IR Studies of Crystalline Methanol Films with Textures

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When amorphous methanol films, deposited at 78 K on a substrate already covered by a thin crystalline methanol layer, are crystallized above 104 K they obtain a growth texture. This can be seen from relative intensity alterations of IR bands related to the hydrogen bondings. Another growth texture is obtained by depositing the film at 145 K. Large spherulites are seen between crossed polarizers. Other alterations of IR bands are observed. From the interpretation of this dichroism we learn about the growth mechanism. The relations of polymer chains with hydrogen bonds to those with covalent bonds are discussed. Isothermal sublimation can be studied from the linear decrease of a single IR band. This allows to determine the heat of sublimation.

1. Introduction

The study of methanol in its solid state has revealed two crystalline phases in which the molecules are connected by OH...O hydrogen bondings and form long chains. From X-ray measurements Tauer and Lipscomb [1] have given evidence that the β-phase below the melting point of 175.4 K has the orthorhombic space group D_{2h}^{17}-CmCm and that the α-phase appears below 157 K by possibly a second order transition. In both phases the polymer zig-zag chains are straight and parallel to each other. In the β-phase the carbon atoms are statistically bent up or down out of the plane formed by the oxygen atoms of one chain and may thermally flip between both positions. In the α-phase this bending is alternately up and down along the chain so that neighbouring chains can come closer together. The probable space group is the monoclinic C_{2h}^{2}-P2_1/m, but this holds without considering the position of the OH hydrogen atoms. By dilatometric studies Staveley and Hogg [2] found a more abrupt change of volume at 157 K so that a first order transition cannot be excluded. Superheating effects in α/β-transition depending on the degree of lattice disorder are observed by Würflinger and Landau [3]. From infrared studies of methanol and its deuterated forms Falk and Whalley [4] have made a thorough space group analysis and linegroup analysis of the spectra in the β- and α-phase. The excitation of both, the symmetric and the antimetric, OH out-of-plane bending modes require that the carbon and/or the OH hydrogen are out of plane of the oxygen atoms. Lattice dynamical calculations and detailed experiments especially concerning the hydrogen bonding and its disorder have been performed by Dempster and Zerbi [5] and by Pellegrini et al. [6]. The strong tendency of methanol molecules to polymerize has been studied experimentally by Van Thiel et al. [7] using a matrix isolation technique. Curtiss [8] made molecular orbital studies of chains up to six molecules, and pseudopotential calculations on hydrogen bonded methanol chains have been reported by Gatti et al. [9]. All these activities demonstrate the outstanding role of methanol as a simple model for hydrogen bonded polymer chains.

The present investigation intents to show closer relations of this polymer to the classical polymers with their covalent bondings. By visual observations of the growth of the condensing crystalline film or of its crystallization from the vitreous (amorphous) state one can learn how to prepare films with prefered growth texture of the methanol chains. This will influence the intensity of IR bands, mainly of the OH hydrogen bonding vibrations.

2. Experimental

All experiments are performed in the high vacuum of an optical cryostat. A polished crystalline plate of potassium iodide is used as the substrate for condensing the methanol film. We have used Merck (very pure) material which was degassed by alternate heating and freezing under vacuum. A vacuum

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valve with precision adjustment is opened for a definite time so that methanol from a 5 cm^3 reservoir can evaporate out of a jet tube onto the substrate. Within 20 sec we obtain a thickness of 10 to 12 μm. The temperature of the substrate is controlled by an iron vs. constantan thermocouple.

The optical transmission between 2.5 μm and 40 μm is measured at 78 K with a Beckman IR-20A and with KI windows on the cryostat. Condensation below 104 K gives amorphous films which can be crystallized by temporary annealing above 110 K. Condensation above 104 K immediately gives crystalline films. From 142 K to 157 K one observes an increasingly fast sublimation of the methanol to the surrounding cold shields. So without breaking the vacuum several films can be prepared and measured successively.

