Polymer Bulletin 2, 543–550 (1980)

Polymer Bulletin

Micro- and Macroconformation of Macromolecules

2. Microconformation of Macromolecules by Fast Exchange NMR-Spectra

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Dedicated to Prof. Dr. Dr. h.c. mult. Hermann Mark on the occasion of his 85th birthday

SUMMARY

An approach is discussed to determine the temperature dependence of the populations of conformers within macromolecules from NMR chemical shift data under fast exchange conditions. It seems to be applicable for subunits which exhibit conformations with two energy levels with an energy difference of about 4 KJ minimum. In case of the meso diad in head- to head polypropylene and of its low molecular weight model compounds the applicability of the method has been verified experimentally. The agreement with findings from the slow exchange spectra of the models is good.

The energy differences of the rotamers are discussed for the low molecular models and for the polymer as well as the rotational barriers determined from the coalescence temperatures.

INTRODUCTION

In the foregoing paper it was reported that with the aid of slow exchange spectra of low molecular weight model compounds being representative for the configuration of the macromolecule - head- to head polypropylenes - the populations of the subunits of the polymer may be interpreted. For polymers exhibiting very low rotational energy barriers the discrete slow exchange signals are not observable, even the realization of those for their low molecular weight models asks for extreme temperatures and superconducting magnet of the NMR instrument.

From the practical standpoint therefore a procedure would have importance, which yields information concerning the temperature dependence of the populations of the subunits within the macromolecules on the basis of fast exchange spectra solely. Such an approach will be presented in the following.

RESULTS AND DISCUSSION

The equilibrium of the populations of the rotational isomeric states within the subunits of a macromolecule changes with the temperature according to BOLTZMANN's law. As the chemical shift of a NMR-signal depends on the spatial arrangement of the chain segments adjacent to the measured atom, consequently in the region of fast

0170-0839/80/0002/0543/$01.60

exchange the chemical shift is changing with the temperature. If one has to assume three staggered conformers for a molecule or its subunit exhibiting non-neglible probability the coalescence signal is determined by both the energy differences and the chemical shifts belonging to the three conformers.

The problem is simplified essentially, if both conformers are mirror images relative to each other and their energy niveaus degenerate consequently. That is the case for many macromolecules. A similar simplification is given, if the energy of one conformer is so high that its population may be neglected.

We like to discuss first molecules with mirror image gauche rotational states of identical energy. The populations p of the gauche and the anti conformers are then:

$$p_a = C \exp(-\varepsilon_a/kT) \qquad p_g = 2\ C \exp(-\varepsilon_g/kT)$$

$$p_g/\ p_a = 2 \exp(-\Delta\varepsilon/kT) \quad . \qquad (\ 1\ )$$

With $p_a + p_g = 3$ for equipartition of the conformers - at infinite temperature - p_a is equal to 1 and p_g equal to 2. Then one can write:

$$p_a = 1 - \Delta p \qquad p_g = 2 + \Delta p$$

$$p_g/\ p_a = (2 + \Delta p)/\ (1 - \Delta p) = 2 \exp(-\Delta\varepsilon/kT) \quad . \qquad (\ 2\ )$$

By rearrangement an expression similar to the tanh function follows:

$$\Delta p = [\exp(-\Delta\varepsilon/kT) - 1]/[\exp(-\Delta\varepsilon/kT) + 1/2] \quad . \qquad (\ 3\ )$$

The chemical shift at fast exchange is composed by the corresponding slow exchange signals:

$$\delta_{coal} = x_a\delta_a + x_g\delta_g \quad . \qquad (\ 4\ )$$

With equ. (1) and $x_a = (1 - \Delta p)/3$ and $x_g = (2 + \Delta p)/3$ the chemical shift of the coalescence signals at a temperature T is:

$$\delta_{coal} = (1 - \Delta p)/3\ \delta_a + (2 + \Delta p/3)\ \delta_g$$

$$\delta_{coal} = \delta_a/3 + 2\delta_g/3 + \Delta p/3(\delta_g - \delta_a) = \delta_{=coal} + \Delta p/3(\delta_g - \delta_a) \qquad (\ 5\ )$$

$$\delta_{coal} = \delta_{=coal} + (\delta_g - \delta_a)/3\ [\exp(-\Delta\varepsilon/kT) - 1]/[(\exp(-\Delta\varepsilon/kT) + 1/2)]$$

Here $\delta_{=coal}$ is the coalescence signal for the equipartition of the conformers. For $\Delta\varepsilon/kT < 0{,}3$ this function runs linear. With the last equation the chemical shift is given as function of the energy difference of the niveaus, the temperature and the shift difference of the signals of the conformers.

