Synthesis and Characterization of Push-pull Polymers Containing Diphenylsiliane Moiety in the Main Chain

Kuk Ro Yoon*, Bong geun So and Soo min Lee
Department of Chemistry, Hannam University, 133 Ojung-Dong, Taeduk-Gu, Daejeon 306-791, Korea

We have synthesized an azobenzene-containing polymer (PEA) and a stilbene-containing polymer (PAS) with second-order nonlinear properties. The second harmonic coefficient (d_{33}) of the poled polymer films was 84 and 36 pm/V for of PEA and PAS, respectively. The poled state of these polymers was stable at least up to 30 h at room temperature. T_g of these polymers appeared in the range from 120 to 160°C and onset of initial weight losses in the range from 260 to 270°C. Silicon moieties in the main chain enhanced the solubility of PEA and PAS in common organic solvents such as chloroform, N-methylpyrrolidinone (NMP), N, N-dimethylformamide (DMF), etc.

keywords: Nonlinear optical polymer, Second harmonic coefficient, Azobenzene, Stilbene

INTRODUCTION

Recently polymers with nonlinear optical (NLO) and electro-optic (EO) properties have been attracting considerable attention because of the potential applications in optical switching, optical telecommunication devices, optical disks, new type of lasers, and photonic large-scale integration (PLSI), etc [1-3]. Considerable efforts have been put to develop polymers with high nonlinear optical coefficients stable over a prolonged period at moderate temperatures. [4] Extensive studies have been done to put nonlinear optical properties on polymers by introducing nonlinear optical chromophores as pendant groups on the polymer backbone or by incorporating them as components of the polymer backbone [5-7]. The backbone chain should have moderate glass transition temperature (T_g) in order to prevent thermal relaxation of the chromophores aligned by poling while maintaining the poling efficiency sufficiently high. It is well known that chromophore structures with an electron acceptor in one end and an electron donor on the other end of a π-conjugated system exhibit high nonlinear optical coefficient.

Generally, for successful applications, the nonlinear optical polymers should have good processibility, high thermal stability, and low optical loss, in addition to high electro-optic coefficient [8-12]. Usually, wholly aromatic polyamides and polyesters have high thermal stability as well as mechanical strength. However, their processibility is rather poor as they have relatively high T_g, high T_m (melting temperature), and poor solubility in organic solvents.

It is well known that flexibility of the main chain can be increased by incorporating hetero-atoms such as silicon which influence the bond angles [13]. Therefore, it is expected that the T_g of a polymer will be lowered by incorporation of hetero-atoms such as Si into the main chain. In addition, because of the difference in electronegativity of silicon (1.90) and carbon (2.55), the Si-C bonds in the main chain are expected to have moderate magnitude of dipole moment. Thus the Si hetero-atoms incorporated into the main chain are expected to help enhance the processibility of the polymer via promoting the affinity of the polymer to polar solvents, i.e. the solubility in such solvents. The C-C bond energy is 346 kJ/mol while that of Si-C is 360 kJ/mol [14-16]. This means that incorporation of Si hetero-atoms into the main chain will enhance the thermal stability of the polymer as well. It has been reported that incorporation of phenylsilane units in the backbone enhances not only the thermal stability of the polymer, but also the processibility by improving the solubility in common organic solvents [13, 17-19].

Kim and collaborators reported novel silicon-containing NLO polyester show effectively electro-optic applications [20]

In this work, we have synthesized two nonlinear optical polymers, namely PEA and PAS. Polymer PEA consist of phenyl silanes connected via amide linkages in the backbone chain and azobenzene moieties in the side chain. The PAS consists of same phenyl silanes but connected via ester linkages in the backbone chain and consist of stilbene moieties in the side chain.

