TABLE I
X-RAY DIFFRACTION RESULTS FOR THE ORTHORHOMBIC AND THE DERIVED PSEUDOMONOCLINIC UNIT CELLS OF TRANSCRYSTALLINE POLYETHYLENE

Orthorhombic[a]	Unit cell parameters — Derived pseudomonoclinic	Mono 1	Mono 2
a = 7.36 Å	a axis, Å	8.46	7.11
b = 4.92 Å	b axis, Å	9.44	5.46
c = 2.534 Å	c axis, Å	2.534	2.534
	γ angle, °	105.0	96.5
Volume 91.76 Å	Volume, Å^3	195.48	97.75
Monomer units in cell = 2	Monomer units in cell	4	2

Cu Kα radiation = 1.5406 Å

d spacing, Å units — Ortho	Mono	Obsd	Intensity	*hkl* — Ortho	Mono 1	Mono 2
	4.559[b]	4.56	M–S		020	$\bar{1}10$
4.090	4.086	4.09	VVS	110	200	110
3.680		3.68	VS	200		
	3.531[c]	3.53	VW		$\bar{2}20$	200
2.947		2.95	W	210		
	2.714[d]	2.71	VVW		220	020
2.460		2.46	S	020		
2.333		2.33	VW	120		
2.253		2.25	W–S	011		
2.196		2.19	VVW	310		
2.154	2.154	2.15	W	111	201	111
2.087	2.076[b]	2.08–2.09	M	201 split	$4\bar{2}0$	310
2.045	2.043	2.04	W	220	400	220
1.921		1.92	VW	211		
1.840		1.85	VVW	400		
1.763				301		
1.737				320		
1.723				410		
1.716		1.71	M	121		
1.659		1.66	W	311		

[a] The parameters of the orthorhombic unit cell were taken from E. R. Walter and F. P. Reding, *J. Polym. Sci.*, **21**, 561 (1956). [b] Appears in all samples. [c] Appears in stretched samples. [d] Appears in unstretched samples.

A different possible full unit cell can also be considered on the *same lattice array*. This cell, as shown by lightly dashed lines in Figure 1, is also consistent with the full translational symmetry of the lattice array and with the adjacent reentry of molecular folds. It accounts very well for all observed "extra" reflections (see Table I) and the agreement between the experimentally measured and calculated d spacings using the derived lattice parameters is excellent. Consideration of the geometry of this cell suggests that the cell is, in effect, a distorted orthorhombic unit cell of polyethylene. This distortion could arise from slightly different polymer chain packing in a skewed lattice array during the growth of folded-chain lamellae as discussed at some length in our earlier publication.[2] The distortion of the orthorhombic unit cell to this skewed lattice array would involve a small decrease in the length of its a axis, a significant increase in the length of its b axis, and an increase in the γ angle to 96.5°, as is shown in Table I (mono 2). By convention, the smallest full unit cell must be consistent with the full translational symmetry of the lattice. Because this one is consistent, we therefore propose that this cell is the most probable one.

Acknowledgment. The authors gratefully acknowledge helpful discussions with Dr. R. J. Roe.

(2) C. Gieniewski and R. S. Moore, *Macromolecules*, **2**, 385 1969).

Poly(hexamethylphosphoramide) and Its Copolymers

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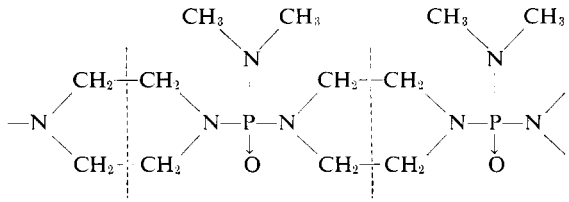
The remarkable properties of hexamethylphosphoramide (HMPA), particularly its ability to dissociate ion pairs into free ions and to dissolve and ionize alkali metals, prompted us to synthesize a polymer of similar structure. This was accomplished by condensing piperazine with dimethylphosphoramidic dichloride ($OPCl_2N(CH_3)_2$) into



