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Dielectric relaxation of cyanoethylated poly(2,3-dihydroxypropyl methacrylate)

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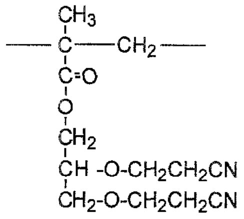
The dielectric properties were studied of a completely cyanoethylated derivative (CN-DPMA) of poly(2,3-dihydroxypropyl methacrylate), which was synthesized by radical polymerization of the monomer with protected hydroxyl groups, followed by deprotection. The experimental results were compared with those already reported for a semiflexible liquid-crystalline polymer with cyanoethyl groups, cyanoethylated *O*-(2,3-dihydroxypropyl)cellulose (CN-DHPC). By the introduction of two cyano groups on the monomer unit, CN-DPMA shows a high dielectric permittivity of 25–26 at 50°C and 1 kHz, which is comparable to the value of CN-DHPC. A study on the temperature dependence revealed two relaxation modes, one being the β-relaxation due to local motions in the side chain and the other being the α-relaxation due to the main-chain motions. The β-relaxation appeared in a temperature region similar to that for CN-DHPC. The fact that only one mode assigned to main-chain motions was detectable for CN-DPMA forms an interesting contrast to CN-DHPC, which shows two main-chain relaxation modes. This difference is attributed to the difference in the backbone flexibility of the two polymers

(Keywords: cyanoethylated poly(2,3-dihydroxypropyl methacrylate); high dielectric permittivity; dielectric relaxation)

INTRODUCTION

Highly dielectric polymers have potential applications as electronic devices such as binding polymers for electroluminescence cells and capacitors. Most of them are cyanoethyl derivatives of polyhydroxyl polymers such as poly(vinyl alcohol)[1] and polysaccharides[2–4]; introduction of moieties with a large dipole moment like cyano groups can greatly increase the dielectric permittivity of these polymers. Methacrylate and acrylate derivatives have also gained much interest due to their easy preparation and high processability. In fact, poly(2-hydroxyethyl methacrylate) (HEMA) and its derivatives (G-HEMA) modified with glycidol were converted into high-performance dielectric polymers by cyanoethylation[5,6]. These patents, however, report only the values of dielectric permittivity and dielectric loss tangent at 25°C but not details of the dielectric properties, in particular the dielectric relaxational processes of the polymers.

The aim of this work is to prepare a highly dielectric poly(methacrylate) derivative and to investigate its dielectric properties as a function of temperature and frequency. As a base polymer, we have adopted poly(2,3-dihydroxypropyl methacrylate) (DPMA), a polymer having two hydroxyl groups per repeating unit. Cyanoethylation of this polymer is expected to give a highly dielectric polymer owing to the high cyano density in this polymer compared with that in the HEMA-based polymers[5,6].



$$\begin{array}{l} \mathrm{CH_3} \\ —\mathrm{C}—\mathrm{CH_2}— \\ \mathrm{C{=}O} \\ \mathrm{O} \\ \mathrm{CH_2} \\ \mathrm{CH{-}O{-}CH_2CH_2CN} \\ \mathrm{CH_2{-}O{-}CH_2CH_2CN} \end{array}$$

Dielectric measurements provide information about the various modes of molecular motions[7,8]. Previously we studied the dielectric relaxation of cyanoethylated *O*-(2,3-dihydroxypropyl)cellulose (CN-DHPC)[9,10], which shows liquid crystallinity due to the semiflexibility of its main chain[11,12]. This polymer exhibits two relaxation modes (α and α') active above the glass transition temperature T_g, as well as the β-mode assignable to local motions in the side chain. The semiflexibility of the cellulose backbone seems to be responsible for the appearance of these two clearly separated relaxation processes above T_g. Like CN-DHPC, the cyanoethyl derivative (CN-DPMA) of DPMA studied here also has cyanoethyl groups in the side chain, but its main chain is more flexible than the cellulose backbone of CN-DHPC. Thus a further aim of this work is to compare the relaxational behaviour of CN-DPMA with that of CN-DHPC, for a clear understanding of molecular relaxation processes in relation to chain flexibilities.

