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Poly(aminophosphazene)s and Protophosphatranes Mimic Classical Strong Anionic Base Catalysts in the Anionic Ring-Opening Polymerization of Lactams

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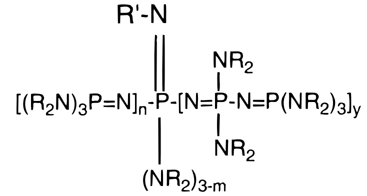
ABSTRACT: Linear very high molecular weight polyamides, such as nylons 6, 7 and 66, have been prepared via the rapid ring-opening polymerization (ROP) of their respective lactams catalyzed by super nonionic poly(aminophosphazene) and protophosphatrane bases. The super nonionic poly(aminophosphazene) bases appear to mimic catalysis by conventional anionic catalysts, but with the added advantage of the toleration of some degree of moisture. Multinuclear liquid and solid-state NMR experiments were used to probe the structure and proton transfer chemistry of P_4-*t*-Bu, one of the most effective lactam ROP poly(aminophosphazene) bases. ^{31}P magic-angle spinning (MAS) results showed the room-temperature structure of P_4-*t*-Bu to be asymmetric and nonprotonated. Variable-temperature ^{31}P MAS NMR experiments on mixtures of P_4-*t*-Bu and ϵ-caprolactam demonstrated the proton transfer chemistry relevant for ROP at elevated temperature. This was confirmed by ^{13}C MAS NMR observation of the ϵ-caprolactam anion in a cross-polarization experiment.

Introduction

The ring-opening polymerization (ROP) of lactams is an important commercial route to polyamides, such as nylon 6 and nylon 12. In the most widely practiced hydrolytic polymerization technology, catalytic amounts of carboxylic acid and amine ends are produced by ring-opening of the lactam after which the ROP ensues by the acid-catalyzed amine group attack on the lactam.[1,2] The reaction may also be catalyzed by protonic acids, by Lewis acids, or by strong bases in the case of anionic polymerization. In the latter, the strong anionic bases play the primary role of generation of lactam anions which are believed to be the species which initiate the ring-opening polymerization of lactams. Generally, the lactam anion is produced by treatment of the lactam with an alkali metal, typically sodium, or an alkali metal hydride, amide, or alkoxide. In the absence of a chain initiator such as an *N*-acyllactam, there can be an appreciable induction period before polymerization ensues.

In the current paper, we would like to report on our recent surprising discovery[3] that the very strong poly(aminophosphazene) and protophosphatrane bases uncovered by Schwesinger[4] and Verkade,[5] respectively, catalyze the rapid ring-opening polymerization of lactams in a way which mimics that by the strong anionic bases discussed above. The only other neutral base reported to catalyze the ROP of lactams, possibly via an anionic mechanism, is pentamethylguanidine with *N*-benzoyllactam chain initiators.[6] The degree of catalysis by this system versus the alkali metal lactams is indicated to be moderate, and the molecular weights demonstrated for the polymers were on the low side (e.g., 2050 Da for poly(ϵ-caprolactam) using *N*-benzoyl-ϵ-caprolactam as the initiator). Recently, one of the Schwesinger bases, P_4-*t*-Bu (see below for description), was reported by Pietzonka and Seebach to catalyze the anionic polymerization of methyl methacrylate.[7]

Table 1. pK_{BH^+}'s of Conjugate Acids of Poly(aminophosphazene) Bases in MeCN



$$[(R_2N)_3P{=}N]_n\text{-}\overset{\overset{\textstyle R'\text{-}N}{\|}}{\underset{\underset{\textstyle (NR_2)_{3-m}}{|}}{P}}\text{-}[N{=}\overset{\overset{\textstyle NR_2}{|}}{\underset{\underset{\textstyle NR_2}{|}}{P}}\text{-}N{=}P(NR_2)_3]_y$$

base	R′	R_2	*m*	*n*	*y*	$^{MeCN}pK_{BH^+}$
P_1-*t*-Bu	*t*-Bu	Me	0	0	0	26.9
P_2-Et	Et	Me	1	1	0	*ca.* 33[a]
P_2-*t*-Bu	*t*-Bu	Me	1	1	0	*ca.* 33.5
P_3-*t*-Bu	*t*-Bu	Me	2	2	0	38.6
P_4-*t*-Bu	*t*-Bu	Me	3	3	0	42.6
P_4-*t*-Oct	*t*-Oct	Me	3	3	0	41.2[b]
P_5-*t*-Bu	*t*-Bu	Me	3	2	1	*ca.* 45.6
P_5-P-*t*-Bu	*t*-Bu	$-(CH_2)_4-$	3	2	1	*ca.* 47
P_7-*t*-Bu	*t*-Bu	Me	3	0	3	*ca.* 45.6

[a] Assumed to be nearly the same as the analogous P_2-*t*-Bu. [b] Schwesinger, R. *Nachr. Chem. Tech Lab.* **1990**, *38*, 1214.

