several million it is no longer valid to use the Debye approximation in good solvent systems. However, if the Ptitsyn equation is then used, ϵ must be adjusted to give the best fit rather than using the *a priori* value calculated from the Mark–Houwink exponent.

As a practical consequence of the wide range of validity of the Debye equation we suggest that chain dimensions of sharp fractions of polymers in the intermediate range of molecular weights be measured by fitting the entire angular envelope to this equation instead of attempting to draw the initial tangent to the low angle data. A gain in precision is thereby effected of approximately fivefold. We also direct attention to the desirability of measuring the scattering intensity as a function of both angle and wavelength and expressing the results as a function of the variable $[\sin(\theta/2)/\lambda']^2$ in order to increase the range of experimental values of P^{-1}.

Acknowledgments. The authors wish to thank Dr. F. Wenger, H. McCormick, and G. Berry for the samples of polystyrene and Mr. R. Buch for the fractions of polydimethylsiloxane.

Nuclear Magnetic Resonance Studies of Polymer Solutions. IV. Polyethylene Glycols

Kang-Jen Liu

Scientific Laboratory, Ford Motor Company, Dearborn, Michigan 48121.

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ABSTRACT: The intramolecular structure of poly(ethylene glycol) (PEG) in solution was studied by a high resolution nmr technique. Most of the experiments were carried out on highly purified oligomeric PEG's, ranging from a trimer to an octamer. The nmr spectra were measured as a function of the chain length. In concentrated solutions, the PEG's are all in states of association, which differ from the individual molecular species. Valuable nmr information concerning the dependence of the intramolecular structure of PEG on its molecular weight may only be obtained from dilute solutions. The protons of the internal ethylenes (E_i) of all PEG'S of various chain length resonate at an identical frequency in their dilute chloroform and aqueous solutions. With the exception of the two outer symmetrical E_i groups, the remaining E_i protons of PEG resonate also at an identical frequency in pyridine. No definite structural information about the chain molecule has been derived from these results alone. In benzene or α-chloronaphthalene, a drastic change in the nmr spectrum of PEG was observed for the hexamer, at which there exist two well-resolved peaks of equal size for the E_i protons, and below which only a single peak was seen. A further change in the nmr spectrum of PEG in benzene or α-chloronaphthalene was observed for the heptamer, at which a new nmr peak appears. This new nmr peak may be referred to as a polymeric peak, which increases with the chain length and, eventually, becomes a predominant peak for high molecular weight PEG. A similar conclusion may also be applied to the nmr results obtained for PEG in carbon tetrachloride. The interaction of the solvent with the E_i groups of the PEG's is generally stronger for the lower PEG's than for the higher members. However, if some specific solvation and complexation are involved, the results may be reversed.

The structure of polyethylene glycol (PEG) has been extensively studied by a number of authors, by various experimental methods, such as X-ray, ir, and dipole moment measurements.[1–7] By measuring the dipole moments of PEG's, ranging from a monomer to a heptamer, in solutions, Kubo, *et al.*,[7] found that the dipole moment of PEG increased progressively with the degree of polymerization. A free rotational model with *trans* and *gauche* minima of equal importance was suggested for these low members of PEG.[7] On the other hand, according to the ir spectra of PEG (mol wt 6000) in the molten and crystalline states, Davison[3] concluded that the conformations of the O(–CH$_2$–CH$_2$–)O portion in PEG are all in the *gauche* form. This conclusion is consistent with the highly crumpled helical structure suggested by X-ray diffraction measurements.[1,2] The higher stability of the *gauche* conformation of PEG was also supported by Mark and Flory from their calculations based on the attractive and repulsive interactions between neighboring segments.[8] Further ir studies of PEG's of various degrees of polymerization revealed that the helical structure of the high members of the PEG series changed into less regular structures of the lower members.[4] Recently, Tadokoro[9] reviewed the structural studies of PEG and stated that the 7/2 helix conformation for high PEG polymer is the most reasonable one at present.