Visual observation is performed by turning the inner tank of the optical cryostat by 90 degrees and watching through strainfree glass windows the growth of the crystalline film between crossed polarizers. Macro photos (1.6/1) are shot with a Canon FT camera. In order to avoid strain birefringence by the KI substrate it has been annealed for 2 hours at 400 °C before mounting. The film is illuminated from behind with an incandescent lamp or sometimes with a high pressure mercury lamp and an interference filter after the condenser.

3. Results

The infrared spectra obtained at 78 K are shown in Figure 1. The amorphous methanol film, condensed at 78 K, gives the dashed curve in Figure 1 a. After annealing at about 110 K for crystallization the same film gives the solid curve in Figure 1 a. Strong alterations are observed in all bands belonging to the OH...O hydrogen bonding vibrations. The stretching mode at about 3235 cm^{-1}, the in-plane bending mode at about 1450 cm^{-1} and the out-of-plane bending mode at about 730 cm^{-1} are split into doublets. These results are already known form other investigators [4–6]. We will use them as a comparison for the spectra in Fig. 1 b and c, where by special preparations we try to grow the crystalline film with a well defined texture. First we condense a very thin film ($d < 0.5$ μm) at 78 K and transfer it to the crystalline state. Then we condense at 78 K the rest of 10 to 12 μm. The dashed line in Fig. 1 b gives the spectrum of the mainly amorphous film. After transferring the whole film to the crystalline state we measure the solid curve in Fig. 1 b. Compared to Fig. 1 a we observe that, concerning the intensities, always the long-wavelength component of the three hydrogen-bonding vibrations has been decreased relative to the corresponding short-wavelength component.

Before describing the film preparation of Fig. 1 c let us report what insight we obtain from visible observations. While in the amorphous state the methanol film remains dark between crossed polarizers, crystallization is noticed by a homogeneous brightening of the film. Condensing the methanol above 104 K produces a transparent film the granulation of which being coarser at higher condensation temperature. Condensing the film between 138 K and 146 K gives well developed plane spherulitic growth with diameters of the single spherulites up to 6 mm. A typical example is shown in Figure 2. The contact boundaries of adjacent spherulites form midverticals of the straight lines connecting their centres. This means that all spherulites have appeared simultaneously and have grown with equal velocity. Any delay and variation of nucleation must be short compared to the time of growing. The lower the condensation temperature the higher in number and smaller in size are the spherulites. At the lowest temperatures of crystalline growth the number of nuclei must be so high that the diameter of spherulites is smaller than the thickness of the film. Therefore no texture can be observed. Only when spherulites have diameters large compared to the thickness of the film, we expect a special growth texture which is different from the other growth texture leading to Figure 1 b.

This texture of plane spherulites, as shown in Fig. 2, resulted in Fig. 1 c. Again we find significant alterations compared to Figs. 1 a and b mainly in the OH...O hydrogen bonding vibrations. Here the long-wavelength component of the two bending modes has been increased relative to the corresponding short-wavelength component. For the stretching mode a similar behavior is not so clearly discernible but cannot be excluded. The most dramatic effect is seen when comparing all three plots in the spectral range of out-of-plane bending of OH...O (at 685 cm^{-1} and 790 cm^{-1}). Because of its small width and probably because of the strongly anharmonic potential the first overtone of the 685 cm^{-1} band at about 1350 cm^{-1} can also be seen and it behaves the same.