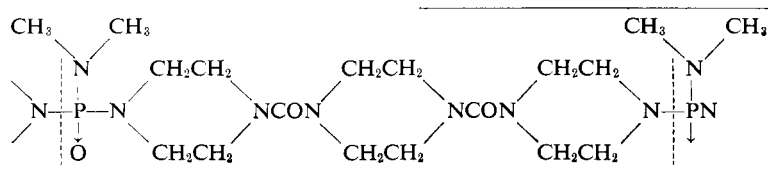
Inspection of the structure of the resulting polymer shows that the recurring units are nearly identical with HMPA and therefore the designation "poly-HMPA" seems to be appropriate for this macromolecule. This work was subsequently extended to some copolymers of a similar structure.

Synthetic Procedure. Dimethylphosphoramidic dichloride was prepared from dimethylamine hydrochloride and an excess of $POCl_3$ following the procedure described by Gordon and Kilby.[1] To obtain anhydrous piperazine the commercial piperazine hexahydrate was dehydrated by heating its mixture with an equal amount of KOH up to 110°. The anhydrous layer was separated from the alkali, mixed with an additional amount of KOH, and finally the diamine was sublimed into the reaction vessel. Thereafter, the required amounts of dry acetone (spectroscopic grade, dried over Drierite for 2 weeks) and of 1,4-diazabicyclo[2.2.2]octane were added to the reactor. The aza compound neutralized the HCl formed in the polycondensation. Finally, the equivalent amount of phosphoramidic dichloride was introduced dropwise into the stirred solution over a period of about 30 min, and then the reacting mixture was heated for 15 hr at 50°. A typical batch contained 5 g of anhydrous piperazine, 50 ml of acetone, 2 equiv of the aza compound, and one equiv of phosphoramidic dichloride.

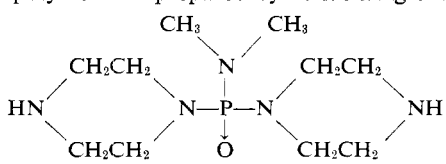
After completion of the condensation the precipitated hydrochloride of the aza compound was removed by filtration and the polymer was then precipitated from the clear solution by pouring it into a 15-fold excess of diethyl ether. The product appeared as a white powder which was filtered and dried in a vacuum oven at 100° for 24 hr. The yield exceeded 80%.

Anal. (theoretical values given in parentheses assume the presence of 1 H_2O/unit). Found: C, 37.5 (37.3); H, 7.97 (8.3); N, 21.1 (21.8), P, 16.4 (16.1).

Preparation of Alternating Copolymers of HMPA Involving CO, Instead of PO, Groups. To modify the properties of poly-HMPA it was decided to synthesize an analogous polymer in which the $>(O)PN(CH_3)_2$ units would alternate either with one or with the two >CO units, *i.e.*

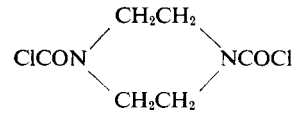


This copolymer was prepared by condensing diamine I



I

with piperazine-1,4-dicarbonyl chloride (II).

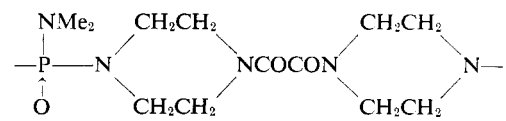


II

In a flask equipped with a condenser and a magnetic stirrer, 7.7 mmol of diamine I and 10.1 mmol of piperazine-1,4-dicarbonyl chloride[2] were dissolved in a mixture of water (30 ml) and chloroform (30 ml). Thereafter, 20 mmol of sodium carbonate was added and the contents were heated to the reflux temperature for 20 hr. The chloroform layer was separated, dried over Drierite, and the polymer was precipitated by pouring the solution into an excess of acetone. After drying at 90° in a vacuum oven the yield of the fibrous polymer was quantitative, its intrinsic viscosity in chloroform at 25° was 0.32 dl/g and $\bar{M}_n$ = 6100 (determined by vapor-phase osmometry). The nmr spectrum in the deuterated chloroform showed the CH_3 protons absorbing at 156 and 166 cps and the CH_2 protons at 196 cps; the integration ratio was 1:4.

