Multiple Dielectric Relaxations in Solid Polyorganophosphazenes

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ABSTRACT: Dielectric properties of solid films of poly(dichloro phosphazene) (PCPN), poly(diphenoxy phosphazene) (PPPN), and poly(difluoroethoxy phosphazene) (PFPN) were studied in the frequency range from 0.1 to 100 kHz. PCPN exhibited only one relaxation peak (named as α process), while PPPN and PFPN exhibited two loss maxima (α and β) in the dielectric loss ε'' curve within the temperature range between 90 and 460 K. The α process for the each sample was seen just above its glass transition temperature T_g, while the β relaxation was observed only for PPPN and PFPN in the region far below their T_g. This result indicates that the β process is due to rotation of the side groups. Based on the simplest two site model, we estimated the amplitude of the rotational oscillation of the side groups and the energy difference between the two sites. Besides these α and β relaxations, PPPN and PFPN showed the mesophase transition at 400 and 345 K, respectively, where the dielectric constant increased step-wise. The dielectric constant in the mesophase was partly attributable to the polarization of the type-A dipoles.

KEY WORDS Polyphosphazene / Poly(organophosphazene) / Poly-(dichloro phosphazene) / Poly(diphenoxy phosphazene) / Poly(difluoroethoxy phosphazene) / Dielectric Relaxation / Primary Process / Side Group / Mesophase / Two-Site Model /

Amorphous polymers exhibit multiple dielectric relaxations since they possess various degrees of freedom for the molecular motions.[1] The processes are usually called α, β, γ, and so on from the one appearing at the highest temperature to those at lower temperatures. We expect that polyorganophosphazene has three types of dipoles being classified by Stockmayer[2] as types A, B, and C. The type-A dipoles correspond to those aligned in the same direction parallel to the chain contour; the type-B, those aligned in the perpendicular direction; and the type-C, those mobile in the side groups.

In our previous study for dilute solutions of poly(diphenoxy phosphazene) (PPPN),[3] we found that PPPN exhibits the dielectric re-laxation conforming to the Zimm theory.[4] This indicates that polyphosphazene has the type-A dipoles whose dipole moment was estimated to be 6.7 D per monomer unit from the relaxation strength. However, in dilute solutions, motions of the type-B and C dipoles could not be observed since the relaxation times were much shorter than the time scale of our experiment. To study the relaxations due to the types B and C dipoles, we have to use either concentrated solutions or bulk films.

At present, a variety of poly(organo phosphazene)s have been synthesized.[5-7] In this study, we carried out dielectric measurement on bulk films of poly(dichloro phosphazene) (PCPN), PPPN, and poly(difluoroethoxy phosphazene) (PFPN). It is obvious

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that PCPN does not possess Type-C dipoles. Therefore, from comparison of the dielectric behavior of PCPN with the other two, we may assign the relaxations due to Type C dipoles in PPPN and PFPN.

Allen et al.[8] reported that PFPN, poly(p-phenylphenoxy phosphazene) and poly(p-chlorophenoxy phosphazene) exhibited two dielectric loss maxima around 250 and 120 K. However, they did not analyse the data in detail and only speculated that the low temperature process was due to Type-C relaxation.

One of the characteristic features of polyphosphazene is that although this polymer has properties of a typical flexible chain in dilute solution,[3,9] it exhibits a mesophase-structure similar to nematic liquid crystals in concentrated solution[10] and in bulk.[5-7,9] In this study, the mobility of the polyphosphazene chains in the mesophase was also analyzed.

EXPERIMENTAL

Samples

PCPN was prepared by thermal ring opening polymerization of cyclo(hexachloro triphosphazene) supplied from Shin-Nisso Chemicals Co., Ltd. The monomer was sealed in a glass ampule together with 2.5% of boron trichloride (BCl_3) in vacuum and allowed to polymerize at 170 to 180 K for ca.100 h. PPPN and PFPN were prepared by substitution of chlorine (Cl) atoms of PCPN with organogroups according to the method reported by Allcock and Kugel.[5] The elemental analysis of PPPN indicated that substitution reaction was almost perfect and the remaining Cl atoms were only 1.3 mol%. The elemental analysis of Cl for PFPN was not successful due to fluorine atoms. However, we estimated the Cl content to be ca. 1% from the carbon content. The weight average molecular weight $\bar{M}_w$ and the ratio of $\bar{M}_w$ to the number average molecular weight $\bar{M}_n$ of PPPN was determined to be

5×10^5 and 2.5 by gel permeation chromatography combined with low-angle light scattering photometry. We did not measure $\bar{M}_w$ of PCPN and PFPN. However, we expect that they also have the values of $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ similar to PPPN since the PPPN and PFPN samples were prepared from the same PCPN.