The high resolution nmr technique was used to study the chain conformation of PEG by Connor and McLauchlan.[10] They measured the temperature dependence of the couplings in the C^{13}–H proton satellite side

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(1) W. H. Barnes and S. Ross, *J. Amer. Chem. Soc.*, **58**, 1129 (1936).

(2) H. Tadokoro, Y. Chatani, T. Yoshihara, S. Tahara, and S. Murahashi, *Makromol. Chem.*, **74**, 109 (1964).

(3) W. H. T. Davison, *J. Chem. Soc.*, 3270 (1955).

(4) Y. Kuroda and M. Kubo, *J. Polym. Sci.*, **36**, 453 (1959).

(5) T. Miyazawa, K. Fukushima, and Y. Ideguchi, *J. Chem. Phys.*, **37**, 2764 (1963).

(6) T. Yoshihara, H. Tadokoro, and S. Murahashi, *ibid.*, **41**, 2902 (1964).

(7) T. Uchida, Y. Kurita, N. Koizumi, and M. Kubo, *J. Polym. Sci.*, **21**, 313 (1956).

(8) J. E. Mark and P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1415 (1965).

(9) H. Tadokoro, *Macromol. Rev.*, **1**, 119 (1967).

(10) T. M. Conner and K. A. McLauchlan, *J. Phys. Chem.*, **69**, 1888 (1965).

TABLE I
BOILING POINTS OF POLY(ETHYLENE GLYCOLS)

	Bp, °C	Pressure, mm
$HO(-CH_2CH_2O-)_3H$	116 ± 1	1.5
$HO(-CH_2CH_2O-)_4H$	105	0.01
$HO(-CH_2CH_2O-)_5H$	134	0.02
$HO(-CH_2CH_2O-)_6H$	168	0.07
$HO(-CH_2CH_2O-)_7H$	186	0.07
$HO(-CH_2CH_2O-)_8H$	213	0.07

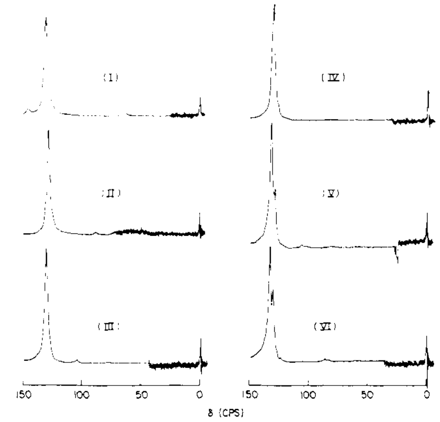


Figure 1. Representative nmr spectra of bulk PEG's at 35°: (I) PEO-600, (II) heptamer, (III) hexamer, (IV) pentamer, (V) tetramer, and (VI) trimer. Cyclohexane, 4% in carbon tetrachloride, was used as an external reference, $\delta = 0$.

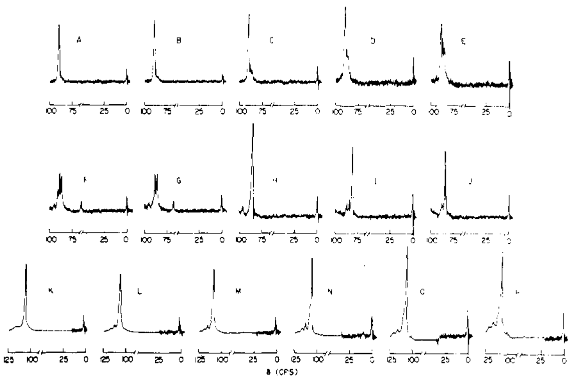


Figure 2. Nmr spectra of PEG's in benzene (A–J, 5%; K–P, 50%) at 35°: (A) PED-20000, (B) PED-4000, (C) PEO-1000, (D) PEO-600, (E) PEO-400, (F) heptamer, (G) hexamer, (H) pentamer, (I) tetramer, (J) trimer; (K) octamer, (L) heptamer, (M) hexamer, (N) pentamer, (O) tetramer, (P) trimer.

bands in PEG. The results seem to indicate that the *gauche* conformation is the most stable one. However, attempts to obtain the energy difference between the *gauche* and *trans* forms were not successful, because the theory used did not fit the experimental results for reasonable values of the parameters involved.

