Second-order nonlinear optical hyperbranched polymers via facile ring-opening addition reaction of azetidine-2,4-dione

Huey-Ling Chang [a,*], Tsung-Yi Chao [b], Chih-Chiang Yang [b],
Shenghong A. Dai [b], Ru-Jong Jeng [b,*]

[a] Department of Chemical and Materials Engineering, National Chinyi University of Technology, Taichung 411, Taiwan
[b] Department of Chemical Engineering, National Chung Hsing University, Taichung 402, Taiwan

Abstract

A new hyperbranched polymeric structure was chosen as a nonlinear optical material. First, a difunctional chromophore, 4-(4′-nitrophenyl-diazenyl) phenyl-1,3-diamine (NDPD) was synthesized, which was then reacted with 4-isocyanato-4′(3,3-dimethyl-2,4-dioxo-azetidino)diphenylmethane (MIA) to form NDPDMIA (A_2 type monomer). The azetidin-2,4-dione functional groups exhibit selective reactivity, which can react only with primary amines under mild conditions. The hyperbranched polymers were synthesized via ring-opening addition reaction between azetidine-2,4-dione (A_2 type monomer) and primary amine (B_3 type monomer). This synthetic scheme comes with easy purification, high yield and rapid synthesis. Chemical structures of the hyperbranched polymers were characterized by FT-IR, ^{1}H NMR, and elemental analysis. The inherent viscosity of hyperbranched polymers in DMSO ranged from 0.15 to 0.22 dLg^{-1}. All of the obtained polymers were soluble in DMF, DMAc, and DMSO. Using *in situ* contact poling, r_{33} coefficients of 6–16 pm/V and their temporal stability at 60 °C were obtained. Optical loss measurement was also achieved by a prism coupling setup.
© 2007 Elsevier Ltd. All rights reserved.

Keywords: Hyperbranched polymer; Nonlinear optics; Azetidine-2,4-dione; Malonamide

1. Introduction

Organic nonlinear optical (NLO) materials have been extensively investigated due to their high bandwidth, large optical nonlinearity and low cost as compared to inorganics [1,2]. Recently, the development of polymers with new chemical structures for NLO materials have become an active field [3–5].

Most of the NLO polymer researches have focused on several types of linear NLO polymers [6–13]. However, the linear NLO polymers usually confront the aggregation-quenching problem. Over the past several years, the concept of using shape modifications on NLO chromophores to improve poling efficiently has been demonstrated to obtain maximum realizable electro-optical (EO) activity [14–16]. Moreover, the NLO chromophores in spherically shaped molecules would not stack in a side-by-side fashion [17,18]. Therefore, the highly branched dendritic macromolecules have drawn

* Corresponding authors. Tel.: +886 4 22852581; fax: +886 4 22854734 (R.-J. Jeng).
E-mail address: rjjeng@nchu.edu.tw (R.-J. Jeng).

considerable interests because of their unique physical and chemical properties, such as low solution viscosity, high solubility, and a large number of terminal functional groups. Dendrimers possess spherical shape, and indeed, dendritic structures containing NLO chromophores have been demonstrated to display large EO coefficients due to their site isolation effects [19]. However, the dendrimers usually require highly complicated and repetitive synthetic routes. By contrast, hyperbranched polymers are easy to synthesize and their three-dimensional spatial separation of the chromophores also endows the polymers with favorable site-isolation effects [20,21].

The hyperbranched polymers are generally prepared by a facile one-pot self-polymerization of AB_x monomers [22–25]. Apart from that, A_2 (difunctional monomer) + B_3 (trifunctional monomer) systems are also adopted to the synthesis of hyperbranched polymers [26,27]. This exhibits the advantage of more available monomers. The first preparation of hyperbranched polymers via the 'A_2 + B_3' approach was reported by Kakimoto [28] and Frechet [29], although the method had been explored to prepare crosslinked polymeric materials more than a century before [30]. The solubility of the low viscosity hyperbranched polymers is superior to that of the corresponding linear ones [31].

In this work, we report the synthesis and characterization of new hyperbranched polymers containing 4-(4′-nitrophenyl-diazenyl) phenyl-1,3-diamine as an NLO chromophore. The difunctional chromophore 4-(4′-nitrophenyl-diazenyl) phenyl-1,3-diamine (NDPD) has been synthesized first, which is then reacted with 4-isocyanato-4′(3,3-dimethyl-2,4-dioxo-azetidino) diphenyl-methane (MIA) to form NDPDMIA (A_2 type monomer). The rationale behind selecting this building block lies in the different reactivity of the isocyanate and azetidine-2,4-dione groups toward amines. The isocyanate group of MIA is the more reactive functional groups which can react readily with compounds possessing amino group, hydroxyl group, or functional groups with active hydrogens. On the other hand, the azetidine-2,4-dione is more selective and could only react with primary amines to form malonamide linkages under mild conditions [32–34]. The A_2 type monomer exhibit high selective reactivity, whose azetidine-2,4-diones can react with aliphatic primary amines rapidly at mild temperatures. Therefore, hyperbranched polymers can be synthesized via ring-opening addition reaction based on NDPDMIA

(A_2 type monomer) and tris(3-aminoethyl)-amine (B_3 type monomer). Moreover, the azetidine-2,4-diones of A_2 monomer are capable of performing ring-opening addition reaction toward aromatic primary amines of tris(3-aminophenyl)phenyl phosphine oxide (TAPPO) at higher temperatures by using 1,8-diazabicyclo(5.4.0.)-undec-7-ene as catalyst. Therefore, this work focused on the synthesis of NLO hyperbranched polymers based on A_2 + B_3 methodology through the ring-opening addition reaction. Thermal behavior of these hyperbranched NLO polymers was studied using differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA). The composition effect on temporal stabilities of the NLO properties was also studied.

