A Nuclear Magnetic Resonance Study of Molecular Motion in Urea- d_4 -Polyethylene Complex

Yasurō HORI, Takeshi TANIGAWA, Shigetaka SHIMADA,
and Hisatsugu KASHIWABARA

Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan.

(Received October 6, 1980)

ABSTRACT: Broad-line proton magnetic resonance spectra were measured for urea- d_4 -polyethylene complex from 125 to 360 K. For comparison, the spectra of the extended-chain crystal of polyethylene, bulk polyethylene, urea- d_4 - n -C₁₈H₃₈ complex, and n -C₁₈H₃₈ were also examined. The NMR spectra of isolated polyethylene which has only an intra-chain interaction and no inter-chain ones were successfully observed for rigid and rotating states. From a comparison of the values of observed and calculated second moments, it was concluded that the polyethylene molecule is freely rotating in urea channels above the transition temperature. A portion of the polyethylene molecule is also freely rotating even 10 K below the transition temperature. The free rotation of guest molecules is probably the cause of the phase transition of urea complexes.

KEY WORDS Broad-Line Nuclear Magnetic Resonance / Molecular Motion / Polyethylene / Urea-Polyethylene Complex /

Urea forms crystalline complexes (inclusion compounds or adducts) with n -paraffins^{1,2} and also with linear polyethylene.³ The urea molecules form a hollow hexagonal channel in which the guest molecules are enclosed with an extended planar zigzag conformation.⁴

Molecular motions of the guest molecules were first studied by Gilson and McDowell⁵ in regard to urea- n -tridecane and - n -hexadecane complexes by the broad-line proton magnetic resonance method. For the urea-hexadecane complexes, they observed a gradual large decrease of the second moment in the temperature range from 77 to about 160 K and a small decrease at about 225 K. The first decrease was assigned to an increasing amplitude of rotational oscillation until an amplitude of 60° is reached at which of course the motion is fully rotational. The second small decrease was explained by an expansion of the urea lattice. By the same method, a series of urea- n -paraffin complexes (from n -C₁₂H₂₆ to n -C₂₀H₄₂) were investigated^{6,7} and essentially the same conclusion was obtained, although the first transition temperature was higher for a higher molecular weight of the guest molecule. Also, the same transition was observed by nuclear

spin relaxation measurements.⁸

On the other hand, the urea-paraffin complexes showed sharp transitions when observed by heat-capacity measurements, and these transitions were associated with the movement of guest molecules rather than that of host (urea) molecules.^{9,10} This transition temperature for urea-hexadecane complex is 152 K.⁹ These transitions were explained as order-disorder (or rotational) transitions of guest molecules by model calculations,¹¹ and have been observed in all urea- n -paraffin complexes (from C₁₂H₂₆ to C₃₆H₇₄).⁷ As in nuclear magnetic resonance (NMR) observations, the transition temperature increased with the molecular weight of guest molecules, but the correspondence of the accurate transition temperatures between NMR measurements and heat-capacity observations has not as yet been clarified.

Recently, Chatani *et al.*^{7,12} examined the crystal structures of urea-paraffin complexes below the transition temperatures and found that the hexagonal crystals (high temperature form) are commonly transformed into orthorhombic crystals (low temperature form). From the temperature dependence of unit cell dimensions, the order-dis-

order transition was found to occur at the same temperature as observed by differential scanning calorimetry (DSC) measurements.⁷

In short, the order-disorder transitions of urea-paraffin complexes were confirmed by many kinds of measurement (NMR, heat capacity, and X-ray), but the observed transition temperatures were slightly different, depending on the method of observation. Also one can conclude that the guest molecules freely rotate above these transition temperatures.

A main subject of this work is the investigation of the molecular motion of polyethylene in the urea-polyethylene complex. In relation to this subject, we have already reported¹³ the molecular motions of peroxy radicals of polyethylene in urea-complexes observed by electron spin resonance. Above 299 K, the whole peroxy radicals were concluded to be freely rotating or vibrating with an amplitude more than 90°. Recently, Yokoyama *et al.* found a similar phase transition of urea-polyethylene complexes by means of DSC¹⁴ and X-ray diffraction.¹⁵ The transition temperatures were 278, 280, and 284 K for 4000, 10000, and 85000 molecular-weights of polyethylene, respectively.

