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Notes

Polymerization of Hexachlorocyclotriphosphazene in the Presence of Carbon Disulfide

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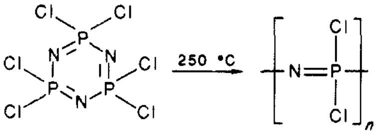
The thermal polymerization of hexachlorocyclotriphosphazene (1) to poly(dichlorophosphazene) (2) is a key step in the synthesis of a wide range of high molecular weight poly(organophosphazenes).[1-3] The polymerization reaction is normally carried out in the molten state, although this can be an unpredictable process unless rigorous precautions are taken with respect to the purity of the cyclic trimer. A number of melt polymerization accelerators have been proposed.[5-10] It is also known that polymerization in the crystalline state can be induced by high-energy irradiation.[11]



1

2 ($n \simeq 15\,000$)

The polymerization of 1 in solution offers a number of potential advantages over the same reaction carried out in the melt. Specifically, the presence of a solvent would be expected to moderate the dramatic viscosity increases that accompany polymerization in the molten phase and perhaps reduce the onset of cross-linking in the later stages of the process. Indeed, evidence exists that the cross-linking process becomes serious only when insufficient $(NPCl_2)_3$ remains in the system to function as a "solvent".

Previous work in other laboratories showed that the use of carbon tetrachloride as a solvent at 270–300 °C yielded polymers with molecular weights up to ≃130 000.[4] The use of toluene, xylene, or hexane as solvents led to reactions with the solvent.[4] Benzene was shown to be a satisfactory, unreactive solvent for polymerization, but accelerators such as benzoic acid, ether, or methanol were needed to enhance the reaction rate.[4,5] In general, polymerizations in solution were found to be one-half to one-third as rapid as those in the molten state, but the molecular weights of the polymers produced in solution were much lower. *o*-Dichlorobenzene has recently been mentioned as a solvent for the catalyzed polymerization of $(NPCl_2)_3$.[12]

We have found that carbon disulfide is an excellent mediator for the thermal polymerization of $(NPCl_2)_3$ to $(NPCl_2)_n$. Within the $(NPCl_2)_3$:CS_2 molar ratio range of 1:3.4 to 1:1.1 and over the 25–250 °C temperature range, it does not react with chlorophosphazenes. Even at these high concentrations of $(NPCl_2)_3$, carbon disulfide functions as a sufficiently effective diluent to permit high conversions of $(NPCl_2)_3$ to poly(dichlorophosphazene), with molecular weights comparable to those obtained by the melt polymerization process. Cross-linking reactions are virtually eliminated, and this is perhaps the most important attribute to this system. However, the presence of carbon disulfide does require the use of high-pressure equipment and rather stringent safety precautions.

Experimental Section

Materials and Equipment. $(NPCl_2)_3$ (Ethyl Corp.) was sublimed and recrystallized from hexane. Tetrahydrofuran (Baker) was dried and distillation from a sodium benzophenone slurry. Sodium spheres (Aldrich) were washed with small amounts of hexane before use. Carbon disulfide (Baker) was dried by distillation from phosphorus pentoxide. Trifluoroethanol was obtained from Halocarbon Products and dried over molecular sieves before use.

^{31}P NMR spectra were recorded on a JEOL PS-100 FT NMR spectrometer. ^{13}C NMR spectra were recorded on a Bruker WP-200 FT NMR spectrometer operated at 52 MHz. Approximate molecular weights were determined with a Waters Associates ALC/GPC 501 instrument fitted with a 120 cm × 1 cm, 10^6-Å Styragel column. The instrument was calibrated with polystyrene standards.

Polymerization of $(NPCl_2)_3$. The following procedure is typical: Weighed samples of $(NPCl_2)_3$ (5.05-15.14 g, 5.1-15.1 mmol) were placed in 15 × 2 cm constricted Pyrex tubes, which were then attached to a vacuum line. Air was removed for 3 h at 0.05 Torr, and the contents were brought to atmospheric pressure by back-flushing the tubes with dry nitrogen. Exactly 3 mL (3.79 g, 49.8 mmol) of freshly distilled carbon disulfide was then syringed into the tubes of puncturing the rubber tubing holding the polymerization tubes attached to the vacuum line. The tubes were then cooled in liquid nitrogen, degassed for 30 min, and finally sealed.