2. Experimental

2.1. Measurements

All chemicals were purchased from Aldrich and were used as received. All reactions were carried out under nitrogen. Infrared spectra were recorded by using a Perkin Elmer Paragon 500 FT-IR Spectrophotometer. ^{1}H NMR spectra were taken on a Varian Gemini-200 FT-NMR spectrometer using $CDCl_3$ and DMSO-d_6. Elemental analysis (EA) was performed on a Heraeus CHN-OS Rapid Elemental Analyzer employing acetanilide as a standard. DSC and TGA were performed on a Seiko SII model SSC/5200. A heating rate of 10 °C/min under nitrogen atmosphere was used. Thermal degradation temperature (T_d) was taken at 5% weight loss. Glass transition temperature (T_g) was measured at the second heating. UV–vis spectra were recorded on a Perkin Elmer Lambda 2S spectrophotometer to measure the dye contents. Solution viscosity of the polymers was measured on an Ostwald–Fenske viscometer in dimethyl sulfoxide (DMSO) solution (0.5 g dL^{-1}) at 30 °C.

2.2. Synthesis of 4-isocyanato-4′(3,3-dimethyl-2,4-dioxo-azetidino) diphenylmethane (MIA) [32–39] (Scheme 1)

The solution of triethylamine (45 g, 0.45 mol) in xylene (100 ml) was added to a solution of methylenedi-p-phenyl diisocyanate (125 g, 0.5 mol) and isobutyryl chloride (38.6 g, 0.362 mol) in the same solvent (250 ml). Reaction mixture was refluxed for 7 h and then cooled to room temperature. The resulting solution was filtered to remove the salt,

and concentrated to about 50 ml. The product was then crystallized from cyclohexane, yielding the compound as white powder (33%) Scheme 1.

IR (KBr): υ (cm^{-1})= 2 260(N=C=O), 1 852(C= O), 1 731 cm^{-1}(C=O).

^{1}H NMR (CDCl$_3$, δ, ppm): 1.40 (s, 6H, –CH$_3$), 3.87 (s, 2H, Ar–CH$_2$–Ar), 6.90. – 7.69 (m, 8 aromatic protons).

Elemental analysis: calculated for C$_{25}$H$_{23}$N$_3$O$_3$: C, 71.24, H, 5.03, N, 8.74; Found: C, 71.32, H, 5.17, N, 8.96.

2.3. Synthesis of difunctional monomer containing chromophores (NDPDMIA)

The difunctional monomer (Scheme 2) was synthesized by the coupling of MIA and the above-mentioned chromophore, NDPD [40]. The NLO chromophore, NDPD (0.4 g, 1.55 mmol) and MIA (1.2 g, 3.75 mmol) were dissolved in N,N-dimethyl-formamide (DMF). The reaction mixture was stirred at room temperature for 14 h. Then the solution was poured into methanol. The precipitate was filtered and purified by column chromatography (silica gel, ethyl acetate/n-hexane = 2:1 as eluent).

^{1}H NMR (DMSO-d$_6$, δ, ppm): 1.39 (s, 6H, –CH$_3$), 3.90 (s, 4H, Ar–CH$_2$–Ar), 7.10 – 8.67 (m, 23H, Ar–H).

Elemental analysis: calculated for C$_{50}$H$_{43}$N$_9$O$_8$: C, 66.88, H, 4.83, N, 14.04; Found: C, 67.70, H, 4.96, N, 14.25.
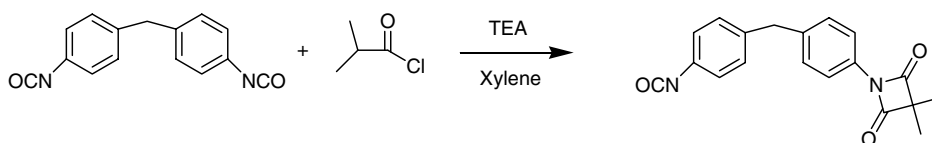
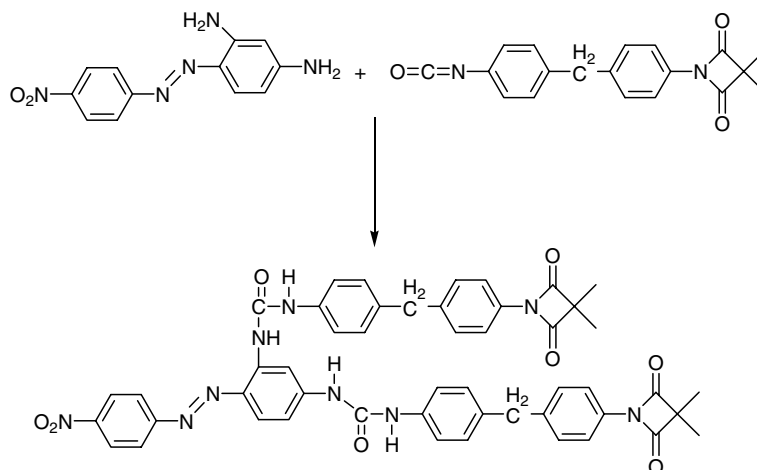## 2.4. Synthesis of NLO polymers

