Polymer Vol. 36 No. 4, pp. 713–718, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/95/$10.00+0.00

The synthesis of phosphinylphosphorimidic hydroxyethyl acrylate and the electrical properties of its polymer produced by ultraviolet-irradiation-induced polymerization

Toyoaki Kimura* **and Meisetsu Kajiwara**
Department of Applied Chemistry, School of Engineering, Nagoya, University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan
(Received 10 September 1993; revised 17 June 1994)

We have replaced the five Cl atoms in dichlorophosphinylphosphorimidic trichloride with oxyethylene acrylate groups. The monomers obtained were polymerized by taking advantage of the double bonds of the acrylic groups. This was done by ultraviolet irradiation in the presence of a sensitizer. It is found from Fourier transform infra-red, ^{1}H and ^{31}P nuclear magnetic resonance spectroscopy and elemental analysis that the obtained substance is the expected one: a new partly inorganic polymer. Volume resistance, dielectric constant and dielectric loss factor were measured over the temperature range from −10 to +70°C and compared with those of other phosphazene polymers together with poly(2-hydroxyethyl acrylate). The result seems to show a relation between dielectric properties and hardness of these polymers. In the present polymer system, anomalous dielectric properties were observed for quick-cooled samples. This anomaly is tentatively explained in terms of -OH dipoles frozen in a metastable state in the polymer.

(Keywords: phosphorus polymer; synthesis; dielectric behaviour)

INTRODUCTION

It is known that phosphorus and nitrogen compounds are effective flame retardants for fibre materials[1]. In this sense phosphazene polymers, $[-P{=}N-]_n$, are essentially non-flammable materials. As a phosphazene polymer, poly(dichlorophosphazene) has been known for a long time[2,3]. Allcock and Kugel have reported that the Cl atoms of poly(dichlorophosphazene) can be replaced by many organic groups[4], which has led to the application of phosphazene polymers in industry.

At present, two types of phosphazene polymers are well known: One type is linear phosphazene polymers, with two organic groups on the P atoms, $[-P(R_1,R_2){=}N-]_n$. The other type is cyclotriphosphazene compounds, with two organic groups on the P atoms, at least one of which possesses a C=C bond by which polymerization proceeds. As for the starting material of linear polyphosphazene, poly(dichlorophosphazene) is synthesized by heating of cyclotri(dichlorophosphazene)[2] or dichlorophosphinylphosphorimidic trichloride (DPPIT)[5], the synthesis of which has been reported by Kahler *et al.*[6]

Hitherto, no attempt has been made to obtain a monomer by replacing the Cl atoms of DPPIT with organic groups in which C=C double bonds are included and to polymerize the monomers by making use of the double bonds. Therefore, we have replaced the five Cl atoms of a DPPIT molecule with oxyethylene acrylate groups and obtained a new polymer by u.v. irradiation in the presence of a sensitizer. Here we will designate the monomer and the polymer as PPI-OEA monomer and PPI-OEA polymer, respectively. One reason that we are interested in this polymer is as follows. We have measured the volume resistance and dielectric constant of the matrix polymer obtained from cyclotri(trifluoroethoxy oxyethylene acrylate)phosphazene (PNF) and compared them with those of the matrix polymer of cyclotri(dioxyethylene methacrylate)phosphazene (PPZ) (the structure of the monomer is shown in *Figure 9*). The former, which has three acrylate parts for crosslinking in one monomer unit, is a rubbery substance and shows higher dielectric constant and lower volume resistance, whereas the latter, which has six acrylate parts for crosslinking, is very hard and shows lower dielectric constant and higher volume resistance. The polymer in this work has five acrylate parts for crosslinking in one monomer unit. From this point of view it is interesting to investigate the electrical properties of this polymer. We have performed elemental analysis, *FT*i.r., ^{1}H n.m.r. and ^{31}P n.m.r. measurements for the monomer. T.g. and d.t.a. measurements were made together with *FT*i.r. measurements for the polymer. Volume resistance, dielectric constant and dielectric loss factor were measured for the polymer, and these values are compared with those of other phosphazene polymers reported.

