of these lines are 1.9, 3.0, and −1.6 kcal per mol (±0.1) for PS-PVK, PMMA-MVK, and PPVK, respectively. Although the number of values of the quantum yield are too small for exact determination, the activation energies obtained are reasonable for the barriers to rotation about carbon–carbon bonds.

Conclusions

At room temperature and above, photochemical reactions may compete with very efficient radiationless processes. Below the glass transition temperature in PMMA-MVK, PS-PVK, and PPVK a temperature dependence exists for the Norrish type II reaction which can be attributed to the changes in the segment mobility of the polymeric molecule. In the case of PMMA-MVK and PS-MVK, higher type II quantum yields are obtained at higher temperatures in the glassy region. In the case of PPVK, the type II quantum yield decreases slightly with increasing temperature. The apparent activation energies obtained from the temperature dependences are 2–3 kcal/mol which are of the same order of magnitude as the energy barriers to rotation around C–C bonds.

In the glass transition region the type II quantum yield increases greatly in all the polymers studied due to the great increase in polymer segment mobility which occurs at this temperature. Above the glass transition region, the type II quantum yields in all polymers studied seem to be constant and, within experimental error, equal to the quantum yields obtained in solution for the same polymer and/or analogous low molecular weight model compounds.

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Crystal Structure of Poly(vinyl chloride) Single Crystals

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ABSTRACT: A refinement of the crystal structure of poly(vinyl chloride) is based on quantitative X-ray intensities obtained from oriented mats of single crystals. The orthorhombic crystal unit cell is very compact, with dimensions a = 10.24 Å, b = 5.24 Å, and c = 5.08 Å. The refined structure places the chains related by the screw axis in the center of the unit cell in such a manner that the C-Cl distance is 4.71 Å, compared with a van der Waals distance of 4.1 Å. This appears to preclude a direct C—H- -Cl hydrogen-bond type of interaction in poly(vinyl chloride).

The first crystal structure analysis of syndiotactic poly(vinyl chloride) was made by Natta and Corradini,[1] using samples of low crystallinity. Later, Natta, Bassi, and Corradini[2] prepared oriented fibers from a mixture of highly crystalline, low molecular weight material and poorly crystalline, high molecular weight material. They were able to deduce the structure and compare calculated X-ray intensities with visually estimated experimental intensities. It has since been possible to produce oriented single crystal mats of very high crystallinity.[3] From these we have obtained accurate quantitative X-ray intensities and have therefore felt it worthwhile to refine the structure.

Experimental Section

Low molecular weight poly(vinyl chloride) was made in butyraldehyde according to the method of Burleigh.[4] The material was fractionated by dissolving it in boiling cyclohexanone, cooling the solution, and separating the crystalline precipitate by ultracentrifugation. Dissolving this precipitate in boiling chlorobenzene and slow cooling of the solution produced single crystals, similar to those characterized by Smith and Wilkes[3] by electron microscopy and electron diffraction. Oriented mats of crystals approximately 0.5-mm thick were collected on fritted-glass filters, washed with acetone and vacuum dried for subsequent X-ray analysis.

Both nickel-filtered copper radiation and zirconium-filtered molybdenum radiation were used to obtain diffraction patterns on flat-plate films in a Statton-Warhus vacuum camera, with the beam parallel to the surface of the crystal mat. Quantitative X-ray intensities were measured from the films with a Joyce-Loebl recording microdensitometer. After the microdensitometer scans were corrected for background and amorphous scattering, the resulting peak heights were used as a measure of the relative intensities.

The 010 reflection, very critical to our subsequent Fourier analysis, was not well resolved in most of our X-ray films. In order to resolve the 010 and 200 reflections, the following special experimental conditions were used: 0.38-mm diameter pinholes set 15.0 cm apart; sample to film distance = 17.0 cm; Cu Kα radiation; vacuum.