For the case one of the three staggered conformations is on such a high energy level that it has nearly no probability we have to write for the temperature dependence of the chemical shift: (5a

$$\delta_{coal} = 1/2\ (\delta_a + \delta_b) + \Delta p/2\ (\delta_a - \delta_g) = \delta_{=coal} + \Delta p/2\ (\delta_a - \delta_g)$$

Experimentally one gets the signal for the equipartition of the conformers extrapolating the coalescence signals measured for the macromolecules versus T_{∞}. The lowest energy conformation follows from the asymptote T = 0 K.

Figure 1 demonstrates this for erythro- diisotactic head- to head polypropylene. For the head- to head erythro- diisotactic polypropylene as well as for its models 2,3-dimethyl butane and meso 3,4-dimethyl hexane the chemical shifts of the methyl carbon atoms in the region of fast exchange are plotted versus 1/T in the figure 1. 2,3-dimethyl pentane is not included. It can exist in three different conformers because of its molecular assymmetry. Therefore analysis of the coalescence signals with respect to conformer population according equ. (5) is not possible. From the slow exchange data published in the foregoing paper it is evident that the methyl signals are reacting very sensitive on the rotational states of the CH-CH bond.

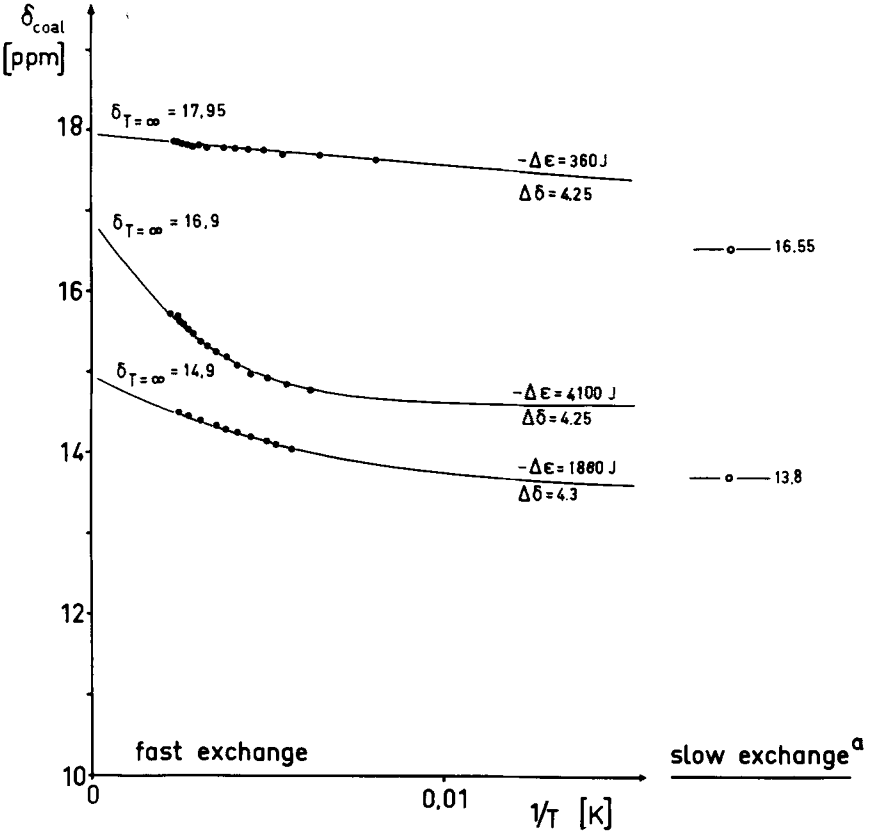

Figure 1: Chemical shift δ of the methyl carbons versus 1/T for erythro- diisotactic H- H- polypropylene (middle), 2,3-dimethyl butane (top) and meso- 2,4- dimethyl hexane (below) in fast (●) and slow exchange (o).

[a] Average chemical shifts of the methyl carbons in the lowest energy conformation from slow exchange spectra.