Results and Discussion

In our work to date, we have only examined four of the polyaminophosphazene bases shown in Table 1. However, these commercially available materials, P_1-*t*-Bu, P_2-Et, P_4-*t*-Bu, and P_4-*t*-Oct, cover a broad enough pK_{BH^+} (MeCN scale) range to characterize the scope of activity of this new class of lactam ROP catalysts. We have also examined the activity of Verkade's protophosphatrane "Super Base", $N[CH_2CH_2N(CH_3)]_3P$.[5] In the case of P_4-*t*-Bu, the base strength is *ca.* 10^{18} times that of diazabicyclo[5.4.0]undecene-7 (DBU),[5] which we have found not to catalyze the ROP of lactams. It appears that to be an effective catalyst (i.e., formation of high-MW polymer in good conversion), the pK_{BH^+} must be greater than *ca.* 27 because the pK_a of lactams from 2-pyrrolidone to laurolactam is 27 when measured in DMSO.[8] The reported pK_{BH^+} is 28.04 (in THF) for P_4-*t*-Bu, and 26.7 (in DMSO) for Verkade's protophosphatrane "Super Base", $N[CH_2CH_2N(CH_3)]_3P$.[5] Note that these values are substantially below those reported in Table I for the poly(aminophosphazene)s in MeCN. (Unfortunately, we have to be somewhat qualitative in

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setting the required base strengths for the poly(aminophosphazene)s because the pK_a for the lactams and the bases have not been measured in the same solvent.) The results shown in Table 2 for the ring-opening polymerization of ϵ-caprolactam indicate that P_1-*t*-Bu is not an effective catalyst whereas P_2-Et and the P_4-R systems give both high MW and good conversion. These materials mimic classical anionic ROP catalysts (e.g. alkali metal hydrides and alkoxides) for lactams in that they (1) give rapid polymer formation after an induction period and (2) are highly responsive to cocatalysis by chain initiators, such as *N*-acetyl-ϵ-caprolactam, which are theorized to stabilize the incipient amide anion.

Ring-Opening Polymerization of Lactams. Table 2 summarizes experimental conditions and results for the ROP of ϵ-caprolactam employing P_4-*t*-Bu, P_4-*t*-Oct, P_2-Et, P_1-*t*-Bu, $N(CH_2CH_2N(CH_3))_3P$, and NaH catalysts. A comparison of entries 1 with 2 with P_4-*t*-Bu shows that although the induction time (entry 1) was relatively short at relatively high temperature (see entry 3 for a polymerization carried out at lower temperature), the reaction was speeded up appreciably when *N*-acetyl-ϵ-caprolactam was added (entry 2). This is consistent with the formation of additional propagation centers in an anionic catalysis mechanism. In all three entries (1–3), high molecular weight polymers were obtained judging from the η_{inh}'s. In fact, the polymer formed in entry 3 exhibited very high molecular weight (Table 3, entry 1). A control experiment in an attempt to ring-open polymerize ϵ-caprolactam without P_4-*t*-Bu catalyst resulted in no polymer formation. Both P_4-*t*-Oct (entries 4 and 5) and P_2-Et (entries 6 and 7) gave polymer, with the former having activity in the same range as P_4-*t*-Bu, whereas the latter was less active. It should also be noted that there is a lower concentration limit at which the poly(aminophosphazene)s exhibit good activity. (The conversion dropped substantially in entry 4 where the catalyst concentration was 0.09 vs 0.18 mol % in entry 5.) As the basicity of the catalyst was reduced to the level of that of P_1-*t*-Bu (entries 8 and 9), the ability to effect the ROP of lactams was virtually lost. Unfortunately, there are no phosphazene bases with reported $^{MeCN}pK_{BH^+}$'s in the range between 27 and 33 such that one would obtain a better estimate of basicity required for their catalytic activity. With respect to the Verkade protophosphatrane "Super Base", $N[CH_2CH_2N(CH_3)]_3P$ with a $^{MeCN}pK_{BH^+}$ of ca. 41,[5] 1 mol % gave high molecular weight nylon 6 polymer (see Table 3, entry 2). It should be mentioned that the volatility of this catalyst at 150 °C is extremely high (by TGA analysis), so that under polymerization conditions—high temperature and atmospheric pressure—the full effect of this catalyst may not have been realized. In fact, the protophosphatrane was not at all effective at 270 °C, possibly due to its volatility. This assertion, however, needs confirmation since one would expect that the volatility of the salt between the base and lactam would be negligible. On the other hand, if there is appreciable free base (see above for relative basicities of protophosphatrane and lactams), its concentration could be reduced through volatilization at high temperature.

