(14) Haddon, R. C.; Stein, S. M.; Chichester-Hicks, S. V.; Marshall, J. H.; Kaplan, M. L.; Hellman, M. Y. *Mater. Res. Bull.* **1987,** *22,* 117.
(15) Haddon, R. C.; Chichester, S. V.; Bowmer, T. N. In Reference 1, p 296.
(16) Oae, S.; Price, C. C. *J. Am. Chem. Soc.* **1958,** *80,* 3425.
(17) Hünig, S.; Baron, W. *Chem. Ber.* **1957,** *90,* 395.
(18) Crossley, M. L.; Dreisbach, P. F.; Hofmann, C. M.; Parker, R. P. *J. Am. Chem. Soc.* **1952,** *74,* 573.
(19) Bordwell, F. G.; Boutan, P. J. *J. Am. Chem. Soc.* **1956,** *78,* 87.
(20) Fitzsimmons, B. W., Shaw, R. A. *J. Chem. Soc.* **1964,** 1735.
(21) Singler, R. E.; Hagnauer, G. L.; Schneider, N. S.; Laliberte, B. R.; Sacher, R. E.; Matton, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1974,** *12,* 433.
(22) Dieck, R. L.; Goldfarb, L. *J. Polym. Sci., Polym. Chem. Ed.* **1977,** *15,* 361.
(23) The microanalytical discrepancy for **12** may result from incomplete combustion of the sample. See ref 13 and 24.
(24) Allcock, H. R.; Fuller, T. J.; Evans, T. L. *Macromolecules* **1980,** *13,* 1325.

Studies of the Phase Transitions in Poly[bis(4-ethylphenoxy)phosphazene] and Poly[bis(4-*tert*-butylphenoxy)phosphazene]. 1. ^{31}P NMR Study

Hajime Tanaka,[†] **M. A. Gomez,**[‡] **A. E. Tonelli,* S. V. Chichester-Hicks, and R. C. Haddon**

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received May 13, 1988; Revised Manuscript Received July 25, 1988*

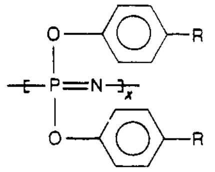
ABSTRACT: The solid–liquid crystalline phase transition of poly[bis(4-ethylphenoxy)phosphazene] has been studied by solid-state ^{31}P NMR. The glass transition of poly[bis(4-*tert*-butylphenoxy)phosphazene] has also been studied. There are a number of transitions in poly[bis(4-ethylphenoxy)phosphazene] which strongly depend on thermal history. The highest premelt transition $T(1)$ around 110 °C is assigned to the solid to liquid crystalline transition from the abrupt change in the mobility of the poly[bis(4-ethylphenoxy)phosphazene] backbone observed by ^{31}P NMR. Three resonances having different chemical shifts are observed at room temperature (below $T(1)$) in poly[bis(4-ethylphenoxy)phosphazene] and assigned to the crystalline, interfacial, and amorphous phases. Poly[bis(4-*tert*-butylphenoxy)phosphazene] has a much higher T_g than poly[bis(4-ethylphenoxy)phosphazene], shows little evidence of crystallinity, and appears to be liquid crystalline both above and below T_g.

Introduction

Recently[1] we have reported preliminary results of a multinuclear NMR study of poly[bis(4-ethylphenoxy)phosphazene]. Polyphosphazenes are unusual among synthetic polymers in that they have an inorganic backbone consisting of alternating N and P atoms. This results in various unique properties,[2–17] such as unusual mechanical and thermal properties and biocompatibility. A wide variety of side groups may be attached to the backbone P atoms leading to a large number of chemically unique polyphosphazenes. It is well-known[18] that most semicrystalline polyphosphazenes have three transitions: T_g, the thermotropic transition from crystalline to mesophase, and the melting transition. Among these transitions, the thermotropic transition is unique and interesting. Furthermore, recently[19–21] it has been found that some polyphosphazenes, whose substituents have the structures $-OC_6H_4X$, have multiple crystalline forms below $T(1)$, the crystal–liquid crystal transition, and their occurrence depends on the crystallization conditions.

These crystalline modifications and the mesophase have been studied mainly by X-ray diffraction, electron diffraction, and thermal analysis. Only a few studies[8,22,23] have been concerned with the dynamic properties of polyphosphazenes. High-resolution solid-state NMR is one of the most powerful methods available for the study of the dynamics and conformations of solid polymers. However, to our knowledge there are no reported studies of the phase transitions in polyphosphazenes by high-resolution solid-state NMR. Generally polyphosphazenes have two kinds of nuclei, ^{31}P and ^{13}C, which are readily observed[23] by NMR. ^{31}P, which is an abundant spin, gives information concerning the mobility and conformation of the backbone, while ^{13}C NMR gives information on the conformation, packing, and mobility of the side groups. Together ^{31}P and ^{13}C NMR provide comprehensive information with which we may begin to understand the physical properties of the polyphosphazenes. Information concerning the backbone mobility and conformation may shed light on the nature of the crystalline and liquid crystalline states in polyphosphazenes.