Results and Discussion

Study of the X-ray patterns showed that the equatorial $hk0$ reflections were considerably sharper than the upper layer line $hk1$ reflections (Figure 1a). A small-angle meridional X-ray long spacing of 61.6 Å (second order = 30.8 Å, Figure 1b), consistent with the crystal thickness measured from electron micrographs,[3] suggests that only about 24 monomer units or 12 repeat units along the chain axis account for the crystal thickness. The sharp equatorial reflections indicate that order is considerable in the lateral directions. The orthorhombic unit cell, whose dimensions we determined to be a = 10.24 Å, b = 5.24 Å, and c = 5.08 Å, is more compact than that observed for less crystalline poly(vinyl chloride).[1,2] The lattice parameters most recently published by Natta[2] and coworkers are a = 10.4 Å, b = 5.3 Å, and c = 5.1 Å with a calculated density of 1.48 g/cm^3. Our calculated density is 1.53 g/cm^3.

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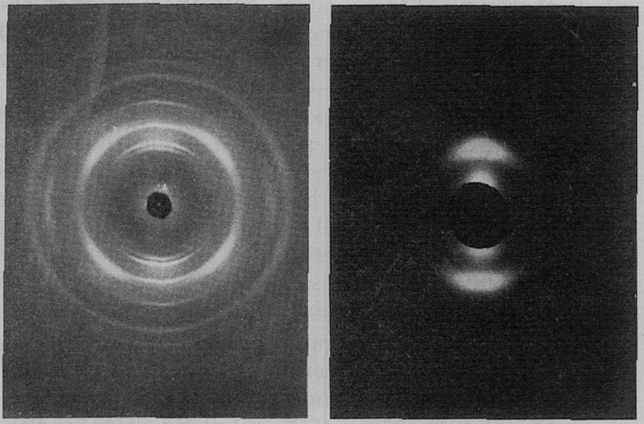

Figure 1. (a, left) X-Ray pattern of poly(vinyl chloride) single crystal mat. X-Ray beam parallel to mat surface; *hk*0 reflections on equator; Mo radiation. (b, right) Small-angle X-ray pattern. X-Ray beam parallel to crystal mat; Cu radiation.

Table I
***Observed and Calculated X-Ray Intensities for Crystalline* Syndiotactic Poly(vinyl chloride)**[a]

*hk*1	n^b	*d* (Å)	F^c	Temp Factor[d]	*LP* Factor[e]	I_{calcd}[f]	I_{obsd}
010	1	5.24	15.0	0.834	14.64	7.3	13
200	1	5.12	31.6	0.826	14.30	31.0	32
110	2	4.66	42.9	0.795	13.01	100.0	100
210	2	3.66	37.0	0.689	10.16	50.2	52
310	2	2.86	34.8	0.543	7.86	27.0	21
020	1	2.62	24.6	0.483	7.17	5.5	*g*
400	1	2.56	18.3	0.466	6.99	2.9	*g*
120	2	2.54	16.1	0.460	6.93	4.3	*g*
220	2	2.33	18.2	0.399	6.33	4.4	*g*
410	2	2.30	37.2	0.389	6.24	17.6	18
320	2	2.08	35.2	0.314	5.59	11.4	10
420	2	1.83	36.5	0.225	4.87	7.6	*g*

[a] Correction factors were based on Mo Kα radiation, $\lambda = 0.7107$ Å. [b] n = multiplicity factor = 1 for *h*00 and 0*k*0 reflections and 2 for *hk*0 reflections. [c] F = calculated structure factor. [d] Temperature factor = $\exp(-2B \sin^2 \theta/\lambda^2)$, best value of $B = 10$ Å^2. [e] *LP* factor = $(1 + \cos^2 2\theta)/\sin 2\theta$. [f] Intensity normalized to $I(110) = 100$. [g] Difficult to measure quantitatively.

Our intensity data support the previous assignment[2] of the space group, *Pcam* (D_{2h}^{11}). Since this symmetry fixes the positions of the repeat units along the *a* and *c* (chain axis) unit cell directions, it is only necessary to refine the position of the chain along the *b* axis and the projection of the Cl–C–Cl angle on the *ab* plane. (This assumes constant bond lengths, which we took to be: C–C = 1.53 Å, C–Cl = 1.76 Å, C–H = 1.10 Å.) Of the ten or so observable equatorial *hk*0 reflections, we were able to measure accurate intensities of seven.

