

# Characterization of brominated poly(4-hydroxystyrene) derivatives containing unsaturated groups

Akira Nagai\*, Junichi Katagiri, Akio Takahashi, Motoyo Wajima and Akio Mukoh

Hitachi Research Laboratory, Hitachi Ltd., 4026 Kuji-cho, Hitachi, Ibaraki 319-12, Japan  
(Received 21 August 1989; revised 8 December 1989; accepted 12 December 1989)

Brominated poly(4-hydroxystyrene) (HS) derivatives containing unsaturated groups such as alkenyl or alkenoyl were investigated with infrared and  $^1\text{H}$  nuclear magnetic resonance spectroscopy. HS derivatives have good thermal properties and their decomposition temperatures were higher than  $300^\circ\text{C}$ . Their thermal degradation behaviour is interpreted by the strength of electron withdrawal of substituent groups. The dielectric constants of HS derivatives can be predicted by the Clausius–Mosotti equation. The calculated values are found to agree with the observed values. The dielectric constants of the polymer can be reduced by replacing hydroxy groups with alkenoyl groups, especially methacryloyl units.

(Keywords: brominated poly(4-hydroxystyrene); dielectric constant; thermal stability; decomposition temperature; flame retardant; thermosetting resin)

## INTRODUCTION

The polymerization of 4-hydroxystyrene has been studied by several authors<sup>1–5</sup>. The methods of polymerization reported gave high yields and high molecular weight polymers. These polymers and their brominated derivatives have been applied to practical uses such as heat resistant composites, photoresists, coatings and adhesives<sup>6–9</sup>. In particular, they have an excellent property as curing agents of epoxy compounds, similar to phenolnovolac resins. Brominated derivatives are flame retardant polymers owing to bromine and have been used as non-flammable insulating materials in electronics industries. These polymers by themselves are not able to form crosslinked networks as a thermosetting resin but a thermoplastic polymer. Moreover, these polymers have high dielectric constants because of the hydroxy groups in their side chains. The dipole moment of the hydroxy group is relatively high.

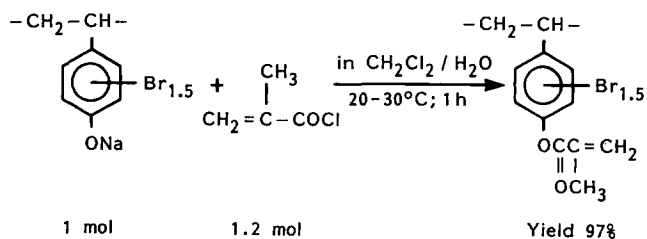
Recently, new derivatives of brominated poly(4-hydroxystyrene) with a low dielectric constant have been synthesized and developed by the substitution of the hydroxy group with unsaturated alkenyl or alkenoyl groups which have a low dipole moment. They can form crosslinkage among the polymer chains<sup>10</sup>. However, the characterization of such new polymers has not been investigated by infrared (i.r.) and nuclear magnetic resonance (n.m.r.) spectra. Moreover, since they are used as thermally stable insulating materials in electronics industries, their dielectric and thermal properties need to be clarified.

This paper reports on the identification of the new polymers and their dielectric and thermal properties.

## EXPERIMENTAL

### Materials

Almost all polymers used were synthesized by the reaction of brominated poly(4-hydroxystyrene) (Maruzen Petrochemical Co. Ltd) with acyl or alkenyl chloride in dichloromethane and water mixed solvent (weight ratio 5:2)<sup>10</sup>. The typical reaction for brominated poly(4-methacryloyloxystyrene) (MC) is shown in *Scheme 1*. This is a phase transfer reaction with two liquid phases. Brominated poly(sodium 4-phenolate) and methacryloyloxy chloride were dissolved in water. The product was insoluble in water but soluble in the organic solvent phase. Therefore, the product was removed from the reaction phase. The yield was 97% and the conversion was estimated to be 99% by titration of unreacted hydroxy groups with potassium hydroxide. MC and brominated poly(4-acryloyloxystyrene) (AC) were purified by reprecipitation with acetone and methanol. Brominated poly(4-allyloxystyrene) (AE), brominated poly((4-methacryloyloxy(2-hydroxypropyl)oxy)styrene) (EPMC), and brominated poly(4-hydroxystyrene) (HS) were also purified by reprecipitation with acetone and n-hexane. All polymers were dried *in vacuo* at  $25^\circ\text{C}$  for  $\approx 20$  h.



