Low-Temperature Poling of Dye-Doped Polymers for Nonlinear Optical Devices

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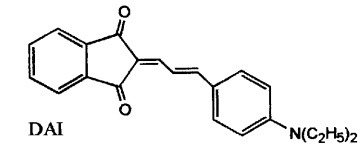
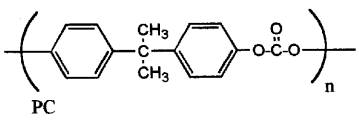
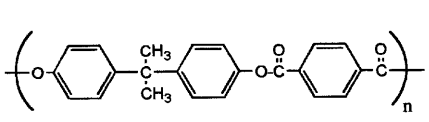
By repeating the corona poling process for several times, dye-doped polymer films were efficiently poled at temperatures significantly lower than T_g. High second-order NLO efficiency (e.g., d_{33} around 100 pm/V) was obtained with a guest dye, 2-(*p*-diethylaminocinnamilidene)-indan-1,3-dione.

Second-order nonlinear optical (NLO) properties of dye-doped poled polymers and sol–gel matrices have been extensively studied because of their ease of film preparation and fabrication for electro-optical devices.[1–8] Usually, dye-doped polymers are poled at high temperatures close to the glass-transition temperatures (T_g) of host polymers, in order to obtain high NLO coefficients.[1–5] In the present paper we report a simple and quite effective method, namely, repeating poling process several times at temperatures significantly lower than the T_g's of the host polymers. The poled polymers obtained by this method revealed high temporal NLO coefficients and slightly improved thermostabilities. A host polymer and a guest dye, 2-(*p*-diethylaminocinnamilidene)-indan-1,3-dione (DAI) of mp 184–186 °C, were dissolved in cyclohexanone, and spin-coated on a slide glass (Iwaki Glass) and dried for 24 h at room temperature, giving a thin film of ca. 2μm thickness with ca. 10 wt% of DAI. As the host polymers, poly(methyl methacrylate) (PMMA) (Wako Chemical, M_W = 15000, T_g = 109 °C), polycarbonate (PC) (Aldrich Chemical, M_W = 64000, T_g = 149 °C), and a copolymer (U-100) (Yunichika, M_W = 100000, T_g = 193 °C) were used as received.





PC



U-100

Corona poling was carried out with a positive needle electrode from a 30-mm distance of the dye-doped film spin-coated on a glass placed on the negative electrode.[2] The spin-coated film was placed in the oven and thermally equilibriated for 10 min at a desired temperature. Then, 10 kV corona field was applied for 10–60 min, followed by cooling with an air fan in 5 min. The poling process was repeated several cycles, and the second-order NLO coefficients were measured at each cycle, by the rotating Maker-fringe method.[4,6] We used a 1064-nm *Q*-switched Nd:YAG laser with a 90-ns pulse width and compared the measured values with d_{11} of quartz (d_{11} = 0.5 pm/V). In the Maker-fringe measurement the polarizations of the input fundamental and the second-harmonic (SH) waves were changed as follows: (1) both the fundamental and the SH were *p* polarized (*p*–*p*), or (2) the fundamental was *s* polarized and the SH was *p* polarized (*s*–*p*), or (3) the fundamental was 45° polarized and the SH was *s* polarized (*sp*–*s*).

A DAI-doped film of the U-100 polymer was corona-poled at 50 °C for 10 min under a 10 kV field strength, in each cycle. On repeating the poling cycle, the value of the d_{33} coefficient increased with the number of the cycle and reached a plateau around 90 pm/V at 10 cycles. Similarly, a value of d_{33} around 95 pm/V was obtained on repeating 3 cycles of the poling at 100 °C. It should be noticed that a high NLO efficiency can be obtained by the repeated poling at a temperature (50 °C) significantly lower than the T_g (e.g., 193 °C) of the host polymers (Figure 1 and Table 1). Though the repeating effects on the

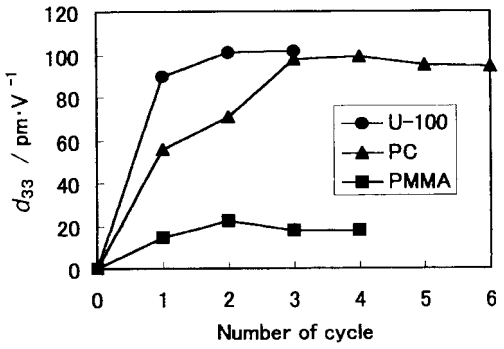


Figure 1. Effects of the poling cycles on the second-order NLO d_{33} coefficients of DAI-doped polymer films. In each cycle, polymer films containing DAI in 10 wt% were poled under 10 kV corona field at 50 ℃ for 60 min.

