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Synthesis and non-linear optical properties of aromatic ester oligomers as chained chromophores

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We synthesized some aromatic ester oligomers consisting of repeating units of oxy-1,4-phenylenecarbonyl group (**ArESn**, $n = 2$–4) as novel non-linear optical (NLO) active chromophores. Some second-order NLO properties for poled polymer films consisting of poly(methyl methacrylate) (PMMA) doped with 10 or 5 wt% **ArESn** and 10 wt% *p*-nitroaniline (*p*NA) were investigated. Comparison of the d_{33} value at the chromophore molar concentration [d_{33} (M)] for these polymer films indicated that the d_{33} (M) value of **ArESn** increases with an increase in *n* and **ArESn** with *n* more than 3 reveals a higher d_{33} (M) value than that of *p*NA. In addition, every **ArESn** has a cutoff wavelength (λ_{co}) of about 300 nm, which is much shorter than the case of *p*NA ($\lambda_{co} = $ ca.450 nm). **ArESn** are concluded to be promising chromophores for second-order non-linear optics. © 1997 Elsevier Science Ltd.

(Keywords: chained chromophore; aromatic ester oligomer; host–guest system)

INTRODUCTION

Organic materials with large second-order non-linearities are currently under development for applications in frequency doubling, optical parametric amplification and electrooptic modulation[1].

For the application of organic non-linear optical (NLO) materials in photonic technologies, the NLO materials with large second-order optical non-linearity and high optical transparency are most desirable. Experimental results have indicated that the use of electron donor–acceptor substituted benzenes, stilbenes, azobenzenes, benzylidenes or tolanes make it difficult to achieve the desired optical transparency for frequency doublers, since the non-linear efficiency–transparency trade-off depends on the nature for the incorporated NLO materials and polymer materials[2].

In order to obtain these molecules, we decided to explore new types of donor–acceptor (D–A) molecules excluding the classical strong D–A pair. In our previous studies[3–6], the second-order hyperpolarizability (β) values of several organic species were evaluated by the hyper Rayleigh scattering (HRS) method at 1.064 μm and semiempirical molecular orbital (MO) calculation. Among these investigations aromatic ester oligomers consisting of repeating units of oxy-1,4-phenylenecarbonyl group were found to have a comparatively large β value in spite of the cutoff wavelength being shorter than 300 nm[5,6]. Furthermore, it was found that generally an oligomer consisting of the *n* number of the repeating units in the rod-shaped structure has a more than *n* times larger $\mu\beta$ value (μ is the calculated

dipole moment) than the sum of the $\mu\beta$ values of the monomeric repeating units. These results may lead a new breakthrough guideline in the preparation a novel organic and/or polymeric NLO materials with both high transparency and large β value. Therefore we used the term 'chained chromophores' for the new types of NLO active chromophores.

In this paper we report the synthesis of aromatic ester oligomers consisting of two to four repeating units of oxy-1,4-phenylenecarbonyl group as chained chromophores (**ArESn**, $n = 2$–4). Some investigations on the NLO properties for poled polymer films consisting of PMMA (host) and **ArESn** (guest) thus synthesized are also reported.

EXPERIMENTS

Materials

p-Anisoyl chloride, *p*-hydroxybenzoic acid, *p*-hydroxy-benzoic acid ethyl ester and ethyl chloroformate were purchased from Tokyo Kasei and were used without further purification. Methyl ethyl ketone (MEK) and triethylamine were purified by distillation under an argon atmosphere. Other reagents and solvents were used without further purification unless otherwise stated.