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EXPERIMENTAL

Materials

Poly(2,3-dihydroxypropyl methacrylate). Following the method reported by Mori *et al.*[13], DPMA was prepared by radical polymerization of the monomer with protected hydroxyl groups, followed by deprotection. The protected monomer, (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate, was synthesized by the reaction of methacryloyl chloride (Tokyo Kasei Kogyo Co.) with isopropylidene glycerol (Nacalai Tesque), which was distilled before use: to a $CHCl_3$ (450 ml) solution of isopropylidene glycerol (1 M) and triethylamine (150 ml), methacryloyl chloride (56 ml) diluted with $CHCl_3$ (56 ml) was added dropwise over a period of 2 h at 5–10°C. After stirring for 48 h at room temperature, the reaction mixture was filtrated to remove liberated triethylamine hydrochloride, followed by washing with aqueous solution of sodium bicarbonate and water. Finally, the remaining trace of water was removed by sodium sulfate. The crude product was purified by distillation under reduced pressure (58–60°C at 1.5–2 mm Hg).

2,2′-Azobis(isobutyronitrile)-initiated radical polymerization of the protected monomer was carried out either in the bulk at 50°C or in a 20 wt% tetrahydrofuran (THF) solution at 65°C with bubbling of nitrogen gas. The product was purified by reprecipitating several times from a THF solution into methanol and dried under vacuum. The obtained polymer with protected hydroxyl groups was deprotected by hydrochloric acid in 1,4-dioxane, and the deprotected polymer was purified by dialysis in water and finally freeze-dried from an aqueous solution. Perfect deprotection was confirmed by infrared (i.r.) and nuclear magnetic resonance (n.m.r.) spectroscopies. Finally two polymers different in molecular weight were obtained, which will be coded DPMA-H and DPMA-L. The weight-average degree of polymerization (DP_w) was determined by light scattering to be 350 for DPMA-L and ~ 5000 for DPMA-H, and the molecular weight distribution index (DP_w/DP_n) was estimated by gel permeation chromatography to be ~ 2 for both samples before deprotection. The light scattering measurements for DPMA-L before and after deprotection revealed that the deprotection proceeded quantitatively without causing main-chain scission[14].

Cyanoethylation. Cyanoethylation was carried out in acrylonitrile by the Michael condensation reaction in the presence of sodium hydroxide as a catalyst[15]. The cyanoethylated polymer was precipitated in water and purified by redissolving in acetone and dialysing against deionized water. During the dialysis, the polymer was precipitated out. The dialysis process was repeated three times using ion exchange resins in order to remove ionic impurities, which can disturb dielectric measurements. Finally, the purified polymer was vacuum-dried to remove the trace of water present. Complete cyanoethylation was confirmed by i.r. and ^{1}H-n.m.r. spectroscopies. The degrees of polymerization of the cyanoethylated polymers may be assumed to be the same as those of the polyhydroxyl polymers. The glass transition temperature was determined to be 3°C by differential scanning calorimetry (d.s.c.).

^{1}H-n.m.r. (DMSO-d_6): 0.8–1.2 (3H, α-CH_3), 1.7–2.1 (2H, CH_2), 2.65–2.8 (4H, CH_2CN), 3.55–3.75 (4H, O–CH_2 in cyanoethyl group), 3.7–4.2 (5H, CH_2–CH–CH_2).

Measurements

Dielectric measurements were conducted on a Hewlett–Packard 4284A Precision LCR meter. An Ohkura EC-7 controller with a copper *versus* constantan thermocoupler was used to control the temperature. The temperature of the sample was measured by either a platinum resistor or another copper *versus* constantan thermocoupler with a Keithley 196 digital multimeter. The whole system was controlled with an Epson model PC-286VE personal computer. A sandwich-type cell was used, which consisted of a pair of circular stainless steel electrodes with a diameter of 1 cm. The polymer film, cast from acetone and vacuum-dried at 50°C, was loaded into the gap between the electrodes and heated to 50°C to make the sample soft and fluid; the two electrodes were tightly pressed against each other by adjusting the film thickness with a polyimide film spacer ~ 30 μm thick. The exact film thickness, from which the cell capacity in vacuum was estimated, was measured with a dial gauge (Mitutoyo) after dielectric measurements. The measurements were carried out isothermally from 77 to 400 K at 48 frequencies ranging from 25 Hz to 1 MHz.