Poly[bis(4-ethylphenoxy)phosphazene] and poly[bis(4-*tert*-butylphenoxy)phosphazene] are typical polyphosphazenes; however they have not been widely studied.[24,25]



R = CH_2CH_3 or $C(CH_3)_3$

Here we focus our attention on the motional and conformational states of these two polyphosphazenes. We mainly report on the crystal–liquid crystal transition in poly[bis(4-ethylphenoxy)phosphazene] and the glass transition in poly[bis(4-*tert*-butylphenoxy)phosphazene]. Comparison of the results observed for poly[bis(4-ethylphenoxy)phosphazene] and poly[bis(4-*tert*-butylphenoxy)phosphazene] permits a discussion of the effects of side-chain bulkiness on the formation of crystal and liquid crystalline phases. The results of solid-state ^{13}C NMR and

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[†] Permanent address: Department of Applied Physics, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan.

[‡] Permanent address: Instituto de Plasticos y Caucho, C.S.I.C., Juan de la Cierva 3, 28006 Madrid, Spain.

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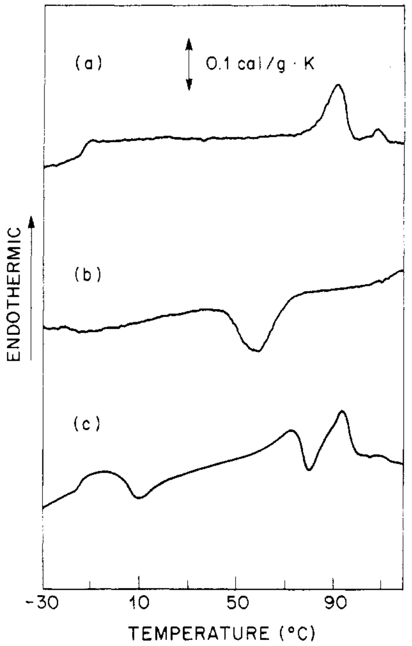

Figure 1. DSC scans of poly[bis(4-ethylphenoxy)phosphazene]. (a) (b) Heating (10 deg/min) and cooling (−10 deg/min) processes; (c) heating process (10 deg/min) of a sample quenched from 120 to −30 °C at −320 deg/min.

X-ray structural studies will be published separately.

Experimental Details

Both poly[bis(4-ethylphenoxy)phosphazene] and poly[bis(4-*tert*-butylphenoxy)phosphazene] were obtained by the Allcock procedure.[26] Polydichlorophosphazene was prepared by heating purified $(NPCl_2)_3$ in a sealed glass tube for 5 days at 250 °C with rigorous exclusion of moisture. Derivatization of $(NPCl_2)_x$ with the 4-ethylphenoxide and 4-*tert*-butylphenoxide residues was accomplished by employing thallium(I) salts of the phenols.[27]

Elemental analysis of the resulting polyphosphazenes showed <0.2% residual chlorine. Gel permeation chromatography indicated an average molecular weight of the order 10^6 for both samples. The polymers are soluble in tetrahydrofuran, chloroform, and benzene. ^{31}P NMR solution spectra in benzene consisted of sharp singlet resonances at −19.3 ppm, poly[bis(4-ethylphenoxy)phosphazene], and −18.7 ppm, poly[bis(4-*tert*-butylphenoxy)phosphazene], relative to external H_3PO_4. ^{31}P NMR spectra (C_6H_6) of the corresponding cyclic trimers $[NP(OC_6H_4\text{-}4\text{-ethyl})_2]_3$ and $[NP(OC_6H_4\text{-}4\text{-}tert\text{-butyl})_2]_3$ exhibited singlet peaks at 8.80 and 8.88 ppm, respectively, relative to external H_3PO_4. Full details of the sample preparations are presented in the preceding article.[27]

^{31}P NMR spectra were recorded on a Varian XL-200 spectrometer at a static magnetic field of 4.7 T. Magic angle sample spinning (MAS) at a speed of ca. 3 KHz was achieved with a Doty Scientific variable-temperature probe, which utilizes a double air bearing design. The temperature was varied from 20 to 135 °C by use of a heated flow and the standard Varian temperature controller. Polyphosphazene in rubbery form was packed in aluminum oxide rotors with Vespel endcaps. A 45-KHz rf field strength was used for the dipolar decoupling (DD) of protons, with a decoupling period of 200 ms. ^{31}P chemical shifts are referenced against external H_3PO_4 (0 ppm).

A Perkin-Elmer DSC-4 was also used to monitor the transitions in poly[bis(4-ethylphenoxy)phosphazene] and poly[bis(4-*tert*-butylphenoxy)phosphazene] by differential scanning calorimetry.

Results and Discussion

Poly[bis(4-ethylphenoxy)phosphazene]. As seen in the DSC measurements shown in Figure 1, the steplike change at −16 °C is caused by the glass transition of the amorphous phase. There are two transitions around 100 °C in the heating process of slowly cooled poly[bis(4-ethylphenoxy)phosphazene]; one transition is located at 90 °C and the other at 110 °C.

