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Structural Aspects of Suspension Poly(vinyl chloride). Small-Angle Neutron Scattering of Rigid and Plasticized Suspension PVC

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ABSTRACT: A comprehensive SANS study on both rigid and plasticized suspension PVC demonstrates the presence of superstructural order in this polymer. Comparison of the experimental scattering invariant data with a tentative two-phase model points to specific penetration of the plasticizer in the noncrystalline regions of PVC. Thermal experiments manifest the gradual and thermoreversible melting of the crystalline regions at temperatures above 80–90 °C. Uniaxial deformation experiments on plasticized PVC confirm the existence of a heterogeneous network-structure in PVC where the crystalline tie-points act as physical cross-links. The observed anisotropic "butterfly" scattering pattern of a uniaxially stretched sample indicates the formation of concentration inhomogeneities as a consequence of the random distribution of the crystalline tie-points in plasticized PVC. The anistropy of the scattering pattern gradually disappears on heating, probably resulting from the increasing mobility of the plasticized interstitial medium.

Introduction

The structural aspects of poly(vinyl chloride) (PVC) continue to be a subject of active research and debate.[1–4] Commercial PVC is generally considered as a semicrystalline polymer with a relatively small crystalline fraction (5–20%) that is believed to be important with respect to the network-like properties of PVC.[5–7] The surprisingly high degree of crystallinity, considering the low stereoregularity, as well as the crystalline morphology are still not clear, however.[8,9] Furthermore, the existence of additional order in the noncrystalline regions of PVC has been reported.[10–12]

An extensive research program has been performed in order to revise the problems related to the characterization and the understanding of the structural order of PVC. On the basis of a series of well-defined suspension PVC samples, polymerized at different temperatures, the structural aspects have been studied by means of scattering techniques, thermal analysis, and electron microscopy, thereby covering the structural order from nanometer up to micrometer level.[13–15] As a part of this research program, the present paper deals with the study of the structural aspects of rigid and plasticized PVC on a length scale up to 1000 Å using small-angle neutron scattering (SANS).

Small-angle X-ray scattering (SAXS) has commonly been applied to examine the microstructure of PVC. Nevertheless, this approach remains rather difficult due to the high X-ray absorption of PVC ($\mu^* = 62$ cm^2/g) and the poor electron density contrast. SAXS studies on rigid PVC have indicated a weak interference maximum with a correlation length of 100–150 Å.[16,17] This maximum was ascribed to a lamellar[16] and nodular[17] semicrystalline morphology, respectively. Other studies on rigid PVC have reported a continuous scattering profile, monotonically decreasing with the scattering angle and with no indication of an interference maximum that could be associated with some structural regularity.[18,19]

The experimental problems connected with the high absorption of X-rays can be alleviated by the use of small-angle neutron scattering (SANS) as a result of the lower neutron absorption of PVC ($\mu^* = 0.24$ cm^2/g). A single SANS study on rigid deuterated PVC has been reported by Walsh et al.[20] who observed a weak interference maximum with a correlation length of approximately 140 Å.

Plasticized PVC samples exhibit a more intense interference maximum which most likely originates from the specific penetration of the plasticizer into the noncrystalline regions, resulting in an enhanced scattering contrast between the crystalline and noncrystalline regions.[21–24] The presence of unplasticized regions in plasticized PVC has also been demonstrated by means of electron microscopy.[24,25] Plasticizer contents up to 50% (v/v) do not seem to affect the structural order of PVC.[24,26,27]

Apart from the lower neutron absorption of PVC, as compared with X-rays, SANS of plasticized PVC occurs under even more favorable conditions. The scattering contrast between the plasticized and unplasticized regions can be further enhanced by deuteration of either the polymer or the plasticizer. Brown et al.[28] observed an

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Table I. Characteristics of the PVC Series

sample	T_{pol} (°C)	K_v[a]	M_w ($\times 10^3$ 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.[30]

intense interference maximum corresponding to 110 Å for PVC plasticized with 50 phr (i.e., number of mass parts per 100 mass parts PVC) deuterated nitrobenzene. A crystallinity of approximately 30% was calculated on the basis of the invariant of a plasticized noncrystalline and unplasticized crystalline two-phase system. Correlation lengths varying between 100 and 200 Å and a crystalline melting temperature of 210 °C have been reported for several annealed plasticized PVC samples with 10% (w/w) deuterated di(n-octyl-d_{17}) phthalate (DOP).[29]

In this SANS study, the present debate with respect to the presence of some superstructural order in rigid PVC is reviewed. The superstructural order in plasticized PVC is explored systematically by altering the volume fraction plasticizer and the tacticity of the PVC sample. The experimental scattering data are verified with a two-phase model, assuming the specific penetration of the plasticizer in the noncrystalline regions. Additionally, the impact of a thermal and/or a mechanical treatment on the small-angle scattering of plasticized PVC is examined.

