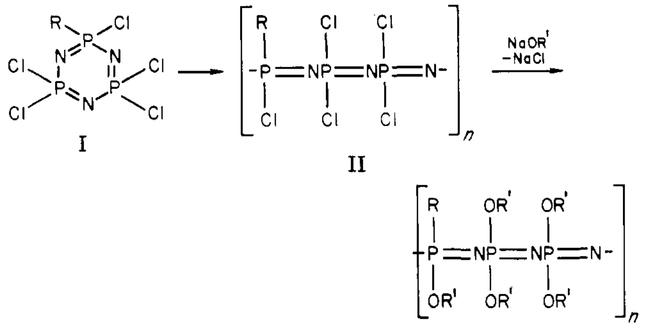
Communications to the Editor

Polymerization of Monoalkylpentachlorocyclotriphosphazenes

The polymerization of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, to poly(dichlorophosphazene), $(NPCl_2)_n$, is a well-known reaction. It constitutes the first step in the synthesis of stable poly(alkoxy- or aryloxyphosphazenes), $[NP(OR)_2]_n$, or poly(aminophosphazenes), $[NP(NHR)_2]_n$ or $[NP(NR_2)_2]_n$. These syntheses are accomplished by the utilization of $(NPCl_2)_n$ as a reactive polymeric intermediate for interactions with alkoxides, aryloxides, or amines.[1-3] A large number of high polymers have now been prepared by this technique, and many of these have considerable fundamental and technological potential.[4-7]

However, it has been recognized for some time that a further extension of this field to yield more-diverse polymers with specific properties (particularly high thermal stability) was dependent on the development of new synthesis routes that would allow alkyl or aryl groups to be linked directly to the skeleton through phosphorus–carbon bonds. The attainment of this goal has been the subject of intensive investigation in our laboratory, with an emphasis to date being placed on substitutive synthesis routes, i.e., on the reaction of organometallic reagents with poly(dihalophosphazenes).[8] The alternative route, the polymerization of per-alkyl- or arylcyclophosphazenes, $(NPR_2)_3$, has so far proved unsatisfactory.[9] However, earlier work by us[10] suggested that phosphazene trimers that contained both phenyl *and* halogeno substituent groups could be converted to low molecular weight polymers, although the steric size of the phenyl groups appeared to be detrimental to the polymerization process.

Recent work in our laboratory has yielded a new synthetic method for the first preparation of monoalkylpentachlorocyclotriphosphazenes (I) by the reaction of $(NPCl_2)_3$ with alkylcopper reagents.[11] We have now found that compounds of structure I undergo thermal polymerization at 210–250 °C to yield high polymers of structure II. If the reaction conditions are controlled carefully, polymers of structure II are not cross-linked and are soluble in a variety of organic solvents, such as tetrahydrofuran, benzene, or toluene. Polymers of formula II are hydrolytically unstable because of the presence of phosphorus–chlorine bonds. Consequently, they were converted to the hydrolytically stable derivatives, III, by treatment with sodium trifluoroethoxide or sodium phenoxide.



I

II

III

$R = CH_3, C_2H_5; OR' = OCH_2CF_3, OC_6H_5$

The following is an example of a typical procedure. Highly purified monomethylpentachlorocyclotriphosphazene, $N_3P_3CH_3Cl_5$ (4.0 g, 0.012 mol), was sealed in an evacuated (0.05 torr) Pyrex tube. The tube was heated at 250 °C for 24 h by which time the viscosity of the polymerizate had risen almost to the point of immobilization. Unchanged $N_3P_3CH_3Cl_5$ was removed from the reaction mixture by sublimation at 70 °C (0.05 torr). The residual polymer (2.5 g) was then dissolved in tetrahydrofuran (50 mL), and this solution was added dropwise to a solution of sodium trifluoroethoxide (prepared from 1.8 g of sodium and 7.5 g of trifluoroethanol) in tetrahydrofuran (100 mL). After the reaction mixture had been heated at 65 °C for 24 h, the polymer III ($R = CH_3$) was isolated by precipitation into dilute hydrochloric acid. Further purification was effected by precipitation from tetrahydrofuran into water or hexane (overall yield = 40%). The product was a colorless, opalescent, film-forming elastomer.

