NMR Study on Poly(vinylphosphonic acid) and Its Dimethyl Ester

Hartmut Komber,* Volker Steinert, and Brigitte Voit

Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069, Dresden, Germany

Received November 30, 2007; Revised Manuscript Received January 14, 2008

ABSTRACT: The microstructure of poly(vinylphosphonic acid) (PVPA) and poly(vinyl dimethyl phosphonate) (PVDMP) prepared by free radical polymerization was studied by a combination of one- and two-dimensional NMR spectra. Whereas ^{13}C and ^{31}P NMR spectra give less stereochemical information a signal split into diad, triad, and, at best, *m*-centered tetrad sequences for the methylene protons of PDMVP could be observed in the ^{1}H NMR spectra. For PVPA our assignments differ from those previously published in the literature. The spectra of both polymers were complicated by the presence of head-to-head regioirregular structures with up to ∼17% for PVPA. For the regioregular part a mainly *atactic* structure was determined for PVPA, whereas PVDMP has an increased content of *isotactic* sequences. The dependency of ^{1}H and ^{31}P signals of PVPA on the degree of neutralization is presented.

Introduction

Poly(vinylphosphonic acid) (PVPA) recently gained increasing interest as model system to study the proton conducting mechanism of phosphonated polymers suggested for applications in fuel cells.[1] A further promising field of application is based on its biocompatibility. Vinylphosphonic acid containing hydrogels show improved cell adhesion and proliferation,[2] and vinylphosphonic acid copolymers give the possibility to integrate biomaterials with natural bone.[3] Besides these up-and-coming applications, vinylphosphonic acid-based polymers and copolymers were used in dental cements[4,5] and suggested as flame retardants,[6,7] separation membrane materials,[8] and conductive blends.[9]

Considering these broad field of applications, the knowledge of the polymer structure is less substantial. Though the microstructure of a huge number of polymers based on monomers with the general structure CH_2═CHR (R = alkyl, aryl, halogen, heteroatom-based functionality, etc.) was characterized in detail by 1D and 2D NMR techniques,[10−12] a first NMR study on PVPA was published only recently by Bingöl et al.[13] The authors described the PVPA structure based on tetrads as *atactic* and found evidence for head-to-head (H−H) and tail-to-tail (T−T) links. The formation of these irregularities was explained by intermediate formation of vinylphosphonic acid anhydride in the radical VPA polymerization in water which cyclopolymerizes under formation of 5- and 6-membered rings. After hydrolysis of these cyclic anhydrides the resulting PVPA would contain H−H/T−T structures.

In our group the copolymerization of VPA and di- and trivinyl functional phosphonic anhydrides both in the reactive solvent acetic anhydride and in dimethylformamide was studied.[14] In the course of the structural characterization of the products and of PVPA obtained by precipitation polymerization of VPA in ethyl acetate, we noticed that the ^{13}C NMR spectrum of the as-synthesized PVPA agreed with that published in ref 13. In contrast, the NMR spectra obtained from VPA/VPA anhydride copolymers after hydrolysis of the anhydride groups to phosphonic acid groups, i.e., PVPA, are complex pointing at structural irregularities. The ^{31}P NMR spectra contain several lines in the 27−35 ppm region, and the signal region in ^{1}H NMR spectra becomes broadened and less structured with increasing anhydrides content in the feed. Finally, the ^{13}C NMR spectra cover the 20−45 ppm region with a multitude of lines but with a relative sharp separation of methine carbon signals (>34 ppm) and methylene carbon signals (<34 ppm). However, the spectra still contain characteristic features of the spectra of PVPA from pure VPA, especially when the anhydrides content was low in the feed. It was concluded from the enhanced polymerization rate compared with polymerization of pure VPA under the same conditions that radical-initiated polymerizations of VPA/VPA anhydrides mixtures with up to 90 mol % anhydrides proceed via a cyclopolymerization mechanism resulting also in 5-membered rings. Thus, we explained the spectra as superposition of structural irregularity (H−T, H−H, and T−T links), tacticity, and, of importance for the ^{1}H and ^{13}C NMR spectra, scalar ^{1}H− or ^{13}C−^{31}P couplings. Because of these different contributions on the spectra, we failed in a detailed signal assignment.

Discrepancies in the interpretation of the PVPA spectra by Bingöl et al.[13] and us[14] initiated this reinvestigation of the ^{1}H, ^{13}C, and ^{31}P NMR spectra of PVPA and its dimethyl ester (PVDMP). Two PVPA/PVDMP pairs were studied: one is based on vinylphosphonic acid (VPA) polymerization (-I) and the other one on vinyl dimethyl phosphonate (VDMP) polymerization (-II) (Scheme 1). The corresponding methylated and acidic form were synthesized by polymer analogous reactions (methylation with trimethylsilyldiazomethane and hydrolysis with HBr, respectively). The analysis of the NMR spectra was accomplished by combination of 1D and 2D techniques. Furthermore, the ^{1}H and ^{31}P chemical shifts of PVPA were followed in dependency on the degree of neutralization.

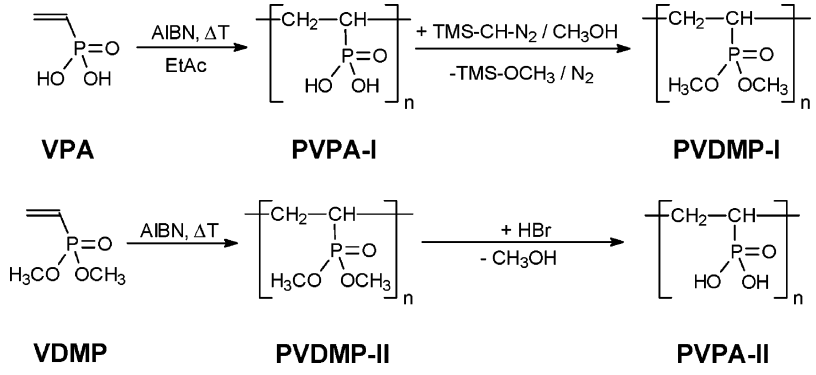
Experimental Section

Polymers. PVPA was synthesized by AIBN-initiated free radical polymerization of VPA in ethyl acetate[14] (sample PVPA-I) but also from poly(vinyl dimethyl phosphonate) (sample PVDMP-II) by hydrolysis with HBr according to ref 13 (sample PVPA-II). PVDMP-II was obtained by radical polymerization of vinyl dimethyl phosphonate (VDMP) in bulk at 60 °C using 2 mol % AIBN as initiator. The reaction was stopped after 12 h (61%

