### Polymer 54 (2013) 3850-3859

Contents lists available at SciVerse ScienceDirect

## Polymer

journal homepage: www.elsevier.com/locate/polymer

### Nonlinear optical hyperbranched polyaspartimide/montmorillonite nanocomposites based on reactive fluorine- or phosphorous-containing organoclays

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### ARTICLE INFO

Article history: Received 1 March 2013 Received in revised form 11 May 2013 Accepted 15 May 2013 Available online 23 May 2013

*Keywords:* Polyaspartimide Organoclay Nonlinear optics

### ABSTRACT

A series of novel hyperbranched polyaspartimide/organoclay nanocomposites were developed for second-order nonlinear optics. The hyperbranched polyaspartimides were synthesized from an azobenzene chromophore bis(4-aminophenyl(4-(4-nitrophenyl)-diazenyl)phenyl)amine (DAC; A<sub>2</sub> type monomer) and a 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-containing trimaleimide (Dopo-trimaleimide; B<sub>3</sub> type monomer) via Michael addition reaction. Moreover, reactive fluorine- and phosphorous-containing organoclays (F-montmorillonite, i.e. F-MMT and P-montmorillonite, i.e. P-MMT) which had been prepared by modifying the high aspect ratio silicate layers of MMTs with two different swelling agents 1,1,1-tris[4-(4-amino-2-trifluoromethylphenoxy)-phenyl]ethane (F-triamine) and (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-yl)tris(4-aminophenyl)methane (P-triamine) were respectively incorporated into the nonlinear optical hyperbranched polyaspartimides. The organoclays were exfoliated and dispersed in the hyperbranched polyaspartimide [EO) coefficients and temporal stability of the hyperbranched polyaspartimides. The hyperbranched polyaspartimide/F-MMT nanocomposite exhibited temporal stability ( $r_{33}(t)/r_{33}(0) = 73\%$ ) at 100 °C, EO coefficient  $r_{33}$  of 20.9 pm/V, and optical loss of 3.0 dB/cm at 1310 nm.

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### 1. Introduction

Hyperbranched polymers with three-dimensional (3D) dendritic architectures have attracted great attention because of their unique properties including low viscosity, good solubility, and multiple functionality, and greater availability relative to the dendrimers [1,2]. Hyperbranched polymers prepared by one-pot polymerization of AB<sub>n</sub> monomers, difunctional monomer (A<sub>2</sub>) and trifunctional monomer (B<sub>3</sub>), or other systems are suitable for largescale production. These hyperbranched polymers have been intensively explored in many areas, including intercalating agent for layered materials [3], drug delivery [4], organic light-emitting devices [5], organic solar cells [6], supramolecular assembly [7], and nanoscale catalysis [8].

Recently, the research field of hyperbranched polymers has also been extended to second-order nonlinear optical (NLO) polymer field due to their 3D dendritic architectures [9–11]. In general, high chromophore contents and the dipole-dipole strong intermolecular electrostatic interactions would bring about the decreased poling efficiency of the NLO polymers. The 3D spatial separation of the NLO chromophores endows the hyperbranched polymers with favorable site-isolation effect [12], which could minimize the strong intermolecular electrostatic interactions among the NLO chromophores with high dipole moment, and thus enhance the optical nonlinearities. Moreover, these hyperbranched polymers with globular shape conformation can be used to improve the solubility and processability, and facilitate the alignment of NLO chromophores during the electric-field poling process [13]. Apart from that, their void-rich topological structure could minimize the optical losses in the NLO polymeric systems [14]. Earlier in 1997, Zhang et al. first prepared a hyperbranched polymer with a second





polymer

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harmonic coefficient, d<sub>33</sub> of 2.8 pm/V, which might be due to the poor poling efficiency of the NLO chromophores under electric field [15]. The rigid NLO chromophores played the role of branching unit, which resulted in the poor poling efficiency of the NLO polymers. A series of guest-host polymers based on the blend of a crosslinkable hyperbranched NLO oligomer and poly(ether sulfone) were reported by Wang et al. [16]. A large d<sub>33</sub> value (65 pm/V) and good temporal stability at 85 °C were obtained for these poled and crosslinked polymer blends. Tang et al. developed an azofunctionalized hyperbranched poly(aryleneethynylene) exhibiting large d<sub>33</sub> values (177 pm/V at 1064 nm) and excellent thermal stability (no decay in d<sub>33</sub> when heated to 152 °C) [17]. In addition, Chao et al. reported a series of  $A_2 + B_3$  hyperbranched NLO polymers through the ring-opening addition reactions of azetidine-2,4dione that showed better NLO properties than their corresponding linear analogs [18]. Shi and co-workers synthesized a rather rigid  $A_2 + B_3$  hyperbranched polytriazole using click chemistry. The effective relaxation temperature  $(T_{ert})$  of this polytriazole was ca. 165 °C [19]. Moreover, Li et al. reported two new azobenzene dyecontaining hyperbranched polytriazoles derived from AB<sub>2</sub> monomers via click chemistry [20]. The T<sub>ert</sub>s of the polytriazoles via dynamic temperature scanning were lower than 120 °C. Later on, the  $T_{\rm ert}$  was improved up to as high as 153 °C for a hyperbranched polyaryleneethynylene prepared through an A<sub>2</sub> + B<sub>3</sub> approach via Sonogashira coupling reaction [21]. Apart from that, several efforts have been made to develop the NLO hyperbranched polymers with large NLO coefficients [22-25]. It was found that the presence of 3D dendritic structure was favorable for the enhancement of EO coefficients of the hyperbranched polymers. However, there is still room for improvement for the long-term NLO stability of the hyperbranched polymeric systems at elevated temperatures.

