JOURNAL OF
Materials
CHEMISTRY
Feature Article

Highly stable, functionalized polyimides for second order nonlinear optics

H. Saadeh, D. Yu, L. M. Wang and L. P. Yu*

Department of Chemistry and The James Franck Institute, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637, USA

Received 12th March 1999, Accepted 2nd June 1999

This paper summarizes our research effort in developing polyimides functionalized with nonlinear optical chromophores for applications in second order nonlinear optical devices. In the past several years, we have developed several general synthetic approaches to these materials. Detailed physical characterization indicated that these materials are quite promising in stabilizing the dipole orientation. Large optical nonlinearity was observed in a few of the systems in which a NLO chromophore exhibiting large $\mu\beta$ value was incorporated. However, a synthetic challenge is to incorporate those NLO chromophores exhibiting better $\mu\beta$ values into polyimide backbones because of the sensitivity of these chromophores towards chemical manipulation. A possible solution by utilizing palladium catalyzed coupling reaction is discussed and an example presented.

Introduction

About two decades ago, a polymeric second order nonlinear optical (NLO) material was disclosed, which stimulated an intensive search for a polymer useful in optical devices.[1–4] These materials were envisioned to possess advantages over inorganic materials, such as fast response time, good processability and low relative permittivity. After many years of research, it becomes apparent that there are three important issues preventing these materials from practical application: the instability of the dipole orientation, inadequate optical nonlinearity and high optical loss.[2–4] Numerous approaches have been developed to tackle these issues and the performances of polymers thus developed have been enhanced. For example, various cross-linkable or high glass transition temperature polymers were developed to enhance the dipole orientation stability at elevated temperatures.[2–11] New chromophores with improved optical nonlinearity have been developed.[12] The origin of optical loss in some of the NLO polymers has been studied, which will help to design strategies to minimize it.[13] However, synthesizing a second order NLO polymer which possesses a combination of properties suitable for extensive device exploration remains a challenge.

Among these polymer systems, polyimides, especially functionalized aromatic polyimides, are promising in the investigation of second-order NLO materials because their high glass transition temperatures can be utilized to stabilize the dipole orientation of the NLO chromophore at high temperatures. Another attractive feature is that the high thermal stability of the polyimides enables them to survive at elevated temperatures during the fabrication of, and operation in, integrated optoelectric devices.[14] Recently, we have developed a series of functionalized polyimides with second order NLO properties.[5–11] Detailed physical and structural analyses have revealed their important features. It seems clear that these polyimides perform better than many other types of polymer materials both in optical nonlinearity and processibility. However, we also recognize the difficulty in synthesizing a polyimide which both contains a NLO chromophore with a large $\mu\beta$ value and remains thermally stable. Various NLO polyimides were also synthesized and investigated by other research groups and significant advances have been achieved.[15] This paper attempts to summarize our own research results and discuss the approaches to issues we encountered.

Results and discussion

Nonlinear optics[16a]

When light interacts with a nonlinear optical material, the optically induced polarization of this material can be described as a power series in the electric field [eqn. (1)]:

$$P=\chi^{(1)}\cdot E+\chi^{(2)}\cdot E\cdot E+\chi^{(3)}\cdot E\cdot E\cdot \mathrm{E}+\ldots \qquad (1)$$

where the expansion coefficients (χ) are known as the first-, second- and third-order susceptibilities, respectively. This bulk nonlinearity originates in the microscopic properties of individual molecules; a similar relationship between the dipole moment and the electric field exists [eqn. (2)]:

$$\mu=\alpha\cdot E+\beta\cdot \mathrm{E}\cdot E+\gamma\cdot E\cdot E\cdot E+\ldots \qquad (2)$$

where α is the polarizability, β is the hyperpolarizability, γ is the second hyperpolarizability of the molecule.

This paper deals with the second order nonlinear optical materials. Noncentrosymmetry is required in the molecules and bulk materials in order for the even-order terms including β and $\chi^{(2)}$ in eqns. (1) and (2) to be nonzero. The microscopic and macroscopic nonlinearity (β and $\chi^{(2)}$) are related to each other and can be expressed by eqn. (3).

$$\chi_{IJK}{}^{(2)}(-\omega;\ \omega_1,\ \omega_2)=Nf_I(\omega)f_J(\omega_1)f_K(\omega_2)$$
$$<\beta_{ijk}(-\omega;\ \omega_1,\ \omega_2)>IJK \qquad (3)$$

where N is the number density of molecules, $f_I(\omega)$, $f_J(\omega_1)$ and $f_K(\omega_2)$ are the Lorentz–Lorenz local field factors at different frequencies, and the term in brackets is a weighted sum of the values of the various β_{ijk}'s, an average of all orientations of the chromophore in the bulk material, such as polymers. Therefore, large molecular hyperpolarizability, high number density and efficient orientation of dipole moments are necessary in order to achieve a large second order NLO effect. However, these three factors are difficult to optimize simultaneously. Large optical nonlinearity generally means large dipole moments in NLO chromophores which impose strong dipole–dipole interactions. These interactions limit the asymmetric dipole orientation.[16b]

In these second order NLO materials, a more interesting phenomenon, the electro-optic (e-o) effect, can be observed. The e-o effect is characterized by the electro-optic coefficient, r, defined in eqn. (4)

$$\Delta\left(\frac{1}{n^2}\right)=rE \qquad (4)$$

where n is the refractive index of the material.

In NLO polymeric materials, a high electric field was used to align the dipole of the chromophore molecules in order to remove the centrosymmetry of amorphous materials. In a poled polymer medium, an ∞mm type symmetry was obtained and the largest e-o coefficient is r_{33}. The e-o effect can be applied in many types of optical devices, such as an integrated-optical modulator (*e.g.* Mach–Zehnder modulator). One important parameter to evaluate the polymeric Mach–Zehnder modulator is the switching voltage V_π (eqn. (5)) which is the voltage needed to change the phase shift by π corresponding to the maximum-to-minimum output intensity,

$$V_\pi = \frac{\lambda h}{n^3 r_{33} L} \tag{5}$$

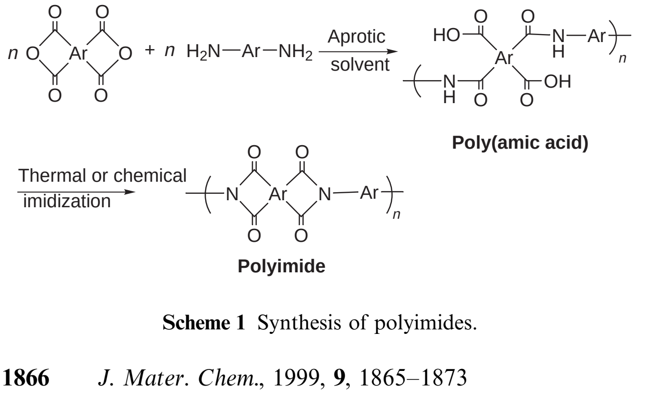
where λ is the wavelength of a TM light, h is the thickness of polymer stack, n is the refractive index of the polymer, and L is the interaction length of the electrode over one arm. It can be seen from eqn. (5) that materials with a large electro-optic coefficient r_{33} need a low switching voltage and a short electrode interaction length to achieve a 180° phase shift. This is the main reason to search for materials with a large r_{33} value.

