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^{1}H and ^{13}C NMR Spectroscopy as a Tool To Probe the Microstructures of Different Types of Poly(vinyl formal)

I. Pollers, P. Adriaensens, R. Carleer, D. Vanderzande, and J. Gelan*

Instituut voor Materiaalonderzoek (IMO), Department SBG, Limburg University, Universitaire Campus, Gebouw D, B-3590 Diepenbeek, Belgium

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ABSTRACT: ^{1}H and ^{13}C NMR spectroscopy has been used to analyze the stereosequence and the comonomer sequence microstructure in poly(vinyl formal) (PVF). The preparation method employed clearly has an effect on the functional group distribution. The results reveal that the heterogeneous modification method shows evidence for a blocky distribution of functional groups whereas samples prepared by the precipitation method exhibit a random distribution.

Introduction

The modification of polymer microstructures by means of postpolymerization chemical reactions is an increasingly active branch of polymer science. Specialty polymers may be obtained through the chemical modification of commercially available polymers. Unique polymer microstructures, many of which cannot be achieved directly through homo- or copolymerization, can be created via this route.[1,2]

Poly(vinyl formal) (PVF) is such a specialty polymer with technological importance; it is mainly used in manufactured enamels for heat-resistant wire insulations for electrical applications and in adhesives, water-resistant fibers, sponges (foamed plastics), implants for the human body, and membranes for reverse osmosis.

PVF is prepared from the condensation reaction of formaldehyde with atactic poly(vinyl alcohol) (PVA) in the presence of an acid catalyst. The formaldehyde reacts with adjacent hydroxyl groups on PVA to form cyclic acetals. The resultant polymer, PVF, is essentially a copolymer of formal rings and unreacted vinyl alcohol. Hence, this complex polymer exhibits both stereosequence and comonomer sequence microstructure.

The properties and applications of a copolymer do not depend only upon the relative contents of functional groups. Several properties, such as degree of crystallinity, melting point, solubility, miscibility, compatibility, and surface tension, vary considerably with the sequence distribution of monomer units and stereochemistry in the copolymer.[3,4] This is of interest when considering the influence of different modification methods.

In the literature, ^{13}C NMR spectra of different forms of acetalized PVA have been discussed.[5,6] The relationship between tacticity of PVA, rate of formalization reaction, and stereochemical configuration of PVF has also been described.[7−12] Different modification methods for the preparation of PVF starting from PVA have been reported,[1,13] and a mathematical reaction scheme for this polymer transformation reaction with incorporation of neighboring group participation effects was made by Boucher and co-workers.[14] The importance of the functional group distribution and the dependence of it on the modification method employed was mentioned.[13] However, a detailed analysis of the stereosequence and comonomer sequence was not described.

In this paper, ^{1}H and ^{13}C NMR are shown to be useful techniques for analyzing the influence of the reaction method on the sequence length and functional group distribution in the modification reaction of PVA to form PVF.

Experimental Section

Materials. Poly(vinyl formal) (PVF) was made from the condensation reaction of atactic poly(vinyl alcohol) (PVA) with formaldehyde. PVA, purchased from Aldrich, was purified by Soxhlet extraction with methanol. Molar mass and intrinsic viscosity were determined by GPC using aqueous salts as the mobile phase (detection by LALLS, refractive index, and viscosity). The results were 123 000 g/mol and 0.998 dL/g for molar mass and intrinsic viscosity, respectively. The level of saponification was more than 0.99. Triad tacticities were determined by inverse-gated decoupling ^{13}C and ^{1}H NMR spectroscopy in DMSO-d_6 solution at respectively 80 and 40 °C. The mm, mr, and rr fractions were respectively 0.21, 0.50, and 0.29 from ^{1}H NMR and 0.23, 0.50, and 0.27 from ^{13}C NMR. These tacticity data are in good agreement with the tacticity reported previously by Wu et al.[15] and Tonelli et al.[16] for almost atactic PVA. Aqueous formaldehyde (37 wt% formalin, stabilized with 10−15% methanol) and paraformaldehyde (90−92%) from Janssen Chimica were used without purification.

Preparation of "Heterogeneous" PVF Samples (PVF-HET). During 24 h, 5 g of granular PVA was swollen with 50 mL of water at room temperature. After mixing with various amounts of formalin (respectively 8.75, 16, 25, and 50 mL for HET a, b, c, and d), 5 mL of H_2SO_4 in 30 mL of H_2O was added. This reaction mixture was stirred at 50 °C for 48 h. After neutralizing the acid with aqueous NaOH, the sample was dried in a vacuum oven at 40 °C followed by freeze-drying (lyophilization).

Preparation of the Heterogeneous Modified PVA Pellets with Different Diameters. PVA pellets with different diameters were obtained by a combination of grinding and sifting. The pellets were ground in a mill under liquid N_2 cooling. The product was sieved. The fraction that remained on a sieve with a mesh size of 50 μm was used to prepare HET e. The fraction that passed through a sieve with a mesh size of 1.7 mm but remained on a sieve with a mesh size of 1 mm was used for the preparation of HET f. The difference in diameter between the pellets in PVF-HET e and f is therefore at least a factor of 20. The heterogeneous modification method (as described above) was used to acetalize these PVA pellets under the same conditions. The amount of formalin used was 3.2 mL for both samples.