The sealed, evacuated tubes were encased in a wire screen jacket and were heated in a thermoregulated oven or pressure vessel under constant agitation. *Caution*: Although well-sealed and annealed glass tubes will withstand the internal pressure on most occasions, explosions can occur. Thus, we recommend that external pressurization within an autoclave be used to balance the internal pressure within the tubes, especially when larger scale reactions are attempted. The polymerization times varied from experiment to experiment (see Results and Discussion). After completion of the polymerization, the tubes were cooled, scored, broken open, and placed in a vacuum sublimator. Carbon disulfide was removed under vacuum, and unchanged trimer and higher cyclic species were separated by vacuum sublimation at 90 °C. The residual polymer was stored in vacuo until used in the halogen substitution step. Further isolation and purification of each cyclic species were accomplished by fractional sublimation followed by fractional recrystallization from hexane.

Derivatization Procedure. Poly(dichlorophosphazene) has a tendency to cross-link while passing through GPC columns; hence, it was converted to its trifluoroethoxy derivative, $[NP(OCH_2CF_3)_2]_n$, before analysis. The following procedure is typical: Sodium trifluoroethoxide was obtained by the reaction of sodium with trifluoroethanol in THF solution. A fourfold excess of the alkoxide was usually employed for each $NPCl_2$ repeating unit in the system.

A solution of poly(dichlorophosphazene) (1% in THF) was added dropwise to a stirred solution of sodium trifluoroethoxide in THF. the reaction mixture was heated at reflux for 72 h. the mixture was then cooled, concentrated, and precipitated into dilute hydrochloric acid. Further purifications were carried out by precipitation from THF into water twice and from THF into hexane twice. The molecular weights of these polymers were estimated by gel permeation chromatographic analysis in THF with the use of polystyrene standards.

Results and Discussion

Inertness of the Solvent. No evidence could be obtained for the incorporation of carbon or sulfur into the poly(dichlorophosphazene). The ^{31}P NMR spectrum of $(NPCl_2)_n$ consisted of a singlet centered at −17.7 ppm. A ^{13}C NMR spectrum of $(NPCl_2)_n$ in benzene-d_6 showed that no carbon atoms could be detected other than in the

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deuteriated solvent. Elemental analysis failed to detect any carbon or sulfur in the polymer. Moreover, all the $NPCl_2$ units in the system were accounted for by the quantitative recovery of cyclic oligomers and polymer. Thus, carbon disulfide appears to be unreactive toward chlorophosphazenes over the 25–250 °C temperature range.

Influence of Polymerization Time. At 250 °C, in 4.75 mol/L solution in carbon disulfide, the conversion of $(NPCl_2)_3$ to $(NPCl_2)_n$ increased from 20% at 10 h to 70% after 144 h. The polymer was un-cross-linked and had a GPC molecular weight near 7×10^5. During the same time period, the yield of higher cyclic species (tetramer through octamer) increased from 2.5 to 11.4%.[13] The polymer molecular weights appeared to be independent of polymerization time at a given concentration but to decrease as the concentration of $(NPCl_2)_3$ in carbon disulfide was lowered.

Source of Higher Cyclic Oligomers. The formation of the cyclic oligomers, $(NPCl_2)_{4-8}$, in the polymerization system is of some mechanistic interest. Preliminary data have been obtained that these higher oligomers are not present during the initial stages of the reaction but that their concentration rises as the amount of high polymer increases. Moreover, solutions of pure $(NPCl_2)_n$ in carbon disulfide yielded mixtures of $(NPCl_2)_{4-8}$ after several days at 250 °C. Thus, we conclude that ring–ring equilibration to yield $(NPCl_2)_{4-8}$ directly from $(NPCl_2)_3$ is probably not a significant source of these products.[14] Instead, thermal depolymerization of $(NPCl_2)_n$ to a mixture of cyclic oligomers may be the main oligomerization pathway.

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References and Notes

(1) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
(2) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(3) Allcock, H. R. *Phosphorus–Nitrogen Compounds*; Academic: New York, 1972.
(4) Patat, F.; Kollinsky, F. *Makromol. Chem.* **1951**, *6*, 292.
(5) Konecny, J. O.; Douglas, C. M.; Gray, M. Y. *J. Polym. Sci.* **1960**, *42*, 383.
(6) Konecny, J. O.; Douglas, C. M. *J. Polym. Sci.* **1959**, *36*, 195.
(7) MacCallum, J. R.; Tanner, J. *J. Polym. Sci., Part B* **1969**, 743.
(8) Kajiwara, M.; Saito, H. *Kogyo Kagaku Zasshi* **1963**, *66*, 621.
(9) Kajiwara, M.; Saito, H. *Kogyo Kagaku Zasshi* **1964**, *67*, 1002.
(10) Fieldhouse, J. W.; Graves, D. F. *Proc. Int. Nat. Conf. Phosphorus Chem. 1981. ACS Symp. Ser.* **1981**, *No. 171*, 315.
(11) Caglioti, V.; Cordischi, D.; Mele, A. *Nature (London)* **1962**, 195, 491.
(12) Kajiwara, M.; Shiomoto, K. *Polymer* **1984**, *25*, 93.
(13) The following percentage yields were obtained for polymer and (in parentheses) total $(NPCl)_2)_{4-8}$: 0 h, 0% (0%); 10 h, 20% (2.5%); 24 h, 30% (2.7%); 41 h, 40% (6.3%); 75 h, 60% (7.2%); 144 h, 70% (11.4%).
(14) Unless $(NPCl_2)_3$ is capable of fragmentation to monomer and linear dimer, it would be difficult to explain the direct formation of $(NPCl_2)_4$ and $(NPCl_2)_5$.

