Diels−Alder "Click Chemistry" for Highly Efficient Electrooptic Polymers

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Organic second-order nonlinear optical (NLO) materials have been intensively studied in the past decade for their potential application in high-speed electrooptic (E−O) devices with very broad bandwidth (up to 200 GHz) and low driving voltages (<1 V).[1−3] One of the main challenges still facing in this field is how to effectively translate high molecular optical nonlinearities ($\mu\beta$), where μ and β are the dipole moment and the first hyperpolarizability of chromophores, into large macroscopic E−O coefficients (r_{33}) and maintain good temporal stability.[4,5] For poled polymers, covalent attachment of high $\mu\beta$ chromophores onto polymer backbones through postfunctionalization methods has been shown to furnish side-chain or cross-linkable NLO polymers with better temporal stability than the simple guest−host systems. However, there are several drawbacks in the commonly used postfunctionalization reactions for making side-chain NLO polymers. For example, the azo coupling,[6] tricyanovinylation,[7] Mitsunobu etherification,[8] Kneovenagel condensation,[9] and catalyzed esterification[5b,c] often generate byproducts or trace amount of residual ionic impurities which significantly attenuate the effective poling electrical field and also cause the dc bias drift during device operation. To alleviate these problems, the selecting criteria for ideal postfunctionalization methods are (i) quantitative conversion with minimum byproducts, (ii) no catalyst required, (iii) free of ionic or polar species, and (iv) mild reaction conditions and good compatibility of a host polymer with various highly efficient but chemically sensitive chromophores. In searching of possible solutions, the "click chemistry" pioneered by Sharpless et al. seems to fit most of these criteria.[10]

The "click"-type reactions, mainly exemplified by Huisgen 1,3-dipolar azide−alkyne or Diels−Alder cycloadditions, have led to reliable and self-directed modular organic reactions to make molecular connections with absolute fidelity.[10] They also inspired a multitude of applications[11−14] in biology, chemistry, and materials science. As a powerful enabling tool, it possesses great potential of meeting the aforementioned stringent criteria for postfunctionalization of NLO polymers to generate comprehensive properties.

Nevertheless, one drawback for these 1,3-dipolar azide−alkyne reactions is the high reactivity between azide and the cyano-containing acceptors that are commonly used for NLO chromophores. This may hinder their general applicability for NLO polymers. To solve this problem, the Diels−Alder cycloaddition was selected as an alternative for generating new series of high-performance NLO polymers. The Diels−Alder reaction involves a ring-forming coupling between a dienophile and a conjugated diene which can be described by a symmetry-allowed concerted mechanism without forming biradical or zwitterionic intermediates.[15] Recently, Diels−Alder cycloadditions have been successfully adopted for fracture self-healing in polymer thermosets[16] and smartly controlled lattice hardening in stable E−O polymers.[5f] These encouraging results have shown the potential and versatility of using these Diels−Alder reactions to create sophisticated properties for polymers.

Here, we describe a new scheme based on the Diels−Alder "click reaction" to functionalize maleimide-containing NLO chromophores onto polymers that possess pendant anthryl-containing diene moieties. The synthetic condition is very mild, and it can quantitatively generate adducts without producing any ionic species. With these advantages, we can adopt some of the concepts recently reported in nanoscale architectural manipulation of macromolecules (their size, shape, and conformation) and the state-of-the-art high $\mu\beta$ chromophores, to design highly efficient E−O polymers. In addition, we can systematically investigate the poling dynamics and temporal stability of poling-induced polar order related to their anchoring positions and the mode (side-on and end-on) of attachments to the polymer backbone. The E−O polymers generated by this methodology have shown large r_{33} values (60 pm/V at 1.3 μm), high temporal stability, and excellent poling characteristics.