In order to enhance the temporal stability of NLO polymers, Odobel and co-workers designed and synthesized two hyperbranched polymers end-capped with azobenzene chromophores through post-functionalization [26]. The synthetic strategy provided a new way to covalently attach the NLO chromophores to the polymers, which could feasibly tune the thermal and NLO properties of the materials through chemical structure modifications. A crosslinkable hyperbranched polyimide which combines the benefits of a high  $T_g$ , good solubility, and high poling efficiency was obtained for a post-poling crosslinking strategy [27]. Another approach is to introduce an inorganic component such as the SiO<sub>2</sub> nanoparticles [28–31], montmorillonites (MMTs) [32–34], or phosphine oxides into the organic NLO materials, yielding organic/ inorganic hybrid materials [35]. Previously, we reported a series of polyimide/MMT [32,33] and poly(amide-imide)/MMT [34] nanocomposites comprising NLO moieties, which showed much better long-term stability at elevated temperatures than those of the pristine polymers. In addition, the NLO-active arylphosphine oxides were incorporated into the polymer matrices to obtain an NLOactive guest-host system with low optical losses [35]. Polymers comprising arylphosphine oxides with excellent thermal stability would prevent the decomposition of materials during the poling process at elevated temperatures.

In this study, a series of novel hyperbranched polyaspartimides were prepared through the Michael addition reaction between amine- and maleimide-containing compounds, which exhibited more favorable properties in the aspect of processing than did the condensation-type polyimides. The NLO hyperbranched polyaspartimides were synthesized in one-pot polymerization between a difunctional azobenzene dye, bis(4-aminophenyl(4-(4-nitro phenyl)-diazenyl)-phenyl)amine (DAC; A<sub>2</sub> type monomer) and a trifunctional 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-ox ide-containing trimaleimide (DOPO-trimaleimide; B<sub>3</sub> type monomer) via  $A_2+B_3$  approach, using *p*-toluenesulfonic acid (*p*-TSA) as catalyst. The thermal stabilities of the hyperbranched polyaspartimides would be further enhanced via the incorporation of the DOPO moieties [36]. The DOPO-trimaleimide was synthesized from the reaction between maleic anhydride and DOPO-containing triamine (P-triamine) and subsequent imidization. Moreover, the Ptriamine with multi-functional groups was chosen as the intercalating agent for MMTs. A reactive organoclay P-MMT was prepared by the intercalation of P-triamine into MMTs. In addition, another reactive organoclay F-MMT was also prepared by the intercalation of a fluorine-containing triamine, 1,1,1-tris[4-(4amino-2-trifluoromethylphenoxy)-phenyl]ethane (F-triamine) in to MMTs [32]. Furthermore, the hyperbranched polyaspartimide/ organoclay based nanocomposites were prepared through the incorporation of F-MMT or P-MMT into the polymeric matrices. One of the amino groups from the intercalating agent would form



Scheme 1. Synthesis of the F-triamine, P-triamine, and DOPO-trimaleimide.

an ionic bond with negatively charged silicates, whereas the rest of the two amino groups in the swelling agent are available for further reaction with the maleimide end groups of the hyperbranched polymer. As a result, the layers of organoclays would be exfoliated and dispersed in the polymeric matrices. Better temporal stability was obtained for these NLO-active hyperbranched polyaspa rtimide/organoclay based nanocomposites.

### 2. Experimental

### 2.1. Materials

All chemicals were purchased and used as received unless otherwise stated. All reactions were carried out under nitrogen. *N*,

*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), acetone, chloroform, methanol (MeOH), etc. were available from Tedia Chemical Co. All reagents and solvents are reagent grade. DMAc was purified through distillation under reduced pressure over CaH<sub>2</sub> and then stored over 4 Å molecular sieves. Montmorillonite, Na<sup>+</sup>-MMT was supplied by Nanocor Co., is a sodium type with a cationic exchange capacity (CEC) of 1.20 mequiv g<sup>-1</sup> and a surface area of 750 m<sup>2</sup> g<sup>-1</sup>. Synthesis of the F-triamine, P-triamine, DOPO-trimaleimide, NLO-active hyperbranched polyaspartimides, and polymer/organoclay nanocomposites are presented in Schemes 1 and 2. NLO chromophore DAC and F-triamine were synthesized according to our previous studies [32,37]. Details of the synthetic procedures are shown as follows:



Scheme 2. Synthesis of the NLO-active hyperbranched polymers and corresponding nanocomposites.

