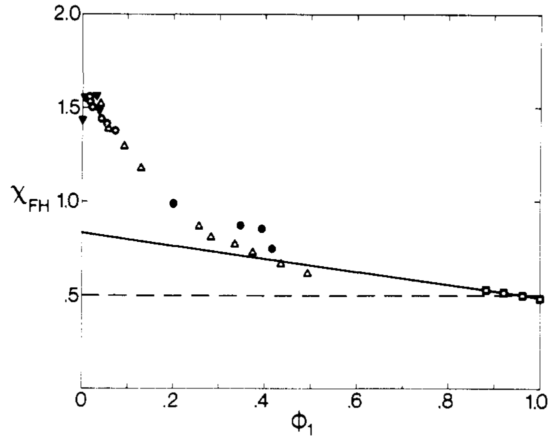

Figure 4. Values for χ_{FH} calculated according to eq 4. Symbols as in Figure 3. Solid line for χ calculated from eq 14 with $\chi_1 = 0.482$ and $\chi_2 = 0.371$.

water content at very low relative humidities, and the effect is also evident when the data are plotted as χ_{FH} vs. ϕ_1 (Figure 4). Possible explanations include an initial hydration of the polymer or disruption of crystalline regions.

In their examination of the activity of organic solvents over liquid-crystalline solutions of poly(γ-benzyl glutamate), Flory and Leonard[8] found that the Henry's law slope, a_1/ϕ_1 at $\phi_1 = 0$, was much less than expected. They obtained a better fit to their experimental data by introducing a new volume fraction term for the mixing of solvent with only the side chains of the helical polymer molecules. In our case, no such assumption was needed to fit the rigid rod theory with a plausible value of χ.

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Crystalline Poly(organophosphazene) Blends and Copolymers

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ABSTRACT: The thermal transition behavior of a number of one-to-one aryloxy poly(phosphazene) copolymers with varied para and meta substituted phenoxy repeat units and several related homopolymer blends has been studied. From DSC experiments on the blends, it is concluded that the crystalline phases, and in some cases the amorphous phases as well, are incompatible. All the copolymers are crystalline and exhibit the $T(1)$ transition to a mesomorphic state typical of poly(phosphazene) homopolymers. Based on the thermal transition behavior, the copolymers can be divided into two classes. Class I copolymers, with similar meta or para substituted repeat units, exhibit $T(1)$ transitions close to homopolymer values and enthalpies at least 75% of theoretical. Class II copolymers, with mixed meta/para substituted phenoxy repeat units, exhibit $T(1)$ values lower than either homopolymer and enthalpies less than one-half the rule-of-mixtures value. The crystalline behavior is attributed to isomorphism. X-ray results on the *p*-chlorophenoxy/*p*-cresoxypoly(phosphazene), a class I copolymer, show that only a single unit cell occurs, while in a typical class II copolymer two unit cells are present. This suggests that class I copolymers exhibit type I and class II type II isomorphism in the sense defined by Natta and by Wunderlich.

Most poly(organophosphazene) homopolymers, with a single type of alkoxy or aryloxy substituent, are semicrystalline materials. These polymers generally exhibit two first-order transitions.[2-5] The lower transition, which is marked by a prominent enthalpy change, is now recognized as representing the transition to a partially ordered state.[5-10] The upper transition represents the true melting point which occurs at 350 to 400 °C in the aryloxy homopolymers and is close to the decomposition temperature.[3-5,9]

Poly(phosphazene) copolymers involving the use of mixed substituents to inhibit the development of crystallinity received early attention.[11] The use of mixed fluoroalkoxy substituents at near equimolar proportions

Table I
Composition of Copolymers $[(RO)_X(R'O)_{(2-X)}PN]_n$

				composition[a]			
				elemental anal.		NMR	
R	R′	% C	% Cl	X	$(2-X)$	X	$(2-X)$
		Copolymers: Class I					
4-ClC_6H_4	4-$CH_3C_6H_4$	55.82	13.41	1.04	0.96	1.06	0.94
4-ClC_6H_4	4-$C_2H_5C_6H_4$	56.91	12.97	1.06	0.94	1.05	0.95
3-$Cl_3C_6H_4$	3-$CH_3C_6H_4$	54.20	13.72	1.14	0.86	1.08	0.92
		Copolymers: Class II					
4-ClC_6H_4	C_6H_5	53.84	14.21	0.92	1.08		
4-ClC_6H_4	3-CH_3C_6H	54.59	14.18	1.14	0.86	1.14	0.86
4-ClC_6H_4	3-$CH_3C_6H_4$[b]	54.48	12.81	1.02	0.98	1.0	1.0
4-ClC_6H_4	3-ClC_6H_4	47.96	23.38				
4-$CH_3C_6H_4$	3-$CH_3C_6H_4$	65.22	0.23				
3-ClC_6H_4	4-$CH_3C_6H_4$	55.08	13.95	1.10	0.90 (2)	1.09	0.91

[a] X and $(2-X)$ are the number of moles of the two substitutents in the copolymer calculated from carbon and chlorine elemental analysis or the number of moles from NMR analysis. [b] Substitution reaction conducted sequentially.

has provided a route to low-temperature, solvent-resistant elastomers which are undergoing commercial development.[3,4,12] Two copolymers, based on mixed aryloxy substituents, have been reported to exhibit rubber-like properties and have been evaluated as fire retardant, flexible, insulating foams.[3,4,13,14] Although it might be expected that copolymers with nearly equimolar proportions of the two substituents would necessarily be amorphous, there is evidence that this is not always the case. A number of aryloxyphosphazene copolymers of the type $[(C_6H_5O)(RO)PN]_n$ and $[(4\text{-}CH_3OC_6H_4O)(RO)PN]_n$, where (RO) represents a variety of para-substituted phenoxy groups, were prepared by Dieck and Goldfarb.[15] Many of these copolymers exhibited endothermal behavior above the glass transition temperature despite the fact that the authors concluded that random substitution had occurred. Direct evidence of the relative reactivities of different aryloxides is not available, but there is little reason to expect that there would be such large differences in reactivity that substitution could lead to block rather than random copolymers, even when the reaction is carried out in the presence of an excess of the nucleophiles. Since the polymers studied by Dieck and Goldfarb were based on phenols with alkyl or alkoxy substituents in the para position, there should be little difference in the relative reactivities. In fact, the elemental analyses were in full agreement with the theoretical values, assuming equimolar substitution.

The work of Dieck and Goldfarb[15] concentrated on the glass transition behavior of aryloxyphosphazene copolymers. The transition behavior of several fluoroalkoxyphosphazene blends and copolymers has been studied by Connelly and Gillham,[16] in this case using torsional braid analysis. In the present investigation, aryloxyphosphazene blends and copolymers have been prepared, where the chain substituents are primarily *m*- and *p*-methyl or -chloro substituted aryloxides. The purpose was to study the nature of crystallinity in these systems and to relate these observations to the known behavior of poly(phosphazene) homopolymers.

To simplify sample designation, blends or copolymers will be designated solely by the two substituents, e.g., phenoxy/*p*-chlorophenoxy copolymer for poly[(phenoxy-4-chlorophenoxy)phosphazene], or by use of the chemical formula $[(C_6H_5O)(4\text{-}ClC_6H_4O)PN]_n$.