As shown in Schemes 1 and 2, we have employed the Diels−Alder cycloaddition to postfunctionalize side-chain E−O polymers. A poly(methyl methacrylate-*co*-anthrylmethyl methacrylate) (**PMMA−AMA)** precursor polymer was prepared by free radical polymerization using 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator.[17] The content of the anthryl moiety in this copolymer was estimated to be ~8.0 mol %. This was further confirmed by comparing the relative integration of the corresponding characteristic peaks in its NMR spectrum. Through the Diels−Alder postfunctionalization, this parent polymer with anthryl diene was reacted with maleimide-functionalized chromophores, such as **2**, **4**, and **7**, to afford **PM-1a**, **PM-1b**, **PM-2**, and **PM-3**, respectively. The structure and purity of these polymers have been verified by gel permeation chromatography (GPC), ^{1}H NMR, UV/vis and mass spectroscopy, and thermal and elemental analysis.

In the side-chain E−O polymers previously made by using postesterification, the typical connection point for side-chain or dendron attachment is limited only through the donor or acceptor end of the chromophores (Chart 1A, **PS-FTC**).[5b,f] Although the chromophore can be structurally shielded from its neighbors to minimize the electrostatic interactions, this head-to-tail linking style creates a quite bulky shape, which causes substantial steric hindrance during poling. As a result, it often needs very high electric field (~150 V/μm) to align the chromophore dipole.

By using the efficient Diels−Alder "click" reaction, different architectures of macromolecules can be created by changing the attaching modes of the chromophore onto polymers. Since both of the donor and acceptor ends were used in the **A**-type side-chain polymers, the alternative site for linking the rod-shaped chromophore is through the center of its bridge. Until now, this approach of making side-chain NLO polymers has only received little attention.[18] By activating the center site of chromophoric bridge, it also creates multiple new placements of chromophores in side-chain dendronized E−O polymers. This provides the possibility to molecular engineer side-chain dendronized E−O polymers with desirable shape for ease of rotation

