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Molecular characterization of a copolymer of 2-allylphenoxyorganocyclotriphosphazene with styrene, methyl methacrylate and vinylbenzyl chloride

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The monomer 2-allylphenoxyorganocyclotriphosphazene was synthesized by reacting hexachlorocyclotriphosphazene with 2-allylphenol, phenol and 2,2,2-trifluoroethanol by phase transfer catalysis in a dichloromethane/alkaline solution. The copolymerizations of 2-allylphenoxyorganocyclotriphosphazene with styrene, methyl methacrylate and vinylbenzyl chloride were investigated. Nine copolymers of 2-allylphenoxyorganocyclotriphosphazene were identified in the solution. These copolymers were characterized by using light scattering, viscometry and ^{31}P n.m.r. spectroscopic techniques. The micelles were observed to hydrodynamically and thermodynamically behave as impermeable spheres. The structure of the micellar shell was determined. The translational diffusion coefficient, Mark–Houwink constants, hydrodynamic radius, micellar weight, aggregation number, characteristic ratio and intrinsic viscosity were obtained. The chains of copolymer were observed to have a high degree of stiffness and a lack of rotational freedom in solution. Copyright © 1996 Elsevier Science Ltd.

(Keywords: phosphazene; phase transfer catalysis; molecular characterization)

INTRODUCTION

A variety of polyphosphazenes having a wide range of substituents at the phosphorus atoms have been synthesized. The interest in this kind of polymer has increased rapidly in recent times not only because of the useful properties that they often exhibit but also due to the excellent means that these polymers provide for exploring the effects of changes in side-group structure on the physical properties of flexible polymer chains[1–9].

The procedure for synthesis, which yields a polymeric material including both inorganic and organic compounds, is vital in the sense that a wide variety of substituents and mixed substituents are attached to the polymer backbone. Variations in the ratio of the content of inorganic material to organic material affect the various physical properties of these polymers. A considerable interest also exists in the preparation and examination of copolymers containing both organophosphazene and organic compound units. The incorporation of organophosphazene units into an organic polymer backbone lowered the glass transition temperature and increased the thermal stability and flame retardation of the copolymer[10]. It is, however, known that the phosphorus atom with a covalent chloride atom in the phosphazene unit is unstable. The 2,2,2-trifluoroethoxy and phenoxy groups were hence used to replace the chloride atom and consequently change the properties of phosphazenes. In this paper, we report the reactions of organofunctional phosphazene monomers having 2,2,2-trifluoroethoxy and phenoxy side-groups with styrene (STY), methyl methacrylate (MMA) and vinylbenzyl chloride (VBC), yielding the copolymers. The objectives of the present study are to investigate the preparation of organophosphazenes and to study the solution properties of these copolymers, by employing intrinsic viscosity, ^{31}P n.m.r. and light-scattering measurements.

EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene (Aldrich), styrene (Janssen), methyl methacrylate (Janssen), vinylbenzyl chloride (TCI), azobis(isobutyronitrile) (AIBN) (TCI), 2,2,2-trifluoroethenol (Merck), phenol (Merck) and other reagents were all reagent grade chemicals.

Analytical equipment

Gel permeation chromatographic analysis was carried out using an instrument (Shimadzu Model LC-6A) equipped with a refractive index detector (Shimadzu, RDI-6A). The measurement was performed in a polymer tetrahydrofuran (THF) solution (5–7 mg/10 ml) by means of two Styragel columns—G2000H and G3000H—at a flow rate of 1.0 ml min^{-1} at 40°C. Approximate calibration of the columns was accomplished with polystyrene standards having a narrow range of molecular weight (Waters Associates). Thermal analysis was conducted at

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10°C min^{-1}, 100 ml of N_2 min^{-1}, for the thermogravimetric system (t.g.a., Du Pont 910) and at 20°C min^{-1}, 100 ml of N_2 min^{-1}, for the differential scanning calorimeter (d.s.c., Du Pont 951). Elemental analysis (EA) was carried out for carbon, hydrogen and nitrogen (Perkin-Elmer 2400). Mass spectra were recorded on a JEOL SX-102A spectrometer. N.m.r. spectra of samples in deuterated chloroform were recorded on an *FT* n.m.r. spectrometer (JEOL, 300 MHz). The incorporated content of compound **I** in the copolymer was determined from the mass fraction of nitrogen.