2.4.1. Linear polymers

The composition for the NLO linear and hyperbranched polymers are showed in Table 1. The linear polymers PL11 (Scheme 3) was synthesized via ring-opening addition reaction. For PL11, NDPD-MIA (2 g, 2.2 mmol) was dissolved in 23 ml of DMF. After complete dissolution, p-xylene diamine (0.3 g, 2.2 mmol) was added to the solution. The mixture was stirred and heated to 60 °C, and further remained under dry nitrogen atmosphere for 5 h. The product was then washed with acetone three times and dried in vacuum at 70 °C for 12 h.

2.4.2. Hyperbranched polymers

HB11, HB32 and HB21 were synthesized by reacting the difunctional compound (NDPDMIA) with tris (2-aminoethyl) amines at different molecular ratios (Scheme 4; Table 1). The difunctional

Scheme 1. Synthesis of 4-isocyanato-4′(3,3-dimethyl-2,4-dioxo-azetidino) diphenylmethane (MIA).

Scheme 2. Synthesis of a chromophore-containing difunctional monomer (NDPDMIA).

Table 1
Compositions of the linear and hyperbranched NLO polymers

| Sample	Composition (molar ratio)
PL11	NDPDMIA/p-xylene diamine (1:1)
HB11	NDPDMIA/tri(2-aminoethyl) amine (1:1)
HB21	NDPDMIA/tri(2-aminoethyl) amine (2:1)
HB32	NDPDMIA/tri(2-aminoethyl) amine (3:2)
PHB11	NDPDMIA/TAPPO (1:1)

compound (NDPDMIA) was dissolved in 23 ml of DMF. After complete dissolution, tri(2-aminoethyl) amine was added to the solution. These mixtures were heated to 60 °C and reacted under a dry nitrogen atmosphere for 4 h, except that the mixture of HB32 was reacted at room temperature. The products were then washed with methanol and water three times and then dried in vacuum at 70 °C for 12 h.

The tris(3-aminophenyl) phenyl phosphine oxide (TAPPO) was synthesized according to the literature [41]. PHB11 was synthesized by reacting the

difunctional compound (NDPDMIA) with TAPPO at equal molecular ratio. The difunctional compound (NDPDMIA, 2 g, 2.2 mmol) was dissolved in 23 ml of DMF. After complete dissolution, TAPPO (0.71 g, 2.2 mmol) was added to the solution and a drop of 1,8-diazabicyclo(5.4.0.)-undec-7-ene was added as catalyst. The mixture was heated to 110 °C and reacted under a dry nitrogen atmosphere for 20 h. The product was washed with methanol and water three times and then dried in vacuum at 70 °C for 12 h.

2.5. Thin film preparation

These polymers were respectively dissolved in DMF. The polymer solution was stirred at room temperature for 3 h, and filtered through a 0.5 μm syringe filter. Thin films were prepared by spin-coating the filtered polymer solution onto indium tin oxide (ITO) glass substrates. Prior to poling
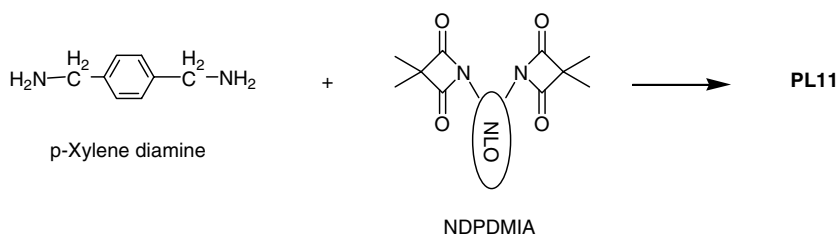
Scheme 3. Synthesis of linear NLO polymer (PL11).
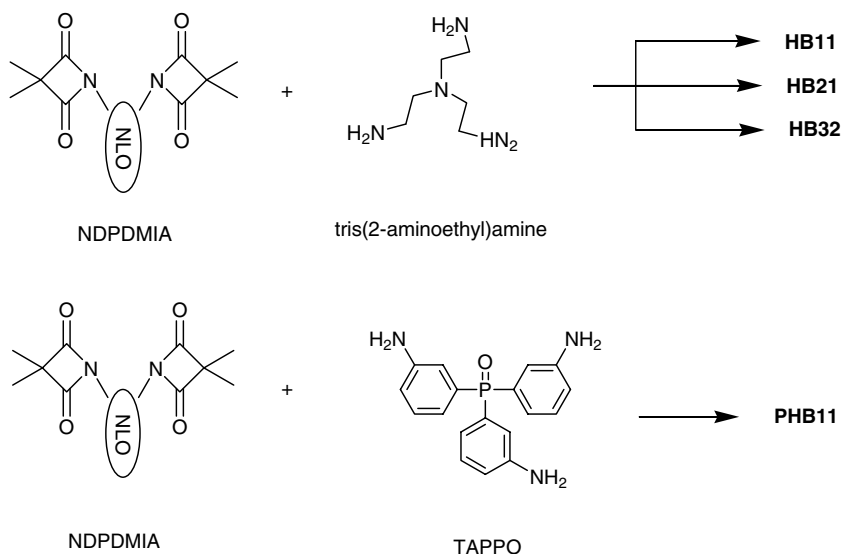
Scheme 4. Synthesis of hyperbranched NLO polymers.