The heats of both transitions are not very large, indicating small differences in order between crystalline phases and the mesomorphic state or a rather small crystalline content. The cooling process is also shown in Figure 1, where only one transition in addition to T_g is observed. These thermal behaviors depend strongly on the prior thermal history of the poly[bis(4-ethylphenoxy)phosphazene] sample. There is a large thermal hysteresis, indicating the first-order character of the transition. Figure 1c shows the DSC scan for quenched poly[bis(4-ethylphenoxy)phosphazene]. Here we observe the glass transition, the crystallization, the melting of one crystalline form, recrystallization to a second crystal form, and the $T(1)$ transition. Details of the effects of crystallization conditions on the phase behavior of poly[bis(4-ethylphenoxy)phosphazene] will be published elsewhere.

The $T(1)$ transition was also observed in the optical microscope as discussed in our previous paper.[1] The transition shows the change in birefringence typical of a transformation from the crystalline to the liquid crystalline state. The liquid crystalline state prevails up to ca. 200 °C, above which only the isotropic melt exists.

Figure 2 presents the temperature-dependent ^{31}P NMR spectra of poly[bis(4-ethylphenoxy)phosphazene] in both the heating and cooling processes. At low temperatures there are three components with different chemical shifts, which correspond[1,28] to crystalline, interfacial, and amorphous phases from low to high field, respectively. This assignment has been confirmed by the real time observation of the crystallization process from the mesophase. Single-scan ^{31}P spectra were recorded at 75 °C after quenching to this temperature from above $T(1)$. This permitted real time observation of the growth of poly[bis(4-ethylphenoxy)phosphazene] crystallinity. Details of real time measurements will be published elsewhere. The crystalline intensity decreases with increasing temperature and completely disappears after the mesomorphic $T(1)$ transition, which is consistent with our optical microscope observations and X-ray measurements. The decrease in crystalline intensity is especially significant close to the lower temperature transition. This implies the partial melting of the sample, or this polymorph and is consistent with the DSC results.[21]

Figure 3 shows the temperature dependence of the ^{31}P line width of the amorphous component. The line width becomes sharper on heating above ambient temperature, then broadens around 85 °C, and after the solid to liquid crystalline transition, becomes very sharp. The line-width broadening observed around 85 °C might be related[21] to the melting of the low-temperature crystalline polymorph and recrystallization to the high-temperature form. The cooling process is qualitatively similar to the heating process, but there is a hysteresis. The crystalline component shows no significant change in its line width.

Figure 4 presents the temperature dependence of the ^{31}P chemical shift of the amorphous component. The chemical shift of the amorphous phase decreases continuously as the temperature increases. A small cusp is observed near the lower temperature transition. This observation coupled with those mentioned above indicates that the transition at 90 °C affects the mobility and conformation of the poly[bis(4-ethylphenoxy)phosphazene] backbone in the amorphous phase. The decreasing chemical shifts mean that the amorphous nuclei are becoming more shielded with increasing temperature, suggesting a more conformationally disordered phase finally transforming to a liquid crystalline phase. This behavior can be understood if the constraints of the crystalline lamellae

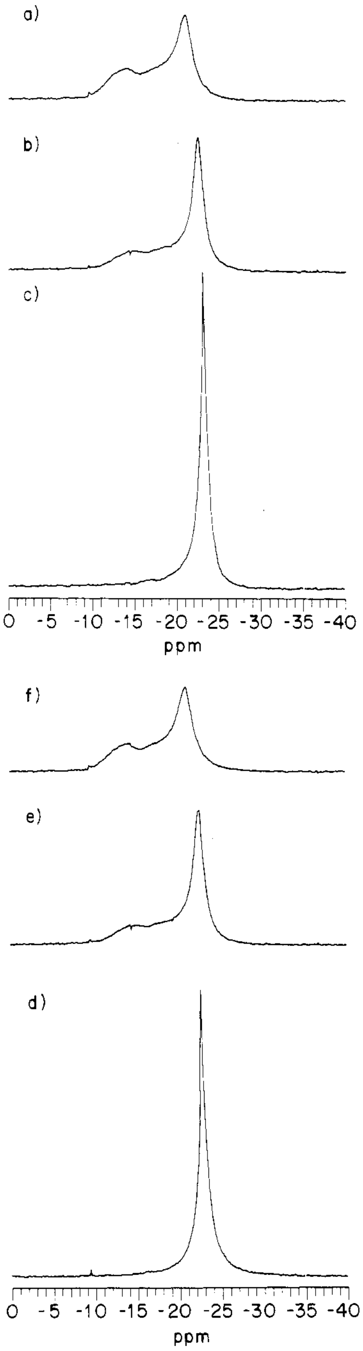

Figure 2. ^{31}P NMR MAS/DD spectra of poly[bis(4-ethylphenoxy)phosphazene] at (a) 23, (b) 80, and (c) 120 °C in the heating process and at (d) 100, (e) 60, and (f) 23 °C in the cooling process.