Films of PPPN and PFPN for dielectric measurement were prepared by compression molding at 400 and 340 K, respectively. The crystallinity of the films thus prepared was measured as follows.

For the PPPN film, a density method was employed. The density of the film and that of an almost perfectly amorphous PPPN containing 5% unsubstituted chlorine were measured by a density gradient method at 25°C using aqueous solutions of zinc chloride as gradient forming liquids. The latter being determined to be 1.237 $g \, cm^{-3}$ was assumed to be the density of 100% amorphous PPPN. The crystalline density was estimated from the X-ray crystallographic data given by Stroh.[11]

The crystallinity of PFPN was determined from the heat of the mesophase transition using the heat of transition reported by Schneider et al.[7]

The crystallinity of PCPN was determined from the jump of the heat capacity ΔC_p at the glass transition temperature with a differential scanning calorimeter (DSC) (Rigaku Denki model 8055 and 8058). We determined the value of ΔC_p for a perfectly amorphous PCPN from ΔC_p measurement of a specimen after directly immersing it into liquid nitrogen.

The glass transition temperatures of the films were also determined with DSC. The results of the characterization were summarized in Table I.

Dielectric measurement was carried out with a capacitance bridge (General Radio 1615-A) and an automatic bridge (Yokogawa-Hewlett-Packard 4270A). Films of PPPN and PFPN for dielectric measurement were coated with evapolated gold to achieve tight contact between the films and the electrodes. The diam-

Table I. Density ρ, crystallinity χ, glass transition temperature T_g, mesophase transition temperature T_1 and melting temperature T_m of the sample films

Sample	ρ	χ	T_g	T_1	T_m
	g cm^{-3}	%	K	K	K
PCPN	1.855	66	211	—	298
PPPN[a]	1.351	61	263	400	620
PFPN	1.475	78	233	347	513

[a] $\bar{M}_w = 5 \times 10^5$; $\bar{M}_w/\bar{M}_n = 2.5$ by LALS-GPC.

eter and thickness of the films were 50 mm and 0.5 mm, respectively. Since the PCPN sample was soft, it was cast from a benzene solution in a cell type electrode, and then sandwitched with another electrode. The distance between the electrodes was controlled with a glass spacer.

RESULTS AND DISCUSSION

Dielectric Relaxations in PCPN, PPPN, and PFPN

Temperature dependences of the dielectric constant ε' and loss factor ε'' for PCPN, PPPN, and PFPN are shown in Figures 1—3, respectively.

For PCPN, we see a loss maximum in the temperature range from 220 to 260 K. Since the glass transition temperature of this polymer was observed around 211 K by DSC, we assigned this relaxation to the primary α process (glass transition process) due to the motion of Type-B dipoles. As seen in Figure 1, no secondary (β) process was found in the range below 200 K. PCPN exhibited high direct current (d.c.) conductivity in the temperature range above 250 K. This is probably due to impurity ions such as Cl$^-$ produced by degradation of the polymer or the monomer. The increase in ε' of PCPN in the temperature range above 270 K is partly due to the fusion of the crystalline part and partly due to interfacial polarization of the sample around the
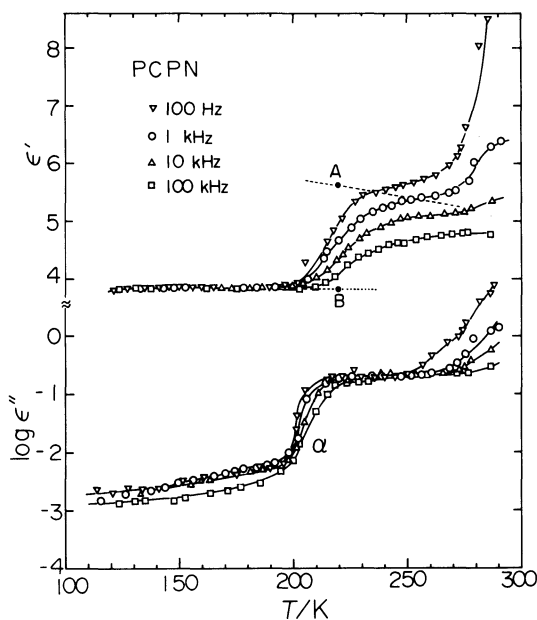