The catalytic activity of the above poly(aminophosphazene)s for the ROP of lactams appears to be general versus alkali metal hydrides. In addition to nylon 6, Table 2 summarizes conditions for the preparation of nylon 7 (entry 14) and nylon 66 (entry 16).

One of the disadvantages of the conventional anionic ROP process is the need to maintain rigorously dry conditions once the catalyst is added to the system. We therefore carried out some qualitative experiments to examine the effect of the presence of moisture on the poly(aminophosphazene)-catalyzed ROP of lactams. Unlike conventional anionic catalysts, it appears that the poly(aminophosphazene) catalysts, typified by P_4-*t*-Bu, maintain significant activity when ca. 0.5 but <1 mol % water (based on ϵ-caprolactam) is added to the polymerization. In an experiment where 0.5 mol % water (equivalent to the P_4-*t*-Bu concentration) was added and the polymerization carried out for 5 min at 270 °C, a 46% yield of polymer with an η_{inh} of 1.3 dL/g (0.5 w/v % in *m*-cresol) was obtained. On the other hand, when the initial concentration of water was reduced via evacuation of the system at <1 mmHg at 90 °C for 30 min, followed by raising the temperature to 270 °C and holding for only 3 min, an 86% yield of polymer was obtained with an η_{inh} of 1.8 dL/g. When the initial water concentration was increased to 1 mol % and then reduced at <1mmHg vacuum at 90 °C (30 min) followed by polymerization at 270 °C (reaction time 100 min), both the polymer yield (32%) and η_{inh} (0.53 dL/g) were reduced versus the above results. When no attempt was made to reduce the initial water concentration from 1 mol %, no polymer was obtained in a polymerization carried out under similar conditions.

In addition to the unusual behavior in the presence of moisture described above, it was demonstrated that P_4-*t*-Bu (0.25 mol % based on ϵ-caprolactam) with 0.32 mol % *N*-acetyl-ϵ-caprolactam as chain initiator could be recycled by conducting a ROP of ϵ–caprolactam to nylon 6 at 270 °C (reaction time 3 min.), extracting the catalyst and unreacted ϵ-caprolactam using MeOH, drying, and employing the resulting mixture for catalysis of a second polymerization under similar conditions. Similar yields (ca. 90%) and molecular weights (η_{inh} of 1.54 versus 1.40 dL/g) were obtained for the fresh and recycled runs, respectively. These results indicate that this class of ROP catalysts is quite robust. However, GC/mass spectroscopy results on P_4-*t*-Bu (mp 207 °C[10]) indicates some degree of thermal degradation of the catalyst: at 185 °C, *tert*-butylamine and a smaller amount of 2-methyl-1-propene were observed, and at 205 °C, larger amounts of the same two materials along with minor amounts of three additional unidentified compounds were observed. These results indicate that the reaction temperature should be kept as low as possible to avoid catalyst decomposition.

Molecular Weights and Molecular Weight Distributions of Polymers. Table 3 summarizes molecular weight and molecular weight distribution data for nylon 6, nylon 7, and nylon 66 prepared using the above poly(aminophosphazene) and protophosphatrane catalysts versus selected hydrolytic and anionic polymerization controls. Conditions for anionic polymerization controls are shown in Table 2 (entries 13 and 15). Nylon 6 and nylon 66 polymers prepared by P_4-*t*-Bu and the protophosphatrane catalysis are characterized by high molecular weights and exhibit linear Mark–Houwink plots with slopes in the same range as for polymer from hydrolytic polymerizations (see entry 1 versus entry 4, Table 3). These results are consistent with polymer virtually free of branches.[9] The MWD's are, in general, broader (particularly for nylon 6 prepared using Verkade's protophosphatrane "Super Base", entry 2, Table 3) than for our anionic controls or commercial nylons which exhibit MWD's (M_w/M_n) in the range of 2. However, under our GPC conditions, a commercial Zytel® 101 nylon 66 resin also exhibited a fairly broad MWD (entry 8, Table 3). In the case of nylon 7, although the molecular weights were high, the MWD was also quite broad (entry 5). The assertion of chain linearity for the