A computer program was written to calculate *hk*0 structure factors and intensities, allowing us to easily vary the Debye–Waller temperature factor *B*, the position of the chain along the *b* axis and the Cl–C–Cl angle. The pertinent correction factors and input parameters were as follows: (1) carbon, chlorine, and hydrogen atomic scattering factors from the International Tables for X-Ray Crystallography (Vol. III]; (2) rotating crystal, zero-layer Lorentz–Polarization factor, $LP = (1 + \cos^2 2\theta)/\sin 2\theta$; (3) unit cell constants $a = 10.24$ Å and $b = 5.24$ Å. Absorption corrections were not necessary because of the small sample size and the use of molybdenum X-ray data.

After trying a number of anisotropic and isotropic temperature factors, we obtained best agreement with an isotropic temperature factor of $B = 10$ Å^2. This compares with values of $B \cong 3$ for single crystals of *n*-hydrocarbons,[5] $B = 10$ for Nylon 77,[6] and B = 17–18 for poly(ethylene adipate)[7] and poly(ethylene terephthalate).[8]

Table II
Atomic Coordinates of Asymmetric Unit of Crystalline, Syndiotactic Poly(vinyl chloride)

Atom	*x*/*a*	*y*/*b*	*x*/*c*
$C_1(CH_2)$	0.250	0.965	0.000
$C_2(CH)$	0.250	0.126	0.250
Cl_1	0.393	0.313	0.250
H_1 (on CH_2)	0.160	0.850	0.000
H_2 (on CH_2)	0.340	0.850	0.000
H_3 (on CH)	0.160	0.241	0.250

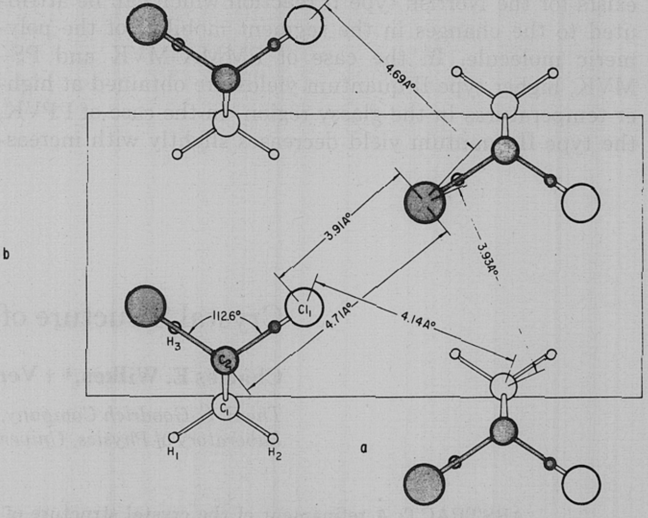

Figure 2. Projection of crystal structure of syndiotactic poly(vinyl chloride) on *ab* plane. C_1 at $z = 0$ and $z = \frac{1}{2}$; C_2 at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ *(shaded).*

As Natta and coworkers previously pointed out,[2] small changes from the equilibrium C–C–Cl angle make little difference in the calculated intensities. We have determined that values of the (equivalent) Cl–C–Cl angle ranging from Natta's 110.7° to approximately 113° give a good fit between observed and calculated intensities. Angles outside this range give poorer results. Optimum agreement was achieved for an angle of 112.6°.

The chain placement in the *b*-axis direction is sensitively determined by the 010 intensity. We have therefore carefully measured this reflection. Our observed value (see Table I) is considerably higher than that assumed by Natta.[2] A refinement of the *b*-axis coordinates (in conjunction with the simultaneous refinement of *B* and the Cl–C–Cl angle) gave best agreement for the coordinates of the independent structural unit given in Table II. Observed and calculated intensities, normalized to $I(110) = 100$, are given in Table I, together with various correction factors. The reliability index, $R = (\Sigma|I_{obsd} - I_{calcd}|)/\Sigma I_{obsd}$, is 0.066.

