

Second-Order Optical Nonlinearity of a Polyamide Derived from 4,4'-[Hexafluoroisopropylidene]dianiline and 4-[*N,N*-Bis(2-carboxyethyl)]amino-4'-nitrostilbene

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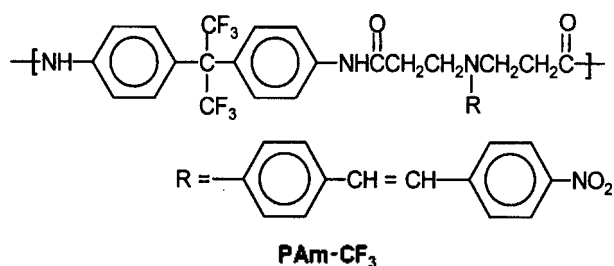
A new polyamide was prepared from 4,4'-(hexafluoroisopropylidene)di-aniline and 4-[*N,N*-bis(2-carboxyethyl)]amino-4'-nitrostilbene. This polymer was cast into thin films by spin coating cyclohexanone solution. After being poled, the electro-optic coefficients of electrode poled polymer films were measured by the reflection measurement technique using an incident laser beam of 1.3 μm . The film poled at the field strength of 1.2 V/ μm exhibited the electro-optic coefficient (r_{33}) of 5.9 pm/V. The relaxation behavior of the poled polymer film was compared with other reported polymers bearing the same NLO chromophores. Due to stiff and highly polar nature of the backbone and also due to formation of interchain hydrogen bonds, this polymer reveals a slower relaxation characteristics. The polymer is amorphous and soluble in various organic solvents.

Introduction

Polymers having chromophores of nonlinear optical (NLO) characteristics have attracted much scientific and technological interests because of their potential applications in the field of optical communications, optical processing, and optical computing.¹ Their advantages over inorganic materials are better chemical, optical, mechanical, and environmental properties, easier processability, and high NLO activities.²⁻⁶ In order to achieve a high second order NLO activity, one usually has to rely on poling of thin polymer films inducing an alignment of chromophores. Such an alignment of chromophores will provide us with non-centrosymmetric structures necessary for the second order NLO activity. Also, polymeric systems have to form good quality films, and chromophores have to be oriented easily at low electric field for practical applications in devices. The long term stability of orientation of chromophores, however, is rather poor due to their relaxant reorientation at elevated temperatures. During past several years, much efforts have been made to retard the relaxation of chromophores by crosslinking of polymer chains,⁷⁻¹² increase in the chain rigidity,¹³ and reduction of chain mobility by interchain hydrogen bonds.^{14,15} Recently, the NLO-active polyamides (See their structures shown below) having improved temporal stabilities of the poled sample due to interchain hydrogen bonding between the nitro group in the NLO-phore and amide group of the polymer backbone were investi-

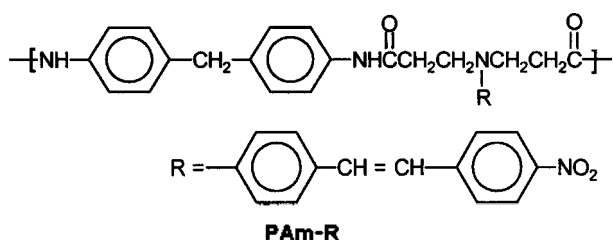
gated by us.¹⁶ However, the long term stability of the polyamide (PAm-R) having dialkylaminonitrostilbene (DANS) chromophore was found to be rather poor. Moreover, this polymer revealed a low breakdown voltage. And it was difficult to orient the chromophores.

In this study, in order to achieve a higher breakdown voltage and also to improve optical quality of polymer films, a new polyamide (PAm-CF₃) having the hexafluoroisopropylidene linking group has been synthesized. The second-order NLO properties of the poled films were studied by measuring their electro-optic coefficients for the incident light of 1.3 μm .