Scheme 1

\* To whom correspondence should be addressed

The i.r. spectra were obtained on a Hitachi 260-50 model spectrometer by the KBr method.

The  $^1\text{H}$ -n.m.r. spectra were obtained on a Hitachi R-250 model FTn.m.r. spectrometer with  $\text{CDCl}_3$  as solvent at room temperature.

The dielectric constants of polymers were measured on a Hewlett Packard 4192A model LF impedance analyser at  $25^\circ\text{C}$  in the frequency range  $10^3$ – $10^6$  Hz. The electrodes were formed on both sides of the sample surfaces with silver paste. The diameter of the electrode was 40 mm. The accuracy in the dielectric constant was estimated to be 2%.

Thermal gravimetric analysis was made with a Sinku-Riko TGD-7000RH model at a heating rate of  $5^\circ\text{C min}^{-1}$  in air.

## RESULTS AND DISCUSSION

### Prediction of dielectric properties from chemical structures

As mentioned in the Introduction, poly(4-hydroxystyrene) (HS) has a relatively high dielectric constant and is not suited for use as an insulating material in electronics industries. To obtain materials with a lower dielectric constant and an ability to form crosslinked networks, we attempted to introduce unsaturated functional groups to HS.

A rough estimation of the dielectric constant of the polymer before its synthesis was made in the design of the most suitable chemical structure of insulating materials. Dielectric constants ( $\epsilon$ ) can be estimated roughly from the sum of the constituent group contributions based on Clausius–Mosotti relation<sup>11</sup>:


$$\epsilon = (1 + 2a)/(1 - a); \quad a = P_m/V_m$$

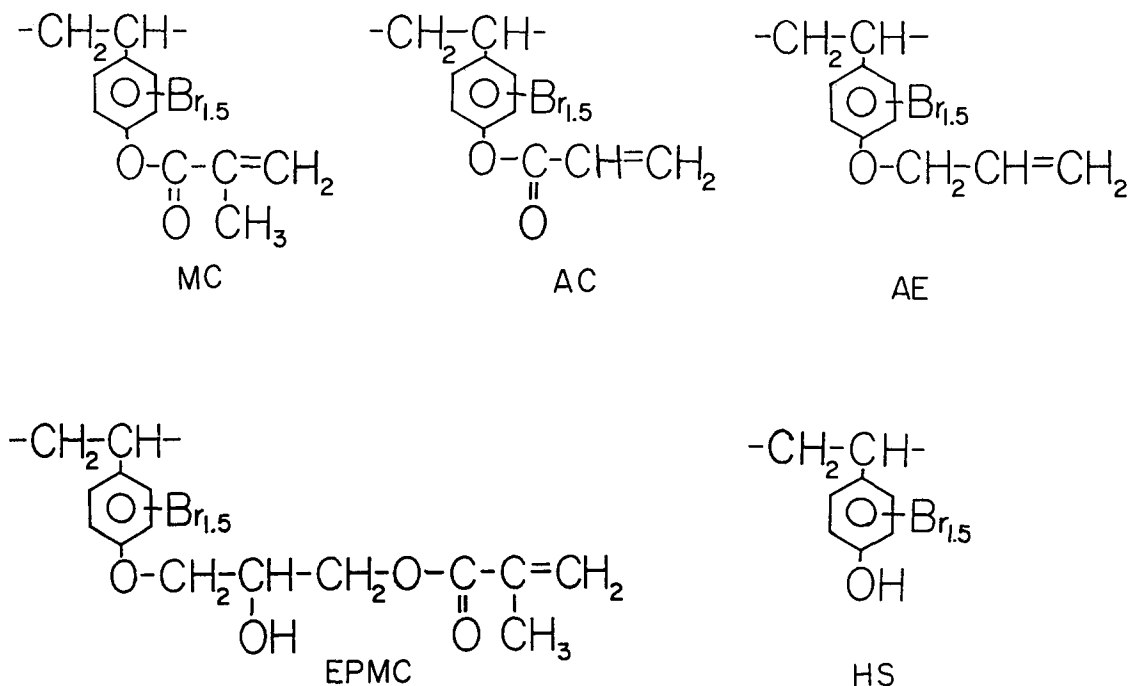
where  $P_m$  is the sum of the molar polarizations of the constituent groups and  $V_m$  is the sum of the molar volumes of the groups. The calculation of these molar quantities for the single repeat (monomeric) unit of the

