

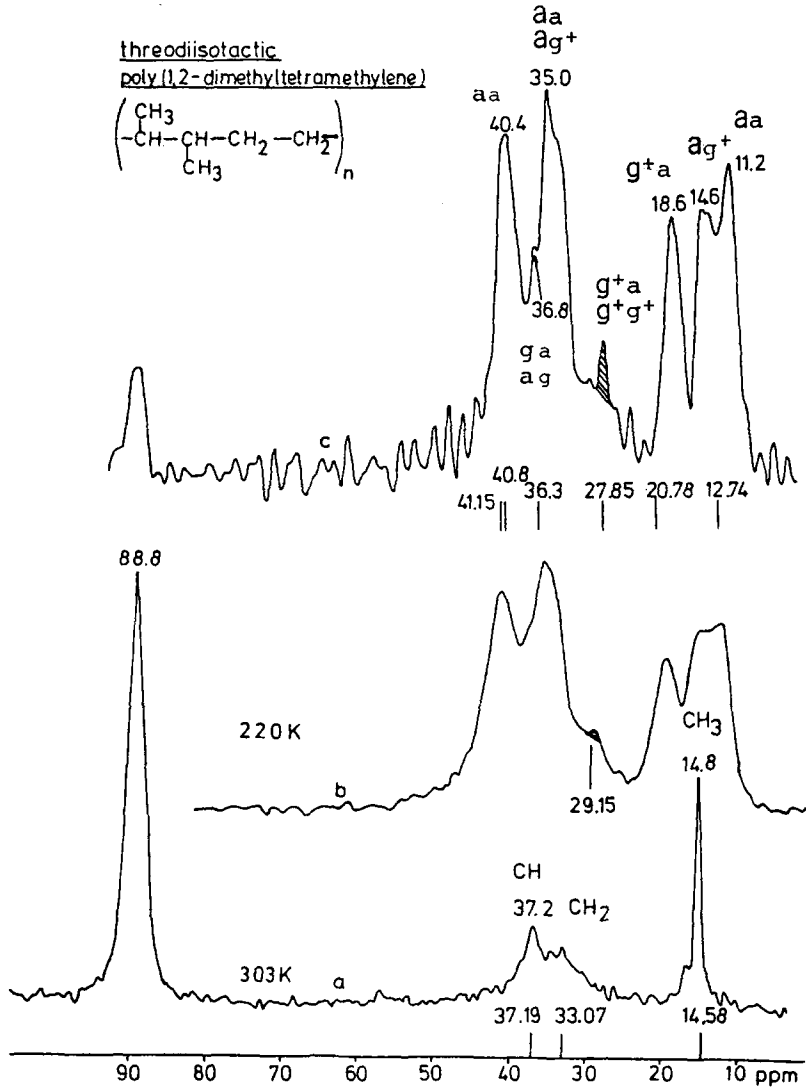
**Micro- and Macroconformation of Macromolecules****10. Conformational Analysis of Amorphous Polymers in the Glassy State by Magic Angle Spinning  $^{13}\text{C}$ -NMR****W. Gronski<sup>1</sup>, A. Hasenhindl<sup>1</sup>, H.H. Limbach<sup>2</sup>, M. Möller<sup>1</sup> and H.-J. Cantow<sup>1</sup>**<sup>1</sup> Institut für Makromolekulare Chemie der Universität Freiburg, Hermann-Staudinger-Haus, Stefan-Meier-Straße 31, D-7800 Freiburg i. Br., Federal Republic of Germany<sup>2</sup> Institut für Physikalische Chemie der Universität Freiburg, Albertstraße 21, D-7800 Freiburg i. Br., Federal Republic of Germany***Herrn Prof. Dr. O. Kratky zu seinem 80. Geburtstag gewidmet***SUMMARY

The first results are reported about the conformational analysis of an amorphous polymer in the glassy state by means of proton enhanced variable-temperature magic angle spinning  $^{13}\text{C}$  NMR experiments. In amorphous threodiiisotactic poly(1,2-dimethyltetramethylene) at 220 K different conformational diads could be resolved and assigned. From the spectrum of the glassy polymer the shift increment associated with a conformational change of main chain bonds from anti to gauche is determined. In addition the populations of the conformations of CH-CH bonds and of CH-CH-CH<sub>2</sub> bond pairs of poly(1,2-dimethyltetramethylene)s are determined in the glassy state and energy differences between these conformations are estimated.