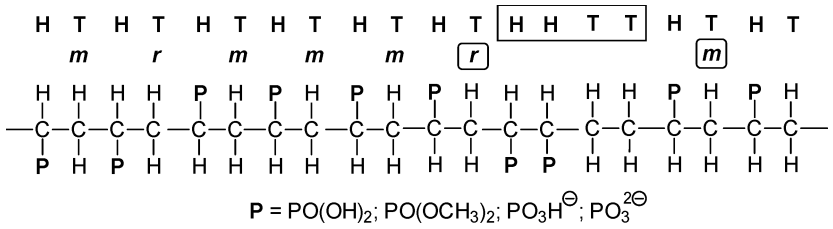
* Corresponding author: Fax +49 351 4658565; e-mail komber@ipfdd.de.

10.1021/ma702662q CCC: $40.75
Published on Web 02/20/2008

Scheme 1. Synthetic Routes to the Poly(vinylphosphonic acid) (PVPA) and Poly(vinyl dimethyl phosphonate) (PVDMP) Samples



Scheme 2. Schematic Structure of Poly(vinylphosphonic acid) and Derivatives Showing Stereosequences and a H−H/T−T Regioirregular Structure with Neighboring Diads



monomer conversion). Volatile components were removed in a rotary evaporator, and the residue was purified by reprecipitation from an acetone solution in diethyl ether. The dimethyl ester of PVPA-I was prepared by esterification with trimethylsilyldiazomethane (sample PVDMP-I). For the methylation reaction PVPA-I was swollen in methanol, and a 2 M solution of trimethylsilyldiazomethane in hexane was added with 50% molar excess. With progress of reaction all polymer becomes dissolved and after 2 h the excess reagent was destroyed by adding acetic acid. The product was isolated by removing the volatile components under reduced pressure and afterward reprecipitated twice as described above. The degree of esterification was 98% (^{31}P NMR).

The weight-averaged molar masses were determined for the dimethyl esters from chloroform solutions by static light scattering using a miniDAWN Tristar detector (Wyatt Technology Corp.): 37 000 g/mol for PVDMP-I and 17 000 g/mol for PVDMP-II.

NMR Measurements. ^{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. The ^{1}H and ^{13}C NMR spectra obtained from polymer solutions in D_2O were referenced on internal sodium 3-(trimethylsilyl)propionate-*2,2,3,3-d*$_4$ ($\delta(^{1}H) = 0$ ppm; $\delta(^{13}C) = 0$ ppm). For solutions in CD_3-OD the residual solvent signal was used as reference ($\delta(^{1}H) = 3.31$ ppm; $\delta(^{13}C) = 49.0$ ppm). All ^{31}P NMR spectra were referenced on external H_3PO_4 ($\delta(^{31}P) = 0$ ppm). The ^{1}H NMR spectra of the samples from the titration experiment were referenced on an external solution of sodium 3-(trimethylsilyl)propionate-*2,2,3,3-d*$_4$ in D_2O ($\delta(^{1}H) = 0$ ppm). The ^{13}C NMR spectra were recorded using the inverse-gated pulse sequence, a 30° ^{13}C pulse, and a delay time of 6 s. ^{1}H NMR spectra were recorded both with and without ^{31}P decoupling. 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.

Titration Experiment. For the titration experiment, 25.5 mL of a 0.05 M (with respect to the repeating unit) solution of PVPA-I in H_2O was titrated with 0.1 M NaOH in 0.05 steps of the neutralization degree (40 titration steps) using the computer-controlled titration system TPC 2000 with a pH electrode of type N 6180 from Schott-Geräte GmbH to determine the pH values. For ^{1}H NMR (with water peak suppression) and ^{31}P NMR measurements, a sample volume of 0.5 mL was taken from the titration solution after each titration step. The polymer concentration of the solution depleted to 0.025 M at a neutralization degree of 2.

Results and Discussion

In the analysis of the NMR spectra of PVPA and its dimethyl ester one has to consider the typical structural features of vinyl polymers.[10−12] The microstructure is determined by the direction of monomer incorporation in the growing polymer chain which usually occurs by reaction of the α-carbon of a growing polymer chain (head = H) with the β-carbon of a monomer (tail = T; H−T link, regioregular) but in few cases also by α- to α-carbon (H−H) and β- to β-carbon (T−T) addition (regioirregular structure). Assuming regioregular addition, stereosequences based on the configuration of consecutive methine carbons and resulting in stereoregular (*isotactic* or s*yndiotactic*) or stereoirregular (*atactic*) polymers characterize the microstructure still further. Depending on the relative configuration of adjacent monomer pairs (diads) one distinguishes *meso* (*m*, same configuration) and *racemic* (*r*, opposite configuration) diads as shortest stereosequences. Scheme 2 illustrates these microstructural features.

^{31}P NMR can be applied to elucidate the PVPA structure because ^{31}P is a nucleus of 100% natural abundance and high NMR sensitivity. However, the presence of phosphorus bonded to the polymer backbone complicates the ^{1}H and ^{13}C spectra by the scalar phosphorus proton ($^{n}J_{PH}$) and phosphorus carbon ($^{n}J_{PC}$) couplings which vary between ~135 Hz for one bond between phosphorus and carbon ($n = 1$) and 5 − 20 Hz for $^{2/3}J_{PH}$ and $^{2/3}J_{PC}$ also depending on stereochemistry.[15] The separation of phosphonic groups on the polyvinyl backbone by only four bonds causes that each proton or carbon experiences scalar couplings with two or three phosphorus each, resulting in line broadening or splitting in dependency on the magnitude of the scalar couplings. Line broadening or splitting by scalar couplings can be suppressed by decoupling techniques. Whereas ^{31}P decoupling of ^{1}H NMR spectra is nowadays an usual technique, the triple resonance experiment resulting in ^{1}H- and ^{31}P-decoupled ^{13}C NMR spectra requires special equipment.