Viscometric measurements

An Ubbelohde-type viscometer was employed to measure the durations of flow of the polymer solution in *N,N*-dimethylacetamide (DMAC). The bath temperature was controlled at 35 ± 0.02°C. The highest concentrations were about 3×10^{-3} g ml^{-1}. Values of the intrinsic viscosity $[\eta]$, the Huggins constant (k_H) and the Kraemer constant (k_K) were estimated according to the Huggins equation ($\eta_{red} = [\eta] + k_H[\eta]^2 C$)[11] and the Kraemer equation ($\eta_{inh} = [\eta] + k_K[\eta]^2 C$)[12] using the least-squares regression method, by simultaneous extrapolation to infinite dilute solution of $\eta_{red} = \eta_{sp}/C$ and $\eta_{inh} = (1/C) \log \eta_{rel}$ *versus* C, where C represents the concentration and η_{sp} and η_{rel} are the specific and relative viscosities, respectively.

Quasielastic light scattering

A Brookhaven Instruments Corp. multiangle light-scattering goniometer with a helium–neon laser light source ($\lambda = 632.8$ nm) was used to measure the intensity fluctuations in the scattered light at 30–120°. The autocorrelation function of the photocurrent was determined using a Brookhaven Instruments Corp. BI-203072-channel, four-bit digital correlator. The samples were prepared by filtering through a 0.45 μm filter. The solvent and temperature were DMAC and 35°C, respectively.

*Synthesis of 2-allylphenoxypentachlorocyclotriphosphazene (**Ia**)*

An aqueous solution (50 ml) of sodium hydroxide (0.5 g, 12.5 mmol), 2-allylphenol (1.34 g, 10 mmol) and tetra-*n*-butylammonium bromide (4 g, 12 mmol, phase transfer catalyst) was prepared and introduced into the reactor (three-necked flask, 250 ml), which was thermostated at the desired temperature (30 ± 0.02°C). Phosphazene reactant ($(NPCl_2)_3$; 3.47 g, 10 mmol) and dichloromethane (50 ml) also maintained at the desired temperature were then added to the reactor. The reaction mixture was agitated for 0.5 h. After reaction, the oil phase was separated from the aqueous phase, washed several times with water and dried with $MgSO_4$. Most of the solvent from the organic phase was removed with an aspirator. A yellowish oil-like product was thus obtained. The products were separated on a pressurized column chromatograph[13]. Thin-layer chromatography indicated the presence of product. A portion (4 g) of the crude oil was chromatographed on silica gel (70 g) and eluted with *n*-hexane–chloroform (33/1) (10–15 ml min^{-1}) to give compound **Ia** (^{31}P n.m.r., δ 22.94 ppm (doublet) and 12.68 ppm (triplet); EA, 24.26% C, 2.04% H, 9.4% N; *m/e* = 445).

*Synthesis of 2-allylphenoxypentaphenoxycyclotriphosphazene (**Ib**)*

An aqueous solution (50 ml) of sodium hydroxide (6 g, 0.15 mol), phenol (7 g, 0.074 mol) and tetra-*n*-butylammonium bromide (1 g, 3 mmol) was prepared and introduced into the reactor (250 ml, three-necked flask, 35 ± 0.02°C). Phosphazene reactant ($(NPCl_2)_3$; 5 g, 144 mmol) and dichloromethane (50 ml) also maintained at the desired temperature were then added to the reactor. The reaction mixture was agitated for 3 h. After reaction, the oil phase was separated from the aqueous phase, washed several times with water, and dried with $MgSO_4$. Most of the solvent from the organic phase was removed with an aspirator. A yellowish oil-like product was obtained at this stage. The products were separated on a pressurized column chromatograph[13]. The analytical results for chloropentaphenoxycyclotriphosphazene were as follows: ^{31}P n.m.r., δ 23.6 ppm (triplet) and 7.7 ppm (doublet); EA, 56.6% C, 3.94% H, 6.7% N; *m/e* = 635; *m.p.* = 53°C.