Synthesis of monomers

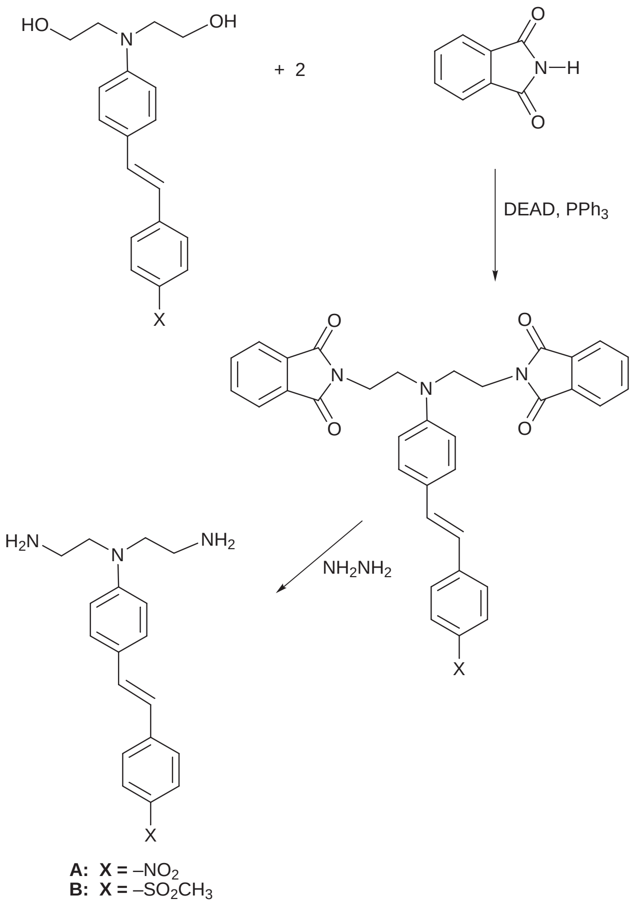
Conventionally, polyimides are synthesized by the polycondensation of dianhydrides and primary diamines *via* a poly(amic acid) precursor which can be subsequently converted into a polyimide either thermally or chemically (Scheme 1).[14] Therefore, to synthesize NLO polyimides, either dianhydrides or diamines can be functionalized with NLO chromophores. However, we have found that the functionalization of diamino monomers is easier than that of dianhydride monomers. Our approach to the synthesis of functionalized polyimides began with the synthesis of nonlinear optical chromophores bearing the diamino moieties. In the past years, we have developed approaches to synthesize both aliphatic and aromatic diamino monomers functionalized with various NLO chromophores (Schemes 2 and 3).[5–11]

In order to keep the functional groups in the chromophore (such as nitro or azo moieties) intact, mild reaction conditions are required. We found that the Mitsunobu reaction can be utilized to achieve that goal.[17] To synthesize aliphatic diamino monomers, the Mitsunobu reaction with modified conditions has been utilized to transform the hydroxy groups into phthalimides which can easily be hydrolyzed to generate diamines. This reaction can be carried out smoothly in THF and monomers A and B as shown in Scheme 2 were synthesized in a reasonable yield.[5,6]

Similarly, the Mitsunobu reaction played a key role in the synthesis of aromatic diamino monomers.[7–11] It is known that the Mitsunobu reaction occurs at room temperature and usually gives a high yield in the alkylation of phenols.[17] The treatment of compounds **4** and **5** with diethyl azodicarboxylate–triphenylphosphine in *N*-methylpyrrolidinone afforded diimido compound **6** in *ca.* 80% yield (Scheme 3). The hydrazinolysis of diimido compounds yielded the corresponding diamino monomers (see Scheme 3). These diamino monomers can be purified after careful recrystallizations. Monomers **F–G** undergo decomposition when hydrazine is used. Methylamine can be used to avoid the side reactions.



Scheme 1 Synthesis of polyimides.

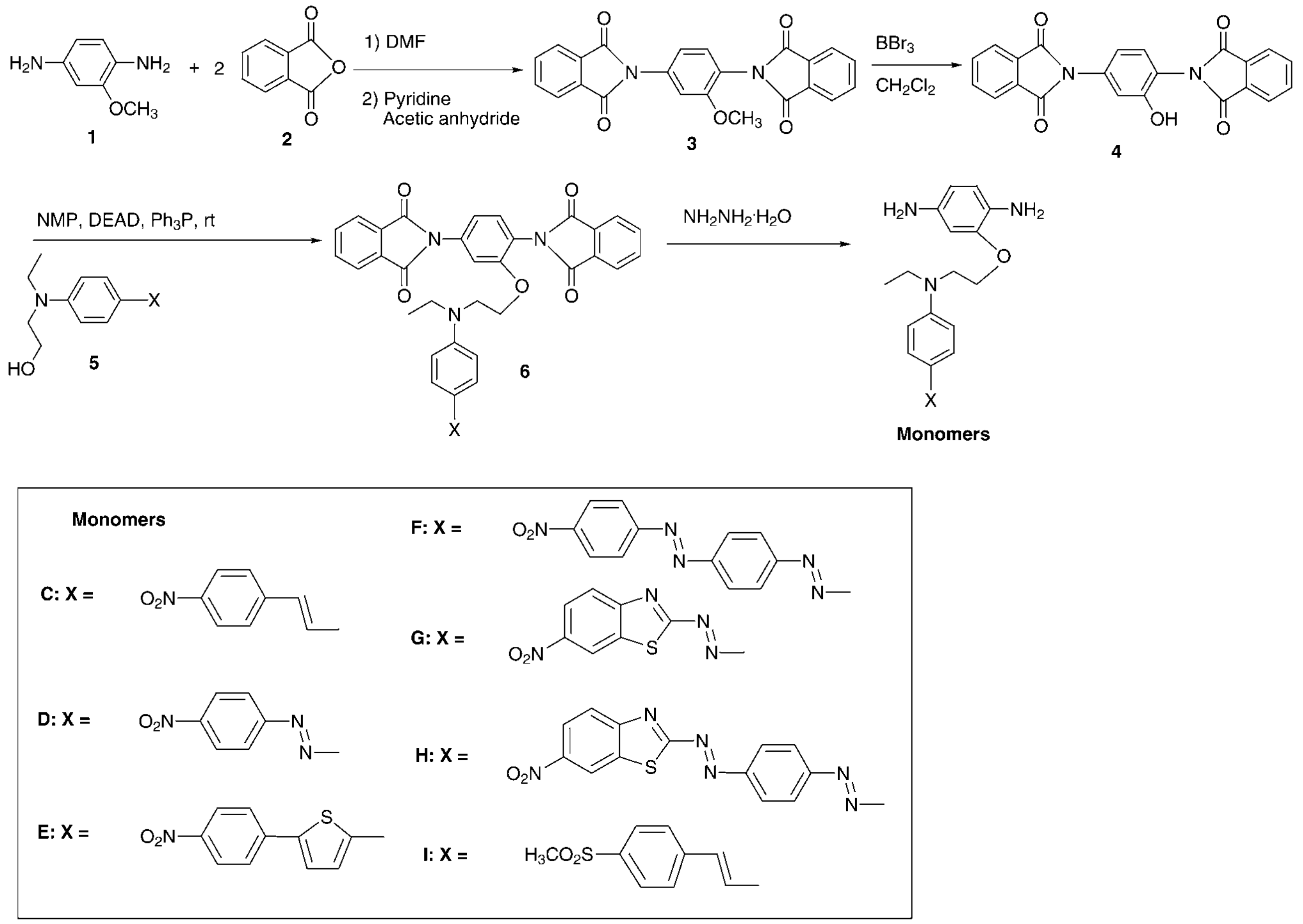


Scheme 2 Synthesis of aliphatic diamino monomers.[5,6]