Table 2. Base-Catalyzed Ring-Opening Polymerization of Lactams[a]

entry no.	lactam (mmol)	base, mol %	N-AcL6, mol %	temp, °C	elapsed time, min	observations and comments	conv %	η_{inh} *m*-cresol/HFIP after MeOH extraction	DSC	
									T_m °C	Δ*H*, J/g
1	L6 (20)	P_4-*t*-Bu 0.25		270	20	The clear water white melt wrapped around the stirrer within 5 min. The stirrer was slowed but the melt remained wrapped around the stirrer. The reaction was allowed to cool after 20 min.	85	1.89/2.57	218 (1st cycle) 212 (2nd cycle)	65
2	L6 (20)	P_4-*t*-Bu 0.25	0.32	270	2	A clear melt was obtained which became very viscous within 2 min and wrapped around the stirrer. Let cool.		1.63/1.74		
3	L6 (20)	P_4-*t*-Bu 0.25		150	0−10	At 1−10 min, the melt was clear and thin.	62	3.34/3.22	220 (1st cycle) 213 (2nd cycle)	78 55
				150−200	10−30	No change in melt viscosity.				
				200−214	30−35	At some point between 30 and 34 min the melt became very viscous and wrapped around stirrer. Droplets of caprolactam appeared on the wall above melt.				
4	L6	P_4-*t*-Oct	0.32	270	1−8	A clear melt with no viscosity increase was observed.	27	0.79/—	206, 220 (1st cycle) 212, 219 (2nd cycle)	99 88
	(20)	0.09			9	No change from above.				
					13	No change. Temperature set to 260 °C.				
					25	A slight increase viscosity was observed at 260 °C. A layer of bubbles was observed atop the melt.				
					35	Unchanged from above.				
					155	A definite viscosity increase was noted.				
					4 h	The somewhat dark melt was allowed to cool.				
5	L6 (20)	P_4-*t*-Oct 0.18	0.32	270	7	The translucent melt climbed stirrer. Stringy fibers formed when stirrer was extracted. The polymer was allowed to cool.	77	1.75/1.83	219 (1st cycle) 217 (2nd cycle)	67 77
6	L6 (20)	P_2-Et 0.25	0.32	220	1	Clear thin melt.				
					2	Clear greenish yellow melt.				
					10	No change. Temperature raised to 250 °C.				
					20	No change. Temperature raised to 260 °C.				
					38	No change. Temperature raised to 270 °C.				
					65	The melt was non-viscous implying little polymerization had occurred.				
7	L6 (20)	P_2-Et 0.50	0.32	270	2	Translucent pale yellowish viscous melt.	71	0.79/0.76	221 (1st cycle) 218 (2nd cycle)	79 90
					2−20	No further increase in melt viscosity. The melt flowed down the side of the reactor when it was tipped.				
8	L6 (20)	P_1-*t*-Bu 0.50	0.32	270	2	Translucent pale yellow nonviscous melt.	0			
					7	No change.				
					30 min to 4 h	Slight darkening in color but no increase in viscosity.				
9	L6 (20)	P_1-*t*-Bu 0.24	0.61	270	4 h	No apparent increase in melt viscosity.	0			
10	L6 (20)	“Super Base”[b] 0.5	0.32	270	30	No increase in viscosity was observed.				
11	L6	“Super Base”[b]	0.32	235	9	The viscosity was on the order of that of maple syrup.				
	(20)	0.5			30	A further increase in viscosity was noted but it was not very high.				
12	L6	“Super Base”[b]	0.32	220	11.5	The viscous melt wrapped around the stirrer.	85	[η] = 2.43 by GPC		
	(20)	1.0			30	The reaction mixture was allowed to cool and a very tough polymer was recovered which yielded long lustrous fibers from a melt pool on a hot surface at 272 °C. The MeOH extract from the polymer was analyzed by FAB MS and found to contain residual “Super Base” with an $m/z + \mathrm{H} = 217.23$ (calcd − 217.16), ϵ-caprolactam, and cyclic oligomers out to a DP of 7.				
13	L6	NaH	0.32	270	0.5	The clear to translucent melt began to wrap around the stirrer. The stirrer was stopped and the reaction allowed to cool.	57	[η] =1.95		
	(20)	0.500.50			2−3	The polymer was analyzed by GPC. $M_n = 30{,}000$.	By GPC	By GPC		
14	L7	P_4-*t*-Bu	0.32	270	1	The initial clear melt became viscous within 1 min.	95	2.1/—	231	73
	(20)	0.25			1−2	The viscous melt wrapped around the stirrer and no flow was evident.			(1st cycle)	
					6	The polymer was allowed to cool.			230 (2nd cycle)	63
15	L7 (20)	NaH 0.5	0.32	220	6	The viscous melt wrapped around the stirrer.	96	1.36/1.41	233 (1st cycle) 230 (2nd cycle)	72 68
					8	The polymer was allowed to cool.				
16	L66 (10)	P_4-*t*-Bu 0.5	none	270	1	A clear thin melt form within 1 min.	73	0.70/1.1	254 (1st cycle)	70
					10	The melt viscosity had noticeably increased. A few dark patches began to appear on the wall of the flask above melt.				
					40	The melt viscosity had further increased.			258	73
					120	The stirrer was extracted from the viscous melt. The polymer yielded fibers from a melt pool on a surface at 262 °C.			(2nd cycle)	