I.r. spectra were recorded on a Jasco FT/IR-8800 spectrometer. ^{1}H-n.m.r. spectra were recorded on a Varian VXR-200. The glass transition temperature was determined on a Perkin–Elmer model DSC-7 differential scanning calorimeter at constant heating and cooling rates of 10 K min^{-1}.

RESULTS AND DISCUSSION

CN-DPMA was found to show a high dielectric permittivity. *Table 1* summarizes dielectric permittivities ε' and dielectric loss tangents tan δ along with the data previously reported for CN-DHPC[9,10] and the cyanoethyl derivatives (CN-HEMA and CN-G-HEMA)[5,6] of HEMA and G-HEMA. The dielectric permittivities of these polymers, which commonly have cyanoethyl groups, should be related to the number density of the cyano group and its mobility at measurement temperature. The dielectric permittivity ε' of CN-DPMA (at 50°C) is comparable to those of CN-DHPC (at 50°C) and CN-G-HEMA (at 25°C). In fact, CN-DPMA contains almost the same weight fraction of cyano groups ($f_{CN} = 0.20$) as CN-DHPC ($f_{CN} = 0.22$) and as CN-G-HEMA with a high dihydroxypropyl content:

Table 1 Dielectric permittivities ε' and dielectric loss tangents tan δ measured at 30°C and 1 kHz

Sample code	ε'	tan δ
CN-DPMA-H	22 (26)[a]	0.12
CN-DPMA-L	21 (25)[a]	0.12
CN-DHPC[b]	29 (29)[a]	0.024
CN-HEMA[c]	20	0.105
CN-G-HEMA[c]	30	0.098

[a] Measured at 50°C and 1 kHz
[b] $MS = 4.5$
[c] Measured at 25°C and 1 kHz

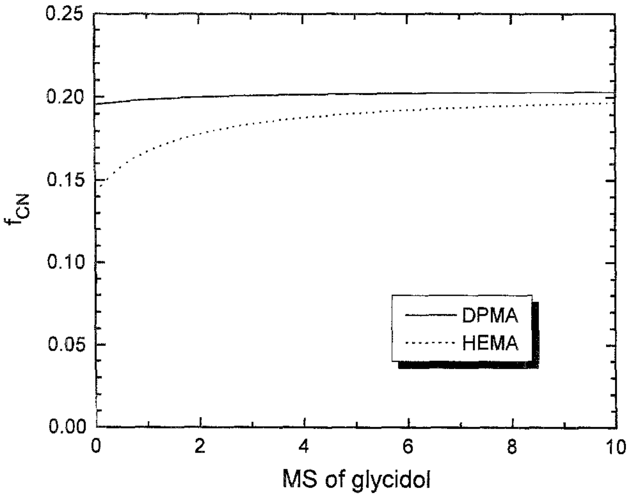

Figure 1 Plot of the weight fraction of the cyano group f_{CN} against the molar substitution *MS* of glycidol for cyanoethyl derivatives of DPMA- (solid curve) and HEMA-based polymers (dotted curve)

Figure 1 shows the calculated values of f_{CN} as a function of the molar substitution *MS* of glycidol per repeating unit. In the case of HEMA (the dotted curve), f_{CN} increases with increasing *MS* in accordance with the experimental observations (compare the ε' values of CN-HEMA and CN-G-HEMA; the *MS* value of CN-G-HEMA was not reported in ref. 6, however). On the other hand, an increase of f_{CN} by the glycidol modification cannot be expected in the case of CN-DPMA (the solid curve in *Figure 1*). For this reason, we did not attempt such modification for DPMA.

Figures 2 and *3* illustrate the temperature dependence of dielectric permittivity ε' and dielectric loss ε'' for CN-DPMA-H and CN-DPMA-L, respectively, at three representative frequencies, 500 Hz, 5 kHz and 50 kHz. In both samples, the dielectric loss curves clearly show two dielectric absorptions (α and β) with the peak temperature increasing with increasing frequency. The β-mode observed mainly below T_g (3°C) is assignable to local motions of the side chain. The α-mode active above T_g should be associated with main-chain motions. The steep rise of each loss curve at high temperatures is ascribed to ionic impurities, which will be discussed later.

