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Schneider B., Stokr J., Doskocilova D., Kolinsky M., Sykora S., Lim D.

Journal of Polymer Science **C16**, 3891-3900 (1968)

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Abstract:

Infrared spectra of PVC in the region of C-Cl stretching vibrations and the β -proton band in NMR spectra of PVC are interpreted, based on the analysis of infrared and NMR spectra of pure stereoisomers of 2,4-dichloropentane and 2,4,6-trichloroheptane. For the interpretation of infrared spectra, only the presence of conformations found to be stable in model compounds has been assumed. The combined evidence of NMR and infrared investigations indicates that interpretations can be found to describe PVC samples prepared by radical polymerization at +50 °C, as atactic, and those prepared at -25 °C, as about 60 % syndiotactic.

Vibrational and NMR Spectra and Molecular Structure of Poly(vinyl Chloride)

B. SCHNEIDER, J. ŠTOKR, D. DOSKOČILOVÁ, M. KOLÍNSKÝ,
S. SÝKORA, and D. LÍM, *Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, Prague, Czechoslovakia*

Synopsis

Infrared spectra of PVC in the region of C—Cl stretching vibrations and the β proton band in NMR spectra of PVC are interpreted, based on the analysis of infrared and NMR spectra of pure stereoisomers of 2,4-dichloropentane and 2,4,6-trichloroheptane. For the interpretation of infrared spectra, only the presence of conformations found to be stable in model compounds has been assumed. The combined evidence of NMR and infrared investigations indicates that interpretations can be found to describe PVC samples prepared by radical polymerization at +50°C. as atactic, and those prepared at -25°C. as about 60% syndiotactic.

NMR and infrared spectra of PVC are expected to be sensitive to the degree of stereoregularity of the sample. However, a reliable quantitative tacticity determination could not be made from either of these methods, due to the lack of an adequate interpretation of the spectra. In NMR spectra, Johnsen's interpretation,¹ based on an assumed zero δ_{AB} shift between the two β protons in isotactic diads, lead to a content of about 60% syndiotactic units in PVC samples obtained by radical polymerization at room or slightly elevated temperature. Tincher's interpretation,² assuming a large δ_{AB} shift, described the same samples as only 45% syndiotactic. The latter interpretation seemed to be favored by the value $\delta_{AB} = 20$ cps found in meso-2,4-dichloropentane.^{3,4} Recently, the zero δ_{AB} interpretation seemed to be strongly supported by double resonance experiments^{5,6} and spectra of deuterated samples^{5,7} all of which exhibit only two prominent (although rather broad) singlets in the region of the methylene protons, and three lines in the region of the methine protons. Quantitative evaluation of the α and β proton bands in these spectra seemed to confirm prevalent syndiotacticity of conventional PVC.^{6,9} The small value of the δ_{AB} shift (10 cps) found in the isotactic trimer model⁸⁻¹⁰ made the concept of a negligible δ_{AB} shift in isotactic sequences of PVC acceptable, even though the large value of the δ_{AB} shift (20 cps) in the hetero-trimer⁸ as well as the shape of the bands in some of the decoupled spectra⁷ indicated that the situation might be much more complicated than has been assumed so far. The complexity of the problem was clearly demonstrated in a recent publication

by Yoshio,⁷ who proved the existence of a wide range of δ_{AB} shifts of β protons in different tetrad sequences of monomer units.

Infrared spectra of PVC depend primarily on the method of sample preparation and on the method of measurement. Differences are mainly observed in the region of C—Cl stretching vibrations. Even though this region has been very thoroughly studied and the frequency range of various conformational structures has been established fairly safely,¹¹⁻¹⁴ an adequate interpretation of the infrared spectrum of PVC in this region has not been presented so far. Conformations of the PVC chain have been determined by Krimm,¹⁵⁻¹⁸ based on C—Cl stretching frequencies measured in films, KBr pellets, and solution. These results have been criticized by Shimanouchi,⁹ who assumes the existence of some of the conformations proposed by Krimm to be improbable on steric grounds, based on an analysis of the conformational structures of the stereoisomers of 2,4-dichloropentane¹⁹ and 2,4,6-trichloroheptane.⁹ However, Shimanouchi does not present a satisfactory explanation of the spectral differences observed between spectra measured in the solid state and in solution. Based on an analysis of vibrational and NMR spectra of the pure stereoisomers of 2,4,6-trichloroheptane, we have attempted to explain some of these discrepancies.