MATERIALS AND METHODS

Materials

Acetic anhydride, thionyl chloride, N-methylpyrrolidinone (NMP), triethylamine (Aldrich), and diglyme (Junsei) were used after purification by vacuum distillation. Ethyl ether, tetrahydrofuran (THF), toluene, n-hexane, and acetone were purified by vacuum distillation over sodium. All other solvents and reagents were analytical-grade quality and used

as received, unless otherwise described.

Synthesis

Di-*p*-tolyldiphenylsilane (DTPS) was synthesized by Grignard reaction of *p*-bromotoluene with dichlorodiphenylsilane in diethyl ether under Li catalyst [20]. White solid of DTPS was obtained with a yield of 87% after purification by recrystallization from ethanol. m.p.: 118-120°C. IR (KBr pellet, cm^{-1}): 1425, 1105, 700 (Si-ph). ^{1}H-NMR (DMSO-d$_6$, ppm): 2.25 (s, 6H, aryl CH); 7.6-7.2 (m, 18H, aryl CH). Anal. Calcd for C$_{26}$H$_{24}$Si (364.56): C, 85.66; H, 6.64. Found: C, 85.88; H, 6.66

Bis(*p*-carboxylphenyl)diphenylsilane (DAPS) was synthesized by oxidizing DTPS with chromic acid (CrO$_3$)^{20}. The yield of DAPS was 75 % after purification by recrystallization from diethyl ether. m.p.:265-268°C. IR (KBr pellet, cm^{-1}): 3500-2400 (carboxylic acid O-H); 1690 carbonyl C=O); 1425, 1105, 700 (Si-Ph). ^{1}H-NMR (DMSO-D$_6$, ppm): 7.6(s, 10H, aryl CH of silyl Ph); 7.8 (d, 4H, aryl *ortho to* Si); 8.2 (d, 4H, aryl CH *ortho to* COOH). Anal Calcd for C$_{26}$H$_{20}$O$_4$Si (424.11); C, 73.57; H, 4.75. Found: C, 73.44; H, 4.81.

Bis(4-chlorocarbonylphenyl)diphenylsiliane) (DCPS) was synthesized by chlorination of DAPS with thionylchloride with a yield of 90%.[20] m.p.: 183-185. IR (KBr pellet, cm^{-1}): 1775, 1735 (aryl C=O); 1425, 1105, 700 (Si-ph). ^{1}H-NMR (DMSO-d6, ppm): 7.5 (*s*, 10, aryl CH of sily Ph); 7.65 (*d*, 4H, aryl CH *ortho to* Si); 8.0 (*d*, 4H, *ortho to* COCl). Anal. Calcd for C$_{26}$H$_{18}$O$_2$SiCl$_2$ (461.12): C, 67.68; H, 3.93. Found: C, 67.92; H, 3.98

A portion of DR19 was dissolved in NMP. An equimolar amount of DCPS solution saturated in NMP was added to the above solution dropwisely using a syringe while stirring at -10°C. After stirring the mixture at -10°C for 30 min, pyridine was added dropwisely. The mixture was stirred under further cooling in a dryice-acetone bath for about 6 h and then at room temperature for another 72 h. Finally the solution was poured into methanol. Polymer PEA was obtained with a yield of 71 %. Anal. Calcd for C$_{32}$H$_{30}$O$_6$SiN$_4$ (570.08): C, 70; H, 4.7, N, 7.7. Found: C, 67.9; H, 4.6, N, 7.9.

Polymer PAS was also prepared from DCPS and DANS-diamine in the similar way except that the reaction was carried out at room temperature. In this case the polymerization yield was about 81%. Anal. Calcd for C$_{44}$H$_{40}$O$_4$SiN$_4$(716.48): C, 72.6; H, 4.8,N,7.6. Found: C, 71.3; H, 4.4, N, 7.2

These polymers were readily soluble in common solvents such as DMF, THF, chloroform, etc. In particular, using chloroform, they can be processed into films of good optical quality by spin casting. The polymerization pathways for PEA and PAS are shown in Scheme 1.