The structure of III ($R = CH_3$; $OR' = OCH_2CF_3$) was confirmed by microanalysis[12] and by the infrared spectrum. A ^{31}P NMR spectrum showed two separate multiplets with peaks at +19.8, +19.5, +17.3, and +16.2 $[P(CH_3)(OCH_2CF_3)]$ and at -8.0, -8.3, -8.7, and -9.1 ppm $[P(OCH_2CF_3)_2]$, respectively.[13] The molecular weight was estimated by gel permeation chromatography to be $\simeq 1 \times 10^6$.[14]

Similarly, the structure of III ($R = CH_3$; $OR' = OC_6H_5$) was confirmed by microanalysis[12] and by ^{31}P NMR spectroscopy. The NMR spectrum showed two resonances as multiplets, the first with peaks at +11.34, +11.05, +10.71, +10.20, and +10.51 $[P(CH_3)(OC_6H_5)]$ and the second at -18.46, -18.58, -18.94, -19.36, -19.53, and -19.77 ppm $[P(OC_6H_5)_2]$. The molecular weight of this polymer was estimated to be $\simeq 1.5 \times 10^6$.

Perhaps the most significant discovery from this work is the ability of only one alkyl group per three repeating units to change the polymer properties from those of a microcrystalline, flexible, but nonelastomeric polymer (as in $[NP(OCH_2CF_3)_2]_n$) to those of a rubbery elastomer. Presumably, this reflects the ability of the methyl groups to disrupt the microcrystallinity. The effect of the alkyl group, R, on the glass-transition temperature of III is of considerable theoretical interest. For polymers of structure III ($OR' = OCH_2CF_3$), the following T_g values (in parentheses) have been determined:[15] $R' = OCH_2CF_3$ (-66 °C), CH_3 (-50 °C), and C_2H_5 (-58 °C).

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References and Notes

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(12) Anal. Calcd for $[-NP(CH_3)_{0.34}(OCH_2CF_3)_{1.66}-]_n$: C, 20.42; H, 2.01; N, 6.49; P, 14.36; F, 44.04. Found: C, 20.54; H, 2.16; N, 6.50; P, 14.51; F. 39.51. Calcd for $[-NP(CH_3)_{0.34}(OC_6H_5)_{1.66}-]_n$: C, 60.52; H, 4.55; N, 6.82; P, 15.09. Found: C, 60.32; H, 4.66; N, 6.71; P, 15.12.

(13) ^{31}P NMR peak positions are relative to aqueous 85% H_3PO_4 used as an external reference. Positive chemical shifts are downfield from H_3PO_4.

(14) The $\bar{M}_n$ molecular weights were determined by gel permeation chromatography comparison with polystyrene standards with the use of 10^6, 10^5, 10^4, and 10^3 Styragel columns in series. The solvent was THF.

(15) The glass-transition temperatures (T_g) were measured with the use of a Chemical Instruments Corp. torsional braid analyzer programmed to operate from −120 to +25 °C, with a temperature variation rate of 2.0 °C min^{-1}.

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Chain Conformation of Phase III Poly(vinylidene fluoride)

Recently Weinhold, Litt, and Lando[1] have produced and studied a crystalline form of poly(vinylidene fluoride), PVF_2, having a chain-axis repeat distance of 9.18 Å and identified as phase III. In a previous paper[2] (henceforth called I) we have suggested two possible chain conformations for this form of PVF_2: *tttgtttg′* and *tgtg′tg′tg* (where *t* represents trans, *g* gauche, and *g′* gauche′). This suggestion was based on an intramolecular conformational analysis using molecular mechanics. The interchain energy and the effects of finite temperature were not taken into account. Because of these omissions, we could not unambiguously choose between the two conformations, although *tgtg′tg′tg* was found to be of a higher intrachain energy than *tttgtttg′*.

We present here preliminary results of the calculation of combined intra- and interchain free energy as a function of temperature. Precise *t*, *g*, and *g′* conformations are used, even though such geometries do not exactly allow the observed fiber axis of 9.18 Å to be computed. The interchain energy is modeled by a mean-field approximation. In calculating the partition function, all the bond lengths and included angles are assumed to be hard variables and remain constant. Only the torsional angle θ is allowed to change. Because in both of the known structures (phases I and II) of PVF_2 every second torsional angle is trans, these are fixed. Consequently, only alternate θ are allowed to vary. We write the Hamiltonian of the system as a functional of the distribution of torsional angles. The free energy and the distribution function $n(\theta)$ are calculated self-consistently in a transfer-integral formalism which has been described at length elsewhere.[3]

