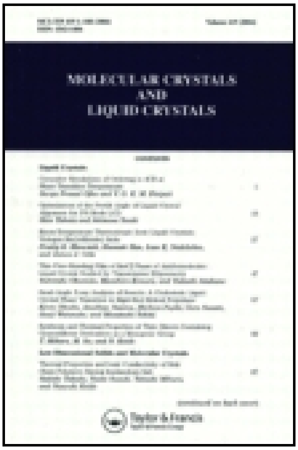

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Tatsumi Kimura [a] , Xuan-Ming Duan [b] , Kimihiko Kamo [a] , Masao Kato [a] , Hiro Matsuda [c] , Shinji Yamada [c] , Takashi Fukuda [c] , Shuji Okada [b] & Hachiro Nakanishi [b]

[a] Department of Materials Science and Technology, Science University of Tokyo, Noda, 278, Japan

[b] Institute for Chemical Reaction Science, Tohoku University, Sendai, 980-77, Japan

[c] National Institute of Materials and Chemical Research, Tsukuba, 305, Japan

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Synthesis and Nonlinear Optical Properties of Polymers Containing Aromatic Ester Oligomers as Chained Chromophores

TATSUMI KIMURA[a], XUAN-MING DUAN[b], KIMIHIKO KAMO[a], MASAO KATO[a]*, HIRO MATSUDA[c], SHINJI YAMADA[c], TAKASHI FUKUDA[c], SHUJI OKADA[b] and HACHIRO NAKANISHI[b]

[a]Department of Materials Science and Technology, Science University of Tokyo, Noda 278, Japan; [b]Institute for Chemical Reaction Science, Tohoku University, Sendai 980-77, Japan; [c]National Institute of Materials and Chemical Research, Tsukuba 305, Japan

We synthesized some aromatic ester oligomers consisting of repeating units of oxy-1,4-phenylenecarbonyl group (**ArESn**, n=2~4) as novel nonlinear optical (NLO) active chromophores and their methacrylate derivatives (**ArESn-MA**, n=2~3). Some second-order NLO properties for poled polymer films of poly(methyl methacrylate) doped with 10 or 5wt% **ArESn** (**ArESn/PMMA**) and **ArESn-MA** homopolymers (**poly(ArESn-MA)**) as well as copolymers with MMA (**poly(ArESn-MA-co-MMA)**) were estimated by the second harmonic generation (SHG) measurement using Nd-YAG laser as light source. Comparison of the d_{33} value at the chromophore molar concentration (d_{33}(M)) for **ArESn/PMMA** films indicated that the d_{33}(M) value of **ArESn** increases with increase in n and **ArESn** with n more than 3 reveal higher d_{33}(M) value than that of *p*NA, in addition, every **ArESn** has cutoff wavelength (λ_{co}) of about 300nm, which is much shorter than the case of *p*NA (λ_{co}=ca.450nm). Moreover, **poly(ArESn-MA)** films exhibited much larger d_{33} values than those of **ArESn/PMMA** films since the formers contain the chromophores in high concentration, however, when the comparison is made by using the d_{33}(M) value the values become less than 1/2 of those in the cases of **ArESn/PMMA** films. This might be caused by a strong interaction acting among the chromophore side chains. Copolymerization of **ArESn-MA** with MMA which is capable of relieving the interaction improved the chromophore orientation considerably.

Keywords: Chained Chromophore; aromatic ester oligomer; poled polymer system; NLO material; transparency

INTRODUCTION

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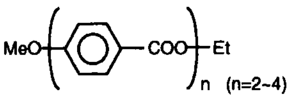
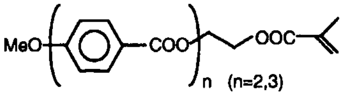
*To whom correspondence should be addressed.

The second-order nonlinear optical (NLO) properties of polymeric materials have been attracting a lot of attention for the development of electro-optic modulators and frequency conversion devices. For the application of NLO materials in the photonic technologies, the NLO chromophores possessing large second-order optical nonlinearity and high transparency are most desirable. However, the NLO materials investigated up to now mostly have the absorptions in visible region even though their second-order hyperpolarizabilities (β) are large. In UV or blue second-harmonic generation (SHG) devices of laser diodes, the absorption cutoff wavelength of materials is requested to be shorter than 400nm and large β has to be achieved even under such absorption restriction. 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. As the first approach to the concept we investigated aromatic ester oligomers consisting of repeating units of oxy-1,4-phenylenecarbonyl group and found that the oligomers have a short cut-off wavelength of about 300nm as well as large β and dipole moment (μ).1) Thus, these compounds are concluded to be promising chromophores for second-order nonlinear optics. We named "Chained Chromophores" for the new types of NLO chromophores.2)

In this paper we report the synthesis of aromatic ester oligomers consisting of 2~4 repeating units of oxy-1,4-phenylenecarbonyl group as chained chromophores (**ArESn**, n=2~4) and their methacrylate derivatives (**ArESn-MA**), and NLO properties of poly(methyl methacrylate) (PMMA) films doped with **ArESn** (**ArESn/PMMA**), PMMA film doped with *p*-nitroaniline (***p*NA/PMMA**) as control and **ArESn-MA** homopolymer (**poly(ArESn-MA)**) and copolymers with MMA (**poly(ArESn-MA-co-MMA)**) obtained by radical polymerization.