---

*To whom correspondence should be addressed

EXPERIMENTAL

Materials

Chlorobenzene, ammonium sulfate, triethylamine and tetrahydrofuran (THF) were Nakarai Tesque guaranteed reagents. Phosphorus pentachloride was obtained from Nakarai Tesque (CP reagent). 2-Hydroxyethyl acrylate (HEA) was Tokyo Kasei extra-pure-grade reagent. The sensitizer for u.v. polymerization was 2-hydroxycyclohexylphenylketone (Irgacure 184, Ciba Geigy).

Synthesis of DPPIT

We have used the method of Emsley[7] because of the high yield of product. Phosphorus pentachloride (83.2 g, 0.4 mol) and ammonium sulfate (13.2 g, 0.1 mol) were put into chlorobenzene (300 ml) in a flask with a condenser. The mixture in the flask was refluxed at 132°C for 2 h. After cooling the flask the contents were filtered to remove unreacted ammonium sulfate. Chlorobenzene in the filtrate was removed in a rotary evaporator and a yellow oily substance was obtained. This substance was refined by distillation at 110–115°C and 0.1 mmHg. The distillation was repeated several times and DPPIT was thus obtained. We designate this refined substance as product **I**.

Synthesis of PPI–OEA monomer and polymerization

DPPIT (5 g) was dissolved in benzene (100 ml) in a flask. HEA (12 g) and triethylamine (10 g) were dissolved in benzene (100 ml), and this solution in a titration flask was added to the DPPIT–benzene solution with mixing. After the addition the solution was kept mixing at room temperature in the dark for 24 h. The triethylamine reacted with HCl (byproduct) to form a complex, which precipitated in the solution. The solution was filtered to take off the triethylamine–HCl complex. The amount of the complex was weighed, and it was confirmed that the five Cl atoms in a DPPIT molecule were replaced by oxyethylene acrylate groups. The filtrate was washed several times with water in a separating flask, dried over sodium sulfate and a clear liquid was obtained after removing benzene by distillation. The liquid product was refined by a liquid chromatograph using a silica gel column and benzene/ethyl acetate mixture (6/1) as a developer. We designate this refined product as product **II**.

PPI–OEA polymer was obtained by u.v. irradiation with a high-pressure mercury lamp (260 W) for 3 min at a position 30 cm from the lamp. In this case 2 wt% 2-hydroxycyclohexylphenylketone was added to PPI–OEA monomer as a sensitizer. We designate the substance obtained as product **III**.

Measurement of dielectric constant and resistance

A PPI–OEA sample was formed into a disc shape (diameter, 30 mm; thickness, 0.3 mm). Electrodes were made by p.v.d. (physical vapour deposition) of Au on the top and bottom surfaces. Dielectric constant, dielectric loss factor and resistance were measured with an impedance meter (Mitamusen D-51S or 12K). D.c. resistance was measured with a digital multimeter (Advantest TR6848). Measurements were always performed in an air bath (Yamato Coolnics CRT-520), the inside of which was kept dry with silica gel.

Analysis of DPPIT, PPI–OEA monomer and polymer

I.r. absorption measurements were performed with an *FT*i.r. spectrophotometer (Nicolet 5DX). ^{1}H n.m.r. and ^{31}P n.m.r. spectra were taken with an n.m.r. spectrometer (JEOL JNM-GX270) at 100 MHz. Elemental analysis was made with an elemental analyser (Perkin Elmer 2400SCHN). T.g. and d.t.a. were measured using a Daini Seikosha SSC/560GH under the condition of flowing air.

RESULTS AND DISCUSSION

DPPIT and the PPI–OEA monomer

The liquid product **I**, obtained from the reaction of PCl_5 and $(NH_4)_2SO_4$, was crystallized at 0°C. The ^{31}P n.m.r. spectrum was taken for this crystal part, and a similar result was obtained as that by Hellioui[5]. The *FT*i.r. spectrum and the elemental analysis gave similar results to those obtained by Emsley[7]. Therefore, product **I** can be assigned as the product of reaction (1):

$$PCl_5 + (NH_4)_2SO_4 \rightarrow \underset{\mathbf{I}}{Cl_3P{=}NP(O)Cl_2} \qquad (1)$$

The result of the elemental analysis of product **II**, obtained from the reaction of DPPIT with HEA, is given in *Table 1*. Data on density and refractive index of product **II** are shown in *Table 2* together with those of HEA. The *FT*i.r. spectrum of product **II** is shown in *Figure 1*, where

