PII: S0032-3861(97)10257-9

Semicrystallinity and polymorphism in PVDF: a solid-state ^{19}F n.m.r. investigation

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Solid-state ^{19}F nuclear magnetic resonance spectroscopy has been employed to investigate the semicrystallinity and polymorphism of poly(vinylidene fluoride) (PVDF). Fast MAS and high-power proton decoupling were applied to separate the spinning sidebands from the relevant spectral range and to remove the effects of dipolar coupling between the protons and the fluorine nuclei. Amorphous and crystalline regions provide distinct chemically-shifted signals. The application of relaxation filters can suppress the signal either of the amorphous or of the crystalline part. The polymorphism, which characterizes the PVDF crystallites, is reflected in spectra of the crystalline part. Some of the variety of possible conversions between the modifications have been exemplified. Variable-temperature experiments demonstrate both crystallization effects and changes in the modifications. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is known for its potential for technical applications based on its mechanical and electrical properties. Especially the piezo- and pyroelectricity, which are extremely high for a polymer, provide possibilities for applications. Many of them have been proposed and realized[1-6]. The semicrystalline nature of PVDF, combined with the occurrence of five crystalline modifications, implies a complicated physical microstructure. The most-frequently described and important polymorphs are the α-phase, which has no net electric dipole moment because of the antiparallel chain arrangement in the unit cell[7], and the β-phase. The β-phase has a parallel arrangement of all-*trans* chains in an orthorhombic unit cell and thus shows a resultant dipole moment in each crystallite, which is important for the strong electric effects of this phase. The chains of the α-phase have a tg^+tg^- conformation. Numerous modes of interconversions between the modifications have been discovered. The combination of stretching followed by poling in high electric fields induces a high proportion of β-crystallites and irreversible dipole reorientations, to give films with usable electrical properties. Solution-state ^{19}F nuclear magnetic resonance (n.m.r.) provides insight into the chain microstructure of PVDF[8]. The main resonance arising from regular head-to-tail polymerizations appears at -91 ppm. There are a couple of further resonances at lower frequency, which reveal reverse arrangements of monomer units. Defect contents of the order of 5% are typical for PVDF[9]. Their influence on the crystallization behaviour has been discussed. Defects may be included in the crystallites if the lamellar thickness is larger then their average distance apart.

However, the degree of crystallinity decreases with the defect concentration. In addition to solution-state n.m.r. studies, a little solid-state n.m.r. work has been reported, mostly dealing with proton and fluorine broad-line experiments[10-12]. ^{1}H–^{19}F cross-relaxation dynamics have been studied[13]. The semicrystalline character of PVDF provides heterogeneous lineshapes and relaxation decays $(T_2, T_{1\rho})$. Spin diffusion effects can be exploited because the typical thickness of lamellae is of the order of 10 nm[11]. Angular dependencies of proton linewidths for drawn film material[12,14] have been measured. Drawing influences mainly the crystalline regions. Attempts have been made to investigate the influence of electric poling procedures on PVDF film material by exploiting the orientational dependencies of linewidths $(\Delta\nu)$, second moments (M_2) and relaxation times $(T_2, T_{1\rho}, T_{2eff})$[14-17]. The irreversible orientation effects due to poling are weak compared to the stretching effect and occur also mainly in the crystalline phase. An approach has been presented to investigate the orientation process in a film *in situ* during the poling process[14,18]. There is a reversible part of the electric polarization, which vanishes after switching off the electric field, and an irreversible contribution. Deuterium n.m.r. investigations of oriented and poled film material have been reported[19], which of course require specially polymerized film material. Chain motions in the α-crystallites of deuterated PVDF have been investigated by two-dimensional exchange ^{2}H n.m.r.[20]. The value of solid-state ^{19}F n.m.r. has been demonstrated when it is possible to apply high-power decoupling to remove the H–F dipolar couplings and fast MAS to suppress the dipolar interaction among the fluorine nuclei, and thus to access the isotropic chemical shift information[21]. Recently, the feasibility of two-dimensional ^{19}F–^{1}H wideline separation (WISE) spectroscopy has been demonstrated[22] for which proton high-power decoupling and fast MAS are also necessary.

