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N-phenylmaleimide polymers for second-order nonlinear optics

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Second-order nonlinear optical properties of the polymers of *N*-phenylmaleimides coupled with nonlinear optical (NLO) chromophores through urethane linkages were investigated. *N*-[4-(Azidocarbonyl)phenyl]-maleimide, the precursor of the isocyanato *N*-phenylmaleimide, was prepared and reacted with NLO chromophores, *N*-(4-nitrophenyl)-L-prolinol (NPP) or 4′-[(2-hydroxyethyl)methylamino]-4-nitrostilbene (ANS) to give monomer **5** or monomer **6**. The monomers were polymerized and copolymerized with methyl methacrylate (MMA) and styrene (ST). The nonresonant linear electro-optic (EO) coefficients, r_{33} values of the copolymers of **5** with MMA or ST corona-poled under 0.6 MV cm^{-1} were found to be about 10–15 pm V^{-1} when measured at 632.8 nm, and those measured at 830 nm were lower by 15–20%. The r_{33} values of the copolymers of **6** with MMA measured at 632.8 nm and 830 nm were 25–35 pm V^{-1} and 8–10 pm V^{-1}, respectively. The homopolymer of **5** showed the excellent thermal stability of the EO coefficient, which retained 85% of its original value when aged at 80°C for 48 h. The EO coefficients of the copolymers were 45–70% of their original values after 48 h at 80°C. At room temperature, no decay of r_{33} values of all polymers was observed over a period of 1 month. © 1997 Elsevier Science Ltd.

(Keywords: second-order nonlinear optics; *N*-phenylmaleimide polymer; thermal stability)

INTRODUCTION

Polymers with nonlinear optical properties have been intensively studied in recent years, but several important properties, such as thermal stability, processability, electro-optical coefficients, and optical loss must be much improved before there are practical applications in electro-optic (EO) and photonic devices[1–3]. These properties are closely related to each other, and enhancement of one property often deteriorates the other properties. For example, the rigid polymers of high glass transition temperature (T_g), or the crosslinked polymer systems for high thermal stability of EO coefficients, usually have difficulties in processing. High concentrations of non-linear optical (NLO) chromophores for high EO coefficients also have adverse effects on processability. These conflicting properties can be optimized by utilizing the radical copolymerization method, which enables us to control the concentrations of the hard and the soft segments as well as of the chromophores.

N-phenylmaleimide is a good candidate for a rigid unit. The polymers of *N*-phenylmaleimide and its derivatives have been known to exhibit high T_gs due to the rigid imide rings in the backbones[4,5]. Recently, Tapolsky *et al.*[6] have reported a bismaleimide functionalized NLO chromophore, which has been polymerized with nucleophilic addition of primary or secondary amines to yield a thermally stable crosslinked matrix. The linear maleimide polymers for NLO have also been reported to show good thermal stability. Ahlheim and Lehr[7] have synthesized NLO maleimide copolymers by polymer reactions of maleic anhydride copolymers with aminoalkyl functionalized azo dyes[7].

In this work the radical polymerization of *N*-phenylmaleimides coupled with NLO chromophores through urethane linkages was investigated. Compound **3**, the precursor of the isocyanato *N*-phenylmaleimide, was easily reacted with hydroxy group or amino group terminated NLO chromophores. Monomers **5** and **6** were polymerized and copolymerized with methyl methacrylate (MMA) and styrene (ST). The contents of the soft segments, and thereby the T_gs of the copolymers, were controlled by varying the monomer feed ratios. Since the polymers possessed urethane bonds, interactions between the polymer chains or the side chain chromophores through inter- or intramolecular hydrogen bondings were expected after poling, which would show a great enhancement of thermal stability of EO activity.