Experimental Section

Synthesis. Poly(dichlorophosphazene) was prepared from the polymerization of phosphonitrilic chloride (>90% trimer) and isolated in a manner similar to that previously described.[3,17] The polymerizations were carried out for 55 to 112 h at 245 °C. Isolated polymer yields were 20–34%.

The poly(aryloxyphosphazene) copolymers were synthesized in a manner similar to that described for the homopolymers,[3,17] except that the mixture of sodium aryloxides was prepared using the corresponding phenols and sodium methoxide (rather than by direct reaction with sodium) followed by azeotropic removal of methanol prior to the addition of poly(dichlorophosphazene).

Analysis. Elemental analyses were conducted by Galbraith Laboratories, Knoxville, Tenn., for carbon, chlorine, and hydrogen, and the results were used to calculate the substituent mole ratios (Table I). The composition of the copolymers was also determined from the relative intensities of each substituent obtained from ^1H NMR spectra taken at 36 °C using a Perkin-Elmer Model R32 90 MHz spectrometer (Table I). An estimate of the trimer content and an examination of the molecular weight distribution were carried out by GPC analysis in tetrahydrofuran using a Waters Anaprep gel permeation chromatograph with refractive index monitor. The column set consisted of 4 ft by $^3/_8$ in. Styragel columns with porosity ratings designated at 5×10^6, 10^6, $(1.5\text{–}7) \times 10^5$, 10^5, 10^4, and 10^3 Å.

Samples for DSC and X-ray analysis were prepared by dissolving the copolymers or mixing the homopolymers in freshly distilled tetrahydrofuran with stirring and gentle heating until an homogeneous solution was obtained (5–10% concentration). Solutions were cast in a leveled 4 in. × 4 in. Teflon mold or in a 100-mL beaker floating on mercury and allowed to evaporate to dryness over a 24-h period. Films were removed and dried in a vacuum oven at 40 °C for 24 h to remove residual solvent. Oriented films were uniaxially stretched nearly to the breaking point, usually 200–300% elongation.

A Perkin-Elmer DSC II equipped with a two-stage intercooler and nitrogen purge was used in collecting the thermal data. Scanning rates of 20 K/min when heating and 40 K/min when cooling were employed. Samples were encapsulated in a standard aluminum pan. A pure sample of indium was used to calibrate the measurement of temperature and enthalpy. Glass transition temperatures were taken as the temperature at which one half of the change in heat capacity had occurred. The temperatures recorded for first-order transitions were taken at the peak maxima and rounded to the nearest degree. Peak areas were measured from the DSC recorder tracer using a Hewlett Packard 9830/B calculator equipped with a Model 9864A digitizer.

X-ray diffraction patterns were recorded photographically in a camera manufactured by W. H. Warhus mounted on a Norelco X-ray generator equipped with a graphite monochromator and copper X-ray tube (20 mA, 50 keV). Exposures of 18 h with a sample-to-film distance of 7.48 cm were used, and powdered aluminum was used to calibrate the sample-to-film distances.

Results

Blends. Figure 1 presents characteristic DSC behavior obtained after the first scan for three of the four blended homopolymer films, each containing poly[bis(*p*-chloro-

Table II
Thermal Data for Poly(organophosphazene) Homopolymers $[(RO)_2PN]_n$; Blends $A[(RO)_2PN]_n + B[(R'O)_2PN]_n$; and Copolymers $[(RO)_X(R'O)_{2-X})PN]_n$[a]

R	R′	T_g(meas), K	T_g(calcd),[b] K	$T(1)$, K	ΔH(meas), cal/g	ΔH(calcd),[c] cal/g
Homopolymers						
C_6H_5		279		433	10.0	
4-$CH_3C_6H_4$		273		427	8.5	
4-$C_2H_5C_6H_4$		255		316	1.1	
4-ClC_6H_4		277 (286)[d]		442	6.6 (7.2)[d]	
3-$CH_3C_6H_4$		248		363	8.3	
3-ClC_6H_4		249		363	5.8	
Blends						
4-ClC_6H_4[d]	4-$CH_3C_6H_4$	282	279	419	3.2	
				435	3.2	7.9
4-ClC_6H_4	3-$CH_3C_6H_4$	249	262	360	2.4	
		277		428	2.6	7.4
4-ClC_6H_4	4-$C_2H_5C_6H_3$	256	265	358	0.5	
		277		380	0.3	
				425	2.5	3.9
4-ClC_6H_4	C_6H_5	278	278	389	1.2	
				403	0.6	
				423	4.6	8.2
Copolymers: Class I						
4-ClC_6H_4	4-$CH_3C_6H_4$	282	275	435 r	6.7	7.5
4-ClC_6H_4	4-$C_2H_5C_6H_4$	271	267	359	3.4	4.0
3-ClC_6H_4	3-$CH_3C_6H_4$	249	249	365	5.2	7.0
Copolymers: Class II						
4-ClC_6H_4	C_6H_5	278	278	350, 367 m	4.2	8.4
4-ClC_6H_4	3-$CH_3C_6H_4$	267	269	352 r	3.6	7.4
4-ClC_6H_4	3-$CH_3C_6H_4$	267	268	347 r	0.5	7.4
4-ClC_6H_4	3-ClC_6H_4	265	263	357 r	3.0	6.2
4-$CH_3C_6H_4$	3-$CH_3C_6H_4$	260	261	329 m	3.1	6.0
3-ClC_6H_4	4-$CH_3C_6H_4$	260	260	339 m	2.6	4.8

[a] A and B are weight fractions of polymers in the blend; X and $(2 - X)$ are the number of moles of the two substituents in the copolymer. [b] From equation 1. [c] From equation 2. [d] Values for later preparation. This sample was used only in the indicated blend. [e] Substitution reaction conducted sequentially: m = multiple endotherms; r = concommitant endotherm/exotherm followed by final endotherm.

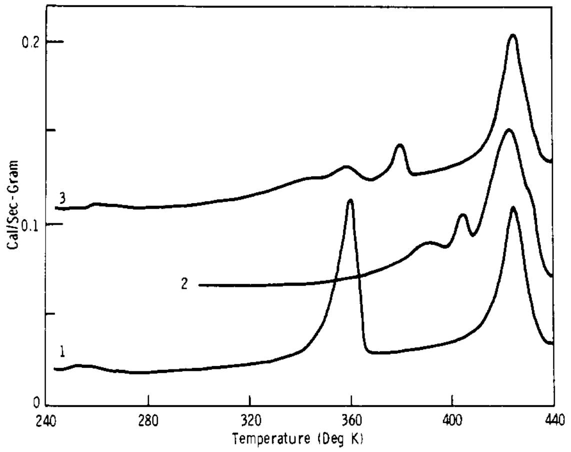

Figure 1. DSC scans of blends of aryloxyphosphazene homopolymers: $[(4\text{-}ClC_6H_4O)_2PN]_n + [(3\text{-}CH_3C_6H_4O)_2PN]_n$ (curve 1); $[(4\text{-}ClC_6H_4O)_2PN]_n + [(C_6H_5O)_2PN]_n$ (curve 2); and $[(4\text{-}ClC_6H_4O)_2PN]_n + [(4\text{-}C_2H_5C_6H_4O)_2PN]_n$ (curve 3).

phenoxy)phosphazene] mixed with a near equal weight of a second polymer component (Table I). Various results taken from the scans are summarized in Table II. Note that in one of the blends a later preparation of poly[(p-chlorophenoxy)phosphazene] was used which proved to have a somewhat higher glass transition temperature (T_g) and enthalpy change at $T(1)$ [values indicated by superscript a]. The two blends for which the homopolymer T_g values differ by at least 20 °C show two T_g values, although the higher T_g is less distinct than the lower transition. From the results in Table II, it can be seen that in each case the two T_g values correspond closely to the homopolymer values indicating amorphous phase incompatibility in these two samples. In the other two blends, the homopolymer T_g values are too close to be resolved so that it is not possible to determine whether there is amorphous phase incompatibility.