Preparation of the "Precipitation" PVF Samples (PVF-PREC). PVA (5 g) in 85 mL of H_2O was stirred for 4 h at 90 °C. The reaction mixture was cooled to 50 °C and different portions of formalin (4, 12.5, 20, and 25 mL respectively for PREC a, b, c, and d) were added. After homogenization, 2.5 mL of H_2SO_4 in 30 mL of H_2O was poured in the reaction

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mixture which was kept at 50 °C for 24 h without stirring. The PVF-PREC b, c, and d samples precipitated during the acetalization reaction, whereas the PVF-PREC a sample (which is soluble in water) was precipitated with acetone. The products were neutralized with aqueous NaOH, dried in a vacuum oven, and freeze-dried.

Preparation of the "Dissolution" PVF Sample (PVF-SOL). PVA (1 g), 0.7 g of paraformaldehyde, 36 mL of 1,4-dioxane, and 1 mL of hydrochloric acid (reagent grade, 35%) were mixed. The reaction mixture was kept at 60 °C for 3 days and then poured into water containing a small amount of sodium carbonate. The polymer was purified by repeated precipitations from the dioxane solution into water. The dissolution method was used to prepare a highly formalized PVA sample.

The PVF-SOL sample used for studying the effect of lanthanide shift reagents on the peak positions in the ^{13}C NMR spectrum was prepared in DMSO-d_6 by adding 108 mM of praseodymium chloride ($PrCl_3 \cdot 6H_2O$, 99.9%, delivered from Ventron) to the above-mentioned PVF-SOL sample.

Preparation of Deuterium-Exchanged PVF-SOL. The hydroxyl protons of a PVF-SOL sample were exchanged by D_2O (99.9 atom % D, Aldrich). The exchange process took place at room temperature, and every 48 h the sample was freeze-dried and fresh D_2O was added. This exchange/freeze-drying cycle was repeated for 3 weeks.

The degree of acetalization (i.e., the percentage reacted hydroxyl groups) is reported in Table 2. All modification methods described were carried out in duplicate and led to reproducible samples.

NMR. The ^{1}H NMR measurements were performed on a Varian Unity 400 spectrometer.

Hu and co-workers[17] already mentioned that care must be taken in preparing samples, in order to observe the PVA hydroxyl proton signal in the ^{1}H NMR spectra clearly. Therefore, freeze-dried samples were dissolved in dry perdeuterated dimethyl sulfoxide (DMSO-d_6), which provides the internal lock and reference signal. The sample concentration was 3% (w/v). Quantitative spectra were recorded at 40 °C, using pulse widths of 10 μs (pulse angle 90°) and pulse intervals of 80 s. Spectra were obtained by accumulation of 8 scans.

The quantitative (inverse-gated decoupling) 100 MHz ^{13}C NMR spectra were obtained at 80 °C. Sample concentration was 7.5% (w/v) in DMSO-d_6. Approximately 20000 free induction decays were accumulated using a 65° pulse of 7.4 μs and a pulse interval of 3 s.

DMSO-d_6 was purchased from Merck (deuteration degree minimum 99.8%). Small amounts of water were removed by activated molecular sieves.

Results and Discussion

The triad tacticities of the starting PVA were checked both by ^{13}C and ^{1}H NMR. The mm, mr, and rr fractions amount to 0.21, 0.50, and 0.29 and 0.23, 0.50, and 0.27 for ^{1}H and ^{13}C NMR, respectively, which means we have an atactic PVA sample which obeys Bernoullian statistics.[15,16]

Poly(vinyl formal) (PVF) is formed when formaldehyde reacts with adjacent hydroxyls on the poly(vinyl alcohol) (PVA) chain to form formal rings. These rings are called meso or racemic, depending on whether the adjacent hydroxyl groups were at the same or opposite sides of the PVA chain. The meso formal ring may take the diequatorial conformation and should be more stable than the racemic formal ring, which may take equatorial−axial or axial−equatorial conformations. These two latter chair forms are energetically nearly equivalent.

In the description of the microstructures of PVF, one has to deal with several aspects. Besides the molecular arrangement of acetal rings and the stereochemistry of the individual ring (meso or racemic), the molecular arrangement and stereoregularity of unreacted hydroxyl groups must also be taken into account. Due to the large number of possible comonomer sequences and stereosequences in PVF, the control of molecular structure in PVF is rather complex. Therefore, it should not be surprising that both ^{13}C and ^{1}H NMR spectra exhibit a complex microstructure.

