Polymer Bulletin 8, 503–510 (1982)

Polymer Bulletin

Micro- and Macroconformation of Macromolecules

11. Glassy Phase Conformational Analysis of Semicrystalline and Amorphous Polymers by Variable-Temperature Magic-Angle Spinning ^{13}C NMR

W. Gronski, M. Möller and H.-J. Cantow

Institut für Makromolekulare Chemie der Universität Freiburg, Hermann-Staudinger-Haus, Stefan-Meier-Straße 31, D-7800 Freiburg i. Br., Federal Republic of Germany

SUMMARY

By variable-temperature proton enhanced magic angle spinning ^{13}C NMR below T_g individual conformational diads could be resolved for glassy phase segments in semicrystalline erythrodiisotactic poly(1,2-dimethyltetramethylene). An assignment based on γ-shift increments associated with anti - gauche conformational transitions is given. In addition an improved interpretation of conformational effects in the glassy phase solid state spectrum of amorphous threodiisotactic poly(1,2-dimethyltetramethylene) is presented.

INTRODUCTION

In the preceding paper of this series [1] we have shown that in amorphous threodiisotactic poly(1,2-dimethyltetramethylene(DMTM)) individual pairs of rotational isomeric states can be resolved by proton enhanced magic angle (PE-MAS) ^{13}C NMR experiments below T_g. It is the purpose of the present communication to demonstrate that a similar analysis can also be carried out for the glassy phase of a semicrystalline polymer. The polymer chosen for these experiments is semicrystalline erythrodiisotactic poly(1,2-DMTM). The conformation of the crystalline phase of this polymer was proven to be $g^+aaag^-aaag^+\ldots$ from the ^{13}C PE-MAS spectrum at 303 K [2] in accordance with X-ray structure analysis [3]. The basis of the NMR conformational analysis was laid in extensive low temperature ^{13}C NMR investigations in solution on model compounds of poly(1,2-DMTM), in particular meso and d,l 4,5-dimethyloctane [4].

EXPERIMENTS AND DISCUSSION

As in our preceding work the low temperature experiments were carried out with a modified variable-temperature MAS BRUKER probehead working in the temperature range between $-150^{\circ}C$ and $+50^{\circ}C$ with a BRUKER CXP 100 NMR spectrometer at 25.14 MHz. Chemical shifts were converted to TMS via the Adamantane solid state signal at 28.7 ppm. Erythrodiisotactic poly(1,2-DMTM) was prepared following literature prescriptions [5]. Thermal transitions according to DSC occur at T_m = 338 K and T_g = 235 K. The molecular weight determined by vapour pressure osmometry is M_n = 12500 g/mol.

1. ERYTHRODIISOTACTIC POLY(1,2-DMTM). A certain complication in the interpretation of the low temperature PE-MAS spectrum arises because of the chemical heterogeneity of the polymer. Besides regular structural units $(\underset{|}{C}H-\underset{|}{C}H-CH_2-CH_2)_n$ of poly(1,2-DMTM) also longer $(CH_2)_n$ (n>2) sequences exist the amount of which as estimated from the ^{13}C solution spectrum in