Experimental

Materials and Methods. The reagents, such as 4,4'-(hexafluoroisopropylidene)dianiline (FDA) and lithium chloride were purchased from Aldrich Chemical Co.. Pyridine, *N*-methyl-2-pyrrolidone (NMP), and triphenylphosphite (TPP) were purified by vacuum distillation before use. 4-[*N,N*-Bis(2-carboxyethyl)]amino-4'-nitrostilbene (BANS) synthesized following the literature procedure¹⁶ was used as a monomer. ¹H NMR and ¹³C NMR spectra were recorded on an FT-80A 300 MHz instrument. IR spectra were recorded on a Shimadzu IR-435 spectrophotometer. Elemental analyses were performed using the Perkin-Elmer EA-240 in-



strument. UV-vis. spectra were recorded on a Shimadzu UV-240 spectrophotometer. Differential scanning calorimetry (DSC) measurements were performed on a Du Pont 910 under nitrogen at a heating rate of 10 °C/min. Thermogravimetric analyses (TGA) were carried out on a Du Pont 951 under nitrogen at a heating rate of 10 °C/min. Wide angle X-ray diffractograms were obtained using nickel-filtered $\text{CuK}\alpha$ ($\lambda=1.5409$ Å) radiation on a Rigaku Geiger X-ray diffractometer. Thickness of the polymer film was measured by using an Alpha step 200 profilometer. Refractive indices were measured by prism coupling method.¹⁷

Synthesis of polymers. NLO active polyamides were prepared by direct polycondensation^{18,19} of the dicarboxylic acid and aromatic diamine monomers. A typical synthetic procedure of PAm-CF₃ polymer is as follows: BANS (0.5 g, 2 mmole), LiCl (0.4 g), TPP (1.2 g) and FDA (0.396 g, 2 mmole) were placed into a 100 mL three-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen inlet and a septum. And pyridine (2 mL) and NMP (8 mL) were added through a syringe. The reaction mixture was stirred at 100 °C for 24 hrs under a nitrogen atmosphere and cooled to room temperature. The reaction mixture was poured into ice water and the precipitated polymer was washed with acetone, dried in vacuum to yield the reddish brown polymer (0.615 g, 90 %).

¹H NMR (300 MHz, CDCl₃, δ ppm) 10.2 (s, 2H, 2NH), 8.1 (d, 2H, 2ArH), 7.7 (d, 6H, 6ArH), 7.5 (d, 2H, 2ArH), 7.4 (d, 1H, C=CH), 7.2 (d, 4H, 4ArH), 7.0 (d, 1H, CH=C), 6.8 (d, 2H, 2ArH), 3.7 (t, 4H, 2CH₂N), 2.6 (t, 4H, 2CH₂C(O)). IR (KBr pellet, cm⁻¹) 3387 (NH stretching), 1663 (C=O), 1610 (C=C stretching), 1512 and 1331 (N-O stretching), 960 (=C-H out-of-plane bending).

Preparation of films. The thin polymer films were prepared by spin coating from 20 wt.% polymer solutions dissolved in cyclohexanone. The solutions were first filtered through a 0.45 μm Teflon membrane filter to remove insoluble particles, then spun onto an ITO glass plate at 800-2000 rpm for 5-15 seconds depending on the desired thickness. It was finally dried in a vacuum oven at 150 °C for 24 hrs. After aluminum electrode was built on the polymer films by thermal evaporation, electrode poling was employed to orient the NLO chromophores at the applied voltage of about 0.2-1.2 V/ μm at a poling current less than 0.2 mA at 185 °C.

Measurement of EO coefficient (r_{33}). The electro-optic coefficient of the poled polymer was measured by using the simple reflection measurement technique.^{20,21} An InGaAs semiconductor laser beam (1300 nm) was incident on the back side of the ITO glass substrate at an angle θ . The beam propagates through the substrate and the polymer layer, and is then reflected back out into the air by the top aluminium electrode. The input beam was set at 45° to the plane of incidence so that the parallel (p-wave) and perpendicular (s-wave) components of the optical field are equal in amplitude. The reflected beam propagates through a Soleil-Babinet compensator, an analyzer, and into a detector. The modulation in the beam was measured using a lock-in amplifier.