Instrumentation

The structures of the synthesized compounds including the polymers were confirmed by ^{1}H-NMR and IR spectra. The ^{1}H-NMR spectra were obtained with 300-MHz and 500-MHz
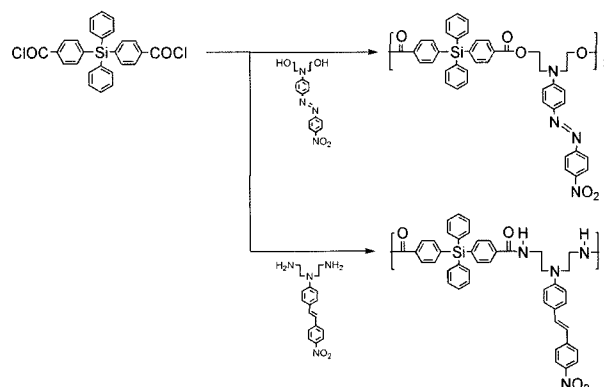
Scheme 1. Synthesis of PEA and PAS

^{1}H-NMR (Varian Gemini) spectrometers and the IR-spectra were recorded using an FT-IR spectrophotometer (Nicolet 205). The thermal properties of the polymers were measured by thermogravimetry (TGA 2050, TA Instruments) and Differential Scanning Calorimetry (DSC 2010, TA Instruments) at a heating rate of 10°C/min under nitrogen atmospheres. UV-Vis spectra were recorded using a diode array spectrophotometer (Hewlett Packard, 8452A). The film thickness was determined using a stylus profiler (α-Step 200, Tencor Instruments) and the refractive index of the sample was measured by the optical transmission technique [21]. The measurement of second harmonic generation (SHG) was performed by Maker fringe interference method.[22] The Q-switched Nd:YAG laser with pulse duration of 25 ns at a repetition rate of 10 Hz was used as fundamental beam. The surface morphology of the spin-coated polymer film was studied using an atomic force microscope (Park Science Instrument Autoprobe CP).

Film casting and poling

Prior to film casting the polymer solution was filtered through a 0.45-μm Nylon membrane filter (Osmonics, DDR04T17LP) to remove dust particles. Film was prepared by spin-casting on glass substrate at room temperature at a spin rate of 1500 rpm. Films were dried for 2 days under reduced pressure at 60°C to remove any residual solvent that might be present in the film. In order to orient the dipoles of the NLO chromophores, the films were poled in a corona-discharge set-up. PEA film was poled at 6.0 kV, 130°C for 1 h and PAS film was poled at 3.0 kV, 170 for °C for 1 h. Poling was performed at a temperature 10°C above T$_g$ of each polymer. The samples were heated at 10°C/min from room temperature to the poling temperature, maintained at that temperature for an hour, then cooled to room temperature with the applied high DC field which was removed after the sample reached room temperature.

RESULTS AND DISCUSSION

The structures of PEA and PAS were confirmed by means

Table 1. Solubility of PEA and PAS in various organic solvents (0.1% (wt./vol.))

Solvent	PEA	PAS
NMP	++	++
DMP	++	++
DMAC	++	++
m-Cresol	++	++
Cyclohexanone	++	++
THF	++	++
Toluene	—	+–
Chloroform	++	—
Acetone	—	—
MeOH	—	—
EtOH	—	—

++: soluble, +–; slightly soluble, —; insoluble

Figure 2. TGA thermograms of PEA and PAS.

of NMR and FT-IR spectra as well as elemental analyses. PEA showed a sharp absorption peak at 1710 cm^{-1} corresponding to C=O stretching vibration of the carbonyl group in the ester linkages. PAS showed a sharp absorption peak at 1651 cm^{-1} corresponding to C=O stretching vibration of the carbonyl group in the amide linkages. In the NMR spectrum of PAS, the peak at 3.5 ppm is assigned to the alkyl group in the chromophore and the peak at 7.4 ppm is ascribed to the aromatic hydrogens in the diphenylsilane unit. The signal at 2.49 ppm orginanates from DMSO-d$_6$ used as solvent and the peak at around 3.30 ppm come from moisture present in the solvent.