polymer will usually suffice for determining a dielectric constant for a given polymer. In the present calculation, the contributions of constituent groups tabulated by Kanamaru<sup>11</sup> were used. The  $a$  values of the representative constituent groups are listed in Table 1. To reduce the dielectric constant of polymers, the hydroxy group is undesirable as the substituent group since it has a high dipole moment. Aliphatic hydrocarbon segments are expected to have a low dielectric constant, but they lead to low glass transition temperature, low modulus and reduced thermal and oxidative stabilities. An attempt was made to introduce the unsaturated functional groups which can polymerize and form crosslinked networks.

According to the above-mentioned concept, HS derivatives with alkenyl or alkenoyl groups in the side chains were synthesized<sup>10</sup>. The chemical structures for HS derivatives are shown in Figure 1. These are linear polymers before thermal curing and, therefore, can be treated as prepolymers for the thermosetting resin. These prepolymers have high solubilities in ordinary organic

**Table 1** Chemical structures and  $a$  values of constituent groups<sup>11</sup>

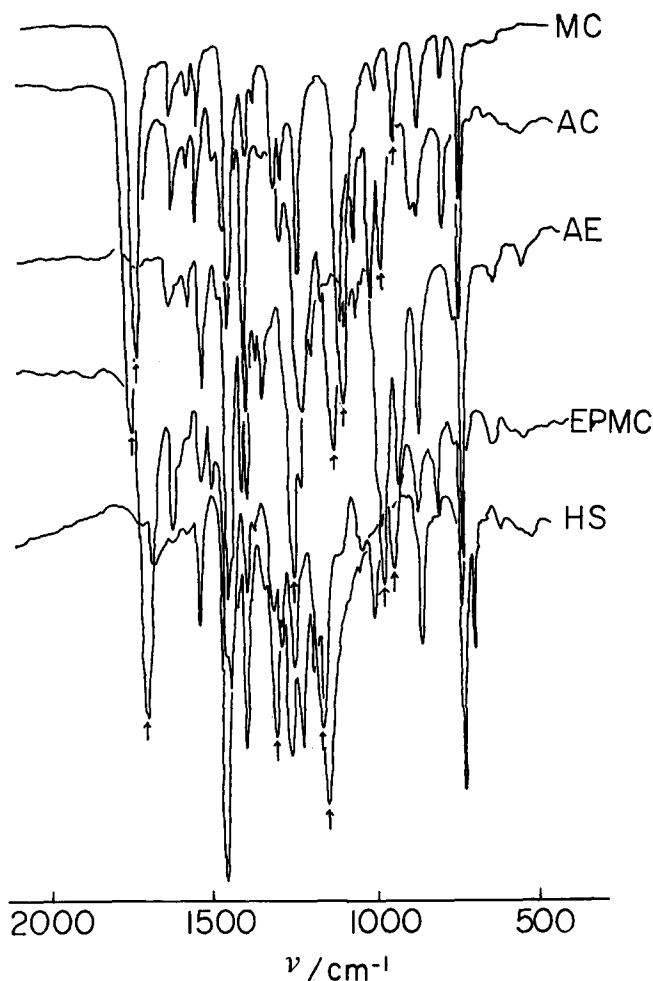
Structure	$a$	$P_m$	$V_m$
$-\text{CH}_3$	0.24	5.7	23.9
$-\text{CH}_2-$	0.29	4.6	15.9
$-\text{CH}-$	0.38	3.6	9.5
	0.38	25.0	65.5
$-\text{CH}=\text{CH}-$	0.38	7.2	18.9
$-\text{Br}$	0.41	12.2	30.0
$-\text{O}-$	0.52	5.2	10.0
$-\text{C}-$	0.54	2.6	4.8
$-\text{CO}-\text{O}-$	0.82	15.0	18.3
$-\text{OH}$	2.06	20.0	9.7