Results and Discussion

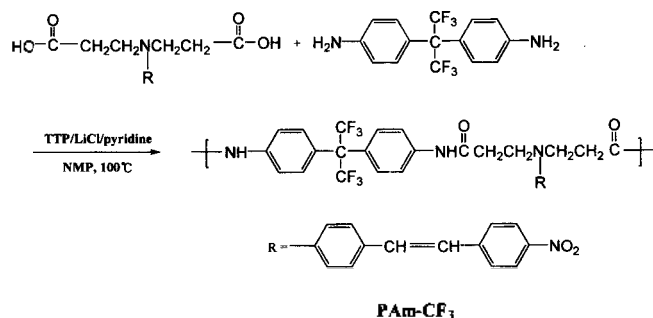
Synthesis and General Properties of the Polymer.

The present polyamide (PAm-CF₃) was prepared by direct polycondensation of the dicarboxylic acid, BANS, carrying NLO moieties and an aromatic diamine in the presence of a mixture consisting of lithium chloride, pyridine and triphenylphosphite, which was reported by Yamajaki *et al.*¹⁸ to be an excellent condensing agent. The synthetic route to the polymer is shown in Scheme 1. This synthetic approach is rather simple and was found to be satisfactory in the present study. The polymerization yield was 90%.

Various spectroscopic techniques were used to study the structures of the polyamide. In the ¹H NMR spectrum of the polyamide, a new peak at 9.9 ppm due to amide proton was clearly be seen. The chemical shifts of stilbene protons were changed from 7.5 and 7.2 ppm to 7.4 and 7.0 ppm after the formation of the new amide bond. At the same time, the chemical shift of methylene units linked to the carbonyl group was changed from 2.7 to 2.5 ppm. When the IR spectra of BANS and the polyamide are compared, the strong absorption at 3400-2600 cm⁻¹ by BANS disappeared because of the formation of the amide linkage. The absorption positions due to stilbene, nitro and trans-vinylene groups, however, remained practically unchanged. The inherent viscosity measured at the concentration of 0.5 g/dL at 25 °C in DMF solution was 0.20 dL/g. The absorption λ_{max} of the UV-Vis. spectrum measured in DMF solution was centered at 456 nm, which is originated from the π - π^* transition of the stilbene unit. The UV absorption edge of the polymer is extended to 600 nm. The extinction coefficients at λ_{max} for the polymer was estimated to be 47500 mol⁻¹ cm⁻¹.

PAm-R polyamide previously prepared¹⁶ could be dissolved in polar aprotic solvents such as NMP, DMF, DMSO, and *N,N*-dimethylacetamide (DMAc), but was insoluble in benzene, chloroform, cyclohexanone, and acetonitrile. The present PAm-CF₃ polymer exhibits much better solubility and is soluble in solvents such as NMP, DMF, DMSO, DMAc, chloroform, and cyclohexanone. The presence of the hexafluoroisopropyl group brings about such an excellent solubility for PAm-CF₃ polymer in a wide variety of the solvents. Also, it was found that the PAm-CF₃ film cast from the cyclohexanone solvent was of much better quality than the film obtained from the DMF solvent.

The glass transition temperature (T_g) of the polymer was determined to be 182 °C using DSC. Since the polar chromophores are directly attached to the main chain, their mobility should be reduced to a large extent leading to a relatively high T_g value. In comparison, the T_g value of PAm-R is significantly lower (164 °C). The reason for this difference can be found from the fact that the hexafluoroiso-



Scheme 1. Synthesis of PAm-CF₃.

propyl linking group existing in the main chain of PAm-CF₃ is much stiffer and more polar than the CH₂ group present in the main chain of PAm-R. Nakamura *et al.*²² showed that the rotation of main chain around the hexafluoroisopropylidene moiety becomes more difficult than that around isopropylidene moieties. This enhanced T_g value for PAm-CF₃ was expected to result in an enhanced temporal stability in the second order nonlinear optical property of this polymer. No crystalline melting transition was detected for the PAm-CF₃ polymer, which implies that the polymer is amorphous. Its amorphous nature could be confirmed by X-ray diffraction analysis.