Figure 1. Temperature dependence of the dielectric constant ε' and loss ε'' for poly(dichloro phosphazene).

electrodes.

As shown in Figure 2, the ionic conductivity in PPPN was lower than that in PCPN. Thus, we could extend temperature range of measurement up to 460 K for this polymer. Around 280 K, we observed a clear loss maximum. We named this process the α process. As in the case of PCPN, we assigned this loss maximum to the relaxation of type-B dipoles in the amorphous region of the sample, since the T_g of PPPN was observed around 263 K by DSC. In the low temperature region below 200 K, we see another small loss maximum. This secondary relaxation process was termed as the β process. It is seen that at the mesophase transition point T_1 ($= 400$ K), both ε' and ε'' of PPPN increased suddenly. This indicates that the PPPN chains in the mesophase become more mobile than in the low temperature phase as discussed in the later section.

As seen in Figure 3, the ε' and ε'' curves for PFPN are similar to those for PPPN. Since the T_g of PFPN was 233 K, we assigned the loss

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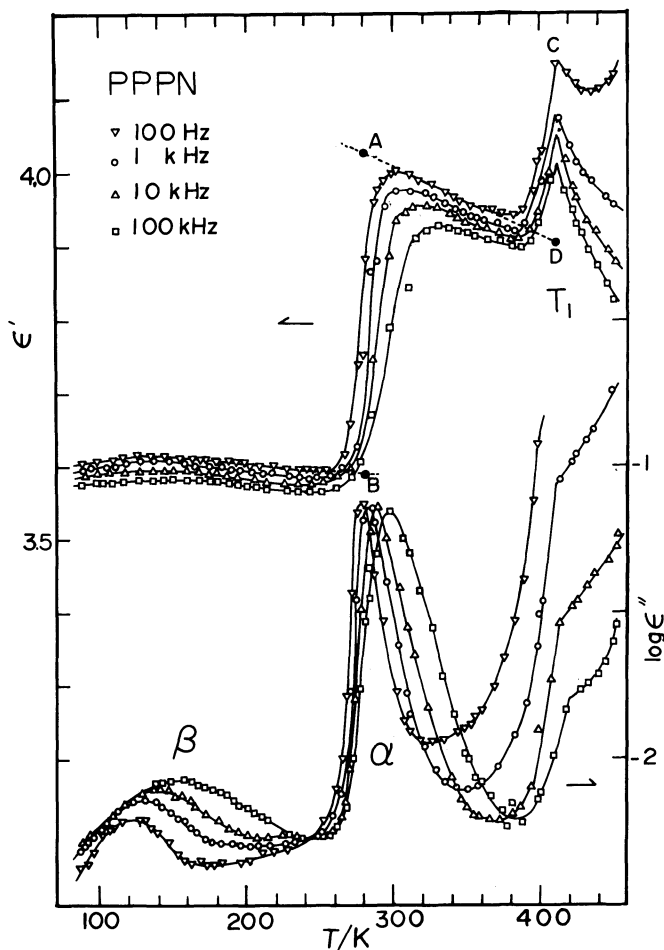
Figure 2. Temperature dependence of ε' and ε'' for poly(diphenoxy phosphazene).

maximum around 230 K to the primary α process and the loss around 120 K to the β process. A sudden increase in ε' and ε'' is also seen at T_1 ($= 347$ K).