Synthesis of polyimides

The polymerization procedure consists of two steps: (1) the polymerization of a diamino monomer with a dianhydride monomer, yielding the poly(amic acid), and (2). the imidization of the poly(amic acid) either by chemical cyclization or thermal cyclization (Scheme 4). Aprotic solvents, such as *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF) or 1-methylpyrrolidin-2-one (NMP) are suitable for the purpose of polymerization. The chemical imidization was effected by adding a mixture of pyridine and acetic anhydride to the NMP solution of poly(amic acid). For the thermal cyclization, a solution of the poly(amic acid) was cast or spin-coated onto a glass substrate, which was then cured at elevated temperatures. Which approach to choose is largely determined by the solubility of the resulting polyimides. Chemical imidization is used to synthesize the polyimides containing hexafluoroisopropylidenediphthalic dianhydride because they are usually soluble in polar solvents. Due to the poor solubility in common solvents, polyimide films synthesized from pyromellitic dianhydride (PMDA) or benzophenone tetracarboxylic dianhydride (BTDA) are prepared from the corresponding poly(amic acid) films by using the thermal approach. From a practical point of view, the soluble PIs have many advantages both in structural characterization and film processing.

Table 1 lists the structural and physical information of the synthesized polyimides. A general observation is that these functionalized polyimides exhibit glass transition temperatures which are consistently lower than those corresponding non-



Scheme 3 Synthesis of aromatic diamino monomers.[7–11]

Table 1 Compositions of polyimides and their thermal properties

Polymer	Dianhydride	Diamine	T_g	T_d
1	BTDA	B	209	420
2	“	D	—	303
3	“	I	230	327
4	PMDA	A	230	340
5	“	B	250	437
6	“	D	—	291
7	“	I	240	367
8	6FDA	C	229	321
9	“	D	235	319
10	“	E	227	322
11	“	F	218	300
12	“	G	200	289

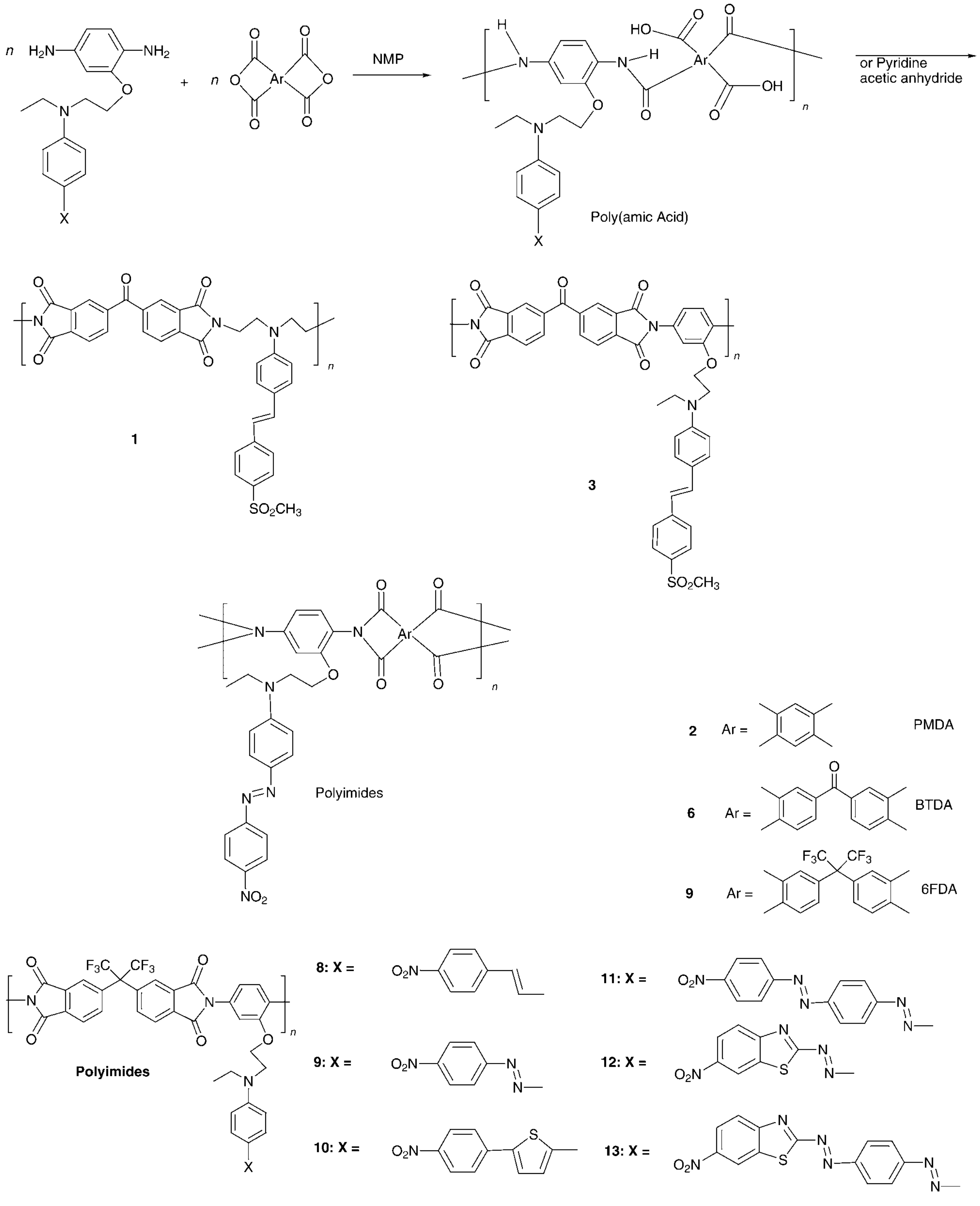
functionalized polyimides. Nevertheless, the T_gs of these polymers are significantly higher than those of most reported NLO polymers.

Physical properties

Structural correlations. These polymers can be classified into a few groups based on the structures with which their physcial properties can be correlated. Several structural parameters can be utilized for this correlation, such as the variations in the structure of diamine, the dianhydride and the NLO chromophores. Such variations affect the glass transition temperature, processibility and optical nonlinearity.