**Figure 1** Chemical structures for brominated poly(4-hydroxystyrene) derivatives

**Table 2** Predicted dielectric constants of brominated poly(4-hydroxystyrene) derivatives

Polymer	$\epsilon_{\text{calc}}$
MC	2.9
AC	3.1
AE	2.7
EPMC	3.8
HS	4.4

**Figure 2** I.r. spectra of brominated poly(4-hydroxystyrene) derivatives

solvents such as acetone and methyl ethyl ketone. Here, the determination of bromine content was determined by both the chemical structure of the starting polymer, HS, and the number of protons in the phenylene ring obtained from n.m.r. measurement of the products.

The predicted dielectric constants of the synthesized polymers are given in Table 2. The dielectric constant decreases on substitution with the alkenyl or alkenoyl group. In particular, the dielectric constants of AE and MC are expected to be <3.

#### Identification of brominated poly(4-hydroxystyrene) derivatives

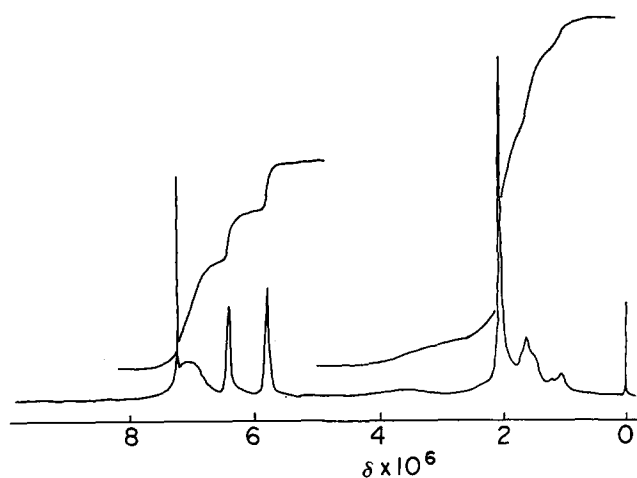
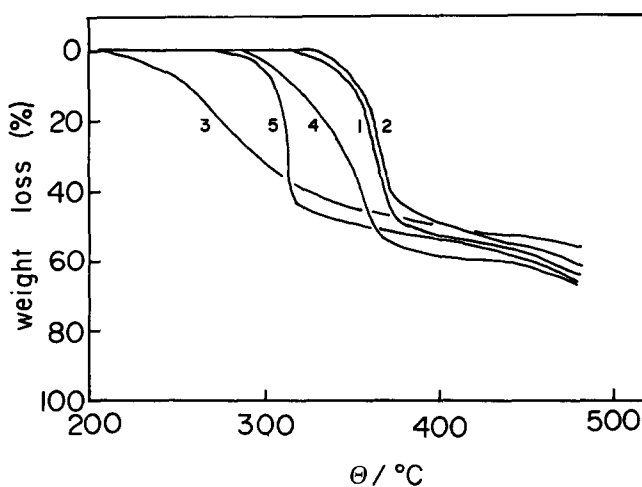
The i.r. spectra of brominated poly(4-hydroxystyrene) derivatives are shown in Figure 2. HS has several absorbance peaks due to the hydroxy group: 3450, 1320, 1150  $\text{cm}^{-1}$ . These peaks disappeared on introducing alkenyl or alkenoyl groups. MC has some peaks at 1750  $\text{cm}^{-1}$  due to the carbonyl group, 1130  $\text{cm}^{-1}$  due to

