AD-A264 913

NTATION PAGE

Form Approved
OMB No 0704-0188

ited to average 1 hour per response, including the time for reviewing instructions, searching existing data sources eviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this urden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson ffice of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
May 18, 1993

3. REPORT TYPE AND DATES COVERED
Technical report

4. TITLE AND SUBTITLE
Synthesis, Characterization, and Modification of Poly(organophosphazenes) that Bear Both 2,2,2-Trifluoroethoxy and Phenoxy Groups

5. FUNDING NUMBERS
N00014-91-J-1194

6. AUTHOR(S)
Harry R. Allcock and Young Baek Kim

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Department of Chemistry
The Pennsylvania State University
152 Davey Laboratory
University Park, Pennsylvania 16802

8. PERFORMING ORGANIZATION REPORT NUMBER
#12

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
4132007

11. SUPPLEMENTARY NOTES
Prepared for publication in MACROMOLECULES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Reproduction in whole or in part is permitted for any purpose of the United State government. This document has been approved for public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

see attached

DTIC
ELECTE
MAY 26 1993
S B D

93 5 25 162

400 343

93-11554

14. SUBJECT TERMS
Polymers, phosphazenes, synthesis, elastomers

15. NUMBER OF PAGES
45

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
unclassified

20. LIMITATION OF ABSTRA
unlimited

Abstract

High molecular weight polyphosphazenes that bear varying ratios of phenoxy and 2,2,2-trifluoroethoxy groups have been synthesized by the reactions of $(NPCl_2)_n$ with sodium phenoxide, $PhO^- Na^+$, and sodium 2,2,2-trifluoroethoxide, $CF_3CH_2O^- Na^+$, using either competitive or sequential exposure to the two nucleophiles. The relative amounts of $NP(OCH_2CF_3)_2$, $NP(OCH_2CF_3)(OPh)$ and $NP(OPh)_2$ units in the polymer are dependent on both the synthesis method and the amounts of $CF_3CH_2O^- Na^+$ and $PhO^- Na^+$ used for the synthesis. The sequential reaction of poly(dichlorophosphazene), $(NPCl_2)_n$, with $CF_3CH_2O^- Na^+$ followed by $PhO^- Na^+$ yields mixtures of polymers that have very different compositions depending on the presence or absence of tetra-n-butyl ammonium bromide or 15-crown-5 ether. The reactions are complicated by the fact that phenoxy groups in $NP(OCH_2CF_3)(OPh)$ units are replaced by 2,2,2-trifluoroethoxy groups at elevated temperatures or at 25 °C in the presence of either 15-crown-5 ether or tetra-n-butyl ammonium bromide. The sodium salt of 3-hydroxypropanol replaces both 2,2,2-trifluoroethoxy and phenoxy groups in these polymers at room temperature in the presence of either tetra-n-butyl ammonium bromide or 15-crown-5 ether. These side group exchange reactions are affected by steric effects. The mechanisms of these reactions are interpreted from the perspective that the reaction of $CF_3CH_2O^- Na^+$ alone with the small molecule model compound, $(NPCl_2)_3$, yields significant amounts of geminally substituted products in the presence of either tetra-n-butyl ammonium bromide or 15-crown-5 ether. The T_g of the mixed-substituent polymers increased as the fraction of phenoxy groups in the polymer increased. For the polymers containing equal amounts of 2,2,2-trifluoroethoxy and phenoxy groups, the polymers with the highest ratio of $NP(OCH_2CF_3)_2$ units had the lowest T_g's. The contact angles of water droplets on the surface of films of these polymers increased as the fraction of 2,2,2-trifluoroethoxy groups increased.

OFFICE OF NAVAL RESEARCH

Grant: N00014-91-J-1194

R&T Code: 4132007

Technical Report No. 12

Synthesis, Characterization, and Modification of Poly(organophosphazenes) that Bear Both 2,2,2-Trifluoroethoxy and Phenoxy Groups

by

Harry R. Allcock and Young Baek Kim

Prepared for Publication in *Macromolecules*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

May 18, 1993

Synthesis , Characterization, and Modification of Poly(organophosphazenes) That Bear Both 2,2,2-Trifluoroethoxy and Phenoxy Groups

Harry R. Allcock* and Young Baek Kim

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802

Abstract

High molecular weight polyphosphazenes that bear varying ratios of phenoxy and 2,2,2-trifluoroethoxy groups have been synthesized by the reactions of $(NPCl_2)_n$ with sodium phenoxide, $PhO^- Na^+$, and sodium 2,2,2-trifluoroethoxide, $CF_3CH_2O^- Na^+$, using either competitive or sequential exposure to the two nucleophiles. The relative amounts of $NP(OCH_2CF_3)_2$, $NP(OCH_2CF_3)(OPh)$ and $NP(OPh)_2$ units in the polymer are dependent on both the synthesis method and the amounts of $CF_3CH_2O^- Na^+$ and $PhO^- Na^+$ used for the synthesis. The sequential reaction of poly(dichlorophosphazene), $(NPCl_2)_n$, with $CF_3CH_2O^- Na^+$ followed by $PhO^- Na^+$ yields mixtures of polymers that have very different compositions depending on the presence or absence of tetra-n-butyl ammonium bromide or 15-crown-5 ether. The reactions are complicated by the fact that phenoxy groups in $NP(OCH_2CF_3)(OPh)$ units are replaced by 2,2,2-trifluoroethoxy groups at elevated temperatures or at 25 °C in the presence of either 15-crown-5 ether or tetra-n-butyl ammonium bromide. The sodium salt of 3-hydroxypropanol replaces both 2,2,2-trifluoroethoxy and phenoxy groups in these polymers at room temperature in the presence of either tetra-n-butyl ammonium bromide or 15-crown-5 ether. These side group exchange reactions are affected by steric effects. The mechanisms of these reactions are interpreted from the perspective that the reaction of $CF_3CH_2O^- Na^+$ alone with the small molecule model compound, $(NPCl_2)_3$, yields significant amounts of geminally substituted products in the presence of either tetra-n-butyl ammonium bromide or 15-crown-5 ether. The T_g of the mixed-substituent polymers increased as the fraction of phenoxy groups in the polymer increased. For the polymers containing equal amounts of 2,2,2-trifluoroethoxy and phenoxy groups, the polymers with the highest ratio of $NP(OCH_2CF_3)_2$ units had the lowest

T_g's. The contact angles of water droplets on the surface of films of these polymers increased as the fraction of 2,2,2-trifluoroethoxy groups increased.

Introduction

The widespread use of poly(dimethylsiloxane) (silicone) elastomers as inert elastomers and biomedical polymers, and the recognition of their shortcomings, has stimulated a search for alternative elastomers with high solvent resistance, good energy absorbing properties, and long-term biocompatibility. Polyphosphazenes offer some of the best alternatives to silicones,[1] mainly because the bulk and surface properties can be tuned over a very wide range by changes in the side group structures. Moreover, surface reactions are possible that can markedly improve adhesion or biomedical interactions.

Two of the first stable polyphosphazenes synthesized and studied were poly[bis(2,2,2-trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$ (2), and poly[bis(phenoxy)phosphazene], $[NP(OPh)_2]_n$ (3).[2,3] Both polymers are semi-crystalline and have two first order thermal transitions at T(1) and T_m.[4-9] The polymers form isotropic melts above the melting temperature, T_m. The additional transitions of $[NP(OCH_2CF_3)_2]_n$ and $[NP(OPh)_2]_n$ at T(1) are due to changes within the crystalline states. The glass transition temperature, T_g, of $[NP(OCH_2CF_3)_2]_n$ is -66 °C and that of $[NP(OPh)_2]_n$ is -6 °C. The T(1)'s of $[NP(OCH_2CF_3)_2]_n$ and $[NP(OPh)_2]_n$ are 80 and 130 °C and the T_m's are 240 and 160 °C, respectively. Both polymers generate hydrophobic surface interactions, as determined by surface contact angles to water, and both are amenable to surface chemical reactions.[10-15] Although these two polymers are microcrystalline film- and fiber-forming species, similar polymers that bear either two different types of fluoroalkoxy or aryloxy side groups are non-crystalline elastomers.[16-20] These elastomers are used commercially in both general technology and in biomedicine.

With respect to the latter use, an early investigation of the biocompatibility and toxicity of several poly(organophosphazenes) showed that polymers with 2,2,2-trifluoroethoxy or aryloxy side groups are biocompatible and sufficiently non-toxic to be potentially useful for bioinert biomedical applications.[21]

$[NP(OCH_2CF_3)_2]_n$ and $[NP(OPh)_2]_n$ have different sets of properties and are immiscible with each other.[22] Nevertheless, materials that combine the attributes of each would be of considerable biomedical and general technological interest. Polymers *co*-substituted with trifluoroethoxy and phenoxy groups may offer the combined advantages of both single-substituent macromolecules and may, in addition, provide elastomeric character due to the decreased degree of crystallinity.

In this study we have synthesized polyphosphazenes *co*-substituted with 2,2,2-trifluoroethoxy and phenoxy groups using various synthesis sequences. The resulting polymers were studied to examine the effects of reaction conditions and the structure of the nucleophile on the polymer composition and physical properties. These polymers were then treated with $CF_3CH_2O^- Na^+$ or the sodium salts of diols to bring about organic side group displacement reactions as a route to otherwise inaccessible polymers with additional new properties. Later work will be devoted to examining the response of living tissues to the surfaces of these various polymers.

Results and Discussion

Synthesis and Composition of Polymers. (a) Competitive Reactions of Sodium 2,2,2-Trifluoroethoxide and Sodium Phenoxide with $(NPCl_2)_n$. $[NP(OCH_2CF_3)_2]_n$ and $[NP(OPh)_2]_n$ are synthesized individually either by the addition of a solution containing an excess amount of the sodium salt of the corresponding alcohol or phenol to a solution of poly(dichlorophosphazene), $(NPCl_2)_n$ (**1**), or by the addition of a solution of $(NPCl_2)_n$ to the sodium salt solution (Scheme I). The reaction of $(NPCl_2)_n$ with excess $CF_3CH_2O^- Na^+$ is rapid, with complete replacement of chlorine being achieved within 4 hrs at room temperature. However, the reaction of $PhO^- Na^+$ with $(NPCl_2)_n$ takes place more slowly, often requiring 72 hrs at 120 °C before total replacement of the chlorine can be achieved. The longer reaction time and the higher reaction temperature required for the complete reaction of $(NPCl_2)_n$ with PhO^- Na^+ can be explained by the more serious steric restrictions imposed by the phenoxy group.

The relative reactivities of $(NPCl_2)_n$ with $CF_3CH_2O^-$ Na^+ and PhO^- Na^+ at room temperature were first estimated by the addition of a THF solution of $(NPCl_2)_n$ to a THF solution containing four equivalents each of $CF_3CH_2O^-$ Na^+ and PhO^- Na^+ (Scheme **I**, reaction a). The recovered organophosphazene polymer contained 80 mole% of 2,2,2-trifluoroethoxy groups and 20 mole% of phenoxy groups as determined by ^{31}P NMR spectroscopy. This result suggests that the reaction rate of $CF_3CH_2O^-$ Na^+ with $(NPCl_2)_n$ is at least four times faster than that of PhO^- Na^+. The polymer contained 60 mole% of $NP(OCH_2CF_3)_2$ units and 40 mole% of $NP(OCH_2CF_3)(OPh)$ units. No $NP(OPh)_2$ units were detected. These different reactivities make it difficult to prepare polymers with predictable compositions by the addition of $(NPCl_2)_n$ to mixtures of the two nucleophiles.

The simultaneous addition of an equimolar mixture of the two reagents to $(NPCl_2)_n$, (method (6) in Tables **1** and **2**, yielded a polymer with 23% of $NP(OCH_2CF_3)_2$ units, 56% of $NP(OCH_2CF_3)(OPh)$ units, and 21% of $NP(OPh)_2$ units. Differences between the structure of this polymer and the one described above can be attributed to the much lower concentrations of the two competing reagents at the reaction sites when the reagents are added to the solution of $(NPCl_2)_n$. The slightly higher amount of trifluoroethoxy groups in the polymer than in the nucleophile mixture may be explained by the higher reactivity of $CF_3CH_2O^-$ than PhO^-. However, method (6) is the simplest route to synthesize polymers that have predictable compositions.

(b) Sequential Cosubstitution. An important objective was to understand the effect of reaction conditions on the formation of the three types of repeating units -- $NP(OCH_2CF_3)_2$, $NP(OCH_2CF_3)(OPh)$ and $NP(OPh)_2$ units. The most probable factors that may affect the formation of these units are the reaction temperature, the inductive and steric effects of the nucleophiles, and the sequence of reagent addition to $(NPCl_2)_n$. To study these factors, polyphosphazenes containing 2,2,2-trifluoroethoxy and phenoxy groups in an approximate ratio of 1:1 were synthesized by various reagent addition sequences (Scheme **I**, reactions d and e). The reaction conditions and product polymer composition are shown in Scheme **II** and Tables **1** and **2**, respectively. Polymers obtained by methods (1) to (6) listed in Table **1** are designated in the following text as polymers **1** to **6**, respectively.

To minimize any inhomogeneous condition that might be caused by a high local concentration of the first reagent added, reagent **A** was added dropwise to the $(NPCl_2)_n$ solution while the mixture was stirred vigorously. Polymers formed by the addition of 50 % equivalents of **A** during either 2 minutes or 60 minutes were identical provided the reaction mixture was stirred vigorously. The fraction of geminal substitution listed in Table **2** is defined by the fraction of **A** reagent molecules that reacted with preformed NP(A)(Cl) units even when unreacted $NPCl_2$ units remained. Therefore, the fraction of geminal substitution increases as more **A** molecules react with NP(A)(Cl).

The results listed in Tables **1** and **2** show that lowering the reaction temperature from 25 to -78 °C did not affect the geminal to non-geminal substitution ratio, since polymers **1** and **2** were essentially identical. However, an increase in the reaction temperature from 25 °C to 50 °C for the initial reaction with trifluoroethoxide increased the proportion of geminally $CF_3CH_2O^-$ substituted units (polymer **3**), a result that may reflect the effect of temperature increases in overcoming the small steric barriers to geminal substitution by this reagent.

On the other hand, when phenoxide ion was the initial reagent, the fraction of geminal phenoxy-substitution was low (polymer **4**), a result that can be explained by the larger steric hindrance imposed by a phenoxy group in an NPCl(OPh) unit compared to that of a 2,2,2-trifluoroethoxy group in an $NPCl(OCH_2CF_3)$ unit.

Further variations in the reaction conditions for method (1) were explored by treating $(NPCl_2)_n$ with various amounts of $CF_3CH_2O^- Na^+$ and $PhO^- Na^+$ in sequence, and these data are listed in Table **3**. The data show that the fraction of geminal substitution increases as the amount of reagent **A** is increased. This may be explained by the higher probability that an NP(A)(Cl) unit will encounter another **A** molecule. The compositions of polymers synthesized by treating $(NPCl_2)_n$ with various amounts of PhO^- Na+ and $CF_3CH_2O^-$ Na^+ in sequence, method (4), are listed in Table **4**. The results in Tables **3** and **4** show that PhO^- gives a lower fraction of geminal substitution compared to $CF_3CH_2O^-$.

