Structural Aspects of Suspension Poly(vinyl chloride). Relationship between Molecular Structure and Structural Order

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ABSTRACT: The structural order of poly(vinyl chloride) (PVC) has been investigated using modified PVC samples. A lack of order in the polymer chain direction is evidenced by comparison between the experimental and the theoretical crystalline wide-angle scattering pattern of PVC. Variation of the molecular structure by specific substitution of chlorine proves to be a very useful tool to acquire some additional information with respect to the structural order of PVC. In this way, it is demonstrated that the isotactic sequences disturb the formation of structural order but do not totally exclude it. The structural order of PVC is preferentially ordered perpendicular to the polymer backbone and consists of short primarily syndiotactic sequences, belonging to different polymer chains or chain segments. The wide variety of size and perfection of these ordered entities as well as the lack of order in the polymer chain direction signifies that the term "crystallinity" in the case of PVC has to be used with some prudence.

Introduction

The structural order of commercial poly(vinyl chloride) (PVC) remains a subject of active research and debate. Commercial PVC is generally considered as a semicrystalline polymer with a crystalline fraction of 5–20%.[1-7] This fraction crystallizes into an orthorhombic unit cell, consisting of two *syndiotactic* chains in the planar zigzag conformation.[8,9] From this viewpoint, the degree of crystallinity of commercial PVC is surprisingly high, considering its low stereoregularity.[10] This phenomenon has been connected with a minimum sequence length for crystallization of 4–6 syndiotactic sequences,[11,12] which is relatively small compared with other semicrystalline polymers.[13,14] Juijn[10] attributed the surprisingly high degree of crystallinity to the incorporation of specific isotactic sequences into the syndiotactic crystal lattice.

As a part of an extensive research program on the characterization and understanding of the structural order of commercial PVC,[15-18] the present paper deals with the study of the relationship between the molecular structure and the formation of structural order. For this purpose, the structural aspects of commercial suspension PVC, butyraldehyde PVC, and some chlorine-substituted PVC samples are compared by means of wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC).

Polymerization of vinyl chloride in the presence of butyraldehyde is known to yield a low molar mass PVC with a relatively high degree of crystallinity.[19-22] This so-called butyraldehyde PVC has been used in several studies on the crystallinity of PVC.[2,23-25]

Complete hydrogenation of PVC with lithium aluminum hydride ($LiAlH_4$) or tributyltin hydride ($(n\text{-}Bu)_3SnH$) in combination with spectroscopic examination has comprised a popular approach toward the elucidation of defect structures in commercial PVC such as chain branching.[26-37] The reductive hydrogenation technique has also been employed in studies on the microstructure of random ethylene–vinyl chloride copolymers with different chlorine contents.[38-42] In contrast to $(n\text{-}Bu)_3SnH$, the hydrogenation with $LiAlH_4$ is reported to be stereoselective as a consequence of its relatively lower reactivity toward syndiotactic triads.[30,31,43] The chlorine substitution of PVC with sodium thiophenate has also been reported as stereoselective.[44-49] In this process, the chlorine atoms are substituted by a bulky phenyl mercaptide group.

The comparison between these chlorine substitution reactions can be very useful to investigate the impact of variation of the molecular structure and stereoregularity on the formation of the structural order of PVC.

Experimental Section

A. Materials. A series of PVC samples were suspension polymerized at different temperatures. Some relevant characteristics of this PVC series are summarized in Table I. The absolute molar masses were calculated using a calibration curve obtained from a set of reference PVC samples (Pressure Chemical Co.). More detailed information on the characterization of this PVC series has been reported elsewhere.[15,16] Butyraldehyde PVC was prepared by a free-radical polymerization in *n*-butyraldehyde at 50 °C.[19-22] The conversion of the reaction was approximately 13%. The weight-averaged molar mass (M_w) and the polydispersity (M_w/M_n) were 2200 g/mol and 1.4, respectively.

Some PVC samples were partially hydrogenated with $LiAlH_4$ and $(n\text{-}Bu)_3SnH$ in 2-methyltetrahydrofuran at 80 °C, according to the procedures described by Starnes et al.[29-31] The chlorine substitution with sodium thiophenate was carried out in a cyclohexanone solution at 50 °C.[44-49]