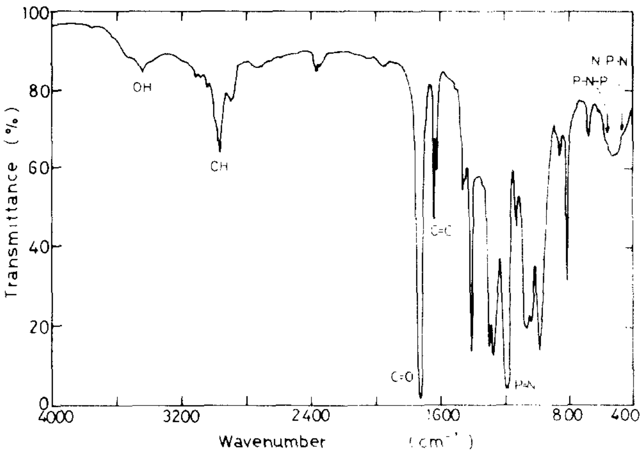


Figure 1 *FT*i.r. spectrum of the reaction product of DPPIT with HEA (product **II**)

Table 1 Elemental analysis of product **II** (PPI–OEA monomer)

	Calculated[a] (wt%)	Experimental (wt%)
C	45.07	44.86
H	5.26	5.61
N	2.10	1.95

[a] Calculated from the structure

$(CH_2{=}CHCOOCH_2CH_2O)_3P{=}NP(O)(OCH_2CH_2COOCH{=}CH_2)_2$

Table 2 Refractive indices and densities of product **II** (PPI–OEA monomer) and 2-hydroxyethyl acrylate (HEA)

	HEA	Product **II**
Density ($g\ cm^{-3}$)	1.06	1.551
Refractive index	1.4500	1.4728

the absorptions of C=O, -P=N-, -P-N-P-, -N-P-N and $-C=CH_2$ are observable. No sharp absorption at $\sim 500\,cm^{-1}$, which corresponds to P-Cl, is observed, implying that the Cl atoms in DPPIT are replaced by oxyethylene acrylate groups. The ^1H n.m.r. spectrum is shown in *Figure 2*. A peak is observed at 4.3 ppm, which can be ascribed to $-CH_2CH_2-$. Let us designate the three protons of $H_2C=CH-$ as $H_aH_bC=CH_c-$. Then the three groups of peaks at 5.8, 6.1 and 6.4 ppm are ascribed to H_a, H_c and H_b, respectively. The ratio of the areas of the peaks at 6.4, 6.1, 5.8 and 4.3 ppm is 1:1:1:4, reflecting the numbers of protons H_b, H_c, H_a and $-CH_2CH_2-$. The ^{31}P n.m.r. spectrum is shown in *Figure 3*. Hellioui *et al.*[5] have reported that peaks around −12 ppm are ascribable to $P(O)Cl_2$ and those around 0 ppm to $=PCl_3$. Therefore, peaks around −3 to 0 ppm and −14 to −12 ppm can be ascribed to $-P(OEA)_3$ and $-P(O)(OEA)_2$.

Data from elemental analysis, *FT*i.r., ^1H n.m.r. and ^{31}P n.m.r. support the following mechanism for the formation of product **II** (PPI-OEA monomer):

$$Cl_3P=N-P(O)Cl_2 + 5HOCH_2CH_2COOCH=CH_2 \rightarrow$$
$$(H_2C=CHCOOCH_2CH_2O)_3P=N-P(O)(OCH_2CH_2COOCH=CH_2)_2 + 5HCl \qquad (2)$$

II

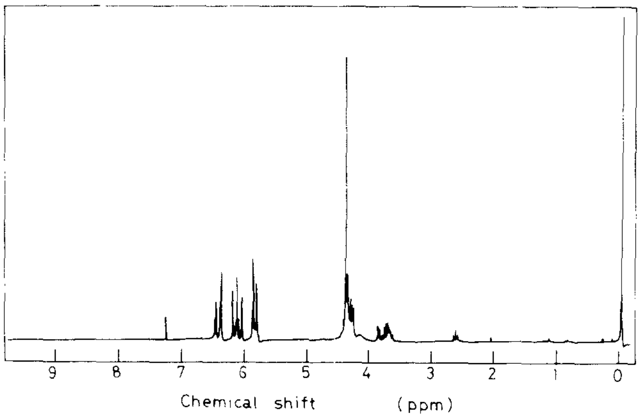


Figure 2 ^1H n.m.r. spectrum of the reaction product of DPPIT with HEA (product **II**)