EXPERIMENTAL

Materials and instrumentation

Compounds **1** and **2** were prepared following the procedures in the literature[8]. All reagents were purchased

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from Aldrich Chemical Co. Maleic anhydride and 2,2'-azobisisobutyronitrile (AIBN) were purified by recrystallization from benzene and methanol, respectively. Reagent grade solvents were dried and purified as follows. Dimethylformamide (DMF) was dried over anhydrous P_2O_5 and purified by distillation. Toluene was distilled over CaH_2. The other reagents were used as received. ^{1}H nuclear magnetic resonance (n.m.r.) spectra were recorded on a Varian-Gemini 200 spectrometer. Infra-red (i.r.) spectra were obtained with the use of a Nicolet Magna-IR 550 spectrometer. Ultraviolet–visible (u.v.–vis) spectra were recorded with a Shimadzu UV-3101 PC spectrophotometer. Gel permeation chromatography (g.p.c.) was carried out with a Waters 150C g.p.c. with a M410 refractive index detector. Thermal analyses were performed by a Dupont 2010 differential scanning calorimeter (d.s.c.) and a 2050 thermogravimetric analyzer (t.g.a.). Elemental analyses were performed by a Carlo Erba 1108 or Perkin Elmer 240C elemental analyzer at Korea Research Institute of Chemical Technology and Korea Basic Research Center.

Synthesis of N-*[4-(azidocarbonyl)phenyl]maleimide (3)*

A solution of sodium azide (0.65 g, 10.0 mmol) in water (25 ml) was added dropwise to a solution of compound **2** (2.07 g, 8.8 mmol) in methylene chloride (35 ml) at 0°C and stirred for 4 h at the same temperature under nitrogen. The reaction mixture was washed with water (40 ml) three times, and dried over anhydrous magnesium sulfate. After filtration and evaporation, the crude product was purified by recrystallization from methylene chloride (yield 75%, mp 120–121°C).

Anal. Calcd for $C_{11}H_6N_4O_3$: C, 54.54; H, 2.50; N, 23.14. Found: C, 54.50; H, 2.44; N, 23.10. ^{1}H n.m.r. [dimethyl sulfoxide (DMSO)-d_6]: δ 7.25 (*s*, 2H, vinyl protons), 7.60 and 8.10 (2*d*, 4H, phenyl protons).

Synthesis of N-*[4-(*N'*-phenoxycarbonylamino)phenyl] maleimide (4)*

To a solution of phenol (0.5 g, 5.3 mmol) and dibutyltin dilaurate (DBTDL, 0.1 ml) in toluene (200 ml) was added compound **3** (1 g, 4.1 mmol) and the solution was refluxed for 3 h. The crude product was isolated by filtration and purified by column chromatography on silica gel (40% ethyl acetate in hexane) and then recrystallization from ethyl acetate–hexane (yield 70%, mp 206–208°C).

Anal. Calcd for $C_{17}H_{12}N_2O_4$: C, 66.22; H, 3.93; N, 9.09. Found C, 66.10; H, 3.91; N, 9.00. ^{1}H n.m.r. (DMSO-d_6): δ 10.43 (*s*, 1H, NH), 7.20 (*s*, 2H, vinyl protons), 7.25–7.35, 7.45, 7.63 (9H, phenyl protons).

Synthesis of monomer 5

To a solution of *N*-(4-nitrophenyl)-L-prolinol (NPP, 4.0 g, 18.0 mmol) and DBTDL (0.1 ml) in toluene (150 ml) was added compound **3** (4.3 g, 18.0 mmol) or compound **4** (5.5 g, 18.0 mmol). The solution was refluxed for 5 h. The crude product was isolated by filtration and purified by column chromatography on silica gel (40% ethyl acetate in hexane) and then recrystallization from ethyl acetate (yield 70%, mp 201–202°C).