INTRODUCTION

In preceding papers of this series the conformation of semicrystalline erythrodiisotactic poly(1,2-dimethyltetramethylene) in the crystalline phase <sup>1)</sup> and of crystalline cyclotetracosane <sup>2)</sup> could be determined by  $^{13}\text{C}$  NMR PE-MAS experiments at room temperature. The conformation in the crystalline phase of the polymer was proven to be  $G^+aaaG^-aaaG^+ \dots$  (big letters for the CH-CH, medium for the CH-CH<sub>2</sub> and small letters for the CH<sub>2</sub>-CH<sub>2</sub> bonds, resp.) in agreement with X-ray analysis. As in polyethylene <sup>3)</sup> the signals of the crystalline and amorphous phases are separated by several ppm. Since the measurements could be performed only at room temperature above  $T_g$  it was not possible to resolve individual conformations because of the rapid interchange between the rotamers on the NMR time scale. The same was found to be true for crystalline cyclotetracosane where the observation of a single sharp signal at room temperature indicated the existence of a highly mobile phase characterized by rapid transitions between anti and gauche conformers of the single bonds. This finding has been verified by DSC and by dielectric measurements <sup>4)</sup>.

After these results it appeared to be tempting to develop a Magic Angle device operating at sufficiently low temperature in order to freeze the mobility of the amorphous or of highly mobile crystalline phases and to detect individual conformations. In view of the large residual line width of  $\sim 50$ - $100$  Hz in  $^{13}\text{C}$  high resolution solid state spectra of amorphous polymers below  $T_g$  <sup>5)</sup> the resolution of conformations in the glassy state seemed to be prohibitive at first sight. Again the ditactic poly(1,2-dimethyltetramethylene)s represent a unique system for conformational studies of glassy polymers.  $^{13}\text{C}$  NMR experiments with low molecular weight analogues, meso and d,1 4,5-dimethyloctane <sup>6)</sup> and 3,4-dimethylhexane <sup>6)</sup> at low temperatures under slow exchange conditions for the CH-CH bond have shown that the chemical shift differences of methylene and methyl carbon atoms can be expected to be large enough to resolve different conformations in the glassy state.

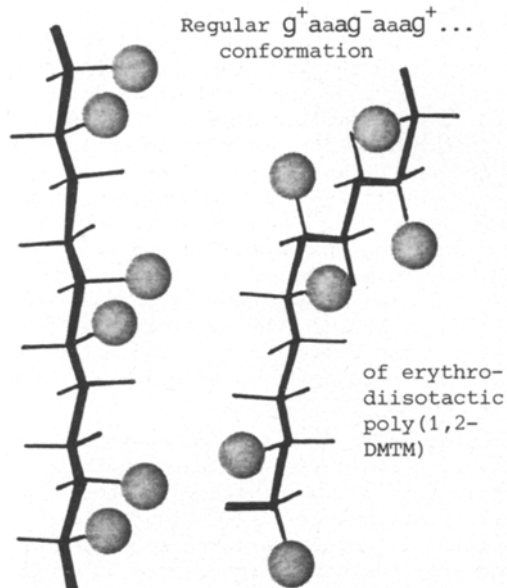


**Figure 1:** Solid state PE-MAS  $^{13}\text{C}$  NMR spectra of amorphous threodiisotactic poly(1,2-dimethyltetramethylene). a): Spectrum at 303 K, 75.42 MHz, chemical shifts of the polymer in  $\text{CDCl}_3$  solution are marked by vertical lines. b): Spectrum at 220 K, 25.14 MHz, the vertical line marks the calculated position of the methylene carbon atom in the  $g^+a(g^+g^+)$  conformation of the  $\text{CH}-\text{CH}$  and  $\text{CH}_2-\text{CH}$  bonds (see text). c): resolution enhanced spectrum b) with assignment of conformations (big letters for the  $\text{CH}-\text{CH}$ , medium for the  $\text{CH}-\text{CH}_2$  and small letters for the  $\text{CH}_2-\text{CH}_2$  bonds), the vertical lines mark the chemical shifts of equivalent carbon atoms in the  $g^+aaag^-aaag^+\dots$  conformation of the crystalline phase of erythrodiisotactic poly(1,2-dimethyltetramethylene). All chemical shifts refer to TMS.