Replacement of Phenoxy Groups by 2,2,2-Trifluoroethoxy Groups. Evidence was obtained that the trifluoroethoxide ion could displace phenoxy groups from $NP(OCH_2CF_3)(OPh)$ units to yield $NP(OCH_2CF_3)_2$ units. For example, the total amount of 2,2,2-trifluoroethoxy groups in polymer **5**, which was synthesized by treating $(NPCl_2)_n$ with equimolar amounts of PhO^- Na^+ and excess $CF_3CH_2O^-$ Na^+ in sequence, followed by heating at 67 °C (method (5)), was significantly higher than 50 %, but the mole fraction of $NP(OPh)_2$ units was almost the same as that in polymer **4**, which was synthesized by treatment of $(NPCl_2)_n$ with equimolar amount of PhO^- Na^+ and excess $CF_3CH_2O^-$ Na^+ in sequence at 25 °C. These results suggest that $CF_3CH_2O^-$ Na^+ can replace the phenoxy groups in $NP(OCH_2CF_3)(OPh)$ units, but not in $NP(OPh)_2$ units. The following examples provide additional evidence for this phenomenon.

A reaction mixture prepared by method (4) (at 25 °C) was divided into two parts. One yielded polymer **4**. The remaining reaction mixture was then heated at reflux (67 °C) overnight to obtain a polymer having an almost identical composition to that of polymer **5**. These results show that, at elevated temperatures, $CF_3CH_2O^-$ replaces phenoxy groups, but only in $NP(OCH_2CF_3)(OPh)$ units. In a separate experiment, a THF solution containing polymer **3** and one equivalent of $CF_3CH_2O^-$ Na^+ was heated to reflux. The composition change at different reaction times is shown in Figure **1** which indicates that $NP(OCH_2CF_3)_2$ units are produced at the expense of $NP(OCH_2CF_3)(OPh)$ units. Phosphorus NMR spectra of the reaction mixture showed a sharp peak at -8 ppm. This peak became larger as the replacement reaction proceeded. The ^{31}P NMR spectra of polymer **3** and the product are shown in Figure **2(a)** and **2(b)**, respectively. The peak from the phosphorus atoms in $NP(OCH_2CF_3)_2$ units in polymer **3**, Figure **2(a)**, is broad (-7 to -13 ppm), while the newly produced peak is relatively narrow with a chemical shift around -8 ppm. The sharpness and the chemical shift suggest that phosphorus nuclei in the newly produced $NP(OCH_2CF_3)_2$ units are similar to those in $[NP(OCH_2CF_3)_2]_n$ which appears as a sharp singlet at -8 ppm. These results suggest that the newly produced $NP(OCH_2CF_3)_2$ units form blocks and this can happen when $CF_3CH_2O^-$ replaces phenoxy groups in $NP(OPh)(OCH_2CF_3)$ units in the vicinity of $NP(OCH_2CF_3)_2$ units, which is the least sterically hindered position.

Polymer **10**, which contained 58 % of $NP(OCH_2CF_3)_2$ and 42 % of $NP((OCH_2CF_3)(OPh)$ units, was heated at reflux in THF (67 °C) in the presence of 3 equivalents of $CF_3CH_2O^- Na^+$. No phenoxy groups were detected in the polymer after 4 days, as determined by ^{31}P NMR spectroscopy. The ^{31}P NMR spectra of polymer **10** and the product are shown in Figure **3(a)** and **3(b)**, respectively. The ^{31}P NMR spectrum of the product showed a relatively narrow singlet at -8 ppm, similar to that of $[NP(OCH_2CF_3)_2]_n$. However, the physical character of this polymer was not identical to that of $[NP(OCH_2CF_3)_2]_n$ synthesized directly by the treatment of $(NPCl_2)_n$ with $CF_3CH_2O^- Na^+$. The ^{31}P NMR spectrum shown in Figure **3(b)** is similar to that of a polymer obtained by Ferrar and coworkers by heating $[NP(OCH_2CF_3)_2]_n$ with $CF_3CH_2O^- Na^+$.[23] The change in the ^{31}P NMR spectrum was explained in that earlier work by the supposition that some of the OCH_2CF_3 groups were replaced by OH groups. Whatever the explanation, it appears that organic side group exchange affects the polymer structure in ways other than would be expected from simple ligand exchange. Polymers isolated after organic side group exchange reactions are generally more brittle than their counterparts that have been prepared by a more direct route. This raises general questions about the relationship of the polyphosphazene structure and properties to synthesis reaction conditions such as reagent concentrations and reaction times.

There are limits to the number of phenoxy groups that can be replaced by trifluoroethoxy groups. For example, a polymer that contained approximately 30 mole% of $NP(OCH_2CF_3)_2$, 20 mole% of $NP(OPh)_2$, and 50 mole% of $NP(OCH_2CF_3)(OPh)$ units was exposed to $CF_3CH_2O^-$. The fraction of $NP(OCH_2CF_3)_2$ units increased as the reaction with $CF_3CH_2O^-$ proceeded, while the fraction of $NP(OPh)_2$ unit did not change. However, replacement of phenoxy groups by 2,2,2-trifluoroethoxy groups ceased after 72 hrs, but a broad ^{31}P NMR peak, centered at 4 ppm, appeared and became larger as the system was exposed to $CF_3CH_2O^-$ beyond that point. The nature of this long-term reaction is not known, but it could involve dehydrofluorination from trifluoroethoxy groups, or perhaps chain cleavage.

The fact that the replacement reaction slows down markedly after a certain number of phenoxy groups in $NP(OCH_2CF_3)(OPh)$ units have been replaced suggests that $CF_3CH_2O^- Na^+$ cannot replace phenoxy groups in polymers that contain more than a certain proportion of phenoxy groups. This may reflect the steric hindrance in regions that contain high concentrations of phenoxy groups. Thus, polymers **16**, **18** and **19**, bearing 73, 82 and 100 mole% of phenoxy groups, were heated at reflux in THF or dioxane in the presence of excess amounts of $CF_3CH_2O^- Na^+$. No change in polymer composition was detected by ^{31}P NMR spectroscopy after 4 days. Thus, polymers that contain 73 % or more phenoxy groups do not undergo phenoxy displacement by $CF_3CH_2O^- Na^+$. This reinforces the view that steric effects control the limit of the organic side group replacement reaction.

Effect of Tetra-n-butyl Ammonium Bromide and 15-Crown-5 Ether on the Reaction Between $NPCl_2$ Units and $CF_3CH_2O^- Na^+$ or $PhO^- Na^+$. The addition of tetra-n-butyl ammonium bromide or 15-crown-5 ether to reactions of the type discussed here provides additional opportunities to control the polymer molecular structure. The rationale behind this approach is as follows. When $CF_3CH_2O^- Na^+$ (sufficient to react with every chlorine atom) is added to $(NPCl_2)_n$, the replacement of chlorine is probably not completely random but is affected by the inductive and steric effects of the side groups already present. Assuming that the electron-withdrawing effect of the CF_3CH_2O group predominates, a phosphorus atom in an $NPCl(OCH_2CF_3)$ unit should be more electrophilic than in an $NPCl_2$ unit, and the regions along the polymer chain that bear the most 2,2,2-trifluoroethoxy groups should be the most electrophilic. If steric effects predominated, the substitution would proceed via a trans-nongeminal pathway. In our previous investigation of the reaction between small molecule hexachlorocyclotriphosphazene and $CF_3CH_2O^- Na^+$ it was found that 2,2,2-trifluoroethoxy groups replace chlorine atoms in a trans-nongeminal pattern.[24] This result suggests that the stereochemistry, at least at the small-molecule level, may be controlled by steric effects. However, the reaction patterns may also be influenced by the nucleophilicity of the organic anion, and this can be controlled by the use of alkyl ammonium halides or crown ethers. The following experiments indicate that such additives can indeed influence the structure of the final product.

The ^{31}P NMR spectrum of a product mixture obtained by adding one equivalent of $CF_3CH_2O^- Na^+$ to $(NPCl_2)_n$ in THF is shown in Figure **4(a)**. The peaks in Figure **4(a)** are relatively broad and not well resolved, presumably because the replacement follows a trans-nongeminal random pathway. When the same reaction was carried out in the presence of either tetra-n-butyl ammonium bromide or 15-crown-5 ether, the ^{31}P NMR spectrum of the reaction mixture was completely different, as shown in Figure **4(b)**.

The spectrum in Figure **4(b)** can be interpreted in terms of two concepts (1) that the product may be a homogeneous polymer containing mostly blocks of $NPCl_2$ and $NP(OCH_2CF_3)_2$ units or (2) that it is a mixture of polymers bearing mostly $NP(OCH_2CF_3)_2$ or $NPCl_2$ units. The broad peak at -10 ppm indicates the formation of $NP(OCH_2CF_3)(Cl)$ units as well. However, this spectrum is consistent with the interpretation that $NP(OCH_2CF_3)_2$ and $NPCl_2$ units are the main repeating units in the product polymer, and that, in the presence of the additives, the system has discriminated against the formation of $NPCl(OCH_2CF_3)$ units.

A polymer synthesized by the sequential reaction of $(NPCl_2)_n$ with equimolar amount of $CF_3CH_2O^- Na^+$ and excess $PhO^- Na^+$ in the presence of 15-crown-5 ether was fractionated. One fraction, obtained by precipitation from methanol, contained 22 mole% of 2,2,2-trifluoroethoxy groups and 78 mole% of phenoxy groups. The unprecipitated polymer was recovered by evaporating the methanol. The recovered polymer contained 65 mole% of 2,2,2-trifluoroethoxy groups and 35 mole% of phenoxy groups. Similar results were obtained for a polymer synthesized in the presence of tetra-n-butyl ammonium bromide. These results show that 15-

crown-5 ether or tetra-n-butyl ammonium bromide induces the formation of polymers that contain ratios of phenoxy and 2,2,2-trifluoroethoxy groups that are very different from those produced in the absence of these compounds.

The effect of tetra-n-butyl ammonium bromide or 15-crown-5 ether was further investigated by comparing the reactions of the small molecule model compound, hexachlorocyclotriphosphazene, with various amounts of $CF_3CH_2O^- Na^+$ in the presence or in the absence of these additives. The reaction mixtures were analyzed by GC/MS and the relative amounts of each 2,2,2-trifluoroethoxy substituted product were determined by the peak areas. In Figures **5-8** the relative amounts of 2,2,2-trifluoroethoxy substituted cyclotriphosphazenes obtained under various reaction conditions are shown. Figure **5** shows that the reaction of hexachlorocyclotriphosphazene with only 1 molar equivalent of $CF_3CH_2O^- Na^+$, in the presence of 60 mole% of tetra-n-butvl ammonium bromide or 15-crown-5 ether, yields an unexpectedly large amount of $[NP(OCH_2CF_3)_2]_3$. Several unidentified products were also detected by GC/MS. The unknown products had molecular weights lower than that of $(NPCl_2)_3$ and some of them contained bromide or chloride. These results correspond to those shown in Figure **5** in that no hexachlorocyclotriphosphazene remained in the reaction mixture. No such side reaction was detected when 15-crown-5 ether was used in a similar ratio.

The results shown in Figures **5-8** illustrate two trends for the reactions in the presence of tetra-n-butyl ammonium bromide or 15-crown-5 ether; (1) Products are formed that contain more 2,2,2-trifluoroethoxy groups than expected, and (2) the production of some isomers is enhanced. These isomers are probably geminally substituted products.

Tetra-n-butyl ammonium bromide has been used to accelerate the synthesis of poly(organophosphazenes) that contain bulky side groups or for reactions of $(NPCl_2)_n$ with poor nucleophiles.[25] For example, sodium *p*-nitrophenoxide does not react with P-Cl bonds in the absence of tetra-n-butyl ammonium bromide, but reaction occurs in the presence of this reagent. $[NP(OPh)_2]_n$ can be synthesized at lower temperatures and with shorter reaction times in the presence of tetra-n-butyl ammonium bromide than in the absence of this reagent. These results were explained by assuming that the tetra-n-butyl ammonium counterion increases the lyophilicity and nucleophilicity of the oxyanions. The results obtained in the present work may be explained in the same manner. The role of 15-crown-5 ether or tetra-n-butyl ammonium bromide may be to increase the reactivity of the incoming nucleophiles to such a degree that the minor steric restrictions imposed by trifluoroethoxy groups already present are overpowered. This would result in larger ratios of geminal substitution, as was observed experimentally.

The ^{31}P NMR spectra of product mixtures formed in the presence of tetra-n-butyl ammonium bromide or 15-crown-5 ether were always more complicated than those obtained without these compounds. Also, the ^{31}P NMR spectra of product mixtures obtained in the presence of tetra-n-butyl ammonium bromide always showed extra peaks which were not present in mixtures obtained in the presence of 15-crown-5 ether or in the absence of additives. These results correspond to the results of GC/MS analysis.

The polymers synthesized by sequential addition of $PhO^- Na^+$ and $CF_3CH_2O^- Na^+$ at 25 °C in the presence of tetra-n-butyl ammonium bromide or 15-crown-5 ether were identical to those synthesized without these additives.

A polymer synthesized by adding a mixture containing 1.2 equivalent of both $CF_3CH_2O^- Na^+$ and $PhO^- Na^+$ to an $(NPCl_2)_n$ solution in the presence of 15-crown-5 ether contained 60 mole% of 2,2,2-trifluoroethoxy and 40 mole% of phenoxy groups. At an early stage in the reaction, the ^{31}P NMR spectrum of the reaction mixture did not show any unusual peaks, but the ^{31}P NMR spectrum of the product mixture taken after 14 hrs showed a small additional sharp peak at -8 ppm which indicates the formation of blocks of $NP(OCH_2CF_3)_2$ units. These results suggest that the higher fraction of 2,2,2-trifluoroethoxy group may be the result of both the faster reaction rate of $CF_3CH_2O^- Na^+$ and the replacement of phenoxy groups by 2,2,2-trifluoroethoxy groups. These results also suggest that phenoxy groups may be replaced by trifluoroethoxy groups at room temperature in the presence of either 15-crown-5 ether or tetra n-butyl ammonium bromide.

Effect of Tetra-n-butyl Ammonium Bromide and 15-Crown-5 Ether on the Replacement of Phenoxy Groups by 2,2,2-Trifluoroethoxy Groups. As a control, no reaction was detected when a solution containing 15-crown-5 ether and polymer **20**, which contained 78 % of phenoxy groups, was heated in boiling THF for 4 days. No reaction occurred even after tetra-n-butyl ammonium bromide was added to the solution. However, when polymer **22** (with 58 % phenoxy groups) was dissolved in THF in the presence of 2 equivalents of $CF_3CH_2O^- Na^+$ and 0.2 equivalent of 15-crown-5 ether, a sharp peak in the ^{31}P NMR at -7 ppm appeared after 10 minutes and no further reaction was detect after 18 hours by ^{31}P NMR spectroscopy. The resulting polymer contained only 2 mole% of phenoxy groups. These results show that phenoxy groups in both $NP(OPh)_2$ and $NP(OCH_2CF_3)(OPh)$ units were replaced by trifluoroethoxy groups. The important point is that phenoxy groups in $NP(OPh)_2$ were replaced under these conditions, but not in the absence of 15-crown-5 ether or tetra-n-butyl ammonium bromide. This is probably related to the higher reactivity of $CF_3CH_2O^-$ in the presence of 15-crown-5 ether. An explanation for the different reactivity of $NP(OPh)_2$ in polymers **22** and **20** is shown schematically in Scheme **III**.