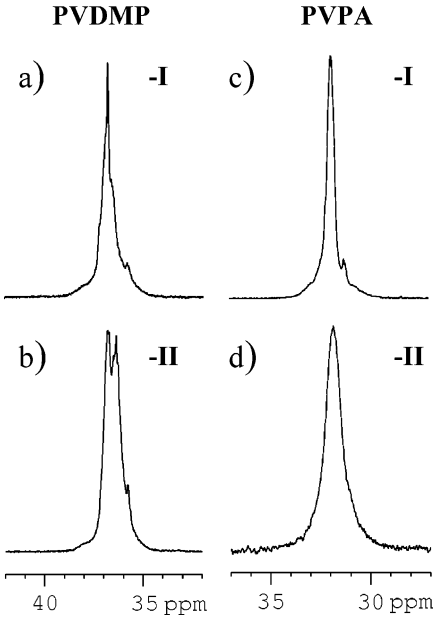


Figure 1. $^{31}P\{^1H\}$ NMR spectra of PVDMP-I and -II in CD_3OD (a, b) and PVPA-I and -II in D_2O (c, d).

Such spectra are not part of this study. Finally, it should be mentioned that the $^nJ_{PH}$ and $^nJ_{PC}$ couplings result in signal splitting in the $^1H-^1H$ and $^1H-^{13}C$ correlation experiments because they are passive couplings not involved in and influenced by the correlation experiments.

Poly(vinyl dimethyl phosphonate). The study was started using the two differently prepared PVDMPs because their dissolution resulted in a lower increase in viscosity and thus higher concentrated solutions could be prepared for ^{13}C NMR measurements than with PVPA. Here, the spectra recorded from solutions in CD_3OD are discussed. The $^{31}P\{^1H\}$ NMR spectra (Figure 1a,b) show a signal in the 35−38 ppm region with a signal splitting varying in intensity for PVDMP-I and -II. This fine structure seems to reflect a splitting due to triad structures, but the separation is too low for a quantification. However, structural differences are obvious. The base of the signals shows an additional broadening possibly due to structural irregularities whereas the shoulder at 35.5 ppm is attributed to end groups.

Figures 2 and 3 depict the $^1H\{^{31}P\}$ and ^{13}C NMR spectra (CH and CH_2 region), respectively, which clearly point at structural differences between both samples. The assignment of the methoxy proton (3.84 ppm) and methoxy carbon signal (56.15 and 55.85 ppm, not shown), respectively, is straightforward based on their chemical shifts. Shoulders on this signal could not be assigned to stereosequences but might be due to end groups or structural irregularities. The methine and methylene carbon regions overlap as revealed by comparison of the DEPT135 and ^{13}C spectrum of PVDMP-II. So, the 31−32.5 ppm signal region results in positive signals in the DEPT135 spectrum (Figure 3c), indicating methine carbon signals but with a different overall shape in comparison to the ^{13}C spectrum (Figure 3b) which is caused by overlap with methylene carbon signals which result in negative DEPT135 signals.

Also, the proton signals are highly overlapped and broadened, and the $^1H-^{13}C$ correlated HMQC spectrum of PVDMP-II delivers first insight in the signal assignments (Figure 4a; methoxy region not shown).

Three regions can be distinguished. Region A covers the methylene group signals showing features which are well-known for methylene groups of other vinyl-type polymers. One can

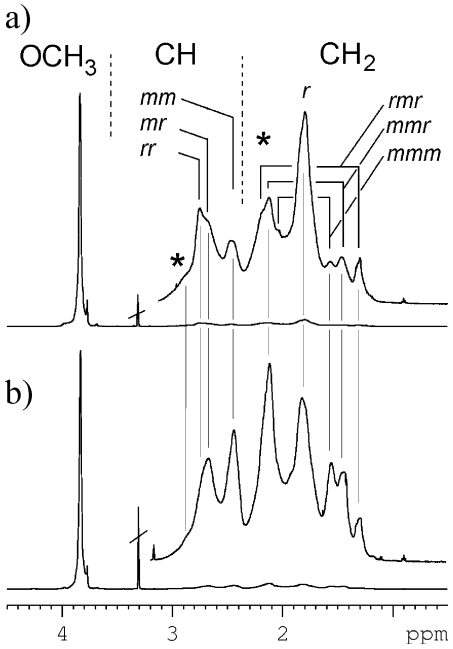


Figure 2. ^{31}P-decoupled ^1H NMR-spectra ($^1H\{^{31}P\}$) of PVDMP-I (a) and -II (b) in CD_3OD. Asterisk indicates the position of methine and methylene signals of H−H/T−T regioirregularities.

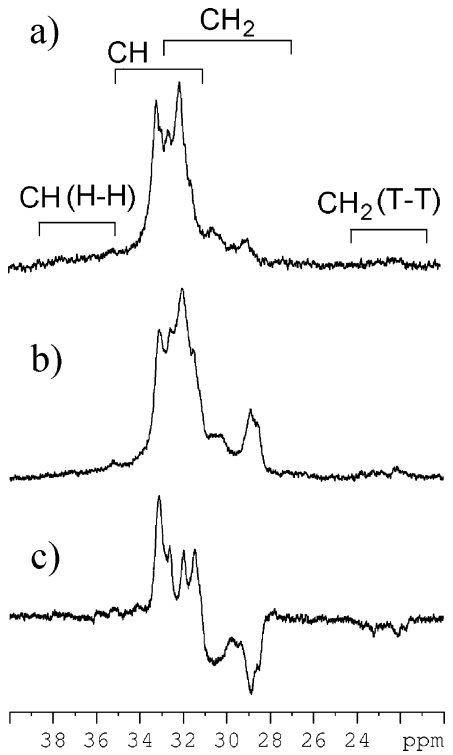


Figure 3. Quantitative ^{13}C NMR spectra (CH and CH_2 region) of PVDMP-I (a) and -II (b) and DEPT135 spectrum of PVDMP-II (c) (solvent: CD_3OD).