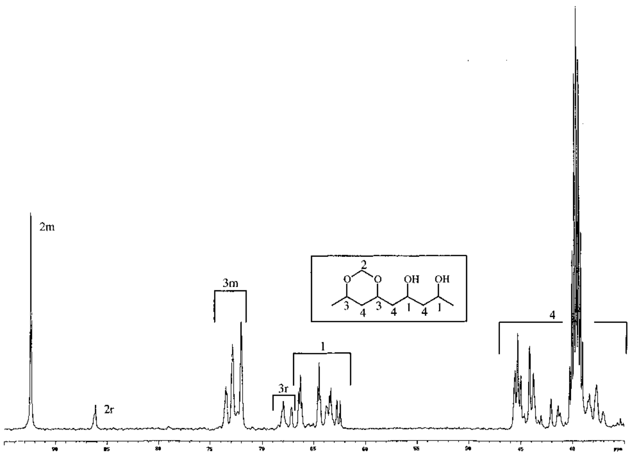


Figure 1. 100 MHz ^{13}C NMR spectrum of a 7.5% solution of PVF-HET c in DMSO-d_6 at 80 °C. Degree of acetalization: 54 (±1)%.

The sequence distribution of functional groups in the resultant PVF polymer depends on the modification method employed.[13,18,19]

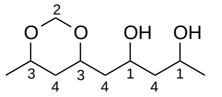
In the "*heterogeneous*" method, the reaction is carried out on water-swollen granular PVA. The formal rings are believed to be distributed selectively and collectively in the amorphous domains.[13,20] This statement will be discussed later.

In the "*precipitation*" method, the reaction initially takes place in an aqueous "solution" of PVA. At approximately 30% acetalization (i.e., the percentage of reacted hydroxyl groups), the acetal precipitates, after which the reaction continues heterogeneously. The PVF-PREC a sample (degree of acetalization < 30%), which is soluble in water, is precipitated with acetone. This method ensures a uniform distribution of functional groups.[13,20]

In the "*dissolution*" method, the reaction is carried out on powdered PVA, suspended in dioxane, a good solvent for the acetal but a poor solvent for PVA. The reaction products (PVF) dissolve as the acetalization proceeds, after which the reaction continues in the homogeneous system. The dissolution method is used to prepare PVA with a high degree of acetalization. It is somewhat surprising that this reaction goes almost to completion with very few unreacted hydroxyl groups remaining. One would expect that, where neighboring groups react in pairs, a significant number of isolated hydroxyl groups would remain unable to react. Assuming random isolation of unreacted hydroxyl groups, Flory's theory[21] predicts that the maximum degree of acetal formation should not exceed 86.5%. Raghavendrachar and Chanda[22] explained higher experimental yields by a nonrandom zipperlike process where the condensation at neighboring hydroxyls is controlled by preexisting acetal groups.

^{13}C NMR Measurements. Peak Assignment. Figure 1 shows the ^{13}C spectrum of PVF-HET c. All resonances in the range 30−50 and 85−100 ppm are methylenes; the resonances from 60 to 75 ppm are methines. The positions of the signals are reported in Table 1.

Table 1. Chemical Shifts for PVF Samples in DMSO-d_6^{a}

			^{13}C NMR chem shift,^{a} ppm 80 °C	^{1}H NMR chem shift,^{b} ppm40 °C
$C_{2m,eq}$			92.4	4.94
$C_{2m,ax}$			92.4	4.62
C_{2r}			86.0	4.78
C_{3m}			71−74	3.84−3.62
C_{3r}			66.7−69	4.12−3.96
C_1	VVV	V_mVV_m	68.2−67.6	
		V_mVV_r	66.7−65.9	
		V_rVV_r	64.7−64.1	
	VVR	V_mVR_r	65.2−65.7	
		V_mVR_m	64.8−65.2	3.96−3.77
		V_rVR_r	63.4−63.8	
		V_rVR_m	63−63.4	
	RVR	R_rVR_r	62.4	
		R_mVR_r	62.7	
		R_mVR_m	63.2	
C_4			30−50	1.0−2.0
mm PVA-OH				4.58
mr PVA-OH				4.39
rr PVA-OH				4.15
new OH				4.42, 4.37, 4.33, 4.29, 4.21

^{a} A vinyl alcohol unit is defined by V and a CHOR unit of a formal ring is defined by R; m and r subindices refer to the meso and racemic orientation of a vinyl alcohol unit or a formal ring with respect to the CHOH unit in question.

Table 2. Degree of Acetalization and Standard Deviation in Parentheses of Different PVF Samples^a

sample	deg of acetalization (%)		% acetal rings in racemic config^d
	^{13}C NMR^b	^{1}H NMR^c	
PVF-HET a	22 (±2)	24.0 (±0.7)	3 (±1)
PVF-HET b	38 (±2)	39.7 (±0.3)	6.2 (±0.9)
PVF-HET c	54 (±1)	54.6 (±0.1)	15.1 (±0.2)
PVF-HET d	67 (±2)	65 (±1)	24 (±1)
PVF-PREC a	27.6 (±0.9)		8 (±1)
PVF-PREC b	35 (±1)	34.1 (±0.6)	11 (±2)
PVF-PREC c	56 (±2)	55.3 (±0.3)	13.32 (±0.02)
PVF-PREC d	63 (±2)	64.5 (±0.4)	15.2(±0.6)
PVF-SOL	94.7 (±0.2)	98 (±3)	34 (±1)

^{a} The ^{1}H NMR spectrum of PVF-PREC a is not used because most of the hydroxyl resonances are masked by water signals (see materials). ^{b} Calculated from ^{13}C NMR spectra shown in Figures 3a and 3b. ^{c} Calculated from ^{1}H NMR spectra shown in Figures 6a and 6b. ^{d} Calculated from ^{13}C and ^{1}H NMR spectra.