Dependence of T_g on Composition for a Compatible Polymer/Oligomer Blend

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Compatible polymer blends have been studied extensively in the past decade.[1,2] One of the goals of this research is to develop materials whose properties can be tailored by varying the ratios of the properly chosen blend components. It can be envisioned that alloys with novel properties somewhat intermediate between the properties of the blend constituents can be developed with minimum expense by utilization of existing polymers.

A relatively rapid way to determine the level of miscibility for mixtures of macromolecules is differential scanning calorimetry (DSC). The presence of a single blend glass transition temperature (T_g), intermediate to the T_g's of the individual components, is the criterion used to define compatibility by this method.[1] A variety of relationships that predict the compositional dependence of T_g for blends and copolymers have been discussed.[3-9] Development of such an equation is important for theoretical reasons and because of the large influence of T_g on macroscopic properties. Couchman[3-5] has derived such a relationship based on entropic considerations:

$$\ln T_g = \frac{x_1 k \ln T_{g_1} + x_2 \ln T_{g_2}}{x_1 k + x_2} \qquad (1)$$

where subscripts 1 and 2 correspond to the blend components, x is the weight fraction of the blend component, $k = \Delta C_{p_1}/\Delta C_{p_2}$, and ΔC_p is the difference in heat capacity below and above the pure component T_g's. It has been mentioned by Couchman[3] that if $T_{g_1} \approx T_{g_2}$ eq 1 yields

$$T_g = \frac{x_1 k T_{g_1} + x_2 T_{g_2}}{x_1 k + x_2} \qquad (2)$$

For the purpose of later discussion we note that if $k = \Delta\alpha_1/\Delta\alpha_2$, where $\Delta\alpha$ is the difference in volume expansion coefficient below and above T_g, eq 2 is identical with the Gordon–Taylor expression.[9] It has also been pointed out[3] that if $\Delta C_{p_1} T_{g_1} \approx \Delta C_{p_2} T_{g_2}$ eq 2 results in the Fox relationship[7] (eq 3) and if $\Delta C_{p_1} \approx \Delta C_{p_2}$ eq 1 simplifies to the empirical equation of Pochan[6] (eq 4):

$$\frac{1}{T_g} = \frac{x_1}{T_{g_1}} + \frac{x_2}{T_{g_2}} \qquad (3)$$

$$\ln T_g = x_1 \ln T_{g_1} + x_2 \ln T_{g_2} \qquad (4)$$

Poly(vinyl chloride) (PVC) has been shown to be compatible or semicompatible with a variety of other macromolecules.[10-24] In a number of instances the Fox equation has provided a good fit to the experimentally determined glass transition temperatures of these blends.[19-22] This may have occurred because the approximations necessary to yield this equation were met. For example, the product of ΔC_p and T_g is believed to be a constant for several polymers.[25] The materials of interest in this investigation, PVC and a styrenic oligomer, will be shown to be thermodynamically miscible. This system offers the opportunity to test the validity of Couchman's equation since it will be shown that for these materials $\Delta C_{p_1} \neq \Delta C_{p_2}$ and $\Delta C_{p_1} T_{g_1} \neq \Delta C_{p_2} T_{g_2}$.

Experimental Section

The blend components used in this study are PVC and an oligomer composed of (w/w) 34% α-methylstyrene, 28% styrene, 25% acrylic acid, and 13% carbitol ester of acrylic acid. The oligomer was provided by J. Allaway of S. C. Johnson & Son, Inc., and the PVC is a stabilized extrusion-grade material provided by Vista Chemical Co. Molecular weights relative to polystyrene standards in tetrahydrofuran were determined via gel permeation chromatography (GPC) by C. Weiss of S. C. Johnson & Son, Inc. (Table I). C. Beatty of the University of Florida prepared the blends by a melt-extrusion process at 160–200 °C. After blending, representative samples were analyzed by GPC to ensure that cross-linking or chain scission had not occurred. Differential