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Interrelations between constitution, configuration and conformation in chlorinated polyalkenamers

1. The polymer components*

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SUMMARY

FTIR-Spectra of poly-1,2-dichloroalkanes are reported as a function of the constitution and of the configuration of the subunits and of the temperature. The intensity of the C-Cl-vibrations of the head-to-head chlorinated polymers with variable tail length seems to be sensitive to changes in configuration and conformation and also to changes in the surrounding of the absorbing group. We conclude from these experiments that an intensity ratio of the different conformers corresponds to every degree of stereoregularity, which is overlapped with the influence of polarity on the absorbance. Assuming that the conformational equilibrium in chlorinated polymers is insensitive against minor disturbances - swelling or blending - the IR-intensity offers information concerning placement and degree of polymer contacts and interactions in polymer blends as well as in plasticized polymers.

INTRODUCTION

1,2 dichloro polymers exhibit a center of high polarity and conformational restriction in their head group and a nonpolar part in their tail. This may provoke polar interactions of intra- and intermolecular type, as well as plasticizing effects. Chlorinated polyalkenamers with head-to-head isomers (HH), threo and erythro, show up different conformations (Fig. 1). Thus, they allow the study of the influence of configuration on conformation.

^{13}C-NMR studies on such polymers and on their low molecular weigt analogs have elucidated interrelations between configuration and conformation, by measurements in solution, under slow and fast exchange conditions (1).

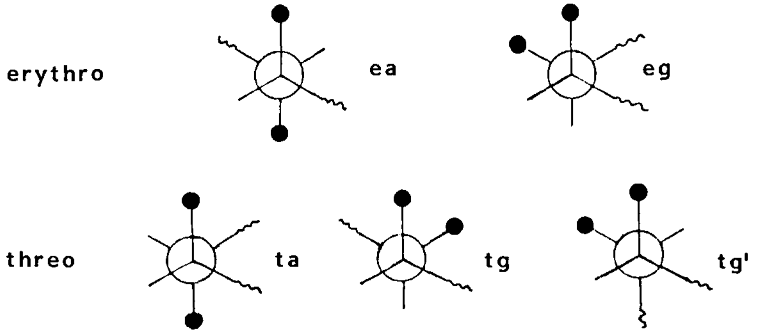

Fig. 1: Configurations and head conformations

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In the IR regime slow exchange occurs exclusively. Thus, this method may be capable to analyze the overlapping effects of conformation and packing.

For head-to-tail polyvinylchloride FTIR-spectroscopy has shown that the influences of stereochemistry and plasticizing may be detected by the conformation sensitive bands (2). Reported infrared spectra of chlorinated cis and trans polybutadiene and their low molecular weight models exhibit significant differences in conformational vibrations (3,4).

In the present investigation the intensity ratios of C-Cl vibrations in polymers listed in Table I are examined with respect to configuration and orientation of the head groups.

EXPERIMENTAL

The series of polymers with the structure $-CHCl-CHCl-(CH_2)_n-$, n=2,3,5,6, was obtained by ionic addition chlorination of polyalkenamers with different cis/trans ratios. Commercially nonavailabe polyolefins have been polymerized by metathesis polymerization. Used catalysts for stereoselective polymerization are $WCl_6/Si(C_3H_5)_4$ and $WCl_6/Al(i\text{-}Bu)_3$, as reported in literature (5,6).

A typical reaction for chlorinating cis polybutadiene (PB) may be described:

1.5 g of high cis PB (Hüls CB10) was dissolved in 500 ml of freshly distilled $CHCl_3$. A small amount of $AlCl_3$ or $FeCl_3$ anhydr. was added, and the mixture was cooled in the dark to temperatures below 0° C. Then gaseous chlorine was bubbled slowly into the solution until it turns yellow. Excess chlorine was removed by nitrogen gas, and after filtration the polymer was precipitated in 1 l methanol. Yield >95%. The high trans PB had to be chlorinated at higher T in suspension. The polymers are given in Table I.