define the resonances of carbons with equivalent and nonequivalent protons. The three carbon signals with magnetically nonequivalent protons are characteristic for methylene groups in *meso* (*m*) diads. The chemical shift difference between the corresponding protons ($\Delta\delta$) increases from 0.56 ppm ($\delta(^1H)$ = 1.55 and 2.11 ppm; $\delta(^{13}C)$ = 28.8 ppm; *mmm*) to 0.71 ppm (1.44 and 2.15 ppm; 30.5 ppm; *mmr*) and 0.90 ppm (1.31 and 2.21 ppm; 32.2 ppm; *rmr*). Such trends in $\Delta\delta$, $\delta(^1H)$, and $\delta(^{13}C)$ for *meso* methylene groups were also observed for structural similar polyacrylates,[16] poly(methyl metharylate),[17]

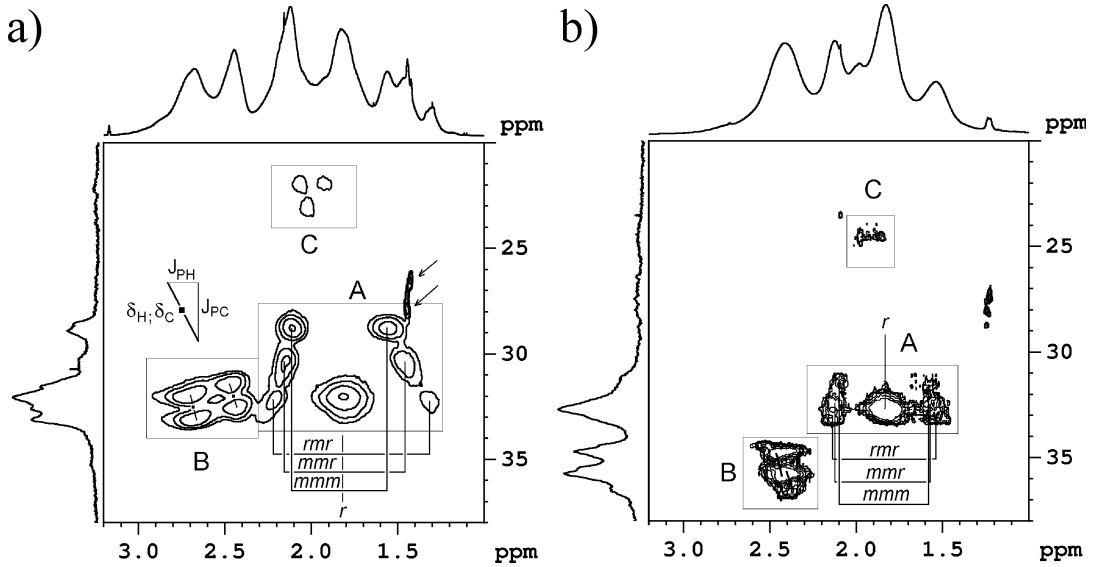


Figure 4. $^1H-^{13}C$ HMQC spectra (CH and CH_2 region) of PVDMP-II (a; solvent: CD_3OD) and PVPA-I (b; solvent: D_2O). The assignment to tetrads is given for the methylene signals. The insert in (a) is to explain the characteristic methine group signal pattern caused by the passive $^1J_{PC}$ (vertical axis) and $^2J_{PH}$ (horizontal axis) couplings; the full square gives the position defining the ^1H and ^{13}C chemical shift of the cross-peak. The arrows point at signals due to AIBN-based end groups.

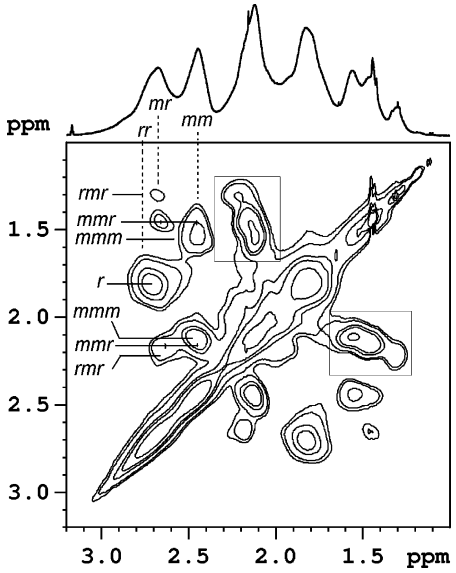


Figure 5. TOCSY spectrum of PVDMP-II (CH and CH_2 region, solvent: CD_3OD, mixing time 20 ms). The assignments are to explain the correlation peaks between methine and methylene protons caused by vicinal couplings. The boxes mark the correlation peaks between the geminal methylene protons of *m*-centered tetrads.

and poly(acrylic acid)[18] and correlated with *mmm*, *mmr*, and *rmr* tetrads, respectively. This assignment also applies for PDMVP as proved by the TOCSY correlations with the methine protons (Figure 5). This confirms the statement of Monaco and Zambelli that for most vinyl polymers the assignment of *m*-centered triads is opposite to that of poly(propylene).[19]

For the *racemic* (*r*) diad neither the magnetically equivalent methylene protons ($\delta(^1H) = 1.81$ ppm) nor the carbon signal ($\delta(^{13}C) = 32.1$ ppm) shows a significant splitting due to tetrads. It can be stated for all methylene signals that the scalar couplings with phosphorus result in signal broadening but cannot be identified as a signal splitting. By contrast, analysis of region B showing the methine group signals requires consideration of scalar phosphorus couplings. The splittings due to $^1J_{PC}$ (~136 Hz) and $^2J_{PH}$ (~17 Hz) couplings which are passive in the $^1H-^{13}C$ HMQC experiment are indicated in Figure 4a. It is obvious that at least two methine proton signals at 2.44 and 2.68 ppm are caused by the polymer microstructure. This also applies for the methine carbons (~31.9 and ~32.5 ppm), but their separation by about 0.6 ppm is superposed by the large J_{PC} coupling (Figure 3). Furthermore, the HMQC spectrum confirms the conclusion from the DEPT spectrum that methine and methylene carbon signals partially overlap. From a TOCSY spectrum recorded with a short mixing time to minimize long distance magnetization transfer the methine proton signals could be well identified by their direct couplings ($^3J_{HH}$) to the neighboring methylene groups in *m* and *r* configuration (Figure 5). The cross-peaks give the following assignments: the signal at 2.45 ppm is from the *mm* triad whereas the signal at 2.68 ppm results from the *mr* triad. The *rr* triad signal is even more low field shifted but less defined due to signal overlap.