Resonances around 92.4 and 86.0 ppm can be assigned to methylene 2 in meso (C_{2m}) and racemic rings (C_{2r}), respectively. Shibatani et al.[7] studied the relationship between the stereostructure of PVA and the acetal formation. They found that the formation of meso formal is favored kinetically and also thermodynamically. This explains the higher intensity of the C_{2m} signal with respect to the C_{2r} signal (see Table 2). The methylene C_2 signal is shifted farther downfield than any other resonance since it is directly attached to two oxygen atoms. Methine 3 is shifted upfield from methylene 2 but downfield from PVA methines since it is in α-position to an OR group instead of an OH group. Furthermore, since two methine 3 carbons exist for each methylene 2 carbon, integration shows that methine 3 carbons in meso rings (C_{3m}) correspond to the resonances in the region 71−74 ppm. Methine 3 carbons in racemic rings (C_{3r}) correspond to resonances from 66.7 to 69 ppm.

For the further analysis of the methine region, a vinyl alcohol sequence is defined by V and a CHOR unit of a formal ring is defined by R; m and r subindices refer to the meso and racemic orientation of the vinyl alcohol sequence or the formal ring with respect to the CHOH unit in question. Expanded regions (60−69 ppm) of the ^{13}C NMR spectra of PVF-HET c, PVF-PREC c, PVA, and PVF-SOL are shown in Figure 2. Assignments of PVA methine resonances are based on previous reports concerning the stereoregularity of atactic PVA.[16,23,24,25] Resonances 68.2−67.6, 66.7−65.9, and 64.7−64.1 ppm are typical patterns for hydroxyl functions with two hydroxyl neighbors, i.e., a **VVV** sequence corresponding with PVA monomer sequences in terms of triad tacticity. These resonances correspond respectively to V_mVV_m, V_mVV_r, and V_rVV_r sequences. The triad effect of a CHOH group is therefore 1.6−1.8 ppm. The remaining splittings (0.1−0.2 ppm) are a result of pentad tacticity.

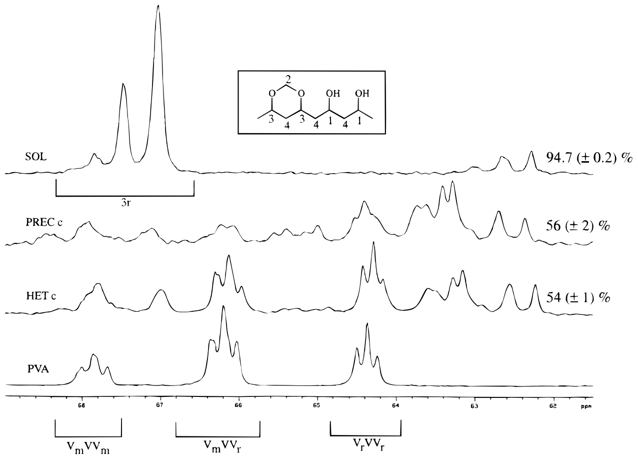


Figure 2. ^{13}C NMR spectra of 7.5% solutions of PVA, PVF-HET c, PVF-PREC c and PVF-SOL in DMSO-d_6 at 80 °C. The degree of acetalization is given on the right side. A vinyl alcohol unit is defined by V; m and r subindices refer to the meso and racemic orientation of a vinyl alcohol unit with respect to the CHOH unit in question.

In samples with a rather low degree of acetalization (PVF-HET a and PVF-PREC a in Figures 3a and 3b), C_{3r} is overlapping with C_1 V_mVV_m carbons; however, the portion of C_{3r} carbons can be derived by taking the double of the intensity of the C_{2r} signal. The remaining signals in the region 62−66.7 ppm are methine 1 resonances of vinyl alcohol sequences with different length (see below). The portion of CHOH groups can be found by subtracting the double of the intensity of the C_{2r} signal from the total intensity in this region.

The tacticity effect of a CHOR unit is clearly visible in the ^{13}C NMR spectrum of PVF-SOL (Figure 2). The three signals in the region 63.2−62.3 ppm represent the tacticity effect of isolated C**H**OH functions, i.e., an **RVR** sequence. Resonances around 62.4, 62.7, and 63.2 ppm correspond respectively to R_rVR_r, R_mVR_r, and R_mVR_m sequences. Formal rings produce a triad splitting of 0.3−0.4 ppm and a pentad splitting of <0.1 ppm.