Reaction of Poly[(2,2,2-trifluoroethoxy)(phenoxy)phosphazenes] with the Sodium Salt of 1,3-Propanediol in the Presence of 15-Crown-5 Ether. As discussed, the high reactivity of the organophosphazene polymers synthesized in this study with alkoxides in the presence of 15-crown-5 ether can be used for the synthesis of new polymers that have hitherto been inaccessible. This provides access to new properties as well as to surface modification reactions. It also opens possibilities for the linkage of other organic groups to a phosphazene chain. For example, the reaction of polymers of the types discussed above with the sodium salts of diols may cause either crosslinking or the formation of polymers with pendent hydroxyl functional groups.

A polyphosphazene containing approximately 39 mole% of phenoxy groups and 61 mole% of 2,2,2-trifluoroethoxy groups (polymer **25**) was treated for 2 hrs at room temperature in the presence of 0.5 equivalents of 15-crown-5 ether with a suspension prepared from a reaction of 8 equivalent sodium hydride and 4 equivalent 1,3-propanediol . The resultant polymer was elastic and was not soluble in THF but was soluble in hot DMSO and pyridine. Thus, it was not crosslinked. A ^{31}P NMR spectrum showed that the polymer contained approximately 33 mole% of phenoxy groups, and the ^{1}H NMR spectrum suggested the presence of approximately 16 mole% of 3-hydroxypropoxy groups. The $NP(OPh)_2$ groups were not affected by the reaction. When polymer **25** was treated for an hour with a suspension prepared from a reaction between 4 equivalents of sodium, 2 equivalents of 1,3-propanediol and 0.1 equivalent of 15-crown-5 ether, the fraction of phenoxy groups remaining in the polymer did not change. The recovered polymer was elastic and was soluble in THF. ^{1}H NMR spectra of the product indicated that the polymer contained approximately 7 mole% of 3-hydroxypropoxy groups. These results show that only the 2,2,2-trifluoroethoxy groups are replaced by 3-hydroxypropoxy group under mild conditions but that phenoxy groups are also replaced under more vigorous conditions.

The much higher toughness and elasticity of the product may be due to the hydrogen bonding of hydroxy groups in the product.

Physical properties. Glass transition temperatures of the synthesized polymers are shown in Figure **9**. The glass transition temperature increases as the fraction of phenoxy groups in the polymer increases. Figure **6** also shows that the T_g's of polymers synthesized by method (4) are higher than those of polymers synthesized by method (1) (which contain more $NP(OCH_2CF_3)_2$ units than polymers synthesized by method (4)). The lower T_g's of these polymers are most likely due to the higher fraction of $NP(OCH_2CF_3)_2$ units.

Most of the mixed-substituent polymers synthesized in this study showed negligible birefringence when observed through a polarizing optical microscope. The glass transitions of most of these polymers could not be detected by DSC analysis if the temperature increase was less than 40 °C/min. Most of the polymers had first order endothermic transitions between 30 and 50 °C as detected by DSC analysis. Some of the polymers showed more than one transition. The first order transitions of some polymers within the temperature range of -100 and 150 °C are listed in Table **5**.

The contact angles of water droplets on the surface of the solvent-cast films of the polymers plotted against the mole fraction of 2,2,2-trifluoroethoxy groups are shown in Figure **10**. The contact angle increases as the fraction of 2,2,2-trifluoroethoxy groups in the polymer increases. The morphology of the surface was critical to the contact angle. Polymers bearing more than 20 mole% phenoxy groups formed opaque films very easily. These opaque films did not show birefringence when observed through a polarizing microscope and it appeared that the opacity was not due to crystallinity. The opaque films gave irreproducible contact angles which were much higher than the expected values. For example, thin, transparent films of polymer **12** had contact angles between 102 to 104 degrees, but opaque films of the same polymer had irreproducible contact angles that varied from 120 to 140 degrees. Scanning electron microscopy showed that the opaque films were highly porous. The SEM micrographs of a transparent film and an opaque film of polymer **12** are shown in Figures **11(a)** and **11(b)**, respectively. It is clear that polymer **12** can form highly porous films with pores of very regular sizes. Thus, the extraordinarily high contact angle of the opaque film is probably related to the surface morphology.[26]

Experimental Section

Materials. Hexachlorocyclotriphosphazene was purified by recrystallization from heptane and by sublimation. The recrystallization and sublimation were repeated twice. Poly(dichlorophosphazene) was synthesized by the thermal ring opening polymerization of hexachlorocyclotriphosphazene at 250 °C.[2] Phenol was dried by boiling with benzene and was then sublimed. Poly(dichlorophosphazene) and sodium were stored and handled in a glove box. 2,2,2-Trifluoroethanol was treated with sodium carbonate and was then distilled and stored over molecular sieves. Tetrahydrofuran and dioxane were freshly distilled from sodium benzophenone ketyl. All the reactions were carried out under a stream of dry argon.

Synthesis of Poly[(2,2,2-trifluoroethoxy)(phenoxy)phosphazenes]. The relative reactivities of $CF_3CH_2O^- Na^+$ and $PhO^- Na^+$ were examined by adding a solution of $(NPCl_2)_n$

(1g, 3.6 mmol, in 200 ml of THF) to a solution containing 14.4 mmol of each of $CF_3CH_2O^- Na^+$ and $PhO^- Na^+$. Sodium 2,2,2-trifluoroethoxide and $PhO^- Na^+$ were synthesized by reacting 2,2,2-trifluoroethanol and phenol separately with excess amounts of sodium in THF for approximately 20 hrs. The polymeric reaction mixtures were stirred at room temperature for approximately 72 hrs. THF was removed by evaporation under reduced pressure. When the mixture became very viscous it was added dropwise to 1 L of vigorously stirred deionized water. The precipitated polymer was recovered by filtration and was then redissolved in a minimum amount of THF. The polymer solution was reprecipitated into water to remove sodium salts until the THF solution of the recovered polymer became clear. Usually two to four reprecipitations were necessary. The polymer was finally purified by precipitation into hexane or heptane.

Polyphosphazenes *co*-substituted with an equimolar amount of trifluoroethoxy and phenoxy units were synthesized as follows. In a 1 L three neck round bottom flask $(NPCl_2)_n$ (2 g, 17.2 mmol) was dissolved in 300 ml of dry THF. A solution of $CF_3CH_2O^- Na^+$ was prepared by adding trifluoroethanol (1.7 g, 17.2 mmol) to a 500 ml three neck round bottom flask containing sodium metal (0.5 g, 21.7 mmol.) and 200 ml of dry THF. The reaction mixture was warmed gently overnight. The $CF_3CH_2O^- Na^+$ solution was transferred into a 250 ml dropping funnel using a canular technique. The $CF_3CH_2O^- Na^+$ solution was then added dropwise to the $(NPCl_2)_n$ solution at room temperature (Method (1)), -78 °C (Method (2)) and 50 °C (Method (3)) during approximately 30 minutes. In practice, the amount of the first added nucleophile (A) was usually slightly less than the amount required to replace 50 % of the chlorine atoms due to the unavoidable experimental losses of the reagent during product transfer. The reaction mixtures prepared by methods (1) and (2) were stirred for approximately 20 hrs before the $PhO^- Na^+$ solution was added. The reaction mixtures prepared by method (2) were stirred at -78 °C for 4 hrs and then warmed to room temperature slowly. The mixtures were stirred for an additional 18 hrs at room temperature. To the reaction mixtures described above were added $PhO^- Na^+$ solutions, prepared from phenol (2.5 g, 25.9 mmol) and sodium (0.7 g, 30 mmol) in 100 ml of dry THF, at room temperature. The reaction mixtures were then refluxed for at least for 48 hrs.

The synthesis of polymers by methods (4) and (5) was carried out in a similar way. In this method, one equivalent of $PhO^- Na^+$ was added to $(NPCl_2)_n$ first and the reaction mixture was stirred at room temperature for approximately 36 hrs and then warmed for approximately 4 hrs to ensure maximum substitution. To this mixture, 1.5 equivalents of $CF_3CH_2O^- Na^+$ was added, the reaction mixture was stirred at room temperature for 18 hrs (method (4)) or for 6 hrs, and was then refluxed for 18 hrs (method (5)). The product was recovered by the same procedure described above.

Polymer **6** was synthesized by the addition of a mixture of 1.2 equivalents of $CF_3CH_2O^- Na^+$ and $PhO^- Na^+$ to a THF solution containing 1 equivalent of $(NPCl_2)_n$. Polymer **7** was synthesized by adding 1 equivalent of $CF_3CH_2O^- Na^+$ solution in THF to a solution containing 1 equivalent of $(NPCl_2)_n$ and 0.1 equivalent of tetra-n-butyl ammonium bromide. Two equivalents of $PhO^- Na^+$ were added to the mixture after approximately 20 hrs and then the reaction mixture was refluxed for approximately 24 hrs.

Polymers having other compositions were prepared by following similar procedures. Polymers with more than 50 mole% of phenoxy groups were synthesized using dioxane as a solvent.

Replacement of Phenoxy Groups in $NP(OCH_2CF_3)(OPh)$ Units. A reaction mixture prepared by method (1) was divided into two fractions. One fraction was concentrated, and the polymer was isolated as described above. The other fraction was heated at reflux overnight. The reaction mixture was treated in the same manner as described above to obtain the polymeric product.

Fractionation of Polymers Synthesized In the Presence of 15-Crown-5 Ether. Three hundred milligrams of a polymer synthesized by the sequential reaction of $(NPCl_2)_n$ with equimolar amounts of $CF_3CH_2O^- Na^+$ and $PhO^- Na^+$ was dissolved in THF and was then added dropwise to methanol. The precipitated polymer was recovered by centrifugation (89.1 mg) and the polymer still dissolved in methanol was recovered by evaporation of the methanol under reduced pressure (206.6 mg).

Reaction of Polymer 12 with Sodium Salts of 1,3-Propanediol. 1,3-Propanediol (0.7g, 9.2 mmol) was added to a sodium hydride suspension (0.8g (60%), 20 mmol) in 30 ml THF. The mixture was refluxed for 36 hrs and was then cooled to room temperature. The remaining sodium hydride was allowed to settle out, and the upper layer of sodium salts of 1,3-propanediol was transferred by a syringe technique into a THF solution containing polymer **12** (0.5 g, 2.33 mmol) and 15-crown-5 ether (0.9 g, 4.1 mmol). The reaction mixture was agitated for 2 hrs and then the mixture was concentrated by evaporation of THF under reduced pressure. The polymer was recovered by precipitation into water and hexane. A similar reaction was carried out using sodium (0.5g, 21.7 mmol), 1,3-propanediol (1g, 13.2 mmol), polymer **12** (1.1 g, 5.13 mmol) and 15-crown-5 ether (0.1 g, 0.45 mmol). The reaction was carried out for 1 hour.

Molecular Weight Determination. Molecular weights of the polyphosphazenes obtained were estimated using a gel permeation chromatography system equipped with a Hewlett-Packard 1090 HPLC system, PLgel 10^5, 10^6 and 10^4 Å columns, a Hewlett-Packard 1037A refractive index detector and a Hewlett-Packard 85B data station. The eluent was THF containing 0.875 g of tetra-n-butyl bromide per one liter. A universal calibration curve was established using polystyrene standards. The number average molecular weight of polymers synthesized in this study were in the region of 1,000,000, and the polydispersity index was approximately 2.5.

Thermal Analysis. Glass transition temperatures and melting temperatures were determined using a Perkin-Elmer DSC 7 system. In a typical run, the temperature was scanned from -120 °C to 90 °C with a temperature increase of 40 °C/min. The temperature was then lowered at a rate of 200 °C/min to -120 °C for the second heating cycle. Glass transition temperatures were determined from the second heating cycle. Glass transitions of some of the polymers were not detectable at lower ramp rates.

Preparation of Films. Polymer films were prepared (1) by dipping glass slides into polymer solutions in THF. The concentration of the polymer solution was approximately 0.1 g/ml, (2) pouring concentrated solutions of the polymer into a mold (1 mm x 30 mm x 3 mm).

After evaporation of the solvent the assembly was immersed in hexane to release free standing films, and (3) pouring concentrated solutions onto glass slides and, after drying, the coated slides were placed in hexane to obtain free standing films.

Contact Angle Measurement. A contact angle goniometer (Ramé-Hart, inc. model 100-00) was used. The polymer films were placed in a chamber saturated with water vapor. Onto each film was placed 1 μl of deionized distilled water. The water droplets were allowed to stand for 3 minutes before estimation of the contact angle.

Composition Determination. The fractions of $NP(OCH_2CF_3)_2$, $NP(OCH_2CF_3)(OPh)$ and $NP(OPh)_2$ units were determined from the integration values of the corresponding phosphorus signals in ^{31}P NMR spectra. The total fractions of trifluoroethoxy and phenoxy groups were determined from ^{31}P and ^{1}H NMR spectra. The total fractions of trifluoroethoxy and phenoxy groups determined using these two spectra corresponded to each other within 2 mole%. Both types of NMR spectra were recorded using a Bruker WP 300 NMR spectrometer equipped with a multinuclear probe. The pulse delay was set to 5 seconds.

GC/MS. A Carlo Erba GC connected to Kratos MS-25 mass spectrometer and a J&W Scientific OB5 capillary column (60 m x 0.25 mm i.d.) was used. The temperature of the oven was raised from 60 to 300 °C at a rate of 20 °C/min. The temperature of the injector was 280 °C. The concentration of the samples were 0.5 to 10 mg/ml and approximately 4μl was injected in a splitless mode.

Acknowledgment. This work was supported by grants from the Johnson & Johnson COSAT Program and the Office of Naval Research.

References

1. Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall; Englewood Cliffs, 1992.

2. Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.

3. Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg . Chem.*, **1966**, *5*, 1709.

4. Allen, P.; Lewis, C. J.; Todd, S. M. *Polymer* **1970**, *11*, 44.

5. Desper, C. R.; Schneider, N. S.; Higginbotham, E. *Polymer Lett. Ed.* **1977**, *15*, 457.

6. Schneider, N. S.; Desper, C. R.; Singler, R. E. *J. Appl. Pol. Sci.* **1976**, *20*, 3087.

7. Sun, D. C.; Magill, J. H. *Polymer* **1987**, *28*, 1243 .

8. Kojima, M.; Magill, J. H. *Makromol. Chem.* **1989**, *106*, 649.

9. Kojima, M.; Sun, D. C.; Magill, J. H. *Makromol. Chem.* **1989**, *189*, 1047.

10. Allcock, H. R.; Visscher, K. B. *Chem. Mater.* **1992**, *4*, 1182.

11. Allcock, H. R.; Fitzpatrick, R. J.; Salvati, L. *Chem. Mater.* **1992**, *4*, 769.

12. Lerner, M.; Tipton, A.; Shriver, D. F.; Dembek, A. A.; Allcock, H. R. *Chem. Mater.* **1991**, *3*, 1117.

13. Allcock, H. R.; Fitzpatrick, R. J. *Chem. Mater.* **1991**, *3*, 450.

14. Allcock, H. R.; Rutt, J. S.; Fitzpatrick, R. J. *Chem. Mater.* **1991**, *3*, 442.

15. Allcock, H. R.; Riding, G. H.; Lavin, K. D. *Macromolecules* **1987**, *20*, 6.

16. Rose, S. H. *J. Polymer Sci.* **1968**, *B6*, 837.

17. Singler, R. E.; Schneider, N. S.; Hagnauer G. L. *Polym. Eng. Sci.* **1975**, *15*, 321.

18. Tate, D. P. *J. Polymer Sci., Polymer Symp.* **1974**, *48*, 33.

19. (a) Penton, H. R. In *Inorganic and Organometallic Polymers*, Zeldin, M.; Wynne, K. J.; Allcock, H. R. Ed.; ACS Synposium Series 360; American Chemical Society: Washington, DC, 1988; Chapter 21, (b) Penton, H. R. *Kautschuk Gummi Kunst.* **1986**, *39*, 301.