Experimental Section

Sample Preparation. Deuterated PVC was obtained by suspension polymerization of 10 g of vinyl chloride-d_3 at 60 °C in a glass reactor which is suitable for the small-scale polymerization of vinyl chloride. A 2-mm-thick sample (2×2 cm^2) was prepared by compression molding for 6 min at 205 °C and a mold clamping force of 200 kN. Prior to compression molding, 2 phr of diocytltin di(thioglycolic acid octyl ester) stabilizer (Ciba Geigy 17 MOK) was added to enhance the thermal stability. Two different PVC/plasticizer systems were prepared: (1) PVC/tetrahydronaphthalene-d_{12} and (2) deuterated PVC/dioctyl phthalate. Tetrahydronaphthalene-d_{12} (TDN), purchased from Aldrich, is a swelling agent for PVC at room temperature. This swelling agent was selected for its commercial availability in a deuterated form and its relatively high deuterium content which secures a sufficient scattering contrast. Deuterated PVC (d-PVC) plasticized with 50 phr dioctyl phthalate (DOP) was also prepared in order to verify the similarities between a commercial PVC/deuterated plasticizer system and a deuterated PVC/commercial plasticizer system. Secondly, the relatively high boiling point of DOP (384 °C) in comparison with TDN (207 °C) enables the performance of temperature-dependent measurements without significant loss of plasticizer. PVC sample (K_v 70) of the PVC series (Table I)[13,14] was plasticized with, respectively, 10, 20, 30, 40, 50, and 75 phr TDN. Three other samples of the PVC series, samples 1 (K_v 47), 5 (K_v 80), and 7 (K_v 100), were plasticized with 50 phr TDN. In case of the plasticized d-PVC sample, 50 phr DOP was added.

Additionally, a plasticized sample of randomly chlorinated polyethylene (CPE) with 50 phr TDN was prepared. CPE samples were obtained by bubbling chlorine gas through a 1% (w/v) solution of high-density polyethylene (HDPE) in 1,1',2,2'-tetrachloroethane at 100 °C.[31] This chlorination method results in a random distribution of the chlorine atoms along the backbone.[32] The chlorine content of the studied CPE sample is 56% (w/w)[31] which is comparable with the chlorine content of PVC (56.7%).

Plasticized samples with a thickness of approximately 1 mm were prepared by compression molding for 1 min at 180 °C and a mold clamping force of 50 kN. In advance, the plasticizer was added homogeneously to the thermally stabilized PVC powder (2 phr dioctyltin di(thioglycolic acid octyl ester)). The applied mold clamping force was restricted to 10 kN for the samples with 50 and 75 phr plasticizer in order to avoid loss of plasticizer. The preparation of a 100 phr PVC/TDN sample was not successful as a consequence of a considerable loss of TDN during the compression molding procedure.

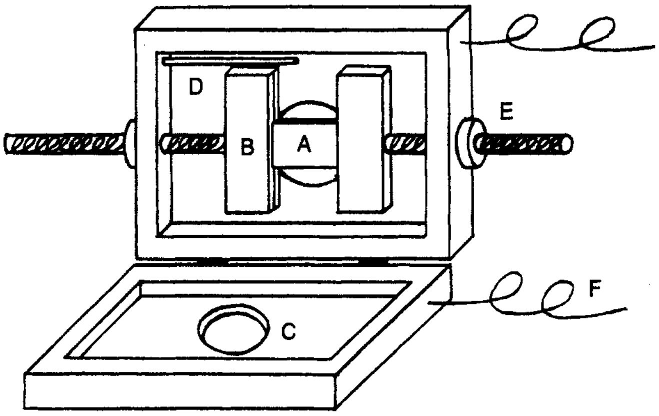


Figure 1. Schematic representation of the oven with a simple uniaxial deformation mechanism. The uniaxial deformation experiments were performed by turning the screws (E) simultaneously: A, sample; B, clamp; C, hole for primary beam (ϕ = 1 cm^2); D, thermocouple, E, screws; F, heating elements.

Instrumentation and Data Processing. The SANS experiments were performed at the SANS facility of the Risø National Laboratory, Roskilde, Denmark. The deuterated rigid PVC sample was studied for three different setups: (1) λ = 15 Å, D = 6 m; (2) λ = 6 Å, D = 3 m; and (3) λ = 3 Å, D = 1 m (λ = wavelength, D = sample-to-detector distance). In case of the plasticized samples, only the two latter setups were used. The radially averaged scattering patterns, measured at different setups, were fitted using a least-squares procedure of the overlapping regions. Pin-hole collimation with a source diameter of 16 mm and a sample diameter of 7 mm was used throughout. All the samples were mounted in the sample chamber without the use of a sample container. The plasticized samples were measured in air at ambient pressure in order to prevent loss of plasticizer during the course of the measurement. The data were corrected for absorption and background and converted into an elastic scattering cross-section by comparison with the scattering of a water standard. The transmission of the deuterated and plasticized samples for setup no. 2 was about 75% and 40%, respectively. In order to perform temperature-dependent measurements in combination with uniaxial deformation, an oven with a simple uniaxial deformation mechanism was constructed (Figure 1).