Generally, three molecular mechanisms for the secondary process are known: the local vibrational motion of the type B dipole, the rotation of the side group, and the motion of the main chains or the side groups in the defects of the crystalline part. Since the β process was seen only in PPPN and PFPN but not in PCPN which does not possess the type-C dipole, we may assign the β process to rotation of the side groups.

Plots of the loss maximum frequency f_m against the inverse of temperature for PCPN, PPPN, and PFPN are shown in Figure 4. It is known that the relaxation time for the primary process conforms to Vogel–Tamman equation.[1] We also see this trend for the α processes of these samples. However, in our frequency range from 0.1 to 100 kHz, the Arrhenius plots are almost linear as shown in Figure 4. Therefore, we determined the activation energy for the α process assuming the plots are linear. The results are listed in Table II. The Arrhenius plots for the β process for PPPN and PFPN also deviated from the linear re-
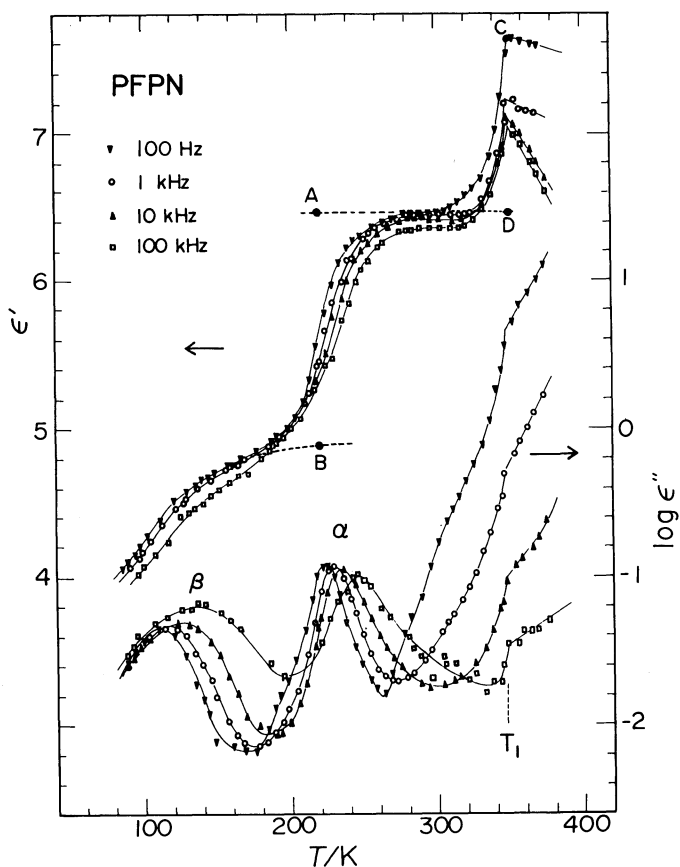
Figure 3. Temperature dependence of ε' and ε'' for poly(difluoroethoxy phosphazene).
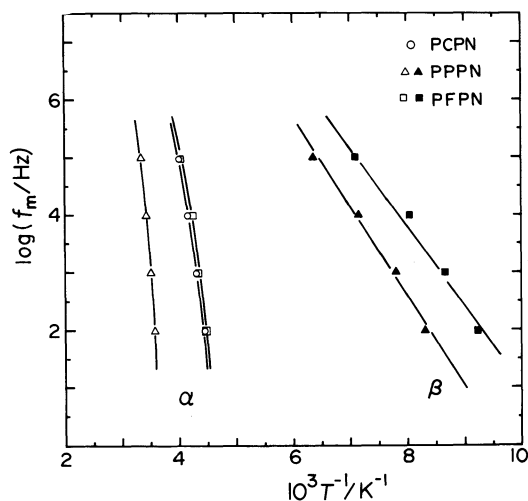

Figure 4. Transition map for PCPN, PPPN, and PFPN. The open and closed symbols represent the α and β processes, respectively.

lation. We determined the activation energy by drawing straight lines as shown in Figure 4. The results are also shown in Table II.

We found that PPPN and PFPN exhibit both the type B and C relaxations. As reported previously,[3] PPPN exhibited the type-A relaxation in dilute solutions. Thus, we conclude that polyorganophosphazene having the type C dipole is classified as a type-ABC polymer.