Nonlinear Optical Properties. For electro-optic experiments, the PAm-CF₃ films 1-4 μm thick were prepared by spin coating 20 wt % cyclohexanone solution on ITO glasses followed by drying at 150 °C. The refractive index of the PAm-CF₃ was measured by the prism coupling method¹⁷ at various wavelengths. The values thus obtained in the TE mode are 1.645 at 0.83 μm and 1.620 at 1.3 μm, which were slightly lower than those of the polymer that contains the methylene bridge instead of the hexafluoroisopropylidene unit.¹⁶ After the polymer films of PAm-CF₃ were poled by electrode poling, the electro-optic coefficients were measured using simple reflection measurement technique^{20,21} and calculated by the following equation.²¹

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{(n^2 - \sin^2\theta)^{3/2}}{(n^2 - 2\sin^2\theta)} \frac{1}{\sin^3\theta}$$

where λ is the optical wavelength, I_m the amplitude of the modulation, I_c the half-intensity point, V_m the modulating voltage, and n the refractive index.

In order to investigate the dependence of the nonlinear optical parameters on the poling voltage, the latter was changed from 0.2 V/μm to 1.2 V/μm. As one can see from the Eq. 1 below, a linear relationship between NLO coefficient ($\chi^{(2)}$ or r_{33}) and the applied poling voltage is expected,

$$\begin{aligned} \langle \xi_j^{(2)} \rangle &= N \beta F \langle \cos^3\theta \rangle \\ \langle \cos^3\theta \rangle &= \mu_0 E / ckT \end{aligned} \quad (1)$$

where N is the number density of the chromophore, β the first order molecular hyperpolarizability, F the local field correction, μ_0 the ground state dipole moment of the NLO moiety, E the local electric field experienced by the dipole, k Boltzmann constant, and T the absolute poling temperature. The factor c equals 0.5 for nonliquid crystalline systems and 1 for liquid crystalline systems. The experimentally obtained r_{33} data are plotted against the poling voltage in Figure 1.

A linear relationship was indeed found within the limits of error of the experimental data. The r_{33} values thus obtained for the poled PAm-CF₃ in the electric field of 1.2 V/μm was 5.9 pm/V for the incident laser wavelength of 1.3 μm. This value was higher than that (3.3 pm/V at the poling voltage of 0.6 V/μm) of PAm-R polymer. The main reason for this can be ascribed to the fact that the dipole orientation or poling is expected to be more efficient for PAm-CF₃ than PAm-R polymer, because the applied poling voltage for the former polymer film could be significantly higher (1.2 V/μm vs. 0.6 V/μm) due to its better quality and capability to stand against the stronger poling field strength than the latter polymer film.

The decay of the electro-optic coefficient at a given temperature was monitored. A PAm-CF₃ film was heated as quickly as possible to a desired temperature and then the time when the film reached and was stabilized at the desired temperature was taken as the initial point of decay *i.e.*, $t = 0$. Figure 2 shows typical EO decay profiles at three different temperatures.

The EO signal of a poled PAm-CF₃ polymer was recorded over 2 h period. The decay process was slow at 100 °C and almost 80% of the initial EO signal was retained. However, the EO signal retained less, almost 70% and 50%, of its initial value at 120 °C and 140 °C, respectively.