For the models, 2,3- dimethyl butane and meso- 3,4- dimethyl hexane, the lines through the points (●) are the plots of the temperature dependence of the coalescence signal according to equ. (5) with the best fitting parameters as given in the figure. The differences of the chemical shifts for the three compounds is due to the effect of the carbon atoms in γ- and δ- position as usually considered in the literature. The curve's extrapolation towards 0 K meets the chemical shift values of the lowest energy conformer of both the models as determined under slow exchange conditions (o). The extrapolation towards T_∞ gives the chemical shifts in case of equipartition of the conformers. They too are in good agreement with the results from the slow exchange spectra. Consequently the chemical shift difference between the conformers in the macromolecule - anti and gauche - is given as $\Delta\delta = 1{,}5\ (\delta_{=\ \mathrm{coal}} - \delta_{o\ \mathrm{coal}})$, in accordance with the chemical shift difference of the models measured in slow exchange. ($\delta_{o\ \mathrm{coal}}$ is the chemical shift of the coalescence signal extrapolated for $T \to 0$.) The fitting of the theoretical function to the measured chemical shift has to be done with equ. (5a) in case of the polymer instead with equ. (5) for the low molecular weight models. In macromolecular chain molecules namely the rotational states of the bonds can not be regarded independent from each other. The conformation around each bond is influenced by the conformation of the adjacent groups . E. g. the g^+ conformation of the head- to head unit may exist with different rotational states of the adjacent bonds as the gauche$^-$ conformation. So the energy level of the gauche$^+$ state has not to be identical with the gauche$^-$ level. Equ. (5) will not fit then the experimental data, as found in our case. Justification for application of the assumings inherent in equ. (5a) can be drawn independently from semiempirical atomistic calculations to be reported in a following paper³⁾. From those calculations it turns out that from 27 theoretically possible conformations to be considered in a three bond system only two exhibit non- negligable probability. These are the a- g^+- g^+ and the g^+- a- g^- conformations. Thus the central head- to head bond in inverted polypropylenes will only exist in anti and in gauche$^+$ conformation. Other conformations show calculated energy levels being at least 20 kJ higher. Consequently for the macromolecules equ. (5a) has to be applied.

Whereas the chemical shift differences between the conformers for the macromolecule and the low molecular weight models are identical, the change of the shift with the temperature shows a different curve as the energy difference between the conformers is not identical. So we conclude that the energy difference between the conformers depends strongly of the chain length: 340 J for 2,3 - dimethyl butane, 1880 J for meso 3,4-dimethyl hexane and 4100 J for the erythro-diisotactic head- to head polypropylene. The $\Delta\varepsilon$ for 2,3- dimethyl butane agrees well with that found by LÜTTKE by proton coupling experiments for the CH protons (355 J). ²⁾ Also the slow exchange data we could evaluate for the model compounds are in good agreement with these results.

From the intensity ratios of the signals of the conformers under slow exchange conditions the populations of the conformers have been determined ¹⁾. Table I presents the populations at 85 K. It is evident that with increasing length of the molecules the gauche$^+$

Table I: Populations of conformers at 85 K.

2,3- dimethyl butane	2.3- dimethyl pentane	3,4- dimethyl hexane	
		meso	dl
a 33 % $g^{\pm}$ 67 %	g^{-} 20 % g^{+} 80 %	$g^{\pm} > 95$ %	$g^{+} > 95$ %

shows up increasing stability if compared with the other conformations. one notes that in those conformations the methyl groups are situated staggerd between two carbons.

In Table II the free standard enthalpy differences between the lowest energy conformers, as determined from the populations, are presented. For the 2,3- dimethyl butane and the meso- 3,4- dimethyl hexane one can not distinguish between both the gauche conformers ($g = g^{\pm}$). Their energy niveaus degenerate.

Table II: Differences in the free energies and in the free enthalpies of activation of the low molecular weight model compounds.