## EXPERIMENTS AND DISCUSSION

The conformational studies in the glassy state were carried out with threodiisotactic poly(1,2-dimethyltetramethylene). The polymer was obtained by hydrogenation of threodiisotactic trans-2,5-poly(trans-trans-hexadiene-2,4) which was polymerized by Ziegler Natta catalysis with  $\text{Co}(\text{aca})_2/\text{AlClEt}_2$  as catalysator<sup>7)</sup>. The polymer does not crystallize under normal conditions and shows a glass transition at 240 K. The variable-temperature  $^{13}\text{C}$  NMR PE-MAS experiments were performed on a BRUKER CXP 100 NMR spectrometer at 25.14 MHz by use of a modified BRUKER MAS probehead. The temperature control is achieved by using a predried and precooled stream of air as propellant. Technical details will be described elsewhere. Figure 1a shows the solid state spectrum of threodiisotactic poly(1,2-dimethyltetramethylene) at 303 K and 75.42 MHz. Figure 1b shows the spectrum of the same polymer at 220 K and 25.14 MHz and Figure 1c the spectrum of Figure 1b after application of the resolution enhancement routine. The chemical shifts of the sample and the Delrin signal of the rotor in the spectrum of Figure 1a are given with respect to TMS, the originally Adamantane related solid state chemical shifts being converted to TMS as described earlier<sup>2)</sup>. In this report the the chemical shifts of the measurements at 220 K have to be considered as approximate only since no standard was used in this experiment and the chemical shifts in Figure 1c were determined with respect to the maximum of the Delrin signal.

The conformational influence on the chemical shift of a given carbon atom is effective through the so called  $\gamma$ -effect, i. e. the relative position of the carbon atoms in  $\gamma$ -position with respect to the observed carbon atom<sup>8)</sup>. The relative position of the  $\gamma$ -carbon atoms depends on the rotational angles of the bonds next but one on either side of the observed carbon atom  $\text{C}^*$  according to the scheme  $\text{C}_\gamma\text{-C-C-C}^*$ . If we assume that the rotational isomeric state model with three discrete conformations, anti(a) and gauche<sup>±</sup>(g<sup>±</sup>), for each bond is realistic also for polymer chains in the glassy state there



Regular  $\text{g}^+\text{aaa g}^-\text{aaa g}^+\dots$  conformation of threodiisotactic poly(1,2-DMTM)

Figure 2

are two magnetically distinguishable  $\gamma$ -positions, the anti and the gauche position. The replacement of an anti by a gauche position always leads to an upfield shift depending on the kind of carbon atom observed and the number of  $\gamma$ -carbon atoms involved as will be shown below. Therefore the assignment in Figure 1c is given in terms of conformations of the bonds next but one on either side of the observed carbon atom, i. e. in terms of diads of conformations of single bonds. The chemical shifts of the carbon atoms in some of the conformational diads can be estimated by comparison with equivalent carbon atoms of the conformation of erythrodiisotactic poly(1,2-dimethyltetramethylene) in the crystalline phase shown in Figure 2 together with the lowest energy conformation of threodiisotactic poly(1,2

dimethyltetramethylene). These estimated shifts are marked by vertical lines in Figure 1c.

