Dielectric relaxation property and alignment behavior of liquid crystalline side-chain polymethacrylate

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Dielectric relaxation properties of a liquid crystalline side-chain polymethacrylate having a 4-cyanophenyl benzoate group in the side chain were investigated in the range 20-106Hz and 50-130℃. The observed dielectric loss spectra reveal δ-relaxation, which contains a component from the dipole reorientation of the mesogenic group. The activation energies obtained were 136.0 kJ/mol in the isotropic phase and 197.3 kJ/mol in the unaligned mesophase. The changes that occur in the amplitudes and shapes of the dielectric loss spectra for a nematogenic side-chain polymethacrylate on going from the nematic to the isotropic phase, and on going from the unaligned to the partially aligned mesophase are described.

1. INTRODUCTION

Liquid crystalline polymers having mesogenic groups in the side-chain are of considerable interest scientifically as hybrid materials and technologically as media for a variety of applications in physical optics and computer technology. Thermotropic liquid crystalline side chain polymers generally consist of polymeric chains to which rigid rod, mesogenic moieties are covalently attached. These chains are usually either members of the acrylate or methacrylate family. A number of the synthesis and thermal properties of liquid crystalline side-chain polymers have been reported. In molecular dynamics field, since the dielectric properties of liquid crystalline side-chain polyacrylate and polymethacrylate including a flexible spacer and alkoxyl groups the mesogenic head group in the side chain have been investigated [1,2], the dielectric

relaxation behavior of unaligned and aligned polysiloxane with an ordinary alkylene spacer and 4-cyanophenyl benzoate as the mesogenic group in the side-chain have been reported [3-9]. As described in ref.10, nowaday dielectric studies are routinely used to probe the molecular dynamics of polar species as a function of frequency and temperature. These results suggest that information on the activation energy, intensity and broadness of the relaxation processes, alignment behavior. In this paper, we describe the results of dielectric measurements on a liquid crystalline side-chain polymethacrylate containing the cyano group as the mesogenic head groups in the side-chain and the alignment behavior.

2. EXPERIMENTAL

The material investigated, poly(4-cyano-

phenyl 4-(6-(methacryloyloxy)hexyloxy)benzo-
ate) (PMCN), was prepared by the free-radical
polymerization of 4-cyanophenyl 4-(6-(metha-
cryloyloxy)hexyloxy)benzoate with AIBN in
THF solution under nitrogen gas. The
chemical structure of PMCN is as follows,

$$\begin{array}{c} CH_3 \\ | \\ +C-CH_2\dagger_n \\ | \\ COO-(CH_2)_6-O-\langle\bigcirc\rangle-COO-\langle\bigcirc\rangle-CN \end{array}$$
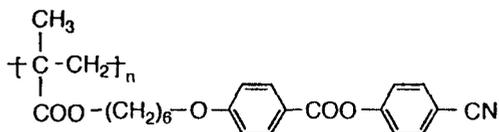
The number-average molecular weight, Mn,
was 6×10^4. The transition temperatures as
judged by DSC were found to be Tg=57°C,
Ti=110.4°C.

The dielectric measurements were made in
the range 20 to 106Hz using HP4284A
Precision LCR meter. Disk samples, 100mm
thickness and 1cm diameter, were prepared
in a three-terminal dielectric cell in which a
PTFE spacer ensured dimensional stability.
The dielectric loss data are presented here as
$G/\omega = \varepsilon$ "Co,where G is the equivalent parallel
conductance of sample, $\omega = 2\pi$ f/Hz, ε " is the
dielectric loss factor and Co is the
interelectrode capacitance in vacua. The
aligned nematic phase samples were
prepared by cooling from isotropic phase with
50-300V rms at 1-10kHz.