Experimental

Sample I was polymerized at +60°C., using benzoyl peroxide as initiator. Sample II was polymerized at -25°C. and initiated by the system 0.5% H_2O_2 , 0.02% $\text{Fe}_2(\text{SO}_4)_3$, and 0.5% ascorbic acid. Details of the polymerization procedure are described elsewhere.²⁰

Infrared spectra were measured on the Zeiss UR 10 and on the Perkin-Elmer 421 spectrometers. NMR spectra were measured on the INM-3-60 spectrometer operating at 60 Mc. and equipped with a variable temperature head.

Infrared Spectra

Infrared spectra of PVC in solution exhibit in the region of C—Cl stretching vibrations two S_{HH} lines at 615 and 638 cm^{-1} , the former being the more intense (Fig. 1a and 2a). These two bands must correspond to all the conformational structures of PVC present in the solution with S_{HH} type* chlorine atoms. From infrared spectra of dimer¹⁹ and trimer⁸ model compounds, the C—Cl stretching vibration of one S_{HH} group is known to lie at 618 cm^{-1} , of two neighboring S_{HH} groups at 610 and 628 cm^{-1} , of three neighboring S_{HH} groups at 608 and 642 cm^{-1} ; the frequencies of four and more neighboring S_{HH} groups will probably not differ much from those of three S_{HH} groups.²¹ From conformational structures found in model compounds, an isolated S_{HH} group is expected to occur in the sequences *isi*, *issi* (*i* designating an isotactic and *s* a syndiotactic diad of mono-

* In the symbols S_{HH} and S_{CH} , the *S* corresponds to a secondary Cl frequency and the *H* and *C* to hydrogen or carbon atoms *trans* to the Cl atom.

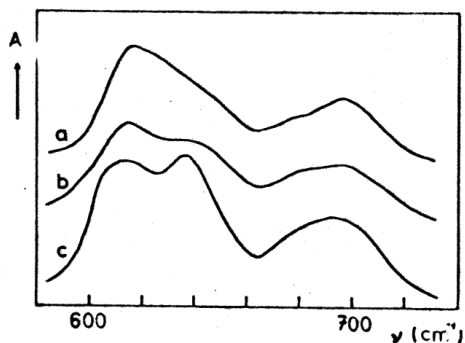


Fig. 1. Infrared spectra of PVC sample I: (a) 10% solution in cyclohexanone; (b) KBr pellet; (c) film evaporated from cyclohexanone solution, washed with CS_2 .

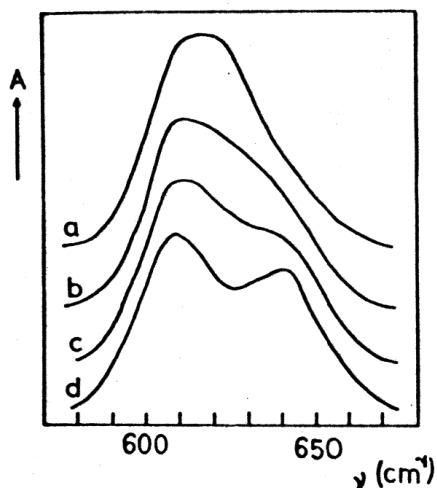


Fig. 2. Expected shape of the S_{HH} band of PVC in solution for various tacticity values. Constructed from the data of Table I for the half-band width 24 cm.^{-1} : (a) 40% s ; (b) 50% s ; (c) 60% s ; (d) 70% s .

mer units, respectively) and in isotactic sequences in the transition point between a right-handed and left-handed helix. In each isotactic sequence only one such transition point can occur. A number of k neighboring S_{HH} groups can arise from sequences of the type $is_{k-1}i$, is_ki , and $is_{k+1}i$. The contents of S_{HH} groups correspond to the content of s diads in the molecule, assuming an equal probability of right-handed and left-handed helices in the isotactic portion of the polymer, and a low content of the folded TTGG form in the syndiotactic part.