In this work, we have used the broad-line proton magnetic resonance technique to study the molecular motions of polyethylene and octadecane in their urea complexes. To study the behavior of the guest molecule itself free from the resonance of protons of the lattice, complexes were prepared by using fully-deuterated urea. In order to compare with the guest molecules in urea-complexes, *n*-octadecane, melt-grown polyethylene, and extended-chain polyethylene were also examined.

EXPERIMENTAL

The following five materials were used for the broad-line NMR study: *n*-octadecane (*n*-C₁₈H₃₈), urea-*d*₄-*n*-octadecane complex (*d*-UPC), melt-grown polyethylene (bulk-PE), extended-chain crystal of polyethylene (ECC-PE) and urea-*d*₄-polyethylene complex (*d*-UPEC). *n*-C₁₈H₃₈ was of reagent grade and used without further purification. In preparing *d*-UPC, the calculated amount of a solution of *n*-C₁₈H₃₈ in isooctane was added to a saturated solution of urea-*d*₄ in deuterated methanol (CH₃OD). Bulk-PE was prepared by the slow cooling of linear polyethylene (Sholex 6050)

from 423 K to room temperature *in vacuo*. ECC-PE was kindly supplied to us by Professor T. Takemura of Kyushu University. *d*-UPEC was made by the indirect method of Monobe and Yokoyama³ which was to replace the hydrocarbon molecules in the *d*-UPC with linear polyethylene molecules (Sholex 6050). The purities of *d*-UPC and *d*-UPEC were determined by the DSC method and materials including neither isolated hydrocarbon, polyethylene nor isolated urea were selected.

These samples were stacked into 18 mm o.d. Pyrex sample tubes and evacuated to 10⁻⁶ torr. The proton magnetic resonance spectra were obtained in JEOL JES-BE-1 spectrometer operating at 40 MHz. Modulation amplitudes ranged from 0.04 to 0.08 mT and appropriate corrections were applied to the experimental second moments. Temperature control was achieved by passing a stream of cooled nitrogen gas through a Dewar lead around the sample. The gas flow was obtained by boiling liquid nitrogen and then heated to the desired temperature. Magnetic field sweep was calibrated with known splitting constants of Mn²⁺ by using a K-band electron spin resonance (ESR) spectrometer operated in the same magnet and the same magnetic field as for the NMR observations.

The signals were recorded by a JEOL spectrum computer, Model JEC-6, and the data obtained were handled by a HITAC 8400 at the NIT Computer Center. Second moments were obtained from the derivative curves by integration in the computer. Sometimes, determination of the base line of the spectrum gave rise to errors in the estimation of second moments. Several ways for determining the base line were tried, and the following simple way looked the best for incurring the least error. The base lines of the spectra were determined according to a computer procedure in which integrals (absorptions) of the left- and right-hand sides of the spectrum were made equal. The measured second moments are accurate to $\pm 0.5 \times 10^{-8} \text{ T}^2$.

The theoretical second moments were calculated using the Van Vleck formulae¹⁶ for a rigid lattice, and the methods of Gutowsky and Pake¹⁷ and Andrew¹⁸ for the moving molecules.

DSC measurements were also carried out for confirming the order-disorder transitions of *d*-UPC and *d*-UPEC.

RESULTS AND DISCUSSION

Urea- d_4 - n -Octadecane Complex (d -UPC) and n -Octadecane (n - $C_{18}H_{38}$)

Examples of proton magnetic resonance derivative spectra for d -UPC at various temperatures are shown in Figure 1. At 123 K, the lowest temperature of measurement, the resonance curve seems to consist of three components, a broad component with a line width of 1.0 mT, a narrower one of 0.25 mT and the narrowest one of 0.1 mT. The line width and intensity of the narrowest component had remained unchanged up to 342 K. This component may be assigned to part of the absorption due to the methyl groups which are freely rotating.¹⁸ The broad component narrowed its line width from 1.0 mT at 123 K to 0.7 mT at 184 K and its intensity became smaller. The middle component did not change its line width, but its intensity became larger.