The results of solubility test of the polymers in various organic solvents are summarized in Table 1. Both polymers are readily soluble in most organic solvents, except in acetone, methanol, and ethanol.

In chloroform, PEA was readily soluble while PAS was insoluble. In toluene, PEA was insoluble while PAS was slightly soluble. It is believed that the silicon moieties in the main chain enhanced the solubility of PEA and PAS in common organic solvents such as THF, NMP, DMF, etc.[14-16]

In the DSC thermograms (Figure 1), the T$_g$ of PEA and

PAS appeared at 120 and 160°C, respectively. The T$_g$ of PAS which has amide linkages in the backbone appeared approximately 40°C higher than the T$_g$ of PEA which has ester linkages in the backbone due to the hydrogen bond between the amide groups. The TGA thermograms of both PEA and PAS (Figure 2) indicate two weight-loss processes. PEA shows an initial decomposition (T$_{id}$) at 250°C which is attributed to the thermal breakdown of the diazo side groups. The second weight loss of PEA which begins approximately from 450°C is believed to be due to mainchain breakdown. PAS shows an initial decomposition at 270°C which is attributed to the thermal breakdown of the stilbene side groups. The second weight loss of PAS, which is also believed to be due to mainchain breakdown, appeared approximately at 450°C.

PEA shows an additional broad absorption with a maximum at 460 nm which is attributed to the DR-19 moieties. The UV-Vis spectra, before and after poling, of PEA and PAS are shown in Figure 3 and Figure 4, respectively. The alignment order parameter of the chromophore was deduced from the spectrum using the following equation:

$$\Phi = 1 - A_1/A_0$$

Figure 1. DSC thermograms of PEA (2nd heating cycle) and PAS (2nd heating cycle).
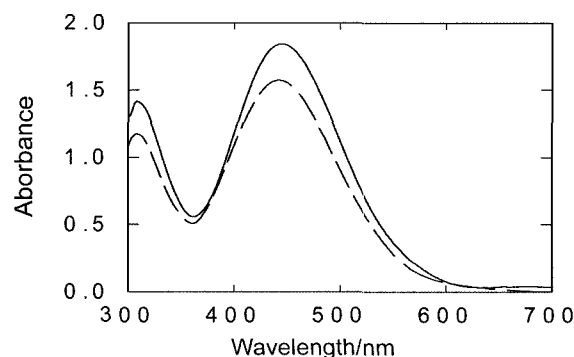
Figure 3. UV-Vis absorption spectra of PAS film coated on ITO substrate before (solid line) and after poling (dashed line). Poled at 3.0 kV and 170°C for 1 h.
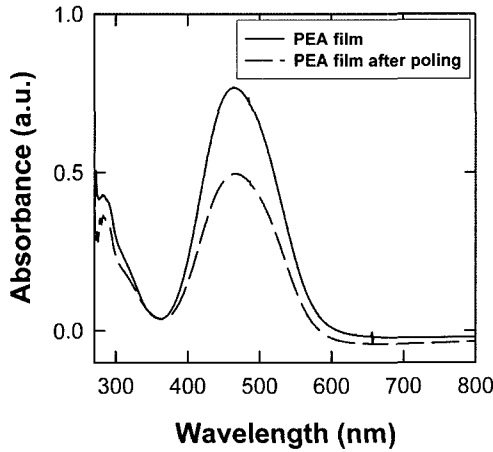
Figure 4. UV-Vis absorption spectra of PEA film coated on ITO substrate before (solid line) and after poling (dashed line). Poled at 6.0 kV and 130°C for 1 h.

Where A_0 and A_1 are the absorbance at the maximum of the polymer film before and after poling, respectively. The estimated order parameters were 0.35 and 0.16 for PEA and PAS, respectively.

