Contribution of the Multiple Charge-Transfer Chromophore to the Orientation Stability of the Poled Polymer Film

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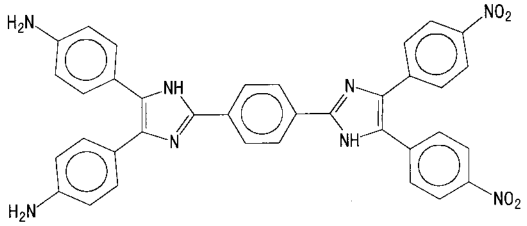
ABSTRACT: One of the novel multidimensional charge-transfer (CT) chromophores, 2-[4-(4,5-di(4-nitrophenyl)imidazolyl)phenyl]-4,5-di(4-aminophenyl)imidazole (DNPIPDAPI), was designed and synthesized; the polyimide was formed with it and 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene (TPTDA) (BMI). The thermal and temporal stability of the poling-induced orientation were evaluated. The temporal orientation of the poled polyimide film with DNPIPDAPI was over 1000 h at 150 °C, retaining 85% of the initial d_{33} value. Comparing with 1-D chromophores, the synthetic multiple CT chromophore possesses a better property in controlling the decay of the SHG activity.

The poled polymers for second nonlinear optics have attracted considerable interest in recent years as promising candidates for applications in high-performance electrooptical devices.[1] However, most polymers suffer from the decay of field-induced second-order nonlinearity, which arises from the relaxation of the induced noncentrosymmetric alignment of chromophore molecules to its original configuration. Significant effort has been devoted to stabilizing the poling-induced alignment, and considerable progress has been achieved by using the poled polymer with high glass transition temperature (T_g).[2−5] The efficient NLO polymers have been designed and synthesized by covalently linking the NLO chromophore to their backbone as a side chain or a structural unit of the main chain. The exhibited high performance of the chromophore-functionalized polyimide, polyurethane, and polyurea is strong evidence of the strategy.[6−8]

To date, the majority of the high-T_g polymers studied in poled polymer films focus on the ones with the one-dimensional dipolar chromophore. The polymers are usually accompanied by a bathochromic shift of the maximum absorption peak and a decrease in thermal stability,[9] which limit their practical application in devices. Therefore, to achieve the nonlinearity−transparency−stability tradeoff of the chromophore and their poled films is one of the most challenging topics. The problem is often intrinsic to the chromophores chosen. In this paper, a new approach to achieve the thermal and temporal stability by introducing a novel multiple charge-transfer (CT) chromophore is reported.

The designed multiple charge-transfer (CT) chromophore, 2-[4-(4,5-di(4-nitrophenyl)imidazolyl)phenyl]-4,5-di(4-aminophenyl)imidazole (DNPIPDAPI) (Scheme 1), has been synthesized successfully.[10] It possesses a larger molecular nonlinearity ($\mu\beta_0 = 550 \times 10^{-48}$esu), a rather blue-shifted absorption ($\lambda_{max} = 384$ nm in THF), and a higher decomposition temperature ($T_d = 377$ °C).[10,11]

Scheme 1



The chromophore-functionalized polyimide (PI3) (Scheme 2) was prepared from 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene (TPTDA) (BMI) and the multiple CT chromophore following the method described before.[12] The thermal stability of the polyimide was investigated by the results of differential scanning calorimetry (DSC) with a Perkin-Elmer 7 series thermal analysis system at a heating rate of 20 °C/min under nitrogen. The result shows that T_g of PI3 is about 235 °C.

To make the high-T_g polyimides and induce orientation order of chromophores, a multistep corona-poling technique at elevated temperature and in-situ SHG measurements as described before were used;[12] the d_{33} of the poled PI3 film was 16.2 pm/V.

To investigate the field-induced orientation stability of PI3, the depoling and the temporal stability experiments had been performed. For the depoling experiment, the decay of the SHG intensity was monitored as a function of temperature without applied field. Figure 1 shows the dependence of d_{33} values of the polyimide on temperature. It can be seen that, upon ramping the temperature from room temperature at a rate of 5 °C/min, d_{33} is almost unchanged until 170 °C. At a higher temperature, relaxation is gradually obvious. When the temperature is over 213 °C, the decrease of the SHG signal becomes more rapid. The half-decay temperature of the sample is as high as 225 °C. The temporal stability of PI3 is shown in Figure 2; it indicates that the poled polymer film of PI3 can be very stable at 150 °C, retaining 85% of the original d_{33} value over 1000 h with 13.6 pm/V.