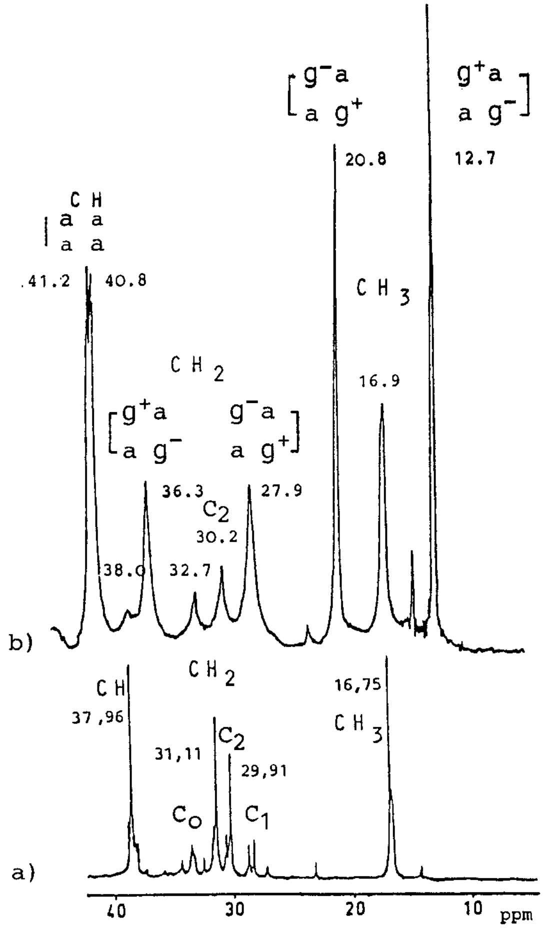

Figure 1. a) ^{13}C NMR spectra of erythrodi-isotactic poly(1,2-DMTM). a) Spectrum in $CDCl_3$solution. b) Solid state PE-MAS spectrum at 303 K, 75.42 MHz, TMS

Figure 1a is ca 50%. Signals of CH_2 carbon atoms in long $(CH_2)_n$ sequences (n>2) which are separated from methine carbon atoms by at least two CH_2 groups are denoted by C_2. The symbols C_1 and C_0 designate separation by one CH_2 group and adjacent methylene carbon atoms, respectively. The CH_2 signal of regular sequences is left unspecified. All resonance positions are found to be in good agreement with calculated positions according to chemical shift increments given by Grant and Paul [6].

In the PE-MAS solid state spectrum at 303 K in Figure 1b signals from two kinds of carbon atoms are observed, carbon atoms of mobile chain segments in the molten amorphous phase and carbon atoms of chain segments in fixed crystalline phase conformations. In the amorphous regions rapid interconversion between conformations takes place, much faster then the frequency differences between the positions of chemically shifted carbon atoms in defined individual conformations. Therefore for the amorphous phase carbon atoms signals near the same positions as in the solution spectrum are expected. By comparison of Figures 1a and 1b the solid state amorphous phase signals of CH and CH_3 carbon atoms are found at 38.0 and 16.9 ppm, respectively, and the signals of CH_2 carbon atoms in regular $-\underset{|}{C}H-CH_2-CH_2-\underset{|}{C}H$ - sequences at 32.7 ppm. The amorphous phase signals C_2 of longer CH_2 sequences at 30.2 ppm appear at the same position as the amorphous phase signal of polyethylene [7]. The remaining C_0 and C_1 signals are either hidden under resonances of greater intensity or are not visible due to their low intensity at the operating conditions (5 ms contact time). In addition to the amorphous phase signals new signals arise which are attributed to fixed conformations in the crystalline phase. As previously explained in more detail the symmetrical splitting of the CH_3 and CH_2 signals about the fast exchange signals and the simultaneous downfield shift of the CH signals is entirely consistent with the g^+a a a g^-a a a g^+.. conformation in the crystalline phase determined by X-ray analysis . Capital letters (a, g) denote the conformations of the CH-CH bonds, medium letters (a,g) the conformations of the $\underset{|}{C}H$-CH_2 bonds, small letters (a,g) the conformation of CH_2-CH_2 bonds.

The conformational influence on the chemical shift mainly arises because of a sterically induced polarization in the C-H bond of the considered carbon atom due to H··H interactions with hydrogen atoms of carbon atoms in γ-position with respect to the observed carbon atom [8]. Replacement of a neighbouring γ-carbon in anti-position by a γ-carbon in gauche position quite generally leads to an upfield shift as has been shown for methyl substituted cyclohexanes [9,10] and perhydroanthracenes [11]. The magnitude of these shift increments has directly be determined from the low temperature solid state PE-MAS spectrum of glassy threodiisotactic poly(1,2-DMTM) [1] and the crystalline phase signals of semicrystalline erythrodiisotactic poly(1,2-DMTM) [2] shown in Figure 1b and Figure 2a. A large upfield methylene carbon shift of - 8.4 ppm results if on one side of the observed CH_2 carbon one γ-carbon in anti-position (CH_3) and the other in gauche-position (CH_2) is transformed to a steric situation where both carbon atoms (CH_2 and CH_3) are in gauche-position. This corresponds to a conformational change from g^+a to g^-a where