Synthesis of aromatic ester oligomers

4-(4'-Methoxyphenylcarbonyloxy)benzoic acid ethyl ester (**ArES2**). *p*-Anisoyl chloride (16.8 g, 98.6 mmol) was dissolved in MEK (20 ml) and the solution was cooled in an ice-bath. To the solution a mixture containing *p*-hydroxybenzoic acid ethyl ester (14.7 g, 88.7 mmol), triethylamine (14 ml) and MEK (50 ml) was added

dropwise under vigorous stirring. The reaction mixture was allowed to stand at room temperature overnight. The precipitate obtained was filtered off. The filtrate was dissolved in chloroform and the solution was washed with $NaHCO_3$ aqueous solution (10 wt%), followed by water. The organic layer was dried over anhydrous Na_2SO_4, the solvent was evaporated, and the residue was recrystallized from acetone to yield 23.6 g (80.0%) of white crystals: MP = 99–100°C; ^1H NMR ($CDCl_3$) δ = 1.40 (t, J = 7.3 Hz, 3H, –COO–CH$_2$CH$_3$, 3.90 (s, 3H, CH$_3$–O–Ph–), 4.35 (q, J = 7.3 Hz, 2H, –COO–CH$_2$CH$_3$), 7.04 (d, J = 8.8 Hz, 2H, aromatic protons of a), 7.34 (d, J = 8.6 Hz, 2H, aromatic protons of c), 8.08 (m, 4H, aromatic protons of b and d); e.i.–m.s. m/e 135, 165, 255, 300 (M^+); Analysis calculated for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37; O, 26.64. Found: C, 68.16; H, 5.37; O, 26.47.

4-Ethoxycarbonyloxybenzoic acid (1). Ethyl chloroformate (16.7 ml, 175 mmol) was added to a chilled (0°C) mixture of p-hydroxybenzoic acid (20.0 g, 145 mmol), sodium hydroxide (11.6 g, 290 mmol) and water (300 ml). The reaction mixture was then acidified with 2 N HCl. The precipitate obtained was filtered and washed with excess water. The resulting solid was recrystallized from a water–acetone mixture to yield 30.3 g (96.6%) of white crystals: ^1H NMR ($CDCl_3$) δ = 1.41 (t, J = 6.8 Hz, 3H, CH$_3$CH$_2$–OCOO–), 4.34 (q, J = 7.2 Hz, 2H, CH$_3$CH$_2$–OCOO), 7.30 (d, J = 8.4 Hz, 2H, aromatic protons of a), 8.15 (d, J = 8.4 Hz, 2H, aromatic protons of b).

4-Ethoxycarbonyloxybenzoyl chloride (2). A mixture of 1 (15.0 g, 71.4 mmol), thionyl chloride (38.7 ml, 546 mmol) and two drops of N,N-dimethylformamide was refluxed for 1 h. After this, the excess thionyl chloride was distilled off and the residue was recrystallized from hexane to yield 10.5 g (64.0%) of yellow solid.

4-(4'-Ethoxycarbonyloxyphenylcarbonyloxy)benzoic acid ethyl ester (3). This compound was prepared from 2 and p-hydroxybenzoic acid ethyl ester using the same procedure as described in the case of **ArES2** to yield 50.0% of slightly brown crystals: ^1H NMR ($CDCl_3$) δ = 1.41 (m, 6H, –COO–CH$_2$CH$_3$ and CH$_3$CH$_2$–OCOO–), 4.37 (m, 4H, –COO–CH$_2$CH$_3$ and CH$_3$CH$_2$–OCOO–), 7.29 (d, J = 8.0 Hz, 2H, aromatic protons of a), 7.35 (d, J = 9.2 Hz, 2H, aromatic protons of c), 8.12 (d, J = 8.4 Hz, 2H, aromatic protons of b), 8.23 (d, J = 8.8 Hz, 2H, aromatic protons of d).