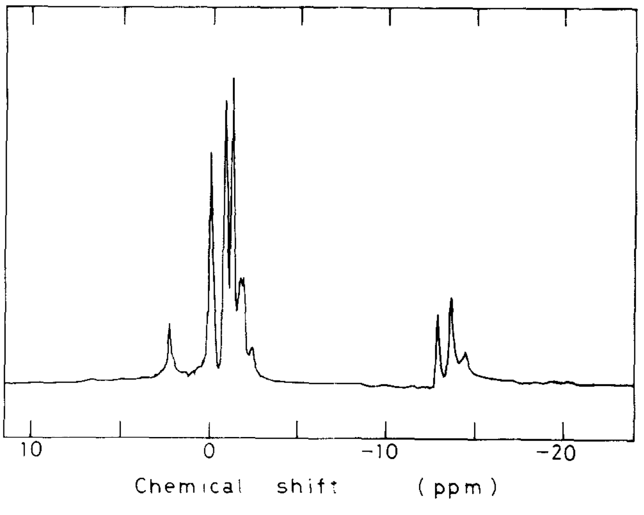


Figure 3 ^{31}P n.m.r. spectrum of the reaction product of DPPIT with HEA (product **II**)

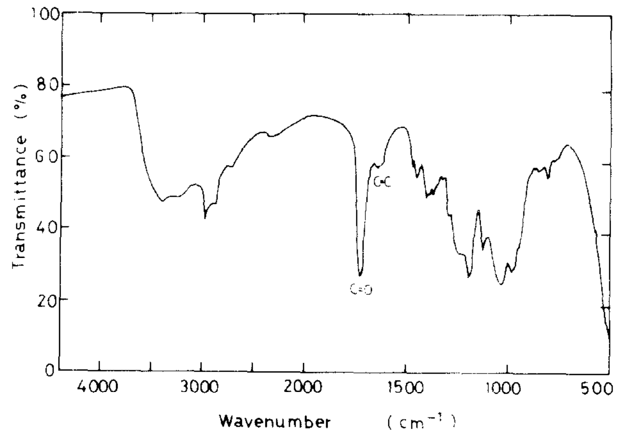


Figure 4 *FT*i.r. spectrum of the PPI-OEA polymer (product **III**) obtained by u.v. irradiation of product **II**

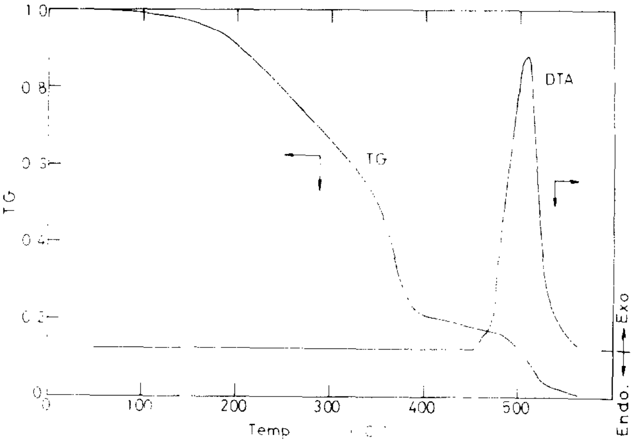
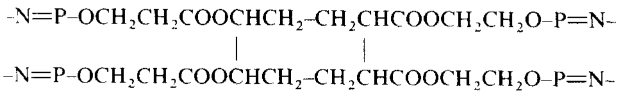


Figure 5 T.g. and d.t.a. trace of the PPI-OEA polymer

As already described, HCl can be removed with triethylamine.

