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Notes

Synthesis and Properties of Low Molecular Weight Polyphosphazenes

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Introduction

Recent studies[1-6] have shown that hydrolytically sensitive polyphosphazenes may find biomedical application as absorbable suturing materials and as substrates for drug delivery systems. Among the problems encountered in carrying out such studies are the low yield (30–40%) of poly(dichlorophosphazene) from the melt polymerization of hexachlorotriphosphazene and the difficulty of controlling the molecular weight of the resultant polymers.

The conventional method[7,8] of thermal ring-opening polymerization of the trimer yields high molecular weight ($\bar{M}_w > 10^6$) polymers, but for subsequent substitution reactions careful purification procedures are required to remove unreacted trimer and partially cross-linked polymer. There are many catalysts[9-18] reported to improve both production yield and reaction time, but purification procedures cannot be omitted. Furthermore, in some particular applications such as drug delivery systems, low molecular weight polyphosphazenes may be more suitable in terms of easy control of biodegradation rate and the solubility of the substituted products. To our knowledge no systematic study has been reported on the synthesis and characterization of low molecular weight polyphosphazenes for such purposes. Here are presented the results of our study on the quantitative conversion of the trimer to low molecular weight ($\bar{M}_w = 10^4$–10^5) poly(dichlorophosphazene) in the presence of more than 2% of aluminum chloride exceeding catalytic amounts.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (Aldrich) used for polymerization was purified by sublimation at 55 °C under vacuum (ca. 0.1 mmHg). Only 60–70% of the material was allowed to sublime to ensure the absence of the cyclic tetramer and other impurities from the sublimate. Aluminum chloride (Aldrich, 99.99%) and sodium (Nakarai) were used as received. Trifluoroethanol (Aldrich) was dried over molecular seives before use. Solvents, such as benzene and THF (Baker), were dried and distilled over sodium benzophenone and CaH_2 under dry nitrogen. All reactions were performed under an atmosphere of dry argon using standard Schlenk techniques.

Measurements. The IR spectra of the polymers were recorded on an Analect FX-6160 FT-IR spectrometer in thin films between KBr disks. ^1H- and ^{31}P-NMR spectra were measured using a Varian Gemini 300 spectrometer in benzene-d_6. The chemical shifts for ^{31}P-NMR are relative to the external standard of triphenyl phosphate. Molecular weights were determined using a Waters Model 590 gel permeation chromatograph equipped with a Waters 410 differential refractometer. The samples were eluted with a THF solution containing 0.1% n-Bu_4NBr through two Waters Ultrastyragel linear columns. Sample concentrations were approximately 0.5% by weight, a typical injection volume being 100 μL, and a flow rate of 1.2 mL/min was used. Molecular weight calibrations were performed using polystyrene standards (Waters Associates) with narrow molecular weight distributions. Thermogravimetric analysis of polymers was carried out on a Perkin-Elmer TGA-2 at a heating rate of 20 °C/min under flowing nitrogen.

Table 1. Phase of Chlorophosphazene Depending on the Content of $AlCl_3$ after Melt Polymerization for 40 h at 240 °C

content of $AlCl_3$ (wt %)	phase of reactant	remarks
0.0	solid phase	trimer major
0.4	transparent rubber	mostly cross-linked
1.0	transparent rubber	mostly cross-linked
2.0	viscous liquid	non-cross-linked
3.0	viscous liquid	non-cross-linked
5.0	viscous liquid	non-cross-linked
10.0	viscous liquid	non-cross-linked