Therefore, there is a general agreement on the conformational features of PEG. However, it is not clear whether the dependence of the conformational arrangements on molecular weight is a smoothly varying function or whether an abrupt transition exists at a certain chain length as the degree of polymerization is increased. In this paper nmr data relevant to this question are shown.

The present experiments were based on the idea that the solvation behavior of the segments in a polymeric structure may be different from those of freely tumbling nonpolymeric segments of the same chain molecule.[11,12] This difference may be amplified experimentally, if certain proper solvents are used. In this study, high resolution nmr spectra of PEG's were measured as a function of chain length in various solvent media.

Experimental Section

Fractions of high molecular weight polyethylene glycol were obtained from Union Carbide and used without further purification. They are essentially pure compounds without any contaminating impurities which may affect the high resolution nmr measurements. Tri- and tetraethylene glycols were obtained from Aldrich and Dow Chemicals, respectively. They were purified by distillation. Penta- and heptaethylene glycols were prepared by condensation of the monosodium salts of mono- and diethylene glycols, respectively, with the dichlorides of the triethylene glycol[13]

$$2HO(-CH_2CH_2O-)_p\,Na + ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl \xrightarrow[16\ hr]{95^\circ} HO(-CH_2CH_2O-)_{2p+3} + 2NaCl$$

where $p = 1$ and 2 for penta- and heptaethylene glycols, respectively. Hexa- and octaethylene glycols were similarly synthesized

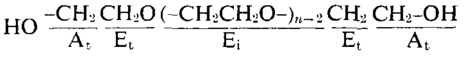
$$2HO(-CH_2CH_2O-)_q\,Na + ClCH_2CH_2OCH_2CH_2Cl \xrightarrow[16\ hr]{95^\circ} HO(-CH_2CH_2O-)_{2q+2}H + 2NaCl$$

where $q = 2$ and 3 for hexa- and octaethylene glycols, respectively. The reaction time of 16 hr was found to be adequate. Prolonged standing at 95° for 3 days as previously reported in the literature[13] is not necessary, and, in fact, makes purification more difficult. These products were isolated by high vacuum distillation, giving sharp boiling points as shown in Table I. The high resolution nmr spectra of the hydroxy protons and of the ethylene protons are quantitatively in accord with the concentrations expected. Pure penta-, hexa-, hepta-, and octoethylene glycols were obtained.

The solvents used were purified in accordance with established procedures. Nmr spectra were obtained using a Varian A-60 spectrometer with a temperature control attachment (Varian Associates, Palto Alto, Calif.). Cyclohexane (4%) in carbon tetrachloride was used as an external standard. The chemical shift is expressed in cycles per second (cps) downfield.

Results and Discussion

Polyethylene glycols can generally be represented by



$$HO\underset{A_t}{\underline{-CH_2}}\,\underset{E_t}{\underline{CH_2O}}\,\underset{E_i}{\underline{(-CH_2CH_2O-)_{n-2}}}\,\underset{E_t}{\underline{CH_2}}\,\underset{A_t}{\underline{CH_2-OH}}$$

In the present report, the ethylene groups at the chain ends and in the parentheses are defined as "terminal ethylene" and "internal ethylene," respectively. All the internal ethylenes are of ether type E_i, whereas the two terminal ethylenes consist of methylenes of both alcohol type (A_t) and ether type (E_t).

Representative nmr spectra of pure PEG'S are shown in Figure 1. All the protons of the ether type, E_i and

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(11) K. J. Liu, *J. Polym. Sci., Part A-2*, **5**, 1199 (1967).