20. Lieu, P. J.; Magill, J. H.; Alarie, Y. C. *J. Fire and Flammability* **1980**, *11*, 167.

21 Wade, C. W. R.; Gourlay, S.; Rice, R.; Hegyeli, A.; Singler, R.; White, J. In *Organometallic Polymers*, Hegyeli, A. Ed.; Academic Press: New York, 1978; pp. 289.

22. Allcock, H. R.; Visscher, K. B. *Manuscript in preparation.*

23. Schmutz, J. L.; Allcock, H. R. *Inorg. Chem.* **1975**, *14*, 2433.

24. Ferrar, W. T.; Marshall, A. S.; Whitefield, J. *Macromolecules* **1987**, *20*, 317.

25. Austin, P. E.; Riding G., H.; Allcock, H. R. *Macromolecules* **1983**, *16*, 719.

26. Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988.

Captions for Figures

Figure 1. Mole percent of $NP(OCH_2CF_3)_2$, $NP(OCH_2CF_3)(OPh)$ and $NP(OPh)_2$ units in the polymer versus reaction time between polymer 3 and $CF_3CH_2O^- Na^+$. (●) $NP(OCH_2CF_3)(OPh)$unit; (■) $NP(OCH_2CF_3)_2$unit; (✖) $NP(OPh)_2$ unit

Figure 2. ^{31}P NMR spectrum of (a) polymer 3 and (b) the product of the reaction of polymer 3 with $CF_3CH_2O^- Na^+$.

Figure 3. ^{31}P NMR spectrum of (a) polymer 20 and (b) the product of the reaction of polymer 20 with $CF_3CH_2O^- Na^+$.

Figure 4. ^{31}P NMR spectra of polymers synthesized by the sequential treatment of poly(dichlorophosphazene) with equimolar amount of $CF_3CH_2O^- Na^+$ and $PhO^- Na^+$ (a) in the absence of 15-crown-5 ether and (b) in the presence of 15-crown-5 ether.

Figure 5. The ratio of cyclic trimeric products from reactions of hexachlorophosphazene with 1 equivalent of $CF_3CH_2O^- Na^+$. (△) without tetra-n-butyl ammonium bromide or 15-crown-5 ether; (○) in the presnece of 60 mole% tetra-n-butyl ammonium bromide; (□) 60 mole% of 15-crown-5 ether

Figure 6. The ratio of cyclic trimeric products from reactions of hexachlorophosphazene with 2 equivalent of $CF_3CH_2O^- Na^+$. (□) without tetra-n-butyl ammonium bromide or 15-crown-5 ether; (○) 4.9 mole% of tetra-n-butyl ammonium bromide

Figure 7. The ratio of cyclic trimeric products from reactions of hexachlorophosphazene with 1 equivalent of $CF_3CH_2O^-Na^+$. (□) without tetra-n-butyl ammonium bromide or 15-crown-5 ether; (○) 3.5 mole% tetra -n-butyl ammonium bromide

Figure 8. The ratio of cyclic trimeric products from reactions of hexachlorophosphazene with 3 equivalent of $CF_3CH_2O^-Na^+$. (□) without tetra-n-butyl ammonium bromide or 15-crown-5 ether; (○) 1.2 mole% of tetra-n-butyl ammonium bromide; (△) 1.1 mole% of 15-crown-5 ether.

Figure 9. Glass transition temperature versus mole percent of TFE group in the polymer. (●) Polymers synthesized by method 4; (■) Polymers synthesized by method 1.

Figure 10. Contact angle versus the mole fraction of 2,2,2-trifluoroethoxy groups in the 2,2,2-trifluoroethoxy-phenoxy-phosphazene polymers.

Figure 11. Scanning electron microscope micrographs of films of polymer **12** on glass slides. (a) a very thin film prepared by dipping the slide glass into a polymer solution ; (b) a thick film prepared on a glass slide by solvent casting

Figure 1.

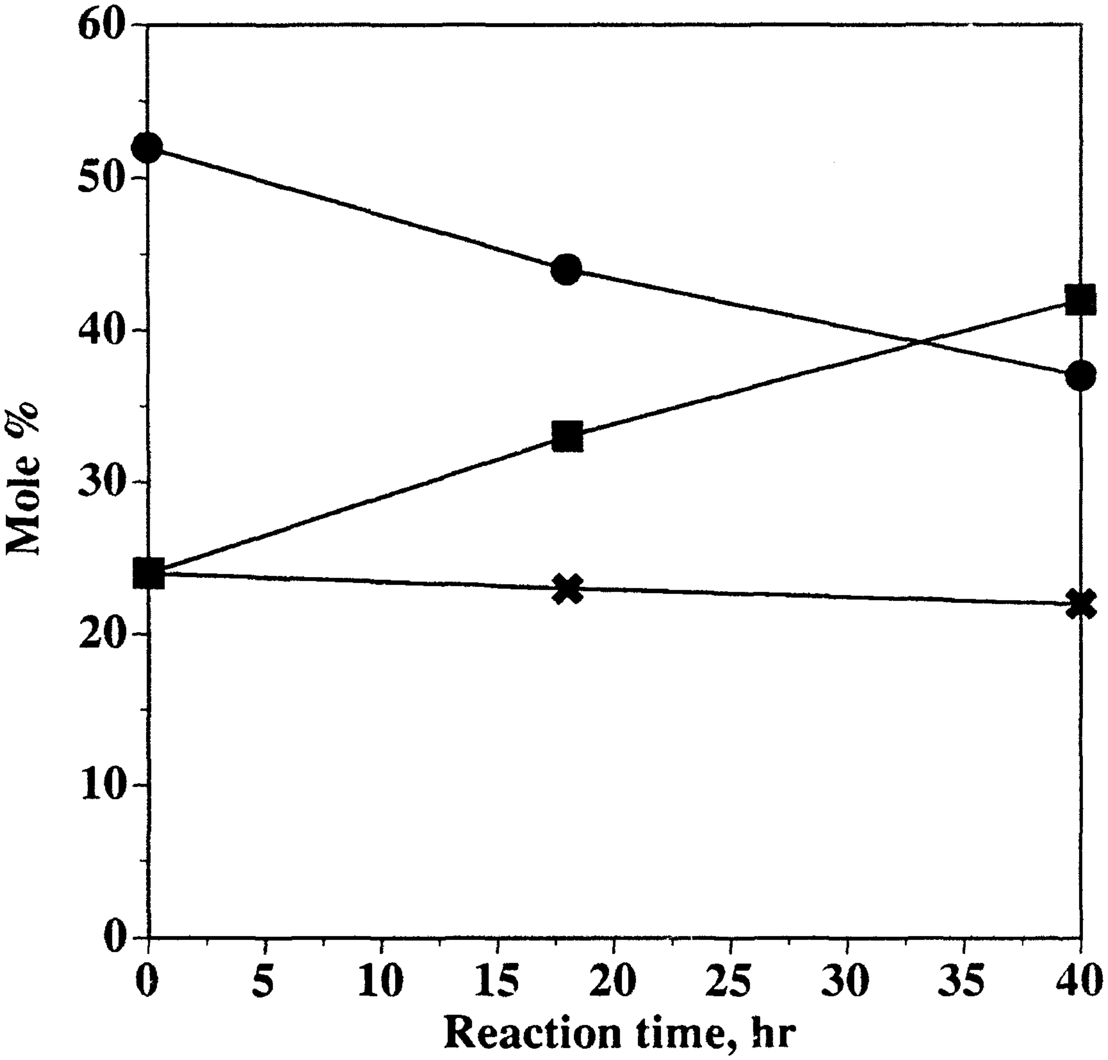


Figure 2(a)

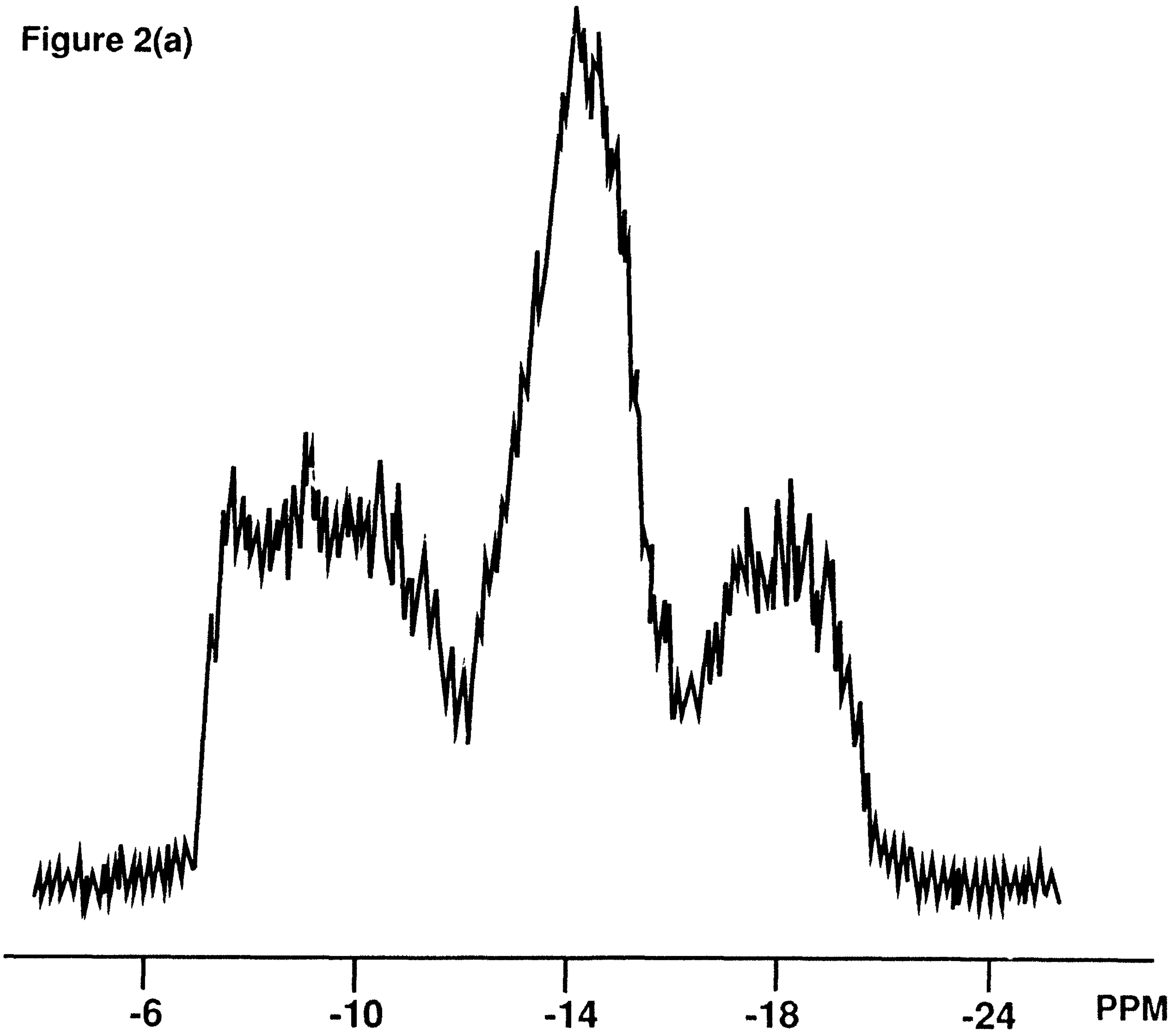
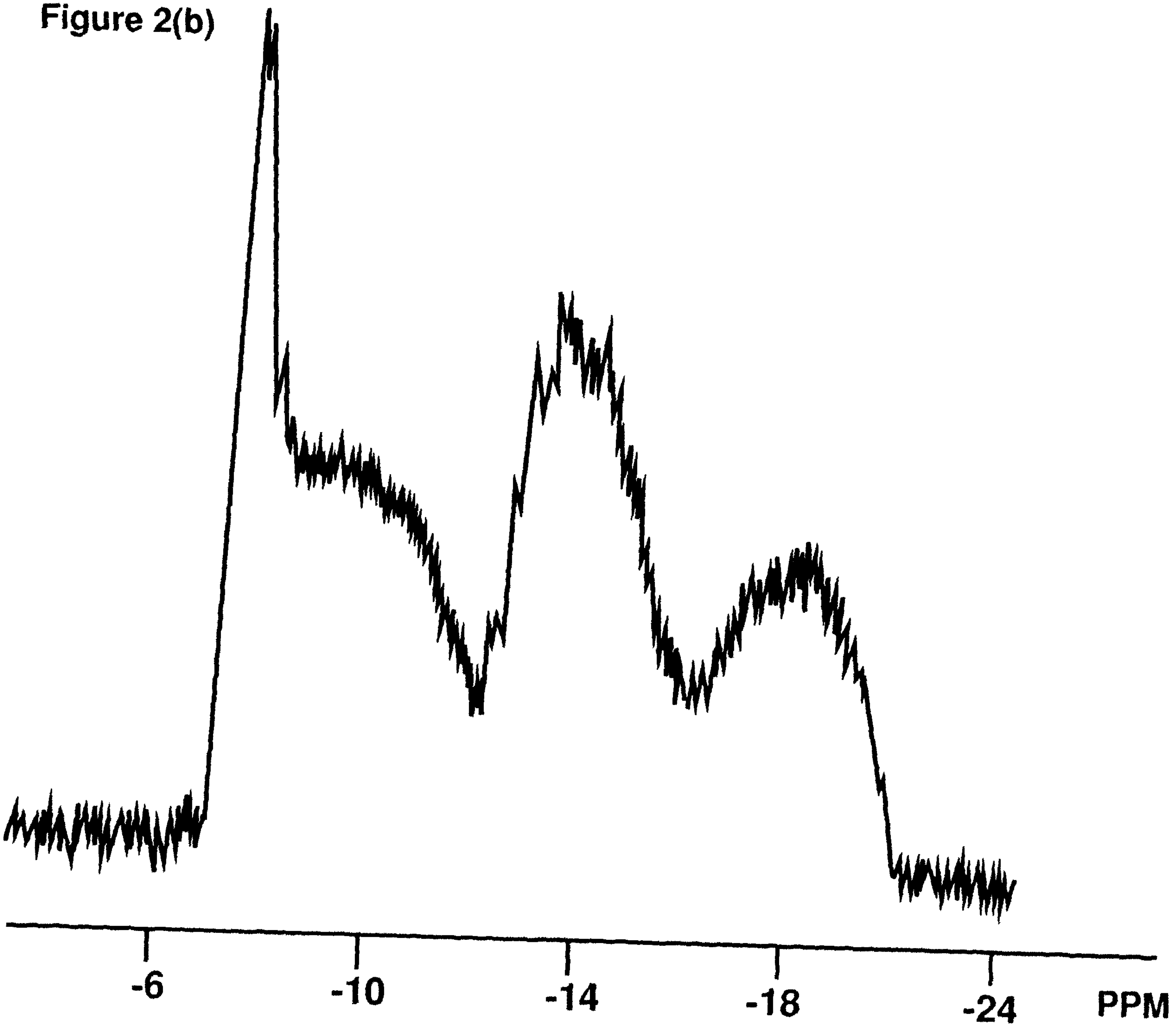


Figure 2(b)