Wide-angle X-ray scattering (WAXS) experiments were performed on stretched plasticized films (50 phr DOP) using a flat film device mounted on a Philips PW1130 conventional X-ray generator (40 kV, 50 mA).

Results and Discussion

SANS of Rigid PVC. The SANS pattern of the fully deuterated rigid PVC sample (Figure 2) exhibits a weak but distinct interference maximum around Q = 0.04 Å^{-1}, corresponding to a correlation length of about 150 Å. This maximum is indicative for the presence of some superstructural order in the deuterated PVC sample. The high scattering intensity at low Q-values originates from the presence of some residual porosity in the compression-molded sample.[14] The intensity of the interference maximum is relatively low considering the degree of crystallinity (5–20%) and the scattering contrast of a simple crystalline/amorphous morphology. The existence of a very wide distribution of crystalline order in commercial PVC[14,15] is most probably on the basis of the poor scattering contrast.

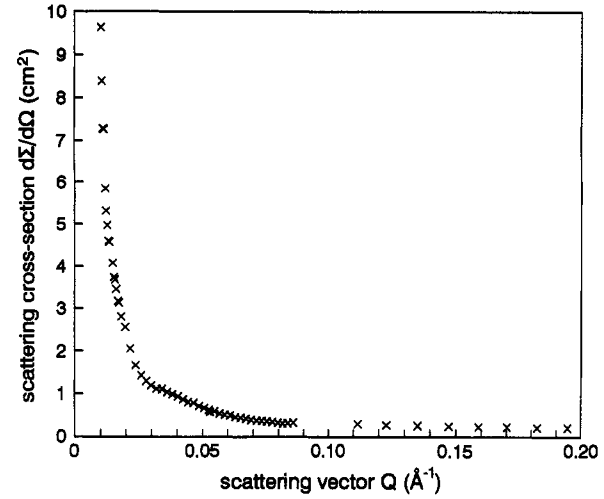


Figure 2. SANS pattern of deuterated PVC.

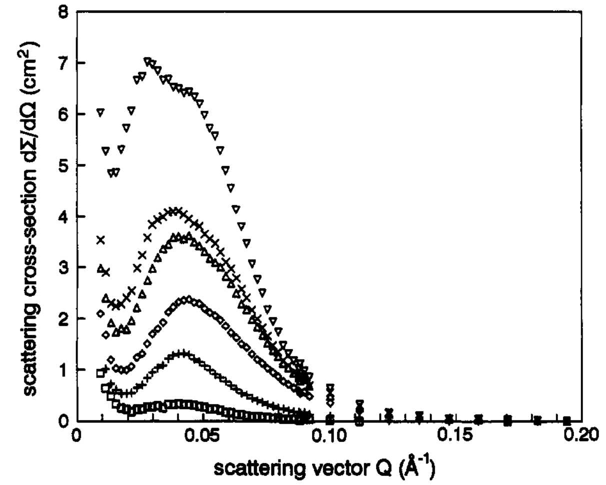


Figure 3. SANS patterns of PVC Sample 4 (K_v 70) with varying volume fractions TDN: □, 10 phr; +, 20 phr; ◇, 30 phr; △, 40 phr; × 50 phr; ▽, 75 phr.

SANS of Plasticized PVC. PVC samples involving a varying volume fraction TDN (ϕ_{TDN}) as well as deuterated PVC plasticized with DOP also exhibit an interference maximum around $Q = 0.04$ Å^{-1}. In the case of the PVC/TDN system (Figure 3), the scattered intensity increases gradually as a function of the volume fraction TDN due to the corresponding enhancement of the scattering contrast.

The apparent shift of the interference maximum with the increase of the volume fraction TDN is not real, but originates from the appearance of a second interference maximum that becomes more pronounced for the highest TDN contents. The observed scattering phenomena are most probably related to the presence of structural order in PVC. This is indicated by the fact that, in contrast to plasticized PVC, the CPE sample plasticized with 50 phr TDN does not show any interference maximum. CPE with such a high chlorine content (56% w/w) is totally amorphous, due to the random position of the chlorine atoms along the polymer backbone.

The dependence of the scattering invariant $\langle \eta^2 \rangle$ on the volume fraction plasticizer ϕ_{plast} can provide additional information with regard to the structural origin of the interference maximum of plasticized PVC. The scattering invariant of a two-phase system is represented by[33]

$$\langle \eta^2 \rangle = \int_0^\infty Q^2 (d\Sigma/d\Omega)(Q)\, dQ = 2\pi^2 V(\rho_1 - \rho_2)^2 \phi_1 \phi_2 \quad (1)$$