The endotherms at $T(1)$ show varied and rather complex behavior. In general, they are broader, occur at lower temperatures, and have smaller individual and combined heats of transition than the values expected on the basis of the homopolymers (compare columns 5 and 6, Table II). Although not illustrated, all four blends exhibit two distinct recrystallization exotherms. A discussion of the distinctive features observed in the individual blends follows.

The heating curve for the *p*-chlorophenoxy/*m*-cresoxy blend in Figure 1 shows two separate and well-defined endotherms occurring at temperatures which can be correlated with the homopolymer $T(1)$ transitions listed in Table II. The enthalpy changes for the two peaks are about 80 and 60%, respectively, of the contribution expected for the *p*-chlorophenoxy and *m*-cresoxy polymers. These results suggest that the crystalline components of the two polymers in the blend are essentially incompatible. However, it is interesting to note that $T(1)$ for the upper peak, representing the *p*-chlorophenoxy polymer, is fully 20 °C below the transition for the pure homopolymer and, in fact, occurs at nearly the same temperature in three of the four blends recorded in Table II. This suggests that the crystalline (*p*-chlorophenoxy)phosphazene phase may accommodate a small amount of the second polymer component. The behavior of the *p*-chlorophenoxy/*p*-

cresoxy blend (not shown) is very similar to that of the *p*-chlorophenoxy/*m*-cresoxy, but it will be noted from Table II that the transition temperatures and enthalpies of the two peaks are closer to the values for the respective homopolymers.

The DSC scan for the *p*-chlorophenoxy/phenoxy blend shows a major peak corresponding to the temperature normally associated with the *p*-chlorophenoxy component and two minor peaks at temperatures which are well below $T(1)$ for the phenoxy homopolymer. The enthalpy change of the major peak is 40% greater than the value expected from the enthalpy of the *p*-chlorophenoxy homopolymer alone. This might be taken to suggest that mixing and cocrystallization of the two homopolymers has occurred. However, since the $T(1)$ temperatures for the two polymers differ by only ten degrees, it is also possible that the separate transitions are not resolved even though the two crystalline phases are essentially incompatible. The broadness of this peak compared to the similar endotherms for the other two blends in Figure 1, as well as the pronounced high-temperature shoulder, supports the latter interpretation.

In the third of the blends illustrated in Figure 1, two minor peaks are observed at temperatures well below that of the main *p*-chlorophenoxy peak but well above $T(1)$ for the *p*-ethylphenoxy homopolymer. There is, in fact, no endotherm which can be identified with the latter component. The enthalpy change for the principal endotherm is fully 76% of that expected for the *p*-chlorophenoxy homopolymer supporting the conclusion that there can be little crystalline phase mixing. It appears likely that the two minor lower temperature peaks also represent the *p*-chlorophenoxy homopolymer rather than mixed crystalline phases. The combined enthalpy of all three peaks is still within the range expected for the *p*-chlorophenoxy component. Thus, the behavior for the blend is very similar to that for the first sample, suggesting that there is little mixing of the two crystalline phases although the absence of a *p*-ethylphenoxy peak indicates that some interaction occurs with the *p*-chlorophenoxy polymer.

In summary, the results on these four blends clearly show that the crystalline phases of the two mixed homopolymers are incompatible. However, some allowance must be made for crystalline phase interactions, including some minor degree of crystalline mixing to account for the differences between the endotherms of the blends and those of the corresponding homopolymers. The state of amorphous phase compatibility is less clear. Two of the blends exhibit amorphous phase incompatibility, but no conclusion is possible in the other two cases where the homopolymer T_g values are too close to be resolved.

Copolymers. The eight copolymers studied in this investigation have been divided into two broad classes. Class I copolymers include three entries where in each case the two comonomers have substituents which occupy the same position on the phenyl ring (see Table I). Class II includes four copolymers which contain differences in the placement of the substituent on the phenyl ring of the two comonomers. The *p*-chlorophenoxy/phenoxy copolymer has also been included in this category. The distinction between the class I and class II copolymers is related to differences in the thermal transition behavior which will be discussed shortly.

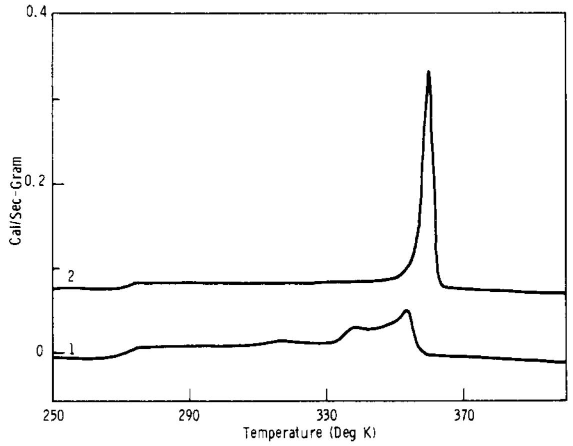

Figure 2. DSC scan of $[(4\text{-}ClC_6H_4O)(4\text{-}C_2H_5C_6H_4O)PN]_n$: initial scan (curve 1); scan after annealing (curve 2).

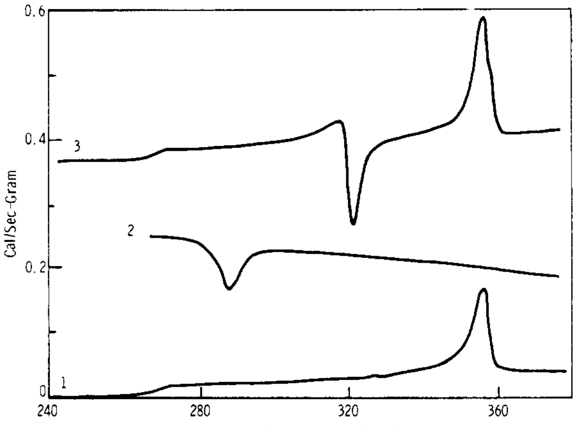

Figure 3. DSC scans of $[(4\text{-}ClC_6H_4O)(3\text{-}CH_3C_6H_4O)PN]_n$: initial heating scan (curve 1); initial cooling scan (curve 2); heating scan after cooling (curve 3).

