Review

Dendronized Hyperbranched Polymer: A New Architecture for Second-Order Nonlinear Optics

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Abstract: Organic/polymeric second-order nonlinear optical (NLO) materials, which rely on the poling-induced non-centrosymmetric arrangement of NLO chromophores, have played a very important role in laser technology and optical fiber communication, due to their ultra-fast response speed, excellent machining performance and low dielectric constant. However, the NLO chromophores have the large dipole moments with strong intramolecular charge transfer, which lead to the intermolecular electrostatic interactions to tend to the centrosymmetric arrangement and decrease the poling efficiency. Since the special three-dimensional spatial separation can minimize these strong intermolecular electrostatic interactions during poling process, dendrimers and hyperbranched polymers have been considered as better topology for the next generation of highly efficient NLO materials. In 2013, by the attachment of low generation dendrimers to the hyperbranched backbone, a new dendritic architecture of dendronized hyperbranched polymer (DHP) was proposed for improving the comprehensive performance of NLO materials. Recent results showed many advantages of DHPs in NLO field, such as easy syntheses, large NLO coefficients and high orientation stability, etc. In this review, the latest advancement of DHPs, including the design principle, synthesis, as well as their application as NLO materials is summarized. The new opportunities arising from DHPs are also summarized in the future perspective.

Keywords: dendronized hyperbranched polymer; nonlinear optics; chromophores

1. Introduction

With the development of economic globalization, people are more committed to the promotion of information globalization. At present, microelectronics materials with electrons as the carriers can hardly meet the requirements of future information communication. Alternatively, optical materials would play more and more important roles in future information communication due to their advantages in parallelism, transmission speed, bandwidth, and electromagnetic interference resistance [1–3]. Second-order nonlinear optical (2nd NLO) material is one of the indispensable keys in optical communication. For example, the electro-optic (EO) modulator, which has been used to modulate the phase and amplitude of light successfully for realizing effective data signal loading onto light wave, is essentially built based on 2nd NLO materials [4–7]. Second-order nonlinear optical (2nd NLO) material is one of the indispensable keys in optical communication. For example, the electro-optic (EO) modulator, which has been used to modulate the phase and amplitude of light successfully for realizing effective data signal loading onto light wave, is essentially built based on 2nd NLO materials [4–7]. To date, all the commercially available 2nd NLO materials are the inorganic crystals [8–10], such as LiNbO₃, GaAs, KTiOPO₄, etc., due to their high stability of NLO coefficients and low-cost large-scale preparation. However, in comparison with the earlier researched inorganic crystal, organic/polymeric NLO materials usually offer potential advantages, such as large and ultrafast responses, low dielectric constants, good processability, and wide range of operating frequencies, and therefore gradually become an important research frontier [11,12].

In terms of symmetry, the non-centrosymmetric arrangement of organic NLO chromophores with donor-π-acceptor (D-π-A) structures is the prerequisite for materials to have macroscopic 2nd NLO activity [13]. The poling process, which was firstly proposed in 1982 [14], has been considered as the most effective and generally way to realize it.
(Figure 1). The chromophores are firstly bonded to (or doped into) the polymer matrix with good film-forming ability, to prepare the polymer film, which is subsequently heated to near or above its glass transition temperature ($T_g$) so that the chromophores can be relatively moved freely; a strong direct current electric field is simultaneously added to induce reorientation of NLO chromophores in accordance with the direction of the electric field; finally, the film is cooled to room temperature to “freeze in” the chromophores with non-centrosymmetric alignment [15–17]. The polymer formed by this poling process was called “poled polymer”. Due to the advantages of ultrahigh NLO effects, easy tailoring ability, excellent processability and mechanical properties of NLO polymers [18], the concept of “poled polymer” directly brought the organic/polymeric 2nd NLO material to a higher level, leading a vigorous development in NLO field, and nearly all the 2nd NLO polymers are “poled polymers” so far.