[a] The monomers of nylons 6, 7, and 66 are expressed by L6, L7, and L66, respectively. [b] “Super Base” = $N[CH_2CH_2N(CH_3)]_3P$.

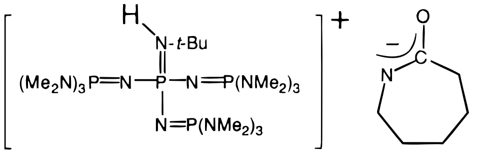
Table 3. Molecular Weights and Molecular Weight Distribution Analyses of Polymers from the Poly(aminophosphazene)-Catalyzed ROP of Lactams Versus Selected Controls

entry no.	polymer	Table 2 entry	M_n	M_w	M_z	M_w/M_n	[η]	a[a]
1	nylon 6	3	50 300	159 000	228 000	3.16	5.33	0.76
2	nylon 6	12	18 000	144 000	415 200	8.00	2.43	0.62
3	nylon 6	13	30 000	77 500	160 000	2.58	1.95	not measd
4	nylon 6[b]		21 000	43 700	65 900	2.08	1.52	0.71
5	nylon 7	14	26 300	104 000	304 000	3.95	2.71	0.62
6	nylon 7	15	23 000	59 000	105 000	2.56	1.72	0.72
7	nylon 66	16	13 500	37 600	68 200	2.78	1.99	0.70
8	Zytel® 101[c]		11 300	35 000	53 000	3.10	1.41	0.69

[a] Slope in Mark–Houwink equation. [b] From American Polymer Standards and prepared via hydrolytic polymerization. [c] Catalyst = none (standard nylon 66 resin from nylon 66 salt strike).

above nylon 6 polymer prepared using P_4-*t*-Bu was supported by the attainment of excellent tensile properties (tenacity (g/denier) = 5.6, elongation = 30%, and initial modulus = 16 g/denier) of spun and then drawn fibers.

Mechanism of Catalysis of ROP of Lactams by Poly(aminophosphazene)s. Initial ^{31}P NMR and ^{13}C NMR evidence for proton transfer such as shown below when P_4-*t*-Bu (0.15 mmol) and ϵ-caprolactam (7.0 mmol) were contacted in the liquid state in an NMR tube at 140 °C was not unequivocal. The ^{31}P NMR spectrum taken at 300 MHz was consistent with the protonated form of P_4-*t* -Bu with chemical shifts at −22.7 (q, 1P, $^2J_{PP}$ = 50 Hz) and 14.1 ppm (d, 3P, $^2J_{PP}$ = 50 Hz) versus reported[5] values for $[HP_4\text{-}t\text{-Bu}]^+CF_3CO_2^-$ of −22.9 (q, 1P, $^2J_{PP}$ = 50.5 Hz) and 13.39 ppm (d, 3P, $^2J_{PP}$ = 50.5 Hz) in THF with CD_3CN external solvent lock. (The neutral P_4-*t*-Bu had reported ^{31}P NMR chemical shifts of −24.44 (q, 1P, $^2J_{PP}$ = 20.2 Hz) and 5.73 ppm (d, 3P, $^2J_{PP}$ = 20.2 Hz) in THF with CD_3CN external solvent lock.) On the other hand, no ^{13}C NMR evidence for a carbonyl resonance associated with an ϵ-caprolactam anion under conditions where the protonated P_4-*t*-Bu appeared prominent and should have been associated with a counter lactam anion. ^{13}C NMR resonances for the unreacted lactam carbonyl carbon at 178.2 ppm and for the low molecular weight polymer carbonyl carbon at 173.4 ppm were observed.)



To explain the anomalous liquid-phase NMR results as well as to determine the structural nature of P_4-*t*-Bu and verify that the initial step in the reaction between P_4-*t*-Bu and ϵ-caprolactam involves proton transfer from the lactam to P_4-*t*-Bu, low- and high-temperature ^{31}P and ^{13}C solid-state MAS NMR studies were undertaken.