where $d\Sigma/d\Omega(Q)$ is the measured scattering cross-section,

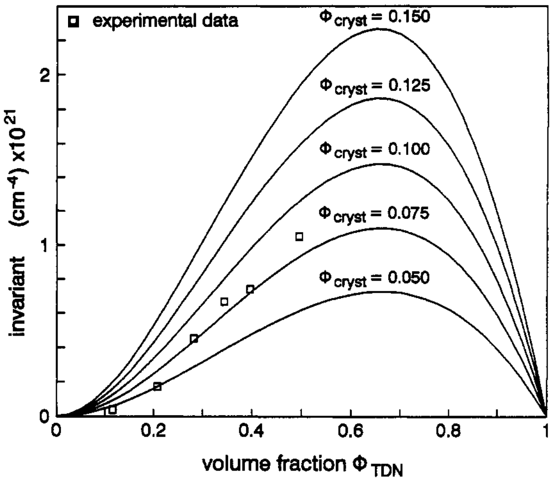


Figure 4. Dependence of the invariant on the volume fraction TDN. The experimental data have been derived from the SANS patterns of Figure 2. The theoretical calculations are based on a two-phase model consisting of plasticized noncrystalline and unplasticized crystalline regions with varying crystalline volume fractions (Φ_{cryst}).

V the irradiated volume, ρ_1 and ρ_2 the scattering densities of phases 1 and 2, respectively, and ϕ_1 and ϕ_2 the corresponding volume fractions. Equation 1 can be applied to describe the theoretical dependence of the scattering invariant on the volume fraction plasticizer for a simple phase-separation between PVC and the plasticizer. However, comparison between the theoretical and the experimental scattering invariant data showed no agreement.[13] On the other hand, a reasonable agreement is obtained on the basis of a tentative model allowing specific penetration of plasticizer into the noncrystalline regions, as suggested in the literature.[21-24] For this purpose, an expression for the dependence of the invariant on the volume fraction ϕ_{plast} has been derived (eq 2), where the scattering densities of the crystalline and noncrystalline phases in rigid PVC have been put equal relative to the scattering density of TDN. This assumption is reasonable in view of the observed small scattering density difference between crystalline and noncrystalline regions.

$$\langle \eta^2(\phi_{plast}) \rangle = 2\pi^2 V(\rho_{PVC} - \rho_{plast})^2 A^2 B \quad (2A)$$

with

$$A = \phi_{plast} + \frac{\phi_{cryst}\phi_{plast} - \phi_{cryst}\phi^2_{plast}}{\phi_{cryst}\phi_{plast} - \phi_{cryst} + 1} \quad (2B)$$

$$B = (1 - \phi_{plast})\phi_{cryst}(1 - \phi_{cryst}(1 - \phi_{plast})) \quad (2C)$$

ϕ_{cryst} is the crystalline volume fraction and ρ_{PVC} and ρ_{plast} are the scattering densities of rigid PVC and the pure plasticizer. The best agreement between the theoretical and experimentally invariant data is realized when a crystalline volume fraction ϕ_{cryst} of 0.05–0.10 is assumed (Figure 4). This value is in agreement with the reported degree of crystallinity of commercial PVC (5–20%). Nevertheless, the experimental scattering invariant data show a positive deviation from the calculated curve. This is most probably connected with the fact that the two-phase model is too simple to describe the super-structural order in plasticized PVC. This is signified by the appearance of the second interference maximum and a significant deviation of Porod's law,[33,34] especially for higher volume fractions TDN. These observations might possibly arise from phase separation between PVC and

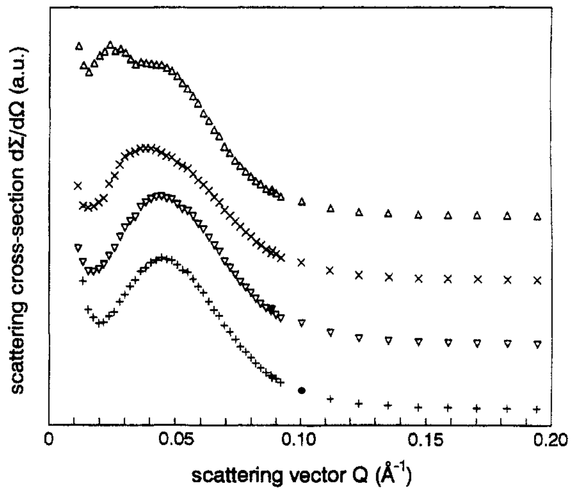


Figure 5. SANS patterns of different plasticized PVC samples (50 phr TDN): +, sample 7; ▽, sample 5; ×, sample 4; △, sample 1. The scattering patterns have been shifted for clarity.

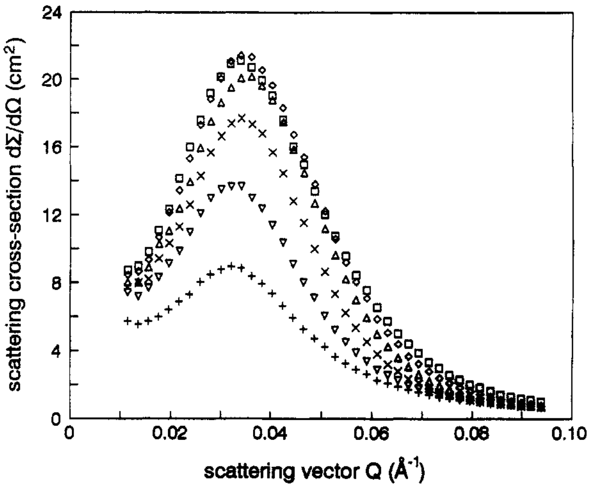


Figure 6. SANS patterns of plasticized *d*-PVC (50 phr DOP) at different temperatures during heating: □, 27 °C; ◇, 77 °C; △, 97 °C; ×, 117 °C; ▽, 137 °C; +, 157 °C.