An aqueous solution (50 ml) of sodium hydroxide (4 g, 0.1 mol), 2-allylphenol (6.5 g, 0.047 mol) and tetra-*n*-butylammonium bromide (4 g, 12 mmol) was prepared and introduced into the reactor (250 ml, three-necked flask, 35 ± 0.02°C). Chloropentaphenoxycyclotriphosphazene ($N_3P_3Cl(OC_6H_4CH_2CHCH_2)_5$; 10 g, 157 mmol) and dichloromethane (50 ml) were then added to the reactor. The reaction mixture was agitated for 8 h. After reaction, the oil phase was separated from the aqueous phase, washed several times with water, and dried with $MgSO_4$. Most solvent from the organic phase was removed with an aspirator. A yellowish oil-like product was thus obtained. The products were separated on a pressurized column chromatograph[13]. Thin-layer chromatography indicated the presence of product. A portion (4 g) of the crude oil was chromatographed on silica gel (70 g) eluted with hexane–chloroform (88/12) (10–15 ml) min^{-1}) to give **Ia** (^{31}P n.m.r., δ 20.85 ppm; EA, 63.8% C, 4.6% H, 5.7% N; *m/e* = 733).

*Synthesis of 2-allylphenoxypenta(2,2,2-trifluoroethoxy)-cyclotriphosphazene (**Ic**)*

This procedure was identical to that of **Ia**, except that phenol was used in place of 2,2,2-trifluoroethanol. The analytical results for chloropenta(2,2,2-trifluoroethoxy)-cyclotriphosphazene were: ^{31}P n.m.r., δ 26 and 13.9 ppm; EA, 18.3% C, 3.0% H, 6.4% N; *m/e* = 655. The analytical results for **Ib** were: ^{31}P n.m.r., δ 16.94 ppm; EA, 29.9% C, 2.5% H, 5.5% N; *m/e* = 763.

*Copolymerization of 2-allylphenoxyorganocyclotriphosphazene (**I**) with **II** (STY, MMA or VBC)*

Compound **I** (1.1 mmol), **II** (5.5 mmol) and AIBN (2 wt%) were added to thick-walled test tubes. The tubes were flushed several times with dry nitrogen in an ice bath, stoppered with rubber serum caps, and then put into an oven heated to 60 ± 0.5°C for 36 h. After reaction, the gels were dissolved in dichloromethane (10–15 ml) and filtered to remove isoluble material. The solution was added dropwise to methanol in order to precipitate the copolymer. The copolymer was filtered, dissolved in dichloromethane and reprecipitated several times. The material was dried and analysed to determine the phosphazene content in the various copolymers.