For comparison, the results of PI1 and PI2 (seen in Scheme 2), which had been reported before,[12,13] are shown in Figures 1 and 2, too. It is clear that the PI3 possesses much better stability than PI1 and PI2.

As is well-known, T_g of the polymer is intimately connected with the poled-order relaxation.[14] With the

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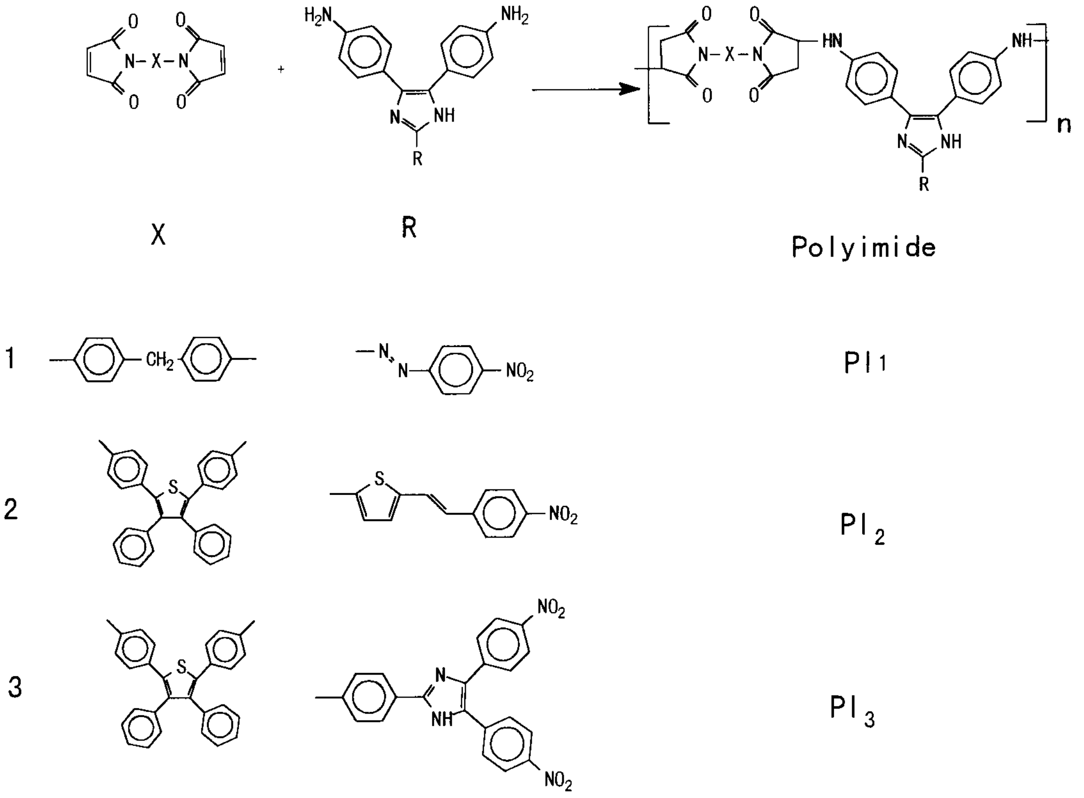
Scheme 2



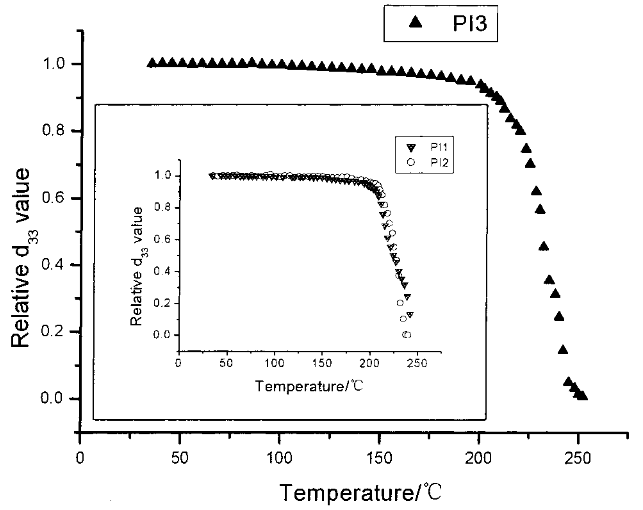


Figure 1. Dependence of orientation stability of polyimide materials on temperature. The heating rate is 5 °C/min.

increase of the T_g, the free volume in polymers decreases and is benefited by the long-term orientation stability. However, T_g of the PI3 is slightly lower than that of PI1 and PI2, which are 250 and 304 °C, respectively, so the better temporal stability of PI3 must arise from another factor besides its high T_g. The structural analysis of the chromophores indicates that the contribution of the multiple charge-transfer chromophore should be an important factor.

