

Thermal dynamics of side-chain copolymethacrylates as studied by the dielectric spectroscopy and relaxation of second-harmonic generation

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A series of copolymethacrylates with different contents of tolane-based mesogenic groups have been synthesized. The mesogenic group content was characterized with ¹H n.m.r. The phase behaviours were determined using a differential scanning calorimeter and optical polarizing microscopy. A smectic A phase was obtained when the mesogenic group content was increased up to 80 mol.%. Dielectric relaxation results indicated that the amplitude of the α -relaxation was suppressed significantly due to the presence of the liquid crystalline phase. The reduction of the molecular motion is beneficial to the enhancement of the temporal stability of the effective second-harmonic coefficient for the polymer with a higher mesogenic group content. Moreover, the second harmonic coefficient is enhanced as the mesogenic group content increases. The self-alignment nature of the liquid crystal phase is favourable for alignment of the NLO-active mesogenic group under an applied electric field and preserving such alignment after removal of the electric field. The relationship between thermal dynamic behaviour and second-order nonlinear optical properties is also discussed. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Side chain liquid crystalline polymers (SCLCPs) exhibiting the desirable mechanical properties of a polymer and the electro-optical properties of a low molecular weight liquid crystal have been studied extensively^{1,2}. SCLCPs with excellent electro-optical properties have potential in electro-optical device applications, such as display, light valve and memory devices. Moreover, SCLCPs with second-order nonlinearity have recently attracted attention because of the self-alignment nature of the liquid crystal (LC) phase^{3–5}. In 1982, Williams et al.⁴ reported that the second-harmonic generation (SHG) of 4-(dimethylamino)-4'-nitrostilbene (DANS) doped SCLCP was considerably larger (100-fold) than could be obtained with a DANS doped PMMA. The second-harmonic (SH) coefficient of a SCLCP containing 20 mol.% chromophore (DR1) was seen to be 1.2 times greater than that of non-mesogenic copolymer with the same doping level, which was reported by Koide et al.⁵ This would be deeply attributed to the LC orientation. The self-alignment nature of the LC phase is helpful for the alignment of the mesogenic group under an applied electric poling field and preserving such alignment after removal of the poling field.

SCLCPs are able to exhibit second-order NLO properties as their NLO-active mesogenic groups are oriented in a

non-centrosymmetric manner by an applied electric field. The NLO properties are determined by the structure of the NLO-active mesogenic group (i.e. NLO chromophore), chromophore density in the polymer and the electric poling efficiency. Moreover, the poling efficiency is closely related to the ease of reorientation of the mesogenic groups. The reorientation of the mesogenic groups is dependent on the chemical structure of SCLCPs. SCLCPs containing a mesogenic group with large dipole moment, large intermolecular distance and a flexible spacer are favourable for the electric poling process^{3,6}. Dielectric relaxation is a useful technique for studying the dynamic behaviour of the polymers, since it measures directly the motions of the ground-state dipole moments of the NLO-active mesogenic groups. In addition, the poling efficiency was also determined by the poling condition of an applied electric field. The poling condition includes poling temperature, poling time and strength of the poling field. The effects of poling condition on the poling efficiency have been studied for the amorphous polymers by Firestone et al.^{7,8}. Furthermore, the poling efficiency and temporal stability of second-order nonlinearity can be obtained by studying the relaxation behaviour of the mesogenic groups. This includes the temperature dependence of the relaxation time, broadening parameter and activation energy.

In this study, a series of copolymethacrylates containing different contents of tolane-based mesogenic groups have

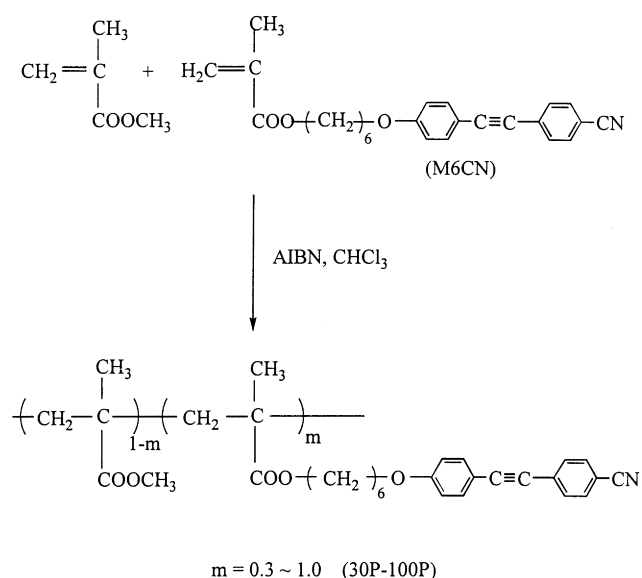
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been synthesized. The phase behaviours of this series of polymers were characterized using a differential scanning calorimeter and optical polarizing microscopy. Moreover, in order to study the relationship among the compositions, thermal dynamic behaviour and NLO properties of the polymers, the relaxation behaviours of the dielectric and SH coefficients were measured by using broadband dielectric relaxation spectroscopy and an in-situ SHG technique. Furthermore, relaxation behaviours were discussed in terms of the polymer compositions of polymer and temperature dependencies.

EXPERIMENTAL

The synthesis of the tolane-based mesogenic group (M6CN) has been reported previously⁹. The copolymethacrylates containing a tolane-based mesogenic group were prepared according to *Scheme 1*. The free radical copolymerizations of the tolane-based monomers and methylmethacrylate were carried out in a Schlenk tube under nitrogen. The polymerization tube, which contained a chloroform solution of the monomer and initiator (AIBN), was degassed under vacuum and finally filled with nitrogen. All polymerizations were carried out at 65°C for 24 h. After the reaction time, the obtained polymers were precipitated in methanol and purified by several reprecipitations from THF solutions into methanol. The content of mesogenic groups was characterized with ¹H n.m.r. for the copolymethacrylates. Moreover, the molecular weights of the polymers were determined by a Viscotek 200 GPC equipped with a differential refractometer and a viscometer.