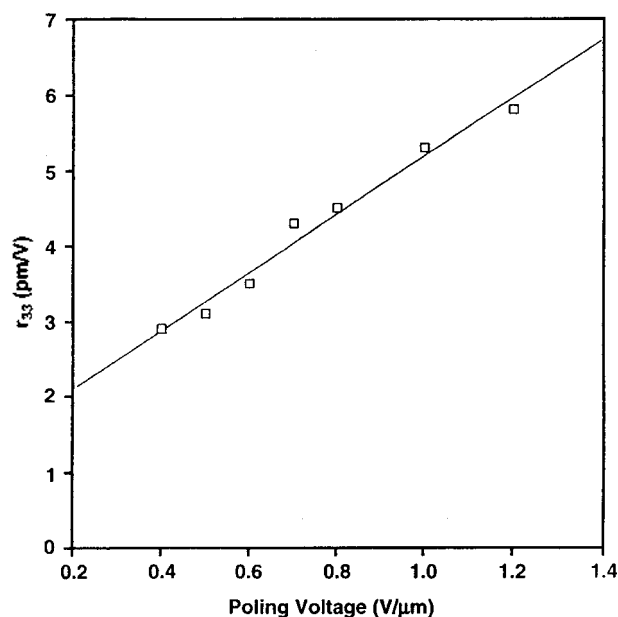


Figure 1. Dependence of EO coefficient, r_{33} , of the PAm-CF₃ Polymer on the poling voltage.

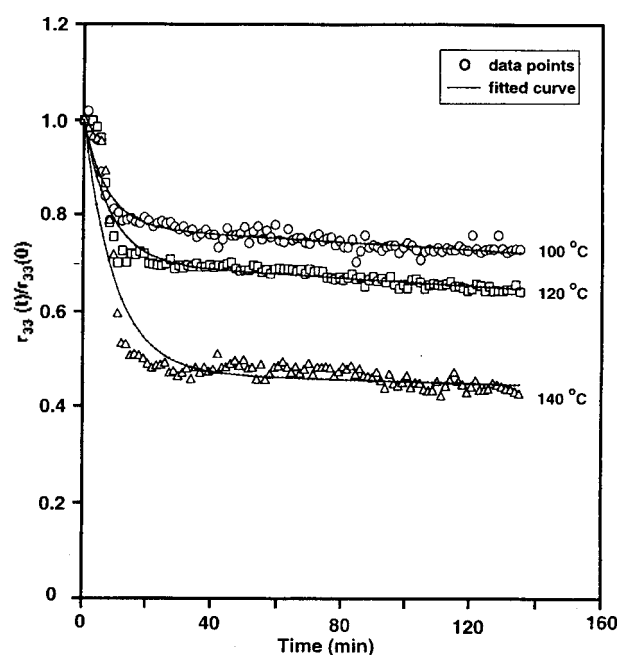
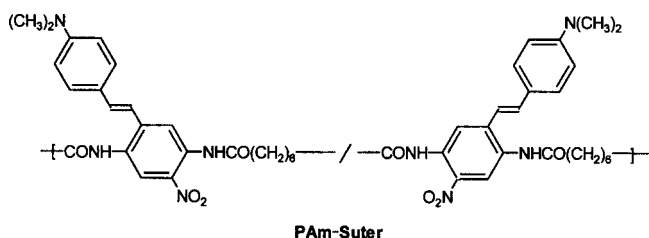
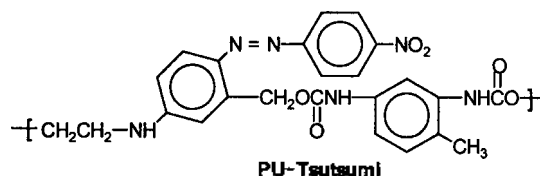


Figure 2. Relaxation of normalized EO coefficients of the PAm-CF₃ polymer at various temperatures.

Suter *et al.*^{23,24} recently reported the second-order nonlinear optical properties and orientational relaxation properties of PAm-Suter ($T_g=176$ °C) based on 2',5'-diamino-4-(dimethylamino)-4'-nitrostilbene (refer to the structure shown below). This polymer contains the NLO-phores as part of the polymer backbone with their dipoles oriented transversely to the polymer main chain:



Second-order nonlinear optical coefficients (d_{33}) up to 40 pm/V at a fundamental wavelength of 1542 nm were reported. Also, Tsutsumi *et al.*²⁵ recently reported the orientational relaxation of transversely aligned chromophores of the linear polyurethane ($T_g=57$ °C, PU-Tsutsumi) that contains the NLO moieties as an integral part of the backbone.