The assignment of these RVR signals was verified by studying the effect of lanthanide shift reagents on the peak positions of PVF-SOL in the ^{13}C NMR spectrum. Adding praseodymium chloride ($PrCl_3$·6 H_2O) clearly has an effect on the signals in the region 63.2−62.3 ppm.

Based on the chemical shift effects of the CHOH and CHOR units on methine 1 signals, resonances in the regions 63−63.8 and 64.8−65.7 ppm can be attributed to CHOH groups surrounded by a formal ring and another hydroxyl function. This sequence is indicated as a **VVR** sequence. The main splitting (1.6−1.8 ppm) is due to the orientation of the neighboring OH group. Resonances 64.8−65.7 ppm are attributed to V_mVR

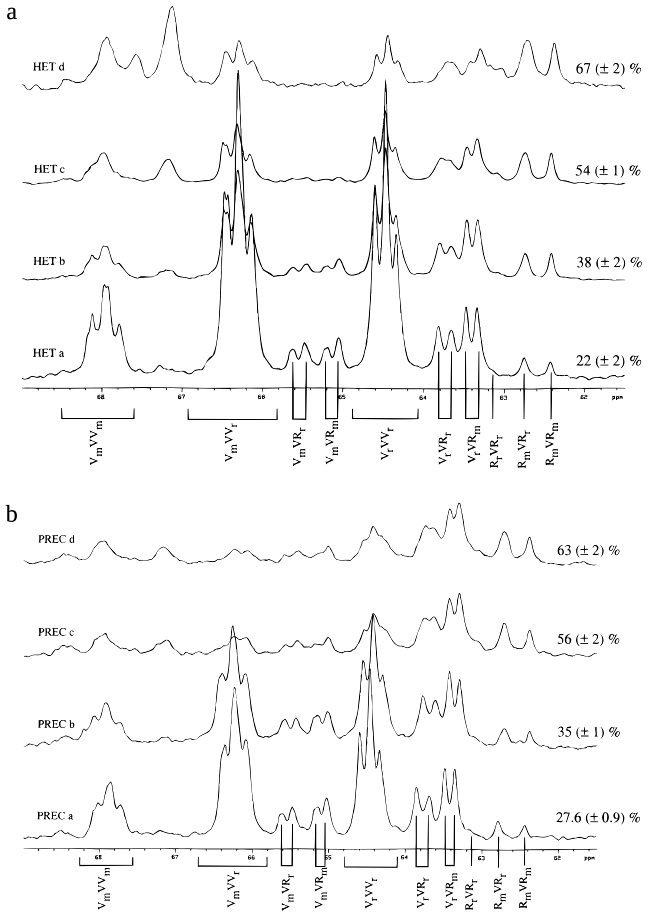


Figure 3. ^{13}C NMR spectra of 7.5% solutions of pairs of PVF-HET (a) and PVF-PREC (b) samples with similar degrees of acetalization, covering the whole range of acetalization degrees in DMSO-d_6. The spectra were obtained at 80 °C. The degree of acetalization is given on the right side. A vinyl alcohol unit is defined by V and a CHOR unit of a formal ring is defined by R; m and r subindices refer to the meso and racemic orientation of a vinyl alcohol unit or a formal ring with respect to the CHOH unit in question.

sequences with this OH group in meso position with respect to the considered CHOH group. In the case of racemic orientation, V_rVR, these resonances are present in the region 63−63.8 ppm. The ring triad effect (0.3−0.4 ppm) also clearly appears. Therefore, V_mVR signals are split up in V_mVR_r resonances (65.2− 65.7 ppm) and V_mVR_m resonances (64.8−65.2 ppm); V_rVR signals are split up in V_rVR_r resonances (63.4−63.8 ppm) and V_rVR_m resonances (63−63.4 ppm). The remaining splittings (0.1−0.2 ppm) are due to pentad effects.

The assignment of the triad effect of the acetal ring, thus whether R_m respectively R_r causes an upfield or a downfield shift, is demonstrated in the following section. With increasing degree of acetalization (see Figures 3a and 3b), one can observe a strong decrease of some V_mVR sequences while the V_rVR sequences remain almost unchanged. Simultaneously, there is an increase of RVR signals around 62.4 and 62.7 ppm, while the resonance around 63.2 ppm is much less affected. The decrease of the V_mVR signals can be correlated with the increase of the R_mVR resonances. Since reaction of a V_mVR_m unit results in an R_mVR_m unit and reaction of a V_mVR_r unit results in an R_mVR_r unit, the RVR signal with an almost constant intensity should be R_rVR_r. Therefore, one can conclude that an acetal ring in meso stereochemical configuration with respect to the vinyl alcohol unit in question causes an upfield shift, whereas an acetal ring in racemic configuration causes a downfield shift.

In summary, in the methine region, we can distinguish VVV, VVR, and RVR sequences. VVV sequences refer to "PVA-like" polymer segments (blocky microstructures) whereas VVR sequences refer to random microstructures. RVR sequences refer to isolated hydroxyl functions.