Finally, a third signal region C is identified in the HMQC spectrum ($\delta(^1H) = 1.8-2.2$ ppm and $\delta(^{13}C) = 21-24$ ppm). The carbons are methylene carbons as can be deduced from the DEPT spectrum (Figure 3c). Their intensity and pattern does not correlate with end groups, and we assign this signal group to the $-CH_2-CH_2-$ structure in T−T regioirregular structures. Unfortunately, the proton signals completely overlap with the signals of the regular structure.

The methine groups of the corresponding H−H irregularity could not be proven in the HMQC spectrum, but there are methine carbon signals of comparable intensity at 35−38 ppm (Figure 3) and a broad proton signal centered at ~2.9 ppm not assigned to triads (Figure 5). For H−H structures similar low-field (methine) and high-field shifts (methylene) compared with the signals of H−T sequences were reported for the classic pair of poly(acrylic acid) (H−T polymer) and poly(ethylene-*alt*-maleic acid) (H−H polymer)[20,21] and also for poly(allyl acetate).[22] Furthermore, the assignment to regioirregular structures is supported by our NMR structural study on the radical-initiated copolymerisation of VPA and VPA anhydrides which results in PVPA with a large amount of H−H/T−T irregularities depending on the anhydride content.[14] Again, the corresponding methine carbon signals are low-field and the methylene carbon signals are high-field shifted compared with the signals of regioregular H−T sequences. With respect to the problems in detecting the signals of the H−H/T−T structure two factors

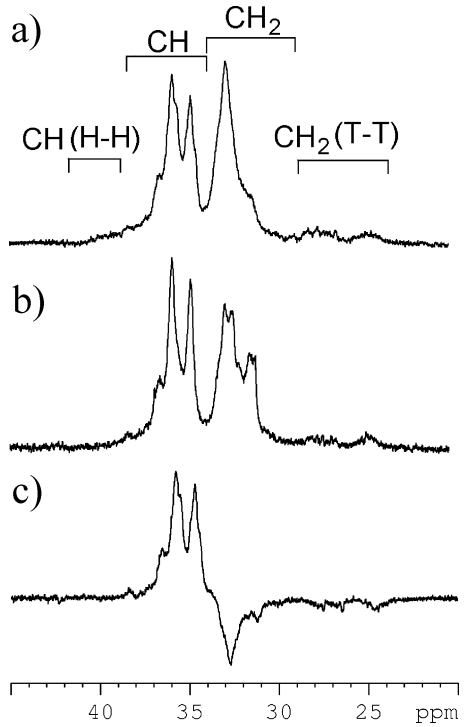


Figure 6. ^{13}C NMR spectra of PVPA-I (a) and -II (b) and DEPT135 spectrum of PVPA-I (c) (solvent: D_2O).

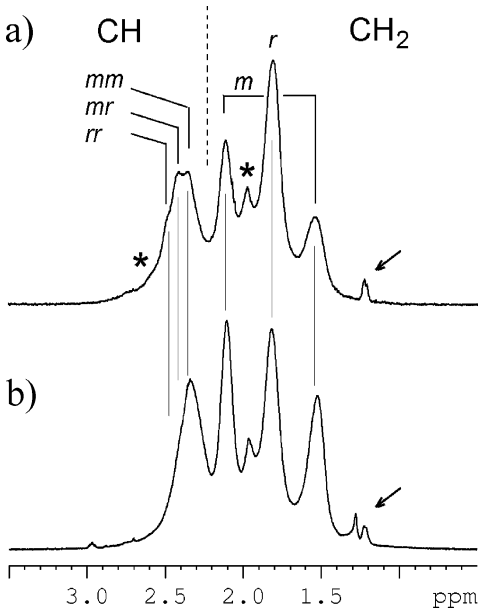


Figure 7. ^{31}P-decoupled ^1H NMR-spectra ($^1H\{^{31}P\}$) of PVPA-I (a) and -II (b) in D_2O. Asterisk indicates the position of methine and methylene signals of H−H/T−T regioirregulatities, and the arrows indicate signals which could be caused by end groups.

have to be considered: first, the total intensity of methine carbons is spread by the signal split due to the one-bond and two-bond P−C coupling, and second the neighboring chiral methine carbons introduce a new stereochemical situation with two arrangements—*erytho* and *threo*—and so increasing number of possible signals.[21] The occurrence of T−T methylene carbon signals for PVDMP-I derived from the parent PVPA-I (Figure 3a) points at regioirregular structure formation also in the VPA polymerization (see later).

In principle, the signal assignments for PVDMP in D_2O solution (see Supporting Information) correspond with those deduced for CD_3OD solution. Signal overlap of methine and methylene carbon signals is lower, but on the other hand, there is no clear tetrad splitting for the methylene protons and the methine proton signal of *mm* triads overlaps with one signal of the *meso* methylene protons.

Poly(vinylphosphonic acid). The PVPA spectra were recorded from D_2O solutions. The ^{31}P spectra show one broad nonstructured signal at 31.9 ppm for PVPA-I and -II (Figure 1c,d). The analysis of the ^1H and ^{13}C spectra was done according to the procedure described for PVDMP. The ^{13}C NMR spectra (Figure 6) are similar to the CH and CH_2 region of the PVDMPs (Figure 3) with the most important difference is that the methine and methylene carbon signals do not overlap as confirmed by the DEPT135 spectrum (Figure 6c). Nevertheless, the quantification of stereosequences is not possible from these spectra.

In addition to the signals of the regular structures, the ^{13}C NMR and HMQC spectra (Figure 4b, region C) provide evidence that also radical VPA polymerization results in regioirregular H−H and T−T structures represented by methylene carbon signals at 23−28 ppm and methine carbon signals at 37−41 ppm.[14] This is in accordance with the spectrum of the methylated PVPA-I (PVDMP-I, Figure 3a) showing T−T signals as discussed in the preceding paragraph. The corresponding methylene proton signals are centered around 2.0 ppm. Again, the HMQC spectra failed at proving the methine group cross-peaks of the H−H connection. For PVPA obtained by hydrolysis of a VPA−VPA anhydride copolymer with a high amount of H−H/T−T structures we found that signals at about 2.2−2.5 ppm represent this methine groups.[14] So, both the methine and methylene proton signals of the regioirregular units completely overlap with the signals of the dominating regioregular structures.