Table I: Characterization of polymers

Polymer	% threo	T_g /K	T_m /K	M_n /g mol^{-1}
PDCTM	>95	330	amorphous	360.000 b)
	80			20.000 b)
	50	320		-
	20	-		30.000 b)
	<5	315		360.000 b)
PDCPM	>95	306		180.000 b)
				626.000 b)
	75	-		-
	25	285		60.000 b)
PDCHM	85	-	-	-
	75	268	330-350 **	25.000 a)
	60	257	-	36.000 a)
			-	17.000 a)
PDCOM	86	-	340-360 **	-
	80	265	-	43.000 b)
	60	-	-	
	40	-	-	
	20	240	315, 310-330 **	38.000 b)

PDC: Polydichloro- TM: -tetramethylene PM: -pentamethylene
HM: -heptamethylene OM: -octamethylene
a) GPC b) osmosis * not determined ** from polarization microscopy

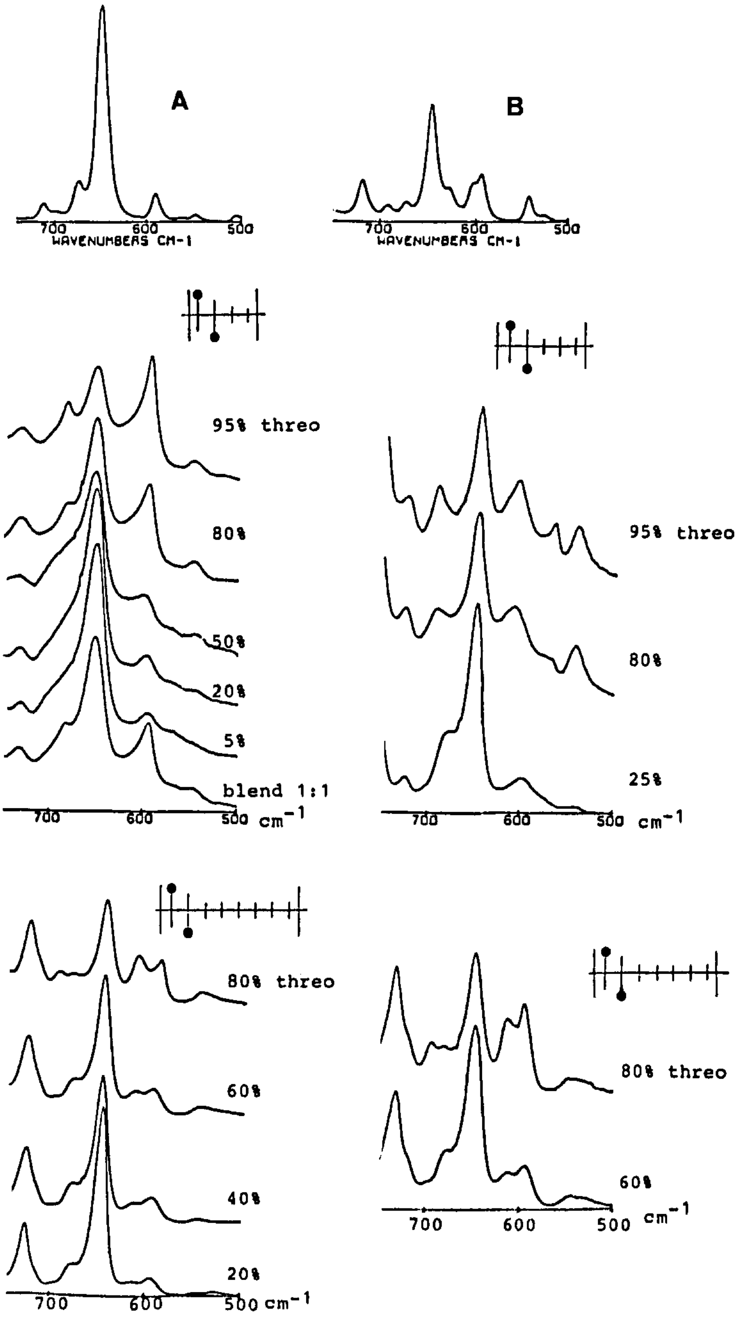

Fig. 2: C-Cl-vibrations of chlorinated polyalkenamers depending on configuration
vibration at 650 cm^{-1}: Cl-anti, at 600 cm^{-1}: Cl-gauche
A: meso 2,3-dichlorohexane, B: d,l 2,3-dichlorohexane

FTIR-spectra were obtained on a Bruker IFS 88 FTIR-spectrometer with 50 or 100 scans with automatic baseline correction.