The thermal transitions of polymers were determined using a differential scanning calorimeter (Seiko SSC/5200 DSC). The thermal transitions were read at the maximum of their endothermic or exothermic peaks. Glass transition temperature (*T_g*) was read at the middle of the change in heat capacity. Heating and cooling rates were 10°C/min in all cases. The transitions were collected from the second heating and cooling scans. A Nikon Microphot-FX optical polarized microscope equipped with a Mettler FP82 hot stage and a Mettler FP80 central processor was applied



Scheme 1 Synthesis of copolymethacrylates containing tolane-based mesogenic group.

toward observing anisotropic textures. Dielectric spectroscopy was determined on a Novercontrol GmbH. Measurements were performed by a Schlumberger SI 1260 impedance/gain-phase analyzer (frequency: 10^{-1} – 10^6 Hz) and a Quator temperature controller. A nitrogen gas heating system ranging from -100 to 250°C was used. The temperature was adjusted within the tolerance of $\pm 0.1^\circ\text{C}$. The polymers were sandwiched between two parallel metal electrode plates with a spacer of $50\ \mu\text{m}$. Moreover, the Winfit 2.3 software was used to analyze the relaxation behaviours of the dielectric relaxations.

The polymer was dissolved in tetrahydrofuran (THF) for film preparation. Thin film was prepared by spin-coating the polymer solution onto indium tin oxide (ITO) glass substrates. The thickness and indices of refraction were measured by using a prism coupler (Metricon 2010). The poling process of the thin films was carried out using the in-situ poling technique. The details of the corona poling set-up were the same as reported previously¹⁰. The poling process was started at room temperature and then the temperature was increased up to the poling temperature (above *T_g*) with a heating rate of $10^\circ\text{C}/\text{min}$. The corona current was maintained at 1 – $2\ \mu\text{A}$ with a potential of $4\ \text{kV}$. Upon saturation of the SHG intensity, the sample was then cooled down to room temperature in the presence of the poling field. Once room temperature was reached, the poling field was terminated. Second harmonic generation measurements were carried out with a Q-switched Nd:YAG laser operating at $1064\ \text{nm}$. Measurement of the second harmonic coefficient, d_{33} , has been discussed previously¹¹ and the d_{33} values were corrected for absorption¹². Relaxation behaviour of the poled sample was achieved by the in-situ SHG technique.

RESULTS AND DISCUSSION

The ¹H n.m.r. spectra of the polymethacrylates 100P and 50P are shown in *Figure 1*. The absorption peaks of protons have been identified for 100P and 50P. For polymers 50P and 100P, the absorption peaks of protons b and c appear at $\delta = 3.85$ – 4.05 . These two protons have no difference in chemical shifts. This demonstrates that these two protons have a similar chemical environment in the polymeric system. Moreover, the proton h shows up at $\delta = 3.45$ – 3.65 for the copolymer 50P. From the integration of the absorption peak areas of protons b, c and h, the mole ratio of the comonomer and mesogenic group was obtained for the copolymer 50P. It was found that the copolymer 50P contains 47 mol.% of the tolane-based mesogenic groups. The compositions, molecular weights and polydispersity of the polymers are summarized in *Table 1*. Their molecular weights were found to be in the range of 1×10^4 – 1.5×10^4 . Only the amorphous phase was observed for polymers with a lower mesogenic group content ($< 65\ \text{mol.}\%$), that is, no LC phase was observed for the copolymers 30P, 50P and 65P. In addition, an LC phase (smectic A) was observed for the copolymers 80P, 90P and 100P. The temperature range and thermal stability of the LC phase were increased with increasing mesogenic group content, whereas *T_g* was decreased with increasing mesogenic group content, due to the plasticizer effect of the mesogenic groups¹³.

Dielectric loss tangent ($\tan \delta$) versus temperature and frequency for the polymers 50P and 100P are shown in *Figure 2*. In *Figure 2a*, the α -relaxation associated with the glass transition was observed for the polymer 50P. The large amplitude of the α -relaxation was obtained due to the