The AFM images of PAS and PEA films after poling are shown in Figure 5. When poled at 3.0 kV, the surface of the
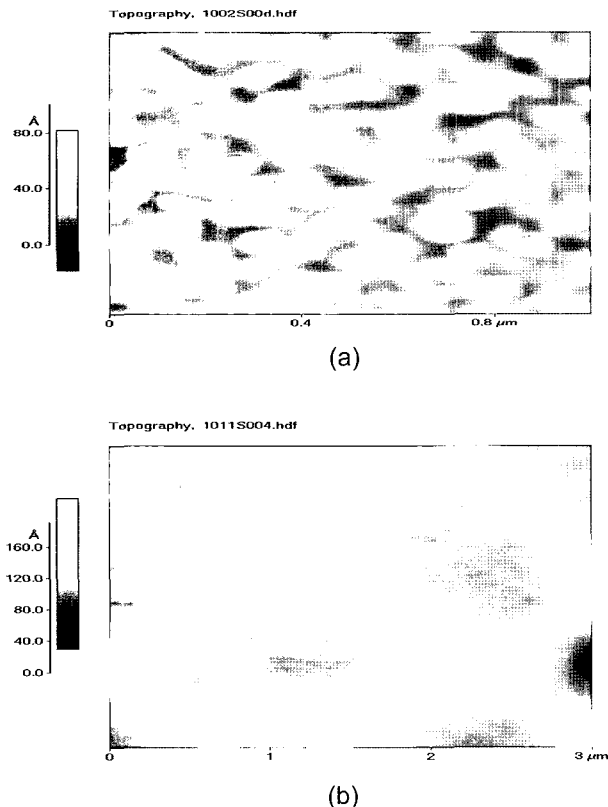
polymer film shows smoother morphology than the film poled at 6.0 kV. The Maker-Fringe patterns of PEA and PAS films are shown in Figure 6 and Figure 7, respectively, with the refractive indices and the thickness. In order to determine the macroscopic second-order susceptibility, $\chi^{(2)}$, of the polymer samples, angular dependence of the SHG signal was recorded and compared with the values obtained from a 1-mm thick Y-cut quartz plate. In the calculation of the effective second harmonic coefficient, d_{33}, correction for the absorption at 532 nm was made [21]. The refractive index of PEA film measured by optical transmission technique [23] was $n_1 = 1.67 + i0.0224$ at 1064 nm and $n_2 = 1.79 + i0.244$ at 532 nm. The thickness of this PEA film measured by alpha step was 120 nm. The refractive index of PAS film measured by optical transmission technique was $n_1 = 1.79 + i0.0056$ at 1064 nm. The thickness of this PAS film measured by alpha step was 95.5 nm. The second harmonic coefficient (d_{33}) observed in the films of PAS and PEA at 1064 nm which were 36 and 84 pm/V, respectively. These values are comparable to those reported in the literatures for nonlinear optical polymers with DANS or DR19 moieties in the side chain [22, 24, 25].

In order to study the temporal stability of the alignment of the chromophores, Maker fringe patterns of PEA and PAS
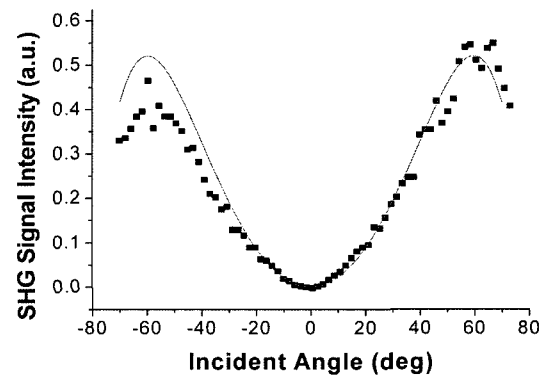

(a)

(b)

Figure 5. AFM images of corona-poled film of (a) PAS (poled at 170°C and 3.0 kV for 1 h) and (b) PEA (poled at 130°C and 3.0 kV for 1 h).