The role of 2-D CT chromophore in controlling the decay of SHG activity was reported before.[15] As reported, the general relationship between the macroscopic second-order nonlinear susceptibility which is related to the averaging of the molecular hyperpolarizability and the NLO coefficient can be represented as shown in eq a[16]

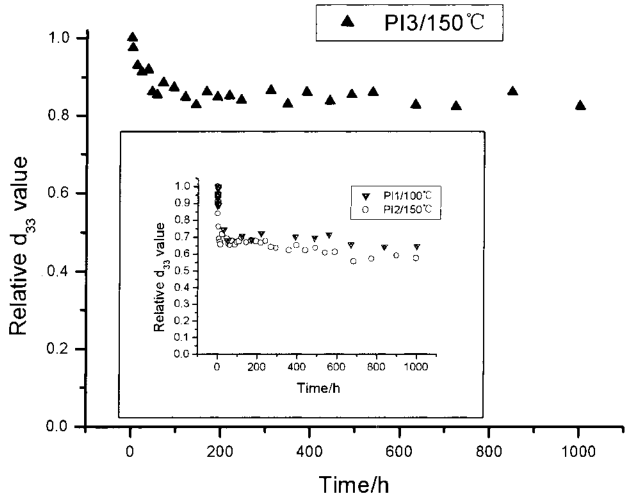


Figure 2. Dependence of orientation stability of polyimide materials on time. PI1 at 100 °C; PI2 and PI3 at 150 °C.

$$d_{IJK} = N f_I^{2\omega} f_J^{\omega} f_K^{\omega} \langle \beta_{IJK} \rangle \quad \text{(a)}$$

$$\langle \beta_{IJK} \rangle = \int \mathrm{d}\phi \int \sin\theta \, \mathrm{d}\theta \int \mathrm{d}\varphi \; b_{IiaJiaKk} \beta_{ijk} G(\theta) \quad \text{(b)}$$

$$\beta_{333} = L_3(p)\beta_{xxx} + 1.5[L_1(p) - L_3(p)]\beta_{xyy} \quad \text{(c)}$$

where N is the number density of chromophore and f terms are the local field factors. In the presence of electrical poling, the $\langle \beta_{IJK} \rangle$ can be deduced from the orientational average of the local-field-corrected molecular second-order optical nonlinearity (β_{ijk}) (eq b), where the rotation matrix aIL between the molecular frame and the laboratory frame is given by the Euler angles (φ, θ, and ϕ); the bIL is the inverse matrix of aIL. $G(\theta)$ is the distribution function. For 2-D CT molecules, both β_{xxx} and β_{xyy} contribute to the second-order nonlinear

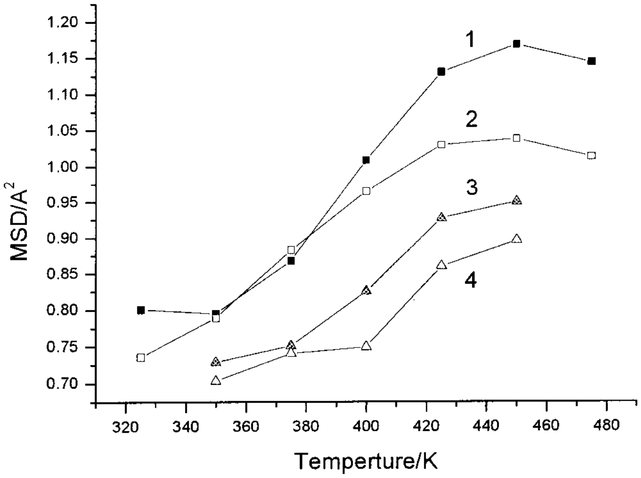


Figure 3. Mean-square displacement of PI2 and PI3. The curves of 1 and 2 show the MSD of pending groups in PI2 and PI3, and the curves of 3 and 4 show the one of main chain of PI2 and PI3, respectively.