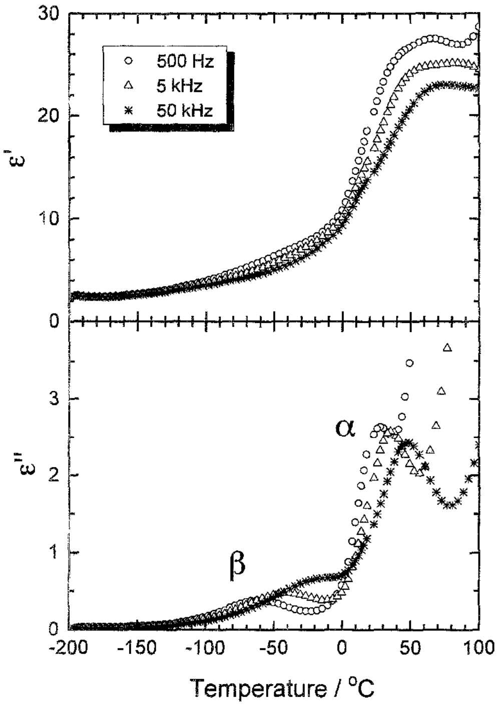

Figure 2 Temperature dependence of dielectric permittivity ε' and dielectric loss ε'' for CN-DPMA-H; f = 500 Hz, 5 kHz and 50 kHz

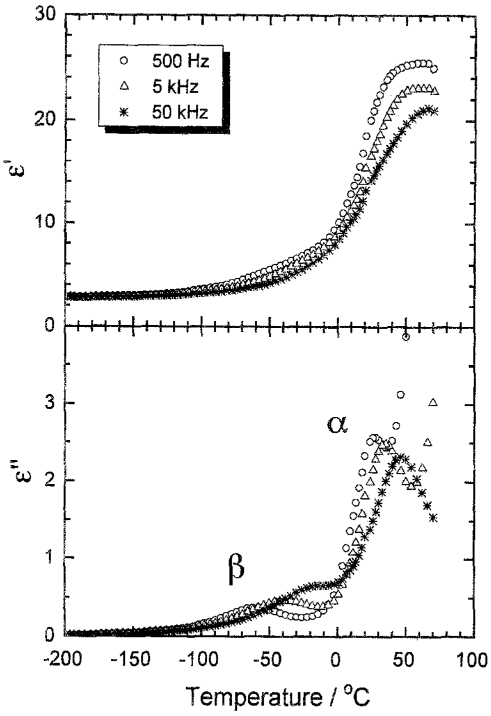

Figure 3 Temperature dependence of dielectric permittivity ε' and dielectric loss ε'' for CN-DPMA-L; f = 500 Hz, 5 kHz and 50 kHz

Figures 4 and *5* show the frequency dependence of ε' and ε'' for CN-DPMA-H and CN-DPMA-L, respectively. Again, ionic impurities are responsible for the increase of ε' and ε'' at low frequencies and high temperature. Both α- and β-relaxation peaks are observed to move towards higher frequencies with increasing temperature. These data were analysed by the following Cole–Cole equation[16].

$$\varepsilon^* = \varepsilon_{\text{inf}} + \frac{\varepsilon_0 - \varepsilon_{\text{inf}}}{1 + (i\omega\tau_0)^b} \tag{1}$$

where ε^* is the complex dielectric permittivity, ω is the angular frequency ($\omega = 2\pi f$, f is frequency), τ_0 is the mean relaxation time, ε_0 and ε_{inf} are the dielectric permittivities in the low- and high-frequency limits, respectively, and b is a parameter characterizing the distribution of the relaxation times. *Figure 6* shows the Cole–Cole plots at several temperatures for CN-DPMA-H, where open circles represent the experimental data and solid curves were calculated by using equation (1). The experimental data were well fitted to the Cole–Cole scheme (see *Figures 4–6*). This analysis gave temperature-dependent values of the mean relaxation frequency f_0 and relaxation strength $\Delta\varepsilon$, and an almost constant value of b, where