ArESn



ArESn-MA

EXPERIMENTAL

NLO Polymers

1) ArESn/PMMA and *p*NA/PMMA

ArESn (n=2~4) were synthesized by the reported methods.2) **ArESn/PMMA** films were prepared by mixing 10wt% (n=2~4) or 5wt% (n=4) of **ArESn** with PMMA (Mn=12,000). ***p*NA/PMMA** film was prepared by mixing 10wt% of *p*NA with PMMA.

2) poly(ArESn-MA) and poly(ArESn-MA-co-MMA)

ArESn-MA (n=2,3) were synthesized based on the similar method used for synthesis of **ArESn**. Homopolymerization of **ArESn-MA** and copolymerization of **ArESn-MA** with MMA were carried out under the condition shown in TABLE I.

TABLE I Conditions of radical homopolymerization of **ArESn-MA** and copolymerization of **ArESn-MA** with MMA.

No.	Composition of monomer mixture (mmol)				Solvent	Solvent vol. (mL)	Temp. (°C)	Time (h)
	ArESn-MA	n	MMA	AIBN				
1	0.30	2	–	0.0015	THF	0.1	60	24
2	0.89	3	–	0.0010	THF	2.0	60	24
3	0.20	3	0.20	0.0040	DMF	1.0	60	24
4	0.10	3	0.20	0.0027	DMF	1.0	60	24

Poling and Second Harmonic Generation (SHG)

The polymer films were prepared by spin-coating from 2~4wt% chloroform solution onto glass or quartz slide and dried (thickness, 0.5~0.6μm). Corona poling of the films was carried out at 5kV/cm (60~90°C) using the equipment reported previously.3) The SHG of the poled films were measured by Maker-fringe method using a Q-switched Nd-YAG laser (1064nm, 8ns, 10mJ/pulse) and the second-order nonlinear optical coefficient (d_{33}) was obtained in usual manner.

RESULTS AND DISCUSSION

Synthesis of ArESn-MA Homo- and Copolymers

The yield, ArESn content, number weight-average molecular weight(Mn) and glass transition temperature (T_g) of the resultant polymers are summarized in TABLE II.

TABLE II Yield, **ArESn** content, $\overline{Mn}$ and T_g of the resultant **poly(ArESn-MA)** and **poly(ArESn-MA-co-MMA)**.

No.	Polymer	Yield (%)	ArESn content (mol%)	$\overline{Mn}$	Tg (°C)
1	poly(ArES2-MA)	65.0	100	40000	75
2	poly(ArES3-MA)	62.4	100	35000	n.d
3	poly(ArES3-MA-co-MMA)(5/5)	63.4	52	21000	n.d.
4	poly(ArES3-MA-co-MMA)(3/7)	62.8	37	17000	n.d.

Absorption Spectra of Polymer Films

The UV/vis spectra of **ArESn/PMMA** films and **ArESn** in acetonitrile as well as those of ***p*NA/PMMA** film and *p*NA in methanol were measured. In these measurements, the spectra of the films were fitted to those of the solutions, respectively.

In the cases of **ArES2** and **ArES3**, the absorption spectrum of the film is almost coincident with that of the solution, suggesting that both chromophores exist in PMMA matrix in a state of molecular dispersion. While, in the case of **ArES4** the absorption spectrum of the film does not coincident with that of the solution although the chromophore content is lower than the other cases, suggesting that **ArES4** exists in PMMA matrix in a mixed state of aggregate and molecular dispersion. It is recognized that *p*NA exist in PMMA matrix in a state of molecular dispersion. As shown in TABLE III,