process, these thin films were dried in vacuum at room temperature for 24 h.

2.6. Poling process, EO coefficient (r_{33}) and optical loss measurements

The poling process for the second-order NLO polymer films was carried out using *in situ* contact poling technique. The poling voltage was maintained for 100 V and the temperature was kept at approximately 10 °C lower than the T_g of the sample for a certain period of time. Upon saturation of the r_{33} signal intensity, the sample was then cooled down to room temperature in the presence of the poling field at which point the poling field was terminated. The thickness, indices of refraction, and optical loss were measured by a Model 2010 Prim Coupler (Metricon[@]) at 830 nm [42,43]. EO coefficients of the poled samples were measured at 830 nm using the simple reflection technique [44].

3. Results and discussion

The reaction mechanism of MIA is described as the following. The intermediate product ketene was formed by the dehydrochlorination of isobutyryl chloride, and then a cycloaddition adduct 2,4-dioxo-acetidino group was obtained from the reactions of isocyanate and ketene. Via controlling the molar ratio of MDI and isobutyryl chloride to 1:0.7, the monosubstituted derivative, MIA could be obtained [32].

This hyperbranched polymers were synthesized based on azetidine-2,4-diones via ring-opening reaction. In comparison with the preparation of dendrimers via convergent or divergent route, the one-pot synthesis of hyperbranched polymers was drastically simplified.

FT-IR was utilized to monitor the reaction process (Fig. 1). The hyperbranched polymer, PHB11 was obtained via the reaction between NDPDMIA (A_2 type monomer) and TAPPO (B_3 type monomer). TAPPO is an aromatic amine capable of performing ring-opening addition reaction toward azetidine-2, 4-diones at higher temperatures by using 1,8-diaza-bicyclo(5.4.0.)-undec-7-ene as catalyst. As shown in Fig. 1a, the –C=O absorption peaks of azetidine-2,4-dione were identified at 1740 and 1855 cm^{-1}. These absorption peaks disappeared after reaction for 20 h (Fig. 1b). This indicates that the ring-opening addition reaction was completed and the absorption peaks of azetidine-2,4-dione were displaced by
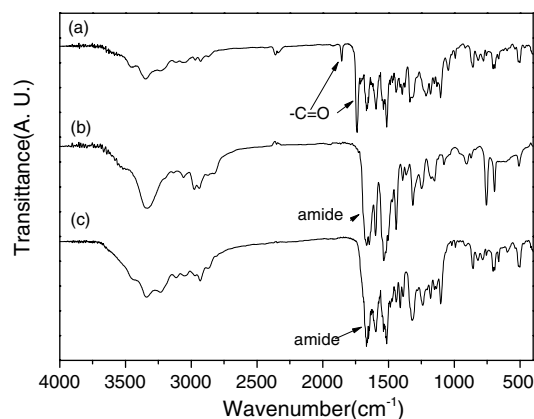

Fig. 1. FT-IR monitoring of NDPDMIA reaction process. (a) pristine, (b) PHB11, reaction for 20 h and (c) HB11, reaction for 10 min.

the emergence of a new absorption peak at 1660 cm^{-1} corresponding to the carbonyl group of malonamide. It is important to note that the ring-opening addition reaction of azetidine-2,4-diones of A_2 monomer toward aliphatic amines are easier to occur as compared to that toward aromatic amines [45]. This is because of higher basicity of aliphatic amines. Therefore, the ring-opening addition reaction could be achieved at lower temperatures for a shorter period of time as shown in Fig. 1c. The absorption band characterized for the carbonyl group of malonamide (1650 cm^{-1}) was observed, meanwhile the absorption peaks at 1740 and 1855 cm^{-1} were disappeared. This indicates that the ring-opening addition reaction is completed. Similar FT-IR spectra were also observed for the rest of samples.