4-(4'-Hydroxyphenylcarbonyloxy)benzoic acid ethyl ester (4). Compound 3 (3.58 g, 10.0 mmol) was suspended in a mixture of pyridine (15 ml), acetone (30 ml) and concentrated ammonia solution (2 ml). After stirring at room temperature overnight the suspension was acidified with concentrated HCl. The resulting precipitate was dissolved in chloroform and the solution was washed with 1 N HCl, followed by water. The organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was recrystallized from an acetone–water mixture to yield 2.10 g (73.4%) of white crystals: ^1H NMR ($CDCl_3$) δ = 1.39 (t, J = 5.7 Hz, 3H, –COO–CH$_2$CH$_3$), 4.40 (q, J = 7.6 Hz, 2H, –COO–CH$_2$CH$_3$), 6.98 (d, J = 8.0 Hz, 2H, aromatic protons of a), 7.38 (d, J = 9.0 Hz, 2H, aromatic protons of c), 8.12 (m, 4H, aromatic protons of b and d).

*4-(4'-(4''-Methoxyphenylcarbonyloxy)phenylcarbonyloxy)benzoic acid ethyl ester (**ArES3**).* This compound was

prepared from p-anisoyl chloride and 4 using the same procedure as described in the case of **ArES2** to yield 68.0% of white crystals: MP = 136–137°C; ^1H NMR ($CDCl_3$) δ = 1.41 (t, J = 6.8 Hz, 3H, –COO–CH$_2$CH$_3$), 3.92 (s, 3H, CH$_3$–O–Ph), 4.41 (q, J = 7.2 Hz, 2H, –COO–CH$_2$CH$_3$), 7.00 (d, J = 8.8 Hz, 2H, aromatic protons of a), 7.37 (m, 4H, aromatic protons of c and e), 8.16 (m, 4H, aromatic protons of b and d), 8.26 (d, J = 8.8 Hz, 2H, aromatic protons of f); e.i.–m.s. m/e 135, 165, 255, 375, 420 (M^+); Analysis calculated for $C_{24}H_{20}O_7$: C, 68.57; H, 4.79; O, 26.64. Found C, 68.61; H, 4.74; O, 26.65.

4-(4'-4''-Ethoxycarbonyloxyphenylcarbonyloxy)phenylcarbonyloxy)benzoic acid ethyl ester (5). This compound was prepared from 2 and 4 using the same procedure as described in the case of **ArES2** to yield 50.0% of slightly brown crystals: ^1HNMR ($CDCl_3$) δ = 1.41 (m, 6H, –COO–CH$_2$CH$_3$ and CH$_3$CH$_2$–OCOO–), 4.38 (m, 4H, –COO–CH$_2$CH$_3$ and CH$_3$CH$_2$–OCOO–), 7.38 (m, 6H, aromatic protons of a, c and e), 8.25 (m, 6H, aromatic protons of b, d and f).

4-(4'-(4''-Hydroxyphenylcarbonyloxy)phenylcarbonyloxy)benzoic acid ethyl ester (6). This compound was prepared from 5 using the same procedure as described in the case of 4 to yield 61.0% of white crystals: ^1H NMR ($CDCl_3$) δ = 1.41 (t, J = 7.6 Hz, 3H, –COO–CH$_2$CH$_3$), 4.39 (q, J = 6.8 Hz, 2H, –COO–CH$_2$CH$_3$), 6.93 (d, J = 8.8 Hz, 2H, aromatic protons of a), 7.37 (m, 4H, aromatic protons of c and e), 8.13 (m, 6H, aromatic protons of b, d and f).

*4-(4'-(4''-(4'''-Methoxyphenylcarbonyloxy)phenylcarbonyloxy)phenylcarbonyloxy) benzoic acid ethyl ester (**ArES4**).* This compound was prepared from p-anisoyl chloride and 6 using the same procedure as described in the case of **ArES2** to yield 34.4% of white crystals: MP = 182–183°C; ^1H NMR ($CDCl_3$) δ = 1.41 (t, J = 7.2 Hz, 3H, –COO–CH$_2$CH$_3$), 3.92 (s, 3H, CH$_3$–O–Ph–), 4.39 (q, J = 7.2 Hz, 2H, –COO–CH$_2$CH$_3$), 7.01 (d, J = 8.8 Hz, 2H, aromatic protons of a), 7.39 (m, 6H, aromatic protons of c, e and g), 8.16 (m, 6H, aromatic protons of b, d and f), 8.30 (d, J = 8.8 Hz, 2H, aromatic protons of h); e.i.–m.s. m/e 135, 255, 375, 495, 540 (M^+). Analysis calculated for $C_{31}H_{24}O_9$: C, 68.89; H, 4.48; O, 26.64. Found C, 68.26; H, 4.40; O, 26.63.