For the H−T structures the HMQC spectrum (Figure 4b, regions A and B) shows a similar signal pattern as discussed for PVDMP; three *m*-centered tetrads and the *r* diad can be assigned for the methylene groups in region A whereas in region B the labeled methine groups signals should represent two of the three possible triads.

However, the chemical shifts of the nonequivalent methylene protons hardly vary for the *mmm*, *mmr*, and *rmr* triads, and in consequence of that, the ^1H NMR spectra (Figure 7) show a lesser sequence splitting than those of the dimethyl esters in CD_3OD. Only the signal of the *r* diad (1.81 ppm) and the two signals of the *m* diad (1.54 and 2.11 ppm) can clearly be distinguished. A broad signal at 2.39 ppm is observed for the methine protons with a slight fine splitting after ^{31}P decoupling. According to the HMQC spectrum, the signal at 1.98 ppm is assigned to the methylene protons of the T−T structures. Finally, a small signal at 1.22 ppm might be caused by end groups.

Although the ^1H and ^{13}C NMR spectra well agree with those published by Bingöl et al.,[13] our signal assignments are very different. For the two ^{13}C signal groups (∼33 and ∼36 ppm) they give an overlap of methine and methylene carbon signals whereas we could prove, i.e., by DEPT, that these are pure methylene and methine carbons signals, respectively. With respect to a description of the polymer structure it is important to note that the four proton signals in the 1.3−2.2 ppm region were assigned to tetrads in ref 13 not considering the nonequivalence of *meso* protons whereas we state a diad splitting with an additional signal due to methylene groups from regioirregular structures.

Titration of PVPA. A 0.05 M solution of PVPA-I in water was titrated with 0.1 M NaOH to follow the ^1H and ^{31}P chemical shifts of PVPA in dependency on the degree of neutralization

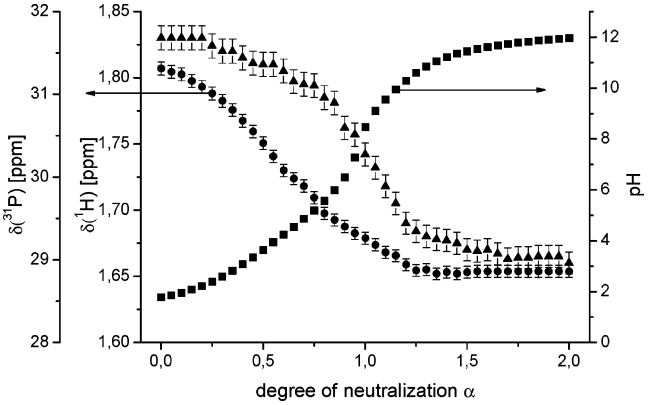


Figure 8. Dependency of the PVPA-I ^{31}P signal shift (weighted mean value, ●), of the ^{1}H chemical shift of the racemic methylene protons of PVPA-I (▲), and of the pH value (■) on the degree of neutralization α (0.05 M at α = 0 stepwise diluted to 0.025 M at α = 2).

α. One aim was to find conditions which result in spectra that allow to extract more microstructural information. However, increasing α results in additional line broadening for the ^{1}H NMR spectra as also observed for poly(acrylic acid).[23] The ^{31}P NMR line of PVPA shows a signal splitting in the region of α = 0.5−1.5 but also a line broadening (see Supporting Information) which cannot be related to stereosequences. Additionally, signals of lower intensity and high-field to the main signal were observed in the course of titration (see Supporting Information). Their α dependency is different to that of the main signal, and on the basis of the aforementioned structure characterization, we assign these signals to the *erythro* and *threo* isomer of the H−H moiety. A different titration behavior of a phosphonic acid group in a 1,3,5-triphosphonic acid and 1,2-diphosphonic acid substructure is to be expected.

The alkylphosphonic acid group is a diprotic acid with significant different pK_a values, e.g., pK_{a1} = 2.5 and pK_{a2} = 8.1 for cyclohexylphosphonic acid.[24] The titration curve in Figure 8 shows the expected dissociation behavior for PVPA which dissociates in two consecutive steps in the same way as alternating maleic acid copolymers.[25−28] Depending on α the ratio of phosphonic acid, monoanion and dianion species in the solution varies. Because of proton-transfer reactions rapid on the NMR time scale, the observed chemical shift represents the concentration-weighted average of the chemical shift of all species in the equilibrium. Figure 8 depicts the chemical shift changes of the ^{31}P NMR signal (weighted mean value) and of the racemic methylene protons signal in addition to the pH value at different α values. The effects over the pH range from 1.9 to 12 are quite small; the ^{31}P signal moves high field by ∼2.5 ppm, and for the racemic methylene protons signal a high-field shift of 0.17 ppm was observed with increasing pH values. Taking into account that at α = 1 the monoanion is the predominating species in the equilibrium, the almost constant ^{31}P value for α > 1 indicates very similar chemical shifts for the mono- and dianion. Because of the lack of data of appropriate 1,3-diphosphonic acids, we compare the ^{31}P data with those of cyclohexanephosphonic acid containing the $-CH_2-CH(PO_3H_2)-CH_2-$ moiety.[24] Here, a significant high-field shift of ∼8 ppm was observed for a similar pH range. However, in discussing data of polyacids, one has to consider that the relative orientation of acid groups fixed on a polymer backbone can vary depending on the ionization state by electrostatic interactions or hydrogen bonding resulting in stereochemical (conformational) chemical shift effects interfering with the deprotonation effect. Finally, the shift changes and their degree of accuracy are too low to determine pK_a values of the acid and monoanion as it was done for alternating ethene− and isobutene−maleic acid copolymers.[28]

Polymer Structure. The final goal of such a study should be to establish the polymerization model which describes the distribution of stereosequences in the polymer.