The ^{13}P solid-state cross-polarization magic angle spinning NMR spectrum (CP-MAS) of P_4-*t*-Bu at room temperature (Figure 1, top) shows four isotropic phosphorus chemical shift peaks of equal intensity at 12.6, −0.16, −3.4, and −25.9 ppm. This was not unexpected for the nonprotonated species in light of a recent article by Schwesinger *et al.*,[4] reporting the X-ray structure of an analogous compound, HPF_6 salt of P_5-*t*-Hept, which showed nonequivalent $[N{=}P(NMe_2)]_3$'s resulting from different degrees of bond stretching from the central phosphorus (*vide supra*). Upon heating the sample to 100 °C, the quantitative Bloch decay MAS spectrum (Figure 1, bottom) shows the collapse of the three downfield resonances observed in the CP-MAS spectrum taken at room temperature to a single isotropic resonance at 3.2 ppm, and the remaining upfield phosphorus resonance (the central phosphorus), which was at −25.9 ppm, now appears at −28 ppm. (It is interesting to note that these results are obtained despite the temperature well below the known melting point for P_4-*t*-Bu of 207 °C.[10]) These latter shifts are now consistent with the nonprotonated species reported previously (*vide supra*).

Figure 1. ^{31}P MAS NMR spectra of neat P_4-*t*-Bu acquired (top) at room temperature using the cross-polarization pulse sequence and (bottom) at 100 °C using a Bloch decay experiment. MAS rate is 8 kHz for both spectra.

Having now established the structural nature of the P_4-*t*-Bu employed in our experiments, we now proceeded to study the reaction of P_4-*t*-Bu with ϵ-caprolactam at various temperatures (80, 100, and 120 °C) and molar concentration ratios of P_4-*t*-Bu to ϵ-caprolactam of 3/1, 2/3 and 0.5/99.5. The latter ratio mimics that typical for catalyzed ROP of lactams. ^{31}P MAS NMR (Bloch decay) spectra were taken to see what effect the P_4-*t*-Bu/ϵ-caprolactam ratio would have on the initial proton transfer reaction prior to polymerization. Some representative spectra are shown in Figure 2. The spectra show that an increase in the amount of protonated P_4-*t*-Bu is found with increasing ϵ-caprolactam content of the mixtures at 100 °C. Protonated/nonprotonated integrated intensities progress from 1.2:1 in the 3/1 mixture (Figure 2b) to 2.5:1 in the 2/3 mixture (Figure 2c). The 0.5 mol % P_4-*t*-Bu result in Figure 2d indicates the exclusive presence of the protonated form. It is also worth noting that as the concentration of ϵ-caprolactam increases, the chemical shifts of the protonated P_4-*t*-Bu move in the downfield direction. We believe this merely results from solvation effects of the ϵ-caprolactam, although not verified. We also observed that at the temperatures given above, the 3/1 ratio exhibited protonated/nonprotonated ratios 0.5:1, 1.2:1, and 2.4:1 (spectra not shown), respectively; i.e., degree of protonation increased with temperature. This result is consistent with the observation of improved catalysis as the temperature is increased by virtue of the higher lactam anion concentration.

Now that we have shown that a proton has been transferred to P_4-*t*-Bu, we have still not determined the source of the proton. In order to verify that the proton source is indeed the ϵ-caprolactam, ^{13}C CP-MAS spectra of both unreacted and reacted ϵ-caprolactam with P_4-*t*-Bu (3/1 ratio) were obtained at room temperature. The