The starting point of the assignment is the observation of the splitting of the methyl resonance in three signals. In principle there are 9 conformational pairs of the CH-CH and CH-CH<sub>2</sub> bonds the rotational angles of which influence the chemical shift of the methyl carbon atoms by  $\gamma$ -interactions between either two methyl groups or a methyl and a methylene group. Some of these conformations, however, have a rather low statistical weight. The  $g^-$  conformation of the CH-CH bond for instance involves energetically unfavourable synaxial positions of the two methyl groups. In fact near  $T_g$ , i. e. near the freezing temperature of the conformations, the fraction of the  $g^-$  conformation is estimated to be ca 0.08 only in contrast to the energetically most favourable  $a$  and  $g^+$  conformations occurring with probabilities of 0.63 and 0.29 respectively. This estimate is made on the basis of <sup>13</sup>C measurements of d,l 4,5-dimethyloctane under slow exchange conditions of the CH-CH bond at the coalescence temperature and on the basis of temperature dependent measurements of the chemical shifts of meso 4,5-dimethylcyclohexane and the corresponding erythrodiisotactic poly(1,2-dimethyltetramethylene) <sup>6</sup>). By the former measurements the energy difference between the  $g^+$  and the  $a$  conformation is estimated to be 1.6 kJ/mol whereas the latter indicate an energy difference of ca 4 kJ/mol between the  $g^-$  and the  $a$  conformation. Even if the  $g^-$  conformation would occur with higher frequency  $g^-$  could probably not be resolved from  $g^+$  because both conformations are subject to the same  $\gamma$ -effects if the adjacent CH-CH<sub>2</sub> bond is in a or  $g^+$  the CH-CH bond being in  $g^+$  or if the CH-CH<sub>2</sub> bond is in a or  $g^-$  in the case of the  $g^-$  conformation of the CH-CH bond. The conformations  $g^-$  and  $g^+$  are again unfavourable in the two respective cases because of the pentane effect. If we consider the more frequent  $g^+$  conformation of the CH-CH bond we can specify the conformation of the adjacent CH-CH<sub>2</sub> bond to be mainly anti because the  $g^+g^+$  pair is unfavourized in consequence of synaxial positions of a methyl group and a methylene group on the other side of the CH-CH bond. According to these considerations a methyl resonance should be present the major intensity of which has to be attributed to  $g^+a$  diads of the CH-CH-CH<sub>2</sub> segment. This resonance should be shifted distinctly downfield with respect to the resonances of conformational diads in which the CH-CH bond is in the preferred  $a$  conformation because the position of a  $\gamma$ -CH<sub>3</sub> group changes from anti to gauche for the reverse conformational change of the CH-CH bond. Therefore the methyl resonance at 18.6 ppm has to be assigned to the  $g^+a$  conformation and the two upfield resonances at 14.6 and 11.2 ppm to conformations of the CH-CH-CH<sub>2</sub> bond pair in which the CH-CH bond is in the preferred anti conformation. The question which conformations of the CH-CH<sub>2</sub> bond have to be assigned to these signals can be answered by inspection of molecular models showing that essentially only the pairs  $aa$  and  $ag^+$  will occur because the remaining  $ag^-$  again involves a synaxial four bond interaction between methyl and methylene groups.  $aa$  must appear upfield of  $ag^+$  because the  $\gamma$ -methylene groups change from anti for  $ag^+$  to gauche for  $aa$ .

The chemical shifts of the methyl carbon atoms in  $g^+a$  and  $aa$  conformations can be compared to the positions of equivalent methyl carbon atoms in the regular  $g^+aaa^-aaa^+...$  conformation of the crystalline phase of erythrodiisotactic poly(1,2-dimethyltetramethylene) <sup>1</sup>) (s. Figure 2). In contrast to the threodiisotactic polymer all conformational sequences of this polymer are asymmetric. Consequently two methyl resonances at 20.78 and 12.74 ppm have been observed for the crystalline phase of the erythrodiisotactic polymer. In the approximation of steric equivalence of CH<sub>2</sub> and

CH<sub>3</sub> groups at a distance of three bonds from the observed methyl group the low field methyl carbon atom of the erythrodiisotactic polymer is equivalent to the methyl carbon atom in the G<sup>+</sup>a conformation of the threodiisotactic polymer while the high field methyl carbon atom of the erythrodiisotactic polymer is equivalent to the methyl group of the aa diad of the polymer under investigation (compare Figure 2 concerning the latter statement). The predicted positions (vertical lines in Figure 1c) are shifted towards lower field by ca 1.5- 2 ppm with respect to the experimentally observed positions. The difference is of similar magnitude as the chemical shift difference of 2.16 ppm between the two stereoregular polymers in solution<sup>6</sup>). The upfield shift of the aa with respect to the G<sup>+</sup>a resonance by -7.4 ppm is similar to the -8.0 ppm separation between the corresponding resonances of the crystalline phase of the erythrodiisotactic polymer indicating that the reason of this shift is essentially of the same origin in both cases, namely the substitution of one γ-carbon atom in anti and the other in gauche position by two γ-carbon atoms in gauche position.