Polymers **1** and **3** have the same NLO chromophore but different polyimide backbones, Polymer **1** is an aliphatic polyimide and **3** an aromatic polyimide. Both polyamic acids exhibited the same absorption maximum at 385 nm. Polyimide **1** has a relatively flexible backbone and polyimide **3** is more rigid. As a result, the glass transition temperature (T_g) (230 °C) of polyimide **3** is higher than that of polyimide **1** (209 °C). Since the temporal stability of the second harmonic generation of the poled polymer is related to the glass transition temperature (the higher the T_g, the better the temporal stability), polyimide **3** should have better stability than the aliphatic polyimide. At room temperature or even higher temperature, for example 100 °C, the difference was not obvious (see Fig. 1). When the temperature was further increased, *i.e.* at 150 °C, polyimide **3** showed an advantage over polyimide **1**. After 800 hours, the SHG signal of polyimide **3** still stabilized at around 100% of the original value. After only 100 hours, the SHG signal of polyimide **1** had already decreased to 90% of its original value. For polyimide **3**, a d_{33} value of *ca.* 45 pm V^{-1} (at 1064 nm) was observed. Polyimide **1** showed a slightly larger d_{33} value, 60 pm V^{-1}, due to a higher density of the chromophore and lower T_g than polyimide **3** (the experimental error is about 20%, which mainly comes from the uncertainty of the reference quartz sample, *ca.* 10%, and the laser beam instability). These d_{33} values were anticipated from the β values of the corresponding NLO chromophore.[13] The electro-optic coefficients of these polyimides were measured at wavelengths of 632 and 780 nm using a reflection technique developed by Teng and Man.[17] A He-Ne laser and a diode laser were used as light sources. The results at 780 nm are presented in Table 2. A slight difference in r_{33} values at 632 nm was noticeable, and they are quite similar to each other at 780 nm. This is consistent with the results found in d_{33} measurements.

Another example is the set of polymers **2**, **6** and **9** which are all aromatic polyimides with the same NLO chromophore. The only difference is the structure of dianhydride used. Polyimides **2** and **6** are insoluble in organic solvents and there is no defined T_g before decomposition. Polyamic acids have



Scheme 4 Synthesis of NLO polyimides.

to be used to prepare films and post-thermal treatments are required to convert them into polyimides. Since the T_gs of insoluble polyimides are not observable, the polymer thin films made from the corresponding poly(amic acid) solutions have to be poled during the imidization process. The imidization temperatures of polyamic acids are approximately 180 °C. After imidization, the dipole was fixed by the polyimide matrix. It seems to be true that the poling efficiency during imidization can not be maximized and as soon as the temperature rises above 200 °C the glass transition temperature can not be reached before decomposition. Thus, the dipole orientation in polyimides **2** and **6** is not optimized. This is reflected in the small d_{33} and r_{33} values of these polymers, although the chromophore densities of these polyimides are comparable with that of polyimide **9**. This trend is consistent with the order parameter measurement results, Φ values of 0.14 and 0.16 were obtained for polyimides **2** and **6**, respectively. In contrast to these polymers, the soluble polymer **9** exhibits a

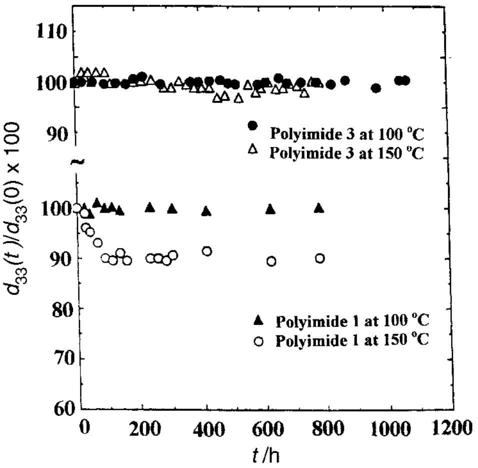


Fig. 1 Temporal stability of SHG signal of polyimides **1** and **3** at various temperatures.

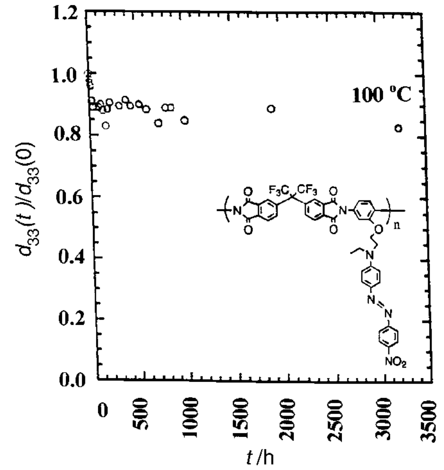


Fig. 2 Temporal stability of SHG signal of polyimides **9** at 100 °C in the air.

T_g of 215 °C and can be corona poled efficiently. Much larger d_{33} and r_{33} values were observed under similar poling conditions.

The nature of the NLO chromophores is also reflected in the optical nonlinearity of the polymers. Polymers **8–11** possess the same polyimide backbone and different NLO chromophores. The $\mu\beta$ value of chromophore **D** (disperse red 1 at 1300 nm) is 751×10^{-31} esu and that of chromophore **C** (DANS at 1300 nm) is 662×10^{-31} esu,[14a] the diaryl thiophene chromophore **E** has a value which is *ca.* 60% of that of DANS,[14b] and **F** has the largest value, 4600×10^{-31} esu at 1300 nm. It can be seen from Table 2 that under identical poling order parameters, polymers **8** and **9** have similar d_{33} and r_{33} values and polymer **10** has the smallest NLO response and polymer **11** the largest NLO response among the four polymers. It can also be seen that as the length of the NLO chromophore increase, the glass transition temperatures of the polymers decrease due to the plasticization effect. Polymers **11** and **12** have a T_g of 218 and 200 °C while others exhibit a T_g of ~239 °C.

Temporal stability of these polymers. As we can see from the introduction, a crucial requirement for these NLO polymers is that they must exhibit a stable dipole orientation at a certain temperature range after electric poling. Different experiments have been designed to investigate this stability. A particularly effective test is to monitor the temporal and thermal stability of the second harmonic generation or the e-o response. Because the thermal relaxation process of the dipole orientation is directly related to the free volume in the polymer, a critical free volume is required for the relaxation of the orientation of the dipole. This critical free volume is related to the glass transition temperature; a high glass transition temperature (T_g) implies a higher orientational stability. It was found that at room temperature, all of the polyimides are stable and there is no decay in the intensity of the second harmonic generation signal. At 100 °C in air, after an initial decay to *ca.* 90% of the original signal, more than 80% of the SHG signals for aromatic polyimides remained after prolonged times (> 1000 h) (see Fig. 2). The SHG signals of all the polyimides remained significantly stable even at higher temperatures. For example, the initial signals only decayed by *ca.* 20% after 800 h at 150 °C in the air, as shown in Fig. 3.

Temperature-dependent SHG measurements yield information on SHG stability as a function of the temperature. Fig. 4 shows such a result for polyimide **8**, where the heating rate is 4 °C min^{-1} and the samples were exposed to the air during the whole measurement. The SHG signal was quite stable until the temperature reached 200 °C (for example, see Fig. 4). A fast decay of the SHG signal was observed when the temperature was close to the polymer's glass transition temperature. The signal completely disappeared when the temperature was above the T_g. However, it was found that the same magnitude of the SHG signal could be recovered from those soluble polyimides after they were re-poled by corona discharging, indicating that the NLO chromophore was not damaged after

Table 2 Physical properties of polyimides

Polymer	$d_{33}^{(532)}$ pm V^{-1}	$r_{33}^{(780\text{nm})}$ pm V^{-1}	$\lambda_{\max}$/nm
1	61	4	385
2	59	7	490
3	46	4	383
4	115	23	438
5	61	5	372
6	69	7	470
7	51	5	383
8	146	24^{a}	440
9	169	25^{a}	477
10	103	24	445
11	—	35^{a}	505
12	—	30^{1}	532

[a] At 1300 nm.