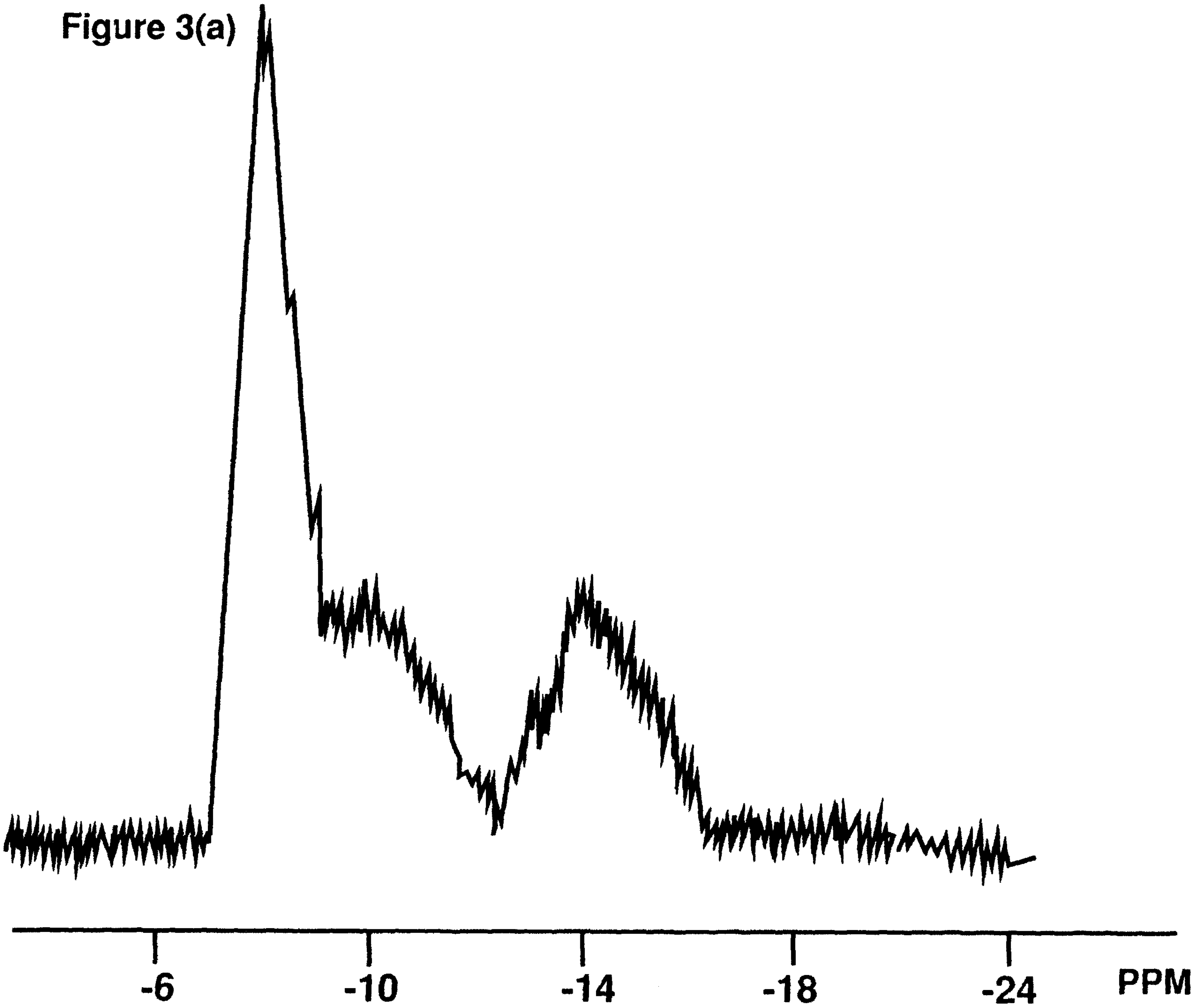


Figure 3(a)

Figure 3(b)

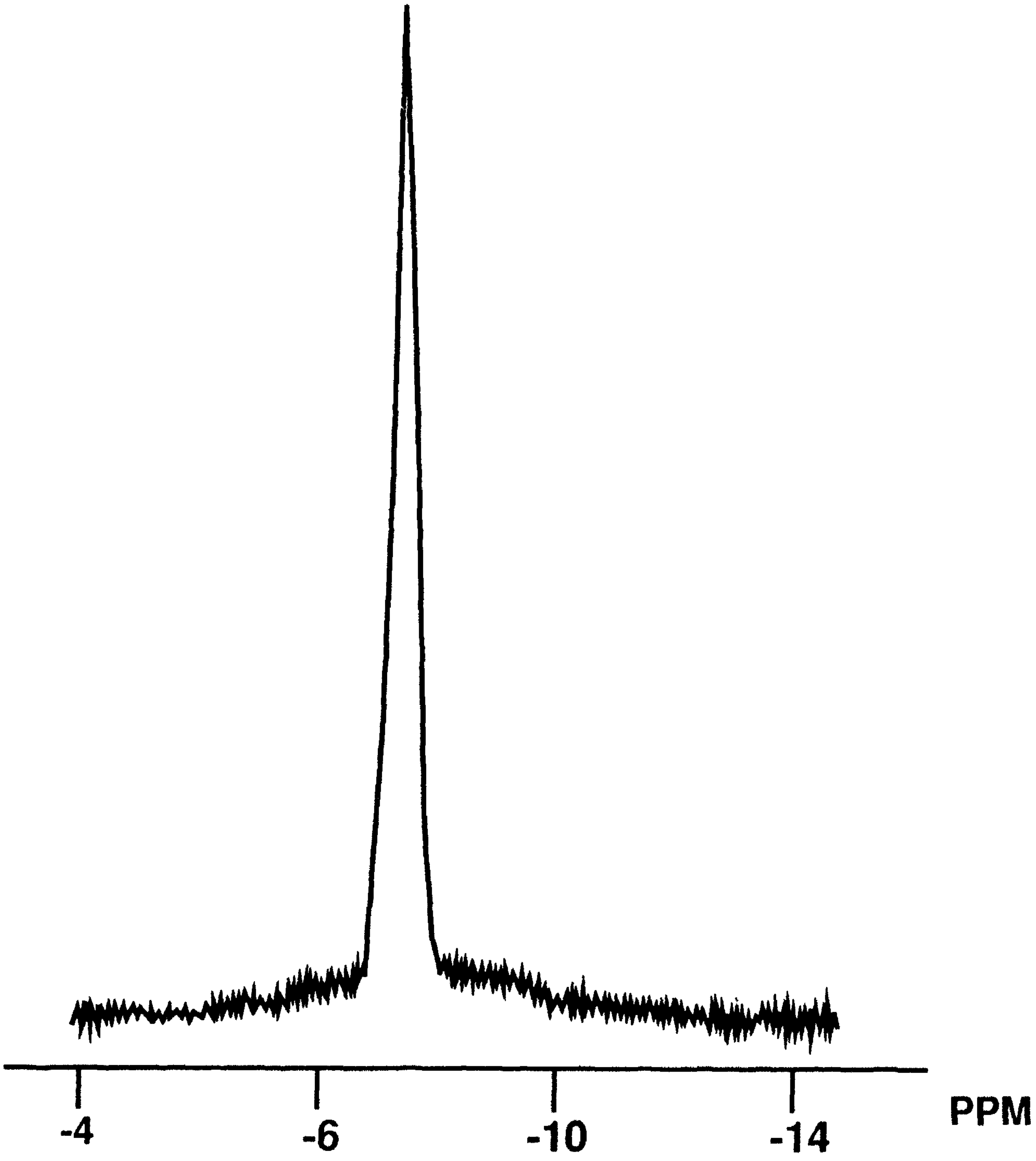


Figure 4(a)

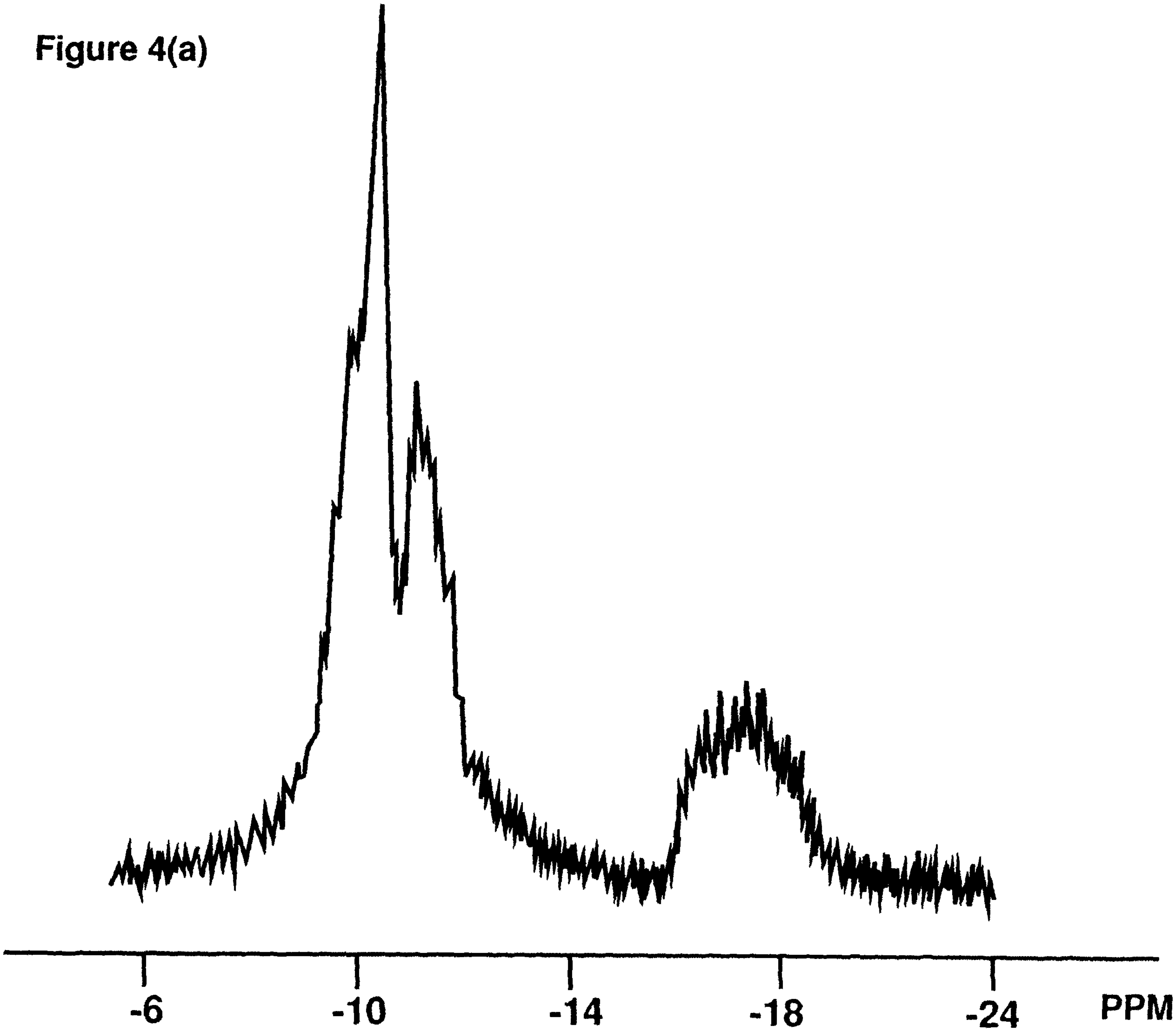


Figure 4(b)

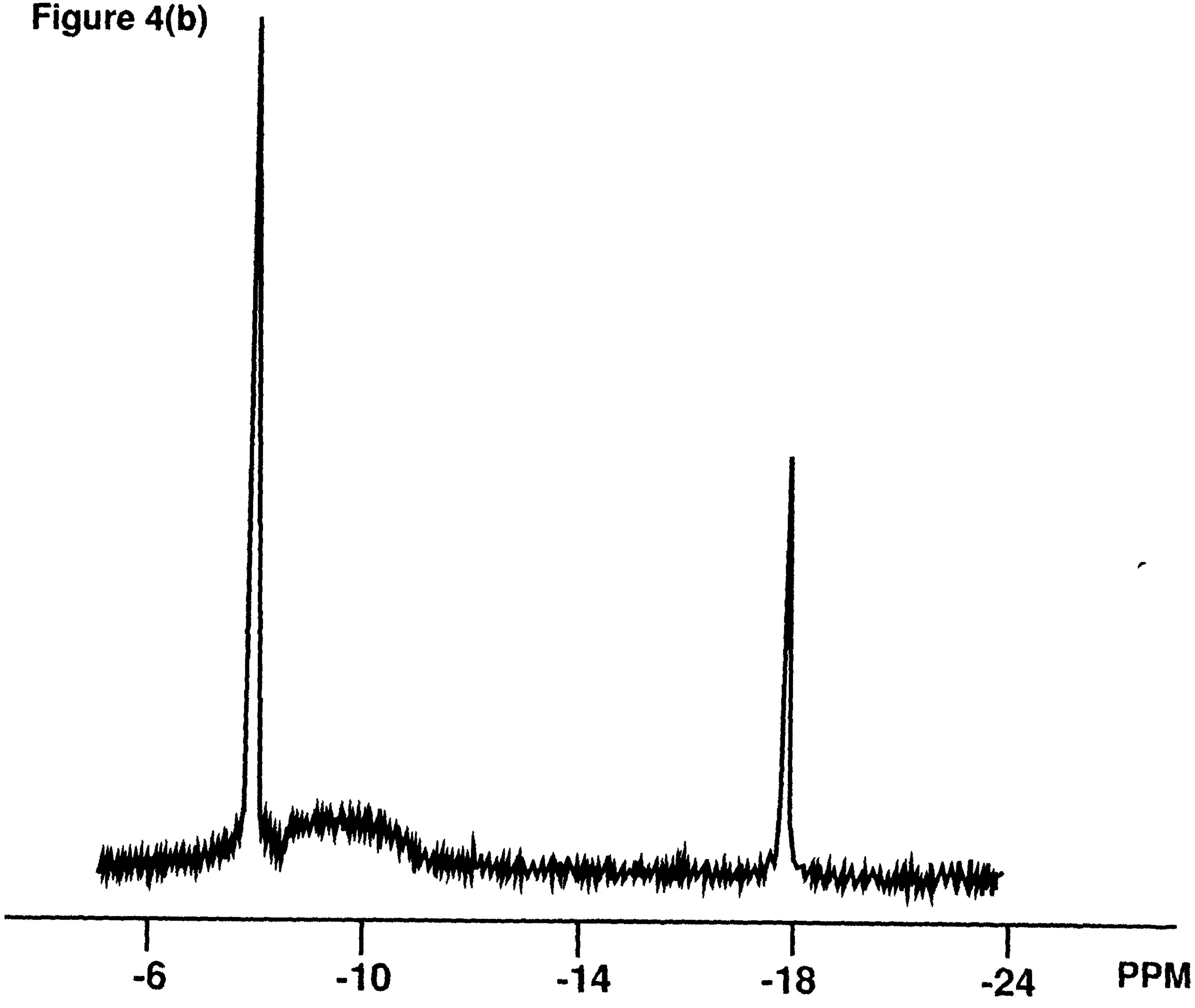
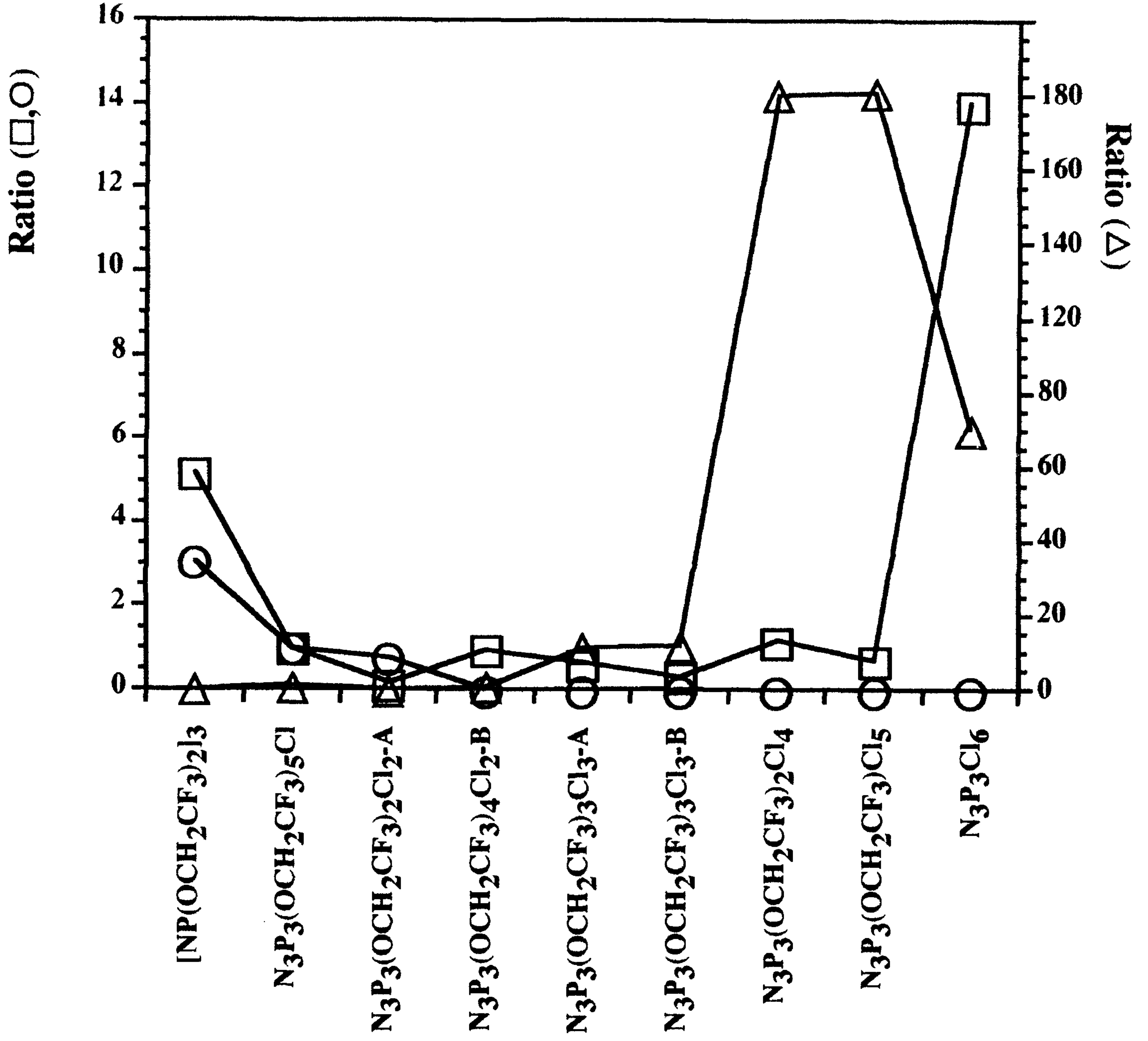