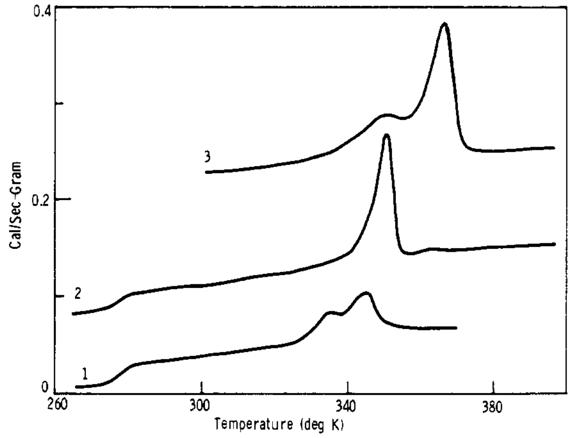

Figure 4. DSC scans of $[(4\text{-}ClC_6H_4O)(C_6H_5O)PN]_n$: initial scan (curve 1); after annealing at 371.1 K (curve 2); after annealing at 365.2 K (curve 3).

The results of elemental analysis on the copolymers are listed in Table I for carbon and chlorine. These values are combined to calculate the substituent mole ratio as well as the residual chlorine on phosphorus (Cl <0.15%). The resulting compositions are very close to the expected one-to-one mole ratios and are in quite good agreement with the values obtained by NMR which also appear in Table I. GPC analyses showed that the substituted trimer content was less than 5% in all cases, except for the *m*-chlorophenoxy/*m*-cresoxy copolymer, which contained 17% trimer. The GPC analyses also indicated that all the copolymers contained the broad distribution of molecular weights ($M_w/M_n > 10$) and high molecular weight ($M_w > 10^6$) typical of organo-substituted poly(phosphazenes).[18] In a few cases absolute molecular weights were obtained by light-scattering measurements and confirmed the high molecular weight of the copolymers.

Typical DSC scans for the copolymers are illustrated in Figures 2 through 4. The three figures will be discussed in detail later, but it is appropriate at this point to make some general observations. The general features of these scans are basically indistinguishable from those obtained with most poly(phosphazene) homopolymers. A single glass transition temperature is observed, but more importantly, all the copolymers exhibit one or more endothermal transitions at higher temperatures indicating that all these copolymers, without exception, are semicrystalline. This thermal transition behavior, like that in the analogous homopolymers, is a manifestation of the transition to a mesomorphic state.[5-10] Accordingly, the transitions are designated $T(1)$ to distinguish them from true melting and in keeping with previous usage. The X-ray diffraction patterns which were taken on several of the samples above the highest recorded $T(1)$ showed only a single reflection with a spacing in the neighborhood of 12 Å, which is indicative of the hexagonal structure characteristic of the partially ordered state in poly(phosphazene) homopolymers above $T(1)$.[6,7] Estimates of the true melting temperature were obtained on solution cast films of several copolymers, using the Perkin-Elmer TMS-1 thermal mechanical analyzer in the penetration mode with a net probe weight of 2 g. Transitions in the range of 350 °C were observed typical of values for the parent homopolymers.[2,3,9] Thus, the indicated melting temperatures do not show the significant reductions in temperature that are apparent in the $T(1)$ values for some of the copolymers (see Table II).

Table II lists the pertinent thermal data as gathered from differential scanning calorimetry along with referenced data for the corresponding homopolymers.[3,9] The T_g of the copolymers can be predicted rather well from the T_g values of the analogous homopolymers by the relationship

$$T_g(\text{calcd}) = xT_{g,x}(\text{meas}) + yT_{g,y}(\text{meas}) \qquad (1)$$

where x and y are the mole fractions of each substituent from Table I. Note that the agreement between experimental and calculated values in Table II is best for class II copolymers in spite of the fact that, except for $[(C_6H_5O)(4\text{-}ClC_6H_4O)PN]_n$, there are differences of the order of 25 K in the T_g value of the homopolymers involved. This clearly indicates the occurrence of a single amorphous phase in the class II copolymers. The results are less decisive for class I since in one case the homopolymer T_g values differ by only 1 °C and in the other two examples the measured values are higher than those calculated from eq 1. The elevation of T_g in these class I copolymers is not in conflict with the occurrence of a single amorphous phase but could arise from the relatively high level of crystallinity in these samples. In their study of the T_g behavior of poly(organophosphazenes), Dieck and Goldfarb[15] only found good agreement between observed and calculated T_g values in about half the samples which they prepared. In the remaining samples, the observed values were also higher than those calculated.

The summary of the endothermal transition data in Table II represents temperatures and heats of transition for annealed samples with the exception of $[(4\text{-}CH_3C_6H_4O)(3\text{-}CH_3C_6H_4O)PN]_n$ which would not recrystallize in a reasonable time span. Annealing at or above $T(1)$ brings about an improvement in the degree and perfection of crystallinity, as indicated by an increase in the transition temperatures and the area under the resulting endotherms compared to those from the initial runs on the solution-cast films. Figure 2 provides an example of the behavior for the *p*-chlorophenoxy/*p*-ethylphenoxy copolymer. The initial copolymer sample displays a broad diffuse transition region which after annealing is transformed into a single, sharp endotherm at 360 K. It should be noted that this stands in marked contrast to the behavior of the corresponding blend (Figure 1, curve 3), where there is a broad, main peak at 423 K as well as several minor peaks at lower temperatures. Note, however, that the minor peaks occurring in the blend are above the transition temperature in the annealed copolymer. The two copolymers whose thermal transition behavior is illustrated in Figures 3 and 4 correspond in choice of substituents to the other two homopolymer blends in Figure 1. This permits an instructive comparison, which underscores the differences in behavior between the copolymers and corresponding blends.

The difficulty in recrystallizing the *p*-cresoxy/*m*-cresoxy copolymer referred to above might be due to residual chlorine on phosphorus, since the value obtained by elemental analysis and listed in Table I is approximately twice the level expected in the best preparations. A cast film of this material also showed very little elongation on cold drawing before tearing occurred, in contrast to the solution-cast films of almost all poly(organophosphazenes) which readily cold draw.[3,9] In this one case, therefore, transition parameters were measured during the first heating cycle on the solution-cast film.

In cases where multiple peaks were observed, the entire area above the base line was included in measuring ΔH (see Figure 4). $T(1)$ was recorded as the temperature of the highest melting component, where the peaks were not resolvable, or as the temperatures of each individual peak where resolution was possible. In several cases, recrystallization did not occur completely on cooling at 40 K/min. In contrast, poly(phosphazene) homopolymers generally crystallize readily and completely under these conditions. But retarded crystallization is observed in homopolymers with bulky substituents, such as phenyl *p*-cresoxy homopolymer $[(C_6H_5\text{–}CH_2\text{–}C_6H_4O)_2PN]_n$ and some of the aryloxy polymers with multiple substituted phenyl rings, such as the 3,5-dimethylphenoxy homopolymer.