These changes in the line shape with temperature can be explained in the following way. The component originating from methyl groups consists of two sub-components, a sharp component, and a middle width component. The absorption due to the methylene groups also has two components: a broad and a middle one. The methyl groups are already freely rotating at the lowest observed temperature and their line shape stays unchanged. On the other hand, the motion of the methylene group becomes vigorous from 123 to 184 K. The ratio of intensities of the broad and middle components changes and the line width of the broad component is narrowed. Therefore, the temperature dependence of the observed spectra from 123 to 184 K can be associated only with the motion of the methylene groups. Finally one observes a sharp spectrum at 184 K and this line shape does not change until at 342 K. These motions of the guest molecule should be discussed in terms of the second moment.

The temperature dependence of the second moment of proton resonance absorption is shown in Figure 2 for both d -UPC and n - $C_{18}H_{38}$. The second moment of d -UPC decreases from $13.5 \times 10^{-8} \text{T}^2$ at 123 K to about $5.5 \times 10^{-8} \text{T}^2$ at 184 K and then gradually decreases to $4.5 \times 10^{-8} \text{T}^2$ at 342 K. This feature is very similar to the results in the literature⁶ and to those on other hydrocarbon-urea complexes.⁵⁻⁷ But our results showed two important features which are different from the

Figure 1. Proton magnetic resonance line shape derivative curves for d -UPC at various temperatures.

Figure 2. Temperature dependence of second moments for n -octadecane and d -UPC.

previous results.⁵⁻⁷ One is the absolute value in the high temperature region. We obtained 5.5 to $4.5 \times 10^{-8} \text{mT}^2$, while values between 2 and $4 \times 10^{-8} \text{mT}^2$ were previously obtained. This difference may be due to the difference in the methods of calculating second moments. These absolute values of second moments at higher temperature will be discussed below. The other difference is that we did not observe a transition due to the lattice expansion around 250 K. If this is considered with the fact that no lattice-expansion transition was observed by heat capacity and X-ray measurements,⁷ it may be concluded that there occurs no

such transition in the urea-paraffin complexes.

For $n\text{-C}_{18}\text{H}_{38}$, the temperature dependence of the second moment showed only a gradual decrease from $24.5 \times 10^{-8} \text{ T}^2$ at 116 K to $14.4 \times 10^{-8} \text{ T}^2$ at 290 K. This is very similar to Andrew's result¹⁸ except for a slight difference in the absolute value. We will not discuss $\text{C}_{18}\text{H}_{38}$ any further but only point out that the differences in temperature dependence and absolute value of the second moments between $d\text{-UPC}$ and $n\text{-C}_{18}\text{H}_{38}$ arise from the fact that the guest molecules in $d\text{-UPC}$ are not interacting with the molecules in the neighbour channels.

We will now discuss the absolute value of the second moment of $d\text{-UPC}$. The rigid lattice second moment¹⁶ of $d\text{-UPC}$ was calculated on the assumption that the molecular structure is the same as that of polyethylene¹⁹ and the methyl groups can come together and approach their Van der Waals radii. The C-H bond length was taken as 1.091 Å, and an angle of 109° was assumed between the hydrogen atoms.¹⁹ Reductions in second moments resulting from the reorientation of methyl groups as well as from rotational oscillation and free rotation of the $n\text{-hydrocarbon}$ chain about its longitudinal axis have been calculated by the methods of Gutowsky and Pake¹⁷ and Andrew.¹⁸ The calculated values are summarized in Table I with the corresponding values for the polyethylene complex. This table also shows the experimental values observed at a number of temperatures.