Important information can also be obtained from the signal intensities. For a given carbon atom the cross polarization relaxation times in different frozen conformations in the glassy state can be assumed to be identical. Therefore the relative intensities are equal to the relative frequencies of the corresponding conformational diads. At present the temperature cannot be located exactly at which the thermal equilibrium is frozen which determines the the observed conformational populations below T<sub>g</sub>. This temperature will probably depend on the thermal history, e. g. velocity of cooling, pressure etc., as in the case of macroscopic observables as volume or enthalpy. In a first approximation it may be assumed that this temperature is identical with the quasistatic T<sub>g</sub> at 240 K as measured by DSC. From the relative intensities of the G<sup>+</sup>a, ag<sup>+</sup> and aa resonances of the methyl carbon atoms (0.27, 0.27 and 0.46 resp. as determined by a Dupont curve resolver) the energy difference between the G<sup>+</sup> and the a conformation of the CH-CH bonds is estimated to be 2kJ/mol. The value of 1.6 kJ/mol derived from <sup>13</sup>C measurements of the low molecular weight analogue d,l 4,5-dimethyloctane<sup>6</sup>) has also to be considered as approximate only because it relies on the estimation of the chemical shift of the G<sup>+</sup> conformer which can only be obtained indirectly from the slow exchange spectrum of meso 4,5-dimethyloctane<sup>6</sup>). The determination of the energy difference from PE MAS measurements in the glassy state has the advantage that the populations of both conformations can be directly determined for the polymer. From the relative intensities of the ag<sup>+</sup> and aa methyl carbon signals one can also estimate the energy difference between the corresponding conformational diads to be 1.1 kJ/mol. This information cannot be obtained from NMR measurements of low molecular weight analogues in solution because it is not possible to reach slow exchange conditions for the conformations of the CH-CH<sub>2</sub> bonds at magnetic fields presently available. With the estimated conformational energy differences one can calculate the chemical shift of the methyl carbon atom of the solid state spectrum at 303 K of Figure 1a. At this temperature all conformations are exchanging fast and therefore the chemical shift of the methyl carbon atom is given by

$$\delta = \sum \delta_{ij} p_{ij} \quad (1)$$

where p<sub>ij</sub> denotes the probability of the conformational diad ij at 303 K and δ<sub>ij</sub> the chemical shift of this diad in the glassy state. The calculation yields 14.3 ppm in reasonable agreement with the experimentally observed position at 14.8 ppm.

The conformational influence on the chemical shift of the methine carbon

atoms mainly arises from rotations about the  $\text{CH}_2\text{-CH}_2$  and  $\text{CH-CH}_2$  bonds next but one on either side of the methine group. The methine carbon atoms in the regular  $\text{a}^+\text{aaa}\text{a}^+\dots$  conformation of the threodiisotactic polymer are equivalent to the methine carbon atoms at 40.8 ppm of the regular  $\text{G}^+\text{aaa}\text{G}^+\text{aaa}\text{G}^+\dots$  conformation of crystalline erythrodiisotactic poly(1,2-dimethyltetramethylene) (s. Figure 2). The equivalence exists with respect to the  $\gamma$ -interactions and also with respect to symmetry at least in the range of two bonds on either side of the observed methine carbon atom. The same equivalence is valid between the low field methine group of the regular crystalline conformation of the erythrodiisotactic polymer at 41.15 ppm and the corresponding regular  $\text{G}^+\text{aaa}\text{G}^+\dots$  conformation of the threodiisotactic polymer. Both methine resonances of the erythrodiisotactic system are near the resonance at 40.4 ppm of the threodiisotactic polymer in the glassy state. Therefore this resonance must be attributed to the methine carbon atom. The small difference of ca 0.3 ppm between the predicted regular  $\text{a}^+\text{aaa}\text{a}^+\dots$  and  $\text{G}^+\text{aaa}\text{G}^+\dots$  conformations of the threodiisotactic polymer demonstrates that rotations about the  $\text{CH-CH}$  bond adjacent to the observed methine group have only a minor effect on the chemical shift of this group. It can be assumed that rotations about the other adjacent bond, the  $\text{CH-CH}_2$  bond, has a similar small influence only. These arguments suggest that the resonance at 40.4 ppm has to be attributed mainly to the  $\text{aa}$  conformation of the  $\text{CH-CH}_2$  and  $\text{CH}_2\text{-CH}_2$  bonds next but one on either side of the observed methine carbon atom. If the anti conformation of one of these bonds is transformed to gauche an upfield shift results which can be estimated to be ca-3.4 ppm from the difference between the positions of the methyl resonances corresponding to  $\text{aa}$  and  $\text{ag}^+$  conformations of the  $\text{CH-CH-CH}_2$  bonds. In fact, there is a small but reproducible shoulder -3.6 ppm upfield from the main methine resonance at 36.8 ppm which is assigned to  $\text{ga}$  and  $\text{ag}$  pairs. The  $\text{gg}(\text{gg})$  diads which should be shifted further upfield cannot be located with certainty.