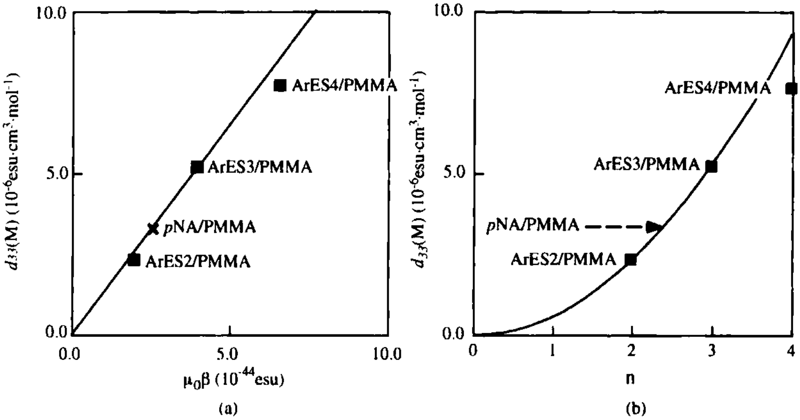
TABLE III UV/vis spsctra and second-order NLO properties of poled **ArESn/PMMA** films, **poly(ArESn-MA)** films, **poly(ArESn-MA-co-MMA)** films and ***p*NA/PMMA** films.

Polymer	Chromophore content		λ_{max}	λ_{co}	d_{33}	d_{33}(M)
	(wt%)	(10^{-4}mol·cm^{-3})	(nm)	(nm)	(10^{-9}esu)	(10^{-6}esu·cm^{3}·mol^{-1})
ArES2/PMMA	10	4.4	263	301	1.0	2.3
ArES3/PMMA	10	3.1	263	302	1.6	5.2
ArES4/PMMA	5	1.2	263	305	0.9	7.6
poly(ArES2-MA)	78	42	263	310	5.3	1.3
poly(ArES3-MA)	83	32	263	310	6.0	1.9
poly(ArES3-MA-co-MMA)(5/5)	69	20	263	310	6.2	3.1
poly(ArES3-MA-co-MMA)(3/7)	64	18	263	310	7.5	4.2
*p*NA/PMMA	10	9.6	371	473	2.8	3.3

UV/vis spectra of all **ArESn/PMMA** films as well as **poly(ArESn-MA)** and **poly(ArESn-MA-co-MMA)** films have cutoff wavelength (λ_{co}) of about 300nm, which is much shorter than the case of ***p*NA/PMMA** film (λ_{co}=473nm).

NLO Properties of Polymer Films

The NLO properties of poled **ArESn/PMMA**, ***p*NA/PMMA**, **poly(ArESn-MA)** and **poly(ArESn-MA-co-MMA)** films are summarized in TABLE III, together with their λ_{max} and λ_{co} in UV/vis spectra. 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. The relationship between the d_{33}(M) value and $\mu_0\beta$ value for **ArESn/PMMA** and ***p*NA/PMMA** films is shown in FIGURE 1(a). Here, the μ_0 value was calculated dipole moment at zero frequency and the β value was evaluated by the hyper Rayleigh scattering method at 1.064mm, respectively.[1)] Except **ArES4/PMMA** film, the plots of **ArES2/PMMA**, **ArES3/PMMA** and ***p*NA/PMMA** films approximately give a linear relationship between increase in the $\mu_0\beta$ value and that in the d_{33}(M) value. An unfavorable effect due to the chromophore aggregate which can not respond to poling was recognized for **ArES4/PMMA** film.



(a) (b)

FIGURE 1 (a)Relationship between $\mu_0\beta$ and d_{33}(M) for **ArESn/PMMA** and ***p*NA/PMMA** films, (b)relationship between the number of repeating units n and d_{33}(M) for **ArESn/PMMA** films.

The relationship between the d_{33}(M) value and the number of monomer units (n) for **ArESn/PMMA** films is shown in FIGURE 1(b). Here, the data for **ArES1/PMMA** film was not plotted because **ArES1** is liquid, making impossible to perform SHG measurement. The curve in FIGURE 1(b) indicates that the d_{33}(M) value roughly increase in proportion to n^2, though the plot of **ArES4/PMMA** is off due to the reason described above. Thus, the results may lead a new guideline for breakthrough to obtain a novel NLO active materials with both high transparency and large β value.

It was expected that **poly(ArESn-MA)** and **poly(ArESn-MA-co-MMA)** films will exhibit much larger d_{33} values than those of **ArESn/PMMA** films since the formers contain the chromophores in high concentration. As shown in TABLE III, apparent d_{33} values of **poly(ArESn-MA)** films are certainly large, however, when the comparison is made by using the d_{33}(M) value the values become less than 1/2 of those in the cases of **ArESn/PMMA** films. Probably, the result was induced by the fact that an effective chromophore orientation by poling could not be achieved by obstruction attributed to a strong interaction occurred among closely gathered chromophore side chains in polymer. It is expected that the interaction between the chromophore side chains is weaken by copolymerization with monomer which is capable of relieving the interaction, thereby improving the chromophore orientation. As expected, copolymerization of **ArESn-MA** with MMA improved the orientational ability of the chromophores considerably as shown in TABLE III. Further investigation is required to obtain chromophores having much higher μ and β values. About this investigation is now under way and the results will be reported in elsewhere.

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