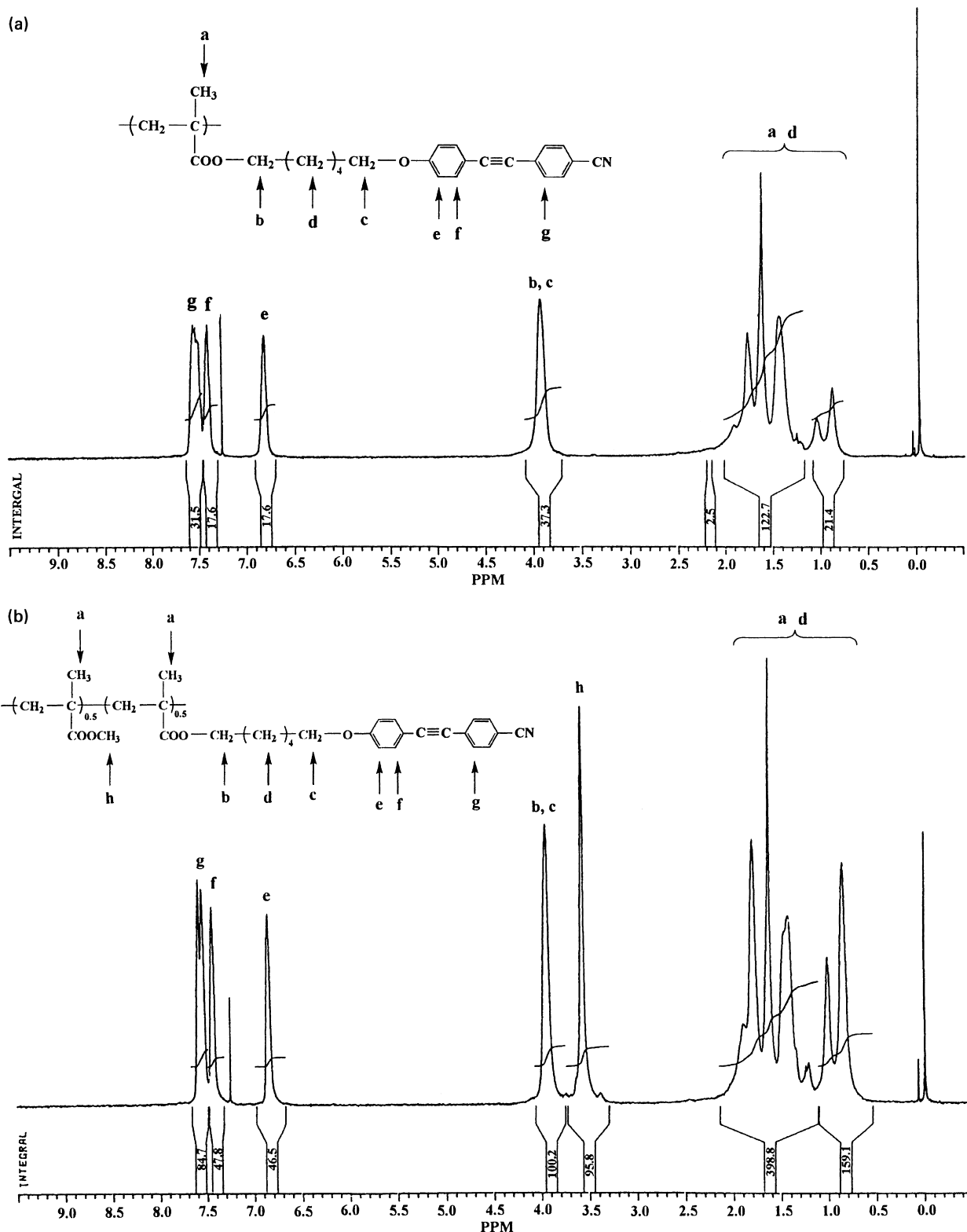


Figure 1 $^1\text{H-NMR}$ spectra of polymers 100P (a), and 50P (b), respectively.

plasticizer effect of the mesogenic groups. Moreover, the δ -relaxation was observed at a higher temperature range, which corresponded to the rotation of the mesogenic group around the polymer backbone. Similar phenomena were observed for the polymers 30P and 65P. On the other hand, a σ -relaxation was observed near the transition temperature of smectic A and isotropic phases for the polymer 100P (Figure 2b), in addition to the α - and δ -relaxations. This relaxation was possibly caused by the transition of LC and

isotropic phases. Moreover, the amplitude of the α -relaxation was remarkably suppressed compared to that of the 50P. This implies that the molecular mobility of the polymer chains was reduced during glass transition for the polymer 100P. According to the literature¹⁴, the α -relaxation is attributed to a combination of motions of the polymer main chain with the mesogenic group. In other words, the relaxation intensity is dependent on the dipole moment and molecular motions of the main chain backbone

Table 1 Molecular weights, phase transitions (°C) and corresponding enthalpy changes (J/g) of the copolymethacrylates

Polymer	m ^a	GPC		Phase transitions ^b (cooling scan ^c heating scan ^d)
		10 ⁻³ \bar{M}_n	\bar{M}_w/\bar{M}_n	
30P	0.28	9.27	1.92	I 77.3 G G 78.0 I
50P	0.47	14.6	2.22	I 66.5 G G 69.2 I
65P	0.63	13.0	1.94	I 64.2 G G 66.1 I
80P	0.78	10.5	1.92	I 80.7(2.0) S _A 57.9 G G 59.1 S _A 81.8(2.4) I
90P	0.87	11.8	1.86	I 90.2(2.2) S _A 53.1 G G 54.0 S _A 93.7(2.8) I
100P	1.00	10.1	1.61	I 108.1(2.5) S _A 46.2 G G 47.0 S _A 111.8(3.0) I

^am, according to the scheme.

^bG, glass; S_A, smectic A; I, isotropic.

^cThe data were obtained from the first cooling scans.

^dThe data were obtained from the second heating scans.

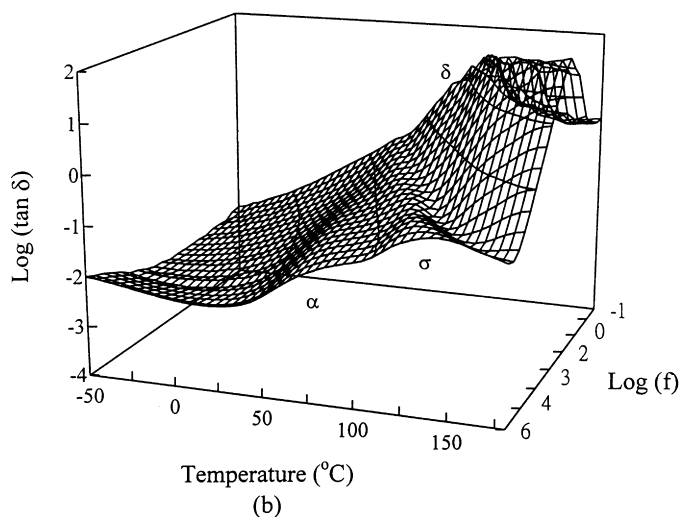
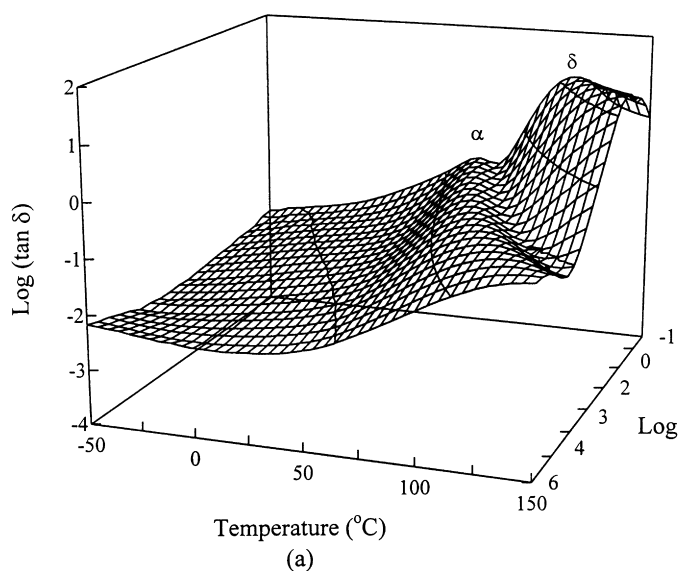


Figure 2 Dielectric loss tangent *versus* temperature and frequency for the polymers 50P (a), and 100P (b), respectively.