Solubility properties in organic solvents are summarized in Table 2. These polymers are soluble in aprotic polar solvents such as dimethylacetamide (DMAc), DMSO, and DMF. The polymers in the other solvents are partially soluble in THF, acetone and ethanol. The polymers PL11, HB11, and HB21 containing aliphatic amine exhibit the better solubility in organic solvents. According to the solubility properties, the molecular weights of these polymers were determined by GPC using DMF as eluent (Table 3). The molecular weights of polymers containing aromatic amine are lower, given the fact that the electron-withdrawing phenyl group decreases the basicity of the amine. As a result, the ring-opening addition reaction of azetidine-2,4-dione groups toward the aromatic primary amines becomes less reactive [39]. The molecular weights are not avail-

Table 2
Solubility properties of the polymers

Polymer	Solvent[a]						
	Acetone	Ethanol	THF	H_2O	DMAc	DMSO	DMF
PL11	±	±	±	–	+	+	+
HB11	±	±	±	–	+	+	+
HB32	–	–	–	–	±	±	±
HB21	±	±	±	–	+	+	+
PHB11	–	–	–	–	+	+	+

+: soluble; ±: partially soluble; –: insoluble.
[a] Abbreviation: THF: tetrahydrofuran, DMAc: dimethylacetamide, DMSO: dimethyl sulfoxide, DMF: N,N-dimethyl formadmide.

Table 3
Thermal properties and molecular weights of the polymers

Sample	T_g (°C)	T_d^{a} (°C)	M_w^{b}	M_n^{b}	PDI (M_w/M_n)[c]
PL11	124	277	53911	20636	2.61
HB11	82	203	21289	11589	1.84
HB21	92	264	21105	9145	2.31
HB32	127	257	–[d]	–[d]	–[d]
PHB11	106	252	11441	6600	1.73

[a] Td was read at the temperature corresponding to 5wt.% loss.
[b] Determined by GPC in DMF with linear polystyrene standards.
[c] PDI = polydispersity.
[d] Not available due to its partially crosslinking.

able for the HB32 sample because it is partially crosslinked. The HB32 sample was prepared from NDPDMIA (A_2 type monomer) reacted with tris(3-aminoethyl)-amine (B_3 type monomer) with a feed ratio of A_2–B_3 of 3/2. Although the A_2 + B_3 approach to hyperbranched polymers holds some merits over the conventional AB_2 polycondensation approach, such as facile preparation and commercial availability of monomers. However, this approach still exhibits the major problem of uncontrollable gelation [45].

The intrinsic viscosities of polymers were obtained by dissolution of the samples in DMSO at 30 °C. The inherent viscosities were in the range between 0.15 and 0.28 dL/g. The inherent viscosities of HB11 and PL11 are much higher than those of HB21 and PHB11. According to previous literature on the relationship between viscosity and molecular weight for hyperbranched polymers reported by Turner et al. [46], the molecular weight for hyperbranched polyesters with $\eta_{inh} = 0.27$ dL/g is ranged from 10,000 to 100,000. Although a direct comparison of our products with those is not strictly valid, a comparison of their physical properties is reasonable.

Thermal properties of the hyperbranched polymer were measured with DSC and TGA (Table 3). Typical DSC thermograms of polymers are shown in Fig. 2. The T_g of hyperbranched polymer, HB32 is the highest one (127 °C) among all the polymers. This is possibly due to the partial crosslinking of HB32. Moreover, the T_g of HB21 polymer is higher than that of HB11. This is because a higher content of azetidine-2,4-dione groups is present in HB21, and the number of phenyl groups is proportional to the azetidine-2,4-dione content. Furthermore, the T_g of PHB11 sample is higher than that of HB11 due to the presence of aromatic amines and phosphorous effect. Typical TGA thermograms of the hyperbranched polymers are shown in Fig. 3. It seems that these hyperbranched polymer show fairly good thermal stability.

Optical properties of these NLO materials are shown in Table 4. Thicknesses of the polymer films are ranged from 0.93 to 1.74 μm, whereas refraction indices are ranged from 1.68 to 1.69 (830 nm). Optical loss is in the range between 5.2 and 7.6 dB/cm (830 nm). It is important to note that the phosphorus containing PHB11 sample exhibits lower optical loss than other samples do. The phosphorus-containing
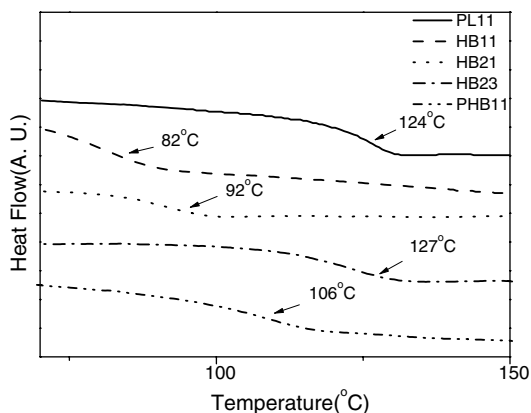
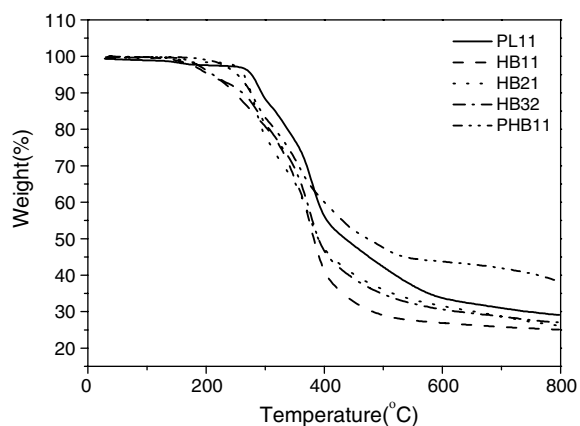Fig. 2. DSC thermograms of the hyperbranched polymers.