(12) K. J. Liu, *ibid., Part A-2*, **5**, 1209 (1967).

(13) R. Fordyce, E. L. Lovell, and H. Hibbert, *J. Amer. Chem. Soc.*, **61**, 1905 (1939).

E_t, are similar and give one absorption peak. The protons of the terminal alcohol type, A_t, are distinguishable from those of E_i and E_t only for the trimer and tetramer. Their hydroxy proton peaks are not included in these spectra.

As the liquid samples are diluted with benzene, all the nmr peaks of PEG's move toward higher magnetic field owing to the "aromatic solvent effect" of the benzene molecules.[14] Two sets of representative nmr spectra of PEG's in benzene at different concentrations, 50 and 5%, are shown in Figure 2. The protons of the terminal ethylenes showing the complicated spin–spin splitting nmr spectra, and become very different from those of the internal ethylenes in benzene solutions. Again the protons of E_i type give one single nmr peak in 50% concentrated solutions. However, in dilute benzene solutions, it is surprising to observe a fine structure of the nmr spectra of the E_i protons because these protons would usually be expected to be equivalent. A close examination of these chain molecules reveals that the E_i protons of the trimer and tetramer may only give a single nmr peak, because they belong to either a single ethylene (trimer) or two symmetrical ethylenes (tetramer) of E_i type. Indeed, single peaks at 81 and 78 cps were observed for the trimer and tetramer, respectively. The pentamer contains three E_i ethylenes, of which two are symmetrical groups (S groups) and one is at the center of the chain molecule (C group). Therefore, the E_i protons of the pentamer may resonate either at a single frequency when S and C groups are equivalent, or at two different frequencies when S and C are not equivalent. Experimentally, a single peak at 84 cps was observed for the pentamer. It seems to indicate that all the E_i groups of the pentamer are indistinguishable. Similarly, one would expect that the E_i protons of the hexamer (two S groups and two C groups) might also resonate at a single frequency. Contrarily, two peaks at 85 and 87 cps were observed for the hexamer. This may be explained by a conformational change of the polymer segments which sets in at $n = 6$. An addition of the seventh unit (P group) to the center of the chain molecule creates a new environment, and, therefore, three peaks at 86, 88, and 90 cps were observed for the heptamer. As the molecular weight is increased beyond the heptamer, further monomer units may all be identified as P groups and resonate at a single frequency. Therefore, it appears that a polymeric type of conformational structure is revealed in an oligomer in benzene when the chain is seven units long. In this sense, this new nmr peak seen in the heptamer, which increases with the chain length, may be referred to as a polymeric peak.

When α-chloronaphthalene was used as a solvent, very similar nmr results were obtained. The spectra are also concentration dependent. In dilute 5% solutions, the E_i protons give a single peak at 90, 84, and 91 cps for the trimer, tetramer, and pentamer, respectively; two peaks at 94 and 96 cps for the hexamer; and three peaks at 94, 96, and 100 cps for the heptamer and higher members of PEG. When the degree of polymerization reaches seven, the peak at 100 cps appears, which grows again into a single predominant peak for high molecular weight polymers. This polymeric peak does not disappear easily with increasing temperature and may be detected even at 130°. Some nmr spectra determined at 130° and 35° are shown on an expanded scale in Figure 3.

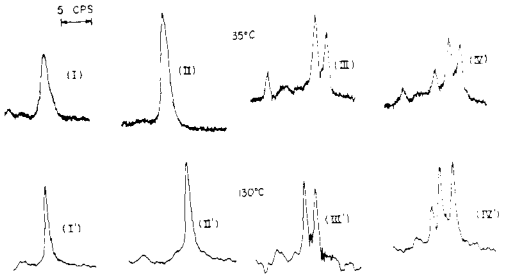

Figure 3. Nmr spectra of PEG's (5%) in α-chloronaphthalene determined on an expanded scale at 35 and 130°: (I, I') tetramer, (II, II') pentamer, (III, III) hexamer, and (IV, IV') heptamer.