The PPI-OEA polymer

PPI-OEA polymer film was obtained by u.v. irradiation of PPI-OEA monomer with the addition of a sensitizer. The *FT*i.r. spectrum of the film is shown in *Figure 4*. The absorption at $1640\,cm^{-1}$ is markedly lower than that in *Figure 1*, indicating that the C=C double bonds of acrylic groups are consumed by the u.v.-induced polymerization. This can also be confirmed by the fact that the film obtained is insoluble in benzene and THF. Therefore, the film has a crosslinked structure such as:



$$\begin{array}{c} -N=P-OCH_2CH_2COOCHCH_2-CH_2CHCOOCH_2CH_2O-P=N- \\ \qquad\qquad | \qquad\qquad\quad | \\ -N=P-OCH_2CH_2COOCHCH_2-CH_2CHCOOCH_2CH_2O-P=N- \end{array}$$

III

Thermogravimetry (t.g.) and differential thermal analysis (d.t.a.) were carried out on the PPI-OEA polymer and the results are given in *Figure 5*. The t.g. curve starts to decrease around 100°C. A sharp decrease appears around 200°C followed by a much sharper one around 350°C. As is seen in the structure **II**, five acrylate units are involved in one monomer unit. The t.g. value (the weight fraction of the polymer remaining) at 350°C is 0.50, as seen in *Figure 5*. This is nearly equivalent to the case in which three acrylate units in one monomer are lost by thermal decomposition, where the t.g. value is given as 0.48. At 490°C the t.g. value is 0.15, which is roughly equivalent to the thermal decomposition of five acrylate units (t.g. = 0.14). At 400°C, where the decay of the t.g. curve becomes much less steep, the t.g. value is 0.21, roughly corresponding to the loss of 4.5 units of acrylate (t.g. = 0.22). At 570°C there remained only a small amount of ash.

The d.t.a. curve shows one endothermic peak at 510°C. This should be due to combustion of PPI–OEA polymer.

Volume resistance of the PPI–OEA polymer

Measurements of the volume resistance were made for the PPI–OEA polymer that was subjected to various cooling treatments. The results are shown in *Figure 6*. In the case of a quick cool (○), the sample was cooled to −10°C and then the measurement was performed from −10°C with increasing temperature. It is seen in *Figure 6* that resistance decreases with increasing temperature from −10°C, shows a minimum at 16–17°C and then tends to decrease again at temperatures higher than the maximum at ~40°C. On the other hand, when the measurement was done with increasing temperature from 26.5°C, the resistance decreases monotonically with increasing temperature (□). In the case of a slow cool the measurement was done with decreasing temperature until −10°C and then with increasing temperature (▽). In this case the minimum value of the resistance is much higher than that of the quick-cooled sample. Finally the quick-cool treatment was repeated again (△) and the result was similar to that of the previous quick-cooled sample (○).

It is obvious from *Figure 6* that the values of resistance in the temperature range from 20 to −10°C depend on the cooling treatments. In the case of the quick cool, resistance shows a minimum at 16–17°C. On the other hand, it is expected that resistance decreases monotonically with increasing temperature if the cooling rate is slow enough.

Dielectric constant of the PPI–OEA polymer

Dielectric constants (ε_r') measured at 120 Hz are shown in *Figure 7* for the sample that was subjected to the same cooling treatments as for the measurement of volume resistance. In the case of the quick cool (○), the measurement was done with increasing temperature from −10°C, and a peak is observed as shown in *Figure 7*. In the cases of no cool (□) and slow-cool treatment (▽), no peak was observed. A peak is seen for the sample that was quick-cooled again (△). Thus, as is seen in *Figure 7*, the quick cool causes an anomalous peak in the dielectric constant–temperature curve, whereas a monotonic increase in dielectric constant can be seen for the slow-cooled sample if the cooling rate is slow enough.

Dielectric constants were measured for the quick-cooled sample using various frequencies. It is found that the size of the anomalous peak is higher when the frequency is lower. It is expected that the anomalous peak in the dielectric constant should disappear if higher frequencies are used. Regardless of frequency, it is expected that the anomalous peak disappars if the cooling rate is slow enough.