Fig. 3. TGA thermograms of the hyperbranched polymers.

functionalities which result in reducing the number density of C–H, O–H and N–H bonds in the intrinsic structures play a key role in lowering the optical loss [13]. EO coefficients resulted from the *in situ* poling process are in the range between 5.9 and 15.7 pm/V (830 nm). The r_{33} of the hyperbranched polymer HB21 is higher than those of the linear polymer PL11 and hyperbranched polymer HB32. This is due to the fact that the partial crosslinking of HB32 results in poor molecular alignment during

the *in situ* poling process. More importantly, under a similar poling condition, the poled films of HB21 and PHB11 exhibited r_{33} values of 14.7 and 15.7 pm/V, which are two times larger than that of PL11, indicating a significant improvement of poling efficiency. The hyperbranched structure of HB21 and PHB11 possibly contributes to such improvement. Dendritic structure is very close to the spherical shape capable of achieving the theoretically predicted optimum poling efficiency by the site isolation effect [19,47]. Hence, the hyperbranched structures containing NLO chromophores have been demonstrated to display relatively large EO coefficients as compared to the linear NLO-active polymer in this work.

Fig. 4 shows the temporal stability of EO coefficient for the poled samples at 60 °C. A fast decay of the EO coefficients was observed at the beginning of thermal treatment. This phenomenon maybe resulted from recovery of bond angle and bond length of the oriented chromophores [48]. The best temporal stability was obtained for the hyperbranched HB32 sample. After being subjected to thermal treatment at 60 °C for 100 h, a reduction of less than 30% in EO coefficient ($r_{33}(t)/r_{33}(t_0)$)
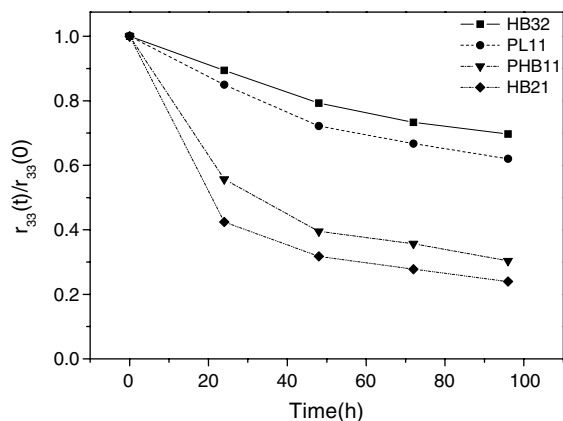

Fig. 4. Temporal stability of EO coefficients for the poled/cured samples at 60 °C.

Table 4
Optical properties and EO cofficients of the NLO polymers

Samples	Dye content (%)	Phosphorus content (%)	Thickness film (μm)	Refraction indices at 830 nm	r_{33} (pm/V) at 830 nm	Optical loss (dB/cm) at 830 nm
PL11	21.7	–	1.62	1.69	6.5	7.6
HB21	23.1	–	1.74	1.68	14.7	6.5
HB32	22.5	–	1.74	1.69	5.9	6.4
PHB11	18.5	2.51	0.93	1.69	15.7	5.2

was observed for both the HB32 and PL11 samples due to the presence of high T_g. On the other hand, a reduction of more than 50% in EO coefficient was observed for HB21 and PHB11 samples. This indicates that the T_g is the sole deciding factor responsible for the temporal stability in this work.

4. Conclusion

A new and rapid synthesis of hyperbranched NLO polymers has been developed. The hyperbranched NLO polymers were synthesized via ring-opening addition reaction based an azetidine-2,4-dione-containing chromophore (A_2 type monomer) and amine-containing compounds (B_3 type monomer). All of the obtained polymers were soluble in DMF, DMAc and DMSO. Using *in situ* contact poling, r_{33} coefficients of 6–16 pm/V and temporal stability at 60 °C were obtained. Optical waveguide measurement was also achieved by a prism coupling setup (830 nm). As compared to the linear NLO-active polymer in this work, these hyperbranched NLO-active polymers have been demonstrated to display relatively large EO coefficients due to their site isolation effects.

Acknowledgements

References

[1] Qin A, Yang Z, Bai F, Ye C. Design and synthesis of a thermally stable second-order nonlinear optical chromophore and its poled polymers. J Polym Sci Part A Polym Chem 2003;41:2846–53.

[2] Haller M, Luo JD, Li HX, Kim TD, Liao Y, Robinson B, et al. A novel lattice-hardening process to achieve highly efficient and thermally stable nonlinear optical polymers. Macromolecules 2004;37(3):688–90.