Unusual for vinyl polymers, both PVDMP and PVPA obtained by free-radical polymerization are not completely regioregular but contain inverted monomer units, i.e., H−H/T−T connectivities. More than occasionally inverted monomer units have been reported only for few radical polymerizations, e.g., of fluoromonomers[8,9,29] and allylesters.[22] Such irregularities result in a higher level of structural complexity (Scheme 2), and with respect to the NMR spectra, the occurrence of regiodefects induces additional chemical shift effects. At best, the new signals do not interfere with the signals of the H−T stereosequences, but in the case of PVDMP and PVPA, this is valid only for the methylene carbon signals of the T−T substructure. Unfortunately, within reasonable measuring time it was not possible to obtain quantitative ^{13}C NMR spectra with a signal/noise ratio, allowing a satisfying accurate determination of signal integrals. To gain quantitative information about the polymer structure, the ^{1}H NMR spectra after line narrowing by ^{31}P decoupling were analyzed. Bearing in mind the signal regions assigned to T−T structures, it is reasonable to determine the signal intensity of one methylene proton of H−T structures from the high-field signal group of the *meso* methylenes and from the high-field half of the *racemic* methylene protons signal, i.e., from the 1.2−1.81 ppm (PVDMP) and 1.25−1.81 ppm (PVPA) region, respectively. Relating this value to the total methylene and methine protons intensity a reasonable estimation of H−H/T−T structures content can be obtained. With good agreement for the PVPA/PVDMP sample pairs a H−H/T−T content of 17 ± 2% was determined for the VPA polymerization (-I) and 8 ± 2 % for the VDMP polymerization (-II). These values are comparable with those found for the aforementioned fluoromonomers and allyl esters. The H−H/T−T structures for samples prepared from VDMP cannot be attributed to intermediate anhydride formation. Moreover, no anhydride formation could be observed by ^{31}P NMR for the VPA polymerization solution in ethyl acetate stored at reaction temperature over 24 h without initiator. Thus, there is also no experimental evidence to consider anhydride formation and cyclopolymerization as a reason for H−H addition in VPA polymerization in ethyl acetate. Accepting the lower H−H content of PVDMP-II compared to PVPA-I as result of higher bulkiness of the dimethyl ester group, we argue the same reason for H−H addition in both polymerizations. Following the discussions in literature,[29] we have to assume that in case of VPA and VDMP polymerization in the monomer addition step the formation of a secondary radical chain end is thermodynamically less preferred to the formation of a primary radical chain end than usual, thus resulting in lower regioregularity. However, this NMR structure study is not appropriate to prove such an assumption.

From the ^{1}H NMR spectra it is obvious that the *m*/*r* ratio is different for the VPA- and VDMP-based polymers (Figures 2 and 7). With the integral of the high-field signal group of the *meso* methylenes representing *m* units and that of the high-field half of the *racemic* methylene protons signal representing *r* units a *m*/*r* ratio of 46 ± 2%/54 ± 2% for VPA polymerization and of 59 ± 2%/41 ± 2% for VDMP polymerization were estimated for the regioregular part, in good agreement for the PVPA/PVDMP sample pairs. Whereas VPA polymerization results in a mainly *atactic* product, a tendency in VDMP polymerization

is observed to form an *isotactic*-rich polymer. At first view this is surprising because an increasing content of *syndiotactic* units is reported for poly(acrylate)s containing bulky ester groups.[30] However, ester groups as triphenylmethyl, diphenyl-2- and -4-pyridylmethyl, and 1-phenyldibenzosuberyl groups result in highly *isotactic* polymers for poly(methacrylate)s prepared by free radical polymerization which is also explained by steric repulsion between ester groups in the monomer addition step but now resulting in *isotactic* segments with helical conformation.[31] With the fact that the bulkiness of a DMP group with a sp^3-hybridized phosphorus atom bonded to the backbone is higher than that of an acrylate group with a sp^2-hybridized, we tend to explain the increased *isotactic* content by the aforementioned formation of helical structures.

A more detailed triad or tetrad analysis on the $^1H\{^{31}P\}$ NMR spectra of PVDMP-I and -II failed. Despite good fits were obtained from spectral line deconvolution based on the aforementioned signals assigned, such characteristic parameters as the CH_2/CH ratio and the ratio of both signal groups from the *meso*-CH_2 group deviate significantly from the expected 2:1 and 1:1 ratios, respectively. This is mainly caused by the H−H/T−T units which can hardly be considered in a deconvolution process because of ill-defined signal position. Furthermore, one has to assume that these microstructure defects also influence the signal positions of the neighboring "regular" repeating units indicated in Scheme 2. We evaded these problems not by adding unspecific lines in the deconvolution input, but we decided to accept the content of H−H/T−T structures and the *m*/*r* ratio as deducible parameters.

Conclusions

A comparative NMR study on the polymer structure of free-radical-polymerized VPA and VDMP was conducted. The parent polymers were converted to the counterpart by polymer-analogous reaction; PVPA can be easily converted to PVDMP by methylation with trimethylsilyldiazomethane, and PVDMP was saponified by hydrobromic acid, resulting in PVPA. The structure of PVPA and PVDMP can be best studied by ^1H NMR where the PVDMP spectra taken in CD_3OD solution with ^{31}P decoupling give best information. For PVPA our study has shown that the ^1H and ^{13}C signal assignments published in ref 13 have to be revised.

The radical polymerization of both monomers, VPA and VDMP, results in products containing significant amounts (17 and 8%, respectively) of H−H/T−T units as regioirregular structures. The probability of their formation is larger for PVPA possibly due to the less bulky phosphonic acid group compared with the dimethylester. In contrast, the higher bulkiness of the dimethyl ester might be responsible for the higher content of *isotactic* sequences in the regioregular domains of PVDMP which result in lower steric interactions than the *isotactic* ones. PVPA is mainly *atactic*. Because of the regioirregular domains and general signal overlap, a deeper going structure analysis is not possible.

The study of the ^1H and ^{31}P spectra of PVPA at different dissociation state revealed a low pH dependency of the NMR signals and did not provide additional structural information.

Acknowledgment. The authors thank Mr. D. Voigt for molar mass determination.