B. Instrumentation and Data Processing. ^{13}C NMR measurements were carried out at 90 °C in a 10% (w/w) mixture of 1,2,4-trichlorobenzene-d_3 and tetrachloroethane-d_2 using a Varian 300-MHz NMR spectrometer. The number of scans was 128 with a pulse angle of 45–50° and a delay time of 10 s. On the basis of the intensities of the ^{13}C NMR triad peaks, 58.5% syndiotactic diads was calculated for the butyraldehyde PVC. The ^{13}C NMR results of the hydrogenated samples are summarized in Tables II and III for sample 4 (K_v 70) of the PVC series. Analogous results have been obtained for other samples of the series. The calculation of the chlorine content and the triad concentrations was based on the eight known resonance peaks for a group of five adjacent carbon atoms, as described in the literature.[37-39,51-58] More detailed information with regard to the interpretation of the ^{13}C NMR data is described elsewhere.[59]

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Table I. Characteristics of the PVC Series

sample	T_{pol} (°C)	K_v[a]	M_w (×10³ g/mol)	M_w/M_n	syndiotacticity α
1	84	47	39	1.8	0.551
2	81	50	41	2.0	0.549
3	64	60	70	1.8	0.559
4	54	70	97	1.9	0.567
5	44	80	140	2.1	0.569
6	36	90	190	2.1	0.564
7	26	100	270	1.9	0.581

[a] K_v is a standard viscosity number which is commonly used in the PVC industry.[50]

Table II. ^{13}C NMR Data on the Hydrogenation of Suspension PVC Sample 4 (K_v 70) with $LiAlH_4$

vinyl chloride content (%)	chlorine content (wt %)	rr (%)	rm (%)	mm (%)	other (%)
100.0	56.7	32.1	48.9	19.0	0.0
89.1	53.8	28.1	32.7	10.9	28.4
79.9	51.0	24.3	22.5	6.1	52.8
68.3	46.9	21.9	12.4	2.7	63.0
46.7	37.5	9.8	4.7	0.6	84.9
38.8	33.2	7.2	2.2	0.0	90.6
32.0	29.1	5.0	1.6	0.0	93.4

Table III. ^{13}C NMR Data on the Hydrogenation of Suspension Sample 4 (K_v 70) with $(n\text{-Bu})_3SnH$

vinyl chloride content (%)	chlorine content (wt %)	rr (%)	rm (%)	mm (%)	other (%)
100.0	56.7	32.1	48.9	19.0	0.0
74.9	49.3	15.3	39.1	6.0	39.6
52.7	40.5	4.7	8.7	0.7	85.9
30.5	28.0	0.3	0.6	0.0	99.1
10.6	11.8				
1.2	1.5				

Differential scanning calorimetry (DSC) experiments were carried out on approximately 20-mg samples using a Perkin-Elmer DSC-7 delta system with a scanning rate of 20 °C·min⁻¹. Prior to the DSC measurements, the thermal history of the samples was eliminated by a standard thermal treatment which consisted of a heating run from 30 to 220 °C with a scanning rate of 20 °C·min⁻¹ followed by immediate quenching in the DSC with a programmed cooling rate of 200 °C·min⁻¹.

Wide-angle X-ray scattering (WAXS) measurements were performed on a Rigaku RU-200B rotating anode, equipped with a horizontal Bragg–Brentano focusing diffractometer and a scintillation counter. Monochromatic Cu K$\bar{\alpha}$ radiation (λ = 1.542 Å) was obtained by a graphite monochromator positioned in the diffracted beam. The scattering patterns were recorded in the reflection mode as a function of the scattering angle 2θ from 10° to 50° with a step size of 0.04° (2θ) and a measuring time of 40 s/step. More detailed information about the experimental conditions of the DSC and WAXS measurements has been reported elsewhere.[15-17]

Results and Discussion

A. Butyraldehyde PVC. The scattering patterns of suspension PVC sample 7 (K_v 100) and butyraldehyde PVC are compared in Figure 1. The crystalline reflections in the scattering pattern of butyraldehyde PVC (Figure 1b) are significantly more intense and sharper, pointing to a comparatively higher degree of crystallinity and crystal perfection. The position and relative intensity of the crystalline reflections of both samples, on the other hand, are in good agreement, implying an identical crystal structure for the two samples. The theoretical diffraction pattern, based on the reported syndiotactic crystal lattice,[9] has also been included in Figure 1. This pattern has been calculated with the computer program CERIUS.[60] The position and the relative intensity of the *hk*0 reflections of both suspension PVC and butyraldehyde PVC are in good agreement with the theoretical diffraction pattern.