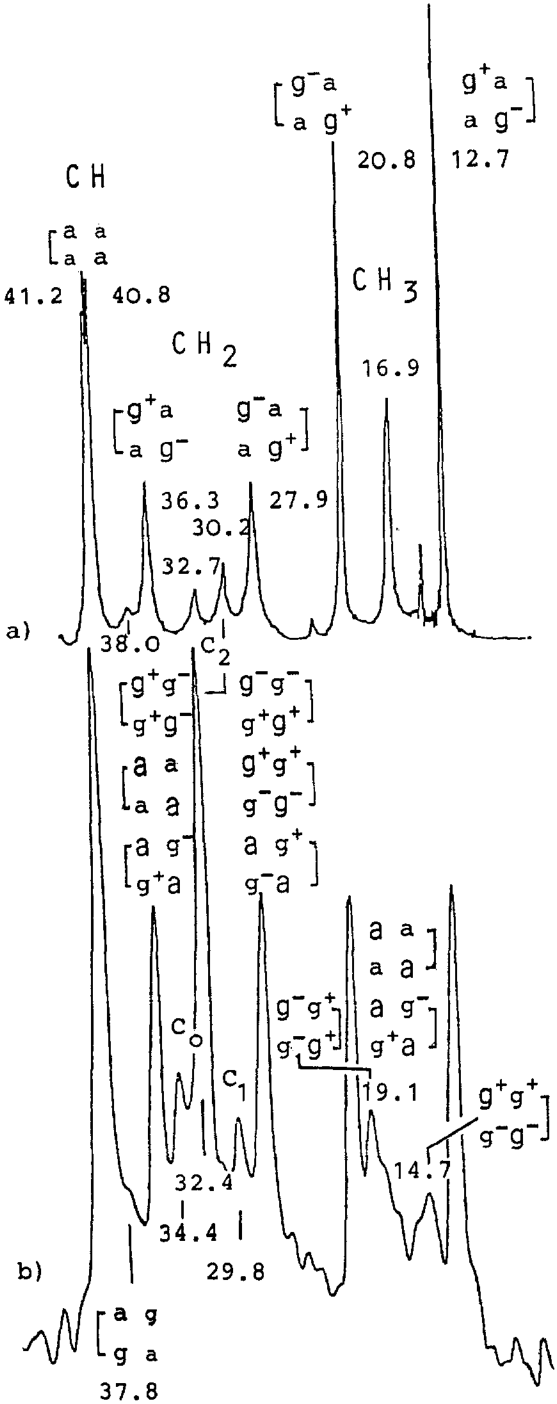

Figure 2. Solid state PE-MAS ^{13}C NMR spectra of erytrodiisotactic poly(1,2-DMTM). a) Spectrum at 303 K, 75.42 MHz, TMS. b) Spectrum at 233 K, 25.14 MHz, TMS

the conformational symbols denote conformations of the bonds next but one on either side of the observed carbon atom, i. e. the CH-CH and CH_2-CH bonds, the rotational angles of which influence the methylene carbon chemical shift through the γ-effect. A shift increment of similar magnitude, - 8.1 ppm, is found for CH_3 carbon atoms if the conformations of the bonds next but one to the CH_3 group, i. e. the CH-CH-CH_2 bond pair are changed from g^-a to g^+a . Also this transition is characterized by the exchange of one γ-gauche atom (CH_2), the other (CH_3) being in anti-position, by an arrangement where both carbon atoms (CH_2 and CH_3) are in gauche-position. The small difference between the two γ-effects seems to indicate that in first approximation only the number of gauche interactions is important for the shift increment but not the nature of the carbon atoms involved in these interactions.