### 2.2. Monomer synthesis

### 2.2.1. Synthesis of P-triamine

Triethylamine (15.15 g, 0.15 mol) was added to a solution of pararosaniline chloride (16.20 g, 0.05 mol) in ethanol (100 mL). The solution was stirred at room temperature under a N<sub>2</sub> atmosphere for 2 h. Subsequently, DOPO (10.9 g, 0.15 mol) was added. The mixture was heated under reflux for 12 h and then cooled to room temperature. The resulting solution was then poured slowly into a mixture of water and MeOH (1:1). The precipitate was filtered off and dried under vacuum at 60 °C to yield the purple product P-triamine (78.5%). IR (KBr): 1193 cm<sup>-1</sup> (P=O), 3448 and 3332 cm<sup>-1</sup> ( $-NH_2$ ). <sup>1</sup>H NMR (400 MHz, *d*-DMSO):  $\delta$  (ppm) = 8.01-8.11 (dd, 1H, P-Ar-H), 7.88-7.90 (d, 1H, Ph-Ar-H), 7.66-7.71 (t, 1H, Ar-H), 7.29–7.36 (m, 2H, Ar-H), 7.22–7.26 (t, 1H, Ar-H), 7.08–7.13 (t, 1H, Ar-H), 6.96 (br, 6H, Ar-H), 6.90–6.93 (d, 1H, O-Ar-H), 6.35– 6.38 (d, 6H, H<sub>2</sub>N-Ar-H), 5.01 (s, 6H, NH<sub>2</sub>). Anal. Calcd. for C<sub>31</sub>H<sub>26</sub>N<sub>3</sub>O<sub>2</sub>P (502.97): C, 73.96%; H, 5.17%; N, 8.35%; O, 6.36%. Found: C, 74.12%; H, 5.23%; N, 8.27%; O, 6.45%. T<sub>d</sub> (TGA in  $N_2$ ) = 345 °C.  $T_m$  (DSC) = 324 °C.

### 2.2.2. Synthesis of DOPO-trimaleimide

P-triamine (1.51 g, 0.3 mmol) was first dissolved in 20 mL DMAc in a 100 cm<sup>3</sup> flask. After the compound was completely dissolved, maleic anhydride (1.77 g, 1.8 mmol) was added. The solution was stirred at room temperature for 18 h, and then acetic anhydride (2.86 g, 2.8 mmol) and sodium acetate (0.41 g, 0.5 mmol) were added to the solution at 70 °C. The solution was stirred for another 1.5 h. The product was purified by re-precipitations into methanol, and dried under vacuum. The precipitate was filtered off and dried under vacuum at 60 °C to yield the yellowish white product (92.5%). IR (KBr): 1213 cm<sup>-1</sup> (P=0), 1716 and 1772 cm<sup>-1</sup> (-C=0 of maleimide), 3094 cm<sup>-1</sup> (-C=C-H of maleimide). <sup>1</sup>H NMR (400 MHz, *d*-DMSO):  $\delta$  (ppm) = 8.03-8.05 (dd, 1H, P-Ar-H), 7.72-7.79 (m, 2H, Ph-Ar-H), 7.40-7.52 (m, 3H, Ar-H), 7.34-7.37 (t, 1H, Ar-H), 7.17-7.22 (d, 6H, Ar-H), 7.13-7.17 (d, 6H, maleimide; CH=CH), 6.90-6.98 (d, 1H, Ar-H). Anal. Calcd. for C<sub>43</sub>H<sub>26</sub>N<sub>3</sub>O<sub>8</sub>P (742.97): C, 69.45%; H, 3.50%; N, 5.65%; O, 17.23%. Found: C, 70.28%; H, 3.42%; N, 5.78%; O, 16.95%.  $^{13}\text{C}$  NMR (DMSO-d<sub>6</sub>,  $\delta$ ) : 62.6 (d,  $J\,=\,92.3\,$  Hz), 118.9, 120.7, 121.2 (d,  $J\,=\,110.6\,$  Hz), 123.6, 124.4, 125.6, 126.3, 128.0 (d, J = 12.2 Hz), 130.0 (d, J = 4.8 Hz), 130.2, 130.9, 131.9 (d, J = 9.2 Hz), 133.9, 134.7, 138.8, 141.9, 150.7 (d, J = 10.9 Hz), 169.7 (d, J = 9.2 Hz). T<sub>d</sub> (TGA in  $N_2) = 448.5 \ ^{\circ}C.$ 

### 2.3. Synthesis of hyperbranched polyaspartimides

Hyperbranched polymers HB11, HB23 and HB12 comprising different contents of DAC were synthesized by reacting the difunctional azobenzene dye DAC with DOPO-trimaleimide at different molecular ratios. The trimaleimide was dissolved in 20 mL of DMF. After complete dissolution, the difunctional compound DAC was added to the solution. The concentrations of all of the reactants were kept well below 0.1 M to avoid the gelation of reaction mixture. These mixtures were heated to 120 °C and reacted under dry nitrogen atmosphere for 78 h, using *p*-TSA (10 wt%) as catalyst. The product was obtained by reprecipitations in methanol, and purified and dried in vacuum at 60 °C for 12 h <sup>1</sup>H NMR analysis of HB12 is shown as follows: <sup>1</sup>H NMR (400 MHz, *d*-DMSO):  $\delta$  (ppm) = 8.38–8.40 (d, NO<sub>2</sub>-Ar-H), 7.72-7.86 (m, -N=N-Ar-H), 7.68-7.70 (m, -Ar-H), 7.10-7.60 (m, -Ar-H), 6.80-7.02 (m, -N-Ar-H, -Ar-H), 6.58-6.65 (m, -N-Ar-H). Moreover, <sup>1</sup>H NMR spectra of HB11 and HB23 were similar to that of HB12.