For the guest molecules in $d\text{-UPC}$, the observed value of $5.5 \times 10^{-8} \text{ T}^2$ at 184 K agrees with the value calculated on the assumption of free rotation. This result leads to the conclusion that there exists only one free rotation of hydrocarbons about the longitudinal axis in $d\text{-UPC}$ above the transition temperature, but translational motion of the guest molecules along the channels as proposed previously⁶ does not occur. The value of $13.5 \times 10^{-8} \text{ T}^2$ at 123 K is lower than that of the rigid lattice, but nearly equal to that for rotational oscillation with an amplitude of 50° . This indicates that the guest molecules are oscillating rotationally at 123 K. The decrease in the second moment from 123 to 184 K can be explained by the increase in the oscillation amplitude. On the other hand, a gradual decrease from $5.5 \times 10^{-8} \text{ T}^2$ at 184 K to $4.5 \times 10^{-8} \text{ T}^2$ at 342 K may be due to the increased twisting of the hydrocarbon chain to give rise to an out-of-plane

Table I. Calculated and observed second moments^a for urea- d_4 - n -octadecane and urea- d_4 -polyethylene complexes
(a) Calculated second moments

	Second moment	
	10^{-8} T^2	
	$n\text{-C}_{18}\text{H}_{38}$	Polyethylene
Rigid lattice	20.97	19.17
Methyl group rotation	16.94	—
Rotational oscillation		
Amplitude ^b 30°	15.51	17.72
60°	12.40	14.17
90°	9.04	10.32
Free rotation	5.20	5.94

(b) Observed second moments

	Second moment	
	10^{-8} T^2	
	$n\text{-C}_{18}\text{H}_{38}$	Polyethylene
	13.5 (123 K)	17.7 (125 K)
	11.6 (145 K)	11.3 (216 K)
	5.5 (184 K)	5.5 (295 K)

^a In 10^{-8} T^2 .

^b The amplitude means 2α in the equation of angular oscillation, $\phi = \phi_1 + \alpha \sin(\omega t)$ in ref 18.

motion of the methylene groups.

Urea- d_4 -Polyethylene Complex ($d\text{-UPEC}$), Bulk Polyethylene (Bulk-PE), and Extended-Chain Crystal of Polyethylene (ECC-PE)

Examples of proton magnetic resonance spectra for bulk-PE, ECC-PE and $d\text{-UPEC}$ at various temperatures are shown in Figures 3, 4, and 5, respectively. The temperature dependence of the second moment of the proton resonance absorption is shown in Figure 6 for bulk-PE, ECC-PE and $d\text{-UPEC}$.

Normal polyethylene having an inter-chain interaction was extensively studied²⁰⁻²² by the NMR method, and the NMR spectra were found to consist of two or three components. The spectra in Figures 3 and 4 for bulk-PE and ECC-PE are essentially the same as those previously reported. The change in the spectrum of bulk-PE with

Figure 3. Proton magnetic resonance derivative curves for melt-grown polyethylene at various temperatures.

Figure 4. Proton magnetic resonance derivative curves for extended-chain crystal of polyethylene at various temperatures.

temperature can be ascribed to immobile and mobile parts. The mobile part giving the narrower component increases with increasing temperature and the associated second moment decreases. As seen in Figure 6, all parts of polyethylene in bulk-PE are rigid below 150 K, and the amorphous part is mobile and the crystalline part is immobile between 200 K and 300 K. The crystalline part becomes mobile above 330 K.

Figure 5. Proton magnetic resonance derivative curves for urea- d_4 -polyethylene complex at various temperatures.

Figure 6. Temperature dependence of second moments for bulk-PE, ECC-PE, and d -UPEC: Δ , ECC-PE; $\square$, bulk-PE; $\circ$, UPEC.

For ECC-PE, the situation is the same as in bulk-PE, but the mobile fraction is smaller than that of bulk-PE.

On the other hand, the temperature dependence of the spectrum and its second moment for d -UPEC was completely different from normal polyethylene. At temperatures above 295 K, the spectra were very sharp and very similar to those of d -UPC at higher temperatures (compare Figure 5(c) with Figure 1(c)). In addition, the line shapes of these spectra remained unchanged from 295 to 360 K. The second moment of d -UPEC in this temperature region is about $5.5 \times 10^{-8} \text{ T}^2$ and just the same as the value calculated for free rotation of the guest molecules.