NLO efficiency are varied with the nature of the host polymers, the ratio d_{33}/d_{31} was larger than 3 (Table 1), implying effective poling in each polymer film. The PMMA film retained low d_{33} coefficients around 20 pm/V whereas PC and U-100 films revealed high values around 100 pm/V, on repeated poling at 50 °C. The poling efficiency, $\phi = (A_0 - A)/A_0$, was also estimated for each poled film from the difference in the electronic absorption maxima before (A_0) and after poling (A): ϕ = 0.22 (U-100), 0.18 (PC), 0.14 (PMMA).

Large orientational changes of the guest molecules are substantially inhibited at low temperatures significantly lower than the T_g's of the host polymers. However, amorphous polymer matrices contain a range of site distributions differing in the

Table 1. Variation in the second-order NLO coefficients of DAI-doped polymer films as a function of repeating cycles of corona poling at 50 °C [a]

Host polymer	T_g / °C	Number of poling cycle	d_{33} / pm/V	d_{15} / pm/V	d_{31} / pm/V
U-100	193	1	89.9	29.7	28.5
		2	100.8	29.7	28.7
		3	101.9	27.4	25.1
PC	149	1	56.0	17.0	16.7
		2	71.0	18.0	17.7
		3	97.7	18.7	18.4
		4	98.8	18.1	17.3
		5	94.8	18.0	17.2
		6	94.5	20.6	18.9
PMMA	109	1	14.4	6.6	6.6
		2	22.2	6.1	6.0
		3	17.9	7.1	7.1
		4	17.9	6.6	6.6

[a] In each cycle, polymer films containing DAI in 10 wt% were poled under 10 kV field strength at 50 °C for 60 min.

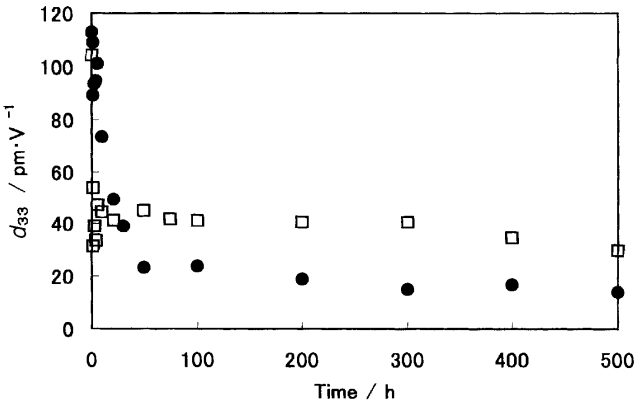


Figure 2. Thermal relaxation of the poled U-100 polymer films at room temperature. (●): Poled once for 180 min, (□): poling for 60 min each cycle was repeated 3 times, under 10 kV corona field at 50 °C.

free volume,[7] and hence there may exist a site with enough free volume which permits orientational response of guest even at low temperatures. The distributions of the site properties and/or free volumes vary with the nature of the host polymers, e.g., PMMA might feature a narrow distribution of the free volume whereas U-100 feature a wide range of free volume distribution.

Figure 2 compares the thermal stabilities of the d_{33} coefficient of the film poled by repeating 3 cycles (60 min × 3) with the film poled once (180 min × 1). Though both films reveal extensive relaxation, slight but significant improvement in the thermostability is seen for the former as compared with the latter. The increased thermostability may be ascribable to an annealing effect, thus, the free volume of the host polymers surrounding the guest would become smaller and hence the mobility of the guest molecules be reduced during the repeating process, while the rapid relaxation in the early stages is pertinent to the heterogeneous distribution of the free volume in the host polymer matrix.

References and Notes

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