The conformational contribution to the chemical shift of the methylene carbon atoms essentially depends on the rotational angles about the  $\text{CH-CH}$  and the  $\text{CH}_2\text{-CH}$  bonds next but one on either side of the observed methylene carbon atom. In the case of an  $\text{aa}$  conformation of these bonds the methylene groups are equivalent with respect to the  $\gamma$ -interactions to the low field methylene group at 36.3 ppm of the crystalline conformation of erythrodiisotactic poly(1,2-dimethyltetramethylene). The methylene groups, however, are not equivalent by symmetry in the same range of three bonds due to the configurational difference of the neighbouring methine carbon atom. Nevertheless, the assignment of methylene carbon atoms with the  $\text{CH-CH}$  and  $\text{CH}_2\text{-CH}$  bonds being in the  $\text{aa}$  conformation to the signal with greatest intensity at 35.0 ppm is unambiguous. The transformation of the anti conformation of the  $\text{CH}_2\text{-CH}$  bond to  $\text{g}^+$  has only the effect of exchanging the positions of the  $\gamma$ -carbon atoms of the chain backbone and the nearest methyl group leaving the total  $\gamma$ -contribution to the chemical shift of the methylene carbon atom constant. Therefore also  $\text{ag}^+$  is assigned to the same signal. The upfield shoulder of this signal could be due either to the latter conformation or to the  $\text{gg}(\text{gg})$  resonance of the methine carbon atoms (s. above). The transformation of the conformation of the  $\text{CH-CH}$  bond from  $\text{a}$  to  $\text{g}^+$  brings both the  $\gamma$ -carbon atom of the chain backbone and the  $\gamma$ -methyl group in gauche position in contrast to the initial situation where only the  $\gamma$ -methyl group is in gauche position. This conformational change induces an upfield shift and therefore the  $\text{G}^+\text{a}$  and  $\text{G}^+\text{g}^+$  conformations have to be assigned to the broad signal in Figure 1b centered at about 29.15 ppm (the hatched peaks are not reproducible). The position was calculated from the position of the  $\text{aa}(\text{ag}^+)$  resonance of the methylene carbon atoms at

35.0 ppm in the glassy state and the methylene chemical shift in solution at 33.07 ppm by means of Eq. 1 applied to the methylene carbon resonance. The calculated position is near the position of the equivalent high field methylene carbon atom of crystalline erythrodiisotactic poly(1,2-dimethyl-tetramethylene) at 27.85 ppm(s. Figure 1).

Although the absolute positions partly deviate considerably from the predicted chemical shifts the overall spectral pattern, particularly the splitting of the methylene resonance, is reproduced satisfactorily. The reasons for the discrepancies between the chemical shifts of equivalent conformations of the erythro- and threodiisotactic polymer can mainly be explained by an unsufficient steric equivalence and partly by the ill defined positions of the resonances in the glassy state. Therefore one cannot establish if also chain packing differences between the crystalline and amorphous polymer account for part of the observed deviations. Effects of chain packing on the  $^{13}\text{C}$  solid state isotropic chemical shifts have been shown to exist by an investigation of n-alkanes in various crystallographic forms 9).

In the case of the methyl carbon atom where the chemical shifts are well defined in the glassy state one can also compare chemical shift differences associated with conformational changes of the CH-CH bond with corresponding shift differences between the two nonequivalent methyl carbon atoms in the gauche conformation of the CH-CH bond of meso 4,5-dimethyloctane in solution under slow exchange conditions 6). In either case the same change of the  $\gamma$ -interactions occur, namely the replacement of two  $\gamma$ -carbon atoms, one in anti and the other in gauche position, by two  $\gamma$ -carbon atoms in gauche position. In order to obtain the shift increment of the methyl carbon atoms in the glassy state associated with the transformation of the CH-CH bond from  $\text{g}^+$  to  $\text{a}$  one has to take the difference between the mean of the chemical shifts of the  $\text{ag}^+$  and  $\text{aa}$  signals weighted with their relative intensities (0.37 and 0.63 resp.) and the shift of the  $\text{g}^+\text{a}$  resonance. This yields the value of -6.1 ppm in good agreement with the corresponding  $\gamma$ -effect of -5.9 ppm determined from the slow exchange spectrum of the low molecular weight compound. The agreement between the  $\gamma$ -effects indicates that major distortions of the bond rotational angles in the glassy state do not occur.