The new structure represents a small change from that proposed by Natta[2]: we find $\Delta y/b = 0.01$. This places the chains related by the screw axis in the center of the unit cell (see Figure 2) approximately 0.1 Å (*i.e.*, 2 × 0.01 ×

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5.24) farther apart along b. It had been suggested from far infrared studies[9] that the C $\cdots$ Cl contact between the above two chains might involve a C—H $\cdots$ Cl hydrogen-bond-type of interaction. Our results indicate that this is not the case, since this distance is a 4.71 Å, compared to a van der Waals contact distance of 4.1 Å.

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Spectrum of Light Quasielastically Scattered from Linear Macromolecules

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ABSTRACT: Based on a simple model of molecular motion, the form factors in the quasielastic scattering of laser light were calculated for flexible and stiff linear macromolecules. This result will play a role of a guiding principle in the analysis of spectra composed of various modes of molecular motion.

Since the pioneering work of Pecora,[2a] quasielastic scattering of laser light has become a powerful tool for the dynamic study of macromolecules.[2b] Under a condition that $dK < 1$ (where d is the representative linear dimension of a scatterer such as the root-mean-square end-to-end distance of a chain, the length of a rod, and K is the absolute value of the scattering vector), the main contribution to the line broadening of light scattered from solutions of macromolecules comes from the center-of-mass motion. Therefore, measurements of spectral densities at $dK < 1$ give a translational diffusion coefficient.[3] This is one of the most important merits of the technique. On the other hand, if spectral densities can be measured under a condition of large dK, it will be found that the internal modes of molecular motion (rotational,[4] stretching,[5] bending[6] etc.) contribute to the line broadening of scattered light. Thus there is a possibility that we can obtain the rotational diffusion coefficient of, and elastic constants of stretching and bending of, a macromolecule in solution as well as its translational diffusion coefficient. In decomposition of a spectrum into components due to various modes of motion, numerical values of scattering form factors at various values of dK must be known.[7-10] Based on a simple model of molecular motion,[11] we present in this paper the scattering form factors of chain molecules.

The Model

A brief summary of our treatment[6] is at first presented. Let a chain molecule be represented by a space curve, $\mathbf{r}(x,t)$, where x is the contour length along the chain $(0 \leq x \leq L)$ and t is the time. The Langevin equation for the Brownian motion of the molecule may be written as[11,12]

$$\rho\partial^2\mathbf{r}/\partial t^2 + \zeta\partial\mathbf{r}/\partial t + \epsilon\partial^4\mathbf{r}/\partial x^4 - \kappa\partial^2\mathbf{r}/\partial x^2 = \mathbf{A}(x,t) \quad (1)$$

where ρ is the linear density, ζ is the friction constant per unit length, ϵ and κ are, respectively, elastic constants of bending and stretching of a chain and $\mathbf{A}(x,t)$ is the fluctuating force acting on the molecule. The elastic constants have been given in terms of γ (the inverse of the statistical length) as[11]

$$\varepsilon = 3kT/4\gamma \quad \text{and} \quad \kappa = 3kT\gamma\mu(\gamma L) \quad (2)$$

where

$$\mu(\gamma L) = [1 - (1 - e^{-2\gamma L})/2\gamma L]^{-1}$$
$$= 1 \text{ (for } \gamma L >> 1) \text{ and } 1/\gamma L \text{ (for } \gamma L << 1) \quad (3)$$

The end-to-end distance of the chain is given in terms of γ as[11-13]

$$\langle R^2\rangle = [\exp(-2\gamma L) - 1 + 2\gamma L]/2\gamma^2 \quad (4)$$

When $\mathbf{r}(x,t)$ and $\mathbf{A}(x,t)$ are, respectively, expanded by an orthonormal set $\{Q(n,x)\}$ as

$$\begin{Bmatrix}\mathbf{r}(x,t) \\ \mathbf{A}(x,t)\end{Bmatrix} = \Sigma_n \begin{Bmatrix}\mathbf{q}(n,t) \\ \mathbf{B}(n,t)\end{Bmatrix} Q(n,x) \quad (5)$$

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