Figure 5


Ratio (□,○)
16
14
12
10
8
6
4
2
0
Ratio (△)
180
160
140
120
80
60
40
20
0
$[NP(OCH_2CF_3)_2]_3$
$N_3P_3(OCH_2CF_3)_5Cl$
$N_3P_3(OCH_2CF_3)_2Cl_2$-A
$N_3P_3(OCH_2CF_3)_4Cl_2$-B
$N_3P_3(OCH_2CF_3)_3Cl_3$-A
$N_3P_3(OCH_2CF_3)_3Cl_3$-B
$N_3P_3(OCH_2CF_3)_2Cl_4$
$N_3P_3(OCH_2CF_3)Cl_5$
$N_3P_3Cl_6$

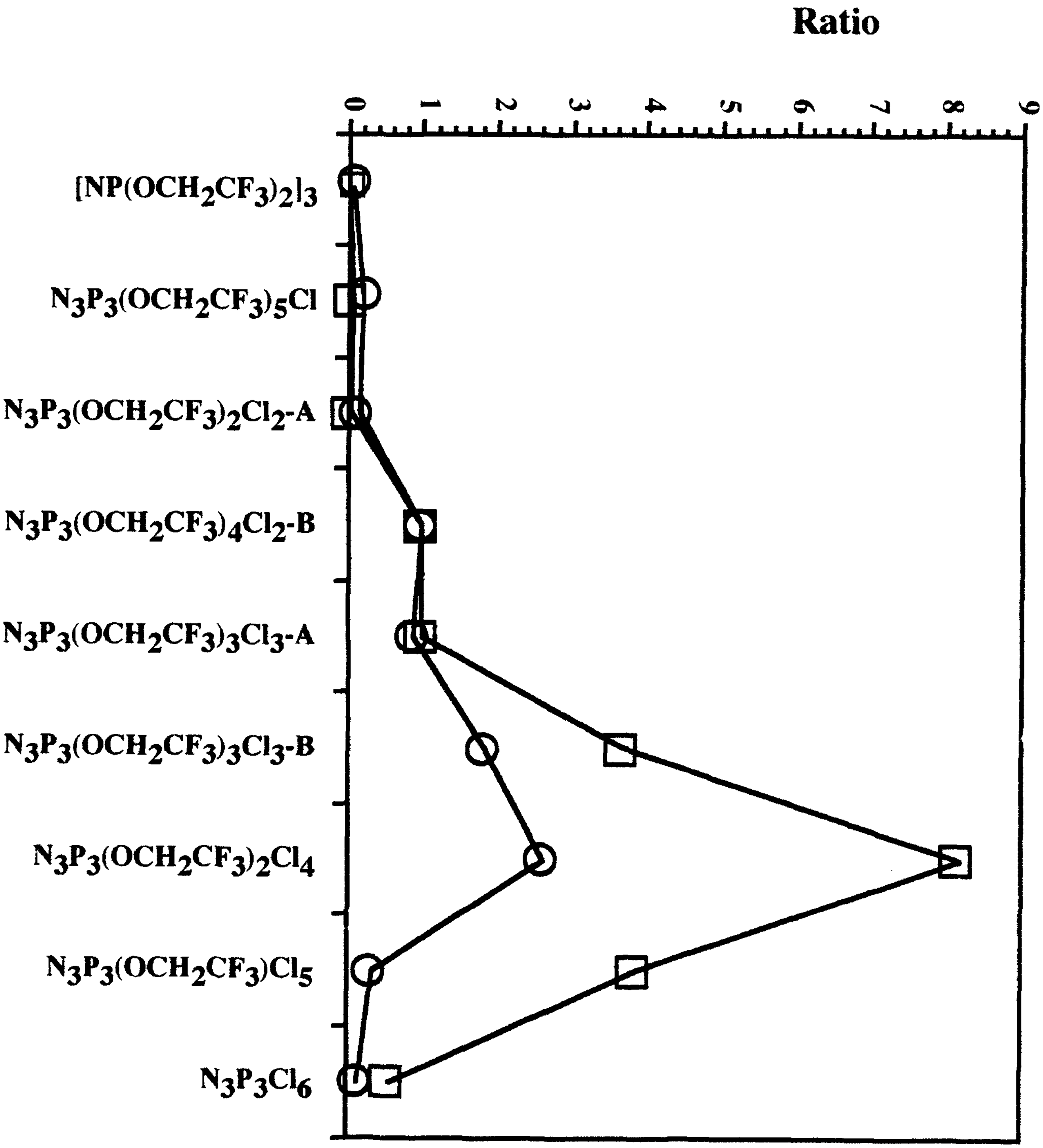

Ratio
0
1
2
3
4
5
6
7
8
9
[NP(OCH$_2$CF$_3$)$_2$]$_3$
N$_3$P$_3$(OCH$_2$CF$_3$)$_5$Cl
N$_3$P$_3$(OCH$_2$CF$_3$)$_2$Cl$_2$-A
N$_3$P$_3$(OCH$_2$CF$_3$)$_4$Cl$_2$-B
N$_3$P$_3$(OCH$_2$CF$_3$)$_3$Cl$_3$-A
N$_3$P$_3$(OCH$_2$CF$_3$)$_3$Cl$_3$-B
N$_3$P$_3$(OCH$_2$CF$_3$)$_2$Cl$_4$
N$_3$P$_3$(OCH$_2$CF$_3$)Cl$_5$
N$_3$P$_3$Cl$_6$

Figure 6

Figure 7

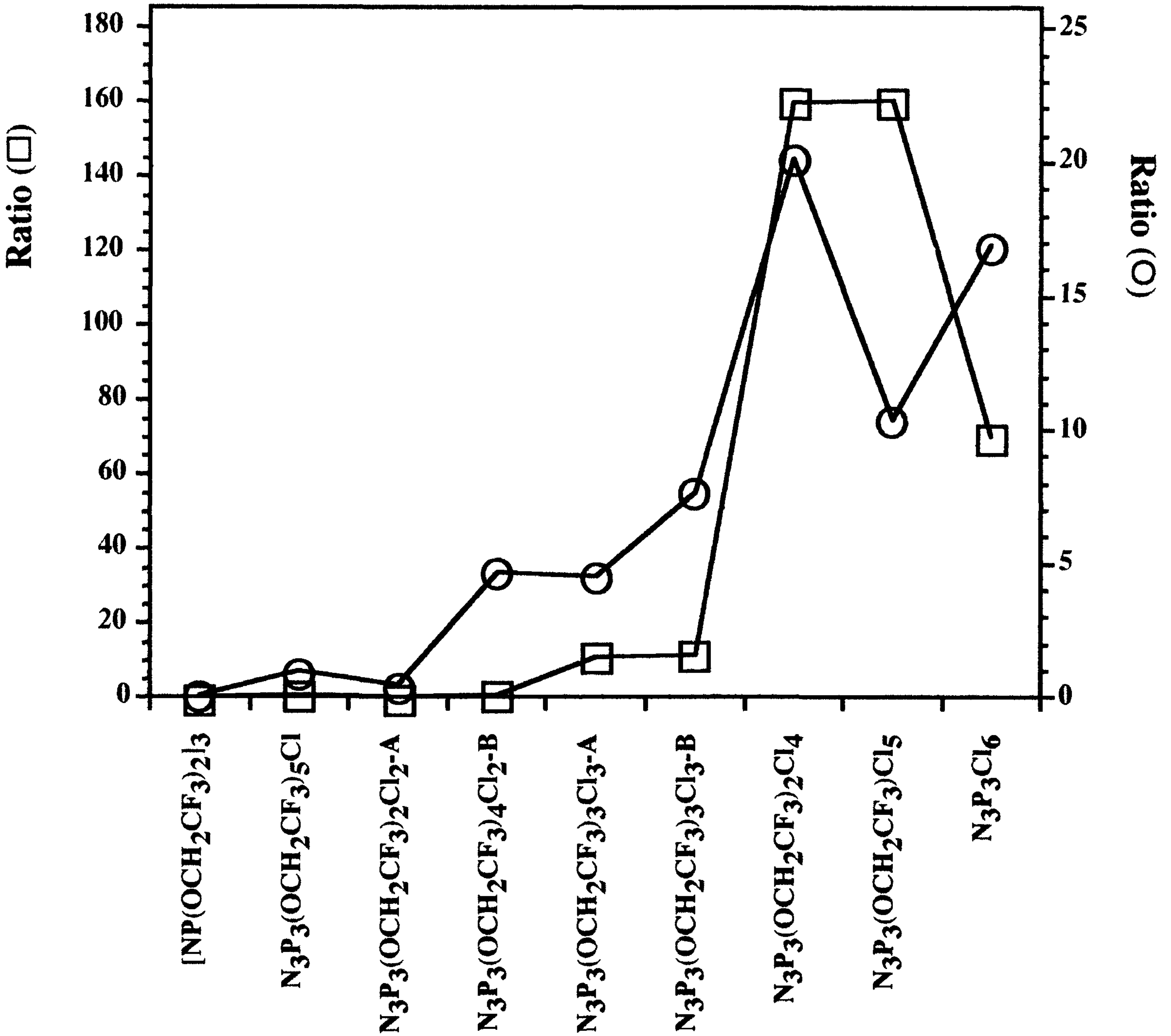

Ratio (□)
Ratio (○)
0
20
40
60
80
100
120
140
160
180
0
5
10
15
20
25
$[NP(OCH_2CF_3)_2]_3$
$N_3P_3(OCH_2CF_3)_5Cl$
$N_3P_3(OCH_2CF_3)_2Cl_2$-A
$N_3P_3(OCH_2CF_3)_4Cl_2$-B
$N_3P_3(OCH_2CF_3)_3Cl_3$-A
$N_3P_3(OCH_2CF_3)_3Cl_3$-B
$N_3P_3(OCH_2CF_3)_2Cl_4$
$N_3P_3(OCH_2CF_3)Cl_5$
$N_3P_3Cl_6$

Figure 8

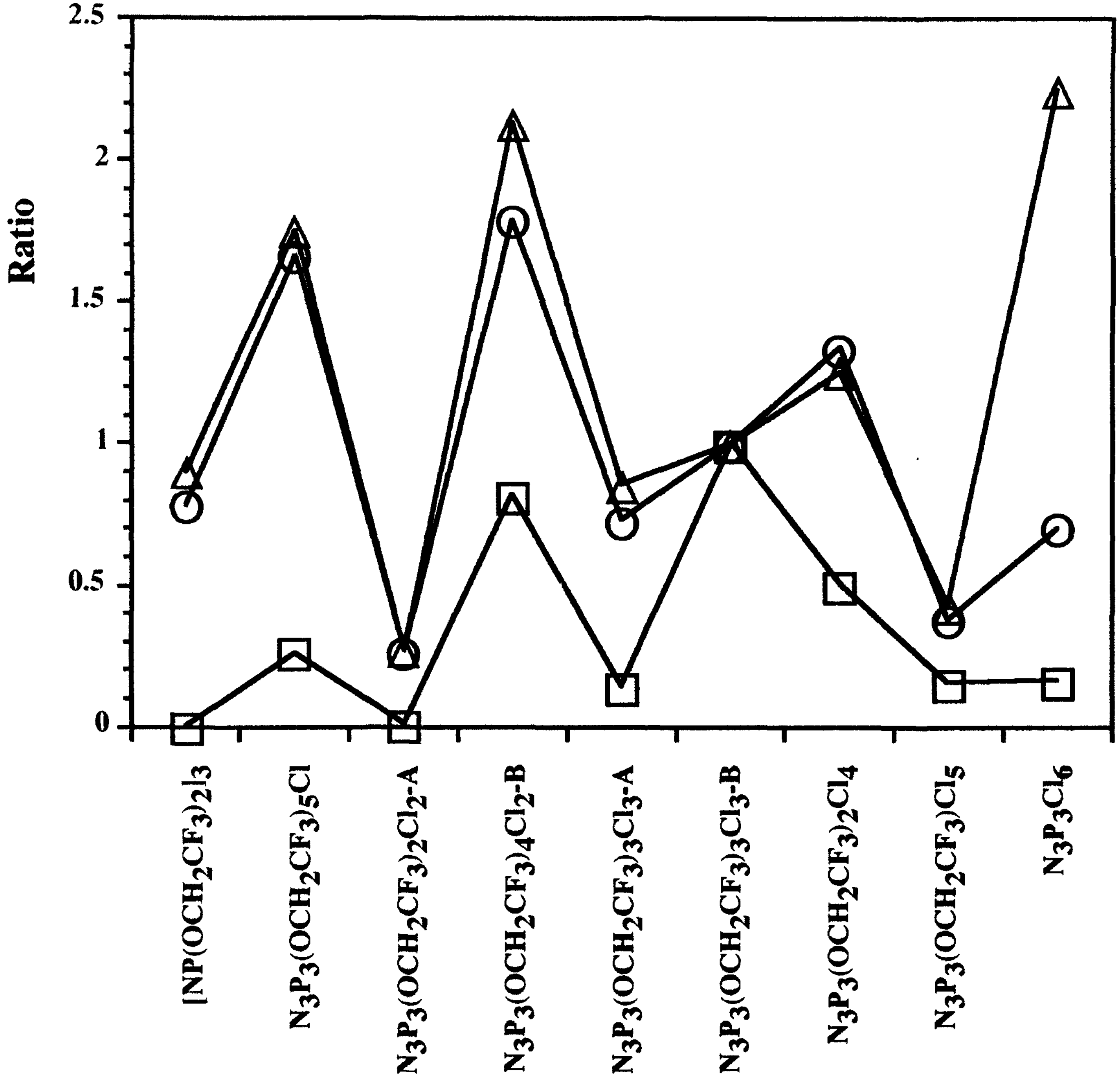

Ratio
2.5
2
1.5
1
0.5
0
$[NP(OCH_2CF_3)_2]_3$
$N_3P_3(OCH_2CF_3)_5Cl$
$N_3P_3(OCH_2CF_3)_2Cl_2$-A
$N_3P_3(OCH_2CF_3)_4Cl_2$-B
$N_3P_3(OCH_2CF_3)_3Cl_3$-A
$N_3P_3(OCH_2CF_3)_3Cl_3$-B
$N_3P_3(OCH_2CF_3)_2Cl_4$
$N_3P_3(OCH_2CF_3)Cl_5$
$N_3P_3Cl_6$

Figure 9.