![Figure 1. The poling procedure for NLO polymers.](image)

However, an unalterable fact is that the strong intermolecular electrostatic interactions among rod-like chromophores are always in existence, which would make the poling-induced chromophore non-centrosymmetric alignment a daunting task and slowly destroy the non-centrosymmetric alignment after poling (Figure 1) [19]. Controlling the shape of chromophores through the introduction of isolation groups is a straightforward, but effective strategy for reducing the interaction, which is proposed by Dalton and co-workers [20,21], and termed as a famous principle of site-isolation principle in designing NLO materials. Subsequent deep research showed that dendritic structures could further
endow the polymer chains with favorable site-isolation effect to the NLO chromophores, making dendritic structures be considered as the next generation topology of highly efficient NLO materials [15,19].

Dendrimers and hyperbranched polymers are the two typical dendritic architectures. When they are used as 2nd NLO materials, there are several differences between them. Dendrimers are defect-free and perfectly monodisperse, leading to better site-isolation effect to show excellent NLO effects [22–24]. In addition, accompanying with the enhanced generation, the dendritic structures gradually become perfect, leading to significantly enhanced NLO effects (Figure 2) [25,26]. However, the syntheses of high generation dendrimers are usually difficult due to the tedious multistep synthetic protocols, limiting their practical applications. As compared with dendrimers, hyperbranched polymers can be synthesized by one-step method, but their linear defects usually lead to relatively lower NLO effects [27]. In addition, the one-pot preparation process usually makes the hyperbranched polymers with relatively high molecular weight, which would endow hyperbranched polymers with excellent stability for NLO effects after poling [28–30].

Figure 2. The design idea of DHP and comparison of the characteristics of different types of macromolecule.

It was natural to consider constructing a new dendritic architecture to inherit the advantages from both dendrimers and hyperbranched polymers. Learning from dendronized polymers, which was firstly developed by introducing dendrimers into traditional linear polymers in the late 1980s, we proposed a new kind of dendritic macromolecules, namely, dendronized hyperbranched polymers (DHP, Figure 2) by linking low generation dendrimers onto a hyperbranched polymer backbone [31]. Recent results showed many advantages of DHPs in NLO filed, such as easy syntheses, large NLO coefficients and high orientation stability, etc. Herein, we would like to summarize the latest advancement of DHPs, including the design principle, synthesis, as well as their application as NLO materials.
2. Synthesis and Topological Structural Optimization of DHP

Dendronized polymer are usually prepared via three methods of graft-to, graft-from and macromonomer [32]. Therefore, there should be also three strategies to synthesize DHPs. However, the highly branched structure of hyperbranched polymer backbones would “protect” their internal reaction sites, leading to strong steric hindrance during grafting process. Therefore, the macromonomer method should be the best choice for DHP syntheses in theory [31]. Till now, almost all the reported DHPs were prepared by such strategy.

In 2013, the first DHP of DHP1 (Figure 3) was prepared through the “A$_3$ + B$_2$” type Suzuki polycondensation between A$_3$-type monomer of borate ester as the branched unit and B$_2$-type monomer with a low-generation NLO dendrimer as the side chain (Scheme 1) [31]. During the polymerization process of normal hyperbranched polymer through the same “A$_3$ + B$_2$” polymerization, cross-linking would usually occur to yield insoluble and infusible polymers, so that the polymerization needed to be controlled strictly. Fortunately, dendritic structures had a larger bulk with a certain steric effect than normal monomers, which can reduce the reactivity and make the hyperbranched polymerization easy to be controlled. Herein, the gelation time of DHP1 was 21 h. As a control, when the normal B$_2$-type monomer without the NLO dendrimer as the side chain was used, the insoluble gel would be yielded after 1 h polymerization. After purification, DHP1 showed high molecular weight of 60 200 g/mol with good solubility and film-forming ability similar to other dendritic NLO macromolecules. After poling, DHP1 demonstrated a high $d_{33}$ value (the second harmonic coefficient, which was used to characterize the second-order nonlinear optical performance) of 133 pm/V (Table 1), larger than that of the corresponding third-generation dendrimer (123 pm/V) [33] and dendronized polymer with the same dendritic NLO side chain (91 pm/V) [34]. In addition, its decay temperature in the $d_{33}$ value was tested as 107 $^\circ$C, still higher than those of both dendrimers and dendronized polymers (both around 70 $^\circ$C). These results revealed that DHP1 can inherit the advantages from both dendrimers (high NLO effects) and hyperbranched polymers (good stability and easy syntheses), indicating that DHP can show highly potential to optimize the comprehensive performance of NLO polymers.