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The aim of the present work was to investigate the extent to which high-resolution ^{19}F n.m.r. (including high-power proton decoupling) can yield information about the domain structure of PVDF, especially with respect to polymorphic form. The effects of processing (including temperature changes and electrical poling) on the polymer have also explored.

EXPERIMENTAL

The n.m.r. experiments have been carried out using a Chemagnetics spectrometer (CMX 200, operating at 200.13 MHz and 188.29 MHz for proton and fluorine nuclei respectively). A commercial (Chemagnetics) double-tuned APEX magic angle spinning (MAS) probe for simultaneous ^{19}F and ^{1}H operation, in conjunction with 4 mm (outer diameter) zirconia Pencil® rotors, was used[23]. Vespel drive tips, spacers, and end-caps have been employed to avoid any unwanted background signal on the fluorine channel. MAS speeds up to approximately 17 kHz were achievable. Experimental parameters were 1.9 μs $\pi/2$ pulse duration (for both ^{19}F and ^{1}H channels) and proton decoupling fields up to 100 kHz. The pulse repetition times were 1 s for the cross-polarization (CP) experiments and 3 s for directly polarized fluorine spectra. The chemical shifts in the fluorine spectra are referenced to the signal for liquid $CFCl_3$ by replacement. Except for the variable temperature experiments, the spectra were acquired at ambient temperature without temperature control. Frictional heating arising from fast MAS has not been considered in this work, though it may be of importance when phase transitions occur.

Different PVDF types have been used in the investigation. Powder material containing the non-polar α-modification and commercial films with different nonpolar(α)/polar(β) ratios were studied. The thickness of the film material ranged from 10 to 25 μm. The estimation of the crystallinities by means of ^{1}H n.m.r. wideline spectra (60 MHz) and X-ray scattering yielded values of (50 $\pm$ 5)% for the powdered material and a slightly increased crystallinity for the films (55%-60%). The polar content (β) of the uniaxially (4:1) stretched 10 μm film has been estimated by means of infra-red (i.r.) spectroscopy to be 80%[24]. The biaxially drawn film material (3:2, thickness 25 μm) contained approximately 65% of the polar phase.

The film samples were metallized by evaporation with aluminium for the electric processing. The electrode areas were 1 cm $\times$ 4 cm. The thermal electret poling method (TEP) has been applied to polarize the samples[3,4]. It must be emphasized that only the material under one electrode has been used. This means that, for 10 mm films, only about 7 mg could be investigated, even though the n.m.r. signal was drastically reduced by the use of combined spin-locked relaxation and cross-polarization for selective experiments. The poling temperature was 80°C, applied for 30 min. After cooling to ambient temperatures, the voltage was switched off. D.c. voltages up to 4 kV could be achieved before breakdown occurred.

RESULTS AND DISCUSSION

Figure 1 demonstrates the influence of magic-angle spinning on the fluorine spectra at rates of up to 6 kHz. There are almost no indications of distinct spectral features if only moderate spinning speeds are applied. When fast MAS was used, the sidebands are moved out of the
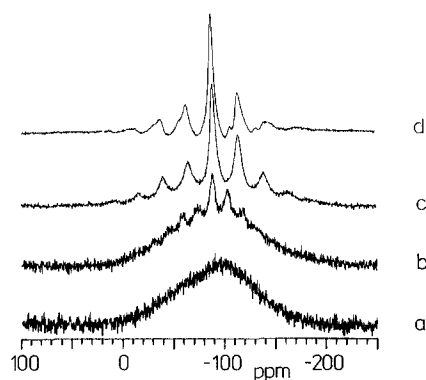