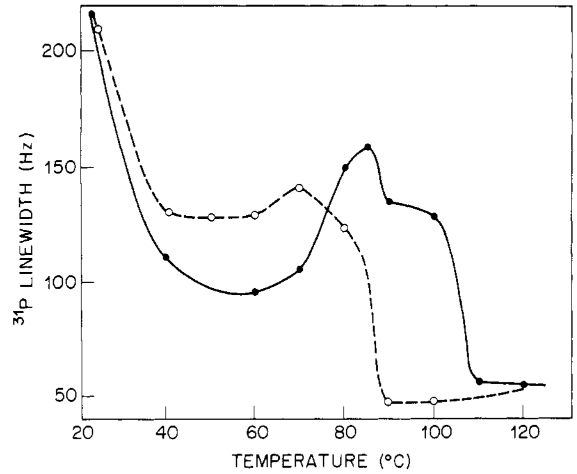

Figure 3. ^{31}P MAS/DD line width of the amorphous component of poly[bis(4-ethylphenoxy)phosphazene] measured during heating (●) and cooling (○).

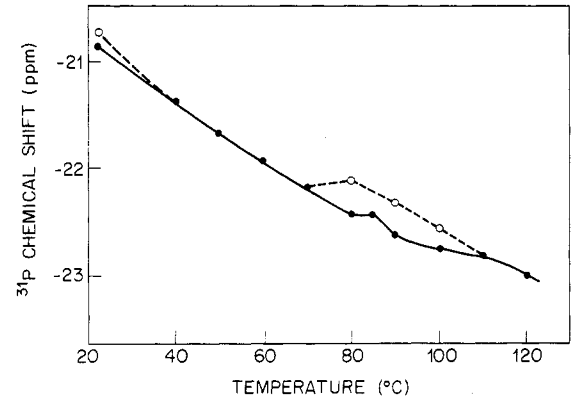

Figure 4. ^{31}P chemical shifts of the amorphous component of poly[bis(4-ethylphenoxy)phosphazene] measured versus H_3PO_4 during heating (●) and cooling (○).

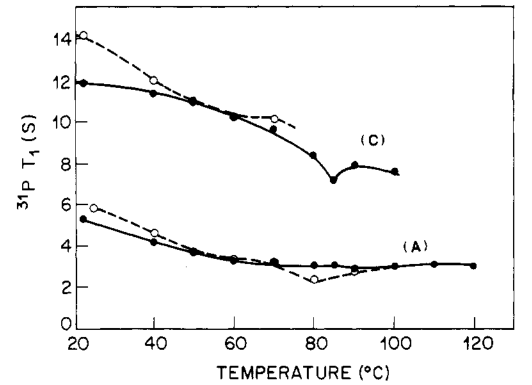

Figure 5. ^{31}P spin-lattice relaxation times, T_1, measured for the amorphous (A) and crystalline (C) components of poly[bis(4-ethylphenoxy)phosphazene] during heating (●) and cooling (○).

affect the conformation of the amorphous backbone. Amorphous chains become less affected by the crystalline constraints as more thermal energy is available. This is also consistent with the observed sharpening of the amorphous line width.

Figure 5 shows the temperature dependence of spin-lattice relaxation times, T_1, measured[29] for both the crystalline and amorphous components. The T_1 of the crystalline phase is longer than that of the amorphous phase as expected. The T_1 of the crystalline phase has a cusp at 85 °C, indicating the motional transition. After the solid to mesomorphic state transition, only one component remains whose T_1 is not very different from that of the amorphous phase below $T(1)$.

The T_1's of the amorphous phase show no drastic change through the $T(1)$ transition, while the line width of the amorphous phase, which is related to the spin-spin relaxation time,[29] T_2, drastically decreases. This behavior is typically observed in polymer systems undergoing a solid to liquid transition. The existence of birefringence above $T(1)$ and the X-ray diffraction pattern consisting of a single sharp equatorial peak strongly indicate the presence of orientational order above the $T(1)$ transition. This is consistent with the typical thermal behaviors reported[3,7,18,21] for other polyphosphazenes.

The temperature dependence of the rate of MAS at constant spinner gas pressure is shown in Figure 6. The spinning rate is generally related to the viscoelastic properties of the sample under the assumption that the sample is homogeneous. Sample homogeneity is obtained by spinning above $T(1)$. The MAS spinning rate under con-

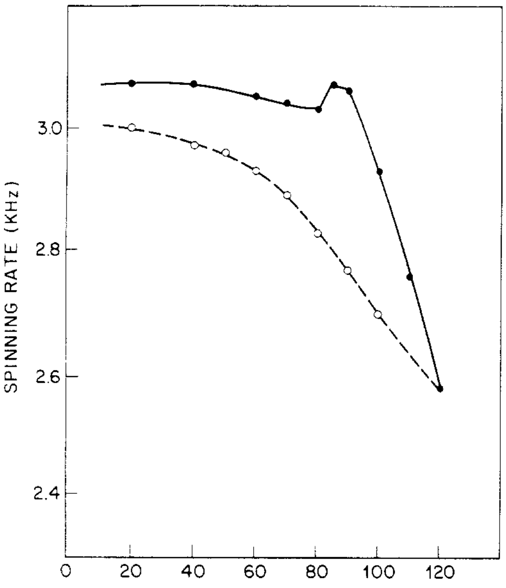

Figure 6. MAS rate at constant N_2 pressure during heating (●) and cooling (○) of poly[bis(4-ethylphenoxy)phosphazene].