### 2.4. MMT intercalated with F-triamine and P-triamine

An example of a preparative procedure for preparing layered silicates with wide d-spacings is shown as follows: Na<sup>+</sup>-MMT  $(1 \text{ g}, 1.20 \text{ mequiv } \text{g}^{-1})$  was placed in a 500 mL flask and dispersed vigorously into 100 mL of de-ionized water at room temperature. In a separate vessel, the precursor intercalating agent (F-triamine: 6.04 g. 1.20 mmol) was acidified with hydrochloric acid (37% in water, 0.18 g, 1.20 mmol, acidification ratio of  $H^+/NH_2 = 1/3$ ) in 100 mL of ethanol. The solution was poured into the flask containing the swelled Na<sup>+</sup>-MMT slurry. The mixture was stirred vigorously at 60 °C for 11 h and then allowed to cool to room temperature. The resulting agglomerated precipitate was collected and washed thoroughly with deionized water to remove any residual ions or free intercalating agents. MMT/F-triamine was dried in a vacuum oven at 70 °C. Organoclay MMT/P-triamine was prepared in a similar manner. The MMTs were intercalated by fluorine- or phosphorouscontaining triamine that are designated as F-MMT and P-MMT, respectively.

# 2.5. Synthesis of hyperbranched polyaspartimide/organoclay nanocomposites

Hyperbranched polymer/organoclay nanocomposites consisting of azobenzene dyes were prepared as the following manner: a suspension solution of MMT was obtained by stirring the modified MMT (F-MMT or P-MMT; 0.15 g or 0.23 g) in DMAc (0.5 mL) for 12 h. The suspension was then added to hyperbranched polymer (HB11; 1 g) in DMAc to form hyperbranched polymer/organoclay samples with different weight ratios (1, 3 and 5 wt% of organoclay P-MMT). These mixtures were heated to 120 °C and reacted under a dry nitrogen atmosphere for 78 h, using *p*-TSA (5 wt%) as catalyst. The product was obtained by re-precipitations of the mixture into methanol, and purified and dried in vacuum at 60 °C for 12 h. The HB11/F-MMT samples with 1, 3 and 5 wt% of F-MMT are designated as HBF1, HBF3 and HBF5, respectively. In addition, the HB11/P-MMT samples with 1, 3 and 5 wt% of P-MMT are designated as HBP1, HBP3 and HBP5, respectively.

### 2.6. Instruments

IR measurements were performed on a Fourier transform infrared (FTIR) spectrometer (PerkinElmer Spectrum). <sup>1</sup>H NMR spectra were obtained with a Varian Gemini-400 using d-DMSO as solvent. Elemental analysis was performed on a Heraeus CHN-OS Rapid Analyzer. Gel permeation chromatography (GPC) was performed in *N*,*N*-dimethylformamide (DMF) as eluant with a Waters Apparatus equipped with Waters Styrogel columns with a refractive index (RI) detector and polystyrene calibration. UV-vis spectra were recorded on a Perkin Elmer Lambda 2S spectrophotometer to measure the dye contents. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a Seiko SII model SSC/5200 at a heating rate of 10 °C/min under nitrogen. Thermal degradation temperature  $(T_d)$ is taken at the position of 5% weight loss.  $T_{\rm g}$  and melting temperature  $(T_m)$  were measured at the second heating. The *d*-spacing of the intercalated MMT was analyzed by an X-ray powder diffractometer (XRD, Shimadzu SD-D1 using a Cu target at 35 kV, 30 mA). The *d*-spacing of the intercalated MMT was analyzed by using Bragg's equation  $(n\lambda = 2 \ d \sin\theta)$ . The value for n = 1 was calculated from the observed values for n = 2, 3, 4, etc. Transmission electronic microscopy (TEM) was performed on a Zeiss EM 902A and operated at 80 kV and samples of approximately 70 nm were microtomed at room temperature.

### 2.7. Thin film preparation and EO properties measurements

hyperbranched polyaspartimide/organoclay These nanocomposites were respectively dissolved in DMF (concentration  $\sim$  10 wt%). The polymer solution was stirred at room temperature for 3 h and filtered through a 0.45 µm syringe filter. Thin films were prepared by spin-coating the filtered polymer solution onto indium tin oxide (ITO) glass substrates. Prior to the poling process, these thin films were dried in vacuum at 60 °C for 24 h. The poling process for the second-order NLO polymer films was carried out using an *in situ* contact poling technique (poling voltage: 100 V; kept at approximately 10 °C lower than the  $T_g$  of the sample). EO coefficients (r<sub>33</sub>) of the poled samples were measured at 830 nm using the simple reflection technique [38]. For the optical loss measurement, a laser beam (830 nm) passed through a linear polarizer and a polarizing beam splitter. Subsequently, the TE polarized light was focused onto a prism coupler that was mounted on a rotation stage. The scattered light was imaged with an infrared-sensitive charge-injection-device camera system. A statistical linear fit of the data to the logarithm of the scattered light intensity versus the distance propagated down the waveguide yielded a slope as the optical loss.