3. RESULTS AND DISCUSSION

3.1 Unalignment behavior

Fig.1 shows plots of the dielectric loss
spectra for unaligned PMCN at different
temperatures from the nematic state to
isotropic state. The overall magnitudes of the
loss peaks are smaller than those observed
for siloxane polymers containing cyano groups
in the mesogenic head group [3-8]. These loss
spectra are broad and bimodal in the sense
that a small high frequency peak is observed
in addition to a main peak. The loss peak is
caused by the response to the probing electric
field of the polar diaryl units at the end of the
side chains. In general the loss peak exhibits
bimodal. The loss curve shows a distinct low
frequency peak and higher frequency shoulder
indicative of two broad component processes,
i.e. the small transverse and large
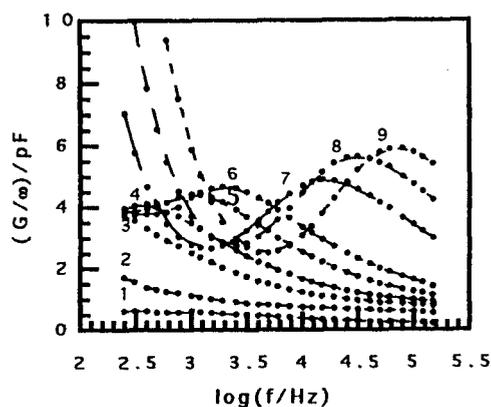
Figure 1. Frequency dependence of the
dielectric loss factor, G/ω
for unaliged PMCN in the temperature
range 59.3 to127.3°C. Curves 1-9
correspond to 59.3, 76.9, 91.1, 94.7, 101.8,
104.8, 113.8, 119.6 and 127.3°C.

longitudinal components of the dipole of the
polar mesogenic group. We labeled these as
δ -and α - relaxation in increasing order of
frequency. The activation energies obtained
from the Arrhenius plots using the relationship
between log fm against 1/T were 136.0kJ/mol
in the isotropic phase and 197.3kJ/mol in the
nematic phase. Both values were equal to
those of polyacrylates and polysiloxane
containing cyano groups in the mesogenic head
group [1-3].

Owing to the very slow variation in the shape
of the δ relaxation with temperature, we were
able to construct a reduced master curve from
ω"/ω"max against log(ω/ωmax) obtained at
different temperature. This was originally

devised to explain the relaxation in polymers in which the polar side chains are attached rigidly to the main chain. This mechanism does not involve a directional change of the side chain group dipole. Consequently, we tried to fit to the WLF equation. The WLF equation has been proposed an empirical equation which describes the temperature dependence of relaxation times in the glass-transition region by Williams,Landel and Ferry [11]. This equation may be written generally as follows,

$$\log a(T) = \frac{-c_1 (T - T_0)}{c_2 + (T - T_0)}$$

in which T_0 is an arbitrary reference temperature and c_1 and c_2 are material constants dependent on the value chosen for T_0. $a(T)$ is shift factor. As shown in Fig.2, the plot may be fitted to WLF equation with $c_1 = -8.86$, $c_2 = 101.6$°C and $T_0 = 113.0$°C, respectively. T_0 is temperature in the vicinity of phase transition Ti.
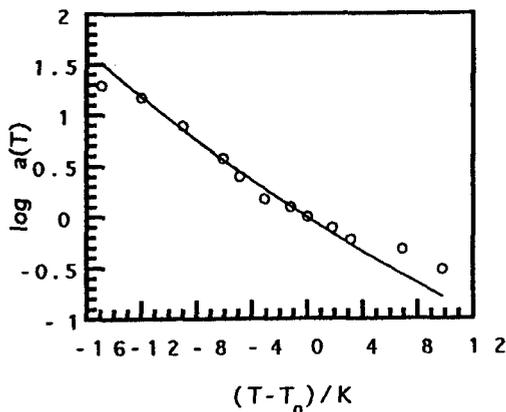
Figure 2. Plot of log a(T) against $(T-T_0)$ for unaligned PMCN. T_0 is an arbitrary reference temperature,113.8°C. Solid line shows WLF equation.

3.2 Alignment behavior

Fig.3 shows representative loss spectra for unaligned and aligned PMCN in the nematic