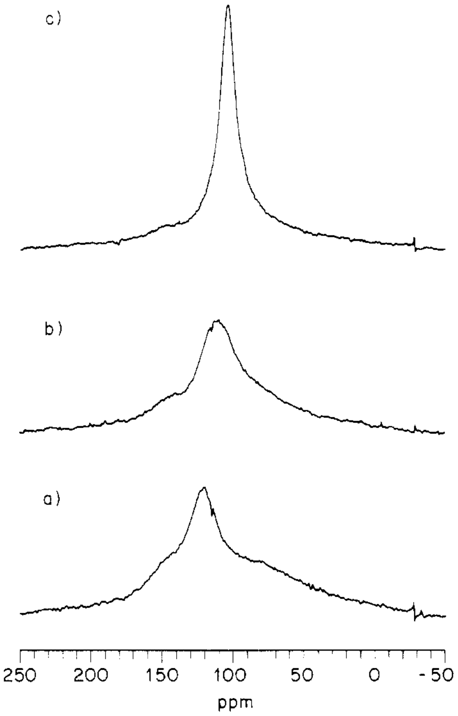

Figure 7. Nonspinning ^{31}P NMR spectra of poly[bis(4-ethylphenoxy)phosphazene] at (a) 23, (b) 70 (cooling), and (c) 90 °C (cooling).

stant N_2 pressure decreases near the $T(1)$ transition, suggesting a softening of the sample.

The powder pattern ^{31}P spectra of poly[bis(4-ethylphenoxy)phosphazene] observed without MAS are presented in Figure 7. In the liquid crystalline state we still observe chemical shift anisotropy. The line width is much broader than with MAS (15 versus <1 ppm), suggesting that the motion is not isotropic and not as rapid as in the true liquid. This is consistent with the existence of liquid crystalline order.

The first transition above T_g (see Figure 1) has a larger heat of fusion than the $T(1)$ transition. The first transition is thought[21] to be the conversion through the melt or disordered phase of one crystalline form to another, and the second, or $T(1)$ transition, is clearly the solid to liquid crystal transformation. It should be noted that the motional and conformational states of the amorphous backbone are affected by this transition. Poly[bis(4-ethylphenoxy)phosphazene] chains in the amorphous phase seem still to be affected by the crystalline phase below the higher $T(1)$ transition. An increase in the line width beginning around 70 °C (see Figure 3) indicates that the second, higher temperature $T(1)$ polymorph constrains the amorphous chains more severely than the lower temperature crystalline polymorph.

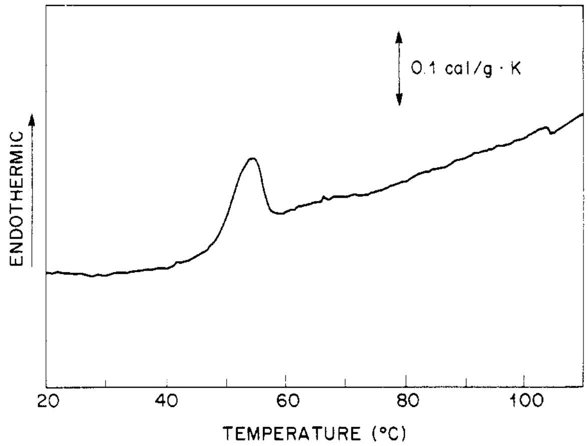

Figure 8. DSC scan (10 deg/min) of poly[bis(4-*tert*-butylphenoxy)phosphazene].

Poly[bis(4-isopropylphenoxy)phosphazene] has been studied by Meille et al.[21] recently, and they found two crystalline forms. The phenomena observed in our poly[bis(4-ethylphenoxy)phosphazene] sample are essentially the same as those seen in poly[bis(4-isopropylphenoxy)phosphazene]. The DSC scan of a quenched sample of poly[bis(4-ethylphenoxy)phosphazene] (see Figure 1c) clearly shows the exotherm after the first transition, indicating recrystallization. This strongly suggests the existence of at least two crystalline forms which are thermally interconverted by passage through the melt or a disordered phase. The difference in the bulkiness of the terminal side-chain groups between these two polyphosphazene polymers does not seem to play a critical role in their phase behavior, and these phenomena also seem to be general in other polyphosphazenes.[3,7,18,21] (Contrast this behavior with that shown by poly[bis(4-*tert*-butylphenoxy)phosphazene] in the next section.)

Poly[bis(4-*tert*-butylphenoxy)phosphazene]. Figure 8 shows the DSC scan of poly[bis(4-*tert*-butylphenoxy)phosphazene]. Its glass transition is observed at 50 °C. No clear $T(1)$ has been detected.