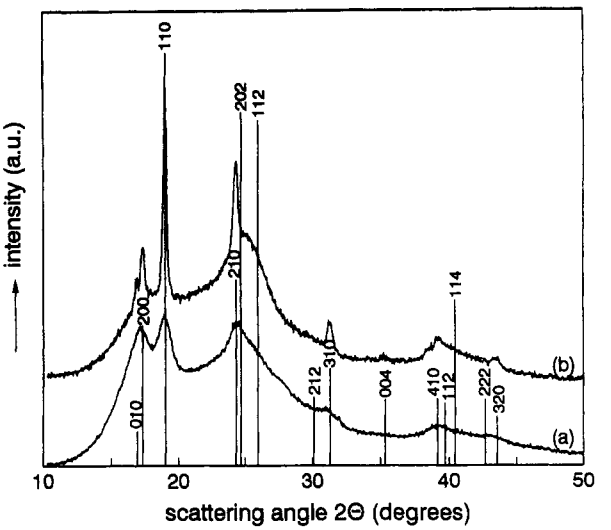

Figure 1. Comparison between the experimental scattering pattern and the theoretical crystalline diffraction pattern: (a) suspension PVC sample 7 (K_v 100); (b) butyraldehyde PVC. The theoretical crystalline reflections are represented by lines. The positions and the relative intensity are based on the syndiotactic crystal lattice reported by Wilkes et al.[9]

The experimentally observed intensities of the *hkl* reflections, however, are significantly weaker than the calculated intensities, signifying a lack of crystalline order in the *c*-direction of the crystal lattice (i.e., the chain direction), as already suggested by Natta and Corradini.[61] Consequently, the structural order of PVC is primarily situated perpendicular to the polymer backbone. In view of the observed difference between the degree of crystallinity of butyraldehyde PVC and the suspension PVC sample 7, a significantly higher syndiotacticity can be expected for the former sample. Surprisingly, the syndiotacticity of the suspension PVC sample 7 (58.1%) is comparable to that of butyraldehyde PVC (58.5%). Some authors[62,63] have also observed such a relatively low stereoregularity for butyraldehyde PVC and attributed the high crystallizability to its low molar mass.

B. Chlorine Substitution. The ^{13}C NMR data of the PVC samples hydrogenated with $LiAlH_4$ (Table II) confirm the reported stereoselectivity of this reaction. The amount of syndiotactic rr triads decreases comparatively less with the degree of chlorine substitution compared with those of the heterotactic rm and isotactic mm triads. The data (Table II) are in line with those reported by Starnes et al.[26-37] A Monte Carlo simulation of the hydrogenation process gives an average syndiotactic sequence length of 2 for a chlorine content of 30%.[59] The impact of the stereoselectivity on the structural order is illustrated in Figure 2. These scattering patterns demonstrate that especially the low-order *hk*0 reflections of the *syndiotactic* crystal lattice become more prominent on hydrogenation with $LiAlH_4$, indicating an increase of the structural order on a small length scale. The gradual shift of these reflections toward larger scattering angles is associated with a more efficient packing of the polymer chains. The appearance of a weak shoulder in the scattering pattern of 21° (2θ) for the samples with a relatively high degree of chlorine substitution (Figure 2e,f) is connected with the crystallization of ethylene sequences. The presence of an additional endotherm at approximately 50 °C in the DSC thermograms of these samples (Figure 3d,e) can also be ascribed to this phenomenon. Additionally, the DSC thermograms (Figure 3) reveal the gradual shift of the glass transition temperature T_g and the broad endothermic region toward lower temperatures with the degree of hydrogenation. The variation of the T_g is connected with

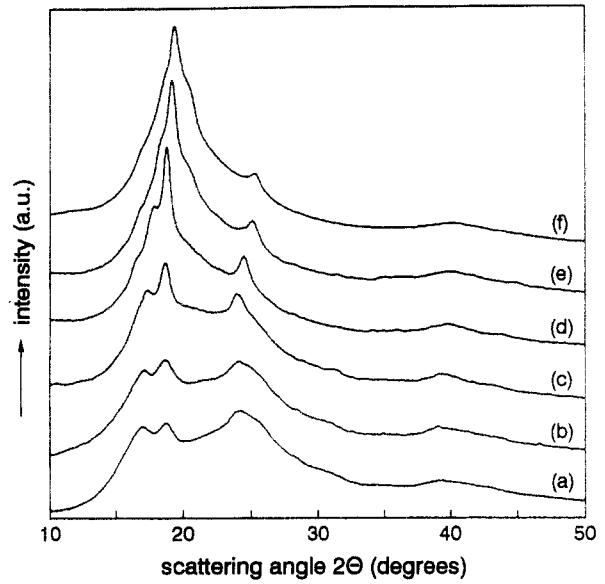

Figure 2. Scattering patterns of suspension PVC sample 4 (K_v 70) hydrogenated with $LiAlH_4$. Chlorine content (w/w): (a) 56.7%; (b) 54%; (c) 47%; (d) 38%; (e) 33%; (f) 29%.