Anal. Calcd for $C_{22}H_{20}N_4O_6$: C, 60.53; H, 4.62; N, 12.84. Found: C, 60.40; H, 4.58; N, 12.70. ^{1}H n.m.r. (DMSO-d_6): δ 9.90 (*s*, 1H, NH), 8.10, 7.60, 7.27, and 6.85 (4*d*, 8H, phenyl protons), 7.20 (*s*, 2H, vinyl protons), 4.30 (*m*, 2H, OCH_2), 4.05 (*m*, 1H, CH), 3.60 and 3.30 (*m*, 2H, NCH_2), 2.10 (*m*, 4H, CH_2CH_2).

Synthesis of monomer 6

To a solution of 4'-[(2-hydroxyethyl)methylamino]-4-nitrostilbene (7 g, 23.5 mmol) and DBTDL (2 ml) in toluene (200 ml) was added compound **3** (5.7 g, 23.5 mmol). The solution was refluxed for 4 h. The crude product was isolated by filtration and purified by column chromatography on silica gel (50% ethyl acetate in hexane) (yield 85%, dec. 225°C).

Anal. Calcd for $C_{28}H_{24}N_4O_6$: C, 65.60; H, 4.72; N, 10.94. Found: C, 64.65; H, 4.34; N, 11.34. ^{1}H n.m.r. (DMSO-d_6): δ 9.83 (*s*, 1H, NH), 8.20, 7.80, 7.55, 7.25 and 6.80 (12H, phenyl protons), 7.40 and 7.15 (*dd*, 2H, vinyl protons), 7.20 (*s*, 2H, vinyl protons), 4.30 (*t*, 2H, OCH_2), 3.75 (*t*, 2H, NCH_2), 3.05 (*s*, 3H, NCH_3).

Homopolymerization

Typical procedure is as follows: A mixture of monomer **5** (1.0 g, 2.3 mmol) and AIBN (3.5 mg) in DMF (1.5 ml) was placed into a polymerization tube (5 ml). After freeze–thaw treatments under nitrogen, the tube was sealed under vacuum. Polymerization was carried out at 80°C for 24 h. The resulting polymer was isolated by precipitation into methylene chloride (50 ml) and purified by reprecipitation from DMF into methylene chloride twice.

Copolymerization

Typical procedure is as follows: A solution of monomer **5** (0.2 g, 0.46 mmol), appropriate amount of comonomer, for example MMA (0.05 ml, 0.46 mmol), and AIBN (1.5 mg) in DMF (2 ml) was charged into a polymerization tube (5 ml). After freeze–thaw treatments under nitrogen, the tube was sealed under vacuum. Polymerization was carried out at 80°C for 24 h. The resulting polymer was isolated by precipitation into methylene chloride/methanol (1/9, 50 ml) and purified by reprecipitation from THF into methylene chloride/methanol twice.

Material processing

For thin film fabrication, a polymer was dissolved in DMF/tetrahydrofuran (THF) (1/0.2). The filtered polymer solution (10 wt%) was spin-coated at 1500 rpm either on indium tin oxide (ITO) precoated glass or normal microslide glass and the films were dried to give an optical quality. The thickness of the film was measured using Tencor P10. The refractive index of the polymer coated on silicon wafer was measured with a Rudolph Auto ELII ellipsometer (Rudolph Research). The wavelength used for this measurement was 632.8 nm and the incident angle was 70°.

For the second harmonic generation (SHG) experiment, we poled the films on microslide glass using the corona poling technique in a wire-to-plane geometry[9,10]. For linear EO coefficient measurement, we deposited the gold electrode on the top of the film and did electrode poling to apply the electric field directly to both gold and ITO electrode.

Measurement of the second-order NLO coefficient, d_{33}

The SHG measurements of the poled samples were carried out with a Q-switched mode locked, Nd^{3+}: YAG laser operating in the TEMoo mode. We followed the standard Maker fringe technique which was already well understood[11]. Assuming Kleinman's symmetry rule, we used the p-p fringe to calculate the d_{33} value. The second harmonic signal was normalized with respect to that from a calibrated quartz crystal for which a value of $d_{11} = 0.5\,\text{pm V}^{-1}$ was assumed[12].