Methods and measurements

Film preparation. The materials were studied in mixtures of 10 wt% of **ArESn** (n = 2–4) and 5 wt% of **ArES4** with a PMMA ($\bar{M}n$ = 12 000). The host–guest films were prepared by spin-coating from a 4 wt% chloroform solution onto a glass or quartz slide at room temperature. The films thus obtained were dried overnight at room temperature. The film thicknesses were 0.3–0.4 μm.
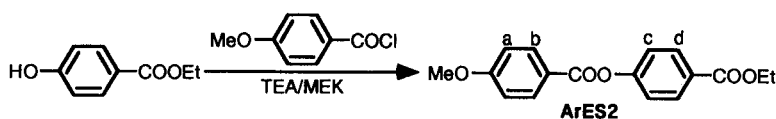
Corona poling. Corona poling of the host–guest films was carried out by using the equipment reported in the previous paper[7]. The corona poling was performed at 5.0 kV cm^{-1} using a sharp tungsten needle as an electrode, which was placed 1 cm above the film surface. The temperature of the film was raised to 60°C for **ArES2/PMMA,** 90°C for **ArES3/PMMA,** 80°C for **ArES4/PMMA** and 90°C for *p*NA/PMMA, respectively. After approximately 20 min, while the voltage was held constant, the temperature of the film was lowered to room temperature.

Characterization of oligomers and host–guest films. Second harmonic generation (SHG) of the host–guest films was measured employing the Maker-fringe method using a Q-switched Nd-YAG laser (Spectrum Physics, DR-2;1064 nm, 8 ns pulse^{-1}, ca. 10 mJ pulse^{-1})[7]. The second-order non-linear optical coefficient (d_{33}) was evaluated by the use of a single quartz crystal plate of 0.5 mm thickness ($d_{11} = 8 \times 10^{-10}$ esu)[8]. Measurements of film thickness were performed using a TALYSTEP (Talor-Hobson). Refractive indices were measured with a Shimadzu AEP—100 ellipsometer. ^1H NMR spectra were recorded on a JEOL EX-400 (400 MHz) spectrometer. UV/vis spectra were obtained on a Shimadzu UV-3000 spectrometer. Mass spectra were measured with Hitachi M-80 e.i.–m.s. spectrometer.
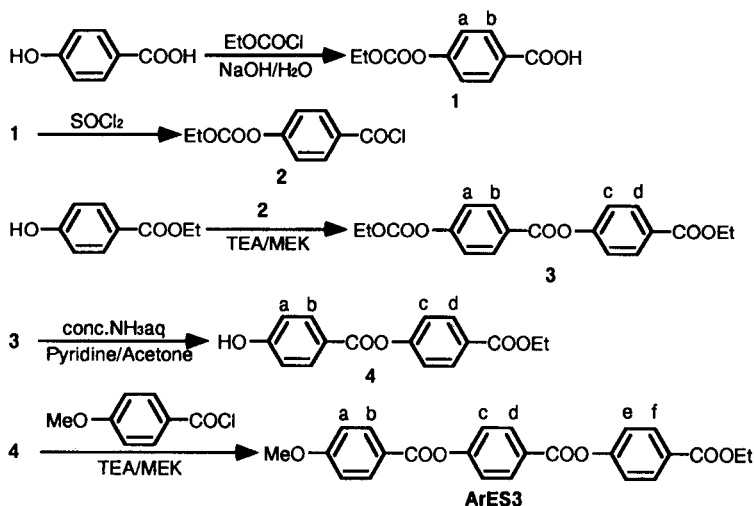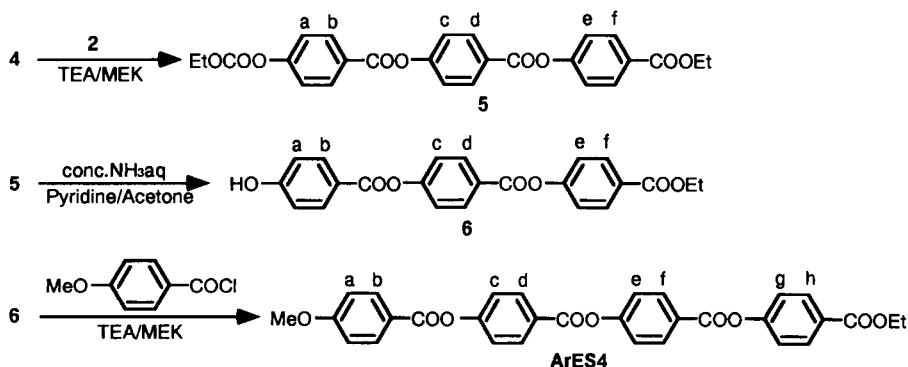
RESULTS AND DISCUSSION