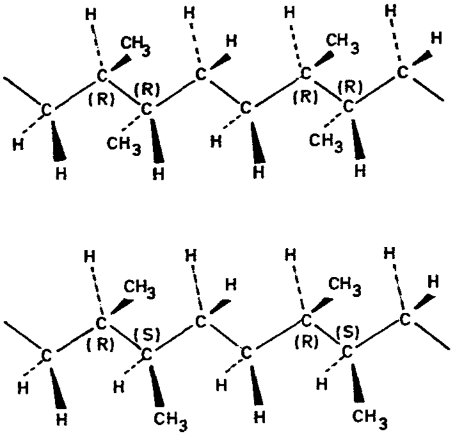

Figure 3. Poly(1,2-DMTM) in all anti conformation. a) erythrodiisotactic chain, b) threodiisotactic chain

For the definition of a specific steric arrangement giving rise to a specific chemical shift not only the specification of the conformation but also the configuration is important. In order to relate a specific steric state to a particular conformation it is necessary therefore to orient the chain in a defined way. For the present definitions the erytrodiisotactic poly(1,2-DMTM) chain is oriented as shown in Figure 3a with all anti chain bonds in the paper plane. Arbitrarily we define the left hand side of the chain as having the higher priority which brings the configuration of all asymmetric carbon atoms into absolute R-configuration. Upon rotation by 180° about a vertical axis in the paper plane the R-chain is changed into a S-chain. The regular conformation of Figure 3a has D_2 symmetry. This also applies to any steric surrounding in the vicinity of a particular carbon atom specified by the conformational angles of the bonds next but one, which define the γ-interactions. This means that a conformational pair in which the original order and the sign of the rotational angles are reversed simultaneously describes a magnetically equivalent situation. In Figure 1b and in Figure 2 equivalent conformations are connected by brackets.

In Figure 2a the effect of "freezing" conformations of amorphous regions below T_g can be seen by the change of the pattern of the amorphous phase signals of the solid state spectrum at 303 K above T_g repeated for comparison in the upper part b) of Figure 2. As expected the fast exchange signal of the CH_3 carbon resonance at 16.9 ppm disapears and new signals from glassy phase conformations not identical with the crystalline phase signals appear at positions symmetrical to the fast exchange signal. The pattern of the glassy state CH_2 signals is more complicated because of the presence of longer irregular $(CH_2)_n$ (n>2) sequences. The enhancement of intensity of the amorphous phase signals with decreasing temperature at fixed contact time (5 ms) is due to changes of the cross polarization time or the proton $T_{1\rho}$ below T_g. A consistent interpretation of the low temperature spectrum is achieved by assuming that the main effects of conformational changes on the chemical shift arise from a change of γ-interactions by conformational transitions about bonds next but one on either side of the observed carbon atom with negligible influence of α- and β-effects due to changes of rotational angles about immediately adjacent bonds. Furthermore we assume that only the number of γ-gauche interactions is important to first approximation but not the nature of the carbon atoms involved.

Glassy phase signals of CH_2 carbon atoms. For the CH_2 carbon chemical shift differences pairs of nonadjacent CH-CH and CH_2-CH bonds have to be considered. Conformational changes of the former bonds change the γ-interactions with CH_2 and CH_3 groups. According to the second assumption these interactions can be classified into three distinct groups. The first group is characterized by one γ-carbon atom in gauche-position on either side, the remaining being in anti-position. This group corresponds to the low field crystalline phase CH_2 signal at 36.3 ppm. The second group involves two γ-gauche interactions on one side and one from the other. The corresponding signal is identical with the high field crystalline phase signal at 27.9 ppm. Since each group contains 4 conformational diads with the same energetic interactions the overlapping resonances of the crystalline and glassy phase signals of these two groups must have equal intensities as it is observed in Figure 3b. The remaining $g^-g^+(g^-g^+)$ diad is characterized by two γ-gauche interactions from both sides of the observed CH_2 carbon atom. Therefore the signal of this conformation should be shifted to high field with respect of the second group by the increment given by the chemical shift difference between the second and the first group if additivity holds for the γ-shift increments. In fact, the appearence of a signal at 19.1 ppm corroborates the proposed assignment scheme. The remaining signals are assigned to prefered conformations of longer $(CH_2)_n$ (n>2) sequences in the glassy phase. The strong signal C_2 at 32.4 occurs at the same position as the crystalline phase signal of the aa conformation in poly(ethylene) and linear alkanes 12) and is therefore assigned to CH_2 groups centered in aa diads. This signal corresponds to the fast exchange C_2 signals in Figure 1a and Figure 1b. Similarly the signals of minor intensity at 34.4 and 29.8 ppm are assigned to the lowest energy conformation of C_0 methylene carbon atoms adjacent to methine carbons and to C_1 methylene carbon atoms separated by one CH_2 group from a methine carbon atom, respectively. These signals are also observed in the solution spectrum of Figure 1a. The reason that higher energy conformations of longer CH_2 sequences are not observed possibly can be explained by a similar behaviour as in poly(ethylene) where discrete ag, gg conformational pairs could not be detected down to temperatures as low as -140° C 13) probably because of a continuous distribution of conformations with only slightly differing chemical shifts. However, further work is in progress to clear up this problem.