Anal. Calcd: C, 48.1; H, 7.58; N, 24.5; P, 7.75. Found: C, 46.4; H, 7.45; N, 22.5; P, 6.54. The hygroscopic properties of the polymer may account for the observed discrepancies, *e.g.*, if 1 H_2O is absorbed for each monomeric unit the results would be C, 46.0; H, 7.74; N, 23.5; P, 7.42.

Alternatively, the diamine I was condensed with oxalyl dichloride giving the following copolymer



The hydrochloride of I (0.016 mol) and sodium carbonate (0.064 mol) were dissolved in 100 ml of water. To this solution, kept in the Waring Blendor, was added rapidly a solution of oxalyl chloride (0.016 mol) dissolved in 100 ml of $CHCl_3$ (free of alcohol). The reaction was over in about 12 min, and the viscous mass was transferred to a rotary evaporator to remove the solvents. The solid residue was extracted with methanol and the filtered methanol solution poured into excess of ether. The copolymer precipitated as a white powder which was filtered and dried; yield 80%; $[\eta]_{25°}$ in methanol 0.40 dl/dr. The polymer is soluble in water as well as in methanol.

Preparation of Diamine I. Diamine I was prepared by treating 100 g of piperazine (sublimed from KOH) with 49.6 g of dimethylphosphoramidic dichloride, $OPCl_2N(CH_3)_2$. The latter was added dropwise to the cold methyl ethyl ketone solution of piperazine containing 67.5 g of 1,4-diazabicyclo[2.2.2]octane. After completion of the addition the mixture was heated for 4 hr to its boiling point, a vigorous stirring prevent-

(1) J. E. Gardner and B. A. Kilby, *J. Chem. Soc.*, 1759 (1950).

(2) D. J. Lymann and S. L. Jung, *J. Polym. Sci.*, **40**, 407 (1959).

ing its overheating. Thereafter, the reacted mixture was cooled to ambient temperature and the precipitated hydrochloride of the aza compound was filtered off. The clear, colorless solution was concentrated in a rotary evaporator and eventually the excess of piperazine was removed by vacuum distillation at 65° (this operation required about 35 hr). The viscous residue was dissolved in 100 ml of ethanol and 40 ml of concentrated HCl solution was then added. The resulting hydrochloride of I was crystallized by adding acetone to the solution until cloudiness appeared and then the mixture was cooled to about −10°. White needles were formed and these were filtered and washed with cold acetone. The yield of product, mp 158°, was about 38%. The analysis corresponded to the empirical composition $(C_{10}H_{24}N_5PO \cdot 2HCl)_2 \cdot 3H_2O$.

Anal. Calcd: C, 33.24; H, 8.11; N, 19.38; Cl, 19.63. Found: C, 33.25; H, 7.71; N, 19.41; Cl, 19.80.

The nmr spectrum in D_2O showed peaks at 157 and 167 (attributed to the CH_3 groups) and at 198 and 203 cps (attributed to the methylenic protons). The integration led to a 3:8 ratio.

Properties of "Poly-HMPA." The resulting polymer is soluble in methylene chloride, chloroform, dimethylformamide, pyridine, acetone, and water. It is insoluble in aliphatic hydrocarbons, cyclohexane, cyclopentane, benzene, carbon tetrachloride, carbon disulfide, and diethyl ether. It precipitates from acetone or acetonitrile solution on addition of very small amounts of water, although it dissolves again when more water is added. Consequently, the polymer is insoluble in wet acetone. The above phenomenon indicates that the interaction of the polymer with water is strong; it probably involves hydrogen bonding causing reversible cross-linking. The importance of such an interaction is shown also by the hygroscopic properties of "poly-HMPA."