In order to be able to treat possible phase III PVF_2 structures, we have extended the theory to describe structures in which the repeat distance along the chain contains eight successive torsional angles. Because all the odd-numbered angles have been kept trans, only the angles θ_{2n} are considered. These are divided into four sublattices θ_{8n}, θ_{8n+2}, θ_{8n+4}, and θ_{8n+6}, which we call the *A*, *B*, *C*, and *D* sublattices. (A formalism in which the alternate torsional angles are divided into two sublattices *A* and *B* has been outlined by Boyle.[4]) The intrachain energy is written in the form

$$V_1 = \int\int U(\theta,\theta') \times [n_{AB}(\theta,\theta') + n_{BC}(\theta,\theta') + n_{CD}(\theta,\theta') + n_{DA}(\theta,\theta')]\,d\theta\,d\theta' \quad (1)$$

and the interchain energy

$$V_2 = \tfrac{1}{4}\int\int\int\int W(\theta_1,\theta_1{}',\theta_2,\theta_2{}') \times [n_A(\theta_1)n_B(\theta_1{}')n_A(\theta_2)n_B(\theta_2{}') + n_B(\theta_1)n_C(\theta_1{}')n_B(\theta_2)n_C(\theta_2{}') + n_C(\theta_1)n_D(\theta_1{}')n_C(\theta_2)n_D(\theta_2{}') + n_D(\theta_1)n_A(\theta_1{}')n_D(\theta_2)n_A(\theta_2{}')]\,d\theta_1\,d\theta_1{}'\,d\theta_2\,d\theta_2{}' \quad (2)$$

The distribution $n_{AB}(\theta,\theta')$ measures the probability that a pair of torsional angles at adjacent *A* and *B* sites will be found at θ and θ'. The mean-field approximation contains the assumption that V_2 can be written as a function of n_A, n_B, n_C, and n_D alone. The function *U* is the change in potential energy resulting from the addition to a chain whose last torsional angle was θ, an additional unit at angle θ'. The function *W* is the energy of a monomeric unit located between segments in the same chain of torsional angles θ_1, $\theta_1{}'$ in the potential of a neighboring chain with angles θ_2 and $\theta_2{}'$. The functions *U* and *W* have been computed using molecular mechanics as exists in the molecular structure determination system CAMSEQ II.[5] The requisite atomic charge densities were computed from the semiempirical molecular orbital scheme[6] CNDO/2.

The resulting transfer-integral expression contains four equations of the form

$$\lambda\psi_A(\theta) = \int\psi_A(\theta')\,d\theta'\int\int\int\exp\{-\beta[V_{AB}(\theta,\theta'') + V_{BC}(\theta'',\theta''') + V_{CD}(\theta''',\theta'''') + C_{DA}(\theta'''',\theta')]\}\,d\theta''\,d\theta'''\,d\theta'''' \quad (3)$$

with

$$V_{AB} = U(\theta,\theta') + \tfrac{1}{2}[h_A(\theta) + h_B(\theta')] \text{ etc.} \quad (4)$$

The function h_i is the mean field at the site *i*. It is related to V_2 through

$$h_i(\theta) = 4\,\frac{\partial V_2}{\partial n_i} \qquad (i = A, B, C, D) \quad (5)$$

These equations are solved iteratively from a starting set of trial functions $n_A{}^0$, $n_B{}^0$, $n_C{}^0$, $n_D{}^0$, which are first used in eq 5 to give V_{AB}, V_{BC}, etc., in eq 4. Hence a new set of n_A, n_B, n_C, n_D results from eq 3 through relations

$$n_i(\theta) = \psi_i\bar{\psi}_i(\theta) \Big/ \int\psi_i(\theta)\bar{\psi}_i(\theta')\theta' \quad (6)$$

with $\bar{\psi}$ the solution of the transposed transfer-integral equation. If more than one such set of solutions is obtained, the one with the lowest free energy is the stable solution. The others are metastable.

In the actual computation, the potentials and distribution functions were found for only six uniformly spaced values of the angle θ (θ = 0° is trans), and the integrations were placed by corresponding uniform summations.

The calculation yields one stable phase and several metastable phases in the low-temperature regime. The chain conformation of the stable low-temperature phase is found to be *tgtg′tgtg′*, the same as the experimental phase II (or α phase). In the high-temperature phase, the gauche and gauche′ states are equally populated, the fractional population increasing with temperature. We identify this as the melt phase. The melting temperature of the α phase is found to be 513 K (Figure 1), which is reasonably close to the experimental value of 460 K. We also find a low-temperature phase with chain conformation *tttttttt*. This is, therefore, identified with the all-trans β phase. It is metastable only with respect to the α phase.

The conformations of the metastable phases that occur with a repeat of eight torsional angles are shown in Table I. The table also contains the free-energy minima of each of these phases and of the α phase and β phase at a

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