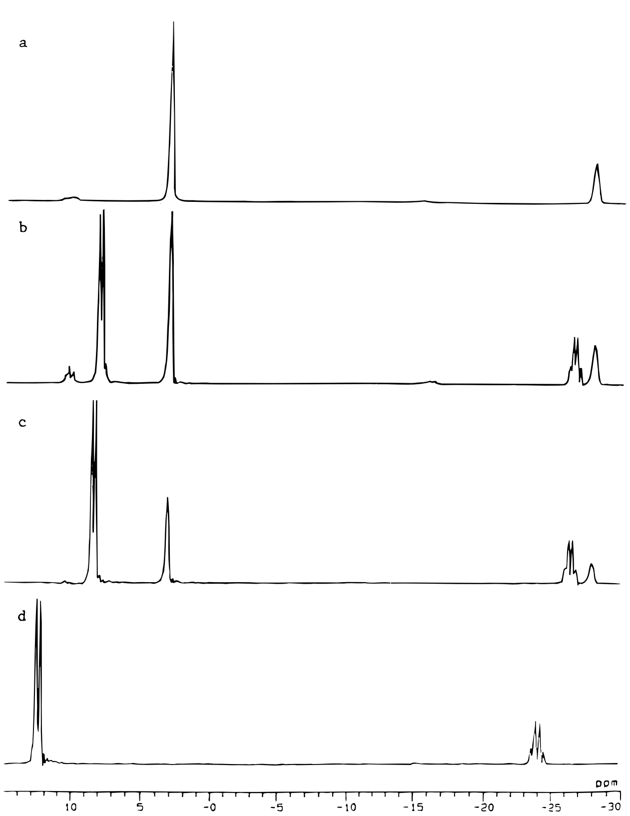


Figure 2. ^{31}P MAS NMR spectra of P_4-*t*-Bu and P_4-*t*-Bu/ϵ-caprolactam mixtures: (a) spectrum of neat P_4-*t*-Bu at 100 °C; (b) spectrum of 3/1 P_4-*t*-Bu/ϵ-caprolactam at 100 °C; (c) spectrum of 2/3 P_4-*t*-Bu/ϵ-caprolactam at 100 °C; (d) spectrum of 0.5 mol % P_4-*t*-Bu in ϵ-caprolactam at room temperature. All spectra were acquired with an MAS rate of 5 kHz.

carbonyl carbon of the unreactive ϵ-caprolactam was found to appear at 181.3 ppm, whereas the reacted lactam appeared at 176.3 ppm. This upfield chemical shift of the reacted versus the unreacted lactam is consistent with the loss of a proton from the lactam nitrogen, leading to the movement of electron density from the nitrogen to the carbonyl carbon, thus leading to a shielding effect.

In summary, we have now shown that the P_4-*t*-Bu compound we started with is the nonprotonated form and once reacted with ϵ-caprolactam, this species was converted to the protonated form with concomitant formation of the ϵ-caprolactam anion. To go back to the solution result which only showed the protonated lactam in the ^{13}C spectrum, it is our belief that the lactam anion was not observed due to its low concentration at the molar ratio of P_4-*t*-Bu used.

Conclusions

Poly(aminophosphazene)s uncovered by Schwesinger and protophosphatranes uncovered by Verkade mimic classical strong anionic base catalysts in their ability to generate lactam anions from lactams, which in turn rapidly catalyze the ring-opening polymerization of lactams to give high molecular weight polyamides. The data suggest that to be effective the $^{\mathrm{MeCN}}pK_{\mathrm{BH}^+}$ must be greater than *ca.* 27. In the case of the poly(aminophosphazene)s, a high degree of robustness is evident based on the maintenance of catalytic activity at high temperature, at least up to 270 °C, and based on, in the case of P_4-*t*-Bu, the fact that the reaction product could be extracted and the extract contained intact P_4-*t*-Bu. Further, the extract was effective in a second polymerization of ϵ-caprolactam.

Experimental Section

All solid-state NMR spectra were acquired on a Chemagnetics CMX-360 solid-state NMR spectrometer operating at a ^1H frequency of 359.97 MHz. The corresponding resonance frequencies for ^{13}C and ^{31}P are 90.53 and 145.73 MHz, respectively. Variable-temperature experiments were performed on a 5-mm Chemagnetics Apex MAS NMR probe, as sample heating in this device was found to be more uniform than in larger diameter probes. ^{31}P MAS rates ranged between 5 and 8 kHz, while ^{13}C experiments were all performed at MAS rates of 5 kHz. Pulse delays for each sample/temperature combination were estimated from the appropriate inversion−recovery-based experiments. ^{31}P chemical shifts are reported on the 85% H_3PO_4 scale using KH_2PO_4 as a secondary reference, while ^{13}C shifts are on the TMS scale established with hexamethylbenzene as a secondary reference.

Materials. The phosphazene bases were obtained from Fluka and used without further purification. Phosphazene bases P_1-*t*-Bu and P_2-Et were received as >98% pure solids, whereas P_4-*t*-Bu and P_4-*t*-Oct were received as 1 M solutions in hexane. 2,8,9-Trimethyl-1-phospha-2,5,8,9-tetraazabicyclo-[3.3.3]undecane, "Super Base", 98%, was obtained from Strem Chemicals and used without further purification. ϵ-Caprolactam from Aldrich was vacuum distilled three times, bp 137 °C at 10 mmHg. ζ-Enantholactam was prepared according to ref 11, bp 122 at 0.45 mmHg. 1,8-Diazacyclotetradecane-2,7-dione containing 6 mol % of its dimer was obtained from the bag filter of the DuPont Co.'s nylon 66 solid-state polymerizer at Parkersburg, WV. The material was sublimed at 240 °C at <1 mmHg and then analyzed by fast atom bombardment mass spectrometry to obtain the ratio of cyclic homologues.[12]