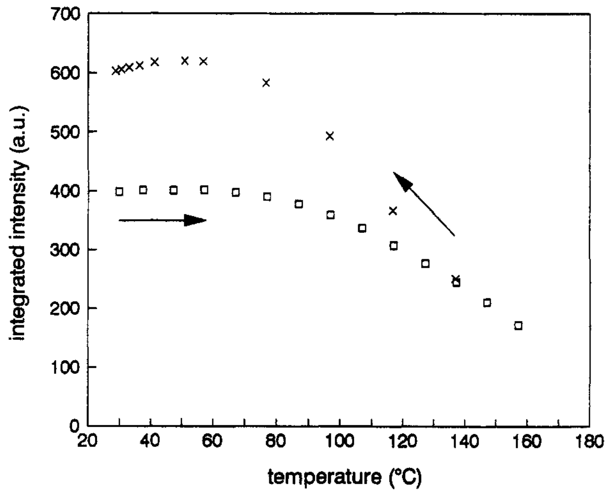


Figure 7. Total integrated scattered intensity as a function of the temperature for plasticized *d*-PVC (50 phr DOP): □, heating; ×, cooling.

TDN at high volume fractions, as indicated by the failure to prepare a plasticized sample with 100 phr TDN. From this viewpoint, the absence of a second interference maximum, in the case of deuterated PVC plasticized with 50 phr DOP, is presumably connected with the relatively better efficiency of DOP as a plasticizer.

SANS patterns of PVC samples (50 phr TDN), polymerized at relatively high temperatures (Table I), also demonstrate the appearance of a second interference maximum (Figure 5). This suggests a lower ability of PVC to absorb plasticizer on increasing the polymerization temperature.

Surprisingly, no dependence of the interference maximum on the volume fraction plasticizer or the tacticity has been observed, which could be indicative for an inhomogeneous distribution of the plasticizer in plasticized PVC.

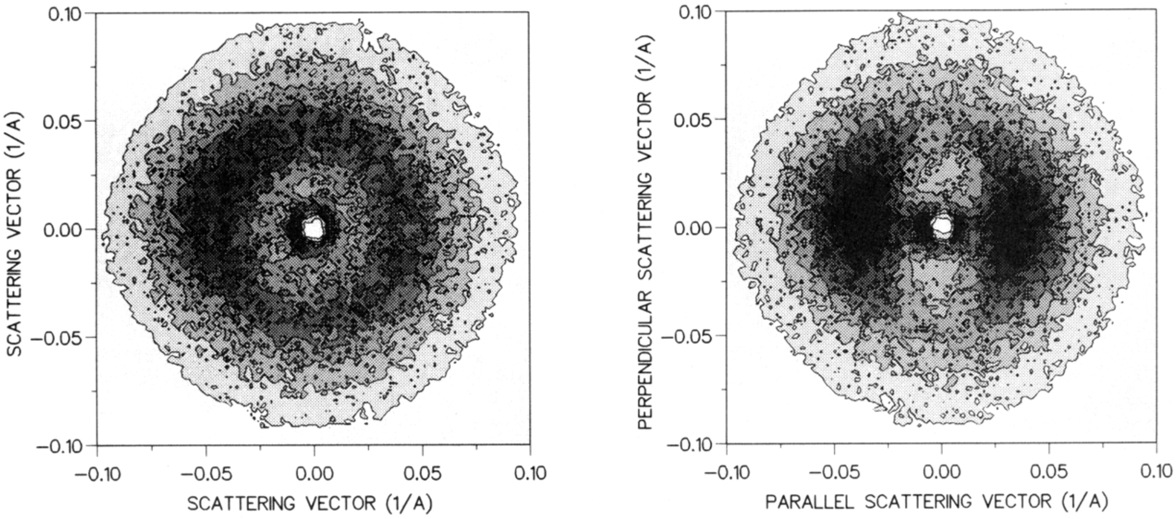
Thermal Behavior of Plasticized PVC. The thermal aspects of the superstructural order in plasticized PVC was subsequently examined. The temperature-dependent measurements on the PVC/TDN system were not successful as a consequence of significant loss of plasticizer at higher temperatures. Alternatively, the measurements have been performed on *d*-PVC with 50 phr DOP. The maximum temperature was restricted to 157 °C in order to avoid thermal degradation of the sample during the course of the measurement. The scattering patterns, obtained during the heat treatment, are depicted in Figure 6. This figure shows that the scattered intensity of the interference maximum gradually changes with the temperature. This change can be visualized more clearly by plotting the total integrated area of the interference maximum at the different temperatures. Such a plot (Figure 7) reveals that the scattered intensity gradually decreases during heating at temperatures above 80–90 °C.