Band intensity calculation was done by a program which simulates IR-bands with harmonic oszillator functions or Gauss and Lorentz curves (7,8).

The samples were prepared by casting films from THF solutions on KBr windows at RT. The samples (15-25 µ thickness) were dried in vacuo for 12h. In the stretching experiment the samples have been crosslinked by γ-rays (.1- .5 mrds) in the presence of 5% divinylbenzene. They have been stretched at $T = T_g + 40^o$ C and quenched to room temperature.

RESULTS AND DISCUSSION

1) Configuration and Conformation

The similiarity of spectra of HH-polymers with different tail length and some related model compounds is evidenced by Fig. 2. From secondary monochloroalkanes to 1,2 dichloroalkanes the C-Cl vibrations change from 615 cm^{-1} and 660 cm^{-1} to 595 cm^{-1} and 650 cm^{-1}, resp. In meso and d, l 2,3-dichlorobutane the 650 cm^{-1} absorption is assigned to the ea (Cl-anti) conformation in the meso (erythro) and ta (Cl-anti) and tg' (Cl-gauche) conformation in the d,l (threo) form (9). Stokr et al. (10) assigned 650 cm-1 to ta (Cl anti) conformation and 595 cm-1 to tg (Cl gauche) conformation, as well as Hörhold et al. (3). We followed this interpretation. The figure shows the C-Cl vibrations of the polymers depending on the configuration in the head group in comparison to their monomer unit model 3,4-dichlorohexane.

In these spectra it can bee seen, that erythro polymers exhibit a higher intensity ratio in the 650 cm^{-1}/595 cm^{-1} vibrations than threo samples. Assuming that the amount of threo all gauche (tg') conformation is neglegible, the intensity ratio 650 cm^{-1}/595 cm^{-1} or 650 cm^{-1}/613 cm^{-1} is connected with the conformational equilibrium for a given head group. This indicates a higher Cl-gauche content in threo arrangements. This ratio is plotted versus the threo content in Figure 4.

In a compatible 1:1 blend of high threo and high erythro polymer the intensity distribution on conformational bands differs from that of the 50% threo sample. This indicates that conformational equilibrium of one head is affected by the conformational situation of the neighbours.

2) Temperature Dependence

In threo samples the Cl-gauche absorption decreases with increasing temperature (Fig. 3). In t-dichlorooctamethylene and t-dichloroheptamethylene, sudden breakdown of the 595 cm^{-1} absorption occurs at relatively low temeratures, perhaps due to opening of hydrogen bond like interactions between chlorine and methine hydrogens in parallel to conformational transitions. From molecular mechanics calculations for glassy PVC (11) this kind of structural order resulted, It is argued that this is caused by dipole interaction. This can be supported for our samples by DSC diagrams with broad peaks and also by anisotropic behaviour with a broad melting region in the polarization microscope. In amorphous erythro polymers the temperature dependence is very low. In semi-crystalline e-dichlorooctamethylene a decrease of all anti structures is found in the 648 cm^{-1} absorption around the melting point at 30°C (DSC). The absorption change with temperature may be insufficient to characterize conformational transitions, because the temperature dependence of the extinction coefficients is yet unknown.

From these results it can be concluded, that in the solid and in the molten state polymer-polymer interactions have great influence on IR absorption in the C-Cl region and may overtone effects of conformational transitions. It can be seen, that IR intensities in the glass and melt react sensitively on changes in intermolecular contacts. Fig. 4 summarizes the results of intensity calculation for the different polymers with respect to stereochemistry.