From these results and a comparison with the results on *d*-UPC, the following conclusion can be derived: the guest polyethylene molecules (infinite-length *n*-hydrocarbon) in the urea channels are freely rotating above 295 K. The difference in the transition temperatures between NMR (295 K) and DSC measurements (282 K) is 13 K, which is comparable with 17 K obtained for urea-*n*-C₁₈H₃₈ complex.

At 125 K, the lowest temperature of measurement, the second moment was $17.7 \times 10^{-8} \text{ T}^2$. This value is slightly smaller than the calculated one for rigid lattice, and corresponds to that of rotational oscillation with an amplitude of 30° as shown in Table I. The other calculated value²³ for rigid lattice by using different C-H bond lengths and H-C-H angles was reported to be $18.1 \times 10^{-8} \text{ T}^2$ for the intra-chain contributions. This value is very close to our experimental value of $17.7 \times 10^{-8} \text{ T}^2$ at 125 K. As mentioned above, the calculated value for a rigid lattice strongly depends on the crystal structure assumed. However, it can be safely concluded that the guest polyethylene in *d*-UPEC is nearly rigid or vibrating with a very small amplitude at 125 K. The above conclusion is supported by the result that in *d*-UPEC, the second moment has a plateau region at temperatures ranging from 125 K to about 150 K, as seen in Figure 6. This indicates that the guest molecules are rigid or vibrating with a constant amplitude at temperatures lower than 150 K and have an increasing amplitude of rotational oscillation at higher temperatures.

From the above discussion we find that the spectrum in Figure 5(a) consists of one component of rigid lattice or of small vibration if any, and arises only from the intra-chain interaction of polyethylene.

As seen in Figure 5(b), the spectra observed at temperatures ranging from 150 to 295 K consist of two components: one spectrum is a broad component whose line width decreases with temperature and whose intensity decreases and the other is a narrower one whose intensity increases with temperature. These spectral changes can be explained as the result of an increase in the amplitude of rotational oscillation of guest polyethylene in *d*-UPEC with increasing temperature. The decrease in the second moment is also due to the same motion.

Molecular Motions of Guest Molecules in Urea Complexes

In the previous sections, the following three conclusions were obtained concerning the molecular motion of guest molecules in urea complexes.

1) The guest molecules both in *n*-C₁₈H₃₈ and in polyethylene complexes are freely rotating above the respective transition temperatures.

2) The transition temperatures observed by NMR are about 15 K higher than those by DSC.

3) At about 125 K, polyethylene molecules are rigid or are at least vibrating with small amplitudes, although *n*-C₁₈H₃₈ molecules are rotating or vibrating with a larger amplitude.

In this section, we discuss the motions in the temperature region in which the second moment decreases with increasing temperature or in which rotational vibration (or rotation) occurs but not completely.

The first characteristic feature is that the second moments of urea complexes decrease gradually over a wide temperature range of about 100 K as compared with the transition region of 10 K observed by thermal measurements. This fact is explained as the decrease in second moments due mainly to the increase in the amplitude of rotational oscillation.^{6,7} Chatani *et al.*⁷ calculated the potential for *n*-C₁₆H₃₄ complex based on the crystal structure. They found four potential minima and a potential barrier of $7.2 \text{ kcal mol}^{-1}$ for the low-temperature form, and six minima and about 1 kcal mol^{-1} for the high-temperature form. This calculation suggests that the free rotations of guest molecules can not occur at temperatures lower than the transition observed by thermal measurements and can occur with a transition from a low-temperature to a high-temperature form.