Measurement of EO coefficient, r_{33}

We measured the linear EO coefficients by way of a simple reflection technique proposed by Teng and Mann[13]. The He–Ne and diode lasers (wavelength 632 nm and 830 nm) were used. In the measurement, the sine wave modulating voltage, r_{33} could be calculated by the following equation.

$$r_{33} = \frac{3\lambda I_{\mathrm{m}}}{4\pi V_{\mathrm{m}} I_{\mathrm{c}} n^2} \frac{(n^2 - \sin^2\theta)^{1/2}}{\sin^2\theta}$$

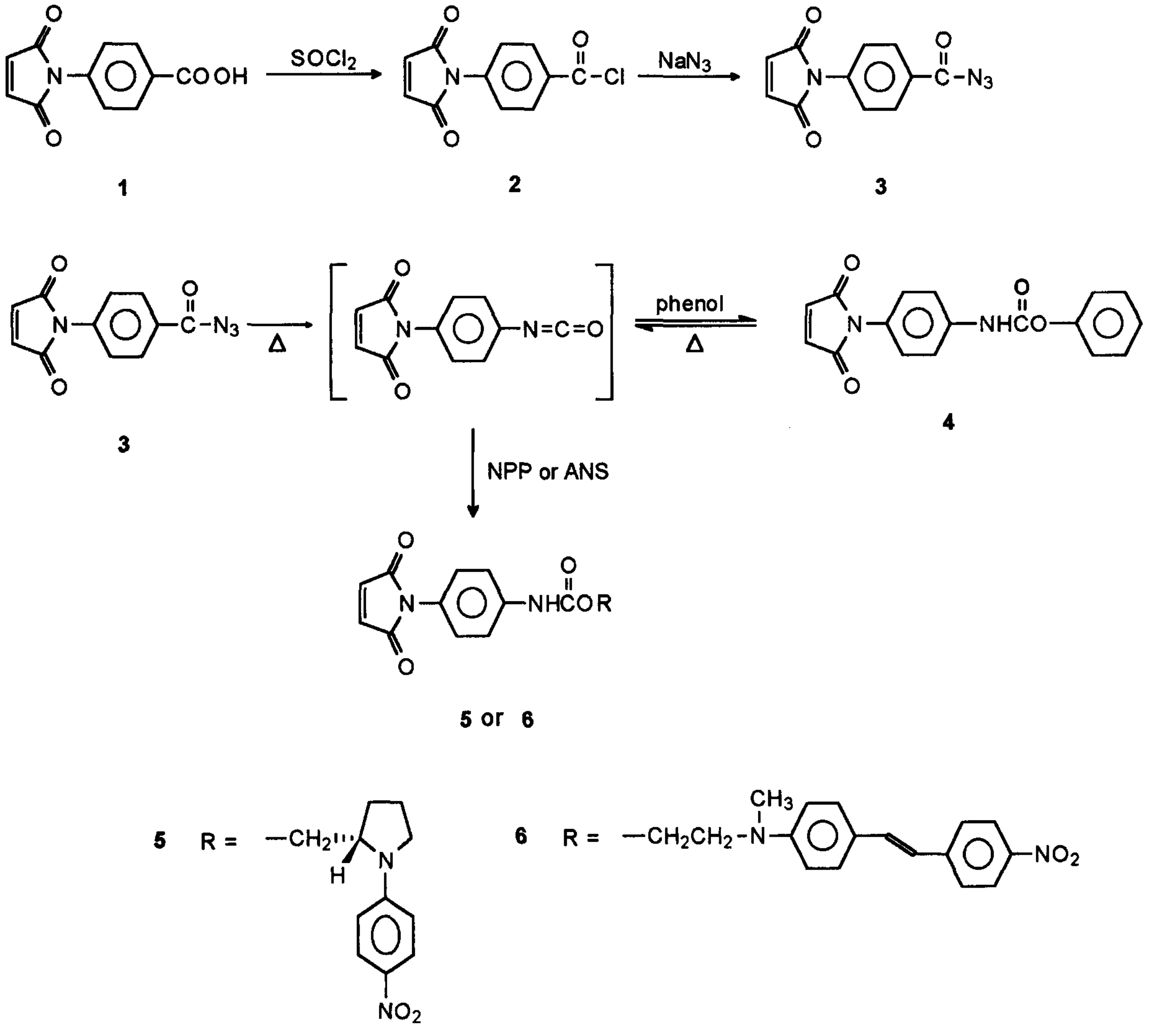
where I_{m} is the amplitude of modulation, V_{m} is the modulating voltage applied to the sample, I_{c} is half the maximum intensity of light, and n is the refractive index of the sample.