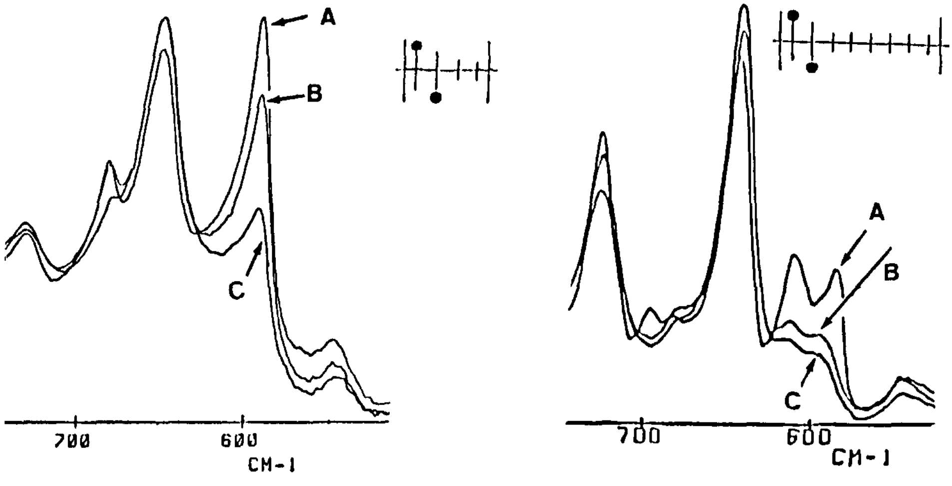

Fig. 3: Temperature dependence of conformational bands of t-PDCTM and t-PDCOM, A: RT, B: 60 °C, C: 120 °C

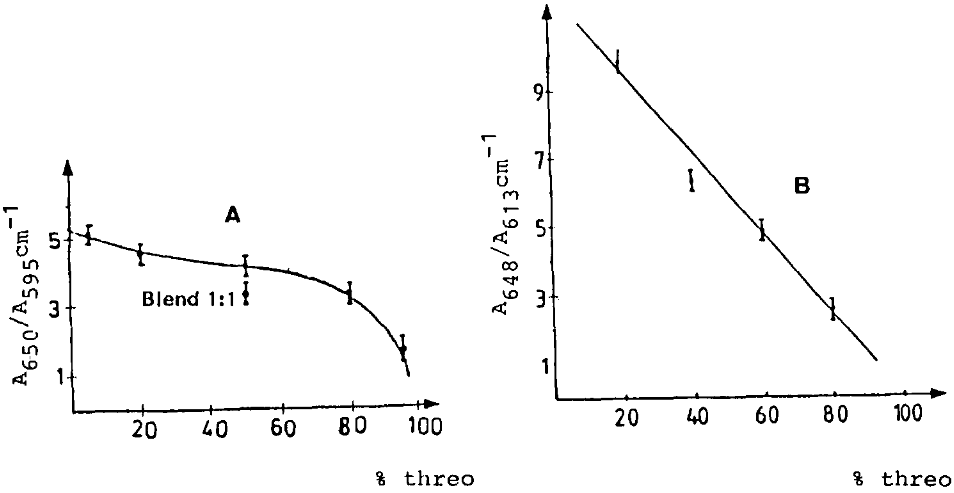

Fig. 4: Intensity ratio of Cl-anti : Cl- gauche vibration and threo content for A: PDCTM, B: PDCOM

3) Orientational Behaviour

IR-dichroism of C-Cl absorption at a stretching degree of 100% is shown in Fig. 6 for three samples. The dichroitic ratio

$$D = A_{\parallel} / A_{\perp} \qquad (1)$$

of the 650 cm^{-1} and 595 cm^{-1} absorption, calculated from band areas, is a function of taillength and head configuration. Samples with long, flexibe tails show lower dichroitic ratios than polymers of higher degree of chlorination. Low chlorinated samples are above T_g at measuring temperature (RT). Viscoelastic relaxation or the imperfect network may be the reason for the small D-values, which increase at higher stretching ratios. D increases with the content threo and in t-dichlorotetra- and -pentamethylene D is different for the anti and gauche conformations (Fig. 5). In erythro

