Physicochemical Characterization of Polyvinyl Chloride). III. Stereoregularity

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SUMMARY

Tacticity of poly(vinyl chloride) (PVC) prepared in the 55 to 160°C range has been determined by the temperature dependence of the intensity ratios of the IR absorption bands at 1434 and 1428 cm^{-1}. Syndiotactic content of these materials varied from 56 to 51%, and the energy difference between two such confirmations ($E_{GG} - E_{TT}$) was found to vary from 2.0 to 2.9 kcal/mole. Differences between activation enthalpies ($\Delta\Delta S_p\ddagger$) for the isotactic and syndiotactic kinetic modes of vinyl chloride addition to the growing polymer chain, and the thermodynamic energy difference between heats of formation ($\Delta\Delta H_p^{\circ}$) of two such stereopolymers, were found to be as follows:

$$\Delta\Delta H_p\ddagger = 0.56 \pm 0.05 \text{ kcal/mole}$$

$$\Delta\Delta S_p\ddagger = 1.2 \pm 0.1 \text{ eu}$$

$$\Delta\Delta H_p^{\circ} = 1.4 \pm 0.13 \text{ kcal/mole}$$

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These results are discussed in the light of published data on PVC tacticity which was obtained by other IR and NMR methods.

INTRODUCTION

The possibility of stereoregulation exists in those polymers which contain asymetric or pseudoasymetic atoms in the backbone chain, and the stereo-specific configurations along such chains are determined during the course of the propagation steps of polymerization [1, 2]. In vinyl type chains these configurations have been (mainly) identified as isotactic and syndio-tactic with the latter predominating in low temperature preparations. X-ray diffraction, NMR, and IR methods have been employed to determine these structures. X-ray diffraction technique, which was the first one to be em-ployed for poly(vinyl chloride) (PVC), showed an identity period of 5.1 Å, characteristic of the unit cell of the syndiotactic planar zigzag chain [3]. But PVC is poorly crystalline and sharp fiber diagrams are not obtained; therefore, x-ray diffraction is not suitable for the tacticity detemination of this polymer. NMR and IR methods, which yield semiquantitative and quan-titative results, have both been widely used for this purpose.

Spectroscopic determination of PVC tacticity has led to the examination of low molecular weight model compounds of this polymer. Two unit mod-els, meso- and dl-2,4-dichloropentanes (DCP), and three unit models, dia-stereoisomeric 2,4,6-trichloroheptanes (TCH), which give well-resolved spectra, have been investigated. NMR spectra examination of these model compounds was done to establish the equivalence or nonequivalence of the methylene protons adjoining asymetric centers [4]. A careful interpretation of the β-CH_2 protons coupled with Bernoulli statistics has yielded some useful data on the tacticity of this polymer [5, 6]. Conformational isomers have also helped in the understanding of the polymer IR spectra, and it has been established that of the three regular structures of PVC, the extended syndio-tactic form dominates [7]. The tacticity-temperature relationship for this polymer has been investigated by several groups of workers, and results have been obtained by the analysis of absorption bands in the 600-700 cm^{-1} (C-Cl stretching bands) and at 1434 and 1428 cm^{-1} (CH_2 bending modes).

Most of the PVC samples used thus far for vibrational spectroscopy studies were prepared at $\leqslant 55°C$; therefore, little data is available in the literature on polymers prepared beyond this temperature. This paper deals with the IR (1434 and 1428 cm^{-1}) determination of the tacticity of PVC prepared at $\geqslant 55°C$. The results obtained are discussed in the light of IR and NMR data published for this polymer.

EXPERIMENTAL

PVC samples used in this study were research samples prepared at temperatures from 55° to 160°C. Samples A-D were prepared at 55°C with varying molecular weights, and Samples E-I were prepared in the 90-160°C range. The IR spectra of these samples were recorded on THF cast films and in solution on a Perkin-Elmer 521 spectrophotometer. Temperature dependence of the intensity ratios of the 1434 and 1428 cm^{-1} absorption bands (assigned to the bending modes of "CH_2" groups) was utilized in the determination of S, the syndiotactic portion of the polymer chain, and $\Delta E(E_{GG} - E_{TT})$, the energy difference between two such confirmations. Numerical values were obtained by using Eq. (1) [8].

$$S = \frac{1 + \exp(-\Delta E/RT)}{1 + \lambda} \tag{1}$$

where $\lambda = D_{1424}/D_{1428}$, was obtained at 300 and 400 k. (Here S is the same as σ in the original equation.)