This phenomenon can be attributed to the melting of crystallites over a broad temperature range.[15,35] The decrease of the scattered intensity with the temperature agrees very well with the reported loss of the dynamic mechanical properties of PVC gels plasticized with dioctyl sebacate and butyl phthalate.[36] During cooling, the total integrated area is even higher than the area at the same temperature during heating, an observation which can be related to an isothermal annealing effect during the course of measurement.

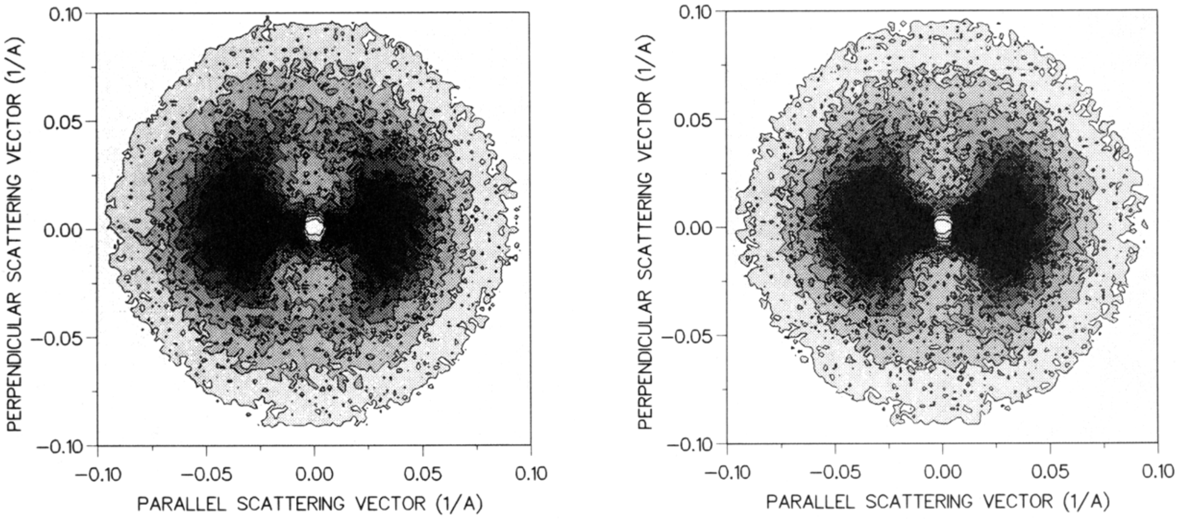
Uniaxial Deformation of Plasticized PVC. The scattering pattern of plasticized PVC is very sensitive to small uniaxial deformation as is demonstrated in Figure 8 for PVC plasticized with 50 phr TDN. As a function of the draw ratio, the isointensity curves show a gradual change of a two-dimensional scattering pattern with the highest scattered intensity parallel to the stretching direction. Analogous effects have been observed for the uniaxial deformation of the deuterated PVC sample plasticized with DOP. Surprisingly, WAXS experiments on the stretched plasticized PVC samples show no orientation of the crystalline and/or noncrystalline structure by uniaxial deformation.

Similar double-winged small-angle scattering patterns with their long axis aligned in the stretching direction have recently been reported by Bastide et al. for uniaxially stretched randomly cross-linked polystyrene gels.[37,38] On the basis of both theoretical considerations[37] and experimental evidence,[38] this so called "butterfly" scattering pattern is ascribed to the occurrence of concentration inhomogeneities as a result of fluctuations in the local cross-linking density. These fluctuations cause variations of the local deformation during uniaxial stretching, leading to inhomogeneous dilution parallel to the stretching direction and an increased scattered intensity parallel to the deformation axis.

Simultaneously, an increase of the correlation distance with the draw ratio was observed, parallel to the stretching direction. An opposite but less pronounced effect occurred



λ=1 λ=1.08



λ=1.21 λ=1.33

Figure 8. Two-dimensional isointensity scattering patterns of plasticized sample 4 (50 phr TDN) for different draw ratios (λ).

perpendicular to the stretching direction because the variation of the sample width and thickness is comparatively less.

The above effects are in good agreement with the scattering phenomena, observed for the uniaxial deformed plasticized PVC. The azimuthal dependence of the scattering pattern (Figure 9), as obtained by radially averaging the $Q = 0.015–0.05$ Å^{-1} region, clearly demonstrates the intensity increase parallel to the stretching direction ($\Omega = 0, 180, 360°$) with the draw ratio and a comparatively lower intensity decrease perpendicular to the stretching direction ($\Omega = 90, 270°$). Besides the increase of the scattering intensity, the scattering function parallel to the stretching direction (Figure 10) also shows the increase of the correlation distance with the draw ratio.