The probability of various isolated syndiotactic and isotactic sequences in a statistical PVC chain is given by the expression $s_n = \sigma^2(1 - \sigma)^n$, $i_n = (1 - \sigma)^2\sigma^n$, where σ is the abundance of an isotactic diad and n is the number of s or i diads in the respective sequence. The expected infrared frequencies and intensities, for sequence distributions calculated by means of the above relation, and using frequency and absorbance values found in dimer and trimer model compounds, are given in Table I. With the aid of this table, the expected spectrum in the region of S_{HH} vibrations may be

TABLE I
Expected Intensities of C—Cl Stretching Bands for
Different Tacticity Values of PVC in Solution

Tacticity, % <i>s</i>	608 cm. ⁻¹ ^a	618 cm. ⁻¹ ^b	628 cm. ⁻¹ ^c	642 cm. ⁻¹ ^d	688 cm. ⁻¹ ^e
70	32	6	4.5	27.5	20
60	25	10	6	19	27
50	18.5	12	6	12.5	33
40	13	14	6	7	40

^a Antisymmetrical C—Cl stretching vibrations of two and more neighboring S_{HH} groups.

^b C—Cl stretching vibration of one S_{HH} group.

^c Symmetrical C—Cl stretching vibration of two neighboring S_{HH} groups.

^d Symmetrical C—Cl stretching vibration of three and more S_{HH} groups.

^e C—Cl stretching vibrations of all S_{CH} groups.

constructed. The form of the expected spectra for several typical cases is shown in Figure 2. A comparison of these theoretical spectra with the experimental spectra of PVC measured in solution indicates that the shape of the S_{HH} band of sample I (Fig. 1a) is comparable to the theoretical spectrum of atactic PVC, and that of sample II (Fig. 3a) resembles the theoretical 60% syndiotactic curve.

The broad band appearing for a solution of PVC at 690 cm.⁻¹ corresponds to S_{CH} type C—Cl stretching vibrations. The spectra of dimer and trimer model compounds indicate that all S_{CH} type stretching vibrations in isotactic sequences lie in this region. In addition to isotactic sequences, S_{CH} type vibrations may also occur in transition units between syndiotactic and isotactic sequences. From the spectrum of the hetero-trimer it is known that the position of this frequency coincides with that of purely isotactic sequences. So far we have not been able to prove the presence of S_{CH} type vibrations corresponding to the folded TTGG conformation of syndiotactic sequences in spectra of model compounds; consequently their location in the spectra of PVC cannot be determined. The content of S_{CH} chlorine atoms may therefore be regarded as corresponding to that of

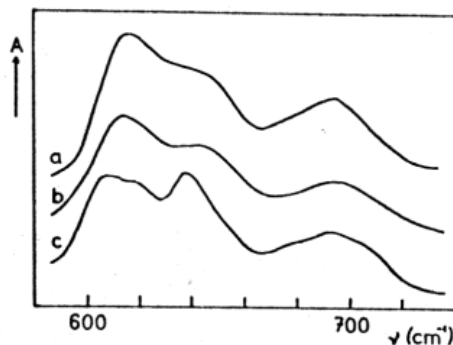


Fig. 3. Infrared spectra of PVC sample II: (a) 10% solution in cyclohexanone; (b) KBr pellet; (c) film evaporated from cyclohexanone solution, washed with CS_2 .

isotactic diads, assuming a low content of the folded TTGG form in syndiotactic sequences.

The integral absorbances of S_{HH} and S_{CH} stretching vibrations determined experimentally in dimer and trimer model compounds are shown in Table II. Even though the content of the folded TTGG form as determined from NMR spectra differs somewhat in model compounds, the ratio of S_{HH} and S_{CH} absorbances remains roughly constant and in the liquid state is equal to ca. 1.5. The tacticity of PVC therefore can also be estimated from the intensity of S_{HH} and S_{CH} bands with this absorbance ratio. The values obtained in this way are in reasonable agreement with those determined from the shape of the S_{HH} band.

TABLE II
Ratio of S_{HH} and S_{CH} Absorbances in Model Compounds

Isomer	1 ^c	2 ^d	3 ^e
iso-2,4-DP ^a	1.5	1	1.5
iso-2,4,6-TCH ^b	0.8	0.5	1.6
hetero-2,4,6-TCH ^b	2.7	2	1.4

^a 2,4-Dichloropentane.

^b 2,4,6-Trichloroheptane.

^c Experimental ratio of S_{HH} : S_{CH} integral absorbances.