RESULTS AND DISCUSSION

Synthesis of monomer

Since NLO chromophores are often bulky and have low nucleophilicity, highly reactive functionalized monomers are required for more efficient coupling reactions. An isocyanate group is very reactive against various nucleophiles. Alcohols and amines are readily added to produce urethanes and ureas, respectively. One of the known methods for preparation of isocyanates is Curtius degradation of acyl azides. *Scheme 1* shows the synthesis of the monomers. Compounds **1** and **2** were prepared according to the literature[8]. Acyl chloride **2** in methylene chloride was reacted with sodium azide in water. Reaction occurred at the interface of an aqueous and an organic layer. The resulting product stayed in the organic layer. Azide **3** was isolated as a solid at room temperature and purified by recrystallization from methylene chloride. The compound was stable at room temperature but slowly decomposed during storage.

In the d.s.c. thermogram of compound **3**, a very sharp and strong exotherm ($\Delta H = -120.5\,\text{kJ mol}^{-1}$) appears at 134°C, which corresponds to the elimination of nitrogen of azide groups and subsequent rearrangement to isocyanate groups. This thermal reaction was also



Scheme 1

confirmed by i.r. spectroscopy (*Figure 1*). The stretching peak of N_3 of compound **3** appears at $2150\,cm^{-1}$. When compound **3** was heated in toluene at 100°C and isolated by evaporation of the solvent, the N_3 peak at $2150\,cm^{-1}$ completely disappeared and newly showed up the stretching peak of isocyanate groups at $2270\,cm^{-1}$. Compound **3** was also polymerizable with radical initiators. No significant degradation of the azide groups was observed if the polymerization proceeded below 70°C. The polymers exhibited similar thermal behaviours to that of the monomer. The polymerization results will be published elsewhere.

Two NLO chromophores, NPP and 4′-[(2-hydroxyethyl)methylamino]-4-nitrostilbene (ANS) were coupled with *N*-phenylmaleimide. The reactions of compound **3** with NLO chromophores were carried out in toluene in the presence of DBTDL. The products were precipitated during reactions. They were purified by column chromatography and recrystallization.

It is very difficult to isolate and shelve an aromatic isocyanate due to its high reactivity against nucleophiles. Compound **3** was a good precursor for the isocyanate compound, but also had trouble with long term storage because of its slow degradation by heat or light. Alternatively, the stable urethane (**4**) was prepared by blocking the isocyanate group generated from compound **3** with phenol. Compound **4** showed a reactivity similar to that of compound **3**, and a long shelf life. Phenol was easily removed on heating above 120°C to regenerate an isocyanate group. Compounds **5** and **6** were also obtained by reacting compound **4** with NPP and ANS, respectively.