$$f_0 = \frac{1}{2\pi\tau_0} \tag{2}$$

$$\Delta\varepsilon = \varepsilon_0 - \varepsilon_{\text{inf}} \tag{3}$$

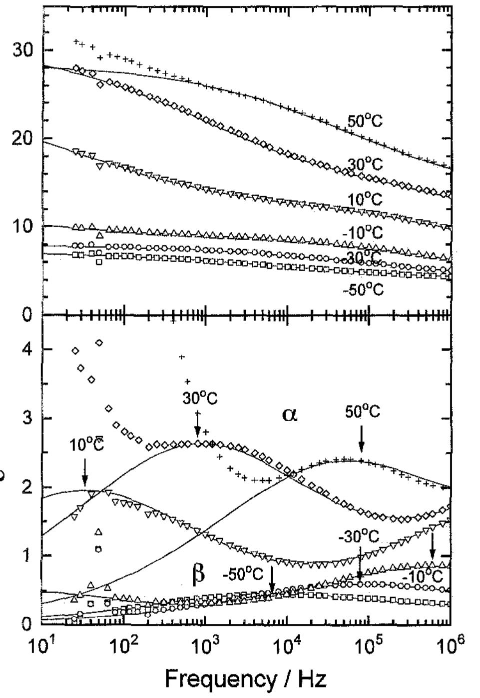

Figure 4 Frequency dependence of dielectric permittivity ε' and dielectric loss ε'' for CN-DPMA-H; open symbols represent experimental data at temperatures of −50, −30, −10, 10, 30 and 50°C, and solid curves were calculated by the Cole–Cole equation

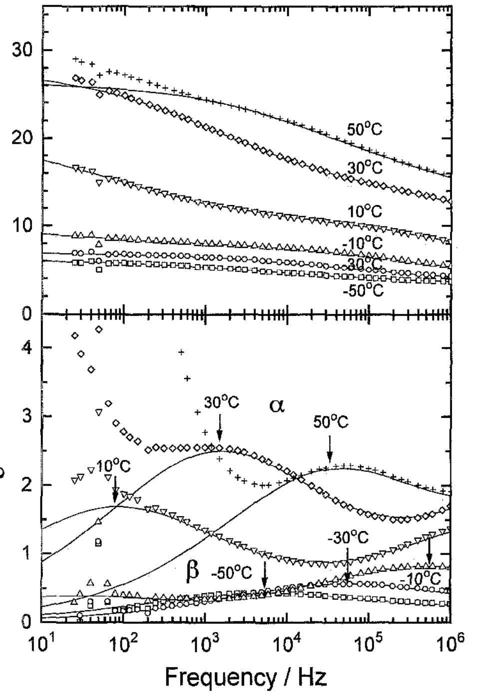

Figure 5 Frequency dependence of dielectric permittivity ε' and dielectric loss ε'' for CN-DPMA-L; open symbols represent experimental data at temperatures of −50, −30, −10, 10, 30 and 50°C, and solid curves were calculated by the Cole–Cole equation

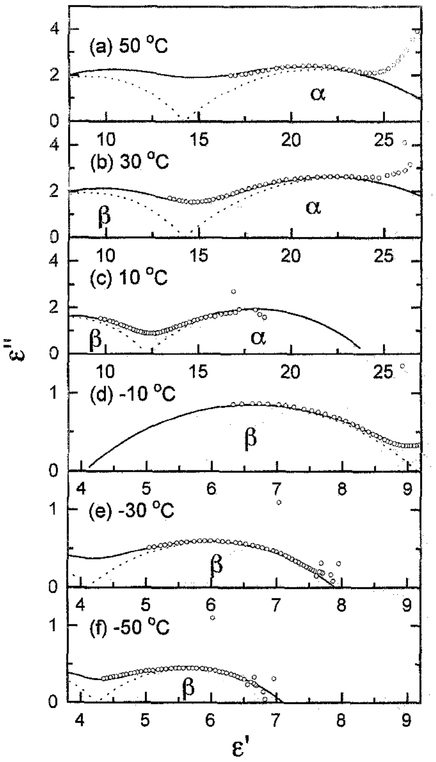

Figure 6 Cole–Cole plot for CN-DPMA-H; open circles represent experimental data at temperatures of −50, −30, −10, 10, 30 and 50°C, and dotted and solid curves are theoretical calculations for the individual relaxations and their sum, respectively