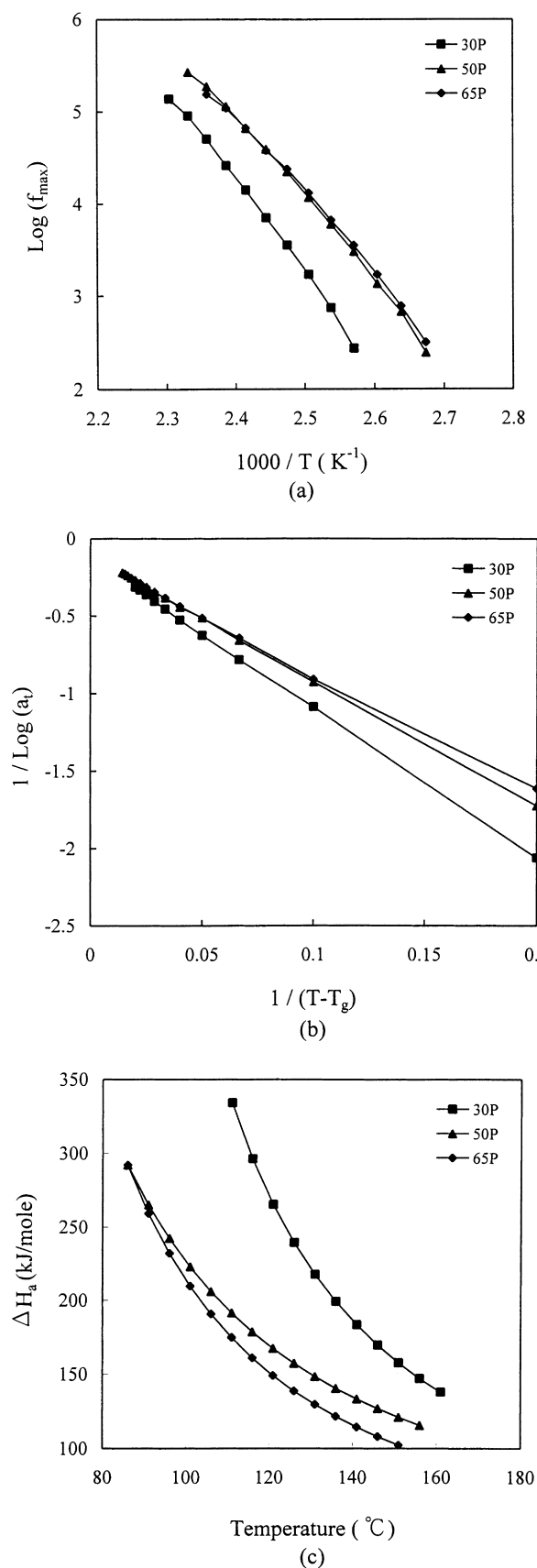


Figure 3 Temperature dependence of the relaxation frequency (f_{max}), shift factor (a_T), and activation energy (ΔH_a) of α -relaxation for polymers 30P, 50P and 65P.

and side chain groups. For the polymer with mesogenic groups, the molecular motions of the main chain backbone and mesogenic groups are mutually affected via the flexible spacer^{3,15}. The self-alignment characteristic of mesogenic groups would reduce the mobility of the main chain backbone and mesogenic groups. Consequently, suppression of the α -relaxation was obtained for the polymers with a higher mesogenic group content. Similar results were obtained for polymers 80P and 90P.

When the relaxation frequencies were plotted as a function of the reciprocal temperature, a nonlinear 'WLF' curve of the α -relaxation was obtained for polymers 30P, 50P and 65P (Figure 3a). Moreover, the relaxation frequency was increased with increasing mesogenic group content, due to the increase of the plasticizer effect. The temperature dependence of the relaxation times has been described by the empirical Williams-Landel-Ferry (WLF) equation^{7,8,16}

$$\log a_T = \log(\tau/\tau_R) = -C_1(T - T_R)/[C_2 + (T - T_R)]$$

where a_T is the WLF shift factor, τ is the apparent relaxation time at temperature T , τ_R is the apparent relaxation time at the reference temperature T_R , and C_1 and C_2 are the WLF constants. The constants C_1 and C_2 can be obtained from the WLF plot of shift factors [$\log a_T$ versus $1/(T - T_R)$]. The temperature dependence of the shift factor for the polymers 30P, 50P and 65P is shown in Figure 3b. Furthermore, the apparent activation energy (ΔH_a) of the α -relaxation can be calculated as follows^{7,8,16}

$$\Delta H_a = 2.303RC_1C_2T^2/(C_2 + T - T_R)^2$$

where R is the ideal gas constant, T_R is defined as the relaxation temperature of the α -relaxation at a lower frequency (0.1 Hz). The temperature dependence of the apparent activation energy for α -relaxation is shown in Figure 3c. The result indicates that the apparent activation energy of α -relaxation was temperature dependent. However, the relaxation time and activation energy were not obtained for the polymers 80P, 90P and 100P, due to the fact that their α -relaxation peaks were suppressed by the self-alignment nature of the LC phase.

The analysis of the dielectric relaxation behaviour for the polymers by a Cole-Cole plot (ϵ'' versus ϵ') provides valuable information about the dielectric relaxation process. Moreover, the relaxation intensity ($\Delta\epsilon_\alpha$), and symmetrical and asymmetrical broadening parameters (α' and β') of the dielectric relaxation can be obtained from the curve-fitting of the Cole-Cole plot by the Havriliak-Negami equation:

$$\epsilon^*(\omega) = \epsilon_U + (\epsilon_R - \epsilon_U)/[1 + (i\omega\tau)^{\alpha'}]^{\beta'}$$

where ϵ_R and ϵ_U represent the relaxed ($\omega \rightarrow 0$) and unrelaxed ($\omega \rightarrow \infty$) values of the dielectric constant, respectively; the ω and τ are the frequency and relaxation times, respectively. Figure 4 shows the typical curve-fitting of the Cole-Cole plot at different temperatures for the polymer 30P. Moreover, the relaxation intensity of the α -relaxation was plotted as a function of temperature for polymers 30P, 50P and 65P (Figure 5a). The α -relaxation intensity was increased with increasing temperature, and then decreased as the temperature further increased. As the temperature increases, an increase in the molecular mobility causes the dipoles to reorient toward the alternating electric field more easily, thereby resulting in an increase of the α -relaxation intensity. However, the large thermal energy results in a randomization of the orientation of the dipoles toward the alternating electric field as the temperature further