the carbonyloxy, and 980  $\text{cm}^{-1}$  representing the double bond. Similarly, AC exhibits peaks at 1750, 1130, 980  $\text{cm}^{-1}$ , respectively. For AE, the peak corresponding to the ether bond appears at 1260  $\text{cm}^{-1}$ , and the double bond gives the peak at 980  $\text{cm}^{-1}$ . Finally, EPMC has peaks at 1710, 1170, 950  $\text{cm}^{-1}$ . These correspond to the carbonyl group, the hydroxy group, and the double bond respectively.

The  $^1\text{H}$ -n.m.r. spectrum of MC is shown in Figure 3. The peak at 7 ppm is assigned to the phenylene ring. The  $\text{CH}_2$  group of the double bond in the side chain exhibits two peaks separated into 6.4 and 5.8 ppm. They correspond to *cis* and *trans* configurations, respectively. The peak for the methyl group of methacryloyl group appears at 2.1 ppm, and the peaks at 1.6 and 1.5 ppm are caused by the protons of the main chain. The integrated intensity of protons at the phenylene ring indicates that the phenyl group contains 1.5 bromine atoms on average.

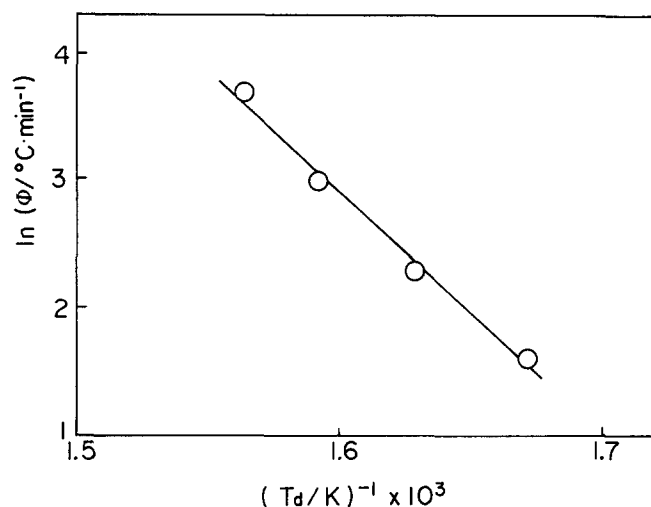
#### Thermal properties of polymers

The thermal degradation behaviour of brominated poly(4-hydroxystyrene) derivatives was investigated by thermogravimetric analysis. As shown in Figure 4, thermosetting polymers except AE are superior to HS, which is a thermoplastic polymer. These thermal characteristics of thermosetting polymers begin to decompose

**Figure 3**  $^1\text{H}$ -n.m.r. spectrum of MC**Figure 4** Thermogravimetric curves of brominated poly(4-hydroxystyrene) derivatives: 1, MC; 2, AC; 3, AE; 4, EPMC; 5, HS

**Table 3** Bromine constants and weight losses of brominated poly(4-hydroxystyrene) derivatives

Polymer	Br content (%)	Weight loss (%)
MC	41	47
AC	43	41
AE	45	—
EPMC	33	52
HS	50	43