The instances of incomplete crystallization for the copolymers are marked with an "r" in Table II. As an illustration, the thermal behavior of an oriented film of $[(4\text{-}ClC_6H_4O)(3\text{-}CH_3C_6H_4O)PN]_n$ is shown in Figure 3. The bottom curve shows the first heating cycle as recorded by DSC. The second curve shows that only about one-half of the area under the endotherm in curve 1 is recovered during recrystallization by cooling at 40 K/min. In this state the sample is quite soft and tearing occurs easily along the stretch direction. The third curve, uppermost in Figure 3, shows that during the second heating cycle on the same sample, the already crystallized material begins to show an endothermal transition, but that further recrystallization occurs concommittantly. The final endotherm which appears at a higher temperature is the one whose parameters are recorded in the table. This fully recrystallized sample has become tougher and resists tearing. The diffraction pattern of the oriented film now shows 16 distinct maxima on the equator and 9 on the first level.

The last column in Table II indicates the calculated maximum attainable heat of transition. The calculation is based on the assumption that substitution occurs randomly, leading to the following proportion of repeat units for equal mole ratios of substituents: 1/4 (RO)P-

Table III
X-ray Data for Phenoxy- and *p*-Chlorophenoxy-Substituted Homopolymers, Copolymers, and Blends[c]

$[(C_6H_5O)_2PN]_n$[a]			$[(4\text{-}ClC_6H_4O)_2PN]_n$[b]			$[(C_6H_5O)(4\text{-}ClC_6H_4O)PN]_n$ annealed at 356.2 K		371.1 K		blend	
hkl	*d*	*I*	*hkl*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
100	16.06	2									
010	13.69	3				13.713	m	13.29	m		
110	11.39	200				11.964	s	11.28	s	11.303	vs
			110	10.98	420						
			020	10.12	429	10.36	m			10.270	ms
$\bar{1}10$	9.921	100				9.452	m				
200	8.289	50	120	8.00	26	8.403	m			8.448	vw (d)
210	7.477	2.4									
120, 020	6.721	25				6.855	m			6.733	vw (d)
$\bar{2}10$	6.408	0.6	200	6.54	35						
			210	6.22	25					6.040	w (d)
			130	5.99	47					5.600	m
220	5.506	1.6									
			220	5.49	217	5.491	m	5.467			
			040	5.06	4	5.069	w	diffuse band		5.020	mw
$\bar{2}20$	4.910	50									
			140,	4.70	60,					4.882	mw
			230		125	4.783	w				
320, 030, 130, $3\bar{2}0$	4.498	50						4.527		4.558	mw
			310	4.26	6					4.300	mw
$\bar{1}30$, 230	4.185	50									

[a] Data taken from E. G. Stroh, Jr., ref 19. [b] Data taken from S. M. Bishop and I. M. Hall, ref 20. [c] vs = very strong; s = strong; m = medium; w = weak; vw = very weak; (d) = diffuse.

(OR), 1/2 (RO)P(OR′), and 1/4 (R′O)P(OR′). Further, if it is assumed that the homopolymer-like units can crystallize to the same extent and degree of perfection that is observed in the homopolymer itself, and that the copolymer-like units (RO)P(OR′) will display enthalpies of transition which are the average of their respective homopolymer analogues, then it can be shown that the maximum enthalpy attainable is:

$$\Delta H_{T(1)} = \tfrac{1}{2}\Delta H_{(\mathrm{RO})\mathrm{P}(\mathrm{OR})} + \tfrac{1}{2}\Delta H_{(\mathrm{R'O})\mathrm{P}(\mathrm{OR'})} \qquad (2)$$

In most instances, the mole fraction of each substituent is not exactly $^1/_2$, so that the actual mole fractions from Table I have been used in the calculation instead.

Two classes of thermal behavior appear in Table II. Those copolymers which are grouped in class I have transition temperatures equal to or higher than one of the corresponding homopolymers. In addition, the observed heats of transition for all three of these copolymers are at least 75% of the calculated maximum value. The copolymers in class II include all those whose transition temperature $T(1)$ is lower than either of their homopolymer analogues. The heat of transition for these copolymers is roughly $^1/_2$ of the calculated maximum value with the exception of $[(4\text{-}ClC_6H_4O)(3\text{-}CH_3C_6H_4O)PN]_n$ which was sequentially substituted. This copolymer, also with a nominal equimolar concentration of the two comonomers, shows much lower values of the enthalpy change and transition temperature. This problem is treated further in the Discussion section.

The DSC scan for $[(4\text{-}ClC_6H_4O)(C_6H_5O)PN]_n$, Figure 4, shows the distinctive response of this copolymer to annealing. The first curve portrays the thermal behavior of the sample as cast and uniaxially oriented. The behavior in the second curve can be produced either by annealing at temperatures just above the barely visible higher temperature peak in curve 2, in this case 371 K, followed by recrystallization on cooling or by scanning to 400 K and recrystallizing on cooling. In either case, the peak at 350 K accounts for almost the total enthalpy change in scan 2, 3.7 cal/g of the 4.3 cal/g total or 88%. Prolonged annealing of the sample at a temperature which lies between the two peaks at 350 and 367 K (i.e., 356 K for about 60 h) produces the dramatic change in behavior which is shown in the third curve. The total enthalpy has increased by 10%, and the higher temperature peak has been enhanced at the expense of the lower temperature peak, accounting for nearly 70% of the total enthalpy change.

The corresponding influence of annealing history on the X-ray diffraction pattern for this copolymer is indicated in Table III. The Table includes Bragg *d* spacings and estimated intensities for the copolymer annealed at both temperatures and for the previously described blend of the corresponding homopolymers. For comparison, literature results from the X-ray powder pattern of $[(C_6H_5O)_2PN]_n$[19] and the X-ray structure investigation of $[(4ClC_6H_4O)_2PN]_n$[20] are also included. The pattern for the copolymer annealed at 371 K is relatively poor, showing only a few discrete lines and a diffuse band from d = 5.478 to 4.527 Å. The discrete lines can be attributed to the phenoxy unit cell while the diffuse band may include lines from the unit cells similar to those of the phenoxy and *p*-chlorophenoxy homopolymers. Annealing at 356 K produces a dramatic change in the X-ray diffraction pattern. The pattern is richer and lines appear whose *d* spacings match both homopolymer patterns. Of these, the four lines matching the *p*-chlorophenoxy structure are unperturbed while the five matching the *d* spacings of the phenoxy structure show a general increase in *d* spacing over that of the homopolymer spacings.

The last two columns of Table III summarize the diffraction patterns of the 1:1 blend of homopolymers. Some lines from the homopolymer structure are missing and others are broadened, denoted by d (diffuse). This is another manifestation of the interaction which gives rise to the broadened endotherms and lower transition temperatures shown in Figure 1 for the blend.