The α Process

The relaxation strengths $\Delta\varepsilon_\alpha$ for the α process of PCPN, PPPN, and PFPN were determined from the jump of the ε' curve. The dotted lines in Figures 1—3 indicate the extrapolation of the ε' curves above and below the α relaxation region. We determined the values of $\Delta\varepsilon_\alpha$ from

Table II. Dielectric properties of polyphosphazene

Sample	$10^{-2}\,T\Delta\varepsilon_\alpha$ K	μ_B D	E_B kJ mol^{-1}	μ_C D	E_a kJ mol^{-1}	U kJ mol^{-1}	ϕ deg
		α process			β process		
PCPN	4.0[a]	0.98	100	—	—	—	—
PPPN	1.23	0.90	140	0.40[b]	29.9	2.8	33
PFPN	3.5	1.59	160	0.59[c,d]	25.9	3.1	38

[a] The experimental uncertainty is ± 1.2.
[b] at 127 K.
[c] at 142 K.
[d] Debye Cm $= 3.333 \times 10^{-30}$

the difference between the points A and B in these figures. For PCPN, this method gave an ambiguous value since the tail of the relaxation process existing in high temperatures overlaps with the α process. The error in determination of $\Delta\varepsilon$ for PCPN was estimated to be *ca.* 30%. Since $\Delta\varepsilon_\alpha$ is approximately proportional to T^{-1}, the values of $T\Delta\varepsilon$ are listed in Table II. We apply the Onsager theory to calculate the effective dipole moment μ per monomer unit:[12]

$$\Delta\varepsilon = \frac{4\pi N \mu^2 \varepsilon_0 (\varepsilon_\infty + 2)^2}{9 k_\mathrm{B} T (2\varepsilon_0 + \varepsilon_\infty)} \quad (1)$$

where N is the number of the dipoles in unit volume of the amorphous part; ε_0, the relaxed dielectric constant; ε_∞, the unrelaxed dielectric constant; and $k_\mathrm{B}T$, the thermal energy. Assuming that the B dipoles in the amorphous region are effective for the α relaxation, we calculated N with χ given in Table I. The effective dipole moments μ_B for the α process thus determined are listed in Table II.

The molecular structure of polyphosphazene with Cl and O–R group is shown in Figure 5, where R represents phenyl and alkyl groups. The perpendicular dipole moment μ_+ of the monomer unit of PCPN should be equal to the vector sum of the bond moments μ for the P–Cl, P=N, and P–N bonds. The P–Cl bond moment μ(P–Cl) was reported to be

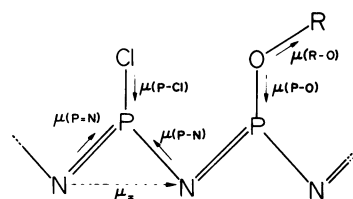**Figure 5.** Analysis of the dipole moment of polyphosphazene.

0.8 D,[13] but the values of the P=N and P–N bond moments (μ(P–N)) are not reported. The parallel component $\mu_=$ of the dipole moment per monomer unit is also given by the vector sum as shown in Figure 5. It is noted that the Cl–P (or P–O) bond is out of the N–P–N plane. If we assume that the P atom is positively charged since electro-negativity of N is higher than P, $\mu_=$ and μ_+ may be given by

$$\mu_= = [\mu(\mathrm{P}=\mathrm{N}) - \mu(\mathrm{P}-\mathrm{N})]\sin(\theta/2) \quad (2)$$

$$\mu_+ = [\mu(\mathrm{P}=\mathrm{N}) - \mu(\mathrm{P}-\mathrm{N})]\cos(\theta/2)$$
$$- 2\,\mu(\mathrm{P}-\mathrm{Cl})\cdot\cos(\psi/2) \quad (3)$$

where θ and ψ denote the N=P–N and Cl–P–Cl angles, and were reported to be 115° and 99°, respectively, by Chatani and Yatsuyanagi.[14] Previously we determined $\mu_=$ to be 6.7 D.[3] Using these values of $\mu_=$ and μ(P–Cl), we estimated μ_+ to be 3.2 D.