### 3. Results and discussion

### 3.1. Synthesis and characterization of monomers

As shown in Scheme 2, a series of NLO hyperbranched polyaspartimides and polyaspartimide/F-MMT (or P-MMT) nanocomposites were synthesized via Michael addition reaction. In comparison with the preparation of dendrimers via a convergent or divergent route, the one-pot synthesis of hyperbranched polymers is drastically simplified. The difunctional NLO chromophore DAC was synthesized by the coupling of *p*-nitrosonitrobenzene and tris(4-aminophenyl)amine according to the methods described in the literature [37]. This chromophore possesses a  $T_{\rm m}$  at 240 °C and a high  $T_{\rm d}$  at 300 °C.

To serve as the intercalating agent, we synthesized the fluorineand phosphorus-containing triamine (F-triamine and P-triamine) according to Scheme 1. According to the literature [32], 1,1,1trishydroxy phenyl ethane (THPE) was reacted with 2-chloro-5nitrobenzotrifluoride in the presence of K<sub>2</sub>CO<sub>3</sub> and DMAc to yield the corresponding trinitro compound (F-trinito), which we then utilized Pd/C as catalyst to produce the fluorine-containing triamine (F-triamine; Scheme 1(a)). FTIR spectra of F-trinitro and Ftriamine are shown in Fig. 1(a) and (b), respectively. As for phosphorus-containing triamine, P-triamine was prepared by the reaction of DOPO and pararosaniline chloride in the presence of ethylene triamine (Scheme 1(b)) [36]. In Fig. 1(c), the spectrum of Ptriamine displayed strong characteristic absorption for phosphine oxide (1193 cm<sup>-1</sup>) and amino group (3432 and 3448 cm<sup>-1</sup>;  $-NH_2$ ) In this work, the P-triamine was further imidized with maleic anhydride to provide a B<sub>3</sub> monomer, i.e. DOPO-trimaleimide with an excellent yield (>90%). Fig. 1(d) shows the FTIR spectrum of DOPOtrimaleimide. The performance of the imidization was confirmed by the formation of imide groups with characteristic absorption bands at 1716 and 1772 cm<sup>-1</sup>. The disappearance of the -NH<sub>2</sub> absorption peak and the presence of the C=C-H absorption peak at 3094 cm<sup>-1</sup> also provided the evidence of imidization. In addition, Fig. 2 showed the <sup>1</sup>H NMR spectra of P-triamine and DOPOtrimaleimide. The amine absorption peak was observed at  $\delta$  = 5.01 ppm for P-triamine (Fig. 2(a)). The characteristic peak at  $\delta$  = 7.13 ppm, assigned to the proton absorption of C=C–H of the maleimide ring, was observed in the <sup>1</sup>H NMR spectrum of DOPOtrimaleimide (Fig. 2(b)). The amine absorption peak at



Fig. 1. FTIR spectra of (a) F-trinitro, (b) F-triamine, (c) P-triamine, and (d) DOPO-trimaleimide.

 $\delta$  = 5.01 ppm was absent for DOPO-trimaleimide. Furthermore, the chemical structures of these monomers are also confirmed by elemental analysis. <sup>13</sup>C NMR spectrum of the DOPO-trimaleimide is shown in Figure S1 (Supporting Information).

# 3.2. Synthesis and characterization of hyperbranched polyaspartimides and their corresponding polyaspartimide/MMT nanocomposites

In this study, compound DAC with diamine group was utilized as the chromophore that is capable of performing Michael addition reaction toward trimaleimide at high temperatures, using *p*-TSA as the catalyst. We prepared amine-terminated hyperbranched polyaspartimide by employing diamine-to-trimaleimide with feed molar ratios of 3:2, 1:1, and 2:1. In Scheme 2, these three hyperbranched polyaspartimides (HB11, HB32 and HB21) were obtained via the reaction of DAC (A<sub>2</sub> type monomer) and DOPO-trimaleimide (B<sub>3</sub> type monomer). Chemical structures of the hyperbranched polyaspartimides were investigated using FTIR spectroscopy (Fig. 3). The absorption of primary amine was located at 3250-3500 cm<sup>-1</sup> for DAC, while a broad band corresponding to the absorption of secondary amine was appeared at 3250-3700 cm<sup>-1</sup> for HB11, HB32 and HB21. Moreover, the absorption peaks of the imide (C=O; 1772, 1716 cm<sup>-1</sup>) and P=O (1193 cm<sup>-1</sup>) groups were also observed. Table 1 summarizes the average molecular weights of the hyperbranched polymers as analyzed by GPC. The weight average molecular weights  $(M_w)$  of the hyperbranched polymers were in the range 9510–10,706 g mol<sup>-1</sup>, with polydispersity (PDI) values in the range of 1.8–1.9. Basically, the functional groups ratio of 1:1 would lead to the highest  $M_w$  among the hyperbranched polymers, and possibly gelation. In order to avoid the gelation of the hyperbranched polymer, the concentration of the reactants was kept well below 0.1 M. Consequently, the difference of the  $M_{\rm w}$  values is insignificant for HB32, HB11, and HB21. We also used TGA to measure the *T*<sub>d</sub>s and char yields of these hyperbranched polymers (Table 2). The DOPO-trimaleimide exhibited excellent thermal stability at about 448.5 °C. This is because DOPO-trimaleimide would form a densely crosslinked network while the sample was heated to the temperatures higher than 220 °C in the TGA thermal chamber [28,39], indicating that the observed high  $T_d$  (448 °C) was actually derived from the densely crosslinked maleimide polymer.