These results indicate that the DSC endotherms at 350 and 367 K are associated with different degrees of order

Table IV
X-ray Data for *p*-Cresoxy- and *p*-Chlorophenoxy-Substituted Homopolymers and Copolymers

$[(4\text{-}CH_3C_6H_4O)_2\text{-}PN]_n$			$[(4\text{-}CH_3C_6H_4O)\text{-}(4\text{-}ClC_6H_4O)PN]_n$			$[(4\text{-}ClC_6H_4O)_2\text{-}PN]_n$[a]		
hkl	*d*	*I*	*hkl*	*d*	*I*	*hkl*	*d*	*I*
110	11.5	s	110	11.5	s			
						110	10.98	420
						020	10.12	429
020	9.31	mw	020	9.21	m			
						120	8.00	26
200	7.24	vw	200	7.40	vw			
						200	6.54	35
030	6.11	w	030	6.07	m			
						130	5.99	47
220	5.58	m	220	5.70	m			
						220	5.49	217
						040	5.06	4
310	4.70	m	310	4.73	m			
320	4.22	w	320	4.18	mw			
						320	4.00	2
						240	4.00	42
240	3.87	w	240	3.91	w			
001	4.87	vw						
002	2.44	w	002	2.44	w	002	2.45	35

[a] Data taken from S. M. Bishop and I. H. Hall, ref 20.

rather than with different unit cells. Annealing at 356 K not only leads to the appearance of X-ray reflections corresponding to the *p*-chlorophenoxy structure but also results in an increase in the number and sharpness of the lines representing the phenoxy structure. Thus, both types of unit cell are present in the sample annealed at 356 K and contribute to the endotherm observed at 367 K.

An attempt was also made to analyze the X-ray diffraction pattern of another class II copolymer, the annealed *p*-chlorophenoxy/*m*-cresoxy copolymer which shows the remarkable rich diffraction pattern referred to earlier. Six of the equatorial lines could be identified with the *p*-chlorophenoxy unit cell. Unfortunately, it was not possible to produce an oriented sample of the *m*-cresoxy homopolymer from which a reference X-ray pattern might be obtained to permit identification of the remaining lines observed in the annealed copolymer.

One class I copolymer system, the *p*-chlorophenoxy/*p*-cresoxy copolymer, was also studied by X-ray diffraction, along with a sample of the *p*-cresoxy homopolymer. These samples were stretched 6× then annealed for 15 min at 180 °C under tension. The X-ray patterns were run at room temperature. The data for the copolymer and *p*-cresoxy homopolymer are summarized in Table IV along with results for the *p*-chlorophenoxy homopolymer taken from the work of Bishop and Hall.[20] The copolymer shows a high level of crystallinity and a large number (27) of resolved lines. There is a very close match between the X-ray pattern for the copolymer and the *p*-cresoxy homopolymer (Table IV) indicating that the copolymer has crystallized in the crystal structure of this homopolymer while the presence of crystals of the *p*-chlorophenoxy structure is definitely ruled out.

The diffraction patterns of the *p*-cresoxy homopolymer and the copolymer have been indexed to orthorhombic unit cells with slightly different lattice parameters (Table V). The lattice parameters were in no way optimized but were simply taken from the experimental values of the 200, 020, and 002 spacings. Thus, the differences in lattice parameters (see Table V) are sufficiently small that the copolymer and the *p*-cresoxy homopolymer structure may be considered identical within the precision of the present data.

Table V
Indexing[a] of Poly[(*p*-cresoxy)phosphazene]

hkl	d_c	d_e	*hkl*	d_c	d_e
110	11.450	11.5	111	4.482	4.50
020	9.310	9.31	121	4.137	4.09
120	7.837	7.85	201	4.044	
200	7.260	7.26	211	3.952	
030	6.207	6.11	221	3.710	3.72
220	5.725	5.58	231	3.389	3.40
130	5.707		041	3.365	
310	4.684	4.70	321	3.221	3.14
040	4.655		331	3.004	
320	4.294	4.22	401	2.911	2.92
240	3.919	3.87	411	2.876	
330	3.817		001	4.870	4.87
400	3.630	3.64	002	2.435	2.438
150	3.607				
420	3.382	3.38			
340	3.355				
510	2.869	2.88			
440	2.863				

[a] d_c, calculated values; d_e, experimental values. Orthorhombic *d* spacings, $a = 14.52$ Å; $b = 18.62$ Å; $c = 4.87$ Å. The similar set of X-ray reflections observed for poly[(*p*-cresoxy)/(*p*-chlorophenoxy)phosphazene] yield an orthorhombic unit cell with $a = 14.72$ Å; $b = 18.42$ Å; $c = 4.86$ Å.

One additional sample which was examined by DSC was a blend of the homopolymer $[(4\text{-}ClC_6H_4O)_2PN]_n$ and the copolymer $[(C_6H_5O)(4\text{-}ClC_6H_4O)PN]_n$, prepared in the ratio 1:4 by weight, to determine whether crystalline phase compatibility in a blend could be improved by the use of a suitably chosen copolymer. The features observed represented a combination of the behavior seen in Figure 1 for the other blends and in Figure 4 for the copolymer component including the response of the copolymer peaks to annealing as shown in Figure 4. Therefore, in this case it appears that crystalline phase compatibility has not been enhanced by the use of a copolymer which contains one of the same substituents as that of the added homopolymer.

Discussion and Conclusions

The interpretation of the endothermal behavior of the copolymers must be approached on the basis of the kind of copolymer which has been synthesized, whether a block copolymer or a random one. The problem is complicated further in that three chemically different types of repeat unit are possible, one of which, the heterogeneously substituted (RO)P(OR′), may have two stereochemical forms. Owing to this tacticity problem with heterogeneously substituted repeat units, only homogeneously substituted repeat units would normally be expected to crystallize in a block copolymer. There are immediate difficulties, however, in any attempt to attribute the observed crystallinity to block copolymer formation. In a competitive substitution reaction with nearly equal reactivities and concentrations of the two aryloxides, no scheme for producing blocks is easily imagined. Furthermore, such blocks would have to be sufficiently long to overcome the nucleation barrier in order for crystallization to occur. To account for the enthalpy observed in class II, these crystallizable blocks must encompass one-half the total number of repeat units, each homopolymer-like unit representing one-quarter of the total (see eq 2). If these blocks are present in such concentration and are sufficiently long to crystallize, then they would probably be incompatible according to the behavior of the blends. The thermal behavior would be similar to that of the blends which exhibit two homopolymer endotherms rather than the single endotherm observed in the annealed copolymer samples.

On the other hand, random copolymers are often amorphous materials when prepared in one-to-one mole ratios. If short crystallizable sequences occur, the glass transition temperature limits the large degree of supercooling required before crystallization can commence. Moreover, as crystallization proceeds the partially crystallized polymer chains impede the diffusion of crystallizable sequences to crystallization sites leading to very low levels of crystallinity at best.

It appears that only if isomorphism of the repeat units can occur will any significant amounts of crystallinity be developed. Wunderlich's treatment[21] of isomorphism, which is an elaboration of a scheme first proposed by Natta et al.,[22] will be followed for the purposes of discussion. Although the examples appearing in Wunderlich's discussion deal entirely with conventional copolymers, the concepts are readily extended to the type of copolymer repeat units which occur in the poly(organophosphazenes). Three types of repeat unit isomorphism are defined. Type 1 exists where the homopolymers of the repeat units have similar crystal structures. The packing restrictions for similar structures require that atoms can only be substituted for other atoms at sites where the difference in their van der Waals radii will not produce a close contact. In all cases, a high constant level of crystallinity can be retained at all compositions. Type 2, known as isodimorphism, is the most commonly found type. Here the homopolymers of the repeat units have nearly identical repeat distances along the chain but differ crystallographically in other respects. Lattice parameters of the copolymer are found to change with composition and reflect the change in the size of the substituent being forced into a unit cell not its own. At intermediate concentrations, distorted homopolymer unit cells of both constituents often coexist. The third type of repeat unit isomorphism occurs when only one of the homopolymer repeat units is crystalline. The other unit, although not capable of crystallization alone, shows isomorphism with the first. A decrease in crystallinity is expected as the crystalline homopolymer unit decreases in concentration. Crystallinity is higher, however, than when there is no isomorphism.

