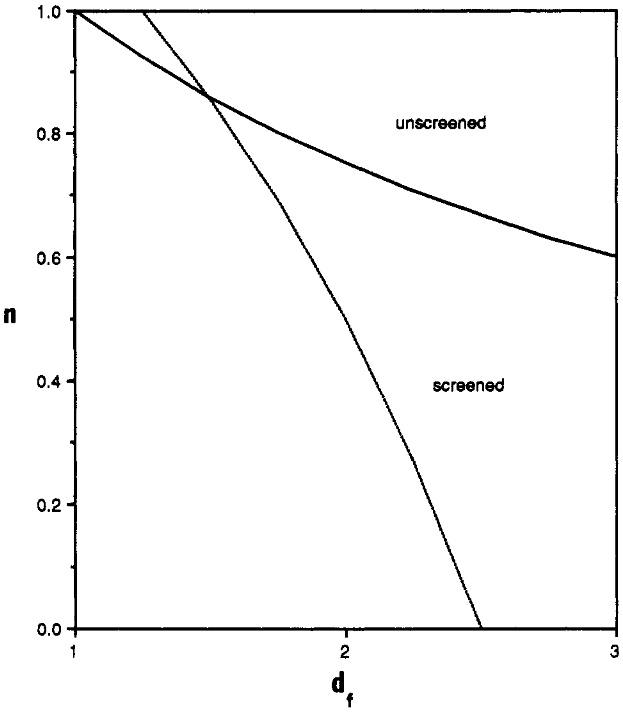

Figure 1. Dependence of n in $d = 3$ on d_f according to eq 6 and 10 for the unscreened and screened cases, respectively.

colation model, eq 7, has been used in writing down this equation. This assumption is valid for the conditions considered here. See ref 29 for more general cases. If only the two-body excluded-volume effect is of concern, $\bar{d}_f > d_f$. If there is only partial screening, then the dimension that appears in the denominator of eq 9 is some appropriate value between d_f and $\bar{d}_f$. Substituting eq 2 in eq 9 gives

$$n = \frac{d(d + 2 - 2d_f)}{2(d + 2 - d_f)} \qquad (10)$$

The dependence of n on d_f for both the unscreened and screened situations (eq 6 and 10, respectively) for $d = 3$ is given in Figure 1. These are to be taken as bounds and reality might lie between depending on the extent of screening. While n for the unscreened case changes from 1 to 2/3 as d_f changes from 1 to 5/2, n changes over the whole range of 0–1 in the same interval of d_f. It is to be noted that a small change in d_f around and above 2 can lead to a substantial change in $\bar{d}_f$ and consequently in the value of n. Specifically, $n = 1/2$ observed by Chambon and Winter corresponds to the situation[30] of $d_f = 2$; i.e., $\bar{d}_f = 4$ (the Zimm–Stockmayer dimension but combined with hyperscaling and not classical theory). The other values of n (in the range of 0.8–0.2) observed by Winter et al.[12-14,25] and Antonietti et al.[24] can be explained by a combination of percolation and either partial or full extent of screening depending on the nature of the particular chemical system.

In spite of the generality of the above-derived result, specific qualitative trends can be predicted. As the cross-linker deficiency is increased, the structure is more open than a fully cross-linked cluster and d_f is lower, leading to an increase in n for fixed extent of screening. If a collection of screened clusters is diluted with chains that are long enough screening is not affected any further and n is relatively insensitive to such dilutions. However, if dilution is performed with small molecular solvent, clusters will expand and n will increase. We finally conclude that the screening of excluded volume in clusters near the gel point can lead to significant changes in the scaling exponent characterizing the viscoelastic properties of such polymeric systems.

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Direct Formation of the Helical Polymer Conformation in Stereospecific Polymer Synthesis. X-ray Crystallographic Determination of Linear Chloral Oligomers[1]

We report the determination of the structure by X-ray single-crystal analysis of the linear oligomers of chloral (dimer to tetramer) that lead to the exclusively isotactic structure for polychloral.