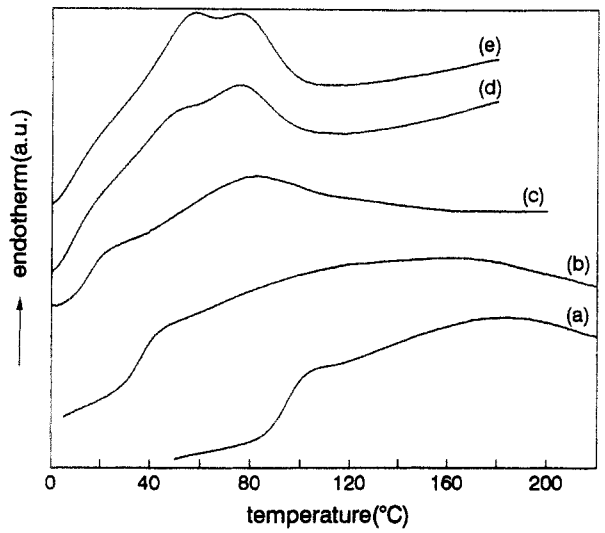

Figure 3. DSC thermograms of suspension PVC sample 4 (K_v 70) hydrogenated with $LiAlH_4$. Chlorine content (w/w): (a) 56.7%; (b) 47%; (c) 38%; (d) 33%; (e) 29%.

the higher chain flexibility of the hydrogenated chain segments. The shift of the endothermic region, pointing to a lower thermal persistence of the structural order,[18] can also be related with the higher chain flexibility. Furthermore, incorporation of ethylene sequences in the syndiotactic crystal lattice could also give rise to a lower thermal persistence of the ordered entities.

The ^{13}C NMR data in Table III do not reveal a significant stereoselectivity for the hydrogenation process with $(n\text{-Bu})_3SnH$. The scattering patterns of these samples (Figure 4) initially show an almost complete annihilation of the structural order (Figure 4b,c). The increase of the structural order (Figure 4d–f) and the crystalline melting temperature (Figure 5) for high degrees of chlorine substitution is related with the increasing crystallizability and the more efficient crystalline packing of the ethylene sequences. Analogous observations have been reported for ethylene–vinyl chloride copolymers with varying chlorine contents.[42]

The chlorine substitution of PVC with sodium thiophenate leads to a rapid annihilation of the structural order as demonstrated in the scattering patterns of Figure 6. Apparently, the bulkiness of the substituted phenyl mercaptide group predominates the effect of the reported

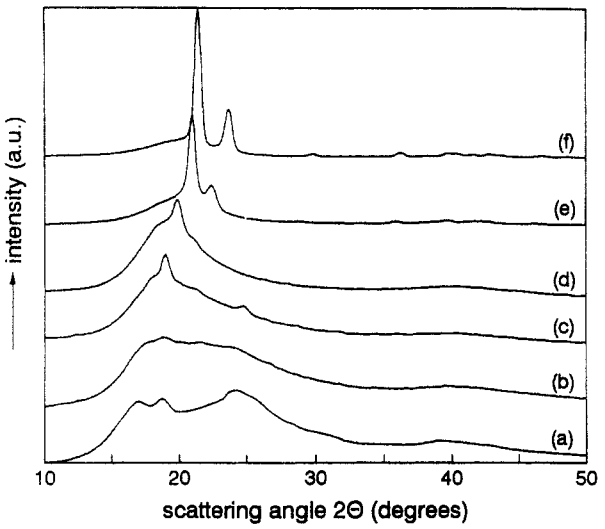

Figure 4. Scattering patterns of suspension PVC sample 4 (K_v 70) hydrogenated with $(n\text{-Bu})_3SnH$. Chlorine content (w/w): (a) 56.7%; (b) 49%; (c) 41%; (d) 28%; (e) 12%; (f) 1%.

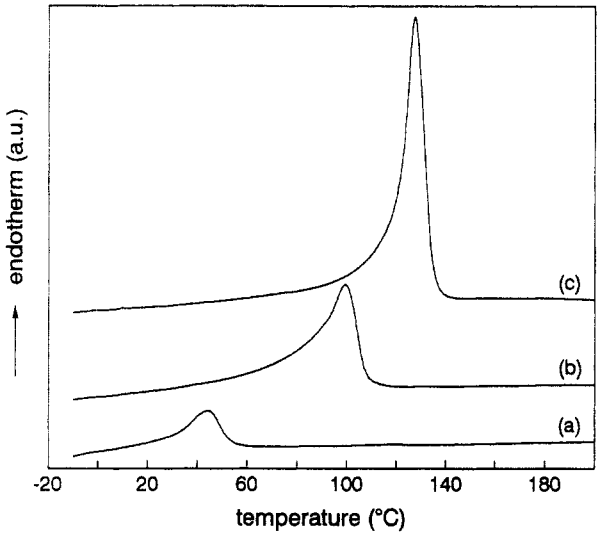

Figure 5. DSC thermograms of suspension PVC sample 4 (K_v 70) hydrogenated with $(n\text{-Bu})_3SnH$. Chlorine content (w/w): (a) 28%; (b) 12%; (c) 1%.

stereoselectivity of this substitution reaction with respect to the formation of the structural order.