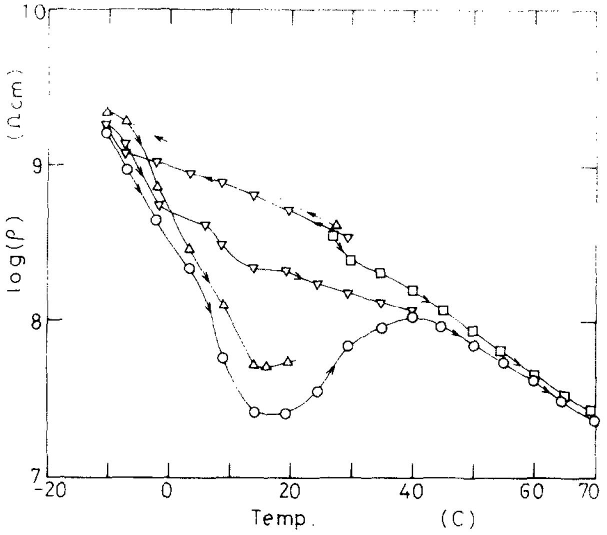


Figure 6 Logarithm of volume resistance of the PPI–OEA polymer vs. temperature: (○) quick cool; (□) without cool; (▽) slow cool; (△) quick cool (second)

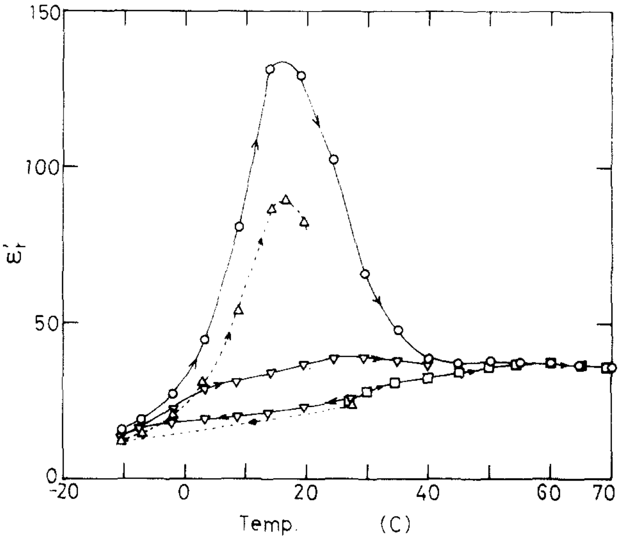


Figure 7 Dielectric constant of the PPI–OEA polymer vs. temperature: (○) quick cool; (□) without cool; (▽) slow cool; (△) quick cool (second)

Dielectric loss factor in the PPI–OEA polymer

Dieletric loss factors (ε_r'') of the PPI–OEA polymer were measured at 120 Hz for the sample subjected to those treatments described above and the results are shown in *Figure 8*. Similar results are obtained to those in *Figure 7*. Dielectric loss factors were measured at several frequencies for the sample subjected to the quick cool. It is also found that the size of the ε_r'' peak is higher when measured at lower frequencies. As is the case for the dielectric constant, dielectric loss factors are expected to increase monotonically if the cooling rate is slow enough.

Comparison of volume resistance and dielectric constant of the PPI–OEA polymer with those of other phosphazene polymers

Some phosphazene polymers with acrylate groups on the P atoms are known[8]. This, it would be interesting to compare the electrical properties of these polymers

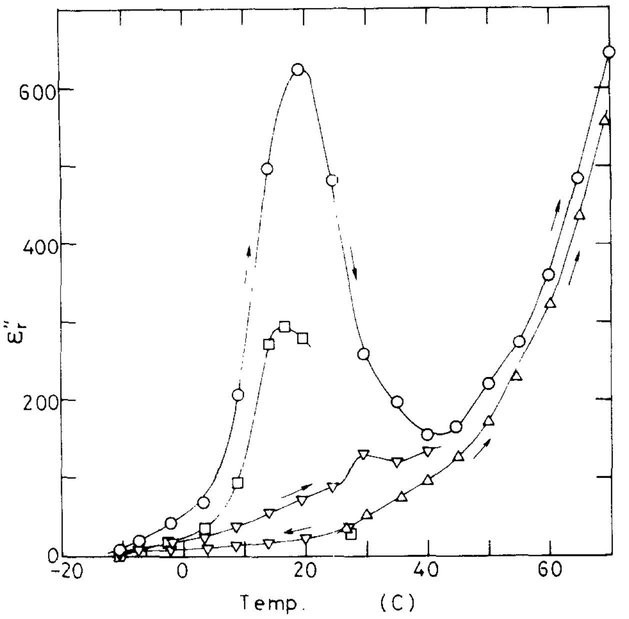


Figure 8 Dielectric loss factor of the PPI–OEA polymer vs. temperature: (○) quick cool; (△) without cool; (▽) slow cool; (□) quick cool (second)