**Figure 5** Arrhenius plot of the decomposition reaction of MC obtained by the Ozawa method

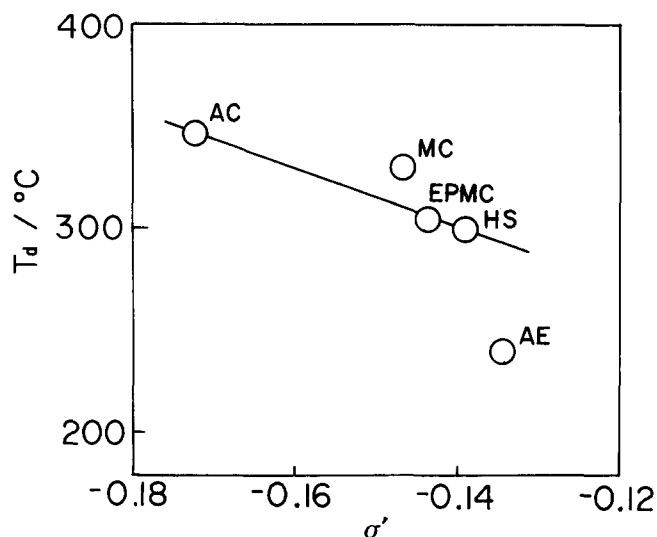
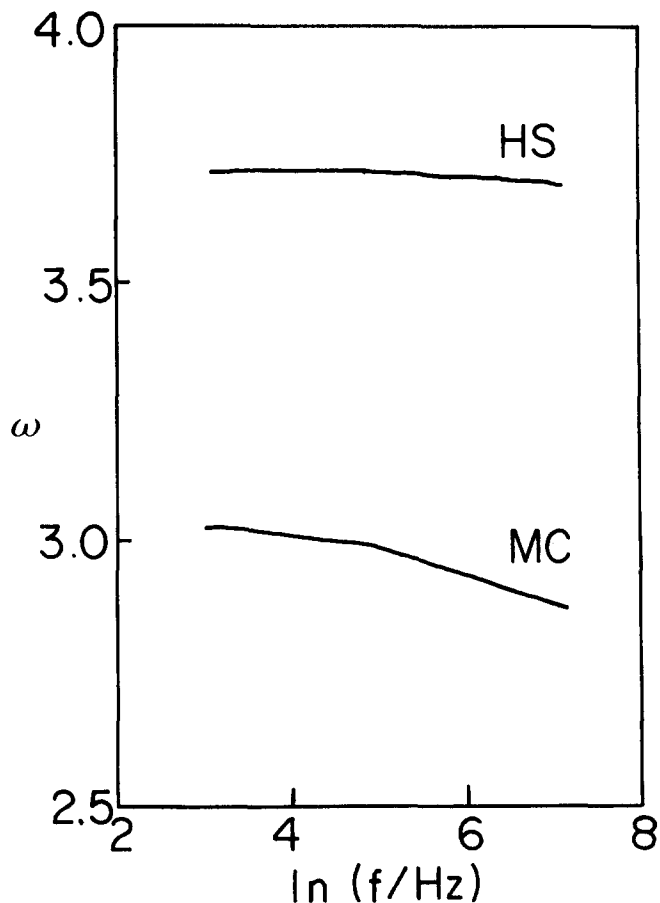
at a temperature as high as 300°C. In particular, MC and AC are superior to the others. These polymers are expected to have low dielectric constants, as given in Table 2. Thus, MC and AC are most suitable for the use in electronics industries.

Although AE is a thermosetting polymer, its decomposition temperature is  $\approx 200^\circ\text{C}$ . Moreover, the decomposition reaction of AE proceeds slowly, unlike the other polymers. The decomposition reaction of almost all the polymers occurs rapidly above a certain temperature. The rapid decomposition reaction of these polymers, except for AE, is presumed to be the result of elimination of bromine from the phenylene ring, judging from the gravity reduction. The approximate bromine content and weight loss of the polymers are listed in Table 3. EPMC exhibits slightly higher weight loss and probably decomposes by simultaneously eliminating both the bromine atoms and the substituent groups.

The activation energy of decomposition reaction for MC was examined by the Ozawa method<sup>12</sup>. The decomposition temperatures at 5 wt% loss, which represents the initial state of the reaction, were measured at several heating rates from 5 to 40°C min<sup>-1</sup>. The activation energy is determined to be 70 kcal mol<sup>-1</sup> from the slope of the Arrhenius plot as shown in Figure 5. This value is similar to the bond dissociation energy of aromatic carbon and bromine (71 kcal mol<sup>-1</sup>)<sup>13</sup>. Judging from this result, it is presumed that the decomposition reaction proceeds by the dissociation of the bromine moiety from the aromatic ring.