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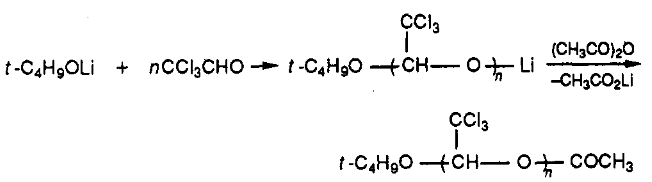
Scheme I[a]



[a] 1, n = 2 (r); 2, n = 2 (m); 3, n = 3 (mm); 4, n = 4 (mmm).

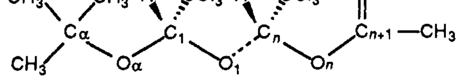
It was recently expressed that it should be possible during polymerization to control not only the stereospecificity (configuration) but also the conformation.[2] The concept that isotactic polymers (stereospecificity) might be formed directly in the helix (conformational specificity) has been stated in early work on stereospecific polymerization of higher aliphatic aldehydes.[3] Some synthetic polymers, most prominently polychloral,[4] but also poly(triphenylmethyl methacrylate),[5] polyisocyanides,[6] and polyisocyanates[7] are known to exist in purely helical structure. The helical conformation of the soluble polymers is rigid even in solution and is caused by the bulkiness of the side groups. The stereochemistry associated with the embryonic stage of the chain growth in stereospecific polymerizations has been of special concern.[4d,8–13]

Many nucleophiles like lithium *tert*-butoxide add to chloral; the first addition product is the *RS* form of a chloral-terminated alkoxide, and the second chloral addition product is formed by stereorandom addition. Subsequent propagating steps of chloral addition force the reaction to become stereoselective and finally stereospecific toward meso addition, which causes the formation of the 4/1 helical conformation of the final isotactic polymer.[4d,9]

Chloral oligomers could be prepared when the chloral polymerization was carried out near the ceiling temperature, using the cryotachensic polymerization technique.[4,14] The oligomerization was carried out at 26 °C after initiation with lithium *tert*-butoxide initiator in methylcyclohexane; the reaction was terminated by acetic anhydride to freeze the oligomer equilibrium (Scheme I). The linear dimer was isolated from the reaction mixture by distillation. In the previous paper[15] it was found by ^{1}H NMR spectroscopy that the dimer fraction is a diastereomeric mixture of the *racemo*-1 and *meso*-2 isomers (1/2 = 25/75). Only the major isomer 2 (mp 72.6–74.0 °C) crystallized from the methanol solution of the mixture. The trimer and tetramer were isolated by gel-permeation chromatography. The trimer and tetramer fractions each contained one diastereomer (3 and 4) highly enriched.[16] Crystals of 3 and 4 were grown from the methanol solutions and showed melting points of 116.2–116.7 °C and 254.0–255.5 °C, respectively. Polychloral has been reported to decompose with some softening resembling melting above 220 °C.[17,18]

The X-ray analysis[19,20] showed that 2[21] is the meso (m) diastereomer (a racemic mixture of the (S,S) and (R,R) isomers), which is the basic minimum configurational sequence of the isotactic polychloral chain. Similarly, 3[22] and 4[23] have been proved to be the linear trimer and tetramer of *mm* and *mmm* configuration, respectively.

Torsional angles for the acetal backbones of 2–4 are summarized in Table I; the angles are given in the (S) form. The schematic representation of the (S) oligomers showing the numbering system is as follows.



