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Dielectric Relaxation in Dilute Solutions of Poly(organophosphazenes): Evidence of the Localized Electronic Structure of the P=N Double Bonds

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ABSTRACT: Dielectric measurements were carried out on dilute benzene solutions of fractionated poly(diphenoxyphosphazene) at a concentration of ca. 0.1%. Loss maxima were observed in the audiofrequency range at 303 K. The relaxation times τ determined from the frequencies of these loss maxima increased with increasing (weight-average) molecular weight M_w of the fractions in proportion to $M_w^{1.7}$. This molecular weight dependence and the absolute values of τ were in agreement with the prediction of the Zimm theory evaluated by using the experimental intrinsic viscosity values. Thus, poly(phosphazene) can be classified as a type A polymer which has components of the dipole moment aligned in the same direction parallel to the chain contour. This strongly suggests that the P=N and N—P bonds are not equivalent in contrast to the current model of the delocalized electronic structure of the P—N backbones. The dipole moment for the parallel component per monomer unit was estimated to be ca. 6.7 D.

Introduction

Dipoles of linear polymers were classified into types A, B, and C by Stockmayer.[1] Type A dipoles correspond to those aligned uniaxially in the direction parallel to the chain contour, and type B dipoles are perpendicular to the chain. On the other hand, type C dipoles are the ones attached to mobile side groups.

The structural formula of the main chain of poly(phosphazene) is usually represented as —(P=N)$_n$—.[2,3] If the poly(phosphazene) molecules actually have this electronic structure, the polymer should be classified as a type A polymer since the chain has no symmetry elements such as a mirror plane or a 2-fold rotation axis. On the other hand, if the π electrons on the double bonds delocalize, the two bonds become equivalent and hence this polymer should not be type A. Allcock[2] discussed these two possibilities of the electronic structure of poly(phosphazenes) and suggested that the latter structure is more plausible, because Giglio et al.[4] suggested on the basis of their X-ray crystallographic study that the bond lengths for the two P–N bonds were the same. Until recently, there existed no other experimental evidences to support or disprove this view. In fact, Tanaka et al.[5] calculated the molecular orbitals of this polymer, assuming the equivalence of the two P–N bonds.

We have studied this problem by means of a dielectric method involving observation of the dielectric normal mode process[1] of dilute solutions of fractionated poly(organophosphazenes). Our preliminary results[6] strongly suggested that the localized electronic structure model appears to be more likely. In fact, a recent X-ray analysis carried out by Chatani and Yatsuyanagi[7] showed that the two P–N bonds of poly(dichlorophosphazene) are not equivalent.

If a polymer has type A dipoles, it should exhibit the dielectric normal mode process due to fluctuation of the end-to-end vector of the molecules.[1] Then, we can easily distinguish type A dipoles from others by the following two characteristic properties. First, the dielectric relaxation due to type A dipoles exhibits a strong molecular weight dependence and can be described by the bead–spring model proposed by Rouse and Zimm.[8,9] According to Zimm's theory, the relaxation times for the normal mode process in dilute solutions are given by[9]

$$\tau = 0.85 M \eta_s [\eta] / RT \qquad (1)$$

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Table I
Molecular Weight M_w, M_w/M_n Ratio, Contents of Chlorine and Fluoroethoxy (FE) Groups, Intrinsic Viscosity $[\eta]$, Common Logarithm of the Dielectric Relaxation Time τ, and Relaxation Strength $\Delta\epsilon$ Divided by Concentration C of Poly(phosphazene) Solution at 303 K[a]

code	$10^{-3}M_w$	M_w/M_n	% Cl	% FE	$[\eta]$[b]	$\log_{10}\tau$	$\Delta\epsilon/C$
CoPPN-100	1000	1.5	1.1	10	165	−4.05	236
CoPPN-60	600	1.5	1.1	10	97	−4.74	169
PPPN-49	490	1.2	12	0	89	−4.68	185
PPPN-38	380	1.6	12	0	66	−4.93	138
PPPN-21	210	1.4	12	0	42	−5.18	134
CoPPN-20	200	2.1	1.1	10	40	−5.32	129
PPPN-11	110	1.7	12	0	35	−5.62	129
PPPN-6	64		12	0	9.0	−6.26	