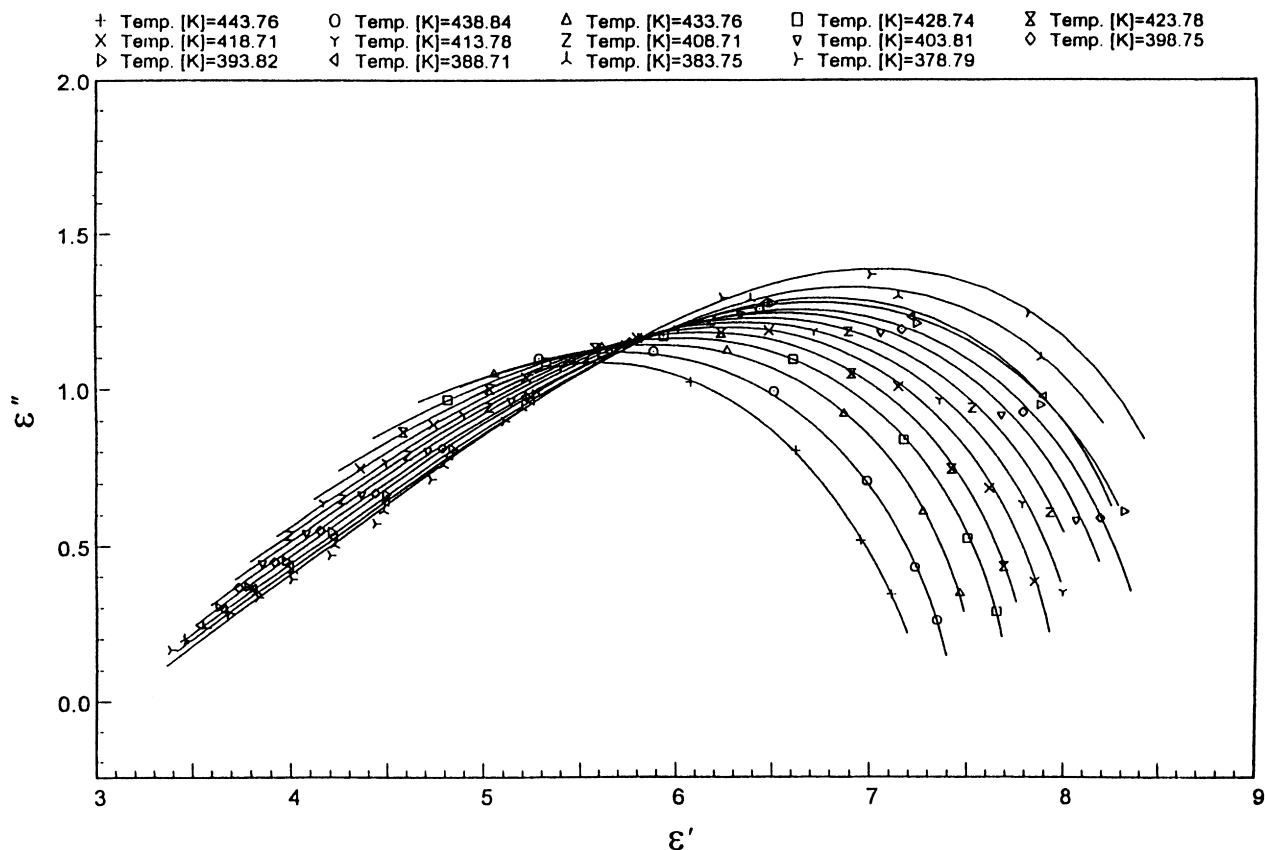


Figure 4 Cole-Cole plot of α -relaxation for polymer 30P at different temperatures.

increases, ultimately leading to a decrease in the α -relaxation intensity¹⁷. Moreover, the temperature effect on the relaxation intensity is increased with increasing mesogenic group content, due to the plasticizer effect.

The temperature dependence of the symmetrical and asymmetrical broadening parameters (α' and β') of the α -relaxation are shown in Figure 5B and C, respectively, for the polymers 30P, 50P and 65P. The parameter α' describes the symmetric width of the relaxation time distribution, and the width increases as α' ranges from 1 to 0; and parameter β' describes the skewness of the relaxation time distribution, and the skewness increases as β' ranges from 1 to 0. In Figure 5b, the broadening parameter decreased with increasing temperature, and then increased as the temperature further increased. A decrease in the broadening parameter reflects the increase of the relaxation time distribution for the α -relaxation. This implies that the molecular mobility for various molecular segments became more diversified as temperature increased. However, the molecular segments with high thermal energy tended to exhibit the similar degree of mobility. As a result, the broadening parameter began to increase as temperature further increased. At this high temperature range, the electric field was no longer effective for switching dipole alignment due to the high thermal energy. This resulted in a decrease of the relaxation intensity for the α -relaxation¹⁷. Furthermore, the polymer with a higher mesogenic content has a larger broadening parameter value, i.e. a narrow distribution of the relaxation time. This suggests that the distribution of molecular segments was more regular or the free volume of the α -relaxation was more homogeneously distributed when a polymer possessed a higher mesogenic group content¹⁸. In Figure 5c, the parameter β' was

increased with increasing temperature, and then decreased as temperature further increased. This indicates that the α -relaxation exhibited a larger degree of skewness of the relaxation time distribution in the lower temperature range. This is because α -relaxation showed up only at the lower frequency range (10^{-1} – 10^2 Hz). Moreover, the relaxation appeared at a broader frequency range (10^2 – 10^5 Hz) as temperature increased. Therefore, the skewness of the relaxation time distribution decreased with increasing temperature. As the temperature further increased, the α -relaxation was present only at the higher frequency range (10^5 – 10^6 Hz), thereby resulting in the increases of the skewness of the relaxation time distribution at a higher temperature range. In addition, a larger asymmetrical broadening parameter value was obtained for the polymer with a higher mesogenic group content. This suggests that a more symmetrical distribution of the relaxation time was present in the polymer with a high mesogenic group content.