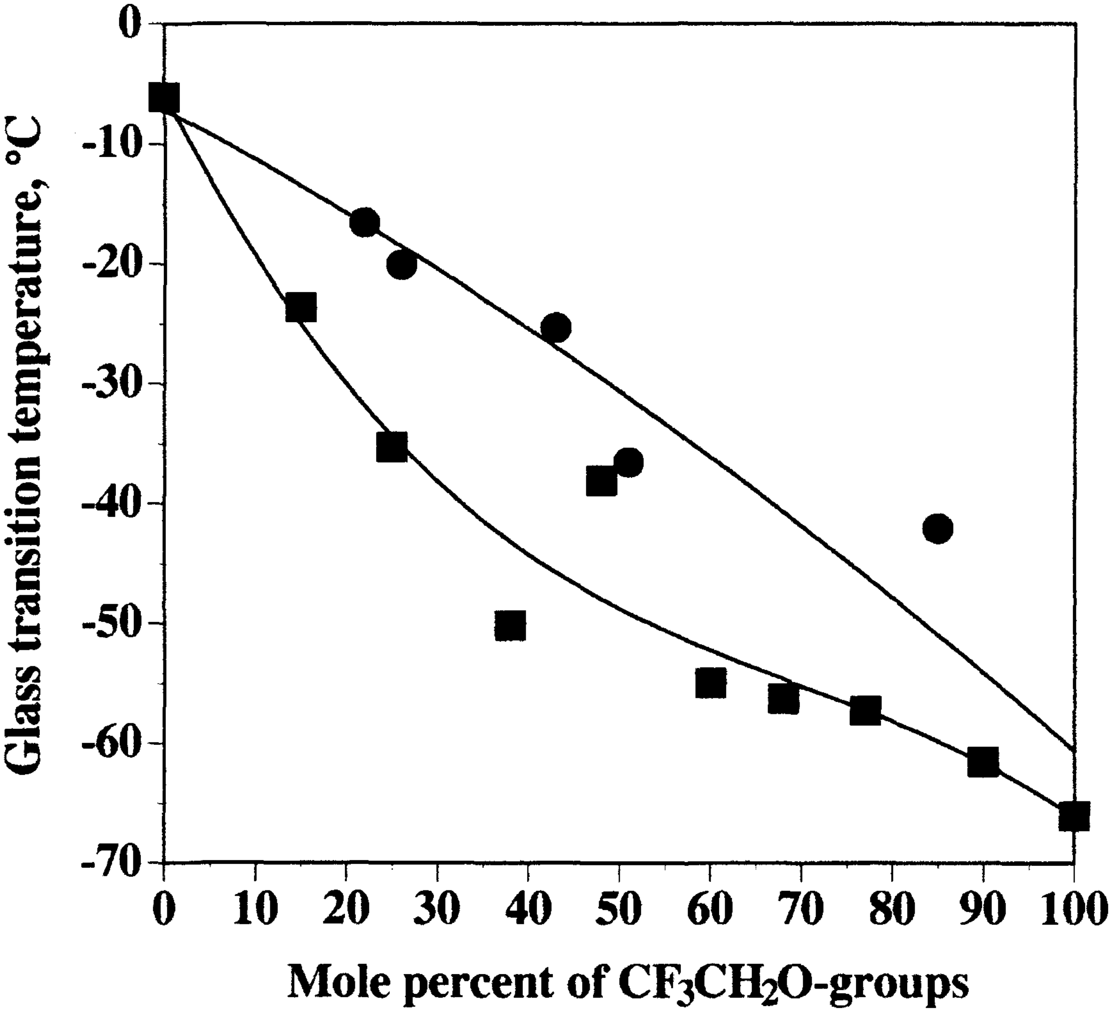

0
-10
-20
-30
-40
-50
-60
-70
Glass transition temperature, °C
0
10
20
30
40
50
60
70
80
90
100
Mole percent of CF3CH2O-groups

Figure10.

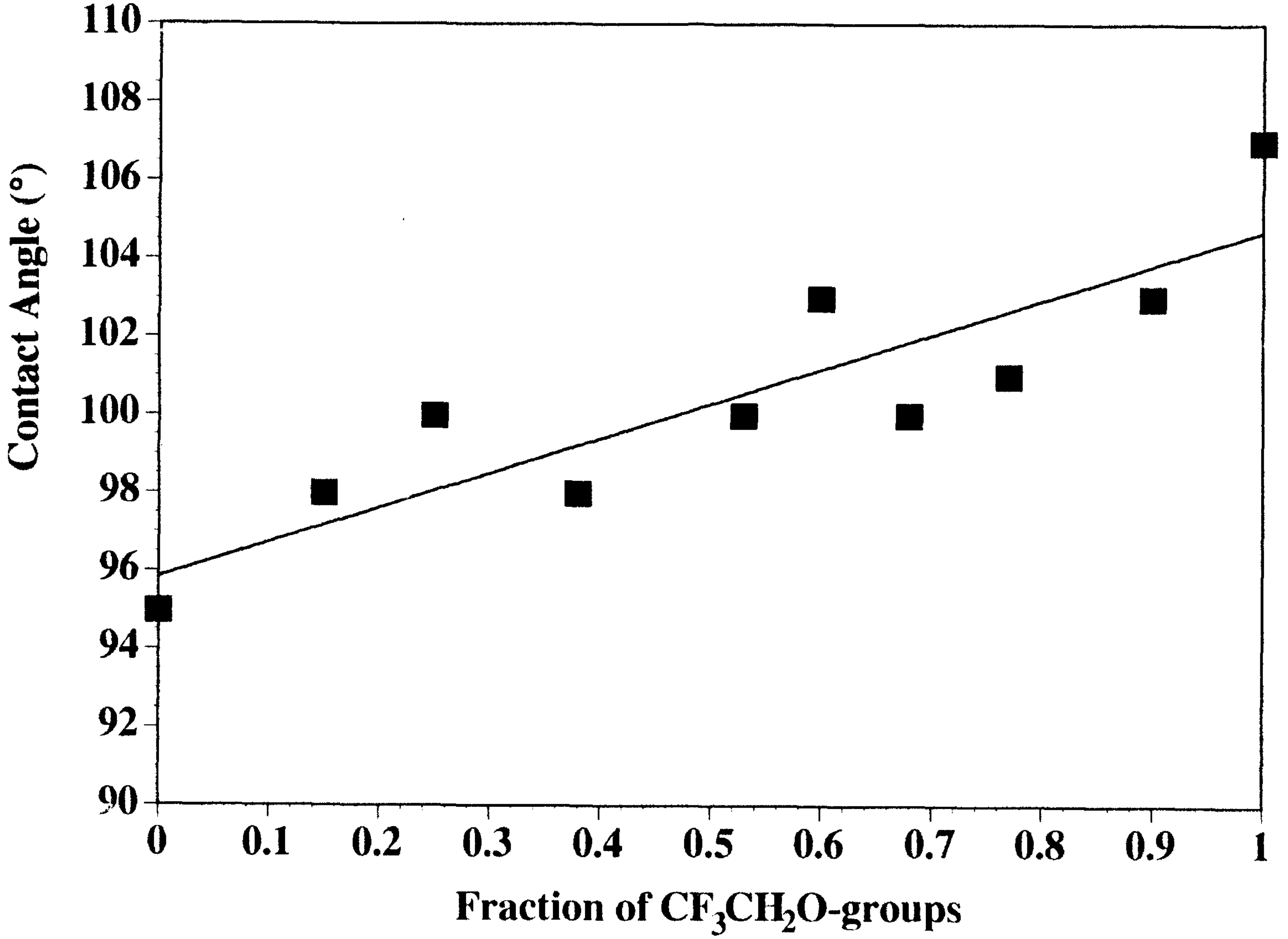

Contact Angle (°)
110
108
106
104
102
100
98
96
94
92
90
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Fraction of CF_3CH_2O-groups

Figure 11(a)

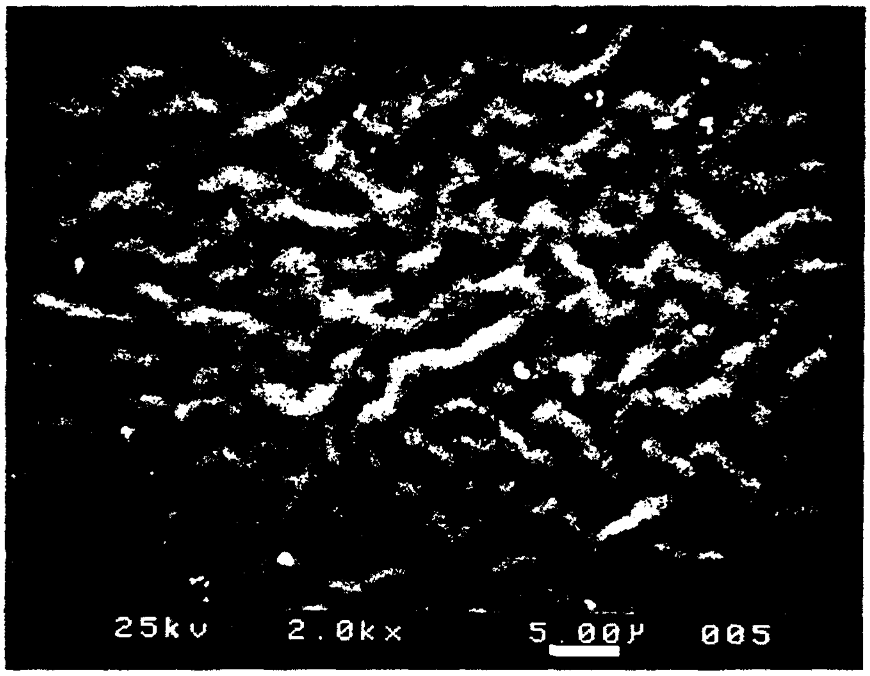


Figure 11(b)

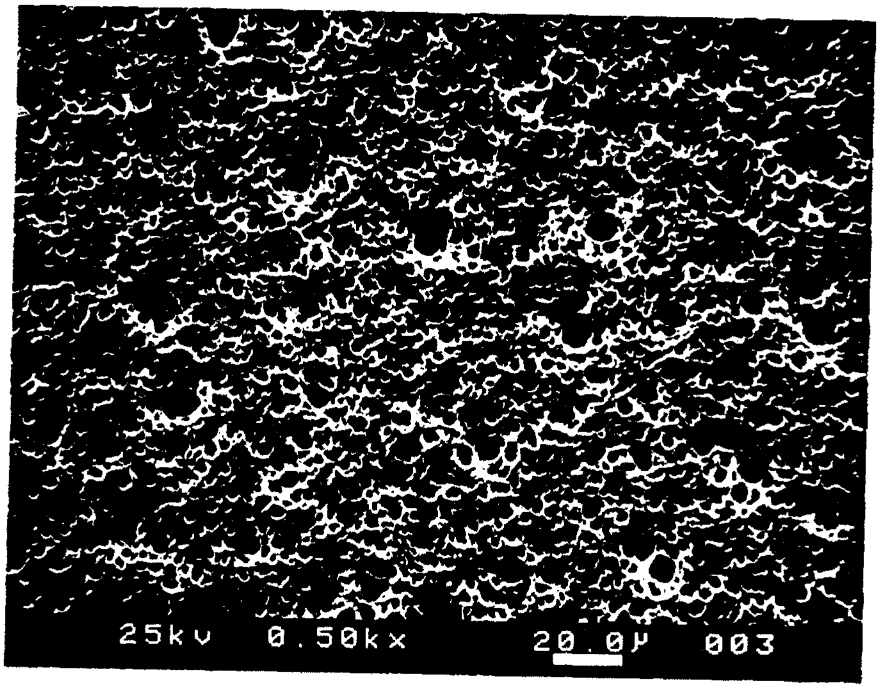


Table 1. Synthesis Methods to Prepare Polyphosphazenes Containing 2,2,2-Trifluoroethoxy And Phenoxy Groups in a Ratio of Roughly 1:1[a].

Method	First Nucleophile Added A (equivalent)	Second Nucleophile Added B (equivalent)	T(A)[b], °C	t(A)[c], hour	T(B)[d], °C	t(B)[e], hour
1	$CF_3CH_2O^- Na^+$ (1)	$PhO^- Na^+$ (1.5)	25	12	25 to 67	48 (25 °C) 24 (67 °C)
2	$CF_3CH_2O^- Na^+$ (1)	$PhO^- Na^+$ (1.5)	-78 to 25	5 (-78 °C) 12 (25 °C)	25 to 67	48 (25 °C) 24 (67 °C)
3	$CF_3CH_2O^- Na^+$ (1)	$PhO^- Na^+$ (1.5)	50	8	25 to 67	48 (25 °C) 24 (67 °C)
4	$PhO^- Na^+$ (1)	$CF_3CH_2O^- Na^+$ (1.3)	25	24	25	72
5	$PhO^- Na^+$ (1)	$CF_3CH_2O^- Na^+$ (1.3)	25	24	67	24
6	$PhO^- Na^+$ (1.2) $CF_3CH_2O^- Na^+$ (1.2)	-	25	72	-	-

[a] The polymers were prepared by the sequential treatment of $(NPCl_2)_n$ first with one reagent and the with another.

[b] T(A) is the temperature of reaction for the first nucleophile.