[3] Li Z, Li Z, Di C, Zhu Z, Li Q, Zeng Q, et al. Structural control of the side-chain chromophores to achieve highly efficient nonlinear optical polyurethanes. Macromolecules 2006;39(20):6951–61.

[4] Ma H, Chen B, Sassa T, Dalton LR, Jen AK-Y. Highly efficient and thermally stable nonlinear optical dendrimer for electrooptics. J Am Chem Soc 2001;123(5):986–7.

[5] Busson P, Örtegren J, Ihre H, Gedde UW, Hult A, Andersson G, et al. Preparation of mesogen-functionalized dendrimers for second-order nonlinear optics. Macromolecules 2002;35(5):1663–71.

[6] Chang CC, Chen CP, Chou CC, Kuo WJ, Jeng RJ. Polymers for electro-optical modulation. J Macro Sci Polym Reviews 2005;45:125–70.

[7] Gong W, Li Q, Li Z, Lu C, Zhu J, Li S, et al. Synthesis and characterization of indole-containing chromophores for second-order nonlinear optics. J Phys Chem B 2006;110(21):10241–7.

[8] Jeng RJ, Chang CC, Chen CP, Chen CT, Su WC. Thermally stable crosslinked NLO materials based on maleimides. Polymer 2003;44:143–55.

[9] Chang HL, Lin HL, Wang YC, Dai SA, Su WC, Jeng RJ. Thermally stable NLO poly(amide–imide)s via sequential self-repetitive reaction. Polymer 2007;48:2046–55.

[10] Jeng RJ, Hung WY, Chen CP, Hsiue GH. Organic/Inorganic NLO materials based on reactive polyimides and a bulky alkoxysilane dye via Sol/Gel process. Polym Adv Technol 2003;14:66–75.

[11] Kuo WJ, Chang MC, Juang TY, Chen CP, Chen CT, Chang HL, et al. Stable second-order NLO semi-IPN system based on bipyridine-containing polyimide and alkoxysilane dye. Polym Adv Technol 2005;16:515–23.

[12] Hsiue GH, Kuo WJ, Lin CH, Jeng RJ. Preparation and characterization of all organic NLO sol–gel materials based on amino azobenzene dyes. Macromol Chem Phys 2000; 201(17):2336–47.

[13] Chen CP, Huang GS, Jeng RJ, Chou CC, Su WC, Chang HL. Low loss second-order non-linear optical crosslinked polymers based on a phosphorus-containing maleimide. Polym Adv Technol 2004;15:587–92.

[14] Luo J, Haller M, Ma H, Liu S, Kim TD, Tian Y, et al. Nanoscale architectural control and macromolecular engineering of nonlinear optical dendrimers and polymers for electro-optics. J Phys Chem B 2004;108(25):8523–30.

[15] Luo J, Ma H, Jen AK-Y. Nanostructured functional dendrimers and polymers for photonics. C R Chimie 2003;6:895–902.

[16] Li Z, Qin A, Lam JWY, Dong Y, Dong Y, Ye C, et al. Facile synthesis, large optical nonlinearity, and excellent thermal stability of hyperbranched poly(aryleneethynylene)s containing azobenzene chromophores. Macromolecules 2006;39(4):1436–42.

[17] Robinson BH, Dalton LR. Monte Carlo statistical mechanical simulations of the competition of intermolecular electrostatic and poling-field interactions in defining macroscopic electro-optic activity for organic chromophore/polymer materials. J Phys Chem A 2000;104(20): 4785–95.

[18] Dalton LR, Steier WH, Robinson BH, Zhang C, Ren A, Garner S, et al. J Mater Chem 1999;9:19–24.

[19] Ma H, Liu S, Luo J, Suresh S, Liu L, Kang SH, et al. Highly efficient and thermally stable electro-optical dendrimers for photonics. Adv Funct Mater 2002;12(9):565–74.

[20] Hecht S, Fréchet JMJ. Dendritic Encapsulation of Function. Angew Chem Int Ed 2001;40:74–91.

[21] Zhu Z, Li Z, Tan Y, Li Z, Li Q, Zeng Q, et al. New hyperbranched polymers containing second-order nonlinear optical chromophores: Synthesis and nonlinear optical characterization. Polymer 2006;47:7881–8.

[22] Huang F, Gibson HW. Formation of a supramolecular hyperbranched polymer from self-organization of an AB₂

monomer containing a Crown Ether and Two Paraquat Moieties. J Am Chem Soc 2004;126(45):14738–9.

[23] Baek JB, Harris FW. Fluorine- and hydroxyl-terminated hyperbranched poly(phenylquinoxalines) (PPQs) from copolymerization of self-polymerizable AB and AB_2, BA, and BA_2 Monomers. Macromolecules 2005;38(4):1131–40.

[24] Che P, He Y, Wang X. Hyperbranched Azo-Polymers synthesized by Azo-coupling reaction of an AB_2 monomer and postpolymerization modification. Macromolecules 2005;38(21):8657–63.

[25] Baek JB, Harris FW. Hyperbranched polyphenylquinoxalines from self-polymerizable AB_2 and A_2B monomers. Macromolecules 2005;38(2):297–306.