Glassy phase signals of CH_3 carbon atoms. The chemical shift of the CH_3 carbon atoms depends on rotations about CH-CH-CH_2 bonds adjacent to the methine carbon atom to which the observed CH_3 carbon atom is bound. Because of energetically unfavourable four-bond interactions between C^*H_3 and CH_3 or CH_2 groups (pentane effect) the following conformations can be excluded: $g^+g^-(g^+g^-)$, $g^-g^+(g^-g^+)$, $g^-g^-(g^+g^+)$ and $ag^+(g^-a)$. The low energy conformations of the crystalline phase have already been assigned in the solid state spectrum at 303 K of Figure 1b. The remaining high energy conformations again can be classified according to whether two or only one γ-gauche carbon atom is present on one side. The former situation holds for the $g^+g^+(g^-g^-)$ diad assigned to the resonance at 14.7 ppm, whereas latter is true for the aa and $ag^-(g^+a)$ diads assigned to the signal group at about 19.0 ppm. The 2 ppm downfield shift of the g^+g^+ resonance with respect to the high field crystalline phase g^+a signal can be explained by the substitution of a γ-gauche CH_2 group by a γ-CH_2 group in anti associated with an $a \rightarrow g^+$ conformational change of the $CH-CH_2$ bond. However, one has to note that this shift increment is smaller than the 3.4 ppm difference for the same substitution in threodiisotactic poly(1,2-DMTM) 1). A difference of similar magnitude between the low field crystalline phase g^-a resonance and the signals of the aa, ag^- diads must be attributed to other effects since the only difference between the two groups consists in the simultaneous interchange γ-CH_3(gauche) ↔ γ-CH_2(gauche) and γ-CH_2(anti) ↔ γ-CH_3(anti). Possibly the methyl carbon chemical shifts are more sensitive to an exchange of chemically different groups in comparable sterical situations than the chemical shifts of the methylene carbon atoms or to differences in chain packing in the crystalline and glassy state.

Glassy phase signals of CH carbon atoms. The chemical shift of the CH carbon atoms depends on rotations about nonadjacent CH_2-CH and CH_2-CH_2 bonds in $-CH_2-CH-C^*H-CH_2-CH_2-$ sequences. The upfield position of the fast exchange CH signal of the amorphous phase at 38.0 ppm with respect to the crystalline phase signals of the aa conformation at 40.8 and 41.2 ppm suggests the presence of signals from $ag(ga)$ and gg conformations upfield of the crystalline phase signals. The small shoulder at 37.8 ppm (also present at other temperatures below T_g) is attributed therefore to the $ag(ga)$ pair. The upfield shift of -3.0 to -3.4 ppm is of the same order as that derived from methine carbon shifts in threodiisotactic poly(1,2-DMTM) 1). The missing gg signal, expected to appear further upfield, is obscured by CH_2 resonances of greater intensity.