The conformation of the acetal backbone of (S,S)-2 is approximating the skew(+)-skew(−)-gauche(+)-skew(−) ($S\bar{S}G\bar{S}$)[24] form. The torsional angles coincide with the results of the conformational energy calculation for (S,S)-2 by Abe et al.[25] The backbone arrangements of (S,S)-2, (S,S,S)-3, and (S,S,S,S)-4 are essentially identical and represent the repeat $G\bar{S}$ sequences from the *tert*-butoxy group to the acetyl group. It is worth noting that the $S\bar{S}G\bar{S}G\bar{S}G\bar{S}$ conformation of (S,S,S,S)-4 is very similar to a unit sequence of a 4/1 helical structure of isotactic polychloral with left-handed helicity (Figure 1). The axis of the helix is parallel to the *c* axis of the crystal, and the repeat distance is 4.81 Å as measured by the atomic distance between O_α and O_5 along the *c* axis. X-ray studies on polychloral film samples that were cold-rolled[26] and on samples that were drawn over a hot pin (at 180–210 °C)[18] indicated that polychloral is isotactic and has the structure of a 4/1 helix. The repeat distance was initially incorrectly given as 6.45 Å[26] and later corrected to approximately 5.2 Å;[18] aliphatic polyaldehydes have 4.8 Å.[27]

Table I
Torsional Angles (deg) for 2–4[a]

	(S,S)-2[b]	(S,S,S)-3[b]	(S,S,S,S)-4
C_α–O_α–C_1–O_1	91.6 (4)	93.3 (6)	92.9 (4)
O_α–C_1–O_1–C_2	−147.5 (3)	−145.1 (5)	−143.7 (3)
C_1–O_1–C_2–O_2	72.2 (4)	66.4 (6)	76.5 (4)
O_1–C_2–O_2–C_3	−127.8 (4)	−133.6 (5)	−135.4 (3)
C_2–O_2–C_3–O_3		81.7 (6)	71.1 (4)
O_2–C_3–O_3–C_4		−115.6 (6)	−137.2 (3)
C_3–O_3–C_4–O_4			70.7 (4)
O_3–C_4–O_4–C_5			−121.4 (4)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] Only one of the two independent molecules in a unit cell is shown, since both adopt essentially identical conformations.

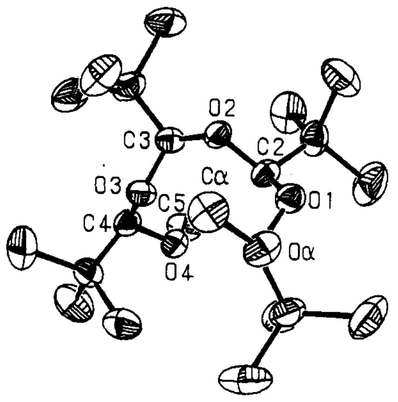


Figure 1. Molecular structure of (S,S,S,S)-4 viewed from the direction of the *c* axis, showing the 50% thermal ellipsoids. Methyl carbons of the *tert*-butoxy and acetyl groups are omitted for clarity.

Conformation of the acetal backbone of 4 in solution has been investigated by ^{13}C NMR spectroscopy,[20] on the basis of the Karplus-type relationship of $^3J_{\mathrm{COCH}}$ long-range coupling constants.[28] The $^3J_{\mathrm{COCH}}$ coupling constants for 4 estimated from the dihedral angles in crystal agreed substantially with the experimental values measured in chloroform-*d* at 35 °C, indicating that the helical conformation of 4 is held even in solution.[20]

The 4/1 helical conformation of the tetramer produced in the polymerizing mixture may account for the exclusive stereospecificity observed in the further propagation process forming the helical isotactic polymer chain of chloral. This may be the first example where the conformation of oligomer formed at the early stage of polymerization is closely related to the conformation of the high molecular weight polymer.

Supplementary Material Available: Listings of positional and thermal parameters for **2**–**4** (5 pages). Ordering information is given on any current masthead page.

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(21) Crystal data for **2** ($C_{10}H_{14}O_4Cl_6$): triclinic, $P\overline{1}$; $a = 11.740$ (4), $b = 17.089$ (6), $c = 9.631$ (4) Å; $\alpha = 107.08$ (3), $\beta = 101.48$ (3), $\gamma = 79.34$ (4)°; $V = 1794$ (1) Å^3; $Z = 4$, D(calcd) = 1.522 g cm^{-3}. The 373 variables were refined with 3719 unique reflections (3° $< 2\theta <$ 50°) with $F_o > 6\sigma(F_o)$ to yield $R = 5.89\%$ and $R_w = 6.57\%$.