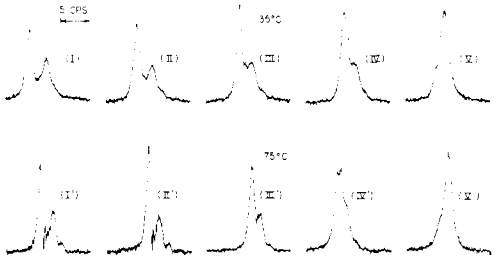

Figure 4. Nmr spectra of PEG's (5%) in carbon tetrachloride determined on an expanded scale at 35 and 75°: (I, I') tetramer, (II, II') pentamer, (III, III') hexamer, (IV, IV') heptamer, and (V, V') PEO-1000.

The conformational changes of PEG may not be restricted to aromatic solvents such as benzene and α-chloronaphthalene only. A similar conclusion may also be drawn from the nmr results obtained for PEG in carbon tetrachloride, although the experimental evidence is not as clear as that obtained in their benzene and α-chloronaphthalene solutions. The nmr spectra of various PEG's in dilute carbon tetrachloride solution taken at 35 and 75° are shown on an expanded scale in Figure 4. The terminal ethylene protons resonate at higher magnetic field (right peak) than those of internal ethylenes. The nmr peak of the E_i protons increases as the polymer chain grows from tetramer to pentamer. The hexamer has a broader E_i peak, and a new peak between the two original peaks appears for the heptamer. It is this poorly resolved new peak which grows eventually into a single predominant peak for high molecular weight polymers.

The E_i protons of all PEG's do not show any resolvable nmr peak in dilute (5%) chloroform or aqueous solutions. Only a single nmr peak was observed in these media for the E_i protons of PEG of any chain length. In dilute pyridine solution, the E_i protons give a single peak at 94 and 92 cps for trimer and tetramer, respectively. A new peak at higher magnetic field appears for the pentamer and grows into a predominant peak for high molecular weight polymers. From these results, no structural information of PEG

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[14] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

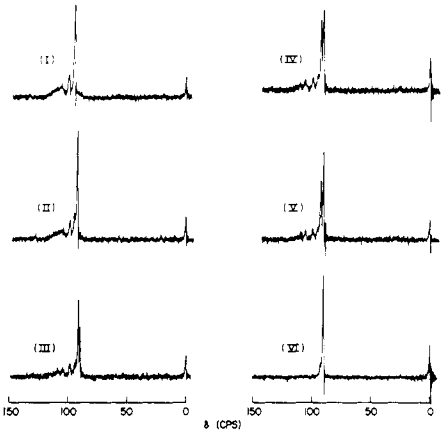

Figure 5. Nmr spectra of PEG's (5%) in pyridine at 35°: (I) trimer, (II) tetramer, (III) pentamer, (IV) hexamer, (V) heptamer, and (VI) PEO-1000.

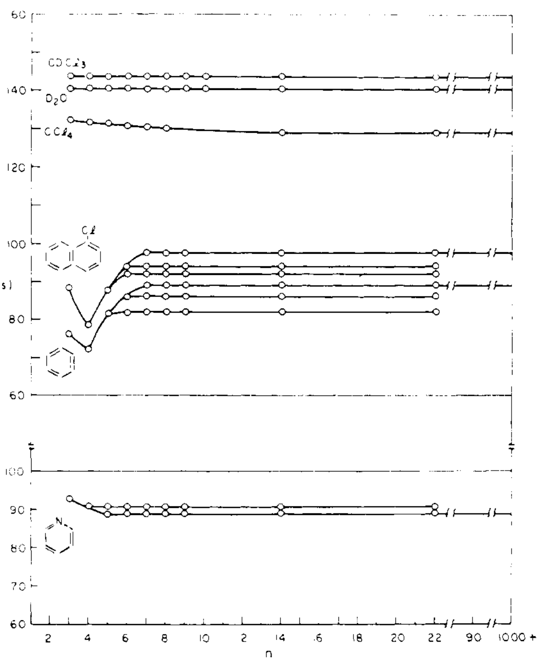

Figure 6. Plots of chemical shift (δ) of the internal ethylene protons of PEG at zero concentration as a function of the chain length.

