Table IV
Side-Group Orientations at Minimum Energy Conformations of the Skeleton and Side Groups

Polymer	Minima[a]	R_1	R_2	R_3	R_4[b]	T_1	T_2	T_3	T_4
$[NP(OCH_3)_2]_n$-A	160:200	C	C	C	C				
	0:200	C	A	C	C				
	0:320	C	B	C	C				
$[NP(OCH_3)_2]_n$-B	160:200	C	C	C	C				
	0:200	C	A	C	C				
	0:320	C	B	C	C				
$[NP(OCH_2CH_3)_2]_n$-A	30:330	C	C	C	C	A	A	A	A
	0:220	C	C	C	C	A	A	A	A
	160:210	C	C	C	C	A	A	A	A
$[NP(OCH_2CH_3)_2]_n$-B	20:340	C	C	C	C	A	A	A	A
	0:180	C	C	C	C	A	A	A	A
	160:210	C	C	C	C	A	A	A	A
$[NP(OCH_2CF_3)_2]_n$	30:330	C	C	C	C	A	A	A	A
	0:180	C	C	C	C	A	A	A	A
	150:210	C	C	C	C	A	A	A	A
$[NP(OC_6H_5)_2]_n$	10:270	A	B	C	B	B	C	C	B
	10:150	A	C	C	C	B	C	C	C
	150:210	C	C	C	C	C	B	C	B

[a] Skeletal torsional angles ϕ and ψ, respectively. [b] Positions A, B, and C are depicted in structures VI and VII. Groups R_2, R_4, T_2, and T_4 are assumed to be represented by mirror images of VI and VII.

is generally believed to be a function of the flexibility of the polymer chains. A low glass transition temperature is an indication of a high chain mobility. High chain flexibility may be a function of two factors: the breadth of the minimum energy wells and the presence of low barriers between the principal wells. Hence, it was of interest to examine the energy surfaces calculated for $[NP(OCH_3)_2]_n$, $[NP(OCH_2CH_3)_2]_n$, and $[NP(OCH_2CF_3)_2]_n$ in a search for clues to the reasons for the low T_g values of these polymers.

The energy surfaces calculated for all three polymers show both broad areas of low potential and low barriers between the main wells. Extensive conformational changes can apparently occur within the wells for all three cases without the surmounting of barriers greater than 1–2 kcal/mol residue. Furthermore, the energy barriers to the transition from one minimum conformation to another are not excessive (<3 kcal/mol residue) for these three alkoxyphosphazene polymers. On the other hand, the surfaces for poly(diphenoxyphosphazene) showed more restricted low-energy areas, with higher barriers (3–5 kcal/mol residue) between conformational minima. Thus, the presumed conformational mobility derived from the energy surfaces, which decreases in the order $[NP(OCH_3)_2]_n \approx NP(OC_2H_5)_2]_n > [NP(OCH_2CF_3)_2]_n \gg [NP(OC_6H_5)_2]_n$, roughly parallels the change in T_g values in the order: −76, −84, −66, and −8 °C. The reversal of the expected order for the methoxy and ethoxy derivatives probably reflects the influence of the longer ethoxy units on reducing intermolecular chain–chain interactions.

Acknowledgment. We thank the Army Research Office for the support of this work.