[c] t(A) is the reaction time allowed for the reaction of $(NPCl_2)_n$ with the first reagent.

[d] T(B) is the temperature of reaction for the second nucleophile.

[e] t(B) is the reaction time following the addition of the second nucleophile.

Table 2. Compositions of Polymers Obtained by Various Methods[a].

Method	2,2,2-trifluoroethoxy groups (mole%)	$NP(OCH_2CF_3)_2$ units (mole%)	$NP(OPh)_2$ units (mole%)	$NP(OCH_2CF_3)(OPh)$ units (mole%)	Fraction of geminal substitution (%)
1	48	16	21	64	16[b]
2	49	16	18	66	17[b]
3	50	24	24	52	24[b]
4	52	15	12	73	12[c]
5	56	36	22	40	
6	52	23	21	56	19[c]

[a], determined by ^{31}P NMR spectroscopy

[b], $$\frac{\left(\frac{[NP(OCH_2CF_3)_2]}{2}\right)}{[Na^{+-}OCH_2CF_3]}\times 100$$

[c], $$\frac{\left(\frac{[NP(OPh)_2]}{2}\right)}{[Na^{+-}OPh]}\times 100$$

Table 3. Compositions of Polymers Synthesized by Method (1).

Polymer	$CF_3CH_2O^- Na^+$ used (mole%)[a]	Trifluoroethoxy groups in the polymer (mole%)[b]	$NP(OCH_2CF_3)_2$ units (mole%)[b]	$NP(OCH_2CF_3)(OPh)$ units (mole%)[b]	$NP(OPh)_2$ units (mole%)[b]	Fraction of geminal substitution
8	100	100	100	0	0	-
9	90	89	77	23	0	0
10	77	79	58	42	0	0
11	68	69	42	53	5	4
12	60	57	34	46	21	17
13	57	57	28	58	14	12
1	48	48	16	64	21	17
14	46	46	17	58	25	19
15	38	41	18	42	39	22
16	25	27	9	36	54	19
17	15	18	3	30	68	8
18	0	0	0	0	100	-

[a], determined by ^1H NMR spectroscopy.

[b], determined by ^{31}P NMR spectroscopy.

Table 4. Compositions of Polymers Synthesized by Method (4)[a].

Polymer	Phenoxy groups (mole%)	$NP(OCH_2CF_3)_2$ units (mole%)	$NP(OCH_2CF_3)(OPh)$ units (mole%)	$NP(OPh)_2$ units (mole%)	Fraction of geminal substitution
19	87	0	29	72	0
20	78	0	45	55	0
21	73	0	54	46	0
22	58	6	73	21	5
23	49	15	73	12	12
24	15	70	30	0	0

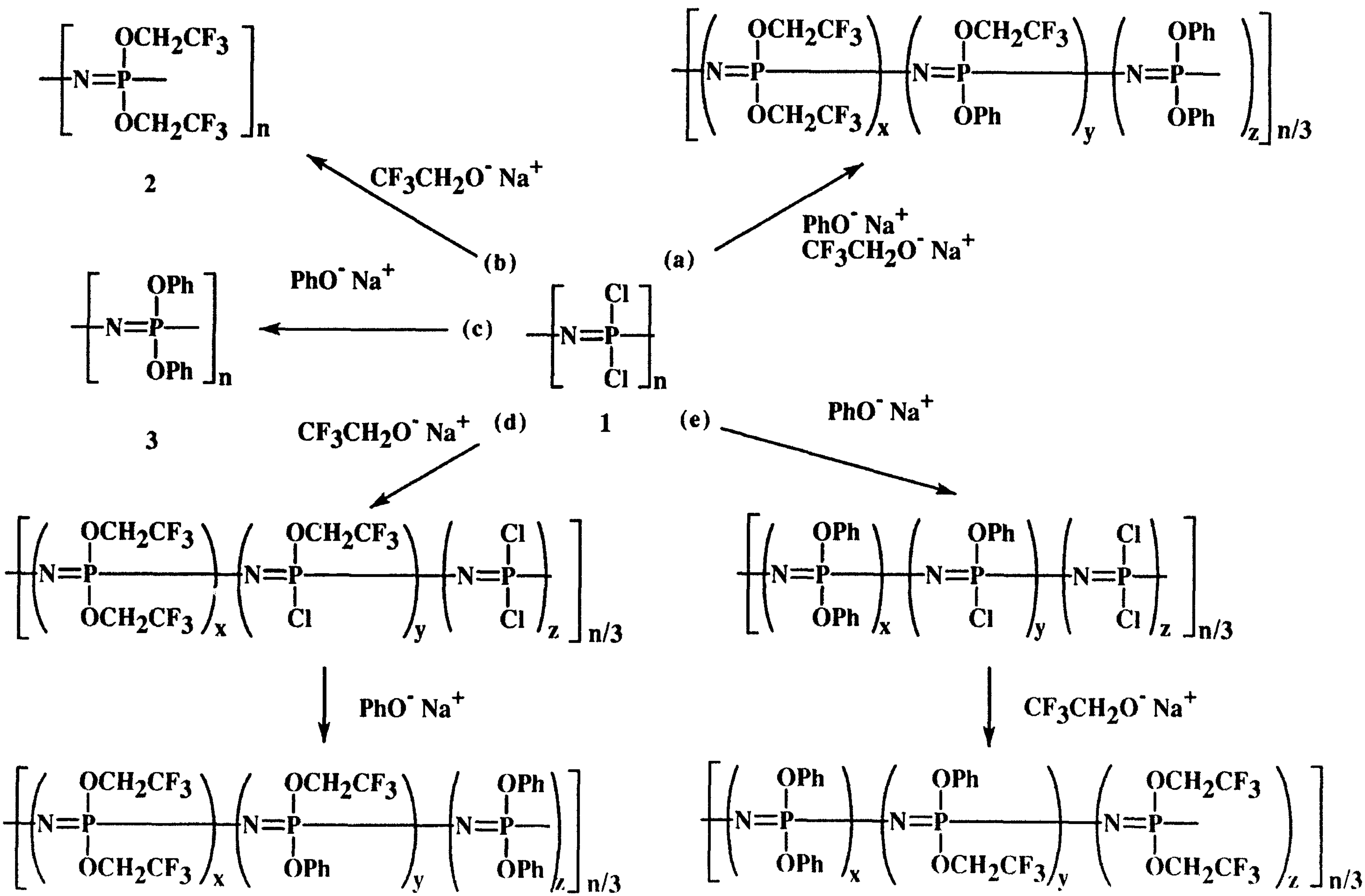
[a], determined by ^{31}P NMR spectroscopy

Table 5. First Order Transition Data of Some Polymers.

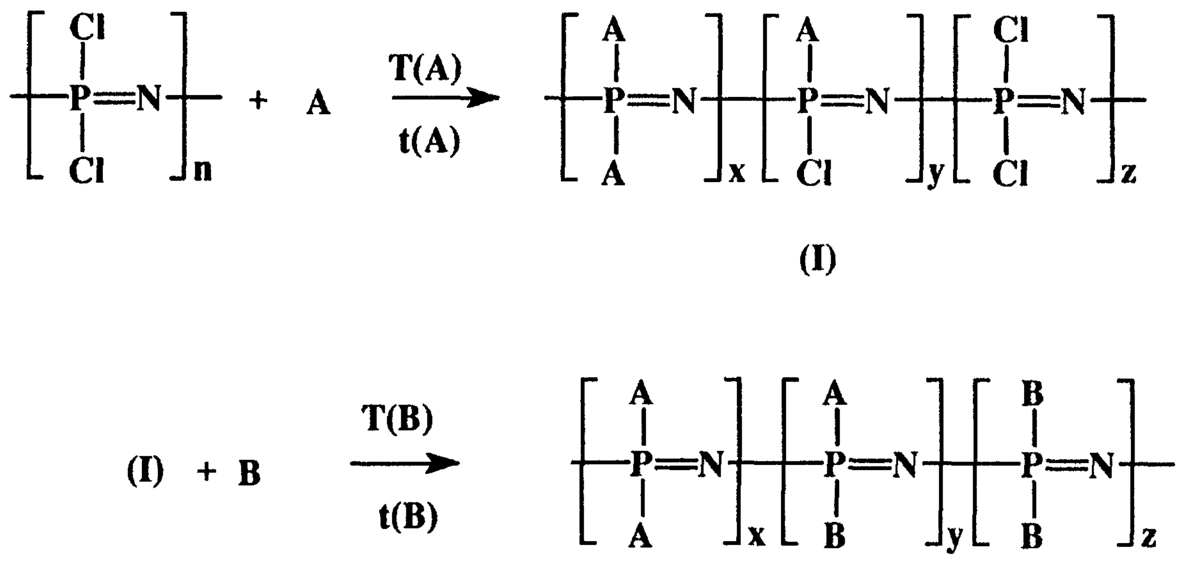
Polymer	Temperature[a], °C	ΔH (J/g)
18	50	4.7
	78	0.7
16	42	0.2
11	40	6.1
10	36	4.8
15	21	2.8

[a], The temperature range for DSC scan was -100 to 150 °C with a temperature of 40 °/min. All results are from the first heating cycle.

Scheme I.

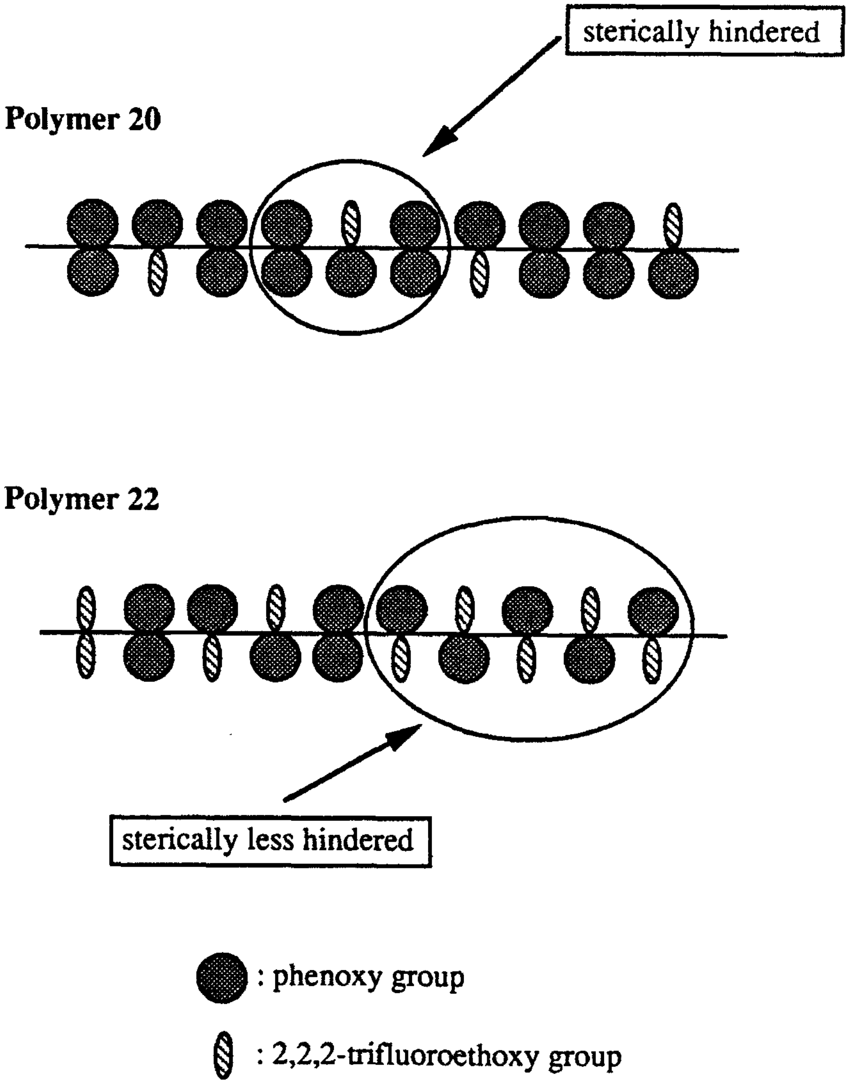


Scheme II



A, B = Sodium 2,2,2-trifluoroethoxide or sodium phenoxide
T(A), T(B) = Temperature at which A or B is added
t(A), t(B) = Reaction times after A or B is added

Scheme III.


sterically hindered
Polymer 20
Polymer 22
sterically less hindered
: phenoxy group
: 2,2,2-trifluoroethoxy group

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)*
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Air Weapons Center
Weapons Division
China Lake, CA 93555-6001

Dr. Elek Lindner (1)
Naval Command, Control and Ocean
Surveillance Center
RDT&E Division
San Diego, CA 92152-5000

Dr. Bernard E. Douda (1)
Crane Division
Naval Surface Warfare Center
Crane, Indiana 47522-5000

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

Dr. Harold H. Singerman (1)
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Eugene C. Fischer (1)
Code 2840
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Defense Technical Information
Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

* Number of copies to forward

ABSTRACT DISTRIBUTION LIST

Dr. Harry R. Allcock
Department of Chemistry
Pennsylvania State Univ.
University Park, PA 16802

Dr. Andrew R. Barron
Department of Chemistry
Harvard University
Cambridge, MA 02138

Dr. Alexander S. Blumstein
Department of Chemistry
University of Massachusetts
Lowell, MA 01854

Dr. Jean M. Frechet
Department of Chemistry
Cornell University
Ithaca, NY 14853

Professor Issifu I. Harruna
Morris Brown College
643 Martin Luther King, Jr. Drive, N.W.
Atlanta GA 30314-4140

Dr. Chris W. Allen
Department of Chemistry
University of Vermont
Burlington, VT 05405-0125

Dr. Kurt Baum
Fluorochem, Inc.
680 South Ayon Avenue
Azusa, CA 91702

Professor Joseph M. DeSimone
Department of Chemistry
The University of North
Carolina at Chapel Hill
Chapel Hill, NC 27599-3290

Dr. Robert H. Grubbs
Department of Chemistry
California Inst. of Technol.
Pasadena, CA 91124

Dr. Robert W. Lenz
Polymer Sci. and Eng. Dept.
University of Massachusetts
Amherst, MA 01002

Dr. Lon J. Mathias
Department of Polymer Science
University of Southern Mississippi
Hattiesburg MS 39406-0076

Dr. Krzysztof Matyjaszewski
Department of Chemistry
Carnegie-Mellon University
Pittsburgh, PA 15213

Pr. Alan G. MacDiarmid
Department of Chemistry
University of Pennsylvania
Chemistry Building
Philadelphia PA 19104-6323

Dr. James E. McGrath
Department of Chemistry
Virginia Polytechnic Inst.
Blacksburg, VA 24061

Dr. James A. Moore
Department of Chemistry
Rensselaer Polytechnic Inst.
Troy, NY 12180-3590

Dr. Bruce M. Novak
Department of Chemistry
University of California
Berkeley, CA 94720

Dr. Virgil Percec
Dept. of Macromolecular Sci.
Case Western Reserve Univ.
Cleveland, OH 44106-2699

Dr. Dietmar Seyferth
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

Dr. Richard R. Shrock
Department of Chemistry, 6-331
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, MA 02139

Dr. James M. Tour
Dept. of Chemistry
Univ. of South Carolina
Columbia, SC 29208

Dr. David M. Walba
Dept. of Chem. & Biochem.
Univ. of Colorado
Boulder, CO 80309

Dr. Robert West
Department of Chemistry
University of Wisconsin-Madison
Madison WI 53706

Dr. Michael E. Wright
Department of Chemistry
Utah State University
Logan, UT 84322