In addition to the dielectric relaxation, thermal dynamic behaviour of the polymers has been studied by an in-situ SHG technique. The time dependences of the SHG intensity during the poling process for polymers 50P and 80P are shown in Figure 6. The results suggest that the poling efficiency (maximum of SHG intensity) was increased with increasing poling temperature at the temperature range between T_g and 15°C above T_g . The enhancement of the thermal energy was favourable for the alignment of the mesogenic group. However, the poling efficiency was reduced as the poling temperature further increased. Two factors are responsible for this. First, the high thermal energy results in a randomization in the orientation of the mesogenic group toward the electric field, and subsequently leads to the decrease of the poling efficiency¹⁹. Secondly,

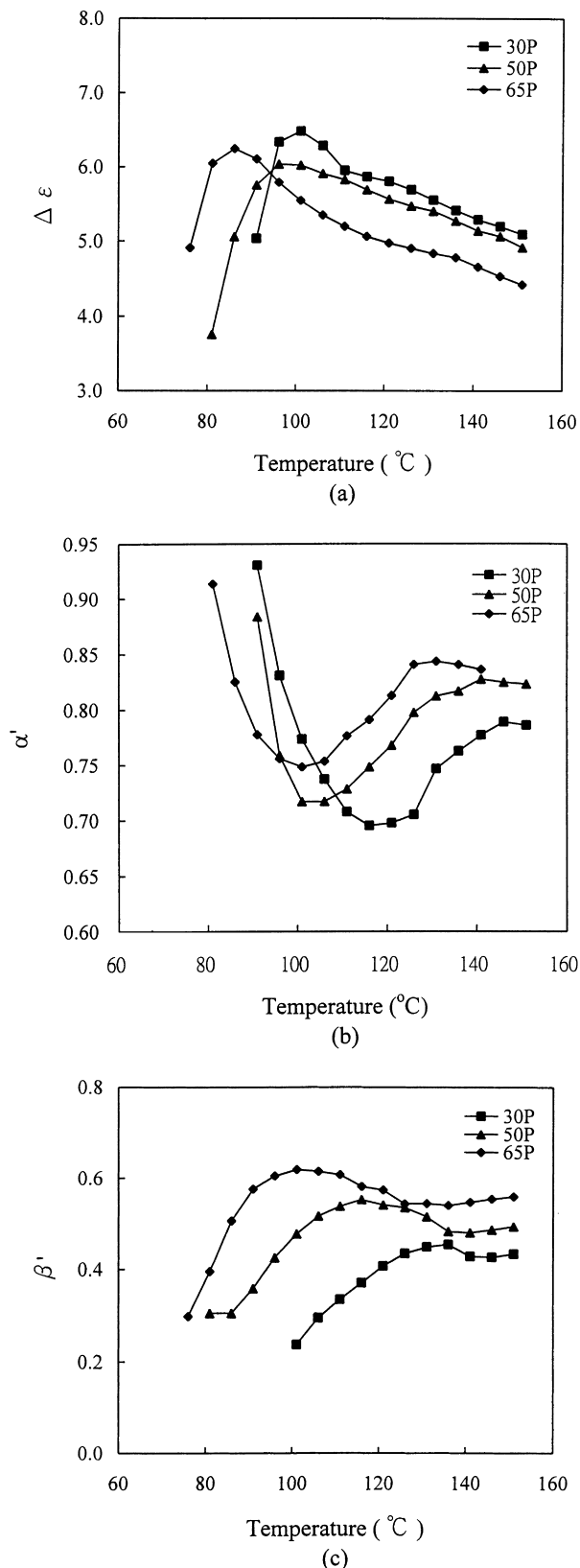


Figure 5 Temperature dependence of the relaxation intensity, and symmetrical and asymmetrical broadening parameters of α -relaxation for polymers 30P, 50P and 65P.

the increase of the conductivity of the polymer film results in the reduction of the internal electric field. This leads to the decrease of the poling efficiency of polymers at a higher poling temperature²⁰. Moreover, similar behaviour of the poling process was also observed for polymers 30P, 65P, 90P and 100P.

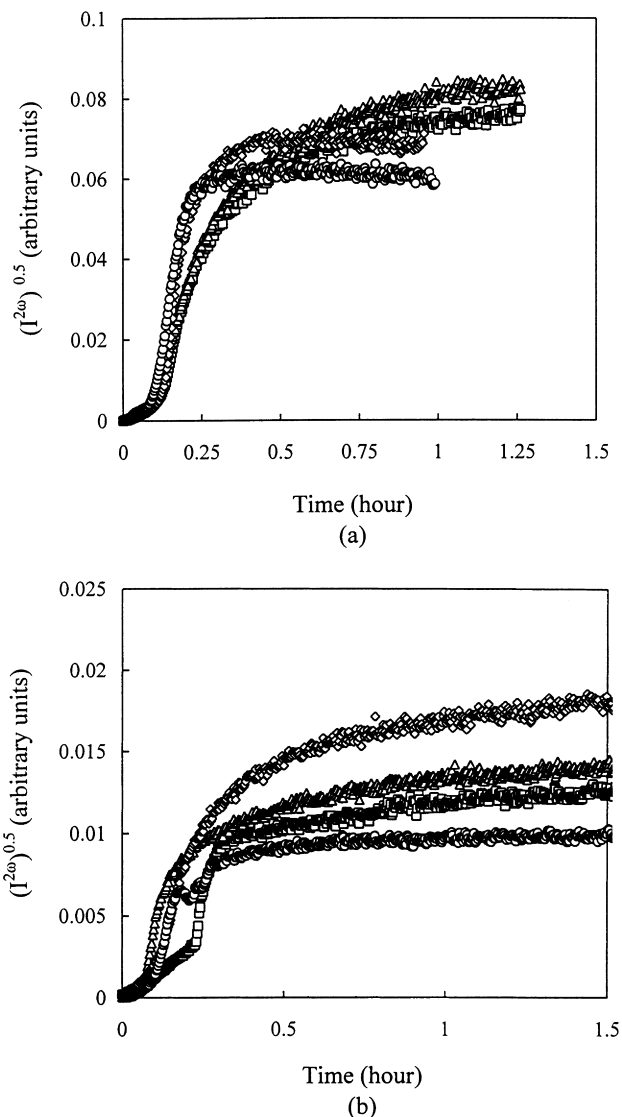


Figure 6 Time dependence of effective second harmonic coefficient during poling process for polymers 50P (a) and 80P (b), respectively ($T - T_g = 0$ (\square), 5 (\triangle), 10 (\diamond) and 15°C (\circ)).