Figure 1 The effect of MAS on CP { ^{1}H} – ^{19}F spectra of powdered PVDF (a) 1250 Hz (b) 2750 Hz (c) 4460 Hz (d) 6090 Hz
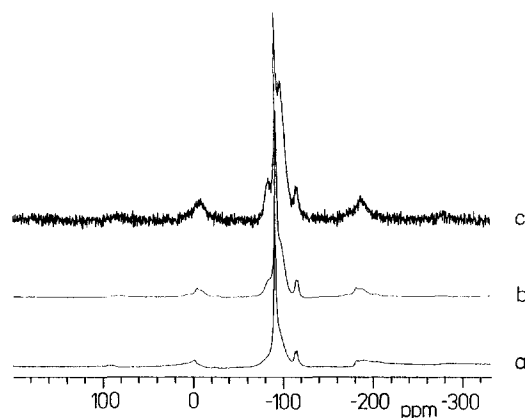

Figure 2 Directly polarized ^{19}F spectra of PVDF film (a) without and (b) with high-power decoupling on the proton channel, MAS at 16.7 kHz (c) CP/MAS spectrum of the same material (contact time 1 ms)

interesting spectral range. We conclude that spin rates in excess of 6 kHz are essential, and in fact we have in practice used significantly higher values. The direct-polarization spectra shown in *Figure 2* were acquired under identical MAS conditions (at spin rates of 16.7 kHz) without and with high-power decoupling. In the same figure, a comparison to the cross-polarization spectrum, also acquired with proton high-power decoupling during acquisition, is given. Without the irradiation of a second frequency for decoupling purposes, the spectrum shows only an intense line around −91 ppm which has some undefined broad wings. We assign this line to the CF_2 main resonance since it can be observed also at this position in solution-state spectra. The smaller resonances at −112 ppm and −115 ppm can be explained by the occurrence of reversed monomer polymerization ($-CF_2-CH_2-CF_2{}^*-CF_2-CH_2-CF_2$ and $-CF_2-CH_2-CF_2-CF_2{}^*-CH_2-CH_2-$ etc.), i.e. head-to-head units. Further smaller resonances due to such chain imperfections have been reported[8] but these are covered by the broad wings of the main resonance in the solid-state spectra. The intensity of these resonances may differ for various materials. Defect percentages obtained from solution-state n.m.r. have been reported to be between 3 and 6%[9]. If decoupling on the proton channel is used, there is a frequency shift due to the Bloch–Siegert effect[25] which is in the order of 2–3 ppm in our experiments, though this can be avoided by using similar 'decoupling' powers when the spectrum of the reference compound is recorded. Some of the spectral features become more pronounced in the
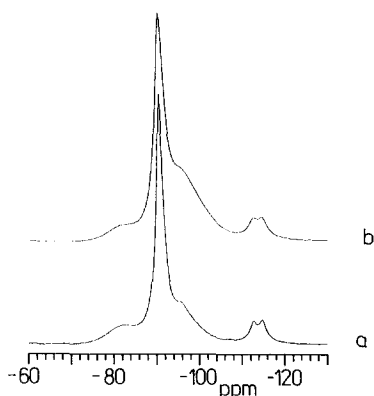
Figure 3 Comparison of directly polarized and high-power decoupled ^{19}F n.m.r. spectra of powdered (a) and bioriented film (b) material (25 μm) at a MAS-frequency of 16.7 kHz

Figure 4 Discriminatory (crystalline-selective) $\{^1H\}-^{19}F$ CP/MAS spectra of (a) PVDF (9 μm biaxially drawn film), (b) melt-crystallized PVDF obtained from (a). Contact time 50 μs, following a preparation spin-locking pulse on the proton channel of duration 40 ms; 12.8 kHz MAS