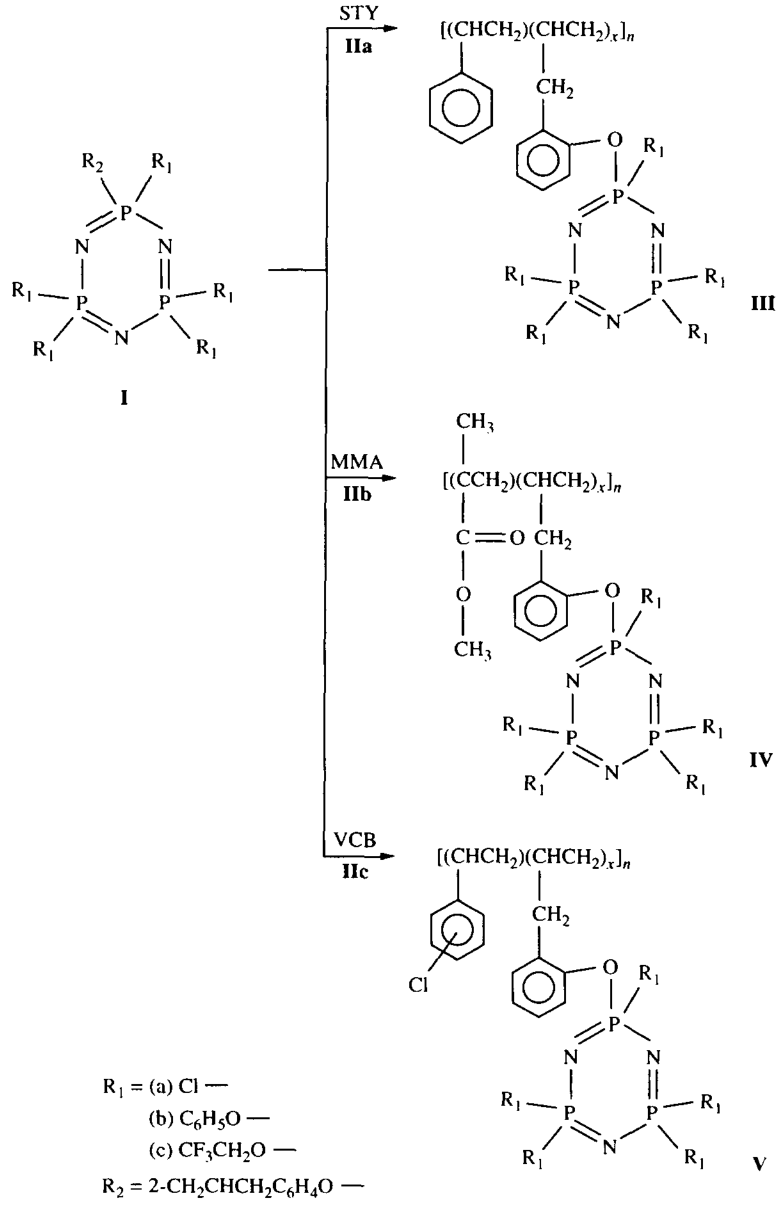
RESULTS AND DISCUSSION

It is known that alkoxy- and aryloxy-cyclotriphosphazenes can be synthesized by conventional nucleophilic substitution, by using the sodium salt of the corresponding alcohols. However, owing to the low solubility of the salts in the solvent and hydrolysis, an elevated temperature, prolonged reaction duration, and inert atmosphere are generally required[14]. On the other hand, phase transfer catalysis is usually applied for the synthesis of organophosphazene[15,16].

When monomer **Ib** or **Ic** was synthesized by reacting **Ia** with phenol or 2,2,2-trifluroethanol, the yield was observed to be low (< 10%). However, chloropentaphenoxycyclotriphosphazene ($N_3P_3Cl(OC_6H_5)_5$) and chloropenta(2,2,2-trifluoroethoxy)cyclotriphosphazene ($N_3P_3Cl(OCH_2CF_3)_5$) were synthesized from the reaction of hexachlorocyclotriphosphazene ($(NPCl_2)_3$) with phenol and 2,2,2-trifluoroethanol, respectively, with phase transfer catalysis in a dichloromethane/alkaline solution. Although the reaction may be controlled by steric effects[17,18], **Ib** and **Ic** were synthesized from the reaction of 2-allylphenol with chloropentaphenoxycyclotriphosphazene and chloropenta(2,2,2-trifluoroethoxy)cyclotriphosphazene, respectively, with phase transfer catalysis. This synthesis was observed to have a high yield (> 80%) as well as a narrow product distribution, and proceeded under mild reaction conditions. These results may be explained by arguing that the tetra-n-butylammonium counterion increases the lypophilicity and nucleophilicity of oxyanions.

Copolymerization reactions are free-radical reactions of 2-allylphenoxyorganocyclotriphosphazenes having chloride, phenoxy and 2,2,2-trifluoroethoxy groups with styrene, methyl methacrylate and vinylbenzyl chloride, respectively. The reactions are shown in *Scheme 1*.

The molecular properties of the nine copolymers are listed in *Table 1*. The gel permeation measurements were performed in a polymer/THF solution (5–7 mg/10 ml) by means of two Styragel columns—G2000H and G3000H—at a flow rate of 1.0 ml min^{-1} at 40°C. The incorporated content of **I** in the copolymer was



R_1 = (a) Cl —
(b) C_6H_5O —
(c) CF_3CH_2O —
R_2 = 2-$CH_2CHCH_2C_6H_4O$ —

Scheme 1

Table 1 Molecular properties of block copolymers

Copolymer	mol% of **I** in copolymer	$M_n \times 10^{-4a}$	M_w/M_n
IIIa	7.89	4.92	1.96
IIIb	2.18	4.18	4.12
IIIc	8.22	3.60	1.39
IVa	2.48	4.89	2.18
IVb	2.48	4.00	3.89
IVc	4.83	3.46	1.47
Va	3.33	5.10	2.02
Vb	2.19	4.74	4.13
Vc	4.61	4.53	1.54

[a] Measured by gel permeation chromatography

Table 2 Viscosity parameters of the copolymers in solution

Copolymer	$[\eta]$ (ml g^{-1})	k_H	k_K
IIIa	51.3	−0.52	−0.35
IIIb	45.9	−0.12	−0.19
IIIc	29.5	−0.21	−0.25
IVa	57.5	−0.48	−0.37
IVb	51.5	−0.11	−0.20
IVc	47.5	−0.18	−0.24
Va	49.8	−0.49	−0.32
Vb	43.7	−0.13	−0.19
Vc	26.2	−0.19	−0.22