The increase of correlation distance with the draw ratio is significantly higher as compared with that of an affinely deformed network.[39] The strong isotropic scattering at low Q values, especially for high ratios, probably results from the formation of voids during the deformation process.

The observed similarities between the small-angle scattering of a randomly cross-linked polystyrene gel and plasticized PVC indicate that plasticized PVC can apparently be considered as a heterogeneous network. The presence of a network structure in plasticized PVC is confirmed by an additional deformation experiment (Figure 11). The azimuthal dependence of the scattering pattern shows that a stretched plasticized PVC sample has a considerable amount of orientation even after 2 days, in spite of the fact that the plasticized system is well above the glass-transition temperature. However, the orientation almost instantly disappears after release of the stress. These observations also imply that the superstructural order in plasticized PVC, as observed with small-angle scattering, is directly associated with the network-like mechanical properties. From this viewpoint, the crystallites can be considered as physical tie-points in a plasticized interstitial medium. The observed heterogeneity of the network-structure in plasticized PVC suggests a random distribution of the crystalline tie-points which is not very unlikely, considering the radical polymerization

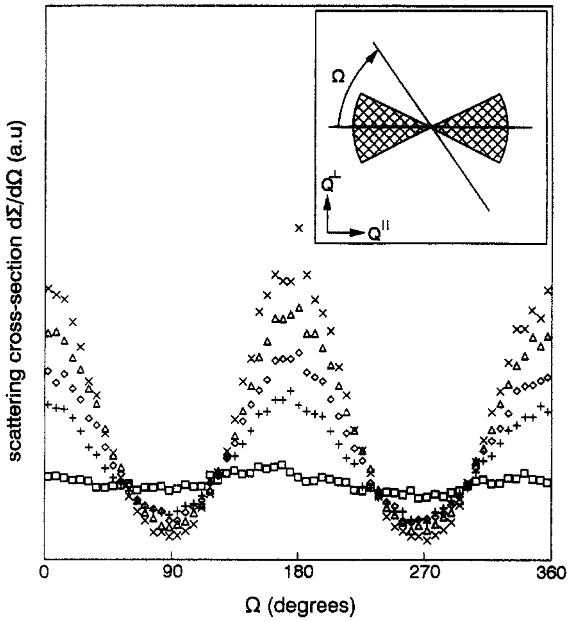


Figure 9. Azimuthal dependence of scattering pattern of plasticized sample 4 (50 phr TDN) for different draw ratios (λ): □, λ = 1; +, λ = 1.08; ◇, λ = 1.21; △, λ = 1.33; ×, λ = 1.54.

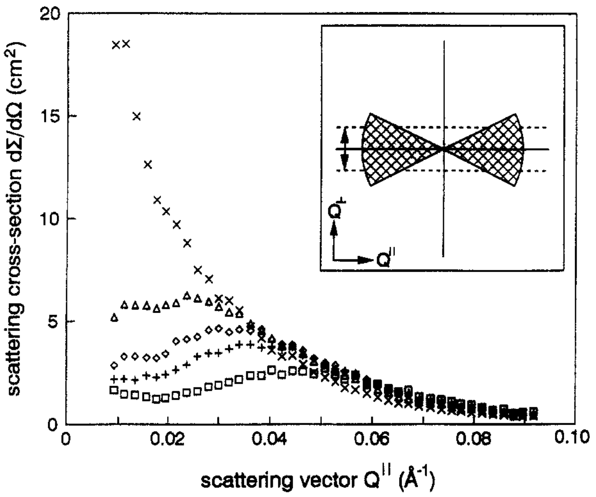


Figure 10. SANS pattern of plasticized sample 4 (50 phr TDN) parallel to the stretching direction for different draw ratios (λ): □, λ = 1; +, λ = 1.08; ◇, λ = 1.21; △, λ = 1.33; ×, λ = 1.54.

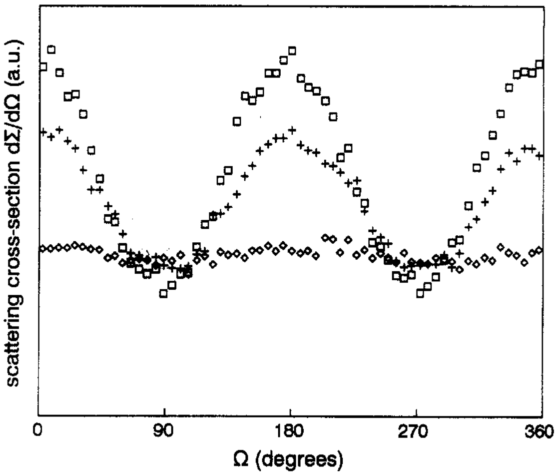


Figure 11. Azimuthal dependence of scattering pattern for plasticized sample 4 (50 phr TDN): □, stretched; +, stretched for 2 days; ◇, 15 min after release of the stress.