The decomposition reactions are expected to depend strongly on polymer structures. It is presumed that the electron withdrawal of substituent groups in the side chain has an effect on decomposition reaction. Thus we examined whether the decomposition temperature could

be interpreted by the Hammett rule. The electron densities on substituent groups ( $\sigma'$ ) were calculated by the modified neglect of diatomic overlap method. The decomposition temperature is plotted in Figure 6 as a function of  $\sigma'$ . It is recognized that the decomposition temperature is well correlated with  $\sigma'$ , except for the case of AE. The decomposition reaction of AE is different from the others. Judging from this result, we conclude that the bond energy between the bromine and the phenylene ring increases with the electron withdrawal of substituent groups.

**Figure 6** Relationship between the decomposition temperatures and the electron densities of substituent groups**Figure 7** Frequency dependence of the dielectric constants of polymers

Dielectric properties of polymers

It has been predicted that MC is suited as a thermo-setting prepolymer in terms of both thermal and dielectric properties. We made dielectric measurements on the cured product of MC to confirm this prediction. A relatively low molecular weight MC ( $M_n=3000$ ) was moulded. The dielectric constant of HS was also measured for comparison. The results are shown in *Figure 7*. The observed and calculated values agree. Thus it is confirmed that the prediction by the Clausius–Mosotti relation is valid.

As shown in *Figure 7*, the dielectric constant of HS does not depend on frequency, in the range  $10^3$ – $10^6$  Hz. On the other hand, the dielectric constant of MC decreases gradually beyond  $10^5$  Hz. It is presumed that this is due to the dielectric relaxation caused by rotation of the methacryloyloxy side chain. Since the methacryloyloxy group is more bulky than the hydroxy group, the motion of the side chain cannot follow the alternating electric field beyond a certain high frequency, i.e.  $10^5$  Hz. But the dipole moment of the hydroxy group can easily follow the alternating electric field at  $10^6$  Hz.

REFERENCES

- 1 Sovish, R. C. *J. Org. Chem.* 1959, **24**, 1345
- 2 Overberger, C. G., Salamone, J. C. and Yaroslavsky, S. *J. Am. Chem. Soc.* 1967, **89**, 6231
- 3 Kato, M. *J. Polym. Sci. A-1* 1969, **7**, 2173, 2405
- 4 Frechet, J. M., Eichler, E., Ito, H. and Wilson, C. G. *Polymer* 1983, **24**, 995
- 5 Hirano, A., Takemoto, K., Packirisamy, S., Yamaguchi, K. and Nakahama, S. *Macromol Chem.* 1985, **186**, 1157
- 6 Fujiwara, H., Takahashi, A., Fujii, K., Nakamura, K., Sekiya, M. and Suzuki, K. *J. Thermoset. Plas. Jpn* 1980, **1**, 92
- 7 Fujiwara, H., Takahashi, A., Fujii, K., Nakamura, K., Suzuki, K., Yamada, T., Horiuchi, H. and Tonogai, S. *J. Thermoset. Plas.* 1981, **2**, 1
- 8 Fujiwara, H., Yoshinari, T., Fujii, K. and Nakamura, K. *J. Thermoset. Plas.* 1984, **5**, 125
- 9 Fujiwara, H. and Matsumoto, T. *J. Thermoset. Plas.* 1987, **8**, 25
- 10 Takahashi, A., Katagiri, J., Nagai, A., Narahara, T., Koochi, H. and Matsuoka, K. Japan Patent 1-96202
- 11 Kanamaru, K. 'Electric Properties of Polymers', Kyouritu, Tokyo, 1981, Ch. 1
- 12 Ozawa, T. *Bull. Chem. Soc. Jpn* 1965, **38**, 1881
- 13 Roberts, J. D. and Caserio, M. C. 'Basic Principles of Organic Chemistry', Japanese Edn., Tokyo Kagaku Dojin, Tokyo, 1970, Ch. 23