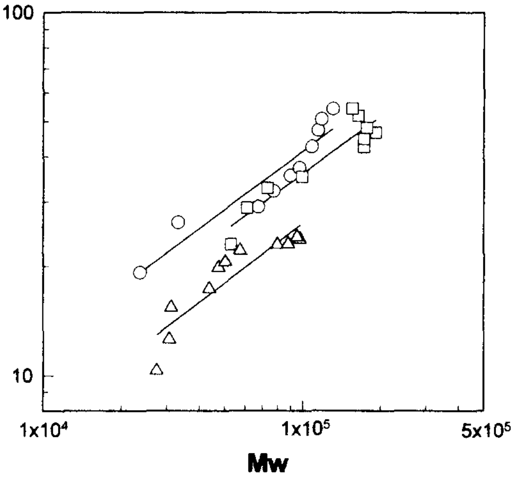


Figure 1 Representation of the Mark–Houwink viscometric equation: ○, STY; □, MMA; △, VBC

determined from the mass fraction of nitrogen. The experimental results of the viscometric measurements are given in *Table 2*. A rough estimate of the experimental uncertainty in the values of $[\eta]$ is about 3%. The Huggins constants were negative in the range −0.11 to −0.52, which are smaller than the values expected for linear and flexible polymers in a good solvent. The values of the Huggins and Kraemer constants reported in the literature for other polyphosphazenes range from very low values, even negative Huggins constants, to very high ones[19–22] and do not normally follow the theoretical relation $(k_H - k_K = 0.5)$[23]. The average values of $(k_H - k_K)$ for **III**, **IV** and **V**, by following the above theoretical equation, were observed to be −0.15, 0.07 and 0.06, respectively. The solvent, DMAC seemed to be poor medium.

The $[\eta]$–molecular weight relationship is described by the Mark–Houwink equation

$$[\eta] = KM^a \qquad (3)$$

where both K and a are constants and dependent on the nature of the polymer, solvent and temperature. The value of a normally ranges from 0.5 to 0.8 for a good solvent. *Figure 1* shows the $[\eta]$–M_w log–log relationship for copolymer **III** prepared in the present study, where a linear plot with $a = 0.53 \pm 0.04$ is obtained.

Information regarding the copolymer size can be derived from the quasielastic light-scattering measurements. The average translational diffusion coefficient of micelles in solution, D, was measured at an angle of 90°. The hydrodynamic radius R_h can then be obtained using the Stokes–Einstein relation

$$R_h = kT/(6\pi\eta_s D) \qquad (4)$$

where η_s is the viscosity of the solvent (1.69 cP for DMAC at 35°C) and k is the Boltzmann constant. No concentration dependence of D was observed in the present study within the concentration range studied. The obtained D and R_h values are listed in *Table 3*. The order of magnitude of R_h is **V** > **III** > **IV**. If the micelles are modelled as hydrodynamically impermeable spheres, then the intrinsic viscosity is related to other properties of solution as[24,25]

$$[\eta] = 10\pi R_h^3 N_A/3M \qquad (5)$$

where N_A is the Avogadro number, and M is the molecular weight of the particle. Since intrinsic viscosity $[\eta]$ is related to the size and shape of a macromolecule, the hydrodynamic radius R_h is expected to have a directly proportional relationship with $[\eta]$. *Figure 2* shows that the slope is about 1.3 ± 0.08.

For impermeable spheres it is reasonable to equate $[\eta]$ with R_h. Thus, combining equations (3) and (4), we

Table 3 Micellar weights and radius from quasielastic light scattering and intrinsic viscosity measurements

Copolymer	R_h (nm)	$\langle s^2\rangle^{1/2}$ (nm)	$D \times 10^8$ (cm^2 s^{-1})	$M_h \times 10^{-7}$	$N_{ag} \times 10^{-2}$
IIIa	75	11	1.79	5.03	5.2
IIIb	61	13	2.20	3.11	1.8
IIIc	48	7.3	2.80	2.35	4.7
IVa	63	12	2.13	3.07	2.8
IVb	54	13	2.49	2.26	1.5
IVc	50	8.6	2.68	3.01	5.9
Va	87	11	1.54	7.06	6.8
Vb	83	13	1.62	6.97	3.6
Vc	56	8	2.40	2.32	3.3