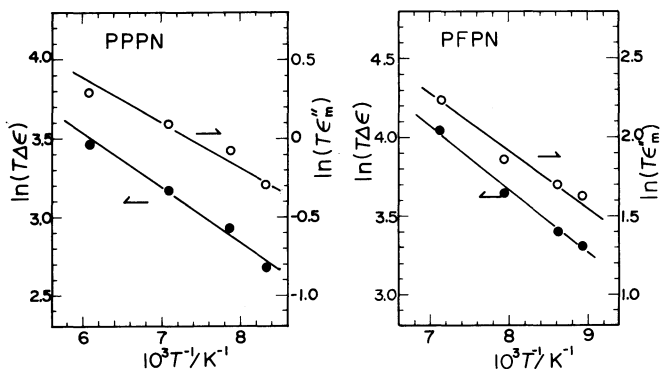It is known that the segmental motion is associated with a co-operative motion of a unit

Figure 6. Temperature dependence of the relaxation strength $\Delta\varepsilon_C$ and maximum value ε_m'' of the loss factor for the β processes of PFPN and PPPN.

composed of several numbers of the perpendicular dipoles. Thus, it is not surprising even if the observed μ_B does not coincide with μ_+. According to the Kirkwood theory,[15] μ_B^2 is equal to $g\mu_+^2$, where g is the factor representing an orientational correlation among the dipole moments in the co-operative motional unit. From the above results, g becomes 0.10 indicating a stronger trend toward antiparallel orientation of the type-B dipoles than ordinary organic polymers whose g is ca. 0.4.[16]

For the analysis of PPPN and PFPN, we need the value of the P–O bond moment μ(P–O), which, however, has not been reported. Therefore, we estimated the perpendicular dipole moment to be 2.85 and 5.02 D for PPPN and PFPN, respectively, assuming that the g factor for PPPN and PFPN is 0.10.

The β Relaxation

The relaxation strength $\Delta\varepsilon_C$ for the β process was determined from the area of the ε'' vs. $1/T$ curve using the following relation:

$$\Delta\varepsilon_C = (2E_a/\pi R) \int_0^\infty \varepsilon'' d(1/T). \qquad (4)$$

We assumed that the $\Delta\varepsilon_C$ thus determined corresponds to the value at the loss maximum temperature T_{max}. The results are shown in Figure 6. From this data the effective dipole moment μ_C for the β process was calculated
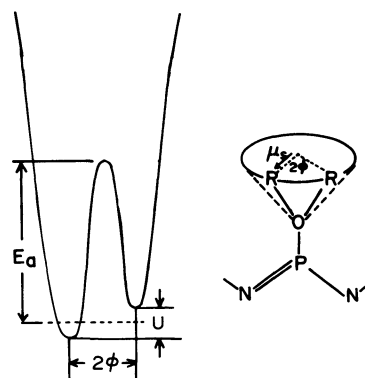

Figure 7. Two-site model for the rotation of the side group of polyorganophosphazene.

with eq 1.

In order to estimate the strength of restriction for motion of the side group, we employ a two-site model[1,17] as illustrated in Figure 7. Since we have no knowledge on the number of the sites in the real systems, the energy difference U and the amplitude ϕ of the oscillation of the side group thus estimated give only rough measure of the restriction. More detailed information will be obtained by calculation of the potential energy as a function of the angle for the internal rotation.[18,19]

The energy barrier E_a in the model is determined from the activation energy for the β process and given in Table II. The effective dipole moment μ_C is given by

$$\mu_C^2 = 4K(\mu_s \sin \phi)^2/(1+K)^2 \qquad (5)$$

$$K = \exp(-U/k_B T) \qquad (6)$$

where μ_s is the dipole moment of the side group projected on the plane perpendicular to the rotational axis (see Figure 7).