Concluding Remarks

Variation of the molecular structure by specific substitution of chlorine proves to be a very useful tool in acquiring some additional information with respect to the structural order of PVC. The observed increase of the structural order as a result of the preferential hydrogenation of the isotactic and heterotactic sequences and the rapid annihilation of the structural order in the case of the introduction of a bulky group indicate that the isotactic sequences in PVC disturb the formation of the structural order but do not totally exclude it. This phenomenon is most probably associated with the intermediate size of the chlorine atom. For instance, the crystallizability of poly(vinyl fluoride) and poly(vinyl alcohol) does not depend significantly on the stereoregularity due to the relatively small size of the vinyl substituent as compared with the chlorine atom, whereas atactic poly(vinyl bromide) and poly(methyl methacrylate) are totally amorphous as a consequence of the relatively large size of the side group. The incorporation of specific isotactic sequences in the syndiotactic crystal lattice, as suggested by Juijn et al.,[10] is in agreement with this supposition. In this way, these

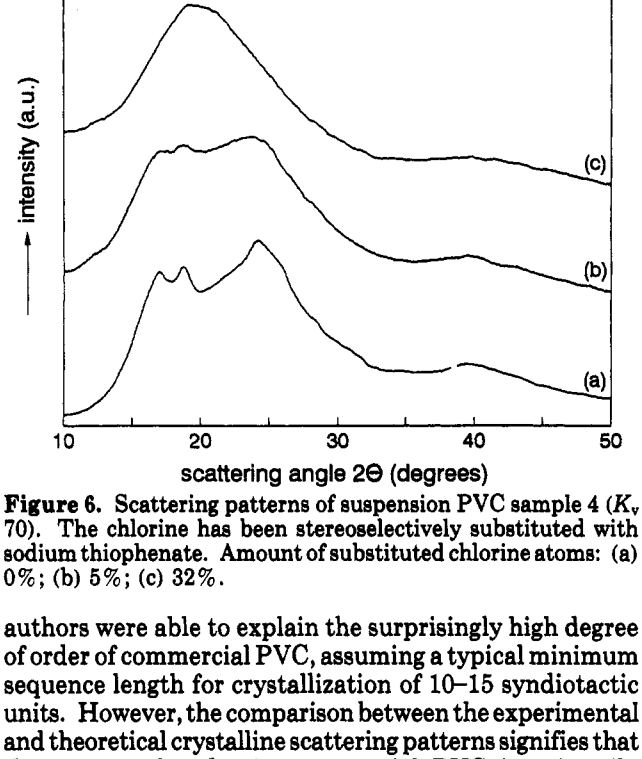

Figure 6. Scattering patterns of suspension PVC sample 4 (K_v 70). The chlorine has been stereoselectively substituted with sodium thiophenate. Amount of substituted chlorine atoms: (a) 0%; (b) 5%; (c) 32%.

authors were able to explain the surprisingly high degree of order of commercial PVC, assuming a typical minimum sequence length for crystallization of 10–15 syndiotactic units. However, the comparison between the experimental and theoretical crystalline scattering patterns signifies that the structural order in commercial PVC is primarily situated perpendicular to the polymer chain. Consequently, the minimum sequence length for crystallization is not very relevant with respect to the formation of the structural order. Furthermore, the relatively high degree of structural order observed at high hydrogenation levels suggests that the presence of short syndiotactic sequences already gives rise to the formation of some local order. From this viewpoint, the structural order in commercial PVC can be related with entities which are preferentially ordered perpendicular to the polymer chain direction and consist of short primarily syndiotactic sequences, belonging to different polymer chains or chain segments. Such ordered entities can have a wide variety of size and perfection as indicated by the wide melting range[17] and the relatively large width of the low-order crystalline *hk*0 reflections.[16] Moreover, the wide variety of size and perfection of the ordered entities as well as the lack of order in the chain direction means that the term "crystallinity" in the case of PVC has to be used with some prudence.

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