[a] Units: $[\eta]$, g^{-1} mL; τ, s; C, g mL^{-1}. [b] $[\eta]$ was measured at 298 K for PPPN and at 303 K for CoPPN.

where M is the molecular weight; η_s, the solvent viscosity; and $[\eta]$, the intrinsic viscosity. Second, the type A dipoles exhibit much longer relaxation times than the types B and C, whose relaxation times are of the order of 10^{-9} to 10^{-10} s in ordinary solvents such as benzene. In this study, we extended the previous work on the dielectric relaxation of poly(organophosphazenes) in order to confirm the electronic structure and also to clarify the dynamic properties of poly(phosphazene) molecules in dilute solutions.

Experimental Section

Materials. First, poly(dichlorophosphazene) (PCPN) was prepared by thermal ring-opening polymerization of cyclohexachlorotriphosphazene supplied by Shin-Nisso Chemicals Co. and Nihon Seika Co. Ltd. In bulk polymerization, the monomer was sealed in a glass ampule with 2.5% of boron trichloride (BCl_3), and the mixture was kept at 170 °C for 70–140 h. In solution polymerization,[3] 20 g of the monomer dissolved in 60 mL of 1,2,4-trichlorobenzene was sealed in an ampule with 0.3 mL of BCl_3 and the mixture was kept at 170 °C for 70 h.

Then, chlorine atoms of PCPN were substituted by phenoxy groups to obtain poly(diphenoxyphosphazene) (PPPN).[2,3,10,11] For the substitution, PCPN was dissolved in dioxane or tetrahydrofuran and refluxed for 70 h with excess sodium phenolate under a dry nitrogen atmosphere. A chemical analysis of the product indicated that PPPN thus prepared still contained 1.1–15% unreacted chlorine. To obtain PPPN fractions of different molecular weight, we fractionated the polymer with benzene and n-hexane. However, difficulty was often encountered because the polymer occasionally underwent gelation or crystallization.

To avoid this difficulty, we prepared a copoly(phosphazene) with randomly substituted phenoxy and trifluoroethoxy groups. The copolymer is obviously less easily crystallizable. The preparation route was almost the same as that for PPPN. Instead of using pure sodium phenolate for substitution, a mixture of sodium phenolate and trifluoroalcoholate of 100/5.3 by weight was used. This copolymer was coded as CoPPN.

These samples were fractionated at 30 °C from benzene solution with n-hexane as the precipitant. The weight-average molecular weight M_w was determined by a gel permeation chromatograph (Toyo Soda HLC-801A) equipped with a low-angle light scattering detector (Toyo Soda LS-8). The characteristics of the samples are listed in Table I.

Methods. Dielectric measurements were carried out for 0.1 wt % benzene solutions in the frequency range from 20 Hz to 100 MHz at 298 K for PPPN and at 303 K for CoPPN. The details of the measurement were described previously.[12] Intrinsic viscosity was determined in benzene at 298 K for PPPN and at 303 K for CoPPN.

For all solutions of PPPN examined here, a relatively large dielectric loss factor ϵ'' was observed. In the low-frequency f region, the slope of the log ϵ'' versus log f plot was −1, but the dielectric constant ϵ' was almost constant. This is a typical behavior of a sample having a relatively large direct current (dc) conductivity due to some impurity ions. We attempted to minimize this effect by repeating dissolution and precipitation in benzene and hexane several times and, afterward, drying the fractions in high vacuum. However, the dc conductivity was not much improved by this procedure. Then, we attempted to purge impurity ions by applying a dc voltage of ca. 300 V/mm to the sample solutions for a few days. Unfortunately this method was also not very effective.