**Fig. 2.** <sup>1</sup>H NMR spectra of (a) P-triamine and (b) DOPO-trimaleimide.



Fig. 3. FTIR spectra of DAC, HB11, HB21, and HB32.

Table 1

Compositions and average molecular weights of the NLO-active hyperbranched polymers.

Sample	Feed molar ratio (DAC/DOPO-trimaleimide)	$M_{ m w}$	M <sub>n</sub>	PDI
HB11	1/1	9510	5056	1.9
HB32	3/2	9397	5130	1.8
HB21	2/1	10,706	5702	1.9

The molecular weight distribution was determined by gel permeation chromatography with polystyrene standards in DMF.

On the other hand, with the introduction of DAC, the  $T_{ds}$  of the resultant hyperbranched polymers were observed at the range of 272–308 °C with the char yields greater than 40% at 700 °C (Figure S2, Supporting Information). As shown in Figure S3 (Supporting Information), similar  $T_{g}$  values were vaguely observed for HB11 (202.1 °C) and HB21 (194 °C), whereas the  $T_{g}$  of HB32 was not detectable from DSC. On the other hand, the UV–vis absorption spectra of hyperbranched polyaspartimides (HB11, HB32 and HB21) are shown in Figure S4 (Supporting Information). The maximal absorption wavelengths of the NLO polymers were observed at ca. 501 nm whereas the cut-off wavelengths of the polymers were located at ca. 780 nm.

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Thermal	properties	of	the	hyperbranched	polymers	and	corresponding
nanocom	posites.						

Sample	Intercalation agent	Contents of organoclay (wt%)	$T_{g}^{a}(^{\circ}C)$	$T_{d}^{b}(^{\circ}C)$
HB11	_	_	202.1	308.2
HB32	_	_	N.D.	308.5
HB21	_	_	194.0	272.3
HBF1	F-MMT	1	212.1	369.9
HBF3	F-MMT	3	230.7	372.6
HBF5	F-MMT	5	219.0	346.8
HBP1	P-MMT <sup>c</sup>	1	155.2, 205.7	349.4
HBP3	P-MMT <sup>c</sup>	3	176.3, 239.7	349.0
HBP5	P-MMT <sup>c</sup>	5	181.5, 228.5	367.5

 $^a\,$  Baseline shift in the second heating DSC traces, with a heating rate of 10  $^\circ\text{C}/\text{min}$  in N\_2.

 $^{\rm b}$  Temperatures at which 5% weight loss were recorded by TGA at a heating rate of 10 °C/min in N2.

<sup>c</sup> Two glass transitions were observed for the HB11/P-MMT samples.

As shown in Scheme 2, organoclays F-MMT and P-MMT were prepared by intercalating MMTs with the swelling agents F-triamine and P-triamine, respectively. By adjusting the acidification ratio of H<sup>+</sup>/NH<sub>2</sub> (1/3), reactive organoclays were formed using Ftriamine or P-triamine as the swelling agent for the silicate layers of MMTs. One of the functional groups of the swelling agents formed an ionic bond with the negatively charged silicates, whereas the remaining functional groups were available for further reaction with maleimide groups of hyperbranched polymer HB11. The organoclavs F-MMT and P-MMT were further respectively embedded into the hyperbranched polyaspartimide HB11 to form the NLO-active nanocomposites. The hyperbranched polyaspartimide HB11 was chosen for further study in preparing the nanocomposites because of its abundant presence of peripheral maleimide groups. By using the swelling agents with trifunctional groups, the organoclays could be easily exfoliated and dispersed in the hyperbranched polymers. Good thermal properties and optical transparency were observed for these hyperbranched polyaspartimide/organoclay nanocomposites. X-ray diffraction patterns of the pristine MMT, swelling-agent-modified MMTs (F-MMT and P-MMT), and hyperbranched polymer HB11/F-MMT (or P-MMT) nanocomposites (HBF1, HBF3, HBF5, HBP1, HBP3, and HBP5) are presented in Fig. 4. For the pristine MMT sample, a strong X-ray diffraction peak at  $2\theta = 6.8^{\circ}$  was caused by the diffraction of the (001) crystal surface of layered silicates, equaling a *d*-spacing of 12 Å. The *d*-spacing values of F-MMT and P-MMT were about 25 and 15 Å, respectively. For all of the HB11/F-MMT (or P-MMT) nanocomposites with different organoclay contents, no diffraction peak in the range  $2-10^{\circ}$  ( $2\theta$ ) was observed in the XRD patterns, implying the presence of disordered form or exfoliation morphology in the samples (Fig. 4). This indicates that the polymer chains could easily permeate into the spaces between the layered structures of modified MMTs. To confirm these results, we further used TEM to visualize the spatial distributions of these nanocomposites (Fig. 5). TEM images indicate that the morphologies of the organoclays changed from intercalation to exfoliation during the in situ polymerization process. The hyperbranched polymer chains would permeate into the galleries of MMTs. The inter-spacings were further expanded and subsequently the MMTs were eventually exfoliated to form individual nanoplatelets. The TEM images of the nanocomposites incorporated with F-MMT or P-MMT indicates that the silicate layers were dispersed in the polymer matrices, exhibiting exfoliated morphology. This is consistent with the XRD study mentioned earlier.