Figure 6. Angular dependence of SHG signal in PEA film poled at 6.0 kV for 1 h. $n1 = 1.67 + i0.0224$ (1064 nm), $n2 = 1.79 + i0.244$ (532 nm), $d_{33} = 86$ pm/V.
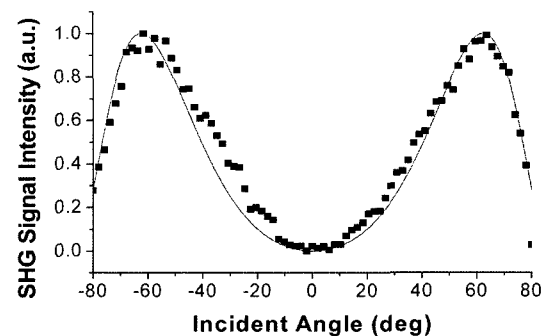

Figure 7. Angular dependence of SHG signal in PAS film poled at 3.0 kV for 1 h. $n1 = 1.79 + i0.0056$ (at 1064 nm), $d_{33} = 36$ pm/V.
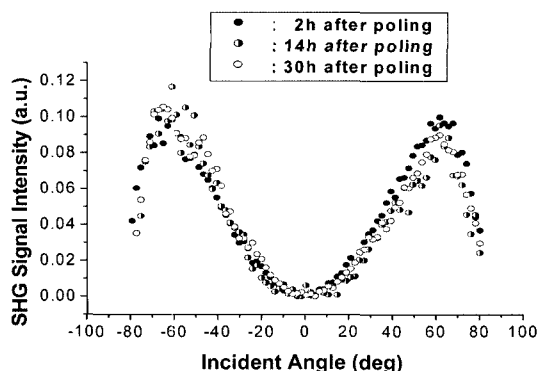
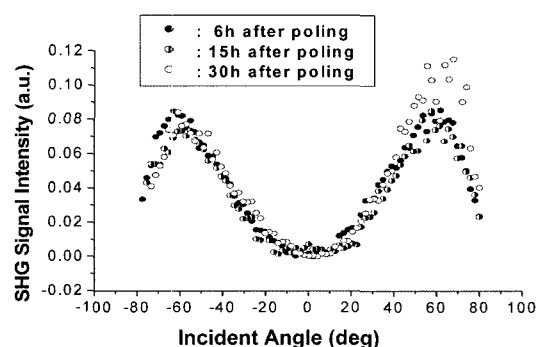Figure 8. Relaxation of SHG in PEA at room temperature.

Figure 9. Relaxation of SHG in PAS at room temperature.

were measured at various time intervals after poling as shown in Figure 8 and Figure 9, respectively. No significant decrease in the intensity of second harmonic signal was observed at least up to 30 h at room temperature in both polymers.

CONCLUSIONS

We have synthesized an azobenzene-containing NLO polymer (PEA) and a stilbene-containing NLO polymer (PAS). The second harmonic coefficient (d_{33}) of the poled polymer films was 84 and 36 pm/V for of PEA and PAS, respectively. The poled state of these polymers was stable at least up to 30 h at room temperature. T_g of these polymers appeared in the range from 120 to 160°C and onset of initial weight losses in the range from 260 to 270°C.

Enhancements of thermal stability as well as the solubility in common solvents were achieved by incorporation of silicon moieties in the main chain of these nonlinear optical polymers.