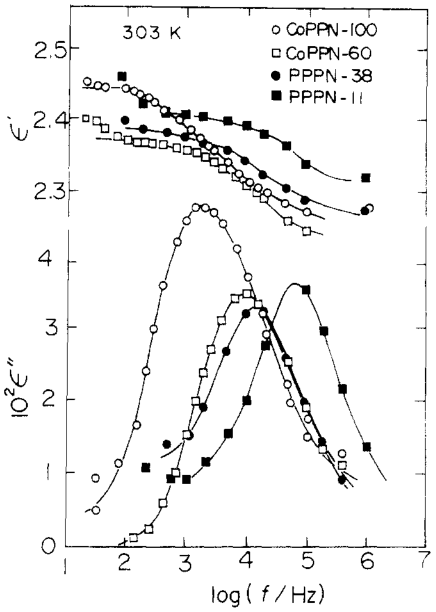

Figure 1. Frequency dependence of ϵ' and ϵ'' calculated by subtracting the contribution of dc conduction for 0.1% benzene solutions of poly(diphenoxyphosphazene) (PPPN) and copoly(phosphazene) with randomly substituted phenoxy and trifluoroethoxy groups (CoPPN).

Thus, we abandoned the attempt at removing the impurities but attempted to subtract the contribution of dc conductivity g_{dc} from ϵ'' by the method proposed by Jones, Stockmayer, and Molinari.[13] They estimated g_{dc} using the following semiempirical equation:

$$g = g_{dc} + K\omega^2 \qquad (2)$$

where g is the observed alternating current conductivity; K, the constant proportional to the relaxation time and strength for the dipolar relaxation process; and $\omega = 2\pi f$, the angular frequency. By plotting g against f^2, we can estimate g_{dc} from the value at zero frequency. The value of g_{dc} was order of 1 μS for the empty cell of 10 pF we employed and was ca. 100 times larger than the second term of eq 2 at 100 Hz. However, this ratio decreases with increasing frequency.

Results and Discussion

Dielectric Relaxation in Dilute Solution of PPPN. Figure 1 shows typical examples of the ϵ' and ϵ'' plotted after subtracting the contribution of dc conductivity. It is clearly seen that the frequency f_m of the loss maximum shifts to the lower frequency with increasing molecular weight.

As usual, the relaxation time, τ, was estimated by

$$\tau = 1/(2\pi f_m) \qquad (3)$$

Figure 2 shows the molecular weight dependence of τ at 303 K for PPPN and CoPPN fractions. The values of τ

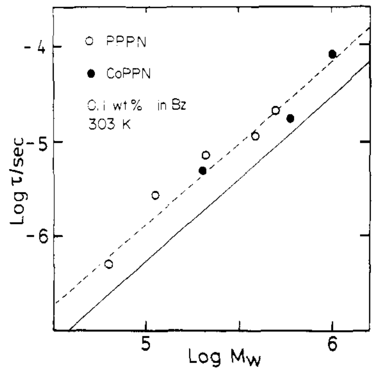

Figure 2. Double-logarithmic plot of relaxation time τ versus molecular weight M_w. Solid line indicates the relaxation time calculated with the experimental $[\eta]$ based on the Zimm theory (eq 1). Dashed line indicates eq 4.

for the PPPN solutions measured at 298 K were reduced to those at 303 K by multiplying it by the ratio of the solvent viscosity η_s at 303 K to that at 298 K, since the friction coefficient for the motion of the molecule is approximately proportional to η_s. For benzene this correction factor was 0.94. Since no appreciable difference in the values of τ between PPPN and CoPPN were seen, we discuss the dielectric behavior without discriminating between these samples.

From the dashed line drawn in Figure 2, the M_w dependence of τ is determined to be

$$\tau \propto M_w^{1.71} \qquad (4)$$

Since τ increases with M_w, the dielectric relaxation shown in Figure 1 should be associated with the overall motion of the molecules. The values of the relaxation times found here are much longer than those for the local segemental motions of the same molecules which are estimated to be on the order of 10^{-10} s from the relaxation time for the type B dipoles observed in bulk and concentrated solutions of PPPN.[14] Thus, the present data strongly indicate that PPPN and CoPPN are a type A polymers.

Using the data of $[\eta]$ listed in Table I, we calculated the theoretical τ values given by the Zimm theory (eq 1) and compared them with the experimental τ values. As seen in Figure 2, the experimental τ values are ca. 0.3 decades larger than the theoretical ones given by the solid line. But the molecular weight dependence of the experimental τ data agrees well with the theoretical prediction. Previously we studied the normal mode process for dilute solutions of *cis*-polyisoprene and observed that the experimental τ values were also ca. 0.3 decades larger than the theory.[15] Thus, we may consider that this discrepancy of the 0.3 decades cannot be the reason to rule out the above mechanism.