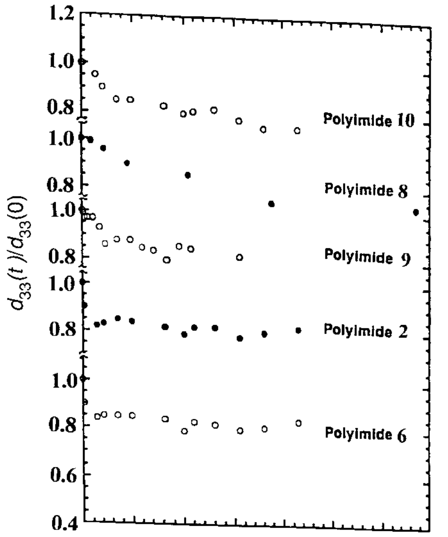


Fig. 3 Temporal stabilty of SHG signal of polyimides **2**, **6**, **8**, **9**, **10** at 150 °C in the air.

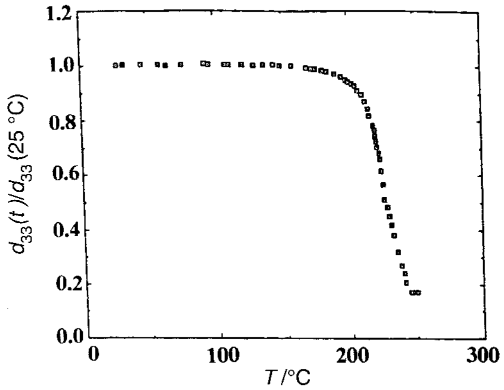


Fig. 4 SHG signal of polyimide **10** as a function of temperature.

experiencing high temperatures. Because of a lower T_g than the others, polymers **11** and **12** start to decay when the temperature reaches 180 °C and 165 °C, respectively.

Poling dynamics and long term stability of the dipole orientation. In order to establish a detailed procedure for corona poling, we studied the poling dynamics on thin films of polymers. Fig. 5 shows the results of the SHG signal as a function of temperature or time for polymer **11**. Several important effects can be seen from these results. First of all, large SHG signals can be observed even at room temperature when the field was turned on. Further heating only helps to increase the SHG signal to a small degree. After the temperature reaches close to the T_g, the SHG signal tends to decrease and eventually disappears if the applying voltage to the corona needle is fixed. This is clearly related to two factors: (1) as the temperature increases, the conductivity of the polymer films increases and thus the effective electric field decreases; (2) high temperature imparts high thermal randomization energy in the NLO dipoles which can compete with the electric poling field. These effects can be minimized when the temperature is reduced, as shown in the cooling curve. As the cooling occurs, physical ageing causes the free volume of the polymer to shrink, thus restricting the chromophore motion and stabilizing the alignment. Because of the physical ageing, the conductivity of the polymer film also changes and the surface accumulates more charges than during the corresponding heating stage. The SHG signal is larger during the cooling stage than the heating stage. This effect can be seen clearly when the voltage is switched off at room temperature; the initial drop of the SHG signal could well be due to the release of the surface charge. After the initial decay, the SHG signal was maintained at a level identical to the maximum during the heating-up process. These results reveal two points: (1) corona poling can be effectively performed at a temperature near T_g; (2) a finite aging time under the corona poling condition may help to enhance the stability of the dipole orientation.

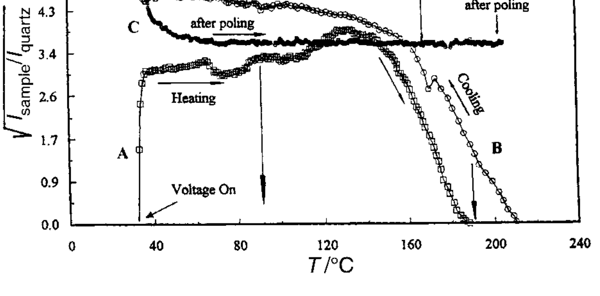


Fig. 5 Poling dynamics as a function of temperature and time of polyimide **11**. Curve A: High voltage was turned on and heating until SHG signal disappeared at a temperature of 185 °C. The heating continued to 210 °C. Curve B: The SHG signal reaches its maximum value on cooling to room temperature while the high voltage was still on. Curve C: High voltage was turned off and the SHG signal stayed stable after 1 h at room temperature.