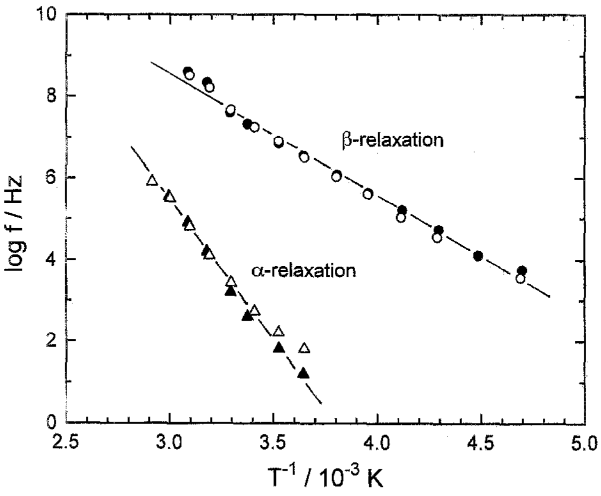

Figure 7 Arrhenius plot for the α (triangles) and β (circles) relaxations for CN-DPMA-H (solid symbols) and CN-DPMA-L (open symbols); the activation energies were estimated to be 126 and 55 kJ mol^{-1} for the α- and β-relaxations, respectively

Figure 7 shows the Arrhenius plot of f_0. The two samples give a common straight line for both α- and β-modes with activation energies of 126 and 55 kJ mol^{-1}, respectively. The activation energy of the β-mode for CN-DPMA is almost exactly the same as that observed for CN-DHPC (56 kJ mol^{-1}). The relaxation parameters estimated at −20°C for the β-mode are also similar to those for CN-DHPC (*Table 2*). These confirm that the β-mode is localized in the side chain, and hence it is independent of the flexibility of the main chain. On the other hand, the activation energy of the α-mode for CN-DPMA is lower than that of the α-mode (146 kJ mol^{-1}) for CN-DHPC, but is higher than that of the α'-mode (72 kJ mol^{-1}) for the same polymer, reflecting the difference of the main-chain motions between the two polymers. We will discuss this matter later. The temperature-independent b value means that the temperature–frequency superposition principle can be

Table 2 Parameters characterizing the α- and β-relaxation modes

Sample code	β (−20°C)			α (20°C)		
	f_0 (Hz)	$\Delta\varepsilon$	b	f_0 (Hz)	$\Delta\varepsilon$	b
CN-DPMA-H	2.1×10^5	4.5	0.38	2.0×10^2	16.5	0.39
CN-DPMA-L	2.0×10^5	4.0	0.41	2.7×10^2	13.4	0.43
CN-DHPC	1.3×10^5	3.9	0.44	1.0×10^5	17.7	0.45

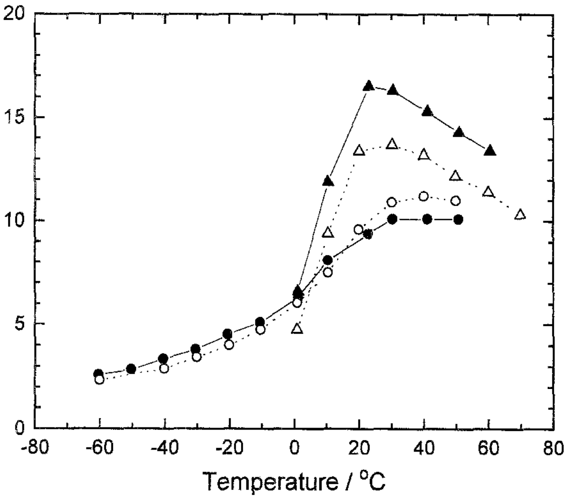

Figure 8 Temperature dependence of relaxation strength $\Delta\varepsilon$ for the α (triangles) and β (circles) relaxations for CN-DPMA-H (solid symbols) and CN-DPMA-L (open symbols)

applied to each relaxation in this system. *Figure 8* shows the temperature dependence of $\Delta\varepsilon$, which characterizes the mobility and number of molecular dipoles. The value of $\Delta\varepsilon$ for the α-mode increased steeply at around T_g with increasing temperature, which indicates that this mode sets in at T_g. The decrease of $\Delta\varepsilon$ with a further increase of temperature above T_g is presumably due to the $1/T$ dependence predicted by the thermal perturbation in the reorientation of dipoles[8]. For the β-mode, $\Delta\varepsilon$ increased slowly with increasing temperature.