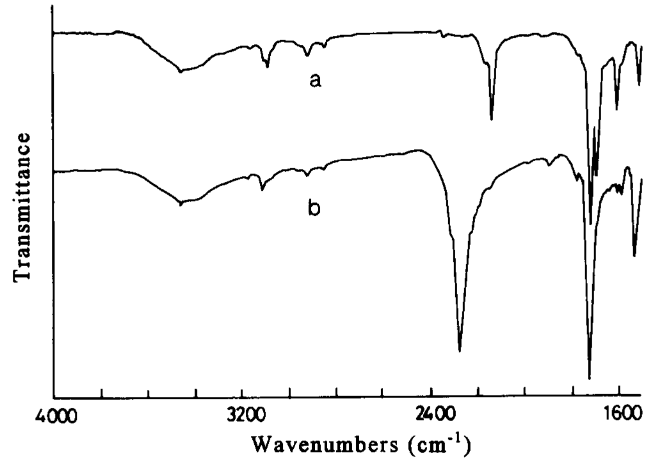


Figure 1 I.r. spectra of: (a) azide compound **3**; (b) the isocyanate compound obtained by heating compound **3** in toluene

Polymerization

Homopolymerization of compound **5** and its copolymerization with MMA were carried out with AIBN in DMF at desired temperatures. The polymerization results are summarized in *Table 1*. The homopolymer was soluble in DMF and DMSO and partially soluble in THF. The molecular weights were measured by g.p.c. in THF to be relatively low, i.e. $M_w = 5000$–8000. In the copolymerization, the contents of NLO chromophores were determined by ^1H n.m.r. spectroscopy, and found to be changed by varying the monomer feed ratios. The copolymers of low contents of NLO chromophores were soluble even in methylene chloride. Molecular weights obtained by g.p.c. were much larger, compared to M_ws of the homopolymers. Many *N*-phenylmaleimide derivatives are known to undergo alternating copolymerization with styrene. Copolymerization of compound **5** with ST also yielded alternating copolymers. Compositions of the copolymers were determined by elemental analyses. With the monomer feed ratios of 0.4–0.6, the contents of maleimide units were found to be close to 50%. The copolymers were soluble in THF, DMF, and DMSO.

Copolymerization of compound **6** with MMA was also carried out in a similar manner. The polymerization results are summarized in *Table 1*. The copolymers were soluble in THF, DMF, and DMSO.

Thermal stability of the polymers was examined by d.s.c. and t.g.a. The homopolymer of compound **5** did not show glass transition up to 250°C. The onset temperature of degradation was 300°C. The copolymers of monomer **5** with MMA had T_gs between 155°C (80% MMA) and 180°C (35% MMA). The alternating copolymer of **5** with styrene showed a glass transition at 208°C. All copolymers began to decompose around 250°C. The copolymers of compound **6** with MMA also showed distinct glass transitions between 175°C (65% MMA) and 195°C (35% MMA). The initial decomposition temperatures were about 250°C.

Second-order nonlinear optical properties

We fabricated the thin films of maleimide polymers and poled these films under proper conditions sequentially. Optically transparent films were obtained from all polymers. In general, the copolymers of high contents of MMA units showed better film forming properties. The film of the homopolymer of compound **5** was a little

Table 1 Polymerization results of *N*-phenylmaleimides

Polymer	M1	M2	[M1] in monomer (%)	Yield (%)	[M1] in copolymer (%)	M_w[a] ($\times 10^3$)	M_w/M_n	T_g (°C)
7a	**5**	MMA	25	78	20	50.8	3.8	155
7b	**5**	MMA	40	70	35	28.4	3.2	163
7c	**5**	MMA	70	68	65	13.9	3.0	180
8	**5**	ST	60	70	55	21.2	3.2	208
9	**5**		100	60	100	5.5	1.6	–
10a	**6**	MMA	33	73	35	18.5	4.2	175
10b	**6**	MMA	50	80	50	16.0	3.6	180
10c	**6**	MMA	86	75	65	12.1	3.1	195