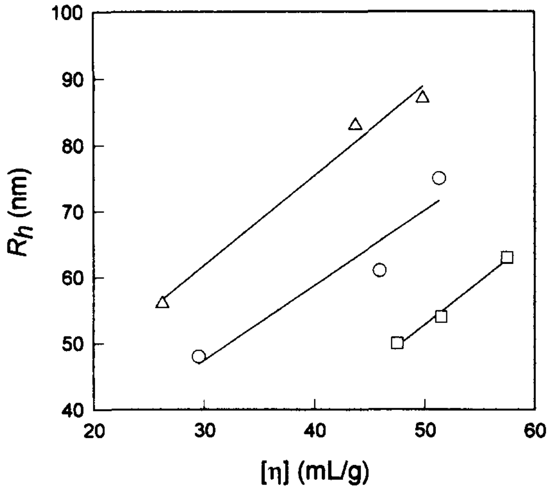


Figure 2 Relationship between the hydrodynamic radius and intrinsic viscosity: ○, **III**; □, **IV**; △, **V**

obtain the hydrodynamic micellar weight M_h as

$$M_h = 10\pi N_A[kT/(6\pi\eta_s D)]^3/3[\eta] \qquad (6)$$

The values of M_h thus obtained are listed in *Table 3*. From the micellar weights and the corresponding unimer molecular weights, the aggregation number $N_{ag}(= M_h/M_w)$ can be obtained. The values of N_{ag} thus obtained are listed in *Table 3*. The aggregation numbers are of the order of a few hundreds, indicating that the micellar solutions have greater turbidity.

The molecular dimensions of the polymeric chains can be calculated from $[\eta]$ and M_w according to the Flory–Fox equation for linear polymers:

$$\langle r^2\rangle^{3/2} = [\eta]M_w/\phi \qquad (7)$$

and

$$\langle r^2\rangle \approx 6\langle s^2\rangle \qquad (8)$$

where Flory's constant $\phi = 250\,\mathrm{mol}^{-1}$ when r is expressed in nanometres and $[\eta]$ in millilitres per gram. The values of the radius of gyration $\langle s^2\rangle^{1/2}$ are listed in *Table 3*. These values can be seen to be in the order **IV** > **III** > **V**. The hydrodynamic radius is more than the calculated value $\langle s^2\rangle^{1/2}$, indicating that a lack of rotational freedom exists in these copolymers and a high degree of stiffness of the chains.

In order to describe chain stiffness in a more quantitative manner, the characteristic ratio C_∞ can be defined as

$$C_\infty = \frac{M_r K_\theta^{2/3}}{2l^2\phi^{2/3}} \qquad (9)$$

where l and M_r are the length and the molecular weight of the repeating unit of polymer, respectively. The value of K_θ was obtained by using the Stockmayer–Fixman equation[26]:

$$[\eta]M^{1/2} = K_\theta + AM^{1/2} \qquad (10)$$

where A comprises the constant ϕ and a function of polymer–solvent parameters that does not depend on molecular weight. From *Figure 3*, the open symbols and dashed lines were calculated by using experimental values of $[\eta]$ and M_w. The solid symbols and unbroken lines were calculated by using experimental values of $[\eta]$ and theoretical values of M_w, obtained as $M_w = ([\eta]/K)^{1/a}$ with the K and a coefficients obtained

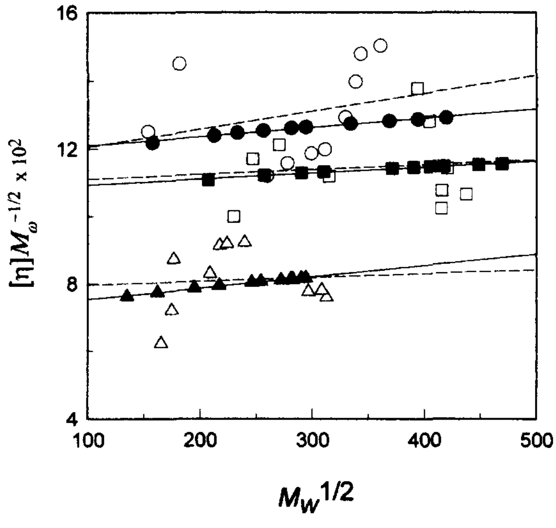


Figure 3 Representation of the Stockmayer–Fixman extrapolation to unperturbed for the copolymer **III**: -○-, -●-, STY; -□-, -■-, MMA; -△-, -▲-, VBC. The straight lines were the least-squares regression lines, fitted by using equation (10)