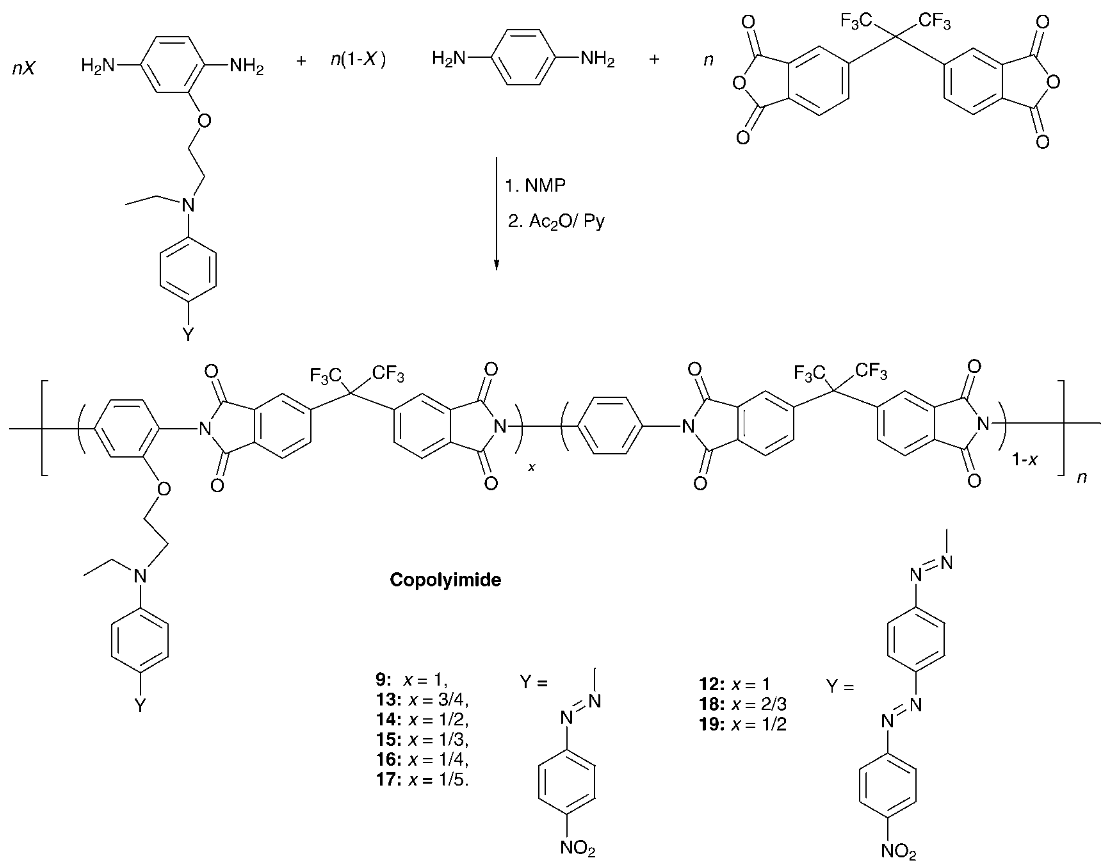
Copolymers

The polymers discussed above show some promising properties both in thermal stability and optical nonlinearity. However, optical engineers are not quite satisfied and they would like to have materials which can survive under the harsher processing conditions common in the semiconductor industry. A higher thermal stability is thus desirable. The above results clearly show that these functionalized polyimides exhibit glass transition temperatures which are consistently lower than those corresponding to non-functionalized polyimides (>300 °C). We can reason that if the common diamino monomers (such as diaminobenzene) are used together with diamino monomers bearing an NLO chromophore and corresponding dianhydrides, NLO copolyimides can be synthesized so that the glass transition temperature of the resulting polymers can be enhanced. The copolymerization approach will offer the opportunity to study the effects of the chromophore loading level (*i.e.* the weight percentage of the chromophore unit in the polymer) on the glass transition temperature (T_g), the thermal stability and the optical nonlinearity. Thorough understanding of these relationships is important to further enhance the performance of NLO materials. It was indeed found that the copolyimides exhibit higher glass transition temperatures and better thermal performance of the NLO properties than our previous polyimides. But, the NLO properties diminished due to the lowering in NLO chromophore loading level. The results indicate that within a tolerable trade-off range in optical nonlinearity, copolyimides are the materials of choice for high thermal stability.

Scheme 5 shows the reaction in which the copolyimides were synthesized *via* the poly(amic acid)s followed by chemical imidization. These copolymers are soluble in solvents such as THF, chloroform, NMP, tetrachloroethane, DMF, and DMSO. Polymers with a relatively low chromophore loading level possess poor solubility in THF and chloroform. Large molecular weight can be obtained after careful purification of the diamino monomers.

DSC studies indicated that as the NLO chromophore loading level decreased, the glass transition temperatures (T_g) of the copolyimides gradually increased (from 235 °C to 278 °C for polymers **9**, **13**–**17** and from 218 °C to 242 °C for polymers **12**, **18**, and **19** (Table 3). The TGA studies showed that the decomposition temperatures (the onset point at which the sample starts weight loss) of these copolyimides were higher than the corresponding glass transition temperatures (320 °C *vs.* 235 °C for polymer **9** and 354 °C *vs.* 278 °C for polymer **17**). It indicated that high temperature poling for a short time is feasible without damaging the NLO chromophores.

Linear optical properties. When the chromophore loading level decreased, the refractive indices decreased (Fig. 6). This feature is interesting because it provides the opportunity to fine-tune the linear optical properties of the polymers to suit the need for device applications. These polymers are birefringent in their pristine films as evidenced by the difference between the refractive indices of the TE and TM modes. The refractive indices of the TE mode (in-plane) are larger than those of the TM mode (out-of-plane) which implies that the polyimide backbone might lie in the plane of the film. The refractive indices of the TE mode did not change after corona electrical poling. The refractive indices of the TM mode became larger after poling and the birefringence became



Scheme 5 Synthesis of copolyimides.

Table 3 Physical properties of polyimides

Polymers	X	Chromophore %	T_g/°C	T_d/°C	Φ	r_{33}/pm V^{-1}
9	1	32.3	235	319	0.18	25
13	3/4	26.8	236	327	0.19	19
14	1/2	19.9	257	342	0.18	11
15	1/3	14.4	267	344	0.17	10
16	1/4	11.3	277	348	0.21	4
17	1/5	9.3	278	354	0.19	3
12	1	39.9%	218	300	0.23	35
18	2/3	31.3%	238	310	0.21	23
19	1/2	25.7%	242	320	0.24	14

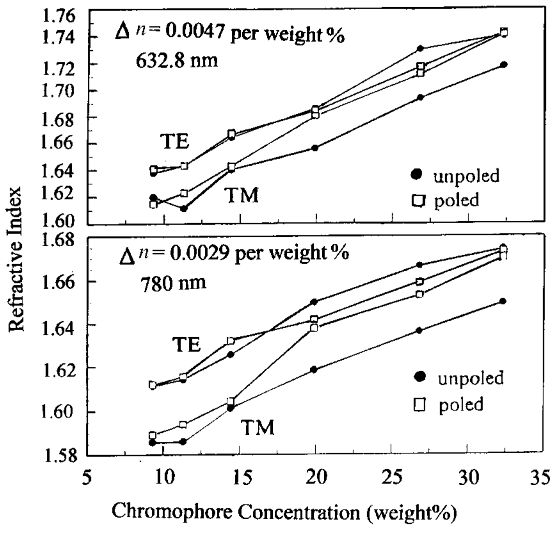


Fig. 6 Refractive index of copolyimides **9**, **13**–**17** as a function of chromophore concentration.

smaller simultaneously. It is caused by the alignment of the molecules of the chromophore along the direction of the applied poling field which is perpendicular to the polymer film plane (out-of-plane).

Nonlinear optical properties. The electro-optic coefficients (r_{33}) were measured using the simple reflection technique at 1300 nm which is beyond the absorption band of the chromophore. A large value of r_{33} was obtained for polymer **11** (r_{33} = 35 pm V^{-1} at 1300 nm). It can be observed that as the chromophore loading level became smaller, values of r_{33} became smaller (Fig. 7).

The temporal stability of SHG for polymers **9**, **13–17** was measured at 180 °C. The copolyimides exhibit a much improved stability, compared with the original polymer **9** and other polyimides we synthesized.[2] Few polymers can survive at such high

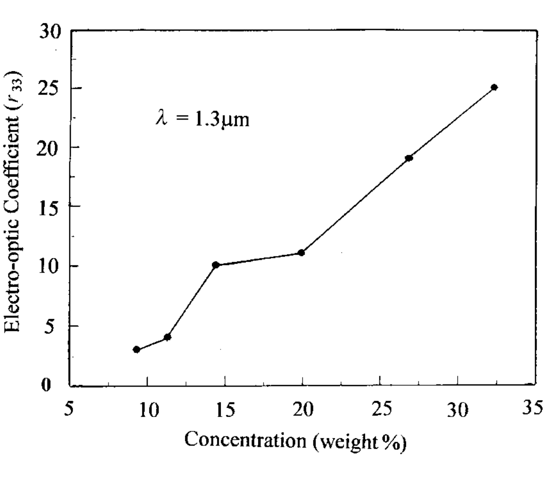


Fig. 7 Electro-optic coefficient of copolyimides **9**, **13**–**17** as a function of chromophore concentration.