Thermal properties of the hyperbranched polyaspartimides (HB11, HB32, and HB21) and nanocomposites (HBF1-HBF5 and



Fig. 4. XRD patterns of (a) Na<sup>+</sup>-MMT, (b) F-MMT, (c)HBF1, (d) HBF3, (e) HBF5, (f) P-MMT, (g) HBP1, (h) HBP3, and (i) HBP5.

HBP1-HBP5) are shown in Table 2. Moreover, DSC and TGA thermograms of the polymers and corresponding nanocomposites are shown in Figs. 6 and 7, respectively. The  $T_g$  and  $T_d$  values of the hyperbranched polyaspartimides were observed in the range 190-205 °C and 272–308 °C, respectively. The Tg values of HB11/F-MMT samples first increased with increasing F-MMT content and then reached a maximum point at the inorganic ratio of 3 wt% as compared to the neat polymer sample. The highest value of  $T_{g}$ (230.7 °C) was observed for the HBF3. This is due to the restriction of the polymer chains by the exfoliated clay platelets. However, further increase of the clay loading (e.g. 5 wt%) was found to be incapable of further enhancing the  $T_g$  of the sample [40]. As shown in Fig. 6(a), the glass transitions were observed clearly at temperatures higher than 210 °C for the HB11/F-MMT samples. This implies that the F-MMT was dispersed uniformly in the polymer matrices of HB11. On the other hand, the  $T_{gs}$  were indistinct at temperatures from 150 to 250 °C for the HB11/P-MMT samples (Fig. 6(b)). Two broad transition bands were observed at about 150-190 and 200-250 °C, respectively. This implies that a rather broad range of distinct local compositions were present in the HB11/P-MMT nanocomposites [40-42]. In addition, Fig. 7 shows TGA thermograms of HB11 and its corresponding nanocomposites (HBF1-HBF5 and HBP1-HBP5). Two weight loss stages were observed in the TGA thermograms. The first degradation stage was observed at 350-450 °C, resulted from the decomposition of the side-chain NLO dyes and phosphorus-containing moieties [32,43]. In addition the second degradation stage was observed at temperatures higher than 500 °C, resulted from the decomposition of the imide linkages. The TGA traces of nanocomposites were found



Fig. 5. TEM micrographs of (a) HBF3, (b) HBF5, (c) HBP3, and (d) HBP5.

to shift toward higher temperature ranges than that of the pristine hyperbranched sample HB11. This is because of the presence of the barrier effect of the MMT layered structures, as well as the strong interaction between the organoclays and hyperbranched polymer. Moreover, higher values of char residues were observed for the HB11/F-MMT and HB11/P-MMT samples as compared to that of the pristine hyperbranched polyaspartimide HB11.

These hyperbranched polyaspartimides (HB11, HB32, and HB21) are soluble at room temperature in polar aprotic solvents such as DMF, DMAc and DMSO, and partially soluble in THF, acetone and chloroform. In addition, the organoclays can be easily swelled and dispersed in aprotic solvents by simple mixing. For all of the nanocomposites, the organoclays could be well-dispersed in DMF, DMAc, and DMSO.

### 3.3. Optical properties of the hyperbranched polyaspartimide/F-MMT (or P-MMT) nanocomposites

The optical losses of the hyperbranched polyaspartimides and nanocomposites were measured based on TE guide modes at 1310 nm, ranged from 2.7 to 4.9 dB/cm. It was reported that the hyperbranched polymers exhibited lower optical loss than the linear ones do due to the void-containing dendritic structure effect [14]. The optical losses of HB11, HB32, and HB21 are 2.7, 3.8, and 3.8 dB/cm, respectively. The HB11 possessed relatively low optical loss value than did HB32 and HB21, which might be due to the

lower dye content of HB11. In addition, the optical losses of HBF1, HBF3, and HBF5 were 2.8, 3.0, and 4.1 dB/cm, respectively, while 3.3, 3.3, and 4.9 dB/cm for HBP1, HBP3, and HBP5, accordingly. The optical loss value increased with increasing content of organoclay for the nanocomposites. Nevertheless, the thermal stability was improved as a result of the organoclay addition. Large optical losses are generally referred to the second harmonic (overtone) vibrational absorption of C-H bond in the near-infrared region, scattering losses from structure defects (voids), and absorption losses from charge-transfer interactions. The introduction of fluorine- or phosphorus-containing functionalities would reduce the number density of C-H, O-H and N-H bonds in the intrinsic structures, which plays a key role in lowering the optical losses of the materials [30,44]. In addition, the optical losses for HB11/P-MMT nanocomposites were larger than those of HB11/F-MMT nanocomposites. This is possibly because the organoclay P-MMT was not distributed uniformly in HB11. As shown in DSC thermograms (Fig. 7(b)), the thermal transitions were much broader when compared to those of the HB11/F-MMT samples [40-42]. The nonuniform distribution of the P-MMT in the polymer matrices of HB11 resulted in larger optical losses of the HB11/P-MMT nanocomposites.