The degree of polymerization of the "poly-HMPA," determined by vapor phase osmometry, is 20–25 and its inherent viscosity in 0.5% chloroform solution is 0.12–0.13 dl/g at 25°. Its nmr spectrum in deuterated chloroform shows two peaks at 155.5 and 165 cps characterizing the two methyl groups, and a peak at 187 cps due to the CH_2 groups. The integration leads to the expected ratio 3:3:8. The polymer softens at 140° and liquifies at 180°. Some decomposition occurs at this temperature as indicated by the slight discoloration of the heated material.

The X-ray spectrum of the powdered polymer showed two rather broad halos corresponding to repeat distances of 5.9 and 12.4 Å. Such spectra are often shown by amorphous polymers, *e.g.*, polystyrene. The halos presumably correspond to the repeat distance along the chain and the interchains spacing, respectively.

Transparent films of poly-HMPA were obtained by depositing 10% chloroform solution of the polymer on microscope slides and then evaporating the solvent under vacuum. The exclusion of moisture was imperative in view of the hygroscopic properties of the material. The films were flexible and tough, but in air they become sticky due to absorption of moisture. Irradiation by γ-rays led to only slight changes in the properties of the film. For example, the bulk of the material was still soluble in water when the film was exposed to 2×10^6 rads of radiation, the insoluble fraction amounting to less than 1%. The inherent viscosity of the irradiated polymer was slightly higher than that of the nonirradiated material; the former was 0.19 dl/g in chloroform solution, while the latter was found to be 0.14 dl/g. The irradiation did not cause any discoloration of the film.

Exposing the film to vapor of $POCl_3$ at 50° did not produce any appreciable effect even after 24 hr of curing. These experiments were performed with polymers terminated by the piperazine moieties. The treatment with $POCl_3$ led to development of faint brown color; however, the treated polymer was still soluble in water and in chloroform.

Cross-linked polymeric films insoluble in water were finally obtained by the following procedure. The previously described synthetic method was modified by adding a mixture of $POCl_2N(CH_3)_2$ and $POCl_3$ (10% on the basis of all Cl atoms) instead of pure $POCl_2N(CH_3)_2$. The reaction mixture was, however, more dilute than the previously described one, namely 0.1 mol of piperazine in 140 ml of acetone. Thus, any cross-linking of the product is minimized. After completion of the reaction 0.02 mol of piperazine dissolved in 40 ml of acetone was added to convert all the end groups into amines. Polymer was then precipitated and isolated in the usual way; the resulting product was soluble in water and chloroform.

The powdery polymer was dissolved in $CHCl_3$ (5% by weight); 0.2% (by weight in respect to the dry polymer) of tin dilaurate was added at room temperature and to the stirred solution 5% of 1,5-naphthalene diisocyanate was introduced with the aid of a syringe. Thereafter, the aliquots of the reacting mixture were spread on tin foil covering glass plates and evened with a Gardner knife. The cross-linking seemed to be completed in about 15–20 min and then the clear films were heated for 2 hr to about 50°. Thus, the solvent was removed and tough transparent films were formed. These were freed from the tin foil by dissolving the latter in mercury.

The resulting films were insoluble in organic solvents and in water, although they swell when in contact with water.

Cross-linking with 2,4-toluene diisocyanate was unsuccessful, presumably due to different reactivities of the two isocyanate groups.

Properties of the Alternating Copolymer. The copolymer is soluble in cold water but precipitates on heating. It dissolves in chloroform and in hot DMF, DMSO, and HMPA but the latter solutions gel on cooling. It is insoluble in acetone, benzene, and hydrocarbons.

Acknowledgment. We are grateful to the U. S. Atomic Energy Commission (Contract At-(30-1)-3949) and to the Petroleum Research Fund administered by the American Chemical Society for the financial support of this investigation. We wish also to thank Dr. P. Luner for his help in developing the films.