![Figure 3. Dendronized hyperbranched polymers of different spatial configurations.](image-url)
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Figure 3. Dendronized hyperbranched polymers of different spatial configurations.

Scheme 1. The polymerization process of DHP1, DHP2, and DHP3.

Table 1. The NLO properties of DHP1–DHP8.

| No.    | \(T_e\) \(^a\) (°C) | \(d_{33}\) \(^b\) (pm/V) | \(T_{onset}\) \(^c\) (°C) | \(T_g\) \(^d\) (°C) | \(T_d\) \(^e\) (°C) |
|--------|----------------------|----------------------|----------------------|----------------------|----------------------|
| DHP1   | 140                  | 133                  | 108                  | 138                  | 285                  |
| DHP2   | 140                  | 122                  | 117                  | 142                  | 291                  |
| DHP3   | 125                  | 166                  | 117                  | (-) \(^f\)          | 283                  |
| DHP4   | 145                  | 40                   | 103                  | 143                  | 275                  |
| DHP5   | 180                  | 36                   | (-) \(^f\)          | 217                  | 274                  |
| DHP6   | 145                  | 101                  | 120                  | 123                  | 297                  |
| DHP7   | 120                  | 179                  | 68                   | 86                   | 245                  |
| DHP8a  | 130                  | 183                  | 111                  | 100                  | 253                  |
| DHP8b  | 135                  | 220                  | 115                  | 82                   | 263                  |

\(^a\) The best poling temperature. \(^b\) Second harmonic generation (SHG) coefficient. \(^c\) The onset temperature for decay in \(d_{33}\) values. \(^d\) Glass transition temperature \((T_g)\) of polymers detected by the DSC analyses. \(^e\) The 5% weight loss temperature of polymers detected by the TGA analyses. \(^f\) Not obtained.

The topological structure of DHP1 can be further optimized. In DHP1, the NLO dendrons were linked as the side chains, making the relaxation of NLO chromophores become relative easier after poling. Therefore, by directly bonded the low generation dendrimers into the hyperbranched polymer backbones, the main chain DHP of DHP2 (Figure 3) was designed in 2015. Similar to DHP1, DHP2 was also prepared by “\(A_3 + B_2\)“ type Suzuki coupling polycondensation (Scheme 1) [35]. During the whole polymerization process, still no cross-linking products were yield. From the \(^1\)H NMR spectra, its degree of branching which was used to characterize the content of branched components in macromolecules was calculated to be close to 1, indicating the perfect dendritic architecture, which led to a high \(d_{33}\) value of 122 pm/V (Table 1). Although this value was slight lower than DHP1, the onset temperature for the decay in \(d_{33}\) value of DHP2 was up to 117 °C, thanks to the main chain improvement.