Functional Group Distribution. With respect to the sequence distribution, Figure 2 shows the difference between the heterogeneous and the precipitation modification methods. In this figure, ^{13}C NMR spectra of PVF-HET c and PVF-PREC c samples with almost the same degree of acetalization (see Table 2) are reported. Clearly, the heterogeneous sample exhibits a blocky distribution of functional groups; the VVV resonances in the regions 68.2− 67.6, 66.7−65.9, and 64.7−64.1 ppm are without doubt present. This means that the formal rings (and therefore also the hydroxyl functions) are more or less grouped. The precipitation sample, on the other hand, shows evidence for a random distribution; the VVV resonances mentioned are of less importance, whereas the signals responsible for RVR and VVR sequences are of major relative intensity.

^{13}C NMR spectra of pairs of PVF-HET and PVF-PREC samples with comparable degrees of acetalization and covering a range of degrees of acetalization are reported in Figures 3a and 3b, respectively. The functional group distribution of the samples with the lowest degree of acetalization (PVF-HET a and PVF-PREC a in Table 2) are comparable. With increasing degree of acetalization, the differences between the two preparation methods, concerning the distribution of functional groups, become more clear. The difference in change of the intensity for the signals in V_mVR sequences compared to those in V_rVR sequences is remarkable. With increasing degree of acetalization, and independent of the preparation method used, one can observe a faster relative decrease of the V_mVR sequences with respect to the V_rVR sequences. This phenomenon is even more evident for the heterogeneous method; in HET c and HET d, the V_mVR sequences have almost fully disappeared. This difference in decrease can easily be explained since meso formal rings are both thermodynamically and kinetically favored. It further confirms the assignment of V_mVR and V_rVR sequences. The V_mVR signals in the region 64.8−65.7 ppm represent tacticity patterns with more vacant iso sequences (to form meso formal rings) than the V_rVR resonances in the region 63−63.8 ppm and are therefore more attractive for the formalization reaction. For the same reason, with increasing degree of acetalization, the order in decrease of the VVV sequences is $V_mVV_m \geq V_mVV_r \gg V_rVV_r$. Again, this effect can be observed for both preparation methods.

The main difference between the heterogeneous and the precipitation methods is reflected in the different relative decreases of the VVV signals with respect to the V_mVR signals as a function of degree of acetalization. In the case of the heterogeneous method, the V_mVR signals disappear faster than the VVV sequences, whereas in the case of the precipitation method, the opposite feature can be observed. Therefore, we can conclude that the acetal rings in the "heterogeneous" samples (Figure 3a) are grouped, whereas in the "precipitation" samples (Figure 3b), they are randomly distributed.

Furthermore, concerning the bandwidth of the VVV signals as a function of degree of acetalization, in the "precipitation" samples, one can clearly observe some broadening effect. On the other hand, the bandwidths in the "heterogeneous" samples are comparable with those of the starting material (PVA) shown in Figure 2.

Degree of Acetalization. The modification reaction logically changes the properties of the polymer. Meso formal rings for example introduce an immobilization effect in the polymer chain because the diequatorial ring cannot transform into a diaxial conformation. Therefore, it is useful to determine the degree of acetalization of the samples and the ratio of meso to racemic formal rings.

The degree of acetalization of the PVF samples was determined by integration of quantitative ^{13}C NMR spectra. It is defined as the percentage of reacted hydroxyl groups and calculated by the following formulas (ratios):

$$200 \times (C_{2m} + C_{2r})/(C_1 + C_{3m} + C_{3r})$$

or

$$100 \times [C_{3m} + (2C_{2r})]/(C_1 + C_{3m} + C_{3r})$$

or

$$100 \times (C_{3m} + (2C_{2r}))/[C_1 + 2(C_{2m} + C_{2r})]$$

where the expressions in the formulas stand for the intensities of the corresponding signals in Figure 1. The degrees of acetalization of the different PVF samples, which are reported in Table 2, are determined by taking the average of the results obtained by all mentioned formulas. These results are in good agreement with those obtained by analysis of the ^{1}H spectra (see below). The average percentage of acetal rings in the racemic configuration calculated from ^{13}C and ^{1}H NMR spectra are also reported in Table 2. With increasing degree of acetalization, the importance of these rings increases.

It is important to note that the heterogeneous preparation method employed is not a surface reaction, as the method described by Matuzawa[26] and Raghavendrachar,[22] but takes place all over the sample. This assumption is confirmed by the following experiment. Under the same conditions, the heterogeneous modification method was used to acetalize PVA pellets with a different bore (thus varying contact area). The PVF samples obtained, HET e and HET f, were identical in degree of acetalization (see Table 2), relative peak intensities, sequence distribution, and stereochemistry.