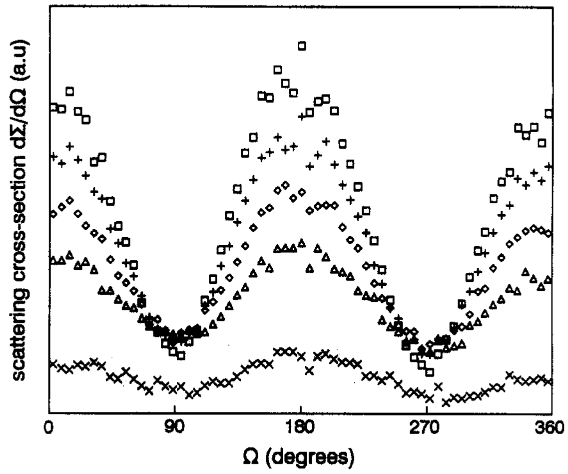


Figure 12. Azimuthal dependence of the scattering pattern for a uniaxially deformed (λ = 1.35) plasticized *d*-PVC (50 phr DOP) for different temperatures: □, 26 °C; +, 46 °C; ◇, 66 °C; △, 86 °C; ×, 106 °C.

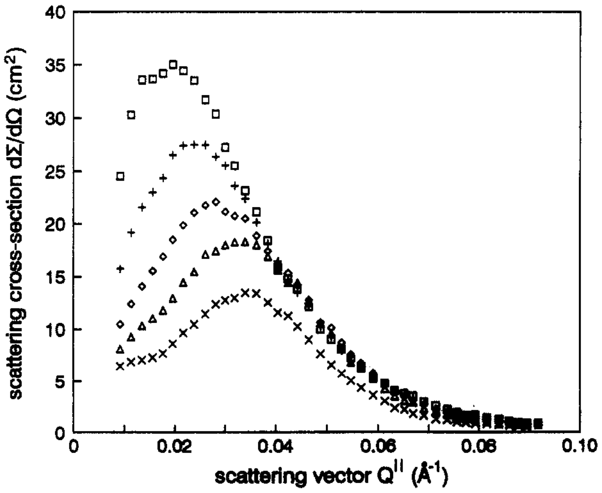


Figure 13. SANS pattern parallel to the stretching direction of uniaxial deformed (λ = 1.35) plasticized *d*-PVC (50 phr DOP) for different temperatures: □, 26 °C; +, 46 °C; ◇, 66 °C; △, 86 °C; ×, 106 °C.

and crystallization process of PVC. The placement of the monomer in the PVC chain is almost random with respect to the stereoregularity. However, the syndiotactic segments crystallize almost exclusively, resulting in very small and imperfect crystallites, primarily ordered perpendicular to the polymer backbone.[15] As determined by the polymerization process, these crystalline tie-points will be located randomly within the polymer. From this viewpoint, the network-structure in plasticized PVC is comparable with a fringed-micelle or nodular type of network-structure.

Thermal Behavior of Uniaxially Deformed Plasticized PVC. The thermal behavior of a uniaxially stretched plasticized d-PVC (50 phr DOP) sample was studied. The azimuthal dependence of the scattering pattern shows a gradual decrease of the degree of orientation on heating between ambient and approximately 80 °C (Figure 12). Simultaneously, the interference maximum shifts back toward higher Q values and the scattered intensity decreases (Figure 13).

These observations can be connected with the annihilation of the concentration inhomogeneities during heating, resulting from the increasing mobility of the plasticized interstitial medium and not from the breakdown of the network-structure. As demonstrated in section D, the melting of the crystalline tie-points starts at temperatures above 80–90 °C. The existence of the concentration heterogeneities proves to be thermoreversible because the orientation phenomena reappeared during cooling of the stretched sample. However, the sample always broke during the cooling procedure, which is tentatively ascribed to the relatively higher cross-linking density of the system by annealing during the course of the measurement.

Conclusions

The scattering pattern of deuterated rigid PVC exhibits a weak but distinct interference maximum, suggesting the existence of some superstructural order. The relatively low intensity might be connected with the wide distribution of crystalline order in PVC. The comparatively high scattered intensity for plasticized PVC originates from the specific penetration of the plasticizer in the noncrystalline regions, as is demonstrated on the basis of a tentative two-phase model. However, the appearance of an additional interference maximum for high volume fractions TDN, probably resulting from phase separation, suggests that our present model for plasticized PVC is still too simple. The gradual disappearance of the crystalline regions at temperatures above 80 °C is completely in agreement with the reported crystalline melting behavior and the loss of the mechanical properties.

Uniaxial deformation experiments on plasticized PVC confirm the existence of a heterogeneous network-structure in PVC where the crystalline tie-points act as physical cross-links. The similarities between the observed scattering phenomena of uniaxially stretched plasticized PVC and those of a stretched randomly cross-linked polystyrene gel suggest the existence of concentration inhomogeneities arising from the inhomogeneous deformation of the randomly cross-linked network. The gradual disappearance of the scattering anisotropy below the melting range of the crystallites can be attributed to the elimination of the concentration inhomogeneities as a consequence of the increasing mobility of the plasticized interstitial medium.

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