^d Ratio of S_{HH} : S_{CH} groups in the molecule.

^e Ratio of S_{HH} : S_{CH} molar integral absorbances.

In infrared spectra of PVC measured in KBr pellets or in films, the intensity of the 638 cm.^{-1} band increases, the band at 615 cm.^{-1} splits into two¹⁹ and the ratio of the integrated absorbances of the S_{HH} and S_{CH} bands increases. The changes observed in the region of the S_{HH} band are similar to those observed upon crystallization of the syndiotactic dimer and trimer.⁸ In these model compounds the ratio of integral absorbances of the symmetrical and antisymmetrical band in the liquid state is equal to 1.0, in the crystalline state it increases to 1.8. A sharpening of both bands is observed upon crystallization. Using an absorbance ratio modified in this respect, the theoretical spectrum of solid atactic PVC has been constructed (Fig. 4). This spectrum agrees well with the experimental spectrum of solid PVC sample I (Fig. 1c). In the composite spectrum the reason of the splitting of the 615 cm.^{-1} band and of the increased intensity of the 638 cm.^{-1} band is clearly demonstrated, and no conformation changes accompanying the liquid-solid transition need be assumed. Spectral changes accompanying the liquid-solid transition in polymers with different tacticity can be explained similarly.

Infrared spectra of PVC measured in the solid and liquid state exhibit also a different ratio of integral intensities of the S_{HH} and S_{CH} bands; this could be due either to the presence of the folded TTGG form, or to a difference of absorbances of the S_{HH} and S_{CH} bands in the solid and liquid states. In model compounds, a band of the folded form could not be

detected around 690 cm^{-1} . A major contribution of the folded form to the spectral changes observed in the polymer therefore seems improbable. The absorbances of the S_{CH} band in the solid state could also not be measured in model compounds. The large changes of absorbances of S_{HH} bands accompanying the solid-liquid transition lead us to the assumption that the changes of the $S_{\text{HH}}-S_{\text{CH}}$ intensity ratio accompanying this transition are also caused by changes of absorbances.

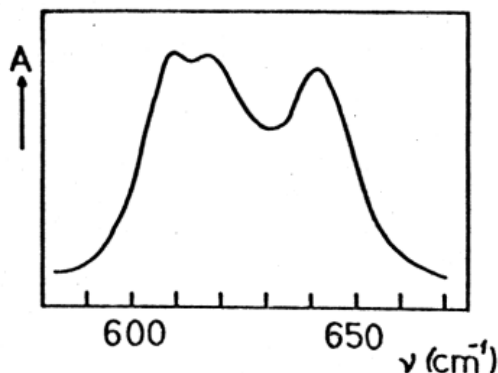


Fig. 4. Expected shape of the S_{HH} band of solid state PVC. Constructed for the half-band width 12 cm^{-1} .

Differences in infrared spectra of PVC measured in KBr pellet and in form of film are probably also due to differences in the degree of order. The same might be true of temperature changes observed in the spectra of solutions of some slightly soluble samples of PVC.

NMR Spectra

Chemical shifts of α and β protons for various configurations of monomer units and their sequences can be calculated by considering the contributions of dispersion interactions and the electrical field of the molecule, following the principles outlined by Buckingham²² and by Schaefer, Reynolds, and Yonemoto.²³ The details of the procedure will be given elsewhere.²⁴ From the results of such calculations, combined with experimental evidence from the trimer model compounds, some conclusions concerning the interpretation of NMR spectra of PVC may be drawn.

α -Proton Band. α -Protons in *ss* and *si* units are fully described by the triad configuration and are therefore expected to produce two quintets in the NMR spectrum. Their calculated shifts agree with the current assignment^{5,6} with $\tau = 5.44$ for the *ss* and $\tau = 5.55$ for the *si* triad, respectively. In *ii* units, however, triad configuration is not sufficient for determining the chemical shift, and pentad configurations have to be considered. The chemical shift is expected to decrease in the series *siis*, *siii*, *iiii*, the *siis* and *siii* pentads being centered around $\tau = 5.77$. A contribution of the *iiii* sequence to the absorption of *si* units cannot be excluded. This effect would evidently decrease syndiotacticity values cal-