[a] Measured by g.p.c. in THF, polystyrene standards

Table 2 Measured r_{33} values of *N*-phenylmaleimide polymers

Polymer	λ_{max} (nm)	Cut off λ (nm)	d_{33} (pm V^{-1})	r_{33} (pm V^{-1} at 632 nm)	r_{33} (pm V^{-1} at 830 nm)
Copolymer **7a**	390	500	7.8	10.6	8.1
Copolymer **8**	390	530	10.2	15.8	11
Homopolymer **9**	393	540	8.5	11.6	8.4
Copolymer **10a**	435	590	16.2	35.2	10.6

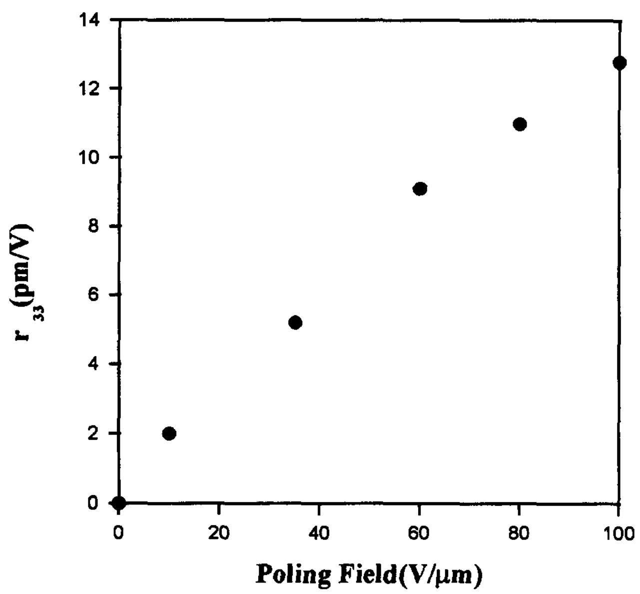


Figure 2 The EO coefficients of copolymer **8** vs poling field

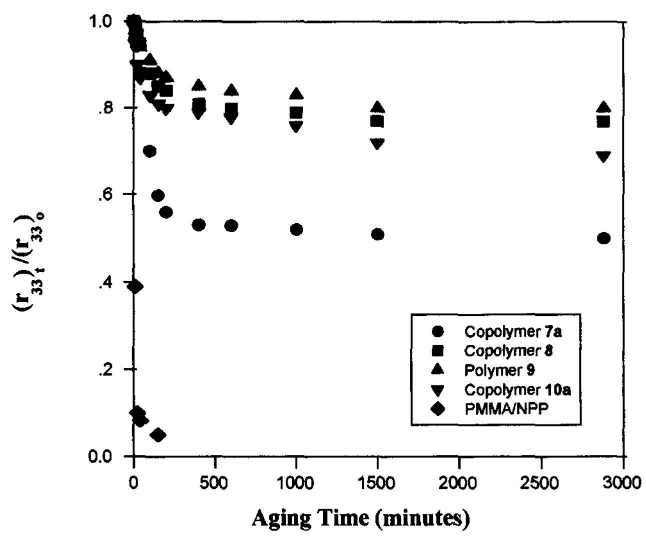


Figure 3 Relaxation behaviour of r_{33} of the polymers at 80°C

brittle. The polymers containing NPP chromophores yielded pale yellow films, while those with ANS gave reddish films. During poling, the polymer films were heated to temperatures 10°C lower than T_gs and kept for 10–20 min. Subsequently, the samples were slowly cooled down to room temperature in the presence of the applied electric field.

In order to investigate the extent of molecular orientation under the poling process, u.v.-vis spectra of the poled and the unpoled films were compared. The thin film (about 0.1 μm thickness) was fabricated on the borosilicate glass. The absorption maximum of the MMA copolymer was observed around 390 nm with a cut-off (100% transmission) at 500 nm prior to poling. In the case of the homopolymer of **5**, the absorption maximum appeared around 393 nm and the cutoff was at about 540 nm. The copolymer of **5** and ST showed λ_{max} and absorption limit at 390 nm and 530 nm, respectively. In the case of copolymer bearing ANS, the λ_{max} was observed around 435 nm and the cutoff was about 590 nm. After poling, the intensities of the absorption maxima of all polymer films decreased by about 15–30% in accord with a general tendency.