may be derived, because further monomer units of high PEG ($n > 5$) are indistinguishable from the central E_i ethylene (C group) of the pentamer in these solvents, and we cannot discriminate between the two possibilities: (a) there is no drastic conformational change of PEG in these systems or (b) the change, if any, cannot be detected by the present experiments (Figure 5).

It is important to note that the concentration dependences of the nmr spectra of PEG's in various solvents clearly indicate the association of the PEG molecules in their concentrated solutions and, accordingly, there is little reason to examine the oligomers of PEG in concentrated solution. Valuable information concerning the dependence of the intramolecular conformation of PEG on its molecular weight may only be obtained in dilute solutions. Generally, the fine structure of the nmr spectra of the E_i protons, if any, can be clearly detected when the concentration of the PEG is less than 10%. By further decreasing the concentration to 1%, the general appearance of the nmr spectra of the E_i protons remains the same, although the resolution of the nmr peaks is slightly improved. All the chemical shifts of the E_i protons of PEG extrapolated to zero concentration in various solvents are summarized in Figure 6.

It is interesting to note that plots of chemical shift of the E_i ethylenes of PEG as a function of chain length are more sensitive in systems containing aromatic solvents. The polymeric nmr peak of the E_i protons of PEG in benzene or α-chloronaphthalene appears always at a lower magnetic field than those nonpolymeric E_i protons. This follows the usual pattern (reported on polyethylene)[12] that solvent molecules interact more weakly with the segments in a polymeric structure than with its freely tumbling nonpolymeric segments, causing the chemical shift of polymeric segments to appear at a lower magnetic field. Moreover, as one compares the trends of chemical shifts of the E_i protons as a function of the chain length (Figure 6), some additional information concerning the solvation behavior of PEG in benzene or α-chloronaphthalene may be deduced. It is not surprising that the chemical shift of the E_i protons of a lower PEG in benzene or α-chloronaphthalene moves toward a higher magnetic field, probably because of its stronger interaction with the aromatic solvent molecules.[11,12] However, it is surprising to note that the E_i protons of the trimer, instead of resonating at a higher magnetic field, resonate at a lower magnetic field than does the tetramer in both benzene and α-chloronaphthalene. This is explainable only if one realizes that both ethylene glycol and diethylene glycol (5%) are insoluble in benzene and α-chloronaphthalene. The trimer is the smallest oligomer which becomes soluble in these solvents. Therefore, it is probable that the triethylene glycol interacts poorly with the aromatic solvent molecules, causing the chemical shift at an unusual lower magnetic field.

The results of chemical shifts of the E_i protons of PEG in pyridine (Figure 6) are inconsistent with those obtained for PEG in benzene and α-chloronaphthalene. In pyridine, the E_i protons of the lower PEG resonate at a lower magnetic field than those of the higher PEG do. Some specific interaction between the PEG and pyridine is probably involved. The complexation between PEG and pyridine was previously reported by Page and Bresler.[15] However, the effect of pyridine on the chemical shifts of the E_i protons has not been elucidated. The present nmr results indicate that the complexation between PEG and pyridine has a downfield effect on the chemical shift of the E_i protons of PEG. Since the pyridine complexes with PEG at the two ends of the chain molecule, the effect decreases as the E_i group moves further away from the two terminal ethylene groups. This explains why the order of the nmr peaks of PEG reverses in pyridine from that in benzene or α-chloronaphthalene. This type of complex formation may also be expected to exist in PEG solutions, using pyridine and benzene as mixed solvents. Indeed, the addition of pyridine to the PEG