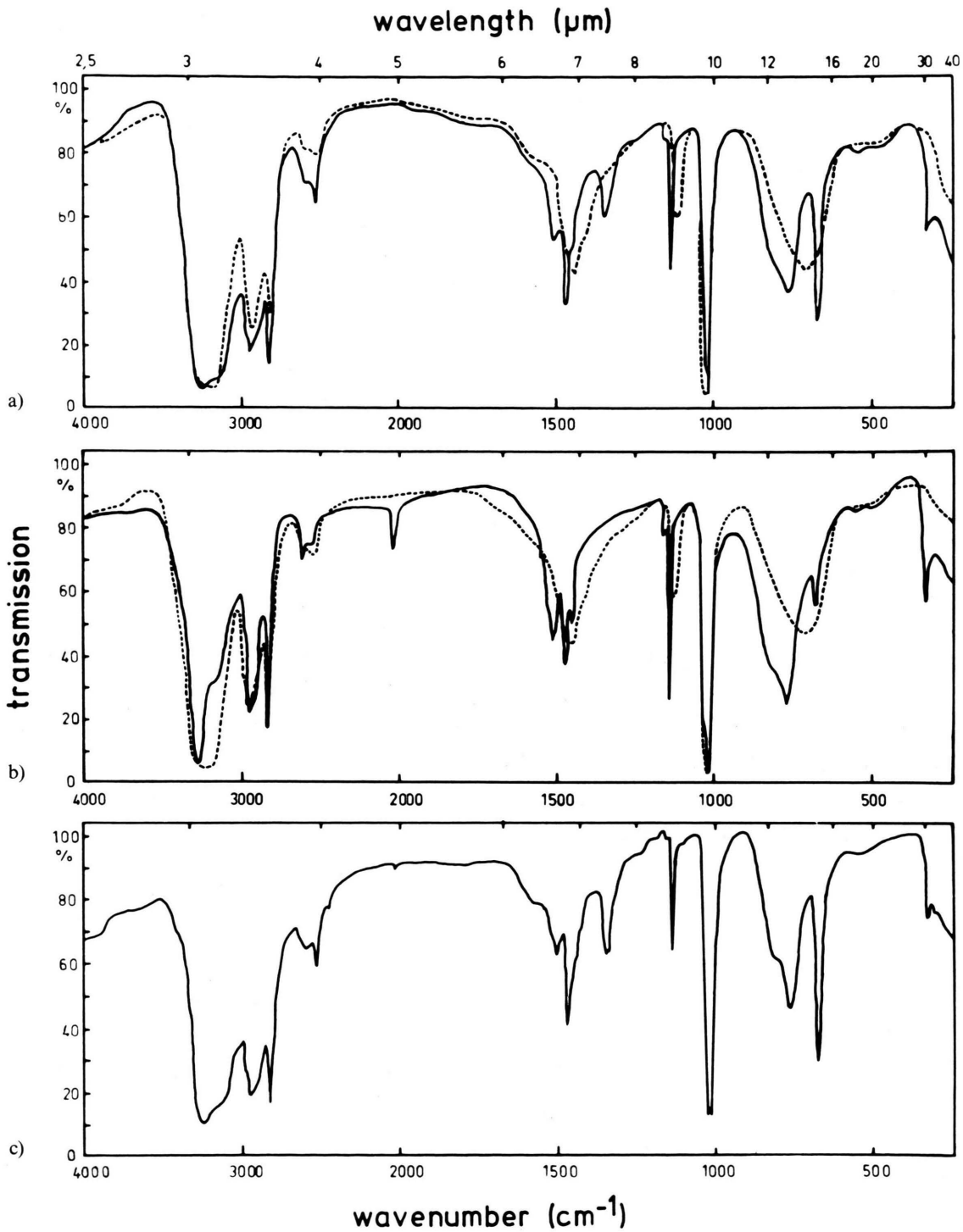


Fig. 1. IR transmission of methanol films (thickness ~ 10 μm) at 78 K. Dashed curves: amorphous (vitreous) film before crystallization. Solid curves: crystallized films. a) without texture, b) texture with polymer chains normal to film plane, c) spherulitic texture with chains in film plane.

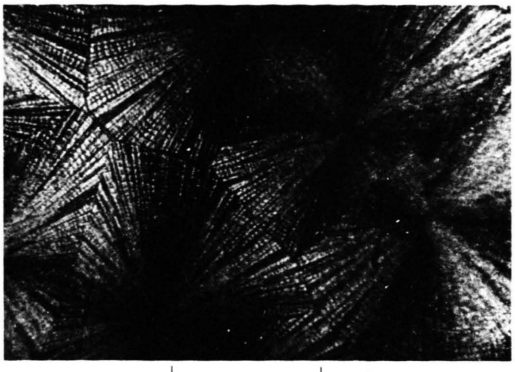


Fig. 2. Large spherulites of methanol film condensed at 145 K. Crossed polarizers.