From $[\eta]$ versus M_w data of these polymers, the Mark–Houwink–Sakurada equation is given by

$$[\eta] = 4.6 \times 10^{-3}\, M_w^{0.75} \qquad (5)$$

The exponent of this equation indicates that benzene is a good solvent for PPPN. Strictly speaking, the Zimm theory[8] neglects the excluded volume effect and thus is applicable only to Θ solutions, predicting that τ is proportional to $M_w^{1.5}$ and $[\eta]$ to $M_w^{0.5}$. However, if the experimental values of $[\eta]$ are used to compensate for the excluded-volume interactions, eq 1 with eq 5 predicts $\tau \propto M_w^{1.75}$, which is in agreement with the observed M dependence given by eq 4. This situation was also seen in dilute benzene solutions of *cis*-polyisoprene.[15]

If the PPPN molecules assume a rodlike conformation, the polymer might also possess molecular weight dependent relaxation times. If this were the case, τ will be proportional to $M_w^{3.2}$.[16] Obviously the present data are not in harmony with this model.

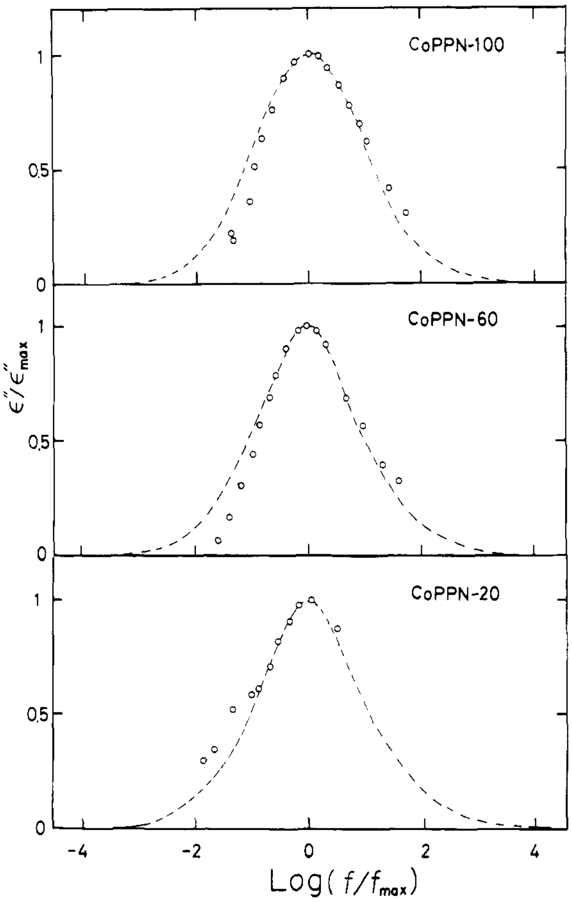

Figure 3. Comparison of the observed and theoretical ϵ'' curves for the CoPPN solutions. The theoretical ϵ'' curves (dotted lines) were calculated on the basis of the Zimm theory by taking the molecular weight distribution into account.

Shape of the Loss Curve. The present samples have broad distributions of molecular weight compared, for example, with anionically polymerized polyisoprene in our previous study.[15] Thus, the distribution of molecular weight may affect the width of the loss curves. Using the empirical M_w dependence of τ and the distribution $w(M)$ of the molecular weight determined by the GPC chromatogram, we calculated the ϵ'' curve by

$$\epsilon''(\omega) = \int_{-\infty}^{+\infty} w(M)\epsilon''_Z(M,\omega)\ \mathrm{d}\log M \qquad (6)$$

where ϵ''_Z indicates the ϵ'' curve given by the Zimm theory. Although the Zimm ϵ''_Z curve is close to the Debye equation, we calculated eq 6 by taking up to the first 19th normal modes of the Zimm theory into account. Figure 3 shows three examples of the results.

It is seen that the experimental values are close to the theoretical values indicated by the dashed lines. On the lower frequency side, the experimental values are slightly smaller than the theoretical values. This may be due to an oversubtraction of the contribution of dc conduction.