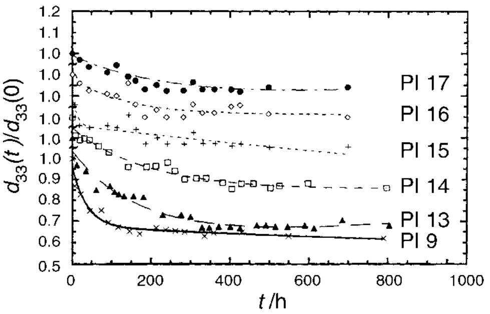


Fig. 8 Temporal stability of SHG signal of copolyimides **9**, **13**–**17** at 180 °C in the air.

temperatures for a long time. The polymer with the higher T_g possessed a higher stability. Fig. 8 shows that polymer **17** with the highest T_g stabilized around 85% of its initial value after 700 h at 180 °C, while polymer **9** with the lowest T_g only exhibited 60% of the original SHG signal after 800 h at the same temperature (Fig. 8). Polymers **12,18,19** displayed no SHG signal decay at room temperature. When the SHG signal of polymer **12** was monitored at 100 °C for 900 h, the decay was noticeable at initial stages and then stabilized at *ca.* 82% of its initial value. Polymers **18** and **19** showed almost identical behavior, since both have a close glass transition temperature. Their signals stabilized at *ca.* 88% and 90% of their initial value, respectively, after 800 h (Fig. 8). These results indicate that these materials are stable enough to withstand the working temperature for device fabrications.

The temperature-dependent SHG was carried out *in situ* by monitoring the SHG signal while the temperature was ramped at 4 °C min^{-1} (Fig. 9). Polymer **16** which has a higher T_g shows much better stability than polymer **13** with a lower T_g. Compared with the onset decay temperature (200 °C) for polymer **13**, the onset temperature of 250 °C for PI 5 is a significant improvement. Polymers **18** and **19** have a higher T_g and showed better stability than polymer **12**. Fig. 9 shows that the SHG signal remained stable for all polymers until reaching the glass transition temperature, where the SHG signal starts to decay rapidly. It completely disappeared as the temperature went above T_g.

Polymers possessing NLO chromophores exhibiting large $\mu\beta$ values

From the above work, we have demonstrated that the thermal stability of the functionalized polyimides is good enough for numerous device applications. The limiting factor is the NLO response—namely, small r_{33} values. To improve this, the incorporation of a NLO chromophore exhibiting a large $\mu\beta$ value is important. However, the majority of the chromophores exhibiting large $\mu\beta$ values sensitive to numerous chemical manipulations. To incorporate these chromophores into a polymer backbone, especially the polyimides backbone, mild reaction conditions are required.

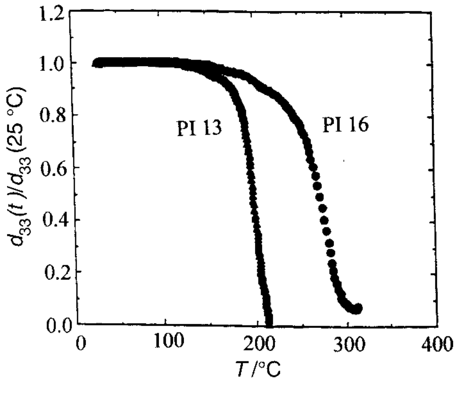


Fig. 9 SHG signal of polyimides **13** and **16** as a function of temperature.

In the past few years, our group has been involved in exploring palladium-catalyzed reactions for polycondensation and gained extensive knowledge about these reactions.[18–21] Two unique features of these reactions are that they can tolerate a variety of functional groups and the reaction condition is mild.[18–21] We have synthesized a series of conjugated photorefractive polymers containing NLO chromophores.[19,22,23] The question is how to utilize these reactions to prepare NLO polyimides which will maintain high thermal stability and processibility. Scheme 6 outlines an approach allowing us to realize that goal. The central step is the synthesis of monomer **K** which contains two bromo groups necessary for palladium-catalyzed reactions and at the same time, contains two NLO chromophores with large $\mu\beta$ values.

Three advantages can be seen from this approach: (1) the arrangement ensures a high NLO chromophore density in resulting polyimides; (2) the bromo groups will be activated by the electron-withdrawing imido and ester groups; (3) the two trifluoromethyl groups render the resulting polymers soluble in polar solvents.

The synthesis of compound **J** has been accomplished in an excellent yield. The next step, attaching the NLO chromophore by utilizing the Mitsunobu reaction, has two options. The first is to attach an NLO chromophore containing a hydroxy group directly to compound **J**. In order for this approach to work, these sensitive groups must be able to survive the Mitsunobu reaction conditions. In the second approach, the sensitive electron withdrawing group is attached after the Mitsunobu reaction.

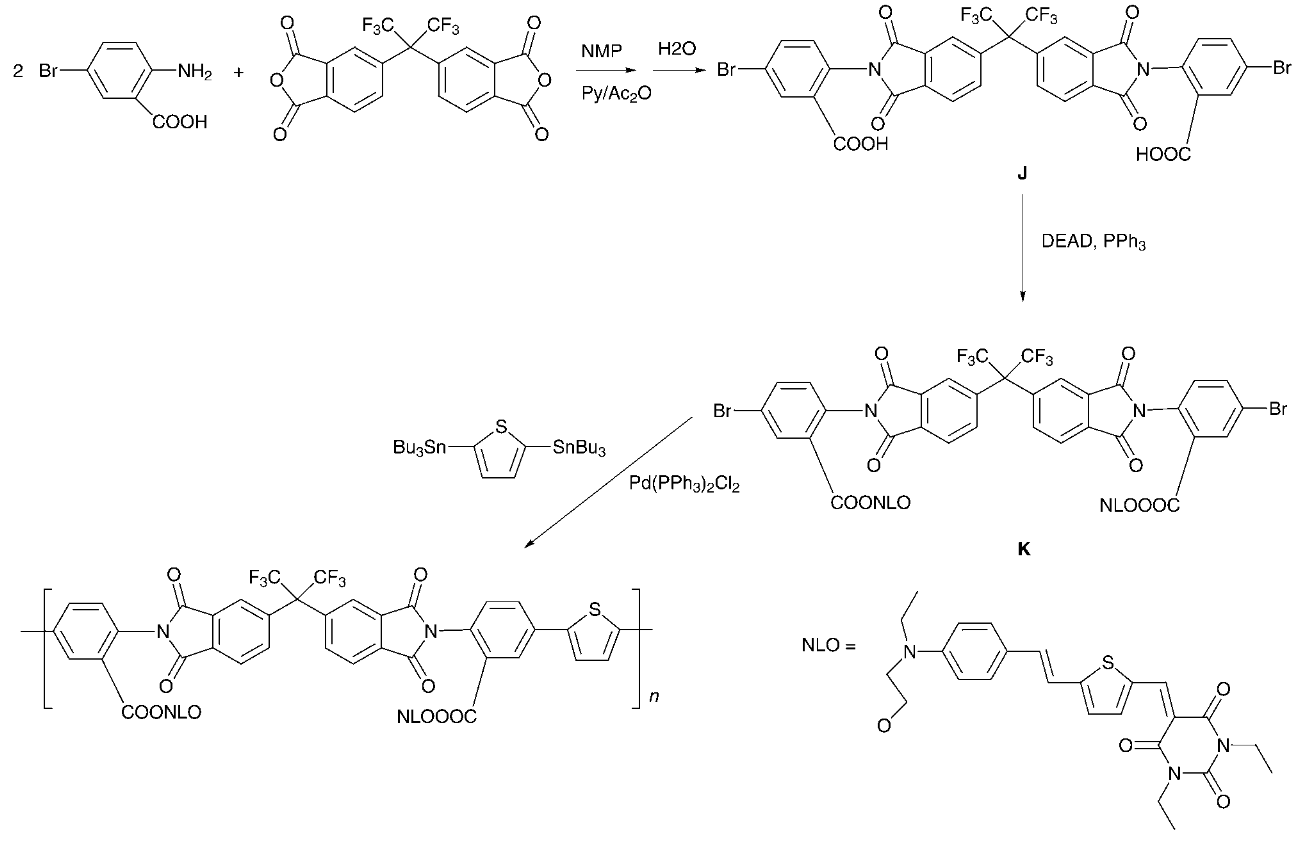
The polymer was synthesized by a typical Stille coupling reaction using THF as a solvent and $PdCl_2(PPh_3)_2$ as a catalytic system. The polymer was soluble in common organic solvents, such as THF, TCE, DMF *etc.* and optical quality films were cast from either THF or TCE for NLO studies. The molecular weight of this polymer, determined by GPC using THF as eluent, was found to be 21000 (M_w) and 13000 (M_n). Spectroscopic studies supported the polymer structure as proposed. DSC studies show that this polymer has a glass transition temperature of 170 °C. Two weight loss temperatures, one at 250 °C and the other at 550 °C were observed by TGA studies, which correspond to the decomposition of the NLO chromophore and backbone, respectively.