The dye contents, EO coefficients ( $r_{33}$ ), and temporal stabilities of the poled polyaspartimide HB11 and nanocomposites HBF3 and HBP3 are summarized in Table 3. The dye contents were determined by UV–vis spectroscopic methods [32]. The maximum



**Fig. 6.** DSC thermograms of the hyperbranched polyaspartimide/organoclay (F-MMT or P-MMT) nanocomposites.



**Fig. 7.** TGA thermograms of the hyperbranched polyaspartimide/organoclay (F-MMT or P-MMT) nanocomposites.

Table 3

Sample	Dye content <sup>a</sup> (wt%)	EO coefficient, r <sub>33</sub> (pm/V) at 830 nm	Optical loss (dB/cm) at 1310 nm	Temporal stability (%), r <sub>33</sub> (t)/r <sub>33</sub> (0) <sup>b</sup>
HB11	38.0	15.3	2.7	28
HBF3	36.9	20.9	3.0	73
HBP3	36.7	12.8	3.3	44

<sup>a</sup> Dye content was determined by UV-vis.

<sup>b</sup> Determined at 100 °C for 100 h.

absorption wavelength ( $\lambda_{max}$ ) of polymer appeared at 500 nm due to the  $\pi - \pi^*$  transition of the NLO chromophore. To generate stable oriented dipoles and large EO coefficients, NLO-active polymers should be aligned and annealed under an electric field. For the hyperbranched polymer HB11 with dye content 38%, an EO coefficient of 15.3 pm/V was resulted from the *in situ* poling process (measured at 830 nm). Moreover, the r<sub>33</sub> value (20.9 pm/V) of the nanocomposite HBF3 was larger than that of the pristine polyaspartimide HB11 (15.3 pm/V). This indicates that the existence of exfoliated silicate platelets did not interfere with the alignment of NLO dyes under the electric field, yet effectively minimized the aggregation of NLO moieties. The chromophore-containing hyperbranched polymer with site-isolation effect tethered on the silicate platelets would arrange in a noncentrosymmetric state under electric field, which is favorable for the enhancement of EO coefficients [32,33]. This site-isolation effect might be more pronounced for the nanocomposite incorporated with the organoclay F-MMTs due to the low surface energy of fluorine containing substituents ( $-CF_3$ ). Therefore, the  $r_{33}$  value of the nanocomposites HBF3 (20.9 pm/V) was much larger than that of nanocomposite HBP3 (12.8 pm/V) despite their similar dye contents (36–38%). The r<sub>33</sub> value of HB11 was reduced by the incorporation of organoclay P-MMTs. This is attributed to the non-uniform distribution of the P-MMTs in the polymer matrices of HB11, resulting in poor poling efficiency of HBP3.

### 3.4. Temporal stability of the NLO hyperbranched polyaspartimide/ F-MMT (or P-MMT) nanocomposites

To investigate the long-term NLO stability of the poled hyper-

branched polymers and nanocomposites, the dipole reorientation of the film was observed by measuring EO coefficient as a function of time at 100 °C. Fig. 8 shows the  $r_{33}$  temporal characteristics for 1.0 - HBF30.8 - HBP30.6 - HBP3



Fig. 8. Temporal stability of EO coefficients for the poled hyperbranched polyaspartimide/organoclay (F-MMT or P-MMT) nanocomposites samples at 100  $^\circ$ C.

the poled HB11, HBF3 and HBP3 samples. A fast decay of the EO coefficients was observed at the beginning right after the thermal treatment. The nanocomposites of HBF3 and HBP3 exhibited better long-term stability as compared to the pristine HB11 polymer. This is because HBF3 and HBP3 exhibited rather higher  $T_{gs}$  (Table 2). The samples with an optimum amount of well-dispersed silicate platelets could effectively enhance the temporal stability at elevated temperatures. This indicates that the mobility of the aligned DAC chromophores in polymer matrices was restricted by the exfoliated layered silicates. Moreover, the fluorine-containing nanocomposite HBF3 exhibited the best temporal stability while retaining 73% of the original r<sub>33</sub> value after being subjected to 100 °C for 100 h. However, only 44% of EO coefficient for the nanocomposite HBP3 was retained after the thermal treatment. This was attributed to the non-uniform distribution of the P-MMT in the polymer matrices of HB11 as mentioned previously. Poor dispersion of P-MMTs in HBP3 resulted in poor temporal stability. Yet, better NLO temporal stability could still be achieved with the addition of a small amount of well-dispersed layered silicates.

#### 4. Conclusion

We have developed a series of novel and thermally stable hyperbranched polyaspartimides consisting of azobenzene chromophores. To further improve the thermal stability, reactive organoclays were incorporated into the hyperbranched polya spartimides. These reactive organoclays were obtained using fluorine- or phosphorus-containing triamine as the intercalating agent for MMTs. One of the amino groups of the intercalating agents formed an ionic bond with the negatively charged silicates, whereas the remaining functional groups were available for further reaction with the hyperbranched NLO polymer. Consequently, the chromophore-containing hyperbranched polymer with siteisolation effect tethered on the silicate platelets would be arranged in a noncentrosymmetric state under electric field. Better EO performance was observed for the polyaspartimide/F-MMT composites as compared to that of the pristine hyperbranched polyaspartimide. Moreover, the presence of chemical bonds between the organoclays and the polyaspartimide chains could enhance the thermal stability of the NLO polymer. The mobility of the aligned DAC chromophores in polymer matrices was restricted by the exfoliated layered silicates. Better temporal stability of EO coefficient at 100 °C was achieved for the NLO-active hyperbranched polyaspartimide/organoclay (F-MMT or P-MMT) nanocomposites than that of the pristine hyperbranched polyaspartimide.

### Acknowledgments

We thank the National Science Council of Taiwan for financial support.

### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2013.05.040.

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