^{1}H NMR Measurements. Peak Assignment. Figure 4 shows the ^{1}H spectrum of PVF-HET c. All resonances in the range 1.0−2.0 ppm are methylene 4 protons; all resonances from 4.52 to 5.55 ppm are methylene 2 protons. C**H**OH (C_1) and C**H**OR (C_3) protons give resonances in the region 3.62−4.12 ppm. Expanded regions (3.5−5.3 ppm) of the ^{1}H NMR spectra of PVF-HET c, PVF-PREC c, PVA, and PVF-SOL are shown in Figure 5. Chemical shift data are collected in Table 1.

A number of workers[15,16] showed that, when DMSO-d_6 is used as solvent, the ^{1}H NMR spectrum of PVA exhibits three distinct hydroxyl proton resonances (4.15, 4.39, and 4.58 ppm), corresponding to the triad sequences rr, mr, and mm. The residual splitting of the hydroxyl lines is ascribed to spin−spin coupling with the methine protons. Moritani and co-workers[27] reported that chemical shifts of hydroxyl protons are mainly determined by triad configurations and are hardly affected by longer range configurations. Therefore, higher order microtacticity of PVA is difficult to determine by proton NMR. Resonances 3.96−3.77 ppm in the spectrum of PVA correspond to C_1 proton resonances, i.e., C**H**OH signals.

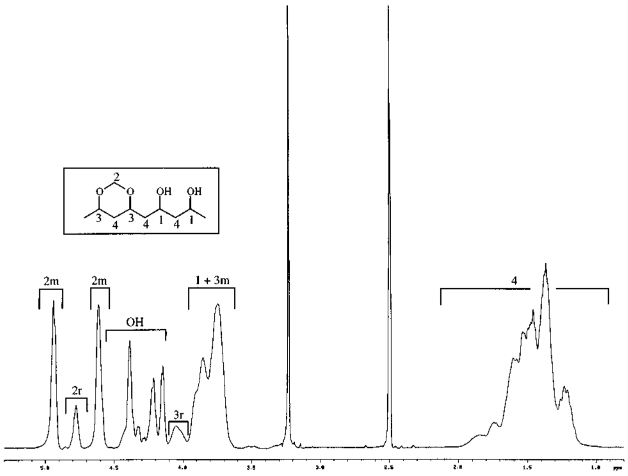


Figure 4. 400 MHz ^{1}H NMR spectrum of a 3% solution of PVF-HET c in DMSO-d_6 at 40 °C. Degree of acetalization: 54.6 (±0.1)%.

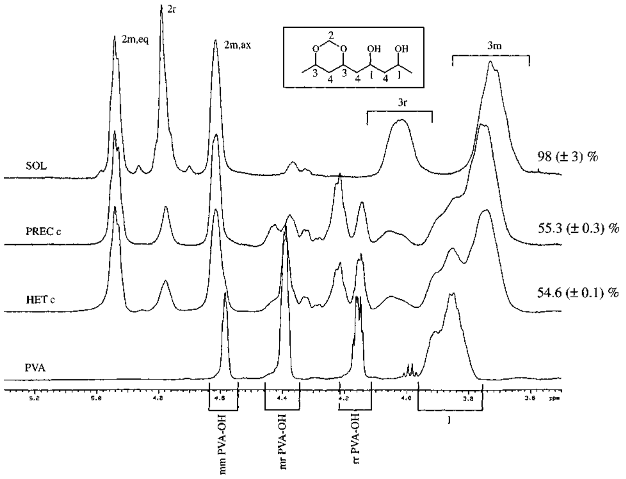


Figure 5. ^{1}H NMR spectra of 3% solutions of PVA, PVF-HET c, PVF-PREC c, and PVF-SOL in DMSO-d_6, recorded at 40 °C. The degree of acetalization is given on the right side.

Chemical shift assignments of PVF (Figure 5, Table 1) are based on previous work of Shibatani.[18] Methylene 2 proton resonances are divided into racemic and meso portions with different chemical shifts due to differences of the steric structures of the polymer. The cis isomer may take the diequatorial conformation preferentially, and therefore the two C_2 protons may be observed as nonequivalent, giving rise to an AB system. Resonances around 4.94 ppm represent the equatorial C_2 proton ($C_{2m,eq}$), and those around 4.62 ppm represent the axial proton ($C_{2m,ax}$). On the other hand, in the trans isomer, these protons can be observed as equivalent because of a rapid inversion between equatorial−axial and axial−equatorial conformations that are energetically equivalent. Therefore, these C_{2r} protons give a single peak at 4.78 ppm.