Polymerization and Derivatization Procedure. Pyrex glass tubes (23 mm o.d. and 10 cm length) were soaked for 24 h in chromic acid solution, followed by washing more than 10 times with distilled water and then drying at 140 °C in an oven. The dried tube was attached to a vacuum line, evacuated, and then flamed out. The cooled tube was loaded in a drybox with 5.0 g (14.4 mmol) of the trimer and appropriate amounts of aluminum chloride as catalyst. The tube was evacuated for 1 h under an ice bath and then sealed under vacuum. The sealed tube was heated at the required temperature in a specially designed reaction oven in which a metal axle holding the tubes was rotated 1 rpm to stir the melted reactant. After polymerization was carried out for the desired time period, the tube was cooled and then moved to the drybox filled with argon gas. The tube was broken, and the entire reaction mixture was dissolved in benzene or toluene and then subjected to a substitution reaction with sodium trifluoroethoxide, followed by purification using the literature procedure.[9] Anal. Calcd for a typical low molecular weight $[NP(OCH_2CF_3)_2]_n$: C, 19.77; H, 1.66; N, 5.76; P, 12.74; F, 46.90. Found: C, 19.80; H, 1.62; N, 5.75; P, 13.00; F, 46.8; Cl, <0.1.

Results and Discussion

Melt polymerization reactions of hexachlorocyclotriphosphazenes were performed using different amounts of $AlCl_3$ as catalyst with variation of both reaction temperature and time. Table 1 lists the phase of the products depending on the content of $AlCl_3$, after thermal polymerization for 40 h at 240 °C. Above a certain amount of $AlCl_3$ (>2.0%), the reactant phase is always liquid without cross-linked polymer and the conversion of trimer is almost quantitative as will be shown later. It is well known that Lewis acids[10,16] such as boron and aluminum trihalides act as initiation catalysts for thermal polymerization of trimer, but in the presence of an excess amount of Lewis acids, propagation is inhibited due to formation of stable acid–base adducts with the trimer.[16] In fact, further extension of the reaction time over 40 h at 240 °C did not result in cross-linked polymers. However, in order to optimize the reaction conditions, the minimum time

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Table 2. Reaction Time Required for Complete Conversion of Trimer to the Polymer

reaction temp (°C)	content of $AlCl_3$ (wt %)	minimum reaction time (h)
240	2	3.0
	5	2.0
	10	0.5
260	10	0.1

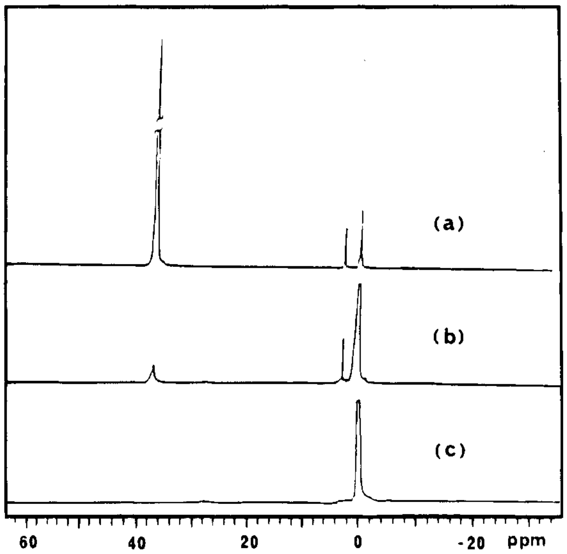

Figure 1. ^{31}P-NMR spectra of a reaction mixture (trimer plus 2.0 wt % of $AlCl_3$) after melt polymerization at 240 °C for 1 (a), 2 (b), and 3 h (c).

required for quantitative conversion of trimer to linear polymers was measured at 240 °C as a function of $AlCl_3$ content: the results are shown in Table 2. Of course, for a given level of $AlCl_3$, longer reaction times are required at lower temperature and vice versa.

We have monitored the thermal polymerization reaction of trimer using ^{31}P-NMR spectroscopy and confirmed almost quantitative conversion of trimer without byproducts. A typical example is illustrated in Figure 1. The trimer peak at 37.8 ppm disappeared completely after thermal reaction for 3 h at 240 °C, and only a polymer peak was observed at −0.2 ppm. It is interesting to note the hexamer peak at 2.6 ppm, which indicates that a considerable amount of hexamer is formed along with the polymer at the initial stage of the thermal reaction, but it is also finally converted to polymer.