REFERENCES

1. Libscomb, G. F., Lytel, R. (1992) Nonlinear Opt. 3, 41.
2. G. F. Libscomb, G. F., Lytel, R., Ticknor, A. J. (1995) Nonlinear Opt. 10, 421.
3. Pradad, P.N., Williams, D. J. (1991) Introduction to Nonlinear Optical Effects in Molecules and Polymers. New York: John Wiley & Sons;
4. Nalwa, H. S. (1997) Handbook of Organic Conductive Molecules and Polymers. In: Nalwa, H. S. ed. John Wiley and Sons.
5. Lee, K. S.; Samoc, M.; Prasad, P. N. (1992) In Comprehensive Polymer Science, S. L. Aggarwal, Russo, S. Eds., Pergamon Press, Oxford.
6. Seymour, R. B. (1988) Polymer Chemistry. New York: Marcel Dekker:
7. Lin, S. B., Hwang, K. S., Tsay, S. Y., Cooper, S. L. (1995) Colloid Polym. Sci. 263, 128.
8. Dalton, L. R., William, H. S. (2001) Chem Mater. 13, 3043
9. Dalton, L. R., Harper, A. W., Wu, B., Ghon, R., Laquirdanum, J., Liang, Z., Hubbel, A., Xu, C. (1995) Adv. Mater. 7, 519.
10. Bonart, R. J. (1968) Macromol. Sci. Phys. B2, 115.
11. Günter, P., Bosshard, Ch., Bosch, M., Liakatas, I., Jager, M. (2000) In Nonlinear Optical Effects and Materials. In: Günter, P., ed., Springer-Verlag, Berlin;
12. Lin, S. B., Hwang, K. S., Tsay, S. Y., Cooper, S. L. (1995) Colloid Polym. Sci. 263, 128.
13. (a) Thames, S. F., Melone. J. (1993) Polym. Sci., Polym. Chem. Ed. 31, 521. (b) So, B. K. (2001) Dissertation for Ph.D. degree, Hannam University, Korea.
14. Cottrell, T. L. (1958) The Strength of Chemical Bonds, 2nd Ed. London: Butterworths;
15. Veneneyev, V. I., Gurvick, L. V., Kondratyev, V. N., Medvedev, V. A., Frankevich, Y. L. (1958) Bond Energies. Ionization Potentials and Electron Affinities. London: Edward Arnold;
16 Pauling, L. (1960) The Nature of Chemcal Bond, Cornell Univ. Press. 3rd Ed. New York: Ithaca;189.
17. (a) Jung, S.-H., Kim, H.-K. J. (2000) Luminescence. 51, 87. (b) Suh, S. C., Shim, S. C., Kim, A. R., Yoo, D. J. (2004) J. Photosci.. 11, 101.
18. Jung, S.-H., Kim, H.-K., Kim, S.-H., Kim, Y.-H., Jeoung, S. -C,. Kim, D. (2000) Macromolecules, 33, 9277.
19. Hamciuc, E., Bruma, M., Köpnick, T., kaminorz, Y., Schulz, B. (2001) Polymer, 42, 1809.
20. Kim, H.K., Ryu, M.K., Shin, S.H., Lee, S.M., Kang,S.J., (1998) J. Polym. Eng,.18, 31.

Table 2. Physical properties of the NLO polymers

Polymer	Monomer	Yield (%)	T_g (°C)	T_{id} (°C)	λ_{max} (nm)	d_{33} (pm/V)
PEA	DCPS, DR19	72	120	260	460	84
PAS	DCPS, DANS-Diamine	81	160	270	456	36

21. Warren, N., Herman, L., Michal, H. (1995) *J. Opt. Soc. Am. B*, **12**, 416.

22. Yu, D., Peng, Z., Gharavi, A., Yu, L. (1995) *Polymers for Second-Order Nonlinear Optics*. In: Lindsay, G., Singer, K. Eds. American Chemical Society. Washington, DC; 172.

23. Cisneros, J. I. (1998) *Appl. Opt.*, **37**, 5262.

24. Liang, Z. Y., Yang, Z. X., Sun, S. J., Wu, B., Dalton, L.R., Garner, S. M., Kalluri, S., Chen, A. T., Steier, W. H. (1996) *Chem. Mater.*, **8**, 2681.

25. Yu, D., Gharavi, A., Yu, L. P. (1996) *Macromolecules*, **29**, 6139.