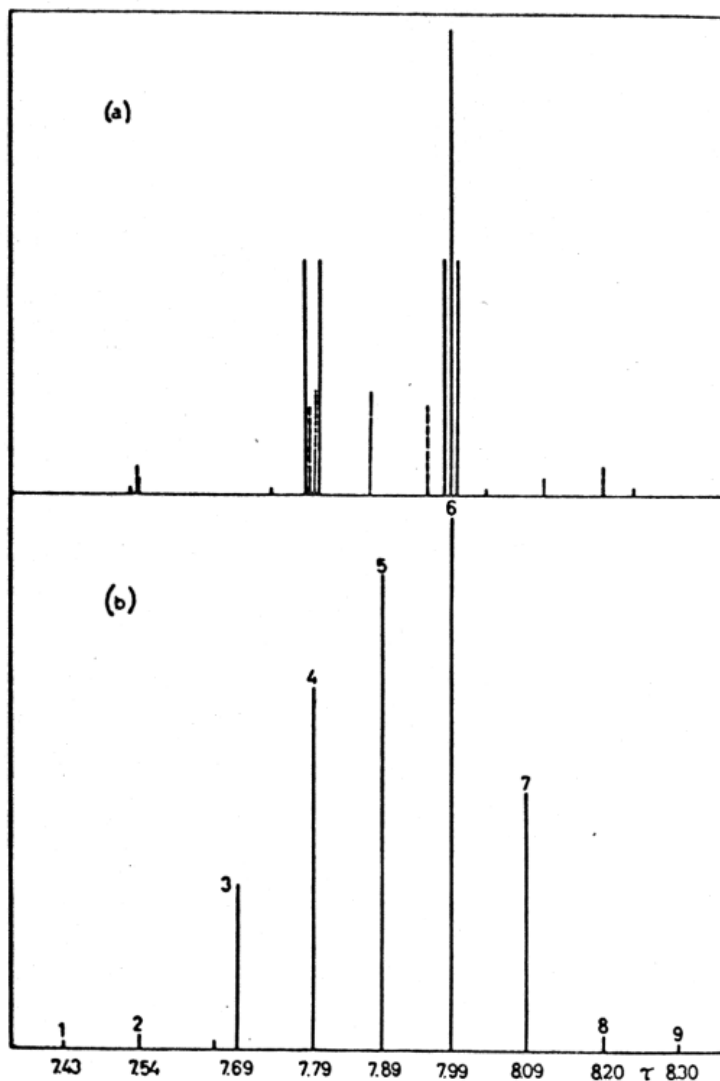


Fig. 5. Assignment of the β proton band of atactic PVC: (a) without α proton interaction: full lines at $\tau = 7.99$ —*sss*, *isi*, *iss* tetrads; full lines at $\tau = 7.79$ —*sii* tetrad, dotted and dashed quartets—*iii* and *sis* tetrads; (b) composite pattern with α proton interaction.

culated from the relative intensity of α proton peaks according to the current assignment.^{6,25}

β Proton Band. The shape of the β proton band is determined by the δ_{AB} shifts of the methylene protons in various tetrad sequences, and by the location of the centers of the corresponding multiplets. δ_{AB} shifts of the two syndiotactic tetrads, *sss* and *isi*, must be zero because of symmetry. The δ_{AB} shift of the *iss* tetrad is expected to be equal to 6 cps, but due to the large value of the geminal coupling constant and to the large half-band width of the polymer spectrum, it may also be regarded as effectively zero. The same is true of the isotactic *sii* tetrad, with an expected δ_{AB} shift of 10 cps or less. From double resonance experiments, band centers of all the three *s* tetrads, and of the *sii* tetrad are known to lie in the vicinity of