A large second-order nonlinearity of $d_{33}=1.6 \times 10^{-7}$ esu (67 pm/V) at a fundamental wavelength of 1064 nm with good thermal stability at the ambient conditions was reported. The second-order NLO values for the both polymers are much higher than the value of PAm-CF₃. We believe that, in spite of the same or similar chromophore structures, the two polymers revealed much higher 2nd-order NLO values than PAm-CF₃ mainly due to much stronger applied maximum poling field strengths. Evidently, the polymer films reported by Suter and Tsutsumi could stand stronger poling fields without breakage.

Oriental stability of NLO-phores of PAm-CF₃ is compared with those of the two polymers, PAm-Suter and PU-Tsutsumi. The decay of the normalized signal intensity could be described by the following the Kohlrausch-Williams-Watts (KWW) stretched exponential function^{26,27}:

$$r_{33}(t)/r_{33}(0) = \exp[-(t/\tau)^\beta] \quad (2)$$

where $r_{33}(t)/r_{33}(0)$ is the intensity ratio of the signal after beginning the measurement normalized to the signal at $t=0$. τ is the characteristic relaxation time that is required for the electro-optic coefficient, $r_{33}(t)$, to decay to $1/e$ of its initial value, $r_{33}(0)$. EO coefficients are usually normalized to unity at $t=0$. β is a measure of width of the distribution of relaxation time and extent of deviation from a single exponential behavior. When $\beta=1$, the time-dependent decay corresponds to a single exponential decay profile. The data points were fitted to Eq. 2 by a least-square routine and the results are summarized in Table 1.

The relaxation time, τ , of the PAm-CF₃ polymer is reduced from 6195 min at 100 °C to 1843 min at 140 °C. Qualitatively, the results show that the disorientation of the im-

Table 1. Effect of Temperature on the Temporal Characteristics of the Electro-Optic Coefficient^a

Polymers	PAm-CF ₃			PAm-Suter ^b			PU-Tsutsumi ^c		
	100	120	140	80	158	167	80	87	90
τ , min	6195	3177	1843	5×10^5	19	4.8	57	45	11
β	0.23	0.25	0.29	0.55	0.27	0.42	0.71	0.65	0.65

^a Parameters were obtained by fitting data (Figure 2) to Eq. 2. ^b The polyamide polymer reported by Suter *et al.*^{23,24} ^c The polyurethane polymer reported by Tsutsumi *et al.*²⁵

posed alignment was more rapid at higher temperature, which is as well expected. The relaxation time, τ , for PAm-CF₃ is lower than that of the PAm-Suter polymer, but greater than that of the PU-Tsutsumi polymer. This means that orientational relaxation of the NLO-phores of the PAm-CF₃ polymer is faster than that of the PAm-Suter polymer, but slower than that of the PU-Tsutsumi polymer. Main reason for a better long-term stability of PAm-CF₃ compared to the PU-Tsutsumi polymer can be ascribed to its high T_g value (182 °C for PAm-CF₃ vs 57 °C for PU-Tsutsumi). A significantly slower relaxation was observed for PAm-Suter than for PAm-CF₃ in spite of its lower T_g value (176 °C for PAm-Suter vs 182 °C for PAm-CF₃). The interesting structural difference between PAm-CF₃ and PAm-Suter lies in the fact that the positions of dialkylamino and nitro groups are reversed. In the PAm-Suter polymer nitro groups are attached to the phenylene rings that are part of the backbone, which, in turn is expected to reduce the mobility of oriented NLO-phores resulting in temporal stability of aligned chromophores as discussed above. The values for β of the PAm-CF₃ polymer range from 0.23 to 0.29 without much change with temperature and largely deviate from 1.