The Cole–Cole plot for the β-mode at low temperatures is asymmetrical (see *Figure 6f*), being broader on the high-frequency side, which suggests that another relaxation mode exists below temperatures of the β-relaxation. This relaxation, however, is too weak and too close to the β-mode to be characterized.

Finally, some words are due regarding the difference in the main-chain relaxation processes of CN-DPMA and CN-DHPC. As already noted, CN-DHPC exhibits two relaxations α and α' that set in at T_g. We have suggested that the α'-mode is associated with a rotational motion of the whole side chain about the main-chain axis, while the α-mode is associated with other centre of mass motions of the main and side chains. We have presumed that the semirigidity of the cellulose backbone is responsible for the appearance of these two clearly separated relaxation processes above T_g. If this interpretation is correct, it is unlikely that CN-DPMA, a more flexible polymer, should also show two relaxations above T_g. One of the incentives for the present work was to confirm this experimentally. As already mentioned, only one relaxation is visible above T_g for CN-DPMA. However, ionic impurities remaining even after an exhaustive purification process may make this statement appear inconclusive. For this reason, we have attempted to quantify the contribution of ionic impurities by assuming the following Schweidler-type dispersion[17,18] for them:

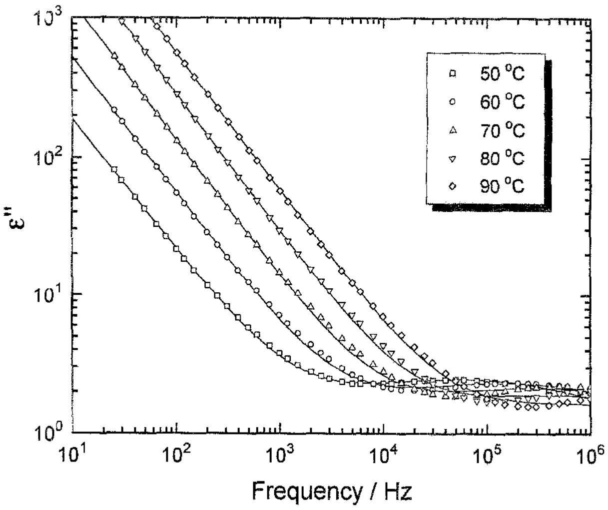

Figure 9 Plots of ε'' against f in logarithmic scale for CN-DPMA-H

$$\varepsilon''_s(\omega) = C \times f^{-m} \qquad (4)$$

In *Figure 9* ε'' is plotted against f in logarithmic scale at several temperatures above 50°C; open symbols represent experimental data. The maxima in the ε'' curves, assigned to the α-relaxation, are observed in a high-frequency region. Because of ionic impurities, ε'' increases steeply with decreasing f. The solid curves in the figure were calculated by using equation (1) with the estimated values of the parameters characterizing the relaxation and by assuming that the contribution of ionic impurities takes the form of equation (4). The experimental data are well fitted to the calculated curves with a common m value of 0.97 and temperature-dependent values of C: no relaxation other than the α-relaxation can be detected. Admittedly, the large contribution of ionic impurities imposes certain limitations on such an analysis, but we may mention that if CN-DPMA had another relaxation with a similar activation energy and a similar relaxation strength to those of the α'-mode of CN-DHPC, it should be visible in these temperature and frequency ranges even in the presence of the ionic impurities. Thus we conclude that this polymer has no such additional relaxation above T_g.

CONCLUSION

Fully cyanoethylated poly(methacrylate) derivative, CN-DPMA, shows a high dielectric permittivity of 25–26 at 50°C and 1 kHz. This high dielectric permittivity arises from the high density of cyano groups, which was attained by the introduction of two cyano groups per monomer unit. This polymer exhibits two relaxations, α and β. The latter mode is observed in the same temperature and frequency regions, and characterized by the same activation energy, as the β-mode of CN-DHPC. This confirms that this relaxation process is localized in the side chain and hence is independent of main-chain flexibility. The α-mode, assigned to main-chain motions, has a lower activation energy than the 'α'-mode of CN-DHPC. Unlike in CN-DHPC, no additional relaxation is observable in CN-DPMA, presumably reflecting the higher main-chain flexibility of this polymer.

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