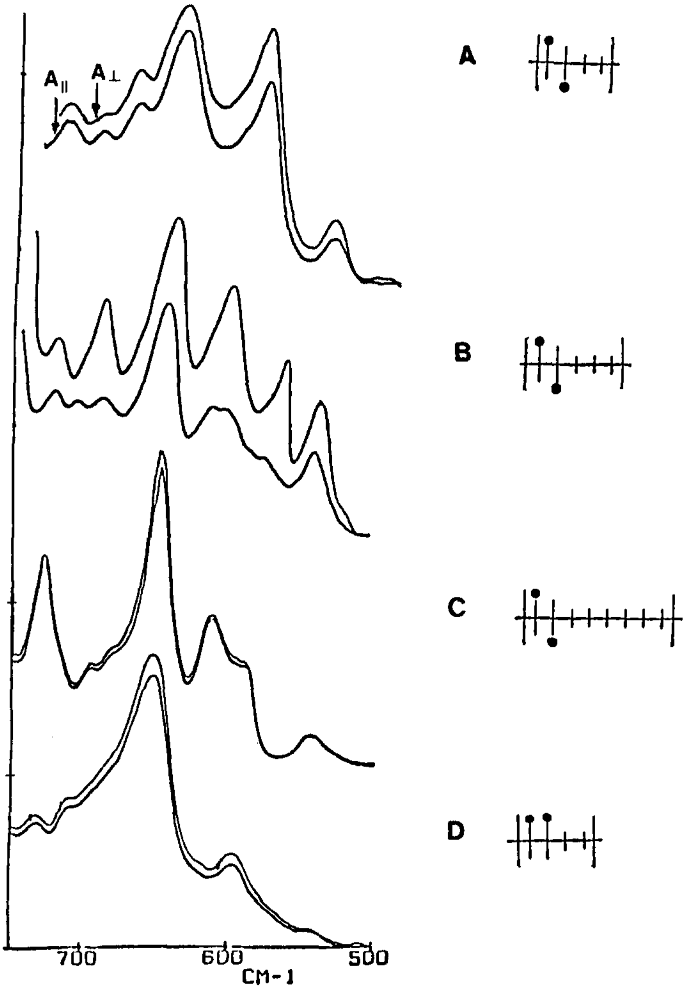

Fig. 5: IR-dichroism of conformation-bands of
A: t-PDCTM, B: t-PDCPM, C: e-PDCOM, D: e-PDCTM

samples no dichroism was detected at 100% stretching degree. One origin of the degree of D is the direction of the C-Cl vibrational transitions moment (angle α) to the chain axis for different conformers. For perfect orientation of all chains the expression for D becomes:

$$D = 2 \cot^2 \alpha \qquad (2)$$

Evaluation of α was done with a program calculating the direction of the C-Cl bond moment with regard to the chain axis for the head group (12). Assuming that the transition moment is identical to the bond moment, the angle α (Fig. 6) was calculated for ideal conformational angles for gauche and anti (180°, 60°) at the 2,3-dichlorobutane unit. Chain axis was the line between C_1- and C_4-atom. Tab. 2 shows the angle α, which is similiar for the ta and tg conformation but different for the tg' isomer. From that identical orientationation for all segments is predicted. In the stretching experiment one may suppose, that all chains are oriented in an average angle Θ around the stretching direction (Fig. 6). Eq. 2 is then modified:

$$D = \frac{2 \cot^2\alpha \cos^2\Theta + \sin^2\Theta}{\cot^2\alpha \sin^2\Theta + (1 + \cos^2\Theta)/2} \qquad (3)$$

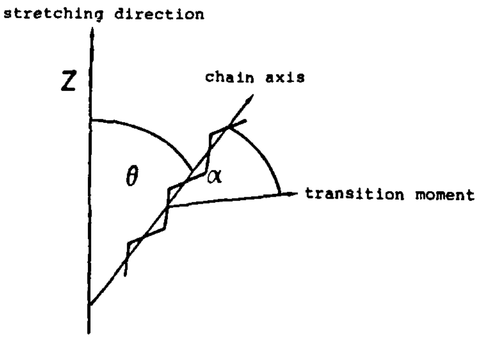

Fig. 6: Geometry of the orientation

In dichlorotetra- and -pentamethylenes different Θ-orientations resulted for a gauche and an anti head segment acording to eq. (3) (Table II).

Table II: IR-dichroism of chlorinated polymers

Polymer	D (ta)	D (tg)	α_{calc}	Θ
threo PDCTM	.89	.67	80°, 81° ta 81°, 82° tg 57°, 58° tg'	51.4° ta 44.4° tg
threo PDCPM	.76	.47		47.3° ta 36.9° tg
erythro PDCTM	0	0		
erythro PDCOM	0	0		

We conclude, that different mechanisms might be possible for orientation of polar and nonpolar segments as the concequence of cooperative processes. These investigations are just at their beginning, they have to be supported by theoretical considerations and by better improved capabilities for measurements under continious stretching in order to prevent viscoelastic flow.

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