The traditional low generation dendrimers were usually conical shape, which is different from the spherical shape, the ideal conformation to minimize chromophore-chromophore interactions proposed by site-isolation principle. As early as 2012, a series of global-like dendrimers were designed by linking the ordinary low generation NLO dendrimers onto a branched core [26]. As a consequence, the \(d_{33}\) value of global-like dendrimer was directly increased by more than a quarter. Inspired by it and the main chain DHP2, the low generation global-like NLO dendrimers were also embedded into the hyperbranched polymer chains to yield DHP3 (Scheme 1, Figure 3) [36]. The \(d_{33}\) value was reasonably enhanced to 166 pm/V (Table 1) without any expense of decay temperature (117 °C, the same to that of DHP2), 36% higher than that of DHP2, thanks to the cooperation of global-like structures of dendronized moieties and the main chain architecture.
Subsequently, the “H-type” chromophore [37], “X-type” chromophore [38], etc., were further utilized to improve the topological structure, and all achieved success. To date, optimization of topological structure of NLO DHPs has still been considered as one of the most effective strategies to improve the comprehensive performance of polymeric NLO materials.

3. Introducing Isolation Chromophores to DHP

According to site-isolation principle, all the isolation groups in the above DHPs were non-polar (such as phenyl rings) or weakly polar (such as triphenylamine, triazole) ones, which could only decrease the intramolecular electrostatic interactions in favor of poling process, but cannot directly contribute to NLO effects. In some special cases, the loading density (calculated by weight, the same below) of NLO chromophores in polymers would be significantly decreased by the over-large isolation group, leading to the reduced NLO coefficients. One of our improvement strategies is to introduce the isolation chromophore [39–42], specifically speaking, it is one with relatively lower $\mu_\beta$ value is used as isolation group of another major chromophore with a larger $\mu_\beta$ value to decrease the intramolecular electrostatic interactions while contributing to NLO performance directly (Figure 4). In addition, the optical transparency of the polymer is also improved. Further deep research indicated that the introduction of isolation chromophores can also improve the $T_g$ value of the polymer, being beneficial to the stability of NLO coefficients.

Therefore, it was reasonable to introduce isolation chromophores into DHPs. However, it seems that the obtained DHPs can hardly show good performance, and the $d_{33}$ values of DHP4–DHP6 were only 40, 36, and 101 pm/V, respectively (Figure 4, Table 1) [37,43,44]. In our previous work, it has been confirmed that the size of suitable isolation group is closely related to the intermolecular electrostatic interactions usually caused by the dipole moment of 2nd NLO chromophores [19]. Therefore, the size of suitable isolation group should become very small when introducing isolation chromophore [45], due to the reduction in dipole moments and intramolecular electrostatic interactions. Herein, in DHP4, there were several isolation groups (one triazole, two phenyl rings, and one co-polymerization unit of fluorene) around each nitroazobenzene chromophore, obviously exceeding the actual...
requirements. Consequently, the loading density of the effective chromophore moieties in DHP4 was only 0.4 (involved both types of chromophores), leading to the low NLO effect. For DHP5, its $T_g$ value was tested as 217 °C, making its thin films difficult to be poling, according to Figure 1. The relatively low $d_{33}$ value of DHP6 was caused by the same reason. Although the high $T_g$ values usually mean high stability of NLO effects, it seems to be meaningless before the films can be poled perfectly.

Based on the above results, we attempted to use flexible chains to construct hyperbranched polymer backbone for NLO DHPs containing isolation chromophores. It has two obvious advantages. Firstly, the size of the flexible chains can be easily adjusted, which can avoid the over-sized isolation group like in DHP4. In addition, the $T_g$ values of the flexible chains are usually much lower than the rigid chain. As early as 2013, it has been confirmed that for DHPs, their $T_g$ values are mainly related to the main chain of polymer, but less to the dendronized side chain [31]. It was therefore expected that the flexible hyperbranched chains could decrease the $T_g$ values of NLO DHPs notably for the easier poling process. In 2016, by using the first-generation NLO dendrimer as the initiator, methyl methacrylate as the monomer, ethylene glycol dimethacrylate as the branching monomer, DHP7 with the chromophore loading density of 0.266 was successfully prepared through one-pot atom transfer radical polymerization to overcome the shortcomings of DHP4–DHP6 [46]. Its $d_{33}$ value was tested as 179 pm/V, the highest value for NLO polymers at that time, confirming the flexible hyperbranched chains were enough to be suitable isolation groups in this system. In addition, its optical transparency was also improved, similar to other successful cases of isolation chromophores, meaning DHP7 would show low optical loss at the usage wavelength.