The maximum absorbance of these bands was obtained by the usual base line method, and I, the isotactic portion of the polymer chain, was calculated as

$$I = 1 - S$$

RESULTS AND DISCUSSION

In Fig. 1 temperature effects on the CH_2 bending modes of syndiotactic and atactic PVC samples are shown, and the tacticity data for all the samples studied are given in Table 1. The 55° preparations (commercial materials) were found to be 56% syndiotactic. For PVC samples prepared in the 50-60°C temperature range, other groups of workers have reported the following values of S: 72% [9], 55% [10], and 54% [2] as determined by IR, and 65% [11], 60% [12], 55% [6, 13], and 51% [14] as determined by NMR. The variation seen in these results is due to the different methods used in the spectral analysis. It is generally agreed, though, that commercial PVC samples are approximately 55% syndiotactic. The value of S for the 90 and 100° material was determined to be 54%. For materials prepared between 80-100°C, the following data for S have been reported: 51% [2] by IR, and

54% [6] and 53% [14] by NMR. PVC samples prepared at 120 and 130°
were observed to have 52% syndiotactic content. By NMR a 120° prep-
paration has been reported to contain 51% [14] syndiotactic content, but in
the same investigation a 60° preparation was found to have the same S
value, too. Atactic or random PVC may be prepared at 160°C.

ΔE values reported in this paper correspond to the energy difference be-
tween GG and TT conformations of the dl-DCP. For this molecule the GG
form has not been detected by IR, indicating that the TT form is the ener-
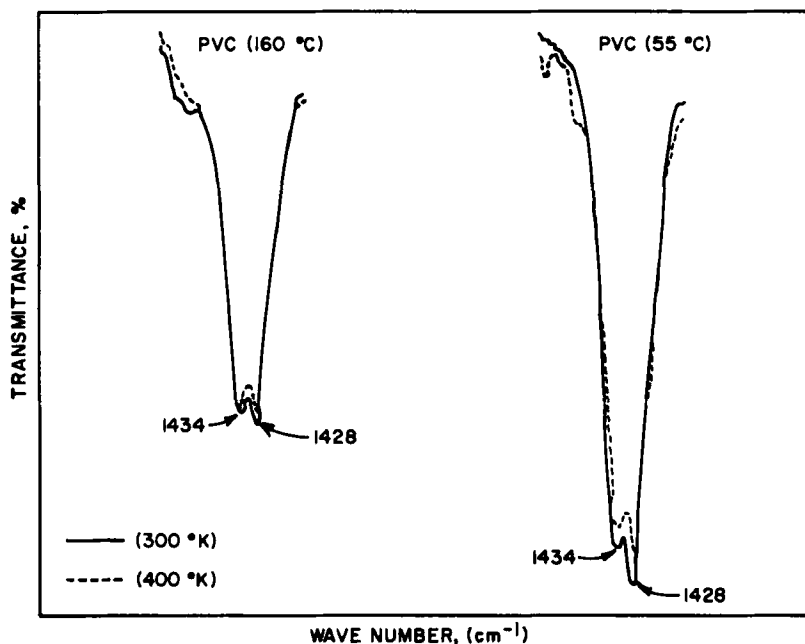

Fig. 1. Temperature effect on the absorption bands of the CH_2 bending
modes of syndiotactic (55°C) and atactic (160°C) PVC samples.

getically favorable conformation. The energy difference between these two
rotational isomers has been estimated as 1.7-2.3 kcal/mole [15], which may
be compared with 2.0-2.9 kcal/mole as found in this investigation for highly
syndiotactic to practically atactic samples. Both the theoretical and exper-
imental ΔE values are not large enough to account for the absence of the GG
form in the IR spectrum of dl-DCP.

Table 1. Tacticity Data for PVC

Sample identification	Temperature of polymerization ($°C$)	$[\eta]$ $25°C$ in THF (dl/g)	ΔE (kcal/mole)	S (Diad) (%)	I (Diad) (%)
A[a]	55	1.135	2.49 (2.29)	56 (56)	44
B	55	0.993	2.28	55	45
C	55	0.940	1.98	56	44
D	55	0.825	2.00	56	44
E	90	0.438	2.33	54	46
F[a]	100	0.390	2.38 (2.44)	54 (54)	46
G	120	0.250	2.68	52	48
H	130	0.145	2.61	52	48
I	160	0.090	2.87	51	49

[a]Measured in film and in solution, and the values within parenthesis correspond to solution measurements. Solution measurement conditions: solvent, 1, 1, 2, 2-tetrachloroethane; concentration, 25 g/liter.