The temperature-dependent ^{31}P NMR MAS/DD spectra of poly[bis(4-*tert*-butylphenoxy)phosphazene] are presented in Figure 9. The spectra are very broad below T_g and sharpen above T_g. There appears to be no significant amount of crystalline phase, which is consistent with the DSC results and X-ray measurements. A small asymmetry observed in the spectra below 80 °C may indicate backbone conformational heterogeneity, probably resulting from a small amount of crystallike order. Above 100 °C this asymmetry disappears. A dramatic change in the line widths of the spinning side bands occurs between 80 and 100 °C.

Figure 10 presents the temperature-dependent ^{31}P line widths, with a narrowing observed around T_g. This line-width narrowing is not as drastic as that observed through the $T(1)$ transition in poly[bis(4-ethylphenoxy)phosphazene], which is consistent with the general properties of the glass transition.

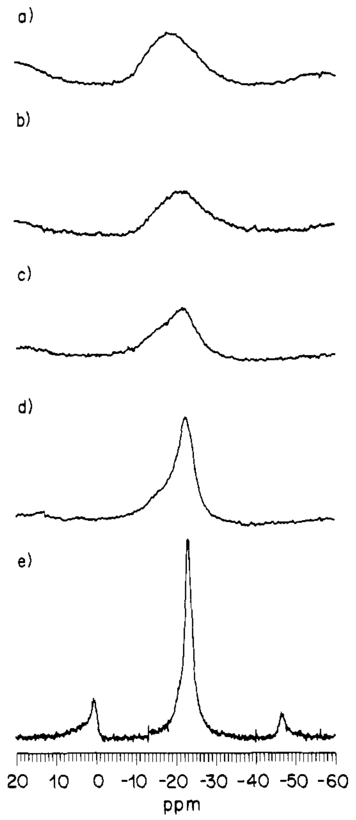

Figure 9. ^{31}P NMR MAS/DD spectra of poly[bis(4-*tert*-butylphenoxy)phosphazene] recorded at (a) 23, (b) 40, (c) 50, (d) 60, (e) 80, and (f) 100 °C.

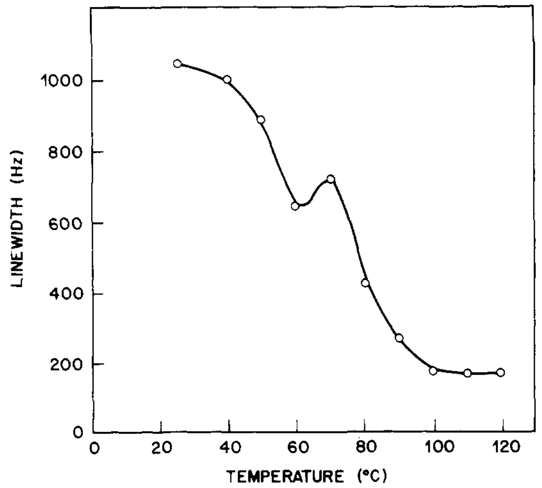

Figure 10. ^{31}P MAS/DD line widths measured for poly[bis(4-*tert*-butylphenoxy)phosphazene].

From optical microscope observations and X-ray diffraction measurements poly[bis(4-*tert*-butylphenoxy)phosphazene] does appear to possess liquid crystalline order either below or above T_g. It may not be too surprising that the liquid crystalline phase becomes glassy below T_g with orientational order if no other ordering, such as crystallization, takes place.

The temperature dependence of ^{31}P T_1's is shown in Figure 11, where T_1 is observed to decrease almost monotonically with increasing temperature. Poly[bis(4-*tert*-butylphenoxy)phosphazene] T_1's are on the slow motion side[29] of the T_1 curve, with motion of the backbone slower than the resonance frequency. Both the line width and T_1 values show an anomaly around T_g. This might be related to some sort of slowing down of the motion or reorganization of the poly[bis(4-*tert*-butylphenoxy)phosphazene] chains around the T_g transition. The transition observed in poly[bis(4-*tert*-butylphenoxy)phosphazene] is not a typical glass transition because it involves the transition from a liquid crystalline glass to a liquid crystal. The phases both below and above T_g have orientational order in contrast to the usual disordered amorphous glasses. The anomaly observed near T_g may be related to the presence of this orientational order. Poly[bis(4-*tert*-butylphenoxy)phosphazene] has a much higher T_g than poly[bis(4-ethylphenoxy)phosphazene], which may be related to the greater bulkiness of the *tert*-butyl moiety terminating the side groups. This difference in T_g probably produces the differences in line width and chemical shift between poly[bis(4-ethylphenoxy)phosphazene] and poly[bis(4-*tert*-butylphenoxy)phosphazene] in the liquid crystalline state.