2. THREODIISOTACTIC POLY(1,2-DMTM). In Figure 4 the solid state PE-MAS spectrum of amorphous threodiisotactic poly(1,2-DMTM) in the glassy phase (c) at 220 K is reproduced in comparison to the solid state spectrum of the melt at 303 K (b) and the signal positions of the solution spectrum (a). The signal positions are referenced to TMS via Adamantane and not to the Delrin rotor signal as in the previous publication 1). They can be directly compared to signal positions in Figures 1 and 3. The structure of the all anti threodiisotactic chain is depicted in Figure 2b. The chain has C_2 symmetry. Therefore conformational diads with reversed order correspond to magnetically equivalent carbon atoms. The assignment in Figure 4c is an improvement of an assignment given in the previous publication 1).

CH_3 carbon signals. For the $CH-CH-CH_2$ bonds the rotational angles of which influence the CH_3 chemical shift the following conformations are excluded because of synaxial interactions: ag^+, g^+g^-, g^-g^+, g^-g^-. Of the remaining conformations all conformations with the CH-CH bond in $g^\pm$ involve one γ-gauche interaction with a CH_2 group on one side and a CH_2 or a CH_3 on the other. Following the same principles as outlined above they are assigned to the methyl resonance at lowest field. The position at highest field is assigned to the aa conformation because it involves a double γ-gauche interaction from one side and a simple γ-gauche interaction from the other. The conformational change from aa to ag^- is associated with the transition of a γ-CH_2 group from gauche to anti. Therefore the latter resonance is shifted to lower field with respect to the former by a small shift increment of 3.4 ppm. In contrast a large shift increment of 7.4 ppm corresponds to the conformational transition from aa to $g^\pm a$ because a double γ-gauche interaction is replaced by a simple γ-gauche interaction.

CH and CH_2 carbon signals. The carbon signals of CH and CH_2 groups in the fast exchange spectra of the melt are closer for threodiisotactic poly(1,2-DMTM)(Figure 4b) than for erythrodiisotactic poly(1,2-DMTM)(Figure 1b). Consequently the splitting of the fast exchange signals into signals of individual conformations below T_g leads to a much stronger overlapping of CH and CH_2 signals in the case of threodiisotactic poly(1,2-DMTM). As for the erythrodiisotactic polymer the 9 possible conformational pairs of nonadjacent CH-CH and CH_2-CH bonds, the rotational angles of which influence the chemical shift of the central CH_2 carbon atom, can be classified into three groups according to a single γ-gauche interaction on both sides of the observed carbon atom, a double γ-gauche interaction from one side, a single