In order to correlate the orientation-relaxation behavior of polymers with their glass transition temperatures, several different relations between T_g , temperature T , and relaxation time τ have been proposed. The Vogel-Tamann-Fischer (VTF) equation (WLF equivalent function)²⁸ is one of them:

$$\tau(T) = A' \exp((T_g - T)/T) \quad (3)$$

where τ has the same meaning as in Eq. 2, A' a system-dependent constant, and T_g the glass transition temperature. Figure 3 shows the scaling plot of the relaxation time for the present polymer. For the purpose of comparison, the results of similar experiments on a polyamide^{23,24} (PAm-Suter, $T_g=176$ °C) and a polyurethane²⁵ (PU-Tsutsumi, $T_g=57$ °C) are also included. As can be seen from Figure 3, the logarithmic τ value for the relaxation of NLO chromophore in the present polyamide is linearly dependent on the reduced temperature, $(T_g - T)/T$, in the temperature range from $T_g - 80$ °C to $T_g - 40$ °C. The results show that the relaxation behavior of PAm-CF₃ favorably compares with PAm-Suter and PU-Tsutsumi. The lower slope indicates that, in the measured temperature regime, the relaxation processes of PAm-CF₃ is less thermally sensitive than the other two polymers. One of possible explanation for the enhanced thermal stability of the oriented chromophores in the PAm-CF₃ polymer is its stiffer backbone due to stronger interchain interactions arising from the presence of strong electron acceptors, CF₃ groups, along the backbone. Another important

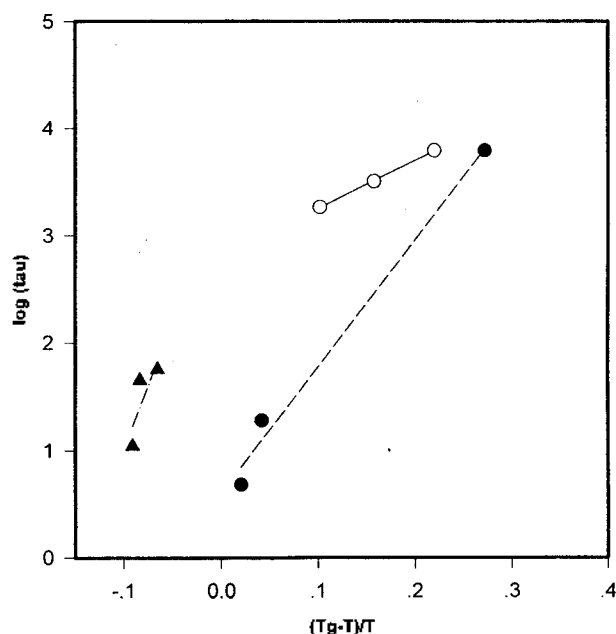


Figure 3. Scaling of relaxation time against $(T_g - T)/T$ (○: PAm-CF₃, ●: PAm-Suter, ▲: PU-Tsutsumi).

reason lies in the fact that hydrogen bondings¹⁶ between the nitro groups and amide hydrogens in PAm-CF₃ are stronger because the nitro groups are free to approach the main chain amide hydrogens due to its longer distance from the backbone.

Conclusion

We have prepared a new polyamide (PAm-CF₃) whose backbone is consisting of the 2,2-diphenylhexafluoroisopropylidene group and the aliphatic amide part to which the dialkylaminonitrostilbene chromophore moieties are attached. This polymer was found to be soluble in a wide variety of polar organic solvents and produce high quality films on spin-coating. The electro-optic coefficient value of this polymer was 5.9 pm/V at the poling field strength of 1.2 V/μm for the incident beam of 1.3 μm. This polymer revealed a lesser temperature dependence of the relaxation behavior when compared with other similar polymers. It also revealed slower relaxation. This is ascribed to the enhanced polar nature and higher rigidity of the backbone of PAm-CF₃ and also to the facile interchain hydrogen bond formation¹⁶ between the nitro group of the chromophore and amide hydrogens in the main chain of the polymer.

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