Synthesis of ArESn

ArES2, ArES3 and ArES4 were synthesized using the modified literature methods[9,10] as shown in *Schemes 1–3*.

The alphabetical indications for the compounds shown in these schemes imply the position of assigned protons obtained by ^1H NMR measurement. ArES2 and ArES3 were obtained in high yield, whereas ArES4 was obtained in low yield. The cause of the difference is now under investigation. Melting points of ArES2, ArES3 and ArES4 were 100, 137 and 182°C, respectively, indicating that melting points of ArESn increases by ca. 40°C, with an increase in the number of the aromatic group ranging from 2 to 4. ArES2 was soluble in alcohol, acetone, acetonitrile and chloroform. ArES3 was soluble in acetone, acetonitrile and chloroform, but slightly soluble in alcohol. ArES4 was sparingly soluble in acetonitrile, chloroform and methylene chloride. Generally the solubility of ArESn decreases with an increase in the number of the aromatic group.

UV/vis spectra. The UV/vis spectra of ArESn/PMMA films and ArESn in acetonitrile ($n = 2, 3$) are shown in *Figure 1* and those of ArES4/PMMA films and ArES4 in acetonitrile are shown in *Figure 2*, respectively. The UV/vis spectra of *p*NA/PMMA film and *p*NA in methanol are also
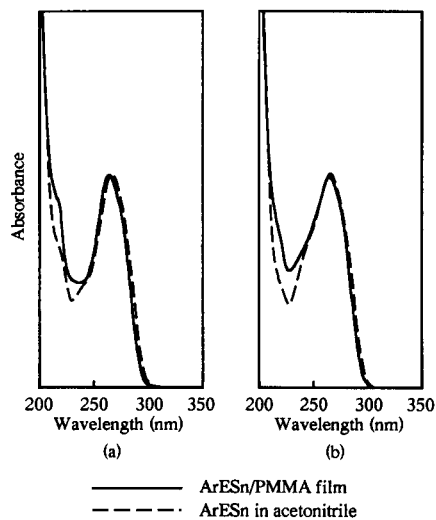

Scheme 1

Scheme 2

Scheme 3

Figure 1 UV/vis spectra of (a) **ArES2/PMMA** film and **ArES2** in acetonitrile; and (b)**ArES3/PMMA** film and **ArES3** in acetonitrile
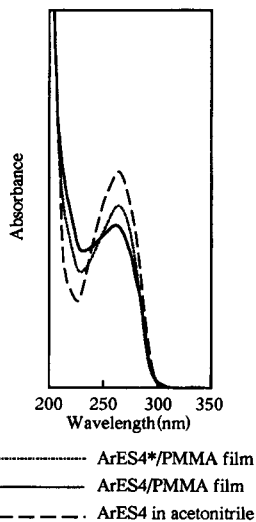