Supporting Information Available: ^1H, ^{13}C, and ^{31}P NMR and $^1H-^{13}C$ HMQC spectra of PVDMP-II in D_2O and ^1H and ^{31}P NMR spectra of PVPA-I in H_2O at different degrees of neutralization α. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Steiniger, H.; Schuster, M.; Kreuer, K. D.; Kaltbeitzel, A.; Bingöl, B.; Meyer, W. H.; Schauff, S.; Brunklaus, G.; Maier, J.; Spiess, H. W. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1764−1773 and references cited therein. (b) Kaltbeitzel, S.; Schauff, S.; Steiniger, H.; Bingöl, B.; Brunklaus, G.; Meyer, W. H.; Spiess, W. H. *Solid State Ionics* **2007**, *178*, 469−474. (c) Lee, Y. J.; Bingöl, B.; Murakhtina, T.; Sebastiani, D.; Meyer, W. H.; Wegner, G.; Spiess, H. W. *J. Phys. Chem. B* **2007**, *111*, 9711−9721.
(2) Tan, J.; Gemeinhart, R. A.; Ma, M.; Saltzman, W. M. *Biomaterials* **2005**, *26*, 3663−3671.
(3) Gemeinhart, R. A.; Bare, C. M.; Haasch, R. T.; Gemeinhart, E. J. *J. Biomed. Mater. Res. A* **2006**, *78A*, 433−440.
(4) Ellis, J.; Anstice, M.; Wilson, A. D. *Clin. Mater.* **1991**, *7*, 341−346.
(5) Adusei, G. O.; Deb, S.; Nicholson, J. W. *Dent. Mater.* **2005**, *21*, 491−497.
(6) Jiang, D. D.; Yao, Q.; McKinney, M. A.; Wilkie, C. A. *Polym. Degrad. Stab.* **1999**, *63*, 423−434.
(7) İmamoğlu, T.; Yağci, Y. *Turk. J. Chem.* **2001**, *25*, 1−9.
(8) Park, C. H.; Nam, S. Y.; Lee, Y. M. *J. Appl. Polym. Sci.* **1999**, *74*, 83−89.
(9) Sahoo, S. K.; Nagarajan, R.; Roy, S.; Samuelson, L. A.; Kumar, J.; Cholli, A. L. *Macromolecules* **2004**, *37*, 4130−4138.
(10) (a) Pham, Q. T.; Pétiaud, R.; Waton, H.; Llauro-Darricades, M.-F. *Proton and Carbon NMR Spectra of Polymers*, 5th ed.; Wiley: New York, 2003. (b) Brandolini, A. J.; Hills, D. D. *NMR Spectra of Polymers and Polymer Additives;* Marcel Dekker: New York, 2002.
(11) Tonelli, A. E. *NMR Spectroscopy and Microstructure: The Conformational Connection*; VCH Publishers: New York, 1989.
(12) Mirau, P. A. *A Practical Guide to Understanding the NMR of Polymers*; J. Wiley & Sons: Hoboken, 2005.
(13) Bingöl, B.; Meyer, W. H.; Wagner, M.; Wegner, G. *Macromol. Rapid Commun.* **2006**, *27*, 1719−1724.
(14) Millaruelo, M.; Steinert, V.; Komber, H.; Klopsch, R.; Voit, B. *Macromol. Chem. Phys.* **2007**, DOI: 10.1002/macp.200700377.
(15) Berger, S.; Braun, S.; Kalinowski, H. O. *NMR Spectroscopy of the Non-metallic Elements*; Wiley: Chichester, 1997.
(16) Kawamura, T.; Toshima, N. *Macromol. Chem. Rapid Commun.* **1993**, *14*, 719−724.
(17) Kawamura, T.; Toshima, N.; Matsuzaki, K. *Macromol. Chem. Phys.* **1995**, *196*, 3415−3424.
(18) (a) Chang, C.; Muccio, D. D.; Pierre, T. St. *Macromolecules* **1985**, *18*, 2154−2157. (b) Beshah, K. *Makromol. Chem.* **1993**, *194*, 3311−3321. (c) Spěáček, J.; Suchopárek, M.; Al-Alawi, S. *Polymer* **1995**, *36*, 4125−4130.
(19) Monaco, G.; Zimbelli, A. *Macromol. Chem. Phys.* **2005**, *206*, 203−209.
(20) Butler, G. B.; Matsumoto, A. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 167−176.
(21) Komber, H. *Macromol. Chem. Phys.* **1995**, *196*, 669−678.
(22) (a) Matsumoto, A.; Iwanami, K.; Oiwa, M. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 211−218. (b) Matsumoto, A.; Kikuta, M.; Oiwa, M. *J. Polym. Sci., Polym. Lett. Ed.* **1986**, *24*, 7−11.
(23) Pearsall, S. K.; Green, M. M.; Morawetz, H. *Macromolecules* **2004**, *37*, 8773−8777.
(24) Ohms, G.; Grossmann, G. *Z. Anorg. Allg. Chem.* **1987**, *544*, 232−240.
(25) Bianchi, E.; Ciferri, A.; Parodi, R.; Rampone, R.; Tealdi, A. *J. Phys. Chem.* **1970**, *74*, 1050−1056.
(26) Kitano, T.; Kawaguchi, S.; Anazawa, N.; Minakata, A. *Macromolecules* **1987**, *20*, 2498−2506.
(27) Reinhard, S.; Steinert, V.; Werner, K. *Eur. Polym. J.* **1996**, *32*, 935−938.
(28) Reinhardt, S.; Komber, H.; Steinert, V. *J. Polym. Sci., Part A: Chem. Ed.* **1996**, *34*, 2415−2419.
(29) Vogl, O.; Qin, M. F.; Zilkha, A. *Prog. Polym. Sci.* **1999**, *24*, 1481−1525.
(30) Matsuzaki, K.; Uryu, T.; Kanai, T.; Hosonuma, K.; Matsubara, T.; Tachikawa, H.; Yamada, M.; Okuzono, S. *Makromol. Chem.* **1977**, *178*, 11−17.
(31) (a) Hatada, K.; Kitayama, T.; Ute, K. *Prog. Polym. Sci.* **1988**, *13*, 189−276 and references cited therein. (b) Nakano, T.; Mori, M.; Okamoto, Y. *Macromolecules* **1993**, *26*, 867−868. (c) Nakano, T.; Matsuda, M.; Okamoto, A. *Polym. J.* **1996**, *28*, 556−558.

MA702662Q