and isotropic phase. As shown in Fig.3, the loss spectra for unaligned nematic phase are broad and asymmetric indicating the presence of two overlapping processes compared with that of the aligned nematic phase. The loss spectra in isotropic phase for the unaligned and aligned nematic phase are fairly symmetric, and intermediate in amplitude. These behavior are all the same as those of a liquid crystalline side-chain polysiloxane [3].
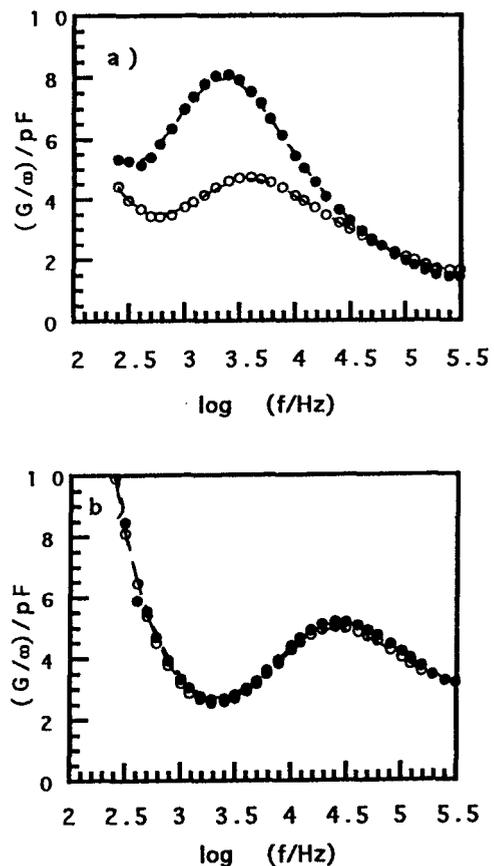
Figure 3. Representative examples of dielectric loss spectra. a).(O) unaligned at 107.7°C; (●) aligned PMCN (50Vrms/1kHz) at 106.6°C. b).(O) 117.8°C, (●) 118.3°C.

The individual loss spectra all cross at a common frequency, i.e. isosbestic point, independent of the alignment of the sample for a given sample temperature as shown in Fig.3(a).

Fig.4 shows plot of the ratio of $(G/\omega)/(G/\omega)_0$, where G/ω and $(G/\omega)_0$ are the height of loss spectra for aligned and unaligned samples, respectively. For the partial homeotropic alignment this ratio is bigger than unity. For a given frequency of aligning field, this ratio changes monotonically and reaching an effective plateau for V>100V. This behavior reveals the change of the director order parameter, Sd. The dynamic relaxation process is expressed by the Fuoss-Kirkwood empirical relaxation function so that this relation is written as,

$$G/\omega = a_\delta \ sech[\beta_\delta \ ln(f/f_{m,\delta})] +$$

$$a_\alpha \ sech[\beta_\delta \ ln(f/f_{m,\delta})] \quad (1)$$

where a_i is the maximum loss factor, (G/ω)max in i-relaxation. In this work, $i=\alpha$ and δ. β is the distribution parameter and $f_{m,I}$ is the critical frequency for i-relaxation. As the ratio of $a_i/\beta_i = A_i$ is proportional to the dielectric increment $\Delta\varepsilon$", the Sd is given by the ratio of $A_{i,\delta}$

$$Sd = (1/2) [(A_{PA,\delta})/(A_{U,\delta}) - 1] \quad (2)$$
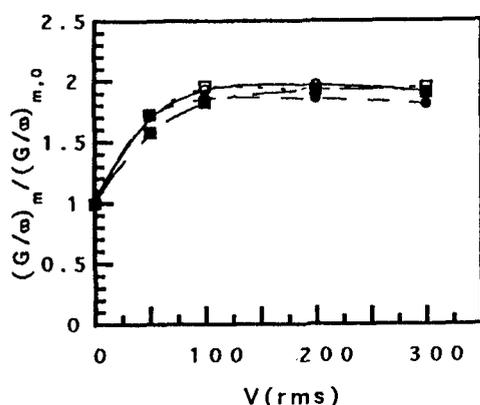
Figure 4. Degree of alignment shown as a function of rms voltage of the aligning field. (O):1kHz, (●):3kHz, (□):5kHz, (■):10kHz. Data recorded at 107.7-104.8°C.

From this equation it can be seen that Sd is in the rang -0.5 to 1.0, Sd =1.0, 0, and -0.5 are fully homeotropic aligned, unaligned, and fully planarly aligned, respectively. The distribution parameters, $\beta_{i,\delta}$ were determined from fitting our data to eq.(1) at 104.8 - 107.7°C in the nematic phase, and then the values of $\beta_{PA,\delta}$ and $\beta_{U,\delta}$ were 0.71 and 0.5, respectively. The values of Sd were able to be estimated using the maximum loss data and the value of $\beta_{i,\delta}$ from eq.(2). This result shows the same behavior as seen in Fig.4. The average value of Sd was 0.36 for V>100V. This value is similar in comparison with that of a polysiloxane containing cyano group in the mesogenic head group [12].

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