The optical quality of the polymers was highly maintained after poling even under 6–7 kV, corona field. This implies that the dielectric breakdown voltages of these polymers are relatively very high.

The linear EO coefficient, r_{33} was measured by a simple reflection technique. The EO coefficient, r_{33} was calculated from the difference of the phase retardation in transverse electric and transverse magnetic mode. The second-order nonlinear coefficient, d_{33} was also measured at 1064 nm of the fundamental wavelength. Measured data for the polymer samples are given in *Table 2*. The r_{33} values at 632 nm are reasonably consistent with the d_{33} values at 532 nm, which is the second harmonic wavelength of Nd^{+3}:YAG laser. The nonresonant linear EO coefficients, r_{33} values of the copolymers of **5** with MMA or ST corona-poled under 0.6 MV cm^{-1} were found to be about 10–15 pm V^{-1} when measured at 632.8 nm. When the film was treated by electrode poling technique, the EO coefficient did not show much difference compared to the above values because the T_gs of the polymers were high enough not to relax the molecular alignment in the gold evaporation bell jar. Copolymers **10a–c** with ANS chromophores exhibited the large EO effect accompanying 25–35 pm V^{-1} of r_{33} value at 632 nm.

To obtain large r_{33} values, the poling efficiency is important as well as the density of the chromophore. The polymers showed larger r_{33} values as the poling field increased. *Figure 2* shows that the EO coefficient of the copolymer of **5** with styrene is directly proportional to the poling field. This implies that the EO coefficient was not saturated even under 1.0 MV cm^{-1}. The r_{33} values of the polymers of **5** were also measured at 830 nm from the diode laser, which were lower than those measured at 632.8 nm by 15–20%. Since at wavelengths above 530 nm, no absorption was observed at all, no resonance enhancement effect at 830 nm was expected. Only the change of the refractive index can reduce the r_{33} value slightly. However, the r_{33} values of copolymers **10a–c** measured at 830 nm were 8–10 pm V^{-1}, which were much smaller than those obtained at 630 nm, 25–35 pm V^{-1}. Therefore, we could consider the contribution of charge transfer resonance to molecular hyperpolarizability, β, of the ANS and EO coefficient at 632 nm.

The long term stability and thermal stability for poled polymers are of critical importance for all nonlinear optical device applications. We examined the relaxation behaviour of the EO coefficients of copolymers **7a**, **8**, **9**, **10a**, and PMMA doped with 10% NPP with the variation of time at 80°C (*Figure 3*). The homopolymer of **5** showed the excellent thermal stability of the EO coefficient, which retained 85% of its original value when aged at 80°C for 48 h. In the copolymers, the NLO chromophores are much diluted with MMA to diminish the side chain interaction. The EO coefficients, r_{33} of the copolymers were 45–70% of their original values after 48 h at 80°C. In general, at the first stage, the EO coefficient rapidly decreased, and then the value slowly approached to a certain value asymptotically at the second stage. At room temperature, no decay of the r_{33} values of any polymer was observed over a period of 1 month. For comparison, the thermal relaxation behaviour of the guest–host system (10 wt% NPP doped poly(methylmethacrylate) (PMMA)) is also plotted in *Figure 3*. Even after 10 min at 80°C, the EO signal decayed rapidly. After 20 min annealing, the EO signal fell to almost zero, indicating that the molecular alignment of the poled film was completely disrupted at the vicinity of the T_g of PMMA.

In summary, we synthesized *N*-phenylmaleimides coupled with NLO chromophores and polymerized them to give a new class of second-order NLO maleimide polymers. The polymers showed fairly large EO coefficient, r_{33}, and second-order nonlinear coefficient, d_{33}, values. We also observed the much improved thermal stability of the dipolar alignment in these polymers.

ACKNOWLEDGEMENT

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