	$\Delta G^o = - RT \ln k_c$ [kJ]	ΔH^o [kJ]
2,3- dimethyl butane	$\Delta G^o_{g-a} = 0,52$	$\Delta H^o_{g-a} = 0,04$
2,3- dimethyl pentane	$\Delta G^o_{g^+-g^-} = 1,04$	
	$\Delta G^o_{g^+-a} > 2,1$	
meso- 3,4- dimethyl hexane	$\Delta G^o_{g-a} > 2,1$	$\Delta H^o_{g-a} > 1,6$
dl- 3,4- dimethyl hexane	$\Delta G^o_{g^+-a} > 2,1$	
	$\Delta G^o_{g^+-g^-} > 2,1$	

A first approximation for the enthalpy difference can be conceived assuming $\Delta S^o = R \ln 2 = 5,7$ J/K as the entropy difference between anti and gauche conformer. With $T\Delta S^o = 484$ J at 85 K ΔH^o follows from $\Delta G^o = \Delta H^o - T\Delta S^o$. Up to now it can not be decided whether the high $\Delta\varepsilon$ between the conformers within the polymer chain compared with meso- 3,4- dimethyl hexane is typical for macromolecules due to cooperative effects on segmental level. Measurements on longer model compounds are planned in order to detect the further tendency of the energy difference with the chain length.

The crucial point of all experimental conformational data is the question, whether the spatial arrangement really is an undisturbed one, whether one can exclude solvent influences on the micro- as well as on the macroconformation over a braod range of temperatures. We critically have chosen conditions for our NMR- experiments to avoid specific solvent effects. So in the slow exchange measurements monodeutero ethane as well as monodeutero propane had no specific influence. Analogously longer alkanes as solvents at higher temperature did not induce any influence on the conformational balance.

Another argument can be given for the validity of the approach that the temperature dependence of the chemical shift can be interpreted by unperturbed conformational changes, assuming "stable" conformers. To this purpose we have measured the ^{13}C- NMR spectrum of cis- 1,2- dimethyl cyclohexane over a broad range of temperatures. This molecule should not show up conformation dependent effects, even if it oscillates between its chair conformations. The signals of the methyl groups turned out to be quite independent on temperature, demonstrating so the absence of temperature dependent solvent shift effects. Below 200 K one observes discrete signals for the equatorial and for the axial methyl group.

At the final part of this paper the rate constants of the transitions between the conformers of the low molecular weight model compounds of the inverted polypropylenes and the activation barriers between the conformers may be discussed. The rate constants of the transition between rotamers can be determined from the coalescence temperatures according to SHANNON-ATIDI and BAR-ELI 4). More conclusive determination of the activation enthalpy is possible only, if the rate constants can be measured over a broader range of temperatures with high exactness. This was not realizable in our case. The coalescence temperatures of the models representative for head-to head polypropylenes were determined using a series of spectra in the low temperature range, some of them given in the foregoing paper1).
The rate constants given in table III are defined as $k_c = 1/\ 2\tau$, according to GUTOWSKY and HOLM 5). For meso 3,4- dimethyl hexane these constants have been determined additionally from the formula being valid for the case only exactly that two signals of identical intensity split up: $k_c = \pi\delta\nu/\sqrt{2}$. The values from both methods agree well. From the rate constants the differences of the free enthalpies of activation can be calculated according to EYRING (with $\kappa = 1$): $k_c = (kT_c/h)\exp\ (\Delta G^{*}/RT)$. The rotational barriers between the conformers turn out to be practically identical. Consequently at least for small molecules the rotational barriers are not depending critically from the length of the substituents.

For the types of molecules investigated here two rotational transitions have to be taken into consideration: At the transition from the gauche$^+$ to the gauche$^-$ conformation or vice versa carbon atoms have to be passed to each other over an eclipsed conformation twice. At the transition from a gauche to an anti conformation however one carbon pair

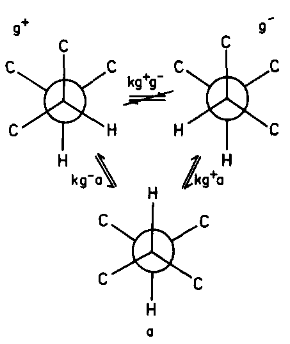

Figure 3: Transitions within a molecule exhibiting gauche$^+$, gauche$^-$ and anti conformation