On the other hand, the result on the second moment of the polyethylene complex does not seem to support the above hypothesis. At 272 K, 10 K below the transition temperature by thermal measurement, at which almost all of the crystals are thought to be in the low-temperature form when estimated from DSC, the second-moment measurements indicate that the amplitude of rotational oscillation of polyethylene is larger than 90° ; *i.e.*, the experimental value is $6.3 \times 10^{-8} \text{ T}^2$, which is smaller than the calculated one of $10.32 \times 10^{-8} \text{ T}^2$ for rotational oscillation with a 90° amplitude. Since the amplitude over 90° means the free rotation in the

case of the low-temperature form of the complex, it can be concluded that part of the polyethylene as guest molecules is freely rotating in the urea channels. The 91% of polyethylene is estimated to be freely rotating even at 272 K, 10 K below the transition temperature observed by thermal measurements. This large proportion of freely-rotating molecules creates certain question as to the activation energy of free rotation in the low-temperature form of crystal and as to the origin of the order-disorder phase transition.

The activation energy must be small, at least smaller than the calculated value of $7.2 \text{ kcal mol}^{-1}$, because almost none of the guest molecules can freely rotate at 272 K if the activation energy is $7.2 \text{ kcal mol}^{-1}$. However, our NMR measurements showed that 91% of polyethylene are freely rotating.

We have two possibilities for the relation between the phase transition and the free rotation of guest molecules. One is that the structure of the host crystal changes to another crystal form and the guest molecules can freely rotate above the transition temperature because the interaction between the host and guest molecules is weak in the high-temperature form. The other is that a certain portion of the guest molecules come rotating freely in the low-temperature form and the complexes transform into a stable form when they have free rotating guest molecules. Our NMR result supports the latter hypothesis.

Acknowledgment. We wish to thank Professor T. Takemura of Kyushu University for supplying the extended-chain crystals of polyethylene. We especially thank Professor F. Yokoyama of Okayama University and Professor Y. Chatani of Osaka University providing important literature and information. The present study was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture.

REFERENCES

1. F. Bengen and W. Schlenk, Jr., *Experimentia*, **5**, 200 (1949).
2. W. J. Zimmerschied, R. A. Dinerstein, A. W. Weitkamp, and R. F. Marschner, *Ind. Eng. Chem.*, **42**, 1300 (1950).
3. K. Monobe and F. Yokoyama, *J. Macromol. Sci. - Phys.*, **B8**, 277 (1973).
4. A. E. Smith, *Acta Cryst.*, **5**, 224 (1952).
5. D. F. R. Gilson and C. A. McDowell, *Mol. Phys.*, **4**, 125 (1961).
6. K. Umemoto and S. S. Danyluk, *J. Phys. Chem.*, **71**, 3757 (1967).
7. Y. Chatani, H. Anraku, and Y. Taki, *Mol. Cryst. Liq. Cryst.*, **48**, 219 (1978).
8. J. D. Bell and R. E. Richards, *Trans. Faraday Soc.*, **65**, 2529 (1969).
9. R. C. Pemberton and N. G. Parsonage, *Trans. Faraday Soc.*, **61**, 2112 (1965).
10. R. C. Pemberton and N. G. Parsonage, *Trans. Faraday Soc.*, **62**, 553 (1966).
11. N. G. Parsonage and R. C. Pemberton, *Trans. Faraday Soc.*, **63**, 311 (1967).
12. Y. Chatani, Y. Taki, and H. Tadokoro, *Acta Cryst.*, **B33**, 309 (1977).
13. Y. Hori, S. Shimada, and H. Kashiwabara, *Polymer*, **18**, 1143 (1977).
14. F. Yokoyama, Y. Ochi, M. Shinohara, and K. Monobe, *Polym. Repr., Jpn.*, **28**, 1862 (1979).
15. F. Yokoyama, private communication.
16. J. H. Van Vleck, *Phys. Rev.*, **74**, 1168 (1948).
17. H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.*, **18**, 162 (1950).
18. E. R. Andrew, *J. Chem. Phys.*, **18**, 607 (1950).
19. S. Kavesch and J. M. Schultz, *J. Polym. Sci. A-2*, **8**, 243 (1970).
20. H. G. Olf and A. Peterlin, *Kolloid Z. Z. Polym.*, **215**, 97 (1967).
21. F. Horii and P. Kitamaru, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 265 (1978).
22. K. Bergmann, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1611 (1978).
23. K. Yamagata and S. Hirota, *Rep. Prog. Polym. Phys. Jpn.*, **5**, 236 (1962).