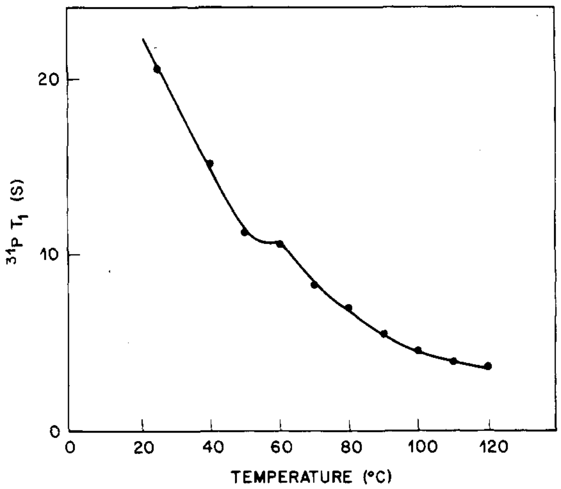

Figure 11. ^{31}P spin-lattice relaxation times, T_1, measured for poly[bis(4-*tert*-butylphenoxy)phosphazene].

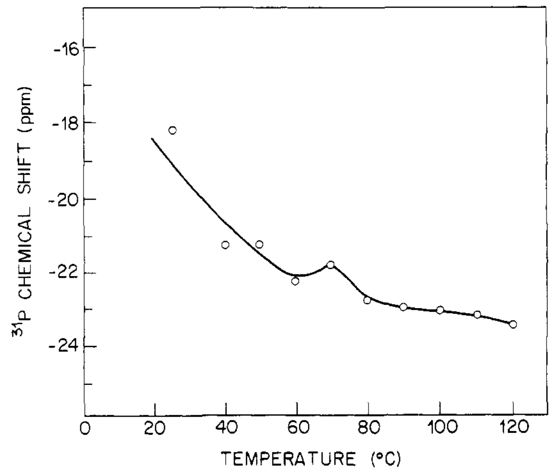

Figure 12. ^{31}P chemical shifts versus H_3PO_4 measured for poly[bis(4-*tert*-butylphenoxy)phosphazene].

Figure 12 shows the temperature dependence of the ^{31}P chemical shifts observed in poly[bis(4-*tert*-butylphenoxy)phosphazene]. As in the case of poly[bis(4-ethylphenoxy)phosphazene], the poly[bis(4-*tert*-butylphenoxy)phosphazene] chemical shifts move continuously upfield with increasing temperature, suggesting a thermally induced conformational disordering.

Conclusions

As pointed out by Allcock et al.,[4,5,30-32] the backbones of polyphosphazenes are inherently flexible because of the nature of the bonding, and this is evidenced by their generally low T_g's. The rotational barriers for the backbone are governed by steric interactions between side chains and can be substantial as in the case of poly[bis(4-*tert*-butylphenoxy)phosphazene] with bulky *tert*-butylphenoxy groups, leading to a T_g significantly above room temperature. The ^{31}P NMR results support the suggestion of flexibility and conformational disorder in the backbone of the amorphous phase and the mesophase. The absence of liquid crystalline order below $T(1)$ in the amorphous phase of poly[bis(4-ethylphenoxy)phosphazene] may be ascribed to the geometrical constraints provided by the crystalline phase. No such constraints appear to exist in poly[bis(4-*tert*-butylphenoxy)phosphazene], which is not crystalline, and liquid crystalline order is observed instead throughout the entire temperature range.

To summarize, we have primarily studied the backbone motional and conformational states of polyphosphazenes by selective excitation of ^{31}P nuclei. The chemical shifts of amorphous backbone ^{31}P nuclei move upfield with increasing temperature, which suggests that the amorphous phase becomes more disordered. At first the amorphous line width in poly[bis(4-ethylphenoxy)phosphazene] decreases with temperature, than it increases as the amorphous chains apparently become more tightly constrained by the higher temperature crystalline polymorph, and finally it is sharply reduced as poly[bis(4-ethylphenoxy)phosphazene] moves into the liquid crystalline state. The motional and conformational state of the side groups should yield important information concerning these transitions. A more detailed companion study including the results of solid-state ^{13}C NMR and X-ray diffraction studies will be published elsewhere.