Table III: Coalescence temperatures T_C, rate constants of the gauche anti transition k_c and differences of the free enthalpy $\Delta G^{\#}$ of model

	signal	T_c [K]	k_c [sec^{-1}]	$-\Delta G^{\#}$ [kJ
2,3- dimethyl butane	CH_3	103	990	18,3
	CH	97	350	18,1
2,3- dimethyl pentane	CH_3(3M)	103	737	18,6
	CH_3(2M)	103	770	18,5
	CH_3(1)	103	780	18,5
	CH_2	103	802	18,5
meso- 3,4- dimethyl hexane	CH_3	102	1290	18,0
	CH_2	102	1105	18,1
	CH	97	424	17,9
dl- 3,4- dimethyl hexane	CH_3	100	410	18,5

only has to pass each other. From semiempirical atomistic calculations 3) we know that the energy of activation has to be around 16 KJ for the gauche- anti and around 30 KJ for the gauche$^+$- gauche$^-$ transition. Consequently the rate of the g^+ - g^- transition is in the order of 10^{10} smaller than that of the g - a transition. Thus the exchange broadening observed in the spectra has to be related to the gauche- anti transition exclusively.

Table III gives the survey over the coalescence temperatures, the rate constants for the conformational transition and the corresponding differences of the free enthalpies according to EYRING for all relevant carbons in the models for inverted polypropylene. It should be noted that the T_C of the dl- 3,4- dimethyl hexane is less exact than that for the other models because of the small effect from fast to slow exchange.

EXPERIMENTAL

The ^1H broad band decoupled ^{13}C magnetic resonance spectra in the region of fast exchange of the conformations were obtained with a BRUKER WH 90 spectrometer operating at 22,625 MHz. The compounds examined were measured in 10 vol- % solutions of monodeuterated n- alkanes, i. e. n- pentane- d_1, n- octane- d_1 and n- decane- d_1 with a few drops of OMTS as an internal reference. Temperature was changed from 160 to 420 K. The slow exchange ^1H broad band decoupled ^{13}C magnetic resonance spectra were obtained with a BRUKER WH 360 operating at 90,51 MHz in 1- monodeutero propane and 1- monodeutero ethane. Shifts given correspond to δ_{CH_3}- ethane = 5,535 ppm.

Monodeuterated n- alkanes were prepared by decomposition of the GRIGNARD substrates of the corresponding n- alkyl bromides with D_2O.

Meso- 3,4- dimethyl hexane was synthesized from cis- 4,5- dimethyl cyclohexane which was prepared according to KWART and MILLER 6) from cis- 1,2,3,6- tetrahydrophthalic acid anhydride. The anhydride was reduced with $LiAlH_4$ in THF to the diol (b.p. 130- 147° C, 5 torr) and converted to the bis- iodine methyl cyclohexene (b. p. 80° C, 10^{-4} torr), which again was reduced in THF with $LiAlH_4$. The cis- 4,5- dimethyl cyclohexene was oxidized with $KMnO_4$ to 3,4- dimethyl adipinic acid. The diethyl ester of the acid was reduced with $LiAlH_4$ to the diol, which was then converted to the p- toluene sulfonate ester. This finally was reduced with $LiAlH_4$ to meso- 3,4- dimethyl hexane (b. p. 117° C).

Erythro- diisotactic head- to head polypropylene was prepared by copolymerization of cis- butene and ethylene with $VCl_4/Al(octyl)_3$ in n- heptane 7). The ^{13}C- NMR spectrum shows that the product contains ∿ 30 % CH_2- sequences longer than two. The head- to tail propylene sequences however exceed 95 % concerning erythro- diisotacticity.

Dr. W. HULL from BRUKER AG, Karlsruhe, we have to thank cordially for the support and help with the slow exchange measurements.

Generous financial support by DEUTSCHE FORSCHUNGSGEMEINSCHAFT and FONDS DER CHEMISCHEN INDUSTRIE is gratefully acknowledged.

REFERENCES

1. RITTER, W., MÖLLER, M. and CANTOW, H.-J.: Polymer Bull. 2, 533 (1980)
2. LÜTTKE, W. and HEINRICH, F.: Chem. Ber. 110, 1246 (1977)
3. BECK, L. and MÖLLER, M.: in preparation
4. SHANNON-ATIDI, H. and BAR-ELI, K.H.: J. Phys. Chem. 74, 961 (1970)
5. GUTOWSKY, H.S. and HOLM, C.H.: J. Chem. Phys. 25, 1228 (1956)
6. KWART, H. and MILLER, L.J.: J. Am. Chem. Soc. 83, 4552 (1961)
7. NATTA, G., D'ALL ASTA, G., MAZZANTI, G., PASQUON, I., VALVASSORI, A. and ZAMBELLI, A.: J. Am. Chem. Soc., 3343 (1961)

Received March 19, 1980