(22) Crystal data for **3** ($C_{12}H_{15}O_5Cl_9$); monoclinic, $P2_1/n$; $a = 16.120$ (5), $b = 27.27$ (1), $c = 10.566$ (5) Å; $\beta = 98.14$ (3)°; $V = 4599$ (3) Å^3; $Z = 8$; D(calcd) = 1.613 g cm^{-3}. The 469 variables were refined with 3066 unique reflections (3° $< 2\theta <$ 45°) with $F_o > 3\sigma(F_o)$ to yield $R = 7.45\%$ and $R_w = 4.72\%$.

(23) Crystal data for **4** ($C_{14}H_{16}O_6Cl_{12}$); monoclinic, $P2_1/a$; $a = 16.795$ (5), $b = 10.952$ (4), $c = 16.587$ (6) Å; $\beta = 113.65$ (3)°; $V = 2795$ (2) Å^3; $Z = 4$; D(calcd) = 1.677 g cm^{-3}. The 353 variables were refined with 2290 unique reflections (3° $< 2\theta <$ 45°) with $F_o > 4\sigma(F_o)$ to yield $R = 4.29\%$ and $R_w = 3.43\%$.

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Estimation of the Free Volume in Polymers by Means of a Monte Carlo Technique

Introduction. During the past 30–40 years, a number of investigators have shown that the diffusion coefficients of small penetrant molecules in polymers, as well as the viscosity of polymers, can be correlated with the polymer free volume (or "empty volume").[1-14] A basic difficulty in such correlations lies in the estimation of the free volume. Bondi and Haward[15,16] have reviewed several definitions of the free volume of condensed phases. The evaluation of the free volume is based at the present time on indirect methods, in some cases involving adjustable parameters, because of the inherent difficulties involved in the determination of the free volume by experimental techniques.

The objective of this study was to develop a more rigorous theoretical method for determining the free volume available within polymers for the diffusion of small penetrant molecules. The method described here is based on the Monte Carlo simulation of the polymer microstructure, such as conceived by Suter and his co-workers.[17-19] Ultimately, this method, in conjunction with molecular dynamics, may allow the prediction of diffusion coefficients of gases in polymers from physicochemical properties of the polymers and of the penetrant gas molecules.

Simulation of Polymer Microstructure. A theoretical determination of the free volume requires an accurate description of the microscopic (atomistic) structure of the polymer. Suter and co-workers[17-19] have recently developed a methodology for obtaining a detailed structure of glassy polymers near their glass transition temperature. The model system was a cube with periodic boundaries, filled with segments from a single "parent" chain. Monte Carlo simulation of a single chain involves the generation of a chain conformation, i.e., a sequence of rotation angles.

The conformation statistics of unperturbed polymer chains are well described by the rotational isomeric state (RIS) theory.[20,21] This theory provides a priori probabilities $p_{\eta;i}$ (bond i in state η) and conditional probabilities $q_{\zeta\eta;i}$ (bond i in state η, given bond $i - 1$ in state ζ). The probabilities $p_{\eta;2}$ and $q_{\zeta\eta;i}$ define an "equivalent Markov process" for the Monte Carlo generation of chain conformations.

The structures obtained with chains generated by this scheme are characterized by excessively high energies. Hence, an initial structure is obtained by using a *modified* Markov process, based on the RIS theory, and incorporating long-range interactions. These interactions are modeled with a finite range modification of the Lennard-Jones potential function in which the potential tail is replaced by a quintic spline. The quintic spline is fitted between the interatomic distances of 1.45σ and 2.30σ, where σ is the interatomic distance where the Lennard-

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