First we determined U. The increase of $T\Delta\varepsilon_C$ with increasing temperature reflects the increase of K. If U is large compared with $k_B T$, eq 1, 5, and 6 predict that logarithm of $T\Delta\varepsilon_C$ is proportional to $-U/k_B T$. This relation was tested in Figure 6 for PPPN and PFPN. In the determination of $\Delta\varepsilon$ from the area of the loss curve, there were ambiguities since the loss curve for the β process was very broad and partly overlapped with the loss due to the α process. Thus, we also attemped to determine U assuming that the maximum value ε_m'' of the loss is proportional to the $\Delta\varepsilon_C$. The plots of ln $T\varepsilon_m''$ vs. $1/T$ is also shown in Figure 6. We see that the U values determined from the two plots are almost similar. The average of the values of U determined by the two methods is given in Table II.

The group moment for phenyl–OCH_3 is reported to be 1.28 D.[20] Thus, we estimated the phenyl–OP bonds of PPPN to be 1.3 D. Using this value and the C–O–P angle of 126°, μ_s for PPPN was estimated to be 1.1 D. On the other hand, estimation of μ_s for PFPN is more difficult than for PPPN since the side group has two degrees of freedom: the rotation around P–O axis and that around CF_3CH_2–O axis. If the rotation around P–O bond is assumed, μ_s becomes 1.1 D since the moment for alkyl–O bond is reported to be 1.28 D.[20] If rotation of CF_3 group is dominant, μ_s becomes 2.2 D from the reported CF_3–CH_2 bond moment of 2.32 D.[20] Using these values of U and μ_s estimated above, we calculated ϕ with eq 5 and 6. For PFPN, $\mu_s = 1.1$ and 2.2 led sin $\phi > 1$ and $\phi = 38°$, respectively. Thus, we adopted the latter value.

Dielectric Behavior in the Mesophase

The jump of ε' at T_1, i.e., the difference of ε' for the points C and D in Figures 2 and 3 may be ascribed to the two mechanisms: One is the onset of a new relaxation process named as the α' process and the other is that the immobilized dipoles in the crystalline phase become mobile by the mesophase transition.

Above T_1, ε' of PPPN at 100 Hz increased with increasing temperature. This indicates that there exists a relaxation process in high temperature region. As reported previously,[3] the normal mode process due to the type-A dipole of PPPN was observed in dilute solutions at 303 K. We expect that in the bulk state, the relaxation time for the type-A dipole becomes much longer than in solution due to entanglement and the increase in the friction coefficient. Hence the relaxation of the type-A dipole is expected to occur at very high temperature. We may ascribe the α' process to the normal mode process.

The jump of ε' at T_1 for the ε' curve at 100 kHz may be due to the release of the dipole in the crystalline part, since the contribution of the type-A dipole is still very small at high frequency. If we assume that the content of the amorphous part does not change by the transition, then the increase in ε' should be ascribed to the orientational polarization in the liquid-crystalline part. Thus, the jump of ε' at T_1 at 100 kHz may be given by

$$\varepsilon'(\text{above } T_1) - \varepsilon'(\text{below } T_1) = \chi\Delta\varepsilon_{\text{meso}} \qquad (8)$$

where $\Delta\varepsilon_{\text{meso}}$ is the total relaxation strength in the perfectly pure mesophase.

We estimated $\Delta\varepsilon_{\text{meso}}$ in PFPN and PPPN to be 11 and 2.9, respectively, assuming that the types B and C dipoles can move freely in the mesophase. The value of $\chi\Delta\varepsilon_{\text{meso}}$ thus calculated by eq 8 is much larger than the observed jump of the ε' which is equal to 0.7 and 0.13 for PFPN and PPPN, respectively. Accordingly the above result indicates that the motion of the dipoles in the mesophase is still restricted strongly. It seems to be reasonable to

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consider that in the mesophase the type-B dipole does not contribute to polarization since the chain has a extended structure in which the type-B dipoles cancel each other. If we assume that only the type-C dipole rotate freely, the theoretical value is still higher than the observed jump of ε'. Thus, we conclude that the type-C dipoles in the mesophase rotate under a constraint.

CONCLUSION

(1) Poly(organophosphazene) exhibits the type-B and type-C relaxations in the solid state. Since it also exhibits the type-A relaxation in dilute solution, this polymer is classified as a type ABC polymer.

(2) The β relaxation in PPPN and PFPN is due to the relaxation of the type C dipoles on the side group.

(3) In the mesophase of PPPN and PFPN, the motion of the side group and the type-B dipoles are restricted.

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