The results of the UV–VIS study showed an absorption maximum at 535 nm. After the molecular dipoles were aligned by corona poling the maximum absorbance was reduced, and an order parameter of 0.21 can be observed. The electro-optic coefficient (r_{33}) was measured in the infrared region at 1.3 μm (using a 5 mW diode laser to avoid resonance enhancement). A large electro-optical coefficient ($r_{33} = 33$ pm V^{-1} at 1300 nm) was obtained. The temperature-dependent SHG experiments on pre-poled samples showed that the SHG signal of this polymer remained stable until reaching the glass transition temperature, where the SHG signal starts to decay rapidly.

These results indicate that the palladium-catalyzed reactions can be applied to prepare high T_g, NLO polyimides. Chemically sensitive NLO chromophores can be tolerated in these reactions. It can be expected that new polyimides and other polymer backbones can be synthesized by following this approach.

Conclusion

Several synthetic approaches have been developed to the synthesis of polyimides bearing different kinds of NLO chromophores. It has been shown that these polyimides possess high thermal stability and tunable optical nonlinearity. The key challenge is the synthesis of NLO polyimides which contain



Scheme 6 Synthesis of polyimides bearing NLO chromophores with large $\mu\beta$ value.

NLO chromophores exhibiting large $\mu\beta$ values and high thermal stability. Palladium-catalyzed coupling reactions were proposed to be a possible solution to this challenge. Preliminary study shows some promising features. Our future work will be focused in this direction.

Acknowledgments

This work was supported by ONR and the National Science Foundation. Support from the National Science Foundation Young Investigator program is gratefully acknowledged. This work also benefited from the support of the NSF MRSEC program at the University of Chicago.

References

1 D. Meredith, J. VanDusen and D. J. Williams, *Macromolecules*, 1982, **15**, 1385.
2 D. M. Burland, R. D. Miller and C. A. Walsh, *Chem. Rev.*, 1994, **94**, 31.
3 L. R. Dalton, A. W. Harper, R. Ghosn, W. H. Steier, M. Ziari, H. Fetterman, Y. Shi, R. V. Mustacich, A. K-Y. Jen and K. J Shea, *Chem. Mater.*, 1995, **7**, 1060.
4 T. J. Marks and M. A. Ratner, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 155.
5 Z. H. Peng and L. P. Yu, *Macromolecules*, 1994, **27**, 2638.
6 S. Y. Yang, Z. H. Peng and L. P. Yu, *Macromolecules*, 1994, **27**, 5858.
7 D. Yu and L. P. Yu, *Macromolecules*, 1994, **27**, 6718.
8 D. Yu, A. Gharavi and L. P. Yu, *Macromolecules*, 1995, **28**, 784.
9 D. Yu, A. Gharavi and L. P. Yu, *J. Am. Chem. Soc.*, 1995, **117**, 11680.
10 D. Yu, A. Gharavi and L. P. Yu, *Macromolecules*, 1996, **29**, 6139.
11 H. Saadeh, A. Gharavi and L. P. Yu, *Macromolecules*, 1997, **30**, 5403
12 S. R. Marder, B. Kippelen, A. K-Y. Jen and N. Peyghambarian, *Nature*, 1997, **388**, 845.
13 C. C. Teng, M. A. Mortazavi and G. K. Boudoughain, *Appl. Phys. Lett.*, 1995, **66**, 667.
14 G. M. Bower and L. W. Frost, *J. Polym. Sci. A.*, 1963, **1**, 3135.
15 Leading references see: (*a*) R. D. Miller, D. M. Burland, M. Jurich, V. Y. Lee, C. R. Moylan, J. I. Thackara, R. J. Twieg, T. Verbiest and W. Volksen, *Macromolecules*, 1995, **28**, 4970; (*b*) T. Verbiest, D. M. Burland, M. C. Jurich, V. Y. Lee, R. M. Miller and W. Volksen, *Macromolecules*, 1995, **28**, 3005; (*c*) T.-A. Chen, A. K.-Y. Jen and Y. Cai, *J. Am. Chem. Soc.*, 1995, **117**, 7295; (*d*). J. Park, T. J. Marks, J. Yang and G. K. Wong, *Chem. Mater.*, 1990, **2**, 229.
16 (*a*) P. Prasad and D. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, John Wiley and Sons, New York, 1991; (*b*) L. R. Dalton, A. W. Harper and B. H. Robison, *Proc. Natl. Acad. Sci. USA*, 1997, **94**, 4842.
17 O. Mitsunobu, *Synthesis*, 1981, 1.
18 Z. N. Bao, W. K. Chan and L. P. Yu, *Chem. Mater.*, 1993, **5**, 2.
19 W. K. Chan, C. Yongming, Z. Peng and L. P. Yu, *J. Am. Chem. Soc.*, 1993, **115**, 11738.
20 Z. Bao, C. Yongming and L. P. Yu, *Macromolecules*, 1994, **27**, 4629.
21 Z. Bao, W. K. Chan and L. P. Yu, *J. Am. Chem. Soc.*, 1995, **117**, 12426.
22 Z. Peng and L. P. Yu, *J. Am. Chem. Soc.*, 1996, **118**, 3777.
23 Q. Wang, L. Wang and L. P. Yu, *J. Am. Chem. Soc.*, 1998, **120**, 12860.

Paper 9/01958H