4. Increasing the Loading Density of Chromophore in DHP

Alternatively, the scientists also directly used the NLO chromophores to construct hyperbranched chains to enhance the effective loading density of chromophore moieties in DHPs. DHP8 (Figure 5) of Li’s work is a typical example. Both DHP8a and DHP8b were synthesized through “$A_3 + B_2$” type Sonogashira polymerization between nitroazobenzene chromophore and low generation NLO dendrimers [47]. The chemical structure of DHP8b was very similar to the above mentioned DHP1, but using nitroazobenzene chromophore instead of triphenylamine as the branched units. As a result, the loading density of the effective chromophore moieties was enhanced from 0.415 to 0.476, leading to an enhanced $d_{33}$ value from 133 to 220 pm/V, which was the highest value for NLO DHPs by using nitroazobenzene as the chromophores at present. From DHP8a to DHP8b, the generation of the introduced NLO dendrimer was enhanced, and the NLO coefficient was also improved from 183 to 220 pm/V. However, the higher generation means the more difficult synthesis, we should find a balance between them. However, from another angle, these results also indicate that the improvement of the dendronized moieties is an effective strategy to further improve the NLO performance of DHPs with chromophores as the hyperbranched architecture.

Accordingly, in the following years, the NLO dendronized moieties have improved to different new types, such as Y-type (the dendronized moieties of DHP9–DHP11 in Figure 6), Janus-type (the dendronized moieties of DHP12 in Figure 6), etc., and the concept of isolation chromophore was also employed for improvement of dendronized moieties in DHPs (DHP 10 in Figure 6) [38,48]. The chromophore hyperbranched architectures have also been improved to the other topological, such as star-type chromophore (the monomer of Mon-3Alk for DHP9–DHP12 in Figure 6). All these attempts and explorations would make the structure–property relationship of NLO DHPs clearer and clearer, laying a solid foundation for the further development of NLO materials with even higher performance in the future.
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In the family of dendritic macromolecules, DHP is one of the latest members, which are usually prepared by the copolymerization between low generation dendrimer and branched monomer. When used in NLO fields, they can inherit the advantages from both dendrimers (high NLO effect) and hyperbranched polymers (good stability and easy synthesis), making them show great potential to optimize the comprehensive performance of NLO polymers. However, due to the time limitation, the related studies are not such thorough, and there are still several issues need to be solved in NLO DHPs. Firstly, the scientists still focus on their structure–property relationships by using simple azobenzene as the chromophores, and no one worked on the NLO DHPs containing high $\mu\beta$-value chromophores. Even though, by using the same nitroazobenzene as the chromophores, the NLO coefficients of DHPs were still lower than high generation dendrimers (220 vs. 299 pm/V [24]), indicating that we should further improve the topological structures of DHPs, and find a balance among high NLO effects and simple syntheses. In addition, although the stability of DHPs is usually high, the “nonlinearity-stability trade off” is still existed in NLO DHPs, which is obvious in DHP4–DHP7 that containing isolation chromophores. Accordingly, some other
strategies in NLO fields, such as photo-crosslinking [49], self-assembly [50], etc., should be also utilized to improve the stability of DHPs without expense of NLO effects. In addition, the emerging artificial intelligence and big data should be helpful to further optimize the comprehensive performance of the DHPs in the future. After scientists’ efforts in the next few years, it is believed that the organic/polymeric NLO materials would finally realize commercialization and affect our daily life.

Besides 2nd NLO, some pioneers have also extended DHPs to some other fields, such as biomedicine [51,52], optical-electric functional materials [53], hydrogels [54], etc. Based on this review, we hope to encourage the further interests of scientists in this young DHP for various applications.

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