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(15) T. F. Page, Jr., and W. E. Bresler, *Anal. Chem.*, **36**, 1981 (1964).

solution in benzene highly disturbs the nmr absorptions of the E_i protons of PEG. For example, the two well-resolved nmr peaks of the E_i protons of hexaethylene glycol collapsed into one unresolved peak when a 10% of pyridine was added to its benzene solution. A further increase in pyridine content causes the collapsed peak to split into two peaks, which are similar to those appeared in its pure pyridine solution. A plot of chemical shifts of the E_i protons of hexaethylene glycol (5%) as a function of pyridine content in the mixed solvent is shown in Figure 7. In order to demonstrate that the result is affected mainly by the complex formation between PEG and pyridine, and is not due to just the presence of a polar solvent, the pyridine in the benzene–pyridine mixed solvent was replaced by another H-bonding polar solvent. When deuterated methanol (15∼25%) was mixed with benzene as a solvent, the two resolved mmr peaks of the E_i protons of hexaethylene glycol remained, although the separation of these two peaks was reduced. This confirms our explanation that a complex formation between pyridine and PEG is the predominant factor which affects the nmr spectra of PEG's in their various mixed pyridine solutions.

In conclusion, we have systematically examined the solvation behavior of PEG as a function of chain length in various solvents. From these results, certain intramolecular conformational changes were detected in dilute benzene, α-chloronaphthalene, and carbon tetrachloride solutions. A polymeric type of conformational structure (P ethylene group) appears only when the degree of polymerization reaches seven. Whether these intramolecular structures are only promoted by the solvent molecules in benzene, α-chloronaphthalene, and carbon tetrachloride, or whether they may also exist in other solvents cannot be determined from the present experiments, and requires further examination.

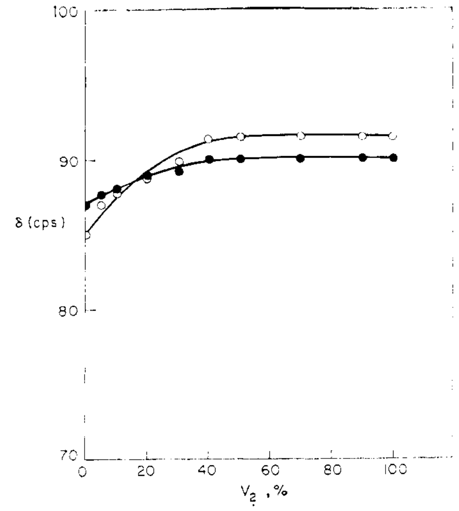

Figure 7. A plot of chemical shifts (δ) of the internal ethylene protons of hexaethylene glycol (5%) as a function of pyridine content (V_2, per cent in volume) in the benzene–pyridine solvent mixture at 35°.

The existence of specialized structures (preferential conformations) in polymer solution, in addition to the well-known polypeptide and nucleic acid systems, has been noted in two other cases of which we are aware. Both polystyrene[16] and polyethylene[12] show characteristic polymeric nmr spectra in solution if, and only if, the chain units reach a certain number. This number is in the neighborhood of 8 for both polystyrene and polyethylene. It is a curious coincidence that the characteristic number of chain units which yield polymeric-type structures in PEG is found to be seven, although the nature of ordered polymeric structures is very different in these three cases.[17] Whether the number 7 or 8 is characteristic of the length of chain sequence necessary to promote a polymeric conformational structure is an interesting subject for further investigation.

Acknowledgment. The author expresses his appreciation to Dr. Robert Ullman for valuable discussions, and to Mrs. S. Lignowski for experimental help.

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(16) F. A. Bovey and G. V. D. Tiers, *Fortschr. Hochpolym. Forsch.*, 3, 139 (1963).

(17) K. J. Liu and R. Ullman, *J. Polym. Sci.*, in press.