References and Notes

(1) This paper is part 29 in a series on phosphorus-nitrogen compounds.
(2) Part 28: H. R. Allcock, R. W. Allen, and J. J. Meister, *Macromolecules*, preceding paper in this issue.
(3) H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.*, **87**, 4216 (1965).
(4) H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem.*, **5**, 1709 (1966).
(5) H. R. Allcock and G. Y. Moore, *Macromolecules*, **5**, 231 (1972).
(6) H. R. Allcock, "Phosphorus-Nitrogen Compounds", Academic Press, New York, N.Y., 1972.
(7) H. R. Allcock, *Chem. Rev.*, **72**, 315 (1972).
(8) H. R. Allcock, *Chem. Technol.*, **5**, 552 (1975).
(9) D. P. Tate, *J. Polym. Sci., Polym. Symp.*, **No. 48**, 33 (1974).
(10) R. E. Singler, N. S. Schneider, and G. L. Hagnauer, *Polym. Eng. Sci.*, **15**, 321 (1975).
(11) S. H. Rose, *J. Polym. Sci., Part B*, **6**, 837 (1968).
(12) G. S. Kyker and T. A. Antkowiak, *Rubber Chem. Technol.*, **47**, 32 (1974).
(13) H. R. Allcock, R. L. Kugel, and E. G. Stroh, *Inorg. Chem.*, **11**, 1120 (1972).
(14) T. M. Connelly and J. K. Gillham, *J. Appl. Polym. Sci.*, in press.
(15) K. D. Gibson and H. A. Scheraga, *Proc. Natl. Acad. Sci. U.S.A.*, **58**, 420 (1967).
(16) The *A* and *B* parameters for an aromatic CH group were calculated with a polarizability estimated from data by Ketelaar and a van der Waals radius slightly smaller than that proposed for a CH_2 group. The method is analogous to the expanded carbon atom approach for methyl groups.
(17) Reference 6, Appendix I, and ref 7.
(18) F. S. Ezra and R. L. Collin, *Acta Crystallogr., Sect. B*, **29**, 1398 (1973).
(19) K. S. Pitzer, *Adv. Chem. Phys.*, **2**, 59 (1959).
(20) J. Ketelaar, "Chemical Constitution", Elsevier, New York, N.Y., 1958, p 91.
(21) R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **42**, 2209 (1965).
(22) D. A. Brant, W. G. Miller, and P. J. Flory, *J. Mol. Biol.*, **23**, 47 (1967).
(23) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
(24) C. P. Smyth, "Dielectric Behavior and Structure", McGraw-Hill, New York, N.Y., 1955, pp 289–311.
(25) G. B. Ansell and G. J. Bullen, *J. Chem. Soc. A*, 2498 (1971).
(26) N. L. Paddock, J. Trotter, and S. H. Whitlow, *J. Chem. Soc. A*, 2227 (1968).
(27) Detailed x-ray analyses of these two polymers are being carried out in our laboratory.
(28) G. Allen, C. J. Lewis, and S. M. Todd, *Polymer*, **11**, 44 (1970).
(29) L. E. Sutton, Ed., *Chem. Soc. Spec. Publ.*, **No. 11**, M 128 (1958).
(30) W. C. March and J. Trotter, *J. Chem. Soc. A*, 169 (1971).

Communications to the Editor

Solubility of Hydrogen in Single Crystalline Polyethylene

In a previous research[1] we were able to demonstrate a far higher solubility of hydrogen in single crystalline mats of linear polyethylene (PE) than in ordinary bulk PE. Per gram of sample the hydrogen solubility was fivefold greater in the single crystalline mats than in the bulk PE, but per gram of amorphous phase in which the hydrogen is believed[1] only to dissolve (studies on cyclopropane solubility[2] in PE agreed also with this conclusion) the solubility in the single crystalline mats at 25 °C and 1 atm of pressure of hydrogen was tenfold greater. (Lowell and McCrum[2] did not observe any enhanced solubility of cyclopropane in their single crystal sample as compared to bulk PE.)

Now, however, we have studied hydrogen solubility[3] in some freeze-dried single crystalline samples which became available to us.[4] Much to our surprise no solubility of hydrogen at all could be detected in these rather fluffy crystals although two attempts at 25 °C and one at 35 °C were made to measure the solubility.

Previously,[5] we had thought that the greatly enhanced solubility of hydrogen in the single crystal mats prepared by hot-filtering was a true solubility because the catalytic effect of hydrogen in promoting alkyl radical decay was tenfold greater than in the case of bulk PE. Now, however, we shall have to withdraw this criterion of true solubility because as shown in another research[6] hydrogen catalyzes the alkyl decay to the same extent in the freeze-dried single crystals as it does in the hot-filtered single crystal mats.

The observation of no hydrogen solubility in the freeze-dried samples indicates that the surface amorphous layer of the single crystals, although serving as the location for the alkyl free radical decay reaction, is not of sufficient depth in these freeze-dried samples to retain molecular hydrogen when the solubility cell is evacuated at 77 K to remove the ambient hydrogen.[7] Apparently, two surface layers of the single crystals have to be in contact to provide suitable sorption sites for the molecular hydrogen to be retained.[8]

Acknowledgment. This research was supported by income from the Chair in Chemistry at Baylor University endowed by a gift from The Robert A. Welch Foundation.

References and Notes

(1) S. Kubo and M. Dole, *Macromolecules,* **7,** 190 (1974).

(2) P. N. Lowell and N. G. McCrum, *Polym. Lett.,* **5,** 1145 (1967).

(3) The complete description of this work will appear in a special volume containing the papers of the "Symposium on Structure-Solubility Relationship in Polymers" held at the San Francisco Meeting of the American Chemical Society, Aug 30–Sept 1, 1976, R. B. Seymour, Ed. To be published by the Academic Press, New York, N.Y.

(4) These samples were brought to us by Dr. G. N. Patel from the laboratory of Professor A. Keller of Bristol University, U.K.

(5) W. Y. Wen, D. R. Johnson, and M. Dole, *Macromolecules,* **7,** 199 (1974).

(6) V. M. Patel and M. Dole, submitted for publication.

(7) S. Kubo and M. Dole, *Macromolecules,* **6,** 774 (1973).

(8) This communication is dedicated to the memory of Dr. Shigeo Kubo who died an untimely death in Japan in 1975.

Mark E. Land and Malcolm Dole*

Department of Chemistry, Baylor University,
Waco, Texas 76703

Received August 1, 1976