Preparation of Polymers. The polymers were prepared according to conditions described in Table 2. The ingredients were placed in a 15 mL round-bottom 2 cm i.d. cylindrical flask contained in a drybox, and in those cases employing P_4-*t*-Bu and P_4-*t*-Oct, the hexane was evaporated in the vacuum chamber. The flask was equipped with a three-necked adapter, a glass shaft with a paddle stirrer blade, and a drying tube and then transferred to a hood and connected to a nitrogen line and a mechanical controller. The reactor was lowered into a Woods metal bath whereupon stirring was begun. After the reaction was complete, the product, after cooling to room temperature, was ground through a 20-mesh screen using a Wiley mill and then Soxhlet extracted overnight with 100 mL of MeOH. The thimble containing the MeOH-insoluble fraction was dried to constant weight in a 100 °C vacuum oven to obtain polymer yields.

Characterization of Polymers. Structure. The ^1H and ^{13}C NMR spectra of the polymers were taken in hexafluoropropan-2-ol-d_2 and were found to be identical to those of authentic samples of nylon 6 via hydrolytic polymerization of ϵ-caprolactam and nylon 66 via catalyst-free condensation of salt strike.

Inherent Viscosities. The inherent viscosity ($\eta_{\mathrm{inh}} = \ln(\eta_{\mathrm{rel}})/c$) values were determined at 30 °C at a concentration of 0.5 w/v % in *m*-cresol and/or hexafluoropropan-2-ol (HFIP) according to the procedure described in ref 13.

Molecular Weight Distribution (MWD). The MWD was determined by size exclusion chromatography combined with laser light scattering and differential viscometry. The experimental setup was as follows: (1) two Phenogel linear size exclusion columns in series, containing cross-linked styrene−divinylbenzene 5 mm packing (each 300 mm × 7.5 mm i.d.; effective molecular weight range about 2000 to about 5 million); (2) carrier: hexafluoropropan-2-ol, 99+ %, (Aldrich Chemical Co.), containing 0.005 M sodium trifluroacetate; (3) concentration detector: differential refractive index detector Model 410 (Water Associates); (4) continuous viscometer: Model 110 (Visotek Corp.); (5) laser light scattering photometer: Model F with 488 nm, 10 mW argon ion laser (Wyatt Technology Corp.); (6) flow rate: 1.0 mL/min at 35 °C; (7) injected 100 mL containing approximately 300 mg of sample dissolved in carrier by Hewlett-Packard Model 1050 autosampler; (8) data processed using TriSEC software, version 2.13.

Thermal Analysis. DSC and TGA measurements were made by using a DuPont 900 series instrument.

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References and Notes

(1) Reimschuessel, H. K. Nylon 6 Chemistry and Mechanisms. *J. Polym. Sci., Macromol. Rev.* **1977**, *12*, 65.
(2) Sekiguchi, H. Lactams and Cyclic Imides. In *Ring-Opening Polymerizations*; Ivin, K. J., Saegusa, T., Eds., Elsevier: London, 1984, Vol. 2, p 809.
(3) Memeger, W. U.S. Patent 5,399,662, 1995.
(4) Schwesinger R.; Hasenfratz, C.; Schlemper, H.; Walz, L.; Peters, E.-M.; Peters, K.; Schnering, H. G. von *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, (9), 1361.
(5) Tang, J.; Dopke, J.; Verkade, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 5015.
(6) Fiala, F.; Kralicek, J. *Angew. Makromol. Chem.* **1978**, *71*, 29.
(7) Pietzonka, T.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, (9), 716.
(8) Valters, B.; Terekhova, M. I.; Petrov, E. S.; Stehlícek, J.; Sebenda, J. *Collect. Czech. Chem. Commun.* **1985**, *50*, 834.
(9) *Lactam-Based Polyamides*. Puffr, R.; Kubanek, V., Eds.; CRC Press” Boca Raton, FL, 1991; Vol. I, p 122.
(10) Schwesinger, R.; Schlemper, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1167.
(11) Coffman, D. D.; Cox, N. L.; Martin, E. L.; Mochel, W. E.; Van Natta, F. J. *J. Polym. Sci.* **1948**, *3*, 85.
(12) Balistreri, A.; Garozzo, D.; Giffrida, M.; Montaudo, G. *Anal. Chem.* **1987**, *59*, 2024.
(13) Sorenson, W.; Campbell, T. W. *Preparative Methods of Polymer Chemistry*, 2nd ed.; Interscience: New York, 1968; p 34.

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