The temporal characteristics of the effective SH coefficient (d_{eff}), after removal of the electric field at temperatures above T_g for the polymers 50P and 80P, are shown in Figure 7. The relaxation of d_{eff} was dependent on the temperature. The d_{eff} decayed rapidly as the temperature increased. Moreover, polymer 80P exhibited a better temporal stability compared to polymer 50P. This is due to the fact that the polymer with a lower mesogenic group content possessed a larger molecular mobility at temperatures near T_g . Dielectric relaxation results indicate that the mobility of the polymer chains was remarkably suppressed during the glass transition for the polymer with an LC phase, i.e. high mesogenic group content, owing to the self-alignment characteristic of the mesogenic group. As a result, a longer relaxation time was obtained for the polymer 80P. The relaxation behaviour is further described by the Kohlrausch–Williams–Watts function (KWW)^{7,8}

$$\Phi(t) = e^{-(t/\tau)^\beta}$$

where Φ represents the normalized relaxation function, τ represents the relaxation time, and β is a constant between 0 and 1 which characterizes correlation effectiveness or the

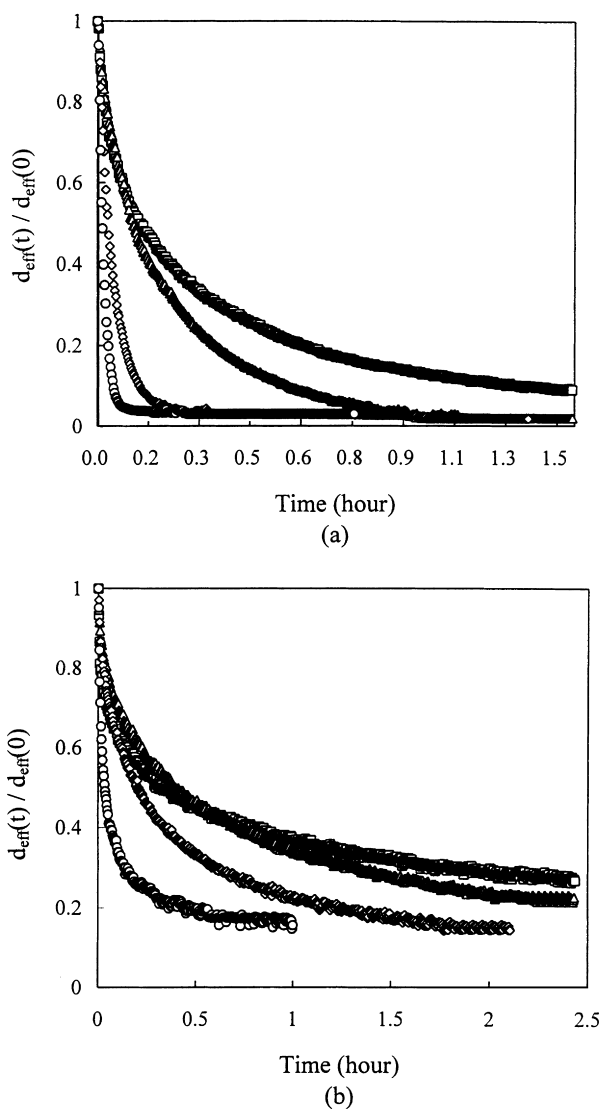


Figure 7 Temporal characteristic of effective second harmonic coefficient at temperatures above T_g for polymers 50P (a), and 80P (b), respectively ($T - T_g = 0$ (\square), 5 (Δ), 10 (\diamond) and 15°C (\circ)).

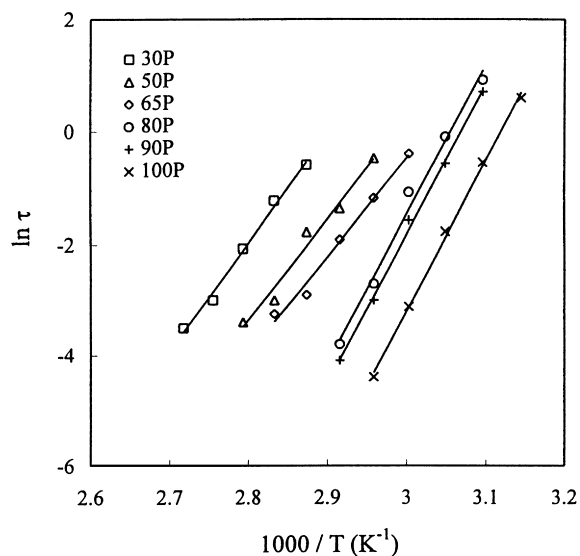


Figure 8 Temperature dependence of the relaxation time of SHG relaxation at temperature around T_g for polymers 30P–100P.

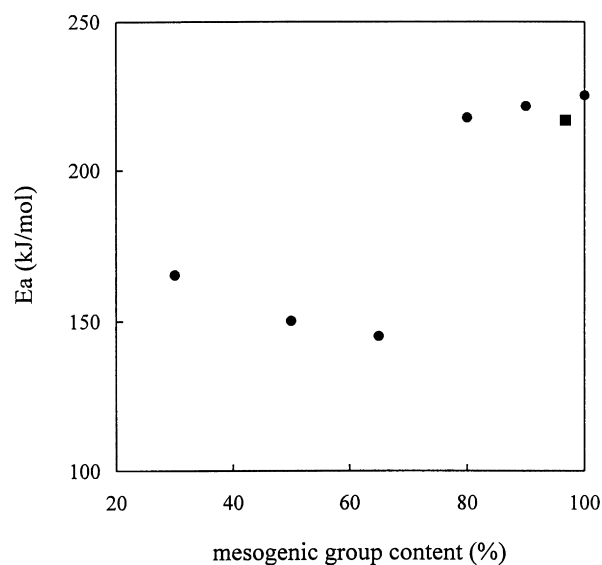


Figure 9 Activation energy of SHG relaxation versus mesogenic group content for polymers 30P–100P.