For crystallinity to occur in a randomly substituted phosphazene copolymer, isomorphism must be assumed to exist between heterogeneously substituted repeat units and each type of homogeneously substituted repeat unit so that the crystallizable unit is sufficiently long to nucleate and crystallize (types 2 and 3). In some cases, isomorphism of all repeat units must be accepted (type 1). To be more specific, however, the homopolymer structure must be known so that a comparison with the X-ray pattern of the copolymer can be made in order to assign the type of isomorphism.

In only a few cases have the crystal structures of the aryloxyphosphazene homopolymers been determined. Bishop and Hall[20] determined the crystal structure of $[(4\text{-ClC}_6H_4O)_2PN]_n$. In the orthorhombic cell a = 13.01 Å, b = 20.23 Å, and c = 4.91 Å. Chains at the four corners of the ab plane of the latter structure are found to have the side groups all pointing in the same direction with respect to the chain axis. A single chain at the center of the plane has side groups all pointing in the opposite direction to those in the corners. The work of Stroh[19] indicates that $[(C_6H_5O)_2PN]_n$ has a monoclinic unit cell with a = 16.22 Å, b = 13.82 Å, c = 4.91 Å, and γ = 82°. The two chains are spaced within 9.9 Å. These differences between the two unit cells are too great to allow type 1 repeat unit isomorphism to occur. However, the fiber repeat distances along c are equal so that the type 2 isomorphism is possible. As discussed earlier, the X-ray diffraction data on this phenoxy/*p*-chlorophenoxy copolymer show that both homopolymer unit cells coexist, a feature often seen in one-to-one copolymers showing type 2 isomorphism. The distortion of the phenoxy lines (see Table III) is probably due to the heterogeneously substituted repeat units cocrystallized with the homogeneous phenoxy ones. The *p*-chlorophenoxy crystal structure apparently can make such an accommodation without distorting the lattice.

Table VI
Comparison of Orthorhombic Unit Cells

	A[a]	B[b]	C[c]
a, Å	14.52	14.72	13.08
b, Å	18.62	18.42	20.23
c, Å	4.87	4.86	4.90
b/a	1.28	1.25	1.55
abc, Å	1317	1318	1297

[a] $[(4\text{-CH}_3C_6H_4O)_2PN]_n$. [b] $[(4\text{-CH}_3C_6H_4O)(4\text{-ClC}_6H_4O)PN]_n$. [c] $[(4\text{-ClC}_6H_4O)PN]_n$. Data taken from S. M. Bishop and I. H. Hall, ref 20.

Although the attempted X-ray examination of the *p*-chlorophenoxy/*m*-cresoxy copolymer lacks the X-ray pattern of the *m*-cresoxy phosphazene homopolymer for comparison, the available data also suggest that two unit cells coexist and contribute to the single sharp endotherm which is observed. By extension, it appears reasonable to identify type 2 isomorphism with all copolymers in class II. Each meta-substituted repeat unit is expected to crystallize in a different unit cell than the para-substituted repeat unit, and the two crystal structures will melt in a single endotherm. The transition temperatures and enthalpy change will depend primarily on the concentration of heterogeneously substituted repeat units cocrystallized in each unit cell. On this basis, the lower transition temperature and crystallinity noted in sequentially substituted $[(4\text{-ClC}_6H_4O)(3\text{-CH}_3C_6H_4O)PN]_n$ may be due to the preference for nongeminal rather than geminal substitution under noncompetitive reaction conditions.

The copolymers in class I, with their higher $T(1)$ transition temperatures and enthalpies, are expected to show type 1 isomorphism in which all three types of repeat unit cocrystallize. This would be most likely to occur with the *p*-chlorophenoxy/*p*-cresoxy copolymer since the difference in van der Waals radii of the chloro and methyl groups is only 0.2 Å. The X-ray data for this system, presented earlier and summarized in Table IV, indicate that the copolymer structure is identical with that of the *p*-cresoxy homopolymer, which is not the same as the *p*-chlorophenoxy homopolymer.

Some insight concerning this situation can be gained from a comparison of the unit cell parameters for the copolymer and the *p*-cresoxy homopolymer (Table V) (reported here for the first time) with the parameters determined by Bishop and Hall[20] for the *p*-chlorophenoxy homopolymer. Table VI shows that there is a striking difference in the b/a ratio (1.25 to 1.28 for the present work, compared to 1.55 for the *p*-chlorophenoxy homopolymer) while c is virtually unchanged. However, the volumes of the three unit cells are quite close, the present unit cells being only 1.5 to 1.6% larger than that of Bishop and Hall. This is not surprising considering the small difference in size between the chloro and methyl substituents. The volume packing fraction is also nearly the same for the two homopolymers and the copolymers. The

Table VII
Packing Parameters for Various Poly(organophosphazene) $[(RO)(R'O)PN]_n$ Unit Cells

R	R	C.I.S.,[a] Å	V/Z,[b] Å^3/monomer
Homopolymers			
4-ClC_6H_4		12.0	324
4-$CH_3C_6H_4$		11.8	329
C_6H_5		9.9	272
Copolymers			
4-ClC_6H_4	4-$CH_3C_6H_4$	11.8	324
4-ClC_6H_4	C_6H_5	two crystal lattices	

[a] C.I.S. = closest interchain spacing. [b] *V/Z* volume per monomer unit.

difference in the b/a ratio probably results from the accomodation of dipole effects associated with the chloro substituent in the *p*-chlorophenoxy homopolymer.

Two anomalies are noted in the present data: equatorial lines indexing as 030 are observed in the homopolymer and copolymer, and a meridional line indexing as 001 is observed in the *p*-cresoxy homopolymer, albeit quite weak. Both lines are ruled out by the symmetry of the space group assigned by Bishop and Hall. Thus the two crystal structures may differ in details of the molecular arrangement although the volume packing fractions are quite similar.

In part, based on the foregoing considerations, we believe it is proper to classify the *p*-cresoxy/*p*-chlorophenoxy copolymer as type 1 isomorphism. Normally the structure of a type 1 copolymer would be expected to exhibit lattice parameters intermediate between those of the two homopolymer crystals. However, in the present case, there probably is insufficient dipole–dipole interaction between chloro groups at the 50:50 copolymer composition to shift the parameters very far away from those of the *p*-cresoxy homopolymer. Quite possibly the expected shift would be observed in copolymers with a fraction of *p*-chlorophenoxy substituents which is larger than 50%, where dipole interactions will become more pronounced. On the other hand, it has already been shown that a one-to-one blend of the two parent homopolymers does not exhibit crystalline phase compatibility. This is not unexpected since unlike the copolymer, the *p*-cresoxy homopolymer in the blend would not be effective in shielding the dipole–dipole interactions between chloro groups of the *p*-chlorophenoxy homopolymer.