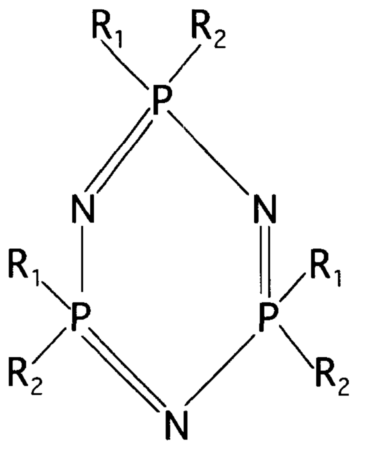


Figure 9 The chemical structure of acrylate-substituted phosphazene monomers: PNF monomer ($R_1 = CF_3CH_2O$–, $R_2 = CH_2$=$CHCOOC_2H_4O$–) and PPZ monomer ($R_1 = R_2 = CH_2$=$C(CH_3)COOC_2H_4O$–)

together with those of poly(2-hydroxyethyl acrylate), namely the polymer of HEA. Volume resistances of PPZ, PNF, PPI–OEA and HEA polymer measured with d.c. at 20°C are shown in *Table 3* together with dielectric constant at 20°C measured at 120 Hz. The chemical structures of PNF and PPZ monomer are shown in *Figure 9*. The PPZ polymer shows the highest volume resistance and the lowest dielectric constant among the polymers in *Table 3*. As already mentioned the hardness of the PPZ polymer is extremely high (equivalent to the hardness of 9H pencils)[9]. The HEA polymer is the next hardest to the PPZ polymer. The volume resistance and the dielectric constant of the HEA polymer follow those of the PPZ polymer. The PPI–OEA polymer is harder than the PNF polymer but much softer than the HEA polymer. The dielectric constant of the slow-cooled PPI–OEA polymer lies between those of the HEA and PNF polymers as is the case of the volume resistance. Here, let us leave the case of quick-cooled PPI–OEA polymer aside for the moment. Then we can say from *Table 3* that the harder the polymer, the higher the volume resistance and the lower the dielectric constant. This seems to imply that in these acrylate polymers some charge carriers or dipoles are included, which result in higher dielectric constant and lower volume resistance when they are mobile, namely when the matrix polymer is soft.

In the case of the quick-cooled PPI–OEA polymer at 20°C the dielectric constant is lower than that of the PNF polymer at 20°C, although the PNF polymer is softer than the PPI–OEA polymer. However, the maximum value of dielectric constant appeared at about 17°C in the quick-cooled PPI–OEA polymer, lower than that of the PNF polymer at about 50°C ($\varepsilon'_r = 200$). A similar tendency is also seen in the case of volume resistance. Namely, the minimum value of the volume resistance of the quick-cooled PPI–OEA polymer is higher than that of the PNF polymer at ~70°C, although at 20°C the quick-cooled PPI–OEA polymer shows lower volume resistance than that of the PNF polymer.

Table 3 Volume resistances (ρ_{dc}) and dielectric constants (ε'_r) of phosphazene polymers at 20°C. Volume resistances were measured with d.c. and dielectric constants at 120 Hz

	ρ_{dc} (Ω cm)	ε'_r
PZZ[a]	3.5×10^{15}	4.7
Poly(2-hydroxyethyl acrylate)[a]	1.7×10^{11}	17
PNF[b]	1.0×10^{8}	42
PPI–OEA polymer[c]	1.4×10^{9}	23
PPI–OEA polymer[d]	3.2×10^{7}	129

[a] T. Kimura and M. Kajiwara, unpublished results
[b] Ref. 8
[c] This work (slow cool)
[d] This work (quick cool)