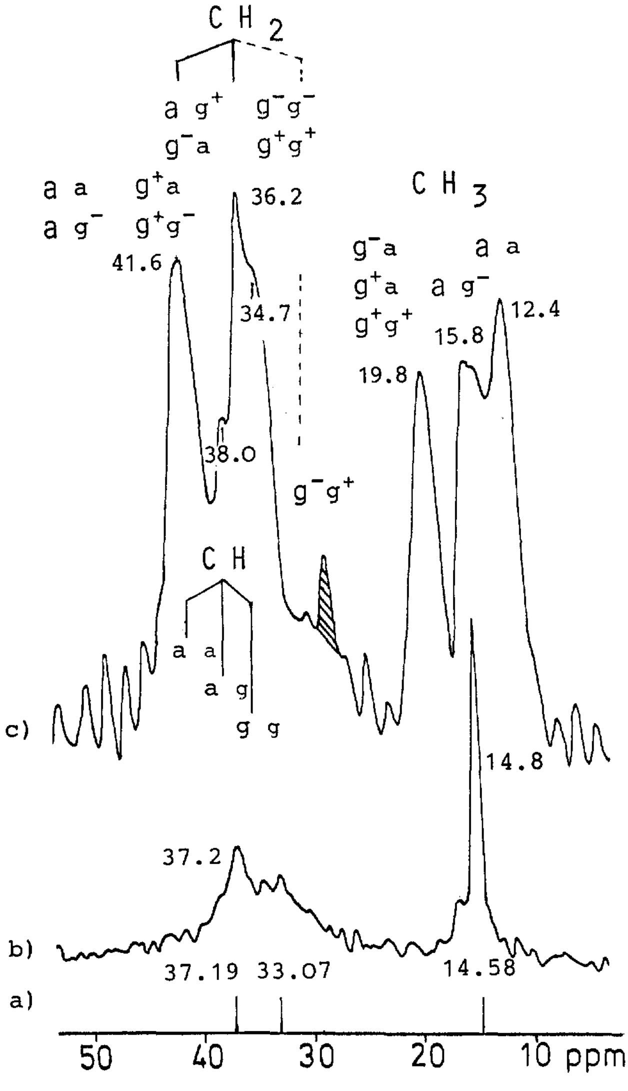

Figure 4. ^{13}C NMR spectra of threodiisotactic poly(1,2-DMTM). a) Signal positions in $CDCl_3$ solution. b) Solid state PE-MAS spectrum at 303 K, 75.42 MHz, TMS. c) Solid state PE-MAS spectrum at 220 K, 25.14 MHz, TMS

from the other and the g^-g^+ diad with double γ-gauche interactions on both sides. According to this classification the corresponding conformations are assigned from high to low field in Figure 4c. Similarly the conformational pairs of nonadjacent CH_2-CH and CH_2-CH_2 bonds responsible for the conformational effect on the CH carbon shift are distributed over the observable resonances. However, due to strong signal overlapping an unambiguous assignment is difficult.

In conclusion it has been demonstrated that variable-temperature magic angle spinning ^{13}C NMR is a very promising method to perform conformational analysis in macromolecular systems, in crystalline as well as in amorphous mobile or glassy phases. In virtue of the simple relationship between intensities and populations of rotational isomeric states the NMR method affords quantitative analysis in a more direct way than infrared spectroscopy. Therefore the method will be useful to relate conformational properties of macromolecules in solid state to other physical variables as deformation, thermal history and crystallization conditions. The potential of the method will be explored in future investigations.

We thank cordially Dr. FÖRSTER, BRUKER Physik AG, Karlsruhe and Mr. A. HASENHINDL, Institute for Macromolecular Chemistry, Freiburg, for the NMR measurements. To Dr. H. H. LIMBACH, Institute of Physical Chemistry, Freiburg, we are indebted for providing measuring facilities. Generous financial support by the DEUTSCHE FORSCHUNGSGEMEINSCHAFT is gratefully acknowledged.

REFERENCES

1. GRONSKI W., HASENHINDL A., LIMBACH H. H., MÖLLER M. and CANTOW H.-J., Polymer Bulletin 6, 93 (1981)
2. MÖLLER M. and CANTOW H.-J., Polymer Bulletin 5, 119 (1981)
3. NATTA G., ALLEGRA G., BASSI I., CORRADINI P. and GANIS P., Makromol. Chem. 58, 242 (1962)
4. MÖLLER M., Doctoral Thesis, Freiburg FRG (1981)
5. NATTA G., DALL'ASTA G., MAZZANTI G., PASQUON I., VALVASSORI A. and ZAMBELLI A., J. Am. Chem. Soc. 83, 3343 (1961)
6. GRANT D. M. and PAUL E. G., J. Am. Chem. Soc. 86, 2984 (1964)
7. EARL W. L. and VANDERHART D. L., Macromolecules 12, 762 (1979)
8. GRANT D. M. and CHENEY B. V., J. Am. Chem. Soc. 89, 5315 (1967)
9. DALLING D. K. and GRANT D. M., J. Am. Chem. Soc. 89, 6612 (1967)
10. MANN G., KLEINPETER F. and WERNER H., Org. Magn. Res. 11, 561 (1978)
11. DALLING D. K. and GRANT D. M., J. Am. Chem. Soc. 94, 5318 (1972)
12. MÖLLER M., CANTOW H.-J., KRÜGER J. K. and HÖCKER H., Polymer Bulletin 5, 125 (1981)
13. GRONSKI W., unpublished results

Accepted October 5, 1982