Presumably the two remaining examples of class I copolymers listed in Table II are also examples of type 1 isomorphism. The *m*-chlorophenoxy/*m*-cresoxy copolymer should be completely analogous to its para-substituted analogue. The pendant groups on the phenoxy rings of $[(4\text{-}ClC_6H_4O)(4\text{-}CH_3CH_2C_6H_4O)PN]_n$ differ in their van der Waals radii so that it would be surprising to find that both substituents fit into a single crystal lattice. However, the *p*-ethyl group has rotational flexibility and, thus, may be able to position itself into the lattice without introducing severe distortion.

It may be possible to generalize the criteria for type I isomorphism in terms of two key parameters which control the packing of diverse repeat units in the various possible unit cells as outlined in Table VII, the closest interchain spacing (abbreviated C.I.S.) and the volume per monomer unit V/Z, calculated from unit cell parameters. The closest interchain spacing is defined as the shortest distance between chain sites in the projection normal to the *c* axis. The premise is that although the different heterogeneous repeat units incorporated in a given crystal may accommodate considerable variations in a, b, a/b, or γ, the volume required by a particular monomer unit and the spacing required in the *c* axis projection are critical parameters. In the case of the *p*-chlorophenoxy and *p*-cresoxy substituents, there is a close match in both parameters, and type 1 isomorphism occurs readily, despite the disparity in the b/a ratios of the homopolymer structures. Between the *p*-chlorophenoxy and the phenoxy substituents, however, the mismatch in these parameters is pronounced. The disparity between the space requirements of the two homopolymers is in the range 16–18%, too large to permit type 1 isomorphism.

None of the copolymer studied here show type 3 repeat unit isomorphism since in all cases the homopolymer repeat units crystallize. Copolymers containing amino or anilino repeat units and aryloxy repeat units might qualify, however, since the amino and anilino homopolymers are amorphous. In fact, a low degree of crystallinity has been observed in $[(4CH_3C_6H_4O)(4\text{-}CH_3C_6H_4NH)PN]_n$ prepared by the sequential substitution route[23] to ensure achievement of equimolar substitution despite differences in reactivity of the substituents.

In summary, the results indicate that many of the aryloxyphosphazene copolymers show well-developed crystallinity despite the apparently random nature of the substitution. Evidence is presented indicating that this crystallinity arises from isomorphism, and examples illustrating all three principal types of isomorphism have been given. Under the circumstances, the occurrence of several technologically important elastomers based on the use of copolymers to block crystallization is somewhat fortuitous. Increasing the differences in the size and nature of the substituents on the phenoxy ring will produce amorphous copolymers, but the poly(phosphazene) unit cell appears to be unusually tolerant of perturbations on a more limited scale. This does not, however, extend to blends of homopolymers which show nearly complete incompatibility of crystalline structure.

The interpretation of the copolymer behavior rests heavily on the assumption that heterogeneously substitued repeat units are incorporated into both homopolymer unit cells in class II copolymers as the condition allowing crystallization to occur. It is remarkable under these conditions that such sharp X-ray patterns can be developed in annealed samples of these copolymers. There is still the need to explain the occurrence of only a single endotherm and, thus, only a single $T(1)$ transition despite the presence of a mixed crystal containing the two types of unit cells which are related to the parent homopolymers. Further evidence on these various problems and other aspects of the behavior reported here might be gained by studying the effects of varying the composition of an appropriate chosen copolymer from class II and from class I. It would also be useful to study the behavior of poly(phosphazene) copolymers with other substituents at the equimolar composition.

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Application of the Virtual Bond Method to the Crystalline Conformations of Isotactic Polystyrene and Poly(methyl methacrylate)

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ABSTRACT: The application of the virtual bond method of analysis to the crystalline conformations of vinyl polymers is discussed. The method can be used if the screw symmetry and the pitch of the helix are known from diffraction data and involves the rotation of the repeat unit about its end-to-end vector or the virtual bond. It enables the determination of the favorable conformations of the helix, by allowing the variation of the skeletal bond angle at the methylene carbon atom. The crystalline conformations of isotactic polystyrene with 12 repeat units per turn and 3 repeat units per turn are discussed. The analysis is restricted to showing that the 12-unit helix is stereochemically possible. Rigorous comparison with the X-ray data is not attempted due to the possible presence of head-to-head sequences in the polymer and its influence on the crystalline domains. The calculations on the five-unit helix of isotactic PMMA show that it occurs close to an unfavorable minimum on the (ϕ_i,ϕ_{i+1}) surface. The calculated energy of the ten-unit helix is lower than that of the five-unit helix of PMMA. The side group rotations play an important role in determining the relative positions of these helical conformations on the overall (ϕ_i,ϕ_{i+1}) domain.

Conformational analysis in terms of the rotations around the skeletal bonds has been used to understand the conformational features of several vinyl polymers.[1-8] Empirical energies of interaction between nonbonded atoms and groups, evaluated for each of the conformations of the dyad, generated by rotations ϕ_i and ϕ_{i+1} as in Figure 1, have been used to calculate the statistical weight parameters and to estimate the unperturbed statistically averaged properties.

The recent work on PMMA[4] and poly(α-methylstyrene)[7] showed that a large value of 122–124° is preferred for the skeletal bond angle C^α–C–C^α (denoted by θ''). Crystallographic results[9] on small molecular analogues support this conclusion. The large deviation from tetrahedral value is due to the bulkiness of the side groups. Similar enlargement of the angle at the bridge atom between repeating units, depending on the size of the substituents, has been observed frequently in di- and polysaccharides.[10] Thus, values of angles greater than 109.5° may have to be used in the calculations depending on the size of the side groups and the intensity of the interaction between them. The energy map, as a function of ϕ_i and ϕ_{i+1}, must therefore be constructed for a range of values of θ'' in assessing the relative stabilities of the conformations and choosing the most preferred conformation. This may not be crucial while calculating the solution properties of these chains, since the range of angles can be substituted by the most probable average value. However, it becomes important when dealing with the crystalline conformations of vinyl chains and in the refinement of crystal structures.

The (ϕ_i,ϕ_{i+1}) map of the energies shows the overall conformational space available to the dyad of the polymer and is useful in calculating the average properties. However, this may be unnecessary when the analysis of a unique crystalline conformation is desired. This is readily accomplished by using the "virtual bond method", which eliminates the need to construct several ϕ_i,ϕ_{i+1} maps for a range of values of θ''. The virtual bond method has been effective in predicting the crystalline conformations of several polysaccharides and copolysaccharides.[11-14] Its application to polypeptides has been briefly discussed before.[11] This method is applicable when the helix parameters are known from diffraction data.

The parameters defining the helical conformation, namely, n, h, $\Delta(360/n)$, and P (repeat distance), can be derived from fiber diffraction data. For the application of the virtual bond method, for a given type of helix, only the monomer geometry is required. The values of θ'' (C^α–C–C^α), ϕ_i, and ϕ_{i+1} are not required, as in other methods; rather, the preferred values of θ'', ϕ_i, and ϕ_{i+1} are obtained as a *result* of the analysis.[11] As shown in Figure 2, the virtual bond is the end-to-end vector of the monomer

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