decoupled spectra, revealing information from relatively immobile regions of the material, which are generally expected to form the crystalline domains. Two new broad peaks at −88 and −98 ppm can be found (*Figure 2b* and *c*). The intensities of the peaks depend on the crystallinity and on the type of material. In material predominantly containing the non-polar α-modification, these two lines are of nearly equal intensity, which reflects the two environments for fluorines in the unit cell. In materials having a high amount of β-modification (two planar all-*trans* chains in the unit cell), the relative intensity of the peak at −88 ppm is reduced and we therefore believe the β-signal is indistinguishable from the low-frequency (−98 ppm) α signal. Directly polarized spectra of α-crystallites containing powder and of film material having a higher amount of β-form are presented in *Figure 3*. The crystalline component is emphasized in the sidebands because of the differences in the mobility-averaged tensor components of the chemical shift for the amorphous component and the crystalline lamellae. Apart from the differences in the shape of the broad wings, the increased degree of crystallinity of the film material leads to a lowered relative intensity of the narrow line which arises from the amorphous regions. For further discussion, results of $\{^1H\}$ → ^{19}F cross-polarization experiments will be used. Compared to the direct polarization of the fluorine nuclei, proton-to-fluorine cross polarization provides spectra which have clearly different structure. The suppression of any background from fluorine-containing components of the probe or rotor is an additional advantage of cross-polarization.

Provided the mobility in the amorphous and crystalline phases are different enough, this will be reflected in the relaxation behaviour of both the ^1H and ^{19}F magnetizations. Above the glass transition temperature, which we have found by means of proton wideline n.m.r. experiments to be at about − 35°C, the chains in the amorphous region rotate about their chain axis. The onset of the α_c-relaxation (rotation of crystallites around the crystalline c-axis) has been reported to occur at about 120°C[26] (confirmed by our own T_2^H results).

Cross-polarization techniques may be used to exploit differences in the molecular mobilities between the domains of the heterogeneous PVDF. By the combination of a long proton spin-locking pulse and a following short contact time for cross polarization, it is possible to suppress almost completely the magnetization of one of the components. The long ^1H spin-locking relaxation conserves the
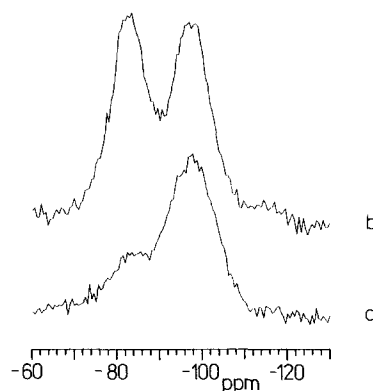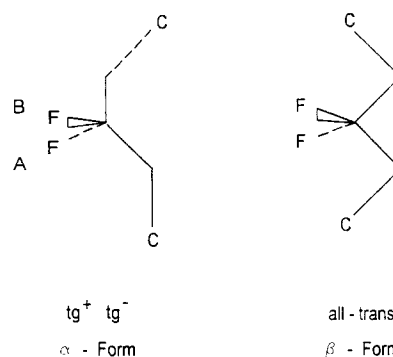

Figure 5 Chain conformations for PVDF to show γ-*gauche* interactions of carbon to fluorine. Left α-form, where F_A has two γ-*gauche* interactions, but F_B has one γ-*gauche* and one γ-*trans*. Right: β-form with two γ-*gauche* interactions for each fluorine

magnetization of the crystalline regions. The short magnetization contact under Hartmann–Hahn conditions also discriminates in favour of the immobile part of the polymer.

Especially if the amorphous component is suppressed, the differences between the polymorphs are more clearly visible. The crystalline-selective spectra of two different PVDF materials are compared in *Figure 4*. It is well known that material produced from the melt contains only the α-modification. In drawn films, the α/β ratio can vary depending on the processing conditions. Under certain circumstances, almost pure β-film material can be obtained. Our evidence shows that both modifications do indeed exist in the films, and we can monitor the α/β-ratio, enabling us to investigate possible interconversions of PVDF modifications.