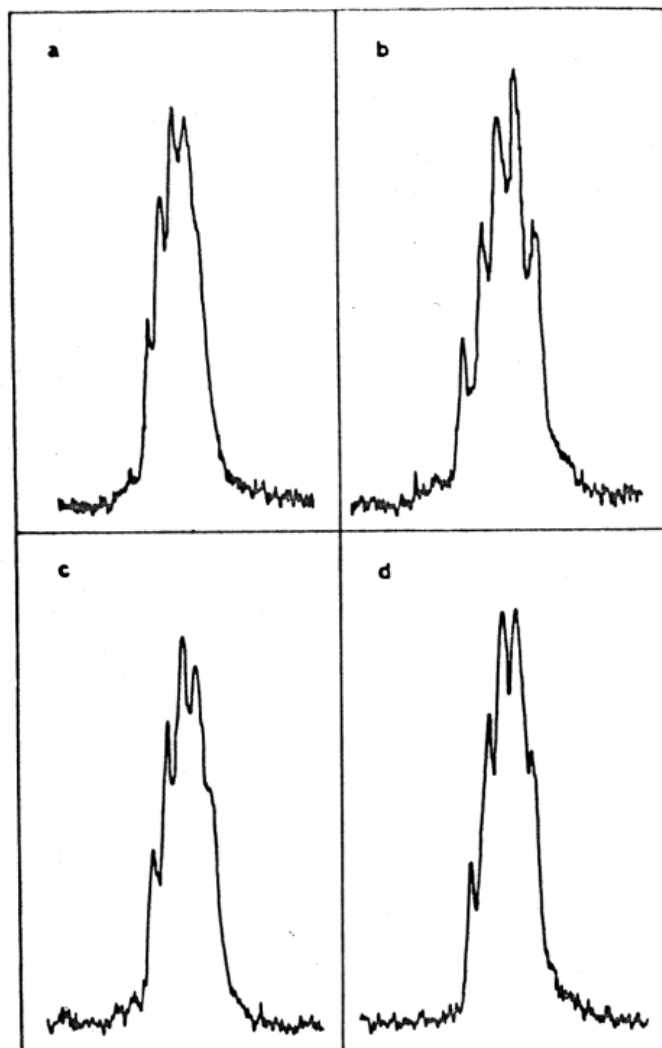


Fig. 6. NMR spectra of the β proton band of PVC, 10% solution in chlorobenzene: (a) sample II, 120°C.; (b) sample II, 160°C.; (c) sample I, 120°C.; (d) sample I, 160°C.

$\tau = 7.99$ and 7.79 , respectively. The δ_{AB} shift of the *sis* tetrad is expected to vary from ca. 21 to ca. 17 cps in the temperature range 20–130°C. The value of the δ_{AB} shift of the *iii* tetrad cannot be checked by analogy with the trimer model, but calculations indicate this value to be in excess of 14 cps. The possibility of the occurrence of δ_{AB} shifts of this order of magnitude in some types of isotactic units has been clearly demonstrated by Yoshino.⁷ The actual position of the band centers of the *sis* and *iii* tetrads is not known. Although in relatively good qualitative agreement with the calculated values, the data obtained by Yoshino⁷ on partly deuterated low molecular weight polymers in chloroform or dichloroethane solution at room temperature cannot be directly transferred to conventional samples dissolved in chlorobenzene at 170°C., as the chemical shifts of various proton groups, e.g., of PVC dimer and trimer model compounds, are known to be strongly temperature- and solvent-dependent. Nevertheless, the actual

values must be compatible with the observed five-line pattern of conventional PVC samples, as well as with the appearance of decoupled spectra, and there are not many alternatives for satisfying this condition. A plausible assignment for a 50% syndiotactic statistical polymer is shown in Figure 5. In Johnsen's two triplet interpretation, this spectrum would be termed as 60% syndiotactic. The assignment of the *sis* and *iii* quartets might be interchanged without essentially affecting the shape of the resulting spectra for tacticity values more than 40% syndiotactic. An experimental verification of this assignment would require the measurement of NMR spectra of a series of samples with a large range of tacticity values. Quantitative evaluation of such spectra is complicated due to the unequal and temperature dependent half-band width of syndiotactic and isotactic bands (Fig. 6). An investigation of these effects is presently in progress and will be the subject of a subsequent communication.

Conclusions

So far it has been generally accepted that PVC samples polymerized by a radical mechanism at about +50°C. are approximately 60% syndiotactic, with samples polymerized at very low temperatures reaching up to 70% syndiotacticity. The combined evidence of the above described NMR and infrared investigations indicates that well-founded interpretations can be found describing the +50°C. samples as atactic, and samples polymerized at -25°C. as about 60% syndiotactic. From the viewpoint of reaction kinetics of polymer formation, these tacticity values are in better agreement with the small tacticity differences observed in samples prepared at widely differing temperatures. In terms of the proposed interpretation, infrared spectra of PVC can be described on the basis of sterically favored conformations found in trimer model compounds, and the consideration of sterically improbable conformers thus seems unnecessary.

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