Table 1. Comparison among Three Chromophores by the Theoretical Calculation

chromophore	1	2	3
β_{xxx}	8003	−10917	−6124
β_{xyy}	456	−457	−2153
β_{xyy}/β_{xxx}	0.06	0.04	0.35

susceptibility (β_{IJK}). The macroscopic second-order susceptibility can be derived from the eq c, where $L_1(p)$ and $L_3(p)$ are the first- and third-order Langevin functions, respectively, and p is expressed by the local field correction factor of Onsager type.

As the traditional one-dimensional chromophores, for the used chromophores of PI1 and PI2, β_{xxx} is far larger than β_{xyy}, which means that β_{333} comes mainly from the contribution of the β_{xxx}. It had been clearly demonstrated that the macroscopic second-order nonlinear susceptibility (β_{IJK}) would decrease as relaxation of the orientational average of Euler angles. But for the chromophore 3 in PI3, which has two crossed intramolecular CT, both β_{xxx} and β_{xyy} contribute to the second-order susceptibility, and the ratio of the tensorial component ($\gamma = \beta_{xyy}/\beta_{xxx}$) is about 1/3 (as shown in Table 1),[11] which is obviously the difference between chromophores 1 and 2, so that the contribution of the β_{xyy} to β_{333} for chromophore 3 cannot be neglected. As reorientation of the chromophore, the decay due to $L_3(p)\beta_{xxx}$ can be compensated by $[L_1(p) - L_3(p)]\beta_{xyy}$.

In addition, the results of the molecular dynamics simulation have given the same explanation. The calculation was performed by using the CERIUS2 program and the DREIDNG2 force field. The results show that, in the case to consider whole repeated unit of the polyimide or pendant group itself only (that is, chromophore), MSDs (mean-square displacements)[17] of PI3 are smaller than those of PI2 for 320−470 K (Figure 3), which means the structure units are more difficult to move for polymer PI3; hence, it is of benefit to control the decay of SHG activity. So, the higher orientation stability of PI3 can be well understood.

In summary, the introduction of a novel multiple charge-transfer (CT) chromophore may be another effective approach to achieve the thermal and temporal stability besides the use of a high-T_g polymer system. For indentifing this conclusion, the other multiple CT chromophores and their poled polymers have been investigated successfully; the detailed results will be published elsewhere.

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(10) Characterization data: mp >300 °C. IR (KBr) cm^{-1}: 3384, 3214, 2913, 1613, 1599, 1515, 1342, 1289, 1181, 1110, 969, 855, 702. ^{1}H NMR (DMSO-d_6) δ ppm: 13.090 (s, 1H), 12.50 (s, 1H), 8.34 (d, 2H, $J = 9$ Hz), 8.23 (d, 2H, $J = 9$ Hz), 8.23 (d, 2H, $J = 9$ Hz), 8.18 (d, 4H), 7.85 (d, 2H, $J = 9$ Hz), 7.23 (d, 2H, $J = 9$ Hz), 6.55 (d, 2H, $J = 9$ Hz), 5.10 (br, s, 4H). ^{13}C NMR (DMSO-d_6), δ ppm: 147.5, 146.7, 146.1, 141.3, 137.5, 136.8, 130.8, 129.4, 128.8, 128.3, 128.0, 126.1, 125.7, 124.2, 124.0, 118.9. *m/z* (FAB), 635 (M$^+$). Anal. Calcd for $C_{36}H_{26}N_8O_4 \cdot 2H_2O$: C, 64.47; H, 4.51; N, 16.70%. Found: C, 64.20; H, 4.42; N, 16.27%.

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(17) The mean-square displacement (MSD) of a molecule is a way to characterize molecule translational motion by using the output of molecular dynamics (MD) simulation, a sequence of time-ordered atom positions and velocities at discrete steps. Let the position of the each atom i at a time t be denoted $\mathbf{r}_i(t)$, and we introduce the scalar displacement $u_i(t,\Delta t) = |\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t)|$ over some interval of time Δt, starting from a reference time t. The translational motion can be characterized by the MSD: $\overline{u^2}(\Delta t) \equiv \langle (1/N)\sum_{i=1}^{N} u_i^2(t,\Delta t)\rangle$. Here $\langle \ldots \rangle$ indicates an ensemble average, and N is the total number of atoms present in a molecule.

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