Figure 2 UV/vis spectra of **ArES4/PMMA** and **ArES4*/PMMA** films, and **ArES4** in acetonitrile
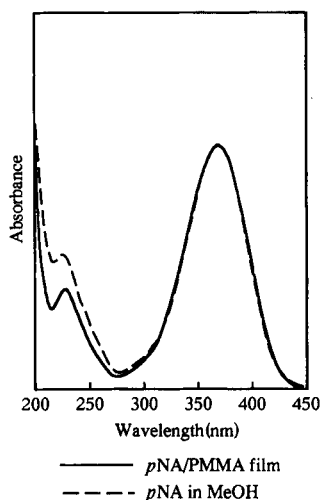

Figure 3 UV/vis spectra of *p*NA/PMMA film and *p*NA in methanol

shown in *Figure 3*. In these figures the spectra of the films were fitted to those of the solutions, respectively. There is recognized no significant difference in the UV/vis spectra between **ArES2/PMMA** film and **ArES2** in acetonitrile [*Figure 1*(a)] as well as those between **ArES3/PMMA** film **ArES3** in acetonitrile [*Figure 1*(b)], suggesting that **ArES2** as well as **ArES3** exists in the PMMA matrix in a state of molecular dispersion. However, there is a significant difference observed in the UV/vis spectra between **ArES4/PMMA** film (mixtures of 5% and 10 wt% **ArES4** with PMMA) and **ArES4** in acetonitrile (*Figure 2*), suggesting that **ArES4** exists in the PMMA matrix in a mixed state of aggregate and molecular dispersion. However, by diluting of **ArES4** concentration in PMMA matrix from 10wt% to 5 wt% (**ArES4*/PMMA**) the proportion of molecular dispersion increased considerably. It is recognized that *p*NA exists in the PMMA matrix in a state of molecular dispersion (*Figure 3*).

The UV/vis spectrum of every **ArESn/PMMA** film has a cutoff wavelength of about 300 nm, which is much shorter than the case of *p*NA/PMMA film (λ_{co} = ca. 450 nm). Thus, **ArESn** has a preferable transparency superior to *p*NA.

Second harmonic generation

The second-order NLO properties of **ArESn/PMMA** and *p*NA/PMMA films after poling treatment are shown in *Table 1*. In this table the d_{33} values of these films are compared together with the d_{33} (M) values which were conveniently converted to the d_{33} values at each chromophore molar concentration. Apparently, **ArESn/PMMA** films reveal a larger d_{33} (M) value than that of *p*NA/PMMA film when *n* is larger than 3. The trend towards an increase in the d_{33} (M) value seems to be considerably improved in the case of **ArES4*/PMMA**; however, it is less in the case of **ArES4/PMMA**. The results might be attributed to the reason that in the case of $n = 2$ and 3 the major part of the chromophores could be responding towards poling treatment since they exist in the PMMA matrix in a state of molecular dispersion, while in the case of $n = 4$ when the concentration is 10 wt% part of the chromophores could be responding towards the poring, since some of them exist in the form of a microcrystal, resisting the orientation by an electric field. This restriction in the orientation is considerably reduced when the concentration is 5 wt% due to the decrease in the microcrystal formation.

In previous papers[5,6] we have shown that calculated dipole moments at zero frequency (μ_0 Debye) and β esu evaluated by the hyper Rayleigh scattering method at 1.064 μm for **ArES2, ArES3, ArES4** and *p*NA are 4.0 and 49 $\times$ 10^{-30}, 5.6 and 71 $\times$ 10^{-30}, 7.8 and 84 $\times$ 10^{-30} (an extrapolated value), and 6.6 and 39 $\times$ 10^{-30}, respectively.