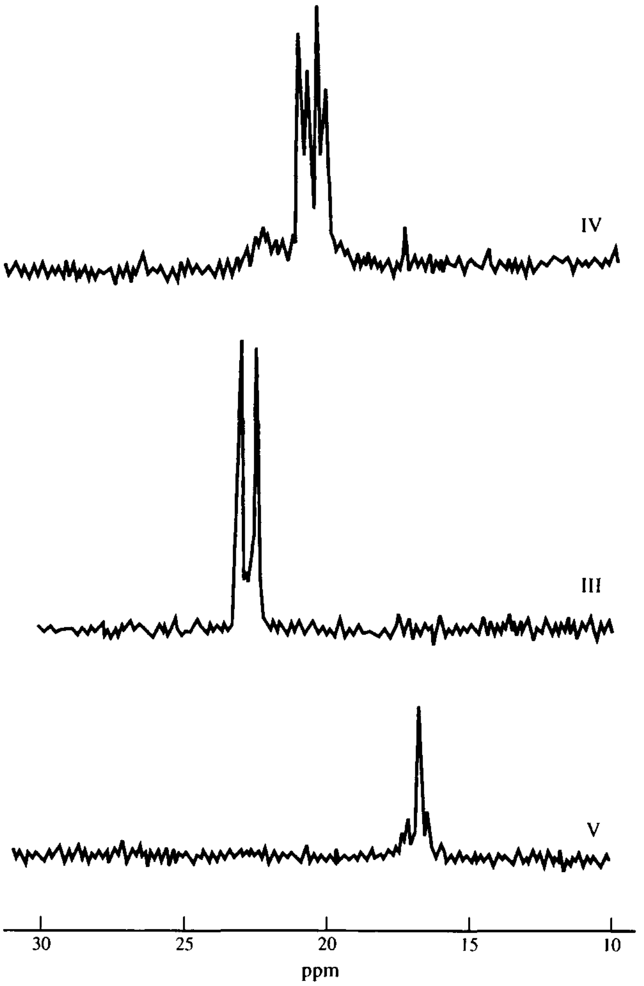


Figure 4 ^{31}P n.m.r. spectra of 2-allylphenoxyorganocyclotriphosphazene copolymers

previously. The six straight lines are the least-squares regression lines, fitted by using equation (10). Although the two fitting procedures are different, the intercepts K_θ, calculated by the least-squares method (extrapolate to $M_w \rightarrow 0$), gave almost identical values. The intercepts for STY, MMA and VBC were 0.117, 0.107 and 0.075 ml mol$^{0.5}$ g$^{-1.5}$, respectively. The uncertainty limit was less than 5%. These intercepts can be converted into the characteristic ratios. The values of the characteristic ratios (C_∞) for STY, MMA and VBC thus obtained were 17.3, 16.5 and 13.8, respectively. It is well-known that the value of C_∞ calculated for a polymer, assuming free rotation, is 3.2[27]. Hence, the high values of C_∞ obtained in the present study indicate a lack of rotational freedom or a high stiffness of the polymer chains.

Figure 4 shows the ^{31}P n.m.r. spectra of 2-allylphenoxyorganocyclotriphosphazene copolymers. A unique singlet is expected from a linear polymer if the chain is long enough. As shown in *Figure 4*, copolymerization is responsible for the two different chemical shifts for copolymers **III** and **IV**. The two signals shift downfield from the monomer, indicating that all the phosphorus atoms are not present in the same environment. The spectra were recorded at least three times for different molecular weights and reacting compound **II**. However, they were observed to be almost identical. The probability of signal in the spectrum being produced by unreacted monomer was omitted from consideration. This phenomenon can arise due to branching or hydrolysis of the copolymers.

CONCLUSION

The monomer 2-allylphenoxyorganocyclotriphosphazene was synthesized by reacting hexachlorocyclotriphosphazene with 2-allylphenol, phenol and 2,2,2-trifluoroethanol by phase transfer catalysis in a dichloromethane/alkaline solution. Molecular characterization of nine copolymers was undertaken using light scattering, viscosimetry and n.m.r. The *a*-value of the Mark–Houwink equation was 0.53. The Huggins constants were negative in the range −0.11 to −0.52 in DMAC solution. The values of the characteristic ratios (C_∞) thus obtained were in the range of 20–27. The high values of C_∞ indicate a lack of rotational freedom or a high stiffness of the polymer chains.

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