4. Discussion

In order to understand this texture dependent strength of the hydrogen bonding vibrations we shall interpret the splitting of the three modes as a cooperative phenomenon of the crystalline state, or better of the isolated chain in the crystal, as already done by Falk and Whalley [4]. In Fig. 3 the three times two vibrational modes of the OH hydrogen motion are illustrated on single OH...O chains. The CH_3 group is only indicated by a dash. The arrows or the ± signs near the hydrogen atoms give the phase of their relative motion in each chain. This motion is nearly parallel (symmetrical mode) or nearly antiparallel (antimetrical mode). Only in the out-of-plane mode it is strongly parallel or antiparallel. The arrows at the bottom show the direction of the electric field E of that IR wave which

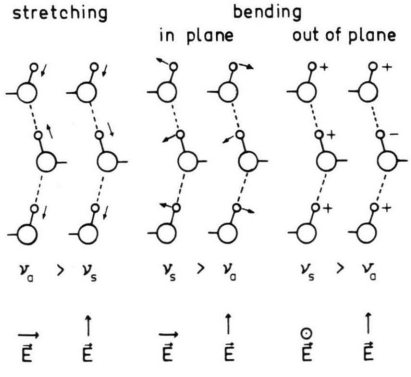


Fig. 3. Vibration modes of OH hydrogen atoms in polymer methanol chain (arrows or ± signs show relative phase, symmetric or antimetric). ***E*** is vector of exciting IR light (see text).

can excite this mode, except the antimetric out-of-plane bending mode. But we know from the experiment that both out-of-plane bending modes are IR active (in α- and β-phase). So we have to conclude, as Falk and Whalley have done, that the carbon atoms and/or the OH hydrogen atoms are not coplanar with the oxygen atoms. Oxygen has to form tetrahedral, instead of planar, bonds. If this is done alternately along the zig-zag chain, the antimetric out-of-plane mode also becomes IR active. In the β-phase there is a rapid interchange of the two puckered collapsed forms of these infinite chains. Therefore the 685 cm^{-1} band remains an allowed IR transition also in the β-phase.

What can we learn from the crystalline films with texture? In order to bring the observed intensity variations of the hydrogen bands in accord with the polarisation requirements of Fig. 3 we have to suppose that spherulitic growth takes place along the OH...O chains, that means they are preferentially aligned parallel to the spherulitic radii. For the texture in Fig. 1 b the OH...O chains would be aligned normal to the film plane. If this alignment would be perfect then the longer wavelength components of all three hydrogen vibrations should have disappeared while the shorter wavelength components should have increased by 50%. The remaining intensity of the 685 cm^{-1} band is a measure of the deviation from a perfect perpendicular alignment of the chains.

On the other hand in a strongly plane spherulitic texture (Fig. 1 c) one would expect in the absorption for the longer wavelength components an increase of 50% and for the shorter wavelength components a decrease of 25%, compared to a film without texture (see Table 1). These expectations are satisfactory for the out-of-plane doublet as seen from Fig. 1 c, but the changes in the two other doublets seem to be less than expected. However if the spherulites prefer to keep the OH...O zig-zag planes more parallel to the film plane then, in this limit, there is no relative change in the stretching doublet and in the in-plane bending doublet (see Table 1). The actual situation could be a mixture of both cases. This would not contradict to what follows now.

From Fig. 2 you may recognize the ring structure of the spherulites. We have chosen this example in order to demonstrate that also in this respect there is no difference in crystallizing behavior between ordinary polymers with their covalent bondings and

Table 1. Relative IR intensities of OH hydrogen bands expected in textured films. $\hat{n}$ = normal to film plane, $\hat{z}$ = direction of chain, $\hat{y}$ = normal to chain plane.