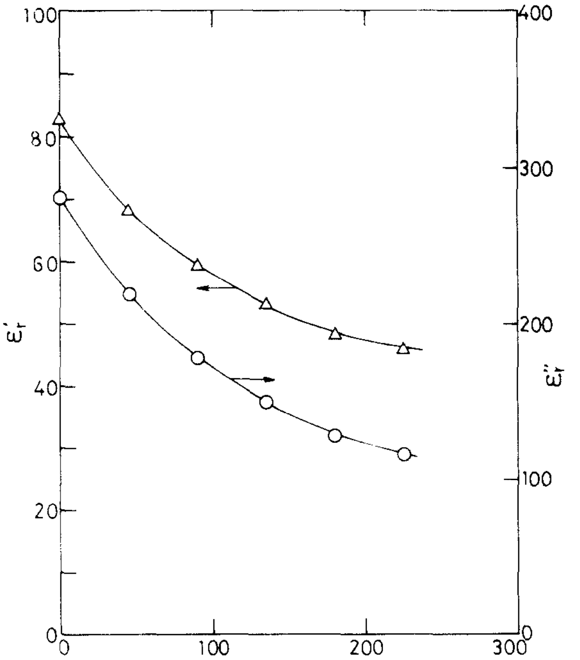


Figure 10 Decay of dielectric constant (△) and dielectric loss factor (○) at 19.6°C measured at 120 Hz

Dielectric properties of acrylate-substituted phosphazene polymers

The result in *Table 3* raises two problems. One is why dielectric constants and dielectric loss factors are high in some acrylate-substituted phosphazene polymer systems. (Dielectric loss factor ε_r'' relates to volume resistance ρ through the relation $1/\rho = 2\pi f \varepsilon_0 \varepsilon_r''$, where f and ε_0 are frequency and permittivity of vacuum, respectively.) The other is that higher ε_r' and ε_r'' are observable only within a narrow temperature range for the quick-cooled PPI–OEA polymer.

Concerning the first problem, it should be noted that higher values of ε_r' and ε_r'' are observable when the polymers are soft and the frequencies of measurement are low. This seems to imply that higher values of ε_r' and ε_r'' result from some permanent dipoles. A speculation has been made for dipoles in PNF polymer: electron transfer from lone pairs of either :O: or :N atoms to COO to form COO$^-$ (ref. 8). An alternative explanation for the higher values of ε_r' and ε_r'' may be –OH dipoles, which are formed during the process of the synthesis of monomers or polymerization. It would be necessary for OH dipoles to orient in some direction in order to give such high dielectric constants (> 100). The *FT*i.r. spectra in *Figures 1* and *4* show the existence of -OH groups. It is interesting to state that an –OH absorption peak is also seen in the *FT*i.r. spectrum of the PPZ polymer.

Concerning the second problem, it is found that higher values of ε_r' and ε_r'' in quick-cooled PPI–OEA polymer decay with time as is seen in *Figure 10*. After the last measurement at 19.6°C for final quick-cooled sample (these are shown as △ in *Figure 7* and as □ in *Figure 8* at 19.6°C) the temperature was maintained at 19.6°C and the decay of ε_r' and ε_r'' was measured. The reasons that higher dielectric constants and loss factors appear only in a restricted temperature range and that those decay with time are speculated as follows. In the quick-cooled polymer OH dipoles are frozen in a metastable state, which gives higher dielectric constants and loss factors during the warming process. The metastable state will be relaxed slowly to a stable state when kept at 19.6°C, as shown in *Figure 10*. Further studies are necessary to clarify these points.

ACKNOWLEDGEMENT

We wish to acknowledge helpful discussions with Dr Y. Kosugi (Nagoya University) on the analysis of ^{1}H n.m.r. spectrum (*Figure 2*).

REFERENCES

1 Lewin, M. and Sello, S.B. 'Flame Retardant Polymeric Materials' (Eds M. Lewin, S. M. Atlas and E. M. Pearce), Plenum, New York, 1975, Ch. 2
2 Stokes, H. N. *Am. Chem. J.* 1895, **17**, 275
3 Staudinger, H. *Chem. Ber.* 1920, **53**, 1073
4 Allcock, H. R. and Kugel, R. L. *J. Am. Chem. Soc.* 1965, **87**, 4216
5 Hellioui, M., De Jaeger, R., Puskaric, E. and Heubel, J. *Macromolecules* 1982, **183**, 1137
6 Kahler, J. US Pat. 2837588, 1985; 2925320, 1960
7 Emsley, J., Moore, J. and Udy, P. B. *J. Chem. Soc.* (*A*) 1971, 2863
8 Kimura, T. and Kajiwara, M. *J. Inorg. Organomet. Polym.* 1992, **2**, 431
9 Kurahashi, A. *Polyfile* 1991 (11), 27