The results mentioned above strongly indicate that the poly(organophosphazenes) are flexible polymers but have the type A dipole moment. Thus, the present dielectric data suggest that the π electrons on the P=N double bonds are localized.

In principle, the asymmetry of the main chain is a sufficient condition but not a necessary condition for the occurrence of the type A polymer. If all the phenoxy

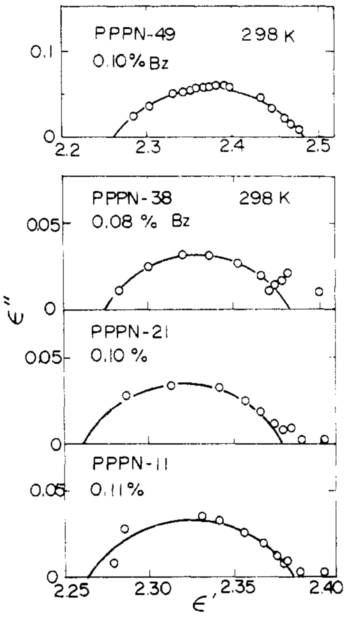

Figure 4. Cole–Cole plots for the representative solutions.

groups orient to the same direction, the polymer could be a type A polymer. However, in our recent study, the side phenoxy groups rotate even in the solid state.[14] Therefore, the possibility of the orientation of all the side groups may be ruled out.

Dielectric Relaxation Strength and Dipole Moment. The dielectric relaxation strengths $\Delta\epsilon$ were determined by Cole–Cole plots and are listed in Table I. Representative Cole–Cole plots are shown in Figure 4. To analyze the data for PPPN and CoPPN together, the values of $\Delta\epsilon$ for the PPPN solutions were reduced to those at 303 K by multiplying them by the temperature ratio 298/303. A double logarithmic plot of $\Delta\epsilon/C$ versus M_w is shown in Figure 5, where C denotes the concentration in unit of polymer weight per unit volume. On the basis of these data, the dipole moment of the PNP chain was estimated as follows.

Generally, the dielectric relaxation strength for the normal mode process is given by[12]

$$\frac{\Delta\epsilon}{C} = \frac{4\pi N_A \mu^2 \langle r^2 \rangle}{3k_B T M} \tag{7}$$

where N_A is the Avogadro constant; μ, the dipole moment per unit contour length of the polymer; and $\langle r^2 \rangle$, the mean-square end-to-end distance. To evaluate μ from $\Delta\epsilon$, we determined $\langle r^2 \rangle$ from $[\eta]$ based on the Flory–Fox equation[17]

$$[\eta] = \Phi \langle r^2 \rangle^{2/3}/M \tag{8}$$

where Φ is the Flory constant, and we put it equal to 2.1 × 10^{21} dL/g. The average value of μ was 2.1 esu. We also calculated the dipole moment per monomer unit to be 6.7 D. This value is 1 order of magnitude larger than the dipole moment of other organic polymers with relatively strong dipole moments.

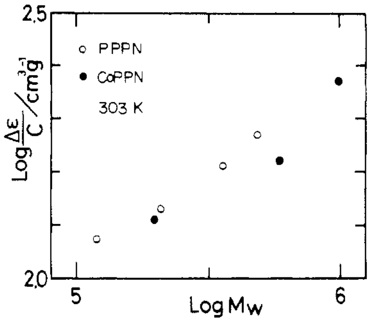

Figure 5. Molecular weight M_w dependence of relaxation strength $\Delta\epsilon$ divided by concentration C.

As is seen from eq 7, the value of $\Delta\epsilon/C$ is proportional to $\langle r^2 \rangle/M$. Thus, the increase in $\Delta\epsilon/C$ with increasing M_w reflects an increase in the dimension due to the excluded-volume effect. The slope of the plot given in Figure 5 is ca. 0.3. This value is larger than the upper limiting value of 0.2.[18] However, since the distribution of molecular weight of the present samples is rather broad, we cannot conclude at the moment that this high value of the exponent is physically meaningful.

Conclusion

Poly(organophosphazenes) exhibit dielectric relaxation depending strongly on the molecular weight. The dielectric relaxation times can be explained in terms of the Zimm theory. Therefore, this polymer has a dipole moment parallel to the chain contour. This suggests the electrons on the P=N double bonds are localized

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