In order to make sure that the tacticity data obtained were free from sample crystallinity effects, the following measurements were made on Samples A and F. S was measured in the film form and in solution and was found to be the same in both media; the ratio of S_{HH} and S_{CH} ($A_{600-640}/A_{690}$) C-Cl stretching bands was obtained in the film and in solution and was found to be 1.7 in both phases; and the density of the films was measured to be 1.404 g/cc. The amorphous density of PVC has been estimated as 1.41 g/cc [16].

If one now combines the tacticity results reported in this paper with those reported by others [6], it is found that over a temperature range of 238° (- 78° to +160°C) the syndiotactic content in PVC changes from 63 to 51%. This is hardly enough to account for the changes in physical properties, particularly crystallinity, that accompany such a temperature change. Perhaps a combination of structural factors, i.e., tacticity, branching, and molecular weight, may be responsible for the changes in physical properties observed.

To obtain kinetic and thermodynamic data for the stereochemical modes of vinyl chloride addition to the growing PVC chain, the following expressions were used:

The differential kinetic activation enthalpies and entropies for the propagation step of vinyl chloride polymerization were calculated from Eq. (2) and (3) [17]:

$$\Delta(\Delta H_p\ddagger) = R \; \partial \; \ln (I/1 - I)/(1/T) \tag{2}$$

$$\Delta(\Delta S_p\ddagger) = R \; \partial \; \ln (I/1 - I) + \Delta(\Delta H_p\ddagger)/T \tag{3}$$

In Fig. 2, ln (I/1 - I) has been plotted as a function of (1/T), and from the slope of the resulting line $\Delta(\Delta H_p\ddagger)$ was calculated. This was then substituted in Eq. (3) to obtain $\Delta(\Delta S_p\ddagger)$. The following values were obtained:

$$\Delta(\Delta H_p\ddagger) = 0.56 \pm 0.05 \text{ kcal/mole}$$
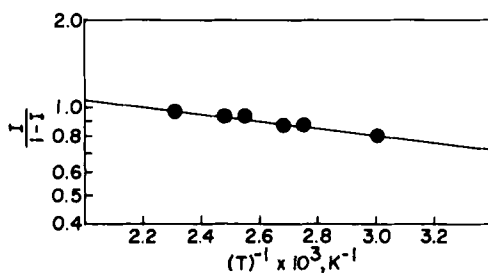
$$\Delta(\Delta S_p\ddagger) = 1.2 \pm 0.10 \text{ eu}$$

Fig. 2. Plot of (I/1 - I) as a function of $(T)^{-1}$ for PVC samples prepared at different temperatures.

The thermodynamic energy difference between the heats of formation of the two steropolymers of vinyl chloride was obtained from Eq. (4). This equation expresses the linear relationship that exists between the thermodynamic ($\Delta H°$) and kinetic ($\Delta H\ddagger$) enthalpies of polymerization [18]:

$$\Delta\Delta H\ddagger(\Delta E\ddagger) = \alpha(\Delta\Delta H°) \tag{4}$$

Substituting for $\Delta(\Delta H\ddagger)$, as previously calculated, and putting $\alpha = 0.4$ in Eq. (4), one obtains

$$\Delta(\Delta H°) = 1.4 \pm 0.13 \text{ kcal/mole}$$

Fordham et al. [1, 19] have calculated $\Delta(\Delta H^\circ) = 1.4 - 1.9$ kcal/mole and $\Delta(\Delta H_p\ddagger) = 0.6$ kcal/mole. On the other hand, Bovey et al. [6] have reported $\Delta(\Delta H_p\ddagger) = 0.31 \pm 0.02$ kcal/mole and $\Delta(\Delta S_p\ddagger) = 0.6 \pm 0.1$ eu.

Two observations may be made from these results: 1) that the free radical polymerization of vinyl chloride is not entirely enthalpy controlled, and 2) that the data reported here agree better with Fordham et al.'s data than with Bovey et al.'s results. It must, however, be borne in mind that Bovey et al. have used a much wider range of temperature in the study of tacticity-temperature relationship, and also that their data are based on triad (i, h, s) analysis. It is also important to point out here that discrepancy in S values is more apparent in PVC samples prepared at low temperatures.

ACKNOWLEDGMENTS

Note Added in Proof: Since this paper was submitted, several papers on PVC tacticity have appeared in the literature. The suitability of 1434 and 1428 cm^{-1} bands for tacticity measurement seems to be equivocal. The structure of PVC is still not fully established. Vibrational spectroscopy (IR and Raman) favor an extended predominantly syndiotactic conformation while NMR spectroscopy indicates nearly atactic conformation with a tendency towards syndiotactic structures at lower temperatures of polymerization (F. A. Bovey and A. R. Shultz, *Amer. Chem. Soc. Polym. Preprints,* 12(2), 25 (1971).

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