The differences between the spectra of the α and β crystalline forms can be understood on the basis of the chain conformation, taking account of the well-known γ-*gauche* shielding effect. The fluorines in the β form are equivalent and have two γ-*gauche* interactions with carbon (*Figure 5*), whereas for the α-form the fluorines are non-equivalent and, because of the tg^+tg^- conformation, one of these two has γ-*gauche* carbons whereas the other has one γ-*gauche* and one γ-*trans* carbon (*Figure 5*). The chemical shift of the β-form is thus expected to nearly coincide with one of the α shifts. The splitting for the α form should equal one γ-*gauche* effect. We measured it to be −16 ppm, which is in good agreement with solution-state estimates[8]. However, the
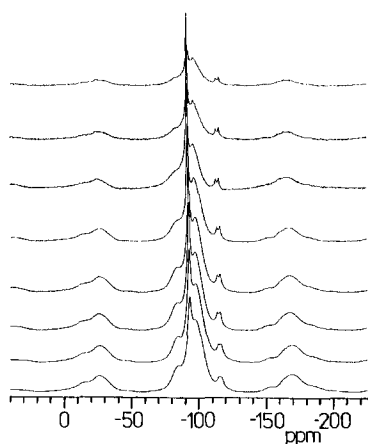
Figure 6 Temperature dependency of {^{1}H}–^{19}F CP/MAS spectra of PVDF (25 μm biaxially drawn film): contact time 1 ms, 12.5 kHz MAS, from bottom: 20, 60, 80, 100, 120, 140, 160, 170°C

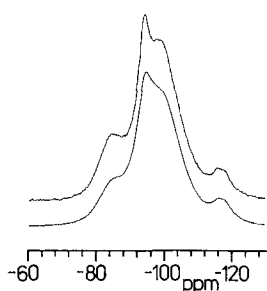**Figure 8** {^{1}H}–^{19}F CP/MAS spectra of unpoled and poled PVDF material. Contact time 50 μs, following a preparation spin-locking pulse on the proton channel of duration 40 ms; 13.0 kHz MAS, spectra acquired at ambient temperatures after poling at (from top): 0 MV m^{-1}, 120 MV m^{-1}, 160 MV m^{-1}

Figure 7 {^{1}H}–^{19}F CP/MAS spectra of PVDF (25 μm biaxially drawn film): contact time 1 ms, 12.5 kHz MAS before (bottom) and after (top) heating in the experiment shown in *Figure 6*. Both spectra were acquired at 30°C

solid-state result is better-founded than those for solution since the conformations are fixed and accurately known. On the other hand, interactions between chains may affect the solid-state measurement. The signals which indicate the head-to-head linkages are almost lost in the spectra of the crystalline phases (*Figure 4*). Thus, the reverse monomer units must occur predominantly in the mobile phase, as might be expected.

PVDF melts in the range from 170 up to 200°C depending on polymorphic form and crystallization[1,2]. Variable-temperature experiments enable dynamical effects to be studied, as well as the influence of thermal effects on the degree of crystallinity and the thermal stability of the modifications. Such variable-temperature fast CP/MAS experiments have been carried out up to 170°C (*Figure 6*). In all these measurements, the same contact time of 1 ms has been used. The cross-polarization efficiency may be a function of the temperature. This is reflected in the absolute intensities and complicates a quantitative description of
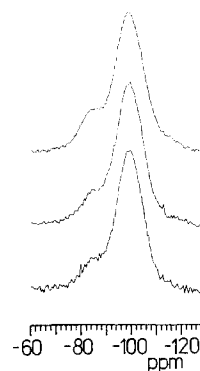
temperature effects on the crystallinity. Nevertheless, a premelting range Δ*T* of about 10 K could be found[27], which causes a clearly decreased CP efficiency and an enhanced amorphous line in the spectrum. The ratio of modifications seems not to be influenced during the heating procedure. However, recrystallization occurs on cooling, providing a slightly increased crystallinity and a higher amount of the α-modification, as shown by a comparison of CP/MAS spectra before and after the treatment up to 170°C (*Figure 7*) However, the measurement of the orientational effect (electrical poling) by means of proton n.m.r. demonstrated that the α$_c$-relaxation destroys irreversibly any orientational effects in films[14,24]. The effect of the interconversion of modifications is more impressive if a sample has been molten and is then crystallized from the melt. A complete transfer to the α-modification can be observed, as expected. When film material is subjected to poling, dipoles tend to orient into the direction of the applied film. Additionally, by applying a strong electric field, the nonpolar α-phase can be interconverted to the polar β-phase. Also a polar analogue of the α-phase can be produced at intermediate electric fields[5]. The orientational effects are not, however, readily accessible by our ^{19}F n.m.r. measurements. The effect of the electric field application on the transformation of the modifications has been proved. *Figure 8* demonstrates results obtained on poled 25 μm (4 cm × 1 cm area) material. The spectrum of the unpoled polymer has been obtained from material around the electrode of the same sample.