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References and Notes

(1) Tanaka, H.; Gomez, M. A.; Tonelli, A. E.; Chichester-Hicks, S. V.; Haddon, R. C. *Macromolecules* **1988**, *21*, 2301.
(2) *ACS Symp. Ser.* **1988**, *No. 360*, 250–312.
(3) Schneider, N. S.; Desper, C. R.; Beres, J. J. In *Liquid Crystalline Order in Polymers*; Blumstein, A., Ed.; Academic Press: New York, 1978; Chapter 9.
(4) Allcock, H. R. *Phosphorous-Nitrogen Compounds*; Academic Press: New York, 1972.
(5) Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22.
(6) Singler, R. E.; Schneider, N. S.; Hagnauer, G. L. *Polym. Eng. Sci.* **1975**, *15*, 34.
(7) Schneider, N. S.; Desper, C. R.; Singler, R. E. *J. Appl. Polym. Sci.* **1976**, *12*, 566.
(8) Alexander, M. N.; Desper, C. R.; Sagalyn, P. L.; Schneider, N. S. *Macromolecules* **1977**, *10*, 721.
(9) Hagnauer, G. L.; Laliberte, B. R. *J. Appl. Polym. Sci.* **1976**, *20*, 3037.
(10) Cheng, T. C.; Mochel, V. D.; Adams, H. E.; Longo, T. F. *Macromolecules* **1980**, *13*, 158.
(11) Kojima, M.; Magill, J. H. *Polym. Commun.* **1983**, *24*, 329.
(12) Masuko, T.; Simeone, R. L.; Magill, J. H.; Plazek, D. J. *Macromolecules* **1984**, *17*, 2854.
(13) Kojima, M.; Magill, J. H. *Makromol. Chem.* **1985**, *186*, 649.
(14) Kojima, M.; Magill, J. H. *Polymer* **1985**, *26*, 1971.
(15) Magill, J. H.; Peterman, J.; Riek, M. *Colloid Polym. Sci.* **1986**, *264*, 570.
(16) Magill, J. H.; Riekel, C. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 287.
(17) Allcock, H. R.; Arcus, R. A.; Stroh, E. G. *Macromolecules* **1980**, *13*, 919.
(18) Sun, D. C.; Magill, J. H. *Polymer* **1987**, *28*, 1245.
(19) Kojima, M.; Satake, H.; Masuko, T.; Magill, J. H. *J. Mater. Sci. Lett.* **1987**, *6*, 775.
(20) Meille, S. V.; Porzio, W.; Allegra, G.; Audisio, G.; Gleria, M. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 217.
(21) Meille, S. V.; Porzio, W.; Bolognesi, A.; Gleria, M. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 43.
(22) Sato, K.; Masuko, T. *Polym. Commun.* **1986**, *27*, 299.
(23) Crosby, R. C.; Haw, J. F. *Macromolecules* **1987**, *20*, 2324.
(24) Singler, R. E.; Hagnauer, G. L.; Schneider, N. S.; Laliberte, B. R.; Sacher, R. E.; Matton, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 433.
(25) Dieck, R. L.; Goldfarb, L. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 361.
(26) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1709.
(27) Haddon, R. C.; Chichester-Hicks, S. V. *Macromolecules*, preceding paper in this issue.
(28) Kitamaru, R.; Horii, F.; Murayama, K. *Macromolecules* **1986**, *19*, 636.
(29) Farrar, T. C.; Becker, E. D. *Pulse and Fourier Transform NMR*; Academic Press: New York, 1971.
(30) Kim, C.; Allcock, H. R. *Macromolecules* **1987**, *20*, 1726.
(31) Allcock, H. R.; Allen, R. W.; Meister, J. J. *Macromolecules* **1976**, *9*, 950.
(32) Allen, R. W.; Allcock, H. R. *Macromolecules* **1976**, *9*, 956.

Polymerization of 3-Silyl-1-hexynes and Polymer Properties[1]

Toshio Masuda,* Kenji Tsuchihara, Kouji Ohmameuda, and Toshinobu Higashimura*

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.

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ABSTRACT: 3-(Dimethyl-*n*-hexylsilyl)-1-hexyne and 3-(dimethylphenylsilyl)-1-hexyne [$HC{\equiv}CCH(SiMe_2R)$-*n*-C_3H_7; R = *n*-C_6H_{13}, Ph; new compounds] formed polymers in excellent yields in the presence of Mo and W catalysts. The highest weight- and number-average molecular weights ($\bar{M}_w$ and $\bar{M}_n$) of poly[3-(dimethyl-*n*-hexylsilyl)-1-hexyne] were ca. 4×10^5 and 2×10^5, respectively ($MoCl_5$–Ph_3Sb as catalyst), while the highest $\bar{M}_w$ and $\bar{M}_n$ of the corresponding phenyl-substituted polymer were ca. 2×10^5 and 8×10^4 (WCl_6–Ph_3Sb). Both of the present polymers were yellow solids, whose structure could be represented as [$-CH{=}C(CHSiMe_2R$-*n*-$C_3H_7)-$]$_n$. They dissolved in many common organic solvents and could be cast from solution into films. Mechanical, thermal, and some other properties of the polymers are discussed.

Introduction

Recently, many polymers have been synthesized from substituted acetylenes by use of transition metal catalysts.[3] Among the polymers, Si-containing polyacetylenes often exhibit unique properties and functions (e.g., high gas permeability[4]); thus their synthesis is an intriguing subject. One of the simplest Si-containing acetylenes is (trimethylsilyl)acetylene. This monomer, however, usually produces a polymer partly insoluble in common organic solvents,[5] and the molecular weight of its soluble fraction is no more than ca. 1×10^4. Monomers in which one of the methyl groups in (trimethylsilyl)acetylene is replaced by other groups such as *n*-hexyl and phenyl also provide only polymers with similar molecular weights.[6]

In a previous paper,[7] 3-(trimethylsilyl)-1-alkynes [$HC{\equiv}CCH(SiMe_3)$-*n*-alkyl, 1] were employed as another