In order to examine the properties of low molecular weight polymers compared with those of the high molecular weight polyphosphazenes, several low molecular weight polymers were prepared using different amounts of $AlCl_3$ at each set of optimum conditions, and their molecular distributions and thermal properties measured are listed in Table 3. It is seen that low molecular weight polymers are obtained when the content of $AlCl_3$ exceeds 2% of the reactant trimer, and the molecular weights decrease slightly with increasing $AlCl_3$ content. T_{10} values of the low molecular weight polymers are remarkably decreased from those of the polymers obtained using catalytic amounts of $AlCl_3$ (<1%), but only slightly decrease with increasing amounts of $AlCl_3$. The production yields of the low molecular weight polymers are all above 90% but not 100% based on the trimer, since the yields were estimated based on the finally recovered polymers substituted with trifluoroethoxide and purified, during the process of which a small amount of oligomer derivatives may be lost. Typical molecular weight distribution curves of the low molecular weight polymers selected from Table 3 are illustrated in Figure 2. While the conventional high molecular weight polymer shows a wide bimodal distribution curve ($\bar{M}_w/\bar{M}_n = 4.9$), all the low molecular weight polymers exhibit narrower monomodal but asymmetric distribution curves, which become increasingly asymmetric as the content of $AlCl_3$ is increased. This trend may be attributed to the fact that the increased amount of catalyst affects both initiation and propagation inducing rapid chain growing to a certain degree at the beginning stage of polymerization, but further growing to a high molecular weight polymer seems to be hindered by formation of the acid–base adducts that were aforementioned.

Table 3. Properties of Low Molecular Weight $[NP(OCH_2CF_3)_2]_n$[a] Depending on the Content of $AlCl_3$ in the Reactant Trimer

			molecular weight distribution[b]			
content of $AlCl_3$ (wt %)	reaction time (h)	yield (%)	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	T_{10}[c] (°C)
0.0[d]	5	<40	34	167	4.9	395
0.2	7	85	43	138	3.2	388
0.4	5	86	42	136	3.2	378
1.0	3	80	27	122	4.5	388
2.0	10	>90	9	29	3.2	326
3.0	10	>90	6	24	4.0	313
5.0	10	>90	5	21	4.2	303
10.0	10	>90	2	9	4.5	300

[a] Melt-polymerized at 240 °C. [b] From GPC. [c] From TGA (T_{10} = temperature of 10% degradation). [d] Melt-polymerized at 256 °C.

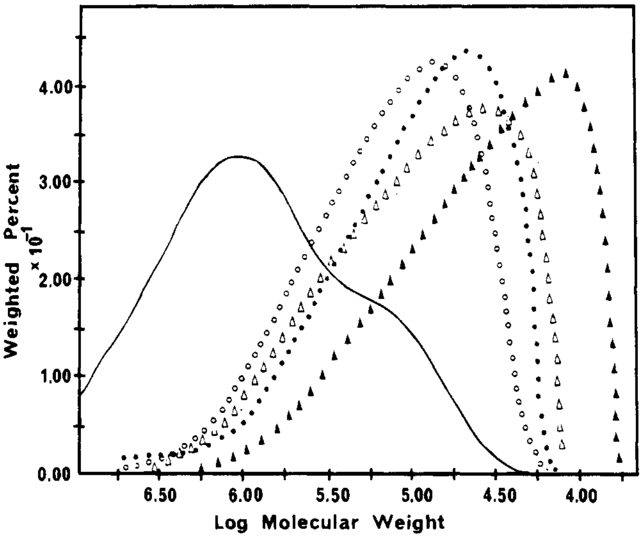

Figure 2. Molecular weight distribution curves depending on the content of $AlCl_3$: (—) blank; (○) 2.0%; (●) 3.0%; (△) 5.0%; (▲) 10.0%.

In conclusion, low molecular weight poly(dichlorophosphazene) ($\bar{M}_w = 10^4-10^5$) can easily be prepared from trimer with almost quantitative yield using appropriate amounts of $AlCl_3$ (2–5% of trimer) and may be used without purification procedures for subsequent substitution reactions for designed purposes.

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