Using these values, the relationship between the $\mu_0\beta$ value and the d_{33} (M) value for **ArESn/PMMA** and *p*NA/PMMA films is demonstrated in *Figure 4*. Except for the **ArES4/PMMA** film the plots of **ArES2/PMMA, ArES3/PMMA, ArES4*/PMMA** and *p*NA/PMMA films approximately give a linear relationship between the increase in the $\mu_0\beta$ value and that in the d_{33} (M) value. The relationship between the d_{33} (M) value and the number of monomeric units (*n*) for **ArESn/PMMA** films is shown in *Figure 5*. Here, the data for **ArES1/PMMA** film was not plotted because **ArES1** is liquid, making it impossible to perform SHG measurement. The curve in *Figure 5* indicates that the d_{33} (M) value roughly increases in proportion to n^2, although the plot of **ArES4*/PMMA** film is off due to the above reason.

Table 1 UV/vis spectra and second-order NLO properties of **ArESn/PMMA** films and *p*NA/PMMA film

Material	Chromophore content		λ_{max} (nm)	λ_{co} (nm)	d_{33} (10^{-9} esu)	d_{33} (M)[a] (10^{-6} esu cm^3 mol^{-1})
	(wt%)	(10^{-4} mol cm^{-3})				
ArES2/PMMA	10	4.4	263	301	1.0	2.3
ArES3/PMNA	10	3.1	263	302	1.6	5.2
ArES4/PMMA	10	2.4	263	305	1.4	5.8
ArES4*/PMMA	5	1.2			0.88	7.6
*p*NA/PMMA	10	9.6	371	473	2.8	3.3

[a] Converted to the d_{33} value at molar concentration.
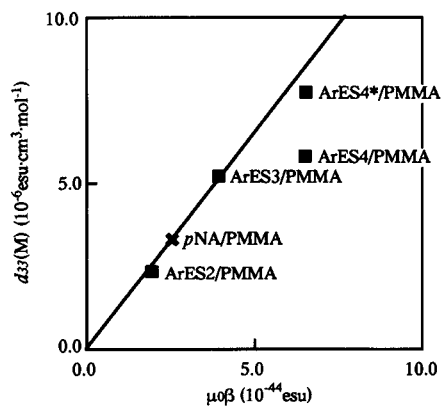
Figure 4 Relationship between d_{33} (M) and $\mu_0\beta$ for **ArESn/PMMA** and *p*NA/PMMA films
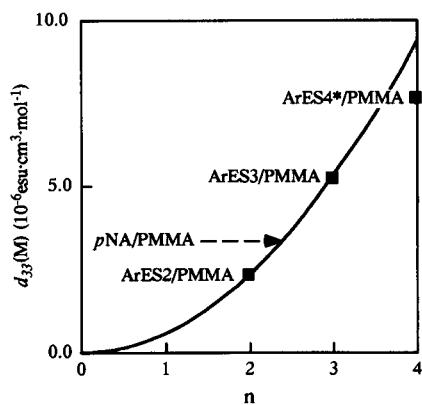
Figure 5 Relationship between d_{33} (M) and the number of repeating units (*n*) for **ArESn/PMMA**

ArESn/PMMA films used here did not show larger d_{33} values as compared with those of the well-known organic NLO active materials. The reason is that there is little possibility of an increase in the chromophore concentration, since the compatibilities of **ArESn** to the host polymer are generally not good. To make the chromophore concentration higher it is preferable that the chromophore is combined with a polymer. Investigations on the synthesis of polymers bearing **ArESn** groups as side chains and their NLO properties are underway. The results will be reported elsewhere in the near future.

In any case, the results obtained here may lead a new guideline for a breakthrough in the preparation of a novel organic and/or polymeric NLO materials with both high transparency and a larger β value.

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