In addition to the  $\gamma$ -effect discussed above another  $\gamma$ -effect can be determined from the spectrum of the glassy polymer which cannot be obtained from the spectra of low molecular weight analogues in solution. This shift increment  $\Delta\delta_{\text{g-a}}$  is associated with the substitution of one  $\gamma$ -carbon atom in anti position by one  $\gamma$ -carbon atom in gauche position for segments with only one  $\gamma$ -carbon atom on the side of the observed carbon atom where the conformational change takes place. This  $\gamma$ -effect controls the conformational influence on chemical shifts in linear alkanes and polyethylene whereas the  $\gamma$ -effect of the first kind is of importance for conformational studies of branched alkanes and related polymers, e. g. polypropylene. The value of this shift increment is  $\Delta\delta_{\text{g-a}} = -3.4$  ppm for the methyl carbon atom and  $\Delta\delta_{\text{g-a}} = -3.6$  ppm for the methine carbon atom. The former value is obtained from the distance between the  $\text{aa}$  and  $\text{ag}^+$  methyl carbon signals while the latter is given by the difference between the  $\text{aa}$  and the  $\text{ga}(\text{ag})$  resonances of the methine carbon atoms. The latter value is of similar magnitude as the increment of -3.3 ppm derived from the difference between the chemical shifts of the crystalline component of polyethylene and of neat cyclohexane assuming that the  $\gamma$ -interaction is transmitted through the bonding electrons 3).

The large difference between the the two kinds of  $\gamma$ -effects shows that this

effect depends strongly on the number of  $\gamma$ -carbon atoms present on the side of the observed carbon atom where the conformational change takes place. The smaller increment associated with the positional change of one  $\gamma$ -carbon atom may be used to calculate the gauche content of the amorphous phase within semicrystalline polyethylene according to

$$\Delta\delta_{\text{NC-C}} = 2p_g\Delta\delta_{g-a} \quad (2)$$

where  $\Delta\delta_{\text{NC-C}}$  is the chemical shift difference between the noncrystalline (NC) and the crystalline (C) components of polyethylene,  $p_g$  the probability of gauche conformations and  $\Delta\delta_{g-a} = -3.6 \pm 0.2$  ppm the  $\gamma$ -increment given by the chemical shift difference of the methine carbon atoms of threodiisotactic poly(1,2-dimethyltetramethylene) in the glassy state. In the derivation of Eq. 2 it is assumed that the  $\gamma$ -interactions on both sides of the observed carbon atom are additive. With the experimental value of  $\Delta\delta_{\text{NC-C}} = -2.36 \pm 0.1$  ppm<sup>3)</sup> the gauche content of the amorphous fraction of polyethylene is  $0.33 \pm 0.03$  which is smaller than the value of 0.37 at 300 K calculated on the basis of an energy difference of 2.5 kJ/mol<sup>10)</sup> including the pentane exclusion principle<sup>11)</sup>. A slightly smaller value was calculated in a previous paper<sup>2)</sup> on the basis of the larger shift increment obtained from slow exchange spectra of low molecular weight compounds in solution. This procedure, however, appears to be less conclusive. The true gauche fraction may be even smaller than the value determined from Eq. 2 if part of the chemical shift differences between equivalent carbon atoms in crystalline erythrodiisotactic and glassy threodiisotactic poly(1,2-dimethyltetramethylene) is attributed to packing differences. The problem can be settled only by the direct measurement of the gauche content in the amorphous phase of a semicrystalline polymer below  $T_g$ .

The results presented in the present and a preceding paper<sup>1)</sup> have shown that problems of microconformational properties of polymers in the solid state can be tackled successfully by means of the  $^{13}\text{C}$  NMR PE-MAS technique at variable temperature. It is a challenge for future research to relate these properties also to the macroconformation of amorphous and semicrystalline polymers.

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