[26] Chen H, Yin J. Synthesis and characterization of negative-type photosensitive hyperbranched polyimides with excellent organosolubility from an $A_2 + B_3$ monomer system. J Polym Sci Part A Polym Chem 2004;42:1735–44.

[27] Liu YL, Tsai SH, Wu CS, Jeng RJ. Preparation and Characterization of hyperbranched polyaspartimides from Bismaleimides and Triamines. J Polym Sci Part A Polym Chem 2004;42:5921–8.

[28] Jikei M, Chon SH, Kakimoto M, Kawauchi S, Imase T, Watanabe J. Synthesis of hyperbranched aromatic polyamide from Aromatic Diamines and Trimesic Acid. Macromolecules 1999;32(6):2061–4.

[29] Emrick T, Chang HT, Frechet JMJ. An $A_2 + B_3$ approach to hyperbranched aliphatic polyethers containing chain end epoxy substituents. Macromolecules 1999;32(19):6380–2.

[30] Odian G. Principles of Polymerization. 3rd ed. New York: Wiley; 1991. pp 125–32.

[31] Kudo H, Maruyama K, Shindo S, Nishikubo T, Nishimura I. Syntheses and properties of hyperbranched polybenzoxazole by thermal cyclodehydration of hyperbranched poly[o-(t-butoxycarbonyl)amide] via $A_2 + B_3$ approach. J Polym Sci Part A Polym Chem 2006;44:3640–9.

[32] Chen CP, Dai SA, Chang HL, Su WC, Jeng RJ. Facile approach to polyurea/malonamide dendrons via a selective ring-opening addition reaction of azetidine-2,4-dione. J Polym Sci Part A Polym Chem 2005;43:682–8.

[33] Chen CP, Dai SA, Chang HL, Su WC, Wu TM, Jeng RJ. Polyurethane elastomers through multi-hydrogen-bonded association of dendritic structures. Polymer 2005;46:11849–57.

[34] Dai SA, Chen CP, Lin CC, Chang CC, Wu TM, Su WC, et al. Novel side-chain dendritic polyurethanes based on hydrogen bonding rich polyurea/malonamide dendrons. Macromol Mater Eng 2006;291:395–404.

[35] Okaniwa M, Takeuchi K, Aai M, Ueda M. One-pot synthesis of dendritic poly(amide-urea)s via curtius rear-rangement. 2. synthesis and characterization of dendritic poly(amide-urea)s. Macromolecules 2002;35(16):6232–8.

[36] Dai SA. Isocyanato-azetidine-diones. Eur Pat Appl 1985: EP0161591.

[37] Tsai CC, Juang TY, Dai SA, Wu TM, Su WC, Liu YL, et al. Synthesis and montmorillonite-intercalated behavior of dendritic surfactants. J Mater Chem 2006;16:2056–63.

[38] Juang TY, Tsai CC, Wu TM, Dai SA, Chen CP, Lin JJ, et al. Organo-clay hybrids based on dendritic molecules: preparation and characterization. Nanotechnology 2007;18: 205606–13.

[39] Dai SA, Juang TY, Chen CP, Chang HY, Kuo WJ, Su WC, et al. Synthesis of N-aryl azetidine-2,4-diones and polymalonamides prepared from selective ring-opening reactions. J Appl Polym Sci 2007;103:3591–9.

[40] Zhou Y, Leng W, Liu X, Xu Q, Feng J. Synthesis of nonlinear optical polyimides containing azodiamine derivative chromophores and their electrooptic and thermal properties. J Polym Sci Part A Polym Chem 2002;40: 2478–86.

[41] Wang TS, Yeh JF, Shau MD. Syntheses, structure, reactivity, and thermal properties of epoxy-imide resin cured by phosphorylated triamine. J Appl Polym Sci 1996;59:215–25.

[42] Shi W, Fang CS, Sui Y, Yin J, Pan QW, Gu QT, et al. Thermal stability and transmission losses of the poled polyimide side-chain thin films. Opt Commun 2000;183: 299–306.

[43] Shi W, Fang CS, Sui Y, Yin J, Pan QW, Gu QT, et al. Poling optimization and optical loss measurement of the polyetherketone polymer films. Solid State Commun 2000; 16:67–71.

[44] Teng CC, Man HT. Simple reflection technique for measuring the electro-optic coefficient of poled polymers. Appl Phys Lett 1990;56(18):1734–7.

[45] Gao C, Yan D. Hyperbranched polymers: from synthesis to applications. Prog Polym Sci 2004;29:183–275.

[46] Turners SR, Walter F, Voit BI, Mourey TH. Hyperbranched aromatic polyesters with carboxylic acid terminal groups. Macromolecules 1994;27(6):1611–6.

[47] Bai YW, Song NH, Gao JP, Sun X, Wang XM, Yu GM, et al. A new approach to highly electrooptically active materials using cross-linkable, hyperbranched chromophore-containing oligomers as a macromolecular dopant. J Am Chem Soc 2005;127(7):2060–1.

[48] Clays K, Coe BJ. Design strategies versus limiting theory for engineering large second-order nonlinear optical polarizabilities in charged organic molecules. Chem Mater 2003;15(3): 642–8.