From the spectrum of PVF-SOL, it becomes clear that the resonances 3.84−3.62 ppm correspond to C_3 protons (i.e., C**H**OR signals) in the meso conformation (C_{3m}) and

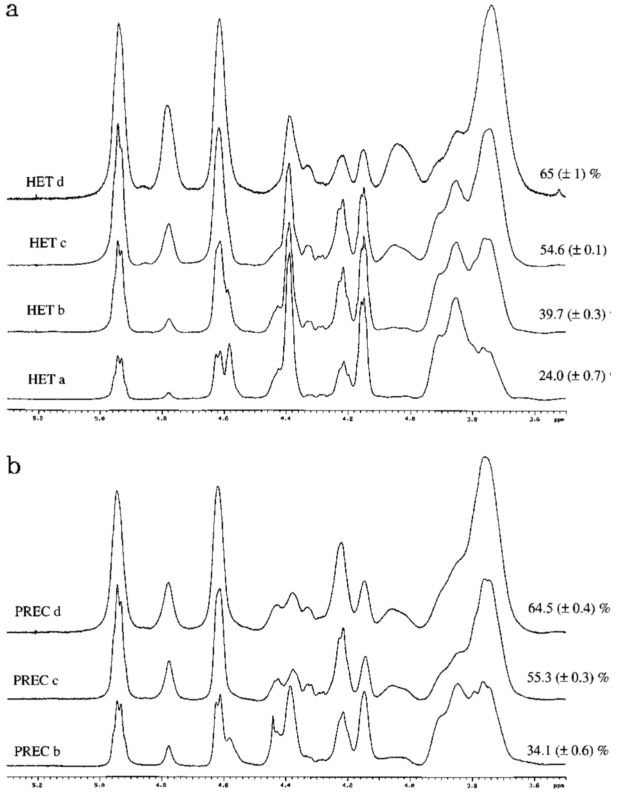


Figure 6. ^1H NMR spectra of 3% solutions of pairs of PVF-HET (a) and PVF-PREC (b) samples with similar degrees of acetalization, covering the whole range of acetalization degrees in DMSO-d_6. The spectra were recorded at 40 °C. The degree of acetalization is given on the right side.

the resonances 4.12−3.96 ppm correspond to C_3 protons in the racemic conformation (C_{3r}).

These assignments are confirmed by integration data; the intensities of the C_{3m} resonances equal those of the C_{2m} signals. The same relation is valid for C_{3r} with respect to C_{2r} signals.

Figures 6a and 6b show respectively the proton spectra of "heterogeneous" and "precipitation" samples as a function of degree of acetalization. When the acetalization reaction proceeds, new proton signals arise in the region 4.48−4.20 ppm. These resonances could be assigned to new hydroxyl signals (new OH), arising from tacticity and sequence effects of the acetal rings. Up to a degree of acetalization of 54−56%, these signals increase (for both modification methods) with increasing degree of acetalization. For higher conversions, these signals become of lower intensity; in the spectrum of PVF-SOL, only signals around 4.37 and 4.33 ppm remain. Therefore, these resonances are not methine C_3 signals, but hydroxyl resonances. This assumption is confirmed by recording a ^1H NMR spectrum of an almost fully deuterium exchanged sample in which these resonances have disappeared.

As can be seen in Figures 6a and 6b, these C_3 signals increase with increasing degree of acetalization, where C_1 proton signals in the area 3.96−3.77 ppm decrease.

Functional Group Distribution. For samples with a rather low degree of acetalization, mm PVA-OH signals overlap with axial C_2 protons in the cis isomer ($C_{2m,ax}$). With increasing conversion, PVA-OH signals logically decrease, with the fastest decrease for the mm PVA-OH signal (regardless of the modification method employed). Analogous to the observations in the ^{13}C NMR spectra, for comparable degrees of acetalization, the PVA-OH signals are more pronounced for the heterogeneously modified samples. This confirms the above-mentioned blocky distribution of functional groups for samples prepared by the heterogeneous method.

Degree of Acetalization. From the proton NMR spectrum, the degree of acetalization is calculated from the following formulas:

$$(C_{2m} + C_{2r})/(C_1 + C_{3m} + C_{3r})$$

or

$$(C_{2m} + C_{2r})/(C_{2m} + C_{2r} + \text{PVA-OH} + \text{new OH})$$

Again, the abbreviations in the formulas stand for the intensity of the corresponding signals in Figure 4. Since $C_{2m,ax}$ resonances (4.62 ppm) overlap with triad mm hydroxyl resonances (4.58 ppm), two times the intensity of the equatorial C_2 protons in the cis isomer ($C_{2m,eq}$) is used as the intensity of the C_{2m} signal. These results, which are in good agreement with the ^{13}C NMR results, are collected in Table 2.

Conclusions

The modification of PVA by means of a postpolymerization acetalization reaction results in a new polymer, PVF, which is a copolymer of formal rings and unreacted vinyl alcohol. To control the properties of this PVF polymer, it is important to have an idea about the polymer microstructure. PVF is a complex polymer because it exhibits both stereosequence and comonomer sequence microstructure. The functional group distribution in PVF depends on the modification method employed. In this work, we used ^{13}C and ^1H liquid NMR spectra to unravel this complex microstructure. It is shown that the methine 1 resonances in the ^{13}C NMR spectra in particular are a very powerful probe to analyze the microstructure of the polymer. The heterogeneous modification method shows evidence for a blocky distribution of functional groups, whereas samples prepared by the precipitation method exhibit random distribution.

The properties and applications of the PVF polymer further depend upon the relative contents of functional groups, expressed in the degree of acetalization. Again, this information can be easily determined both from ^{13}C and ^1H liquid NMR spectra.

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