High voltage poling provides, together with the effect of the orientation of dipoles, a transformation from the nonpolar to the polar modification. The irreversible part of the changes of modifications can be accessed by our n.m.r. measurements.

To some extent, the ^{19}F results can be used to extract

Table 1 Results from ^{19}F NMR for PVDF materials

Material	α (%)	β (%)	Crystallinity (%)	Head-to-head (%)
Powder	100		47...50	5
9 μm untreated	32	68		
Melt crystallized	100			
10 μm	13	87	55...57	5
25 μm untreated	30	70		
Poled (4 kV)	20	80		
After annealing (170*deg;C)	35	65		

numerical values for both the crystallinity (by exploiting the differences in the mobility of amorphous and crystalline chains) and for the ratio of the distinct polymorphs in the material (based on the spectral differences) (*Table 1*). Proton n.m.r. spectroscopy provides only information about the crystallinity. I.r. spectroscopy can also distinguish between the PVDF polymorphs, but the properties influenced by the semicrystallinity of PVDF cannot be accessed by i.r. In contrast, i.r. spectroscopy (and partly also ^{1}H wideline n.m.r.) is valuable for the investigation of orientation problems. Here, the crystallinity has been estimated by deconvolution of the directly-polarized ^{19}F n.m.r. spectra. The lineshapes of the immobile PVDF regions have been used, which have been estimated by the discrimination experiment which suppresses the signal of the mobile part. The crystalline part can be isolated by a long proton spin-locking pulse (40 ms), followed by a very short contact time (50 μs). It has been proved that the cross-polarization efficiencies for all crystalline resonances are identical within experimental error[17]. The sidebands have to be incorporated in any quantitative treatment of the intensities. However, individual deconvolutions for each sideband (differences caused by the different tensor patterns of the mobile and crystalline phases) were used. The resonances arising from reversed monomer units have been assigned to the amorphous phase because of their almost complete absence in the spectra of the crystalline phase. The modification ratios have been estimated from cross-polarization spectra obtained after long pre-contact proton spin-locking and a short contact time, followed by deconvolution. There are some limits for the accuracy and reproducibility. Free nonlinear fit procedures fail because of the number of parameters. The linewidths have been set to fixed values in the deconvolution for both the crystalline resonances and the amorphous lines. This procedure provides relative errors of the order of $\pm 5\%$.

CONCLUSIONS

It has been demonstrated that solid-state $\{^1$H$\}$ → ^{19}F double-resonance NMR provides valuable tools for the investigation of fluorinated polymers which have a high percentage of protons. Fast MAS is required to reduce the dipolar interactions between the fluorine nuclei and to separate the spinning sidebands from the interesting spectral range.

Especially, the relatively immobile chains in the crystalline regions require the application of proton high-power decoupling to completely remove the proton-fluorine interaction. The information provided by the fluorine chemical shifts in the solid state is of special interest because of the occurrence of various polymorphs for PVDF. The semicrystalline nature of PVDF provides molecular mobilities which differ for the amorphous and the crystalline regions above the glass transition temperature.

Differences in spin-locked relaxation and in the cross-polarization dynamics can be used to suppress the amorphous signal and to obtain the spectrum of the crystalline phase. Isolated spectra of the crystalline phase of different polymorphs can be obtained. Conversions among the modifications induced by annealing (β to α), melt crystallization (β completely to α) and poling in electric fields (α to β) have been exemplified.

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