	stretching		bending			
			in-plane		out-of-plane	
	a	s	s	a	s	a
no texture (6 cases)	$\frac{2}{6}$	$\frac{2}{6}$	$\frac{2}{6}$	$\frac{2}{6}$	$\frac{2}{6}$	$\frac{2}{6}$
normal texture $\hat{z} \parallel n$ (2 cases)	$\frac{1}{2}$	0	$\frac{1}{2}$	0	$\frac{1}{2}$	0
spherulic texture (twisted chains) $\hat{z} \perp \hat{n}$ (4 cases)	$\frac{1}{4}$	$\frac{2}{4}$	$\frac{1}{4}$	$\frac{2}{4}$	$\frac{1}{4}$	$\frac{2}{4}$
spherulic texture (flat chains) $\hat{z} \perp \hat{n}$ and $\hat{y} \parallel \hat{n}$ (2 cases)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$

the polymer methanol with its hydrogen bondings. The ring systems have a single period around 0.15 mm. According to the explanation of Keller [10] and of Point [11] this effect arises from the rotation of the optical axes of the birefringent material, when the lamellar crystals are twisted along the spherulitic radii. Under special growth conditions this happens synchroneously within one spherulite. Unfortunately the refractive indices of methanol crystals are not known yet. They could give another test for our view that, different from ordinary chain polymers, methanol chains be ordered radially within the spherulite. There is one argument by which we could easier understand this difference. While ordinary polymers have very stable bondings around their crystallization temperature, OH...O hydrogen bonds are by a factor of 10 weaker (0.26 eV). So around 150 K each hydrogen bond may thermally break and reform after an average time of about 100 seconds. This allows to unravel the amorphous skein during crystallization.

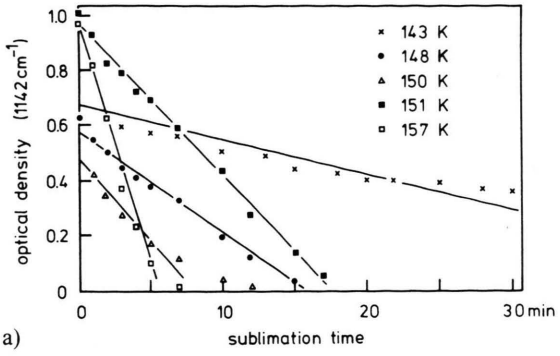
Let us finally make some remarks on the different intensities of the OH hydrogen bonds. Strong or very strong and broad bands are the two stretching bands and the symmetric out-of-plane bending band, while the other three are less broad and have only medium strength. It could be worthwile to consider the possibility of splitting into longitudinal and transversal modes, as known from ionic crystals in the reststrahl range. This view gets support by the fact that strong enough internal electrical fields are consistent with just those modes. A study of these bands in relation to the film thickness could shed more light onto such questions.

5. Conclusion

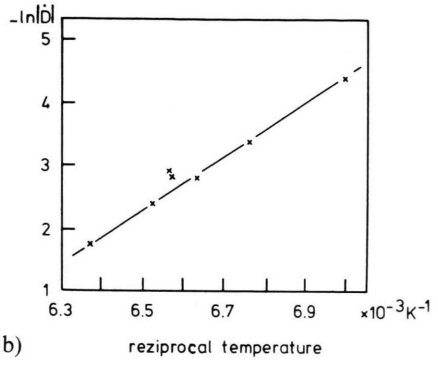
We have reported on techniques to influence the texture of crystalline methanol films by special preparations. Such films show the relative increase or decrease of special IR vibration bands belonging to the hydrogen bondings. This allows to draw conclusions about the special growth texture. A big help is the visual inspection of the films between crossed polarizers. This reveals the formation of large spherulites and allows to optimize their growth conditions. The formation of a single crystalline methanol film and its IR studies with linear polarized light can be a goal for future investigations. Also one would like to determine the three refractive indices of the α- and β-phase. To reach at least part of these goals, namely, to guide the crystal growth into a special direction within the film plane has already been tried in the following experiment. First 90% of the KI substrate are covered and we condense methanol at 145 K which gives spherulitic growth. Then while condensation is continued the cover is suddenly removed. The visible texture between crossed polarizers shows that crystallization has pursued normal to the straight boundary of the cover. Unfortunately some single nuclei produced a competitive spherulitic growth (which gave parabolic boundaries with the uniformly directed growth area). If these nuclei can be avoided (next time we shall try to move the cover more slowly away) we are nearer to the goal of a single crystalline methanol film.