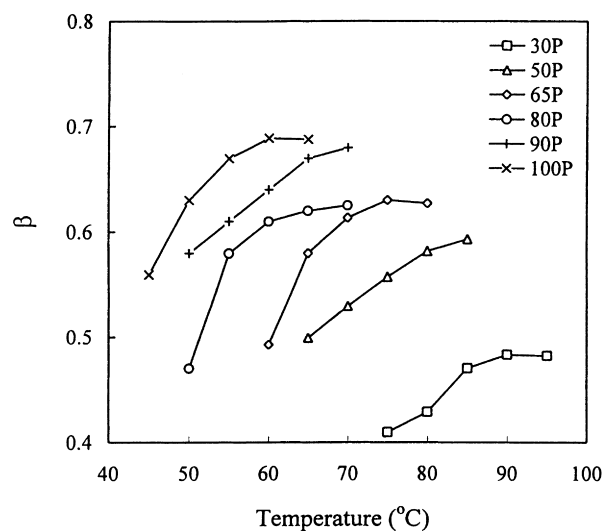


Figure 10 Temperature dependence of the broadening parameter of SHG relaxation for polymers 30P–100P.

parameter of the relaxation time distribution. The relaxation times of the d_{eff} at temperatures near T_g are plotted as a function of the reciprocal temperature, and straight lines (similar to the characteristics of an Arrhenius plot) were obtained for the polymers (Figure 8). Moreover, the relaxation activation energies of the polymers were obtained by curve-fitting with the Arrhenius equation and are shown in Figure 9. For polymers 30P, 50P and 65P, the relaxation activation energy decreases with increasing mesogenic group content, due to the plasticizer effect of the side chain group. Moreover, these polymers have a smaller activation energy compared to the polymers containing higher mesogenic contents (80P, 90P and 100P). The self-alignment nature of the mesogenic groups leads to the suppression of the molecular motion at temperatures near T_g , thereby resulting in a higher relaxation activation energy of d_{eff} for polymers with LC phase. In addition, the parameter, β , of relaxation time distribution was discussed in terms of the temperature and compositions (Figure 10). For all of the polymers, the value of the parameter, β , was increased with

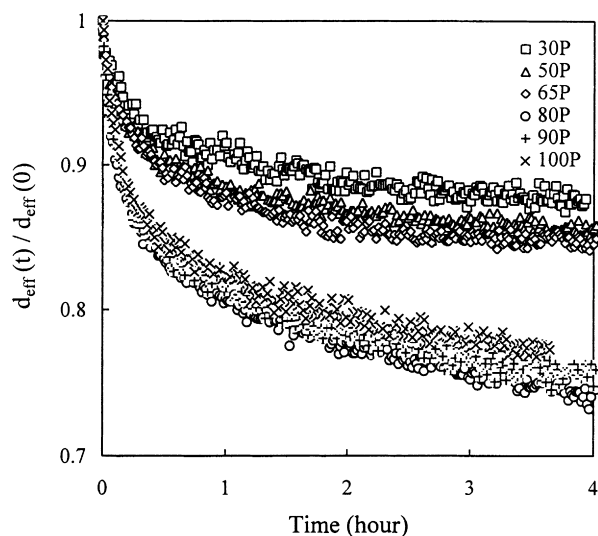


Figure 11 Temporal characteristic of effective second harmonic coefficient at room temperature for polymers 30P–100P.

Table 2 The thickness, refraction indices and second harmonic coefficient (d_{33})

Samples	d (μm) ^a	n_{532}^b	n_{1064}^b	d_{33} (pm/V) ^c
30P	1.08	1.37	1.30	3.7
50P	1.12	1.41	1.32	4.2
65P	1.02	1.42	1.34	4.5
80P	0.95	1.44	1.35	6.2
90P	1.08	1.45	1.36	7.4
100P	0.89	1.47	1.38	8.9

^a d : thickness of the polymer film.

^b n : refraction indices at wavelengths 543 and 1064 nm.

^c d_{33} : second harmonic coefficient.

increasing temperature. This suggests that the poling efficiency of the electric field was increased with increasing temperature at the temperature range between T_g and 15°C above T_g . This also agrees with the results of the dielectric relaxation. The intensity of the α -relaxation was increased with increasing temperature, and the dipole-moments of the polymer chains are favourable for the response of the electric field for the polymers in this temperature range ($T - T_g < 15^\circ\text{C}$). Furthermore, a higher value of the parameter was obtained for the polymers containing a higher mesogenic group content, due to the self-alignment characteristics of mesogenic groups.

The temporal characteristics of d_{eff} for all of the polymers at room temperature are shown in *Figure 11*. For polymers 30P, 50P and 65P, the temporal stability was decreased with increasing mesogenic group contents, due to the plasticizer effect of the side chain group. Moreover, these three polymers have a better temporal stability at room temperature compared to polymers 80P, 90P and 100P. This is due to the fact that the polymers with a lower mesogenic group content (30P, 50P and 65P) have a higher α -relaxation temperature. For polymers 80P, 90P and 100P, the temporal stability at room temperature was increased with increasing content of the mesogenic group despite their similar T_g values. These results indicate that the self-alignment nature of the NLO-active mesogenic group is beneficial to the enhancement of the temporal stability. In addition, the refraction indices and SH coefficient (d_{33}) of the poled polymers are summarized in *Table 2*. The d_{33} values for

these polymers are in the range of 3.7–8.9 pm/V. The d_{33} value is enhanced as the density of the mesogenic group increases. This indicates that the steric effect among the NLO-active mesogenic groups does not occur even at high chromophore content. This is different from S'heeren's result²¹ that in an amorphous NLO polymer system the SH coefficient initially increases with the increasing chromophore density and subsequently decreases after reaching a maximum. This is because at the high chromophore content, the polymer in this work exhibits LC phase, whereas the polymer in S'heeren's work does otherwise. LC behaviour indeed has a positive effect on the second-order NLO properties.

CONCLUSION

The effects of mesogenic group content on the dielectric behaviour and second-order nonlinearity of copolymermethacrylates containing NLO-active tolane-based mesogenic groups have been studied. The self-alignment characteristic of the mesogenic group results in reduction of the molecular mobility during glass transition for the polymer containing a higher mesogenic group content (above 80 mol.%). As a result, a better temporal stability of SH coefficient was obtained for this type of polymer at temperatures near T_g . Moreover, the temporal stability of effective SH coefficient at room temperature was increased with increasing content of the mesogenic group for copolymers with LC phase. This indicates that the self-alignment nature of the NLO-active mesogenic group is beneficial to the enhancement of the temporal stability. In addition, the d_{33} value is enhanced as the density of the mesogenic group increases. The steric effect among the NLO-active mesogenic groups does not occur even at high chromophore contents. It is concluded that liquid crystal behaviour plays an important role in enhancing the second-order NLO properties.

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