6. Appendix: An optical method to measure the heat of sublimation

It is possible to perform the sublimation of the methanol film at a constant temperature. Because of the good thermal conductivity of the potassium iodide crystal a sufficient homogenity of the temperature within the sublimating film is guaranteed. Only at the very end of the sublimation one can detect small deviations from a homogeneous reduction of the thickness of the film by observing between crossed polarizers the disappearance of the



a)



b)

Fig. 4. Isothermal sublimation of CH_3OH film. a) Optical density D of CH_3 rocking mode (1142 cm^{-1}) as function of time (parameter is temperature T). b) Slope $|\dot{D}|$ from a) logarithmic vs. reciprocal T.

birefringence. In order to obtain an accurate measure of the relative film thickness out of the IR absorption we have chosen the rocking mode of CH_3 at 1142 cm^{-1} which in the crystalline state has a very sharp band well isolated from other absorption. In Fig. 4a the optical density D in the maximum of this band is plotted as a function of time. Sublimation temperatures range from 143 K to 157 K. The 143 K run has been followed up to 50 min and the straight lines have been found by least squares fits. The thickness and with it the optical density decrease linearly with time. So the slope of $D(t)$ should be proportional to $\exp(-\Delta H_s/k_B T)$, where ΔH_s is the heat of sublimation. Figure 4b shows $|\dot{D}|$ as a function of T^{-1}, and from the straight line we obtain a heat of sublimation $\Delta H_s(150\,K) = 35.7 \pm 0.7$ kJ/Mol. This value can be compared with the known heat of vaporization $\Delta H(20\,°C) = 35.81$ kJ/Mol [12]. Within the accuracy of our measurements, which probably could be improved, we see no difference. The reason is obvious. In both cases hydrogen bonds have to be broken. The van der Waals contribution from the interbonding of adjacent methanol chains is smaller and is about the same in the crystalline and in the liquid state. Also the PV contribution at 20 °C (about 0.3 KJ/Mol) can be neglected.

The sharp band at 1142 cm^{-1} has also been used by us to study the isothermal crystallization of amorphous methanol films. We did not apply Avrami's equation [13] but only tried to get the initial power law from a double logarithmic plot of the optical density D against the time t. For films without texture we obtained out of more than 50 measurements the power $n = 1.9 \pm 0.6$. A significant T dependence of n could not be found. From our view of a spherulitic growth with constant velocity starting from a constant number of nuclei we would rather expect $n = 3$ for three-dimensional growth. So the result obtained is not yet satisfactory.

[1] K. I. Tauer and W. N. Lipscomb, Acta Cryst. **5,** 606 (1952).
[2] L. A. K. Staveley and M. A. P. Hogg, J. Chem. Soc. **1954,** 1013.
[3] A. Würflinger and R. Landau, J. Phys. Chem. Sol. **38,** 811 (1977).
[4] M. Falk and E. Whalley, J. Chem. Phys. **34,** 1554 (1961).
[5] A. B. Dempster and G. Zerbi, J. Chem. Phys. **54,** 3600 (1971).
[6] A. Pellegrini, D. R. Ferro, and G. Zerbi, Mol. Phys. **26,** 577 (1973).
[7] M. Van Thiel, E. D. Becker, and G. C. Pimentel, J. Chem. Phys. **27,** 95 (1957).
[8] L. A. Curtiss, J. Chem. Phys. **67,** 1144 (1977).
[9] C. Gatti, G. Pacchioni, P. Fantucci, S. Polezzo, and V. Valenti, Mol. Phys. **38,** 1865 (1979).
[10] A. Keller, J. Polymer Sci. **39,** 151 (1959).
[11] J. J. Point, Bull. Acad. Roy. Belg. **41,** 982 (1955).
[12] J. D'Ans and E. Lax, 2nd Ed., p. 1397, Berlin 1949.
[13] M. Avrami, J. Chem. Phys. **9,** 177 (1941).