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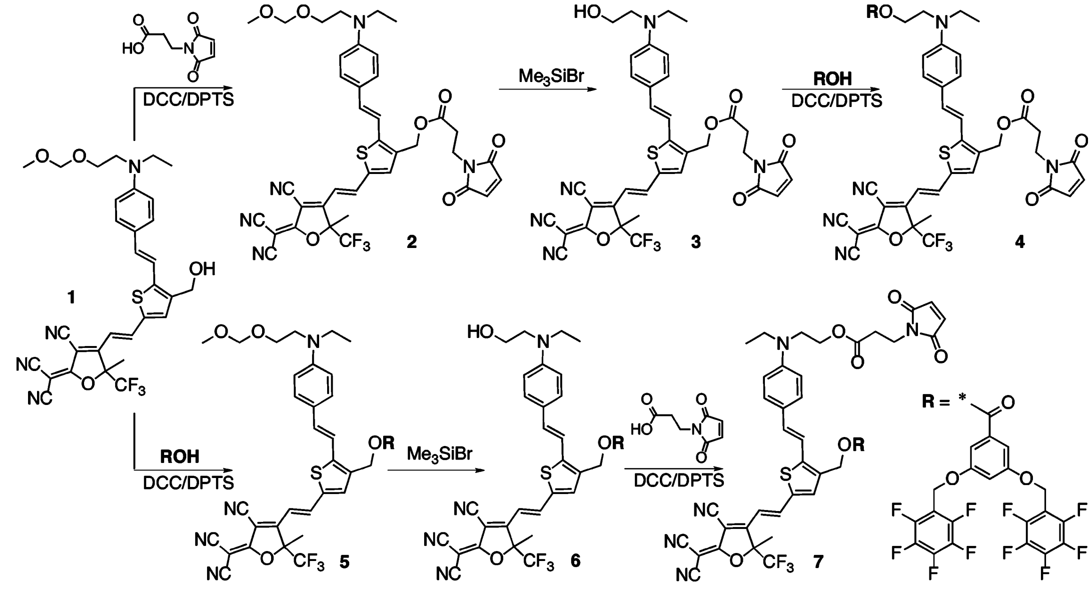
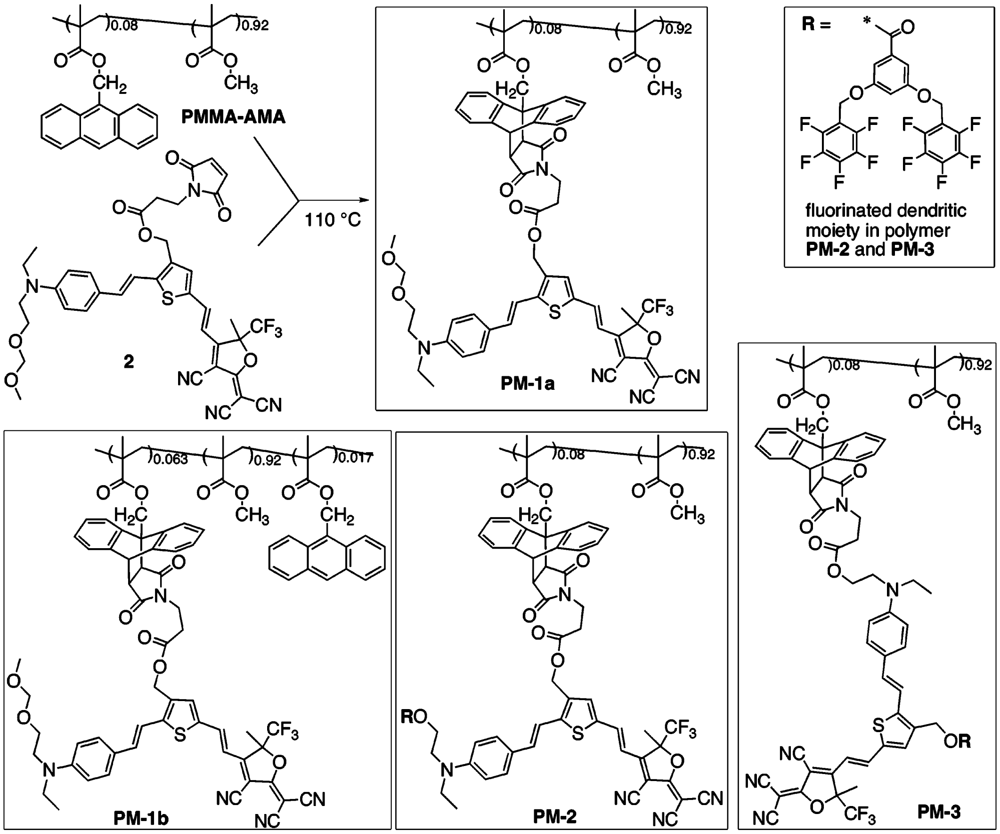
Scheme 1. Synthesis of Chromophoric Derivatives Functionalized with Maleimido and/or Dendritic Moieties, 2, 4, and 7[a]



[a] DCC = 1,3-dicyclohexylcarbodiimide; DPTS = 4-(dimethylamino)pyridinium-4-toluenesulfonate.

Scheme 2. Synthesis of Side-Chain NLO Polymers PM1−3 by Using the Diels−Alder Postfunctionalization

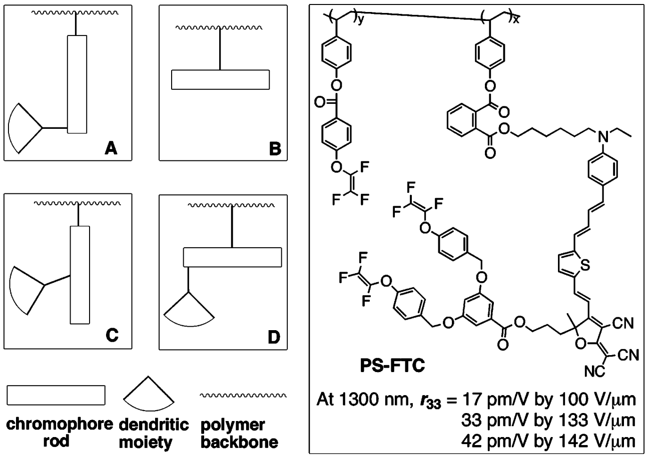


during poling (Chart 1**B**−**D**).[5g] In this new series of side-chain polymers, **PM-1a** and **PM-1b** are the ones that bear the center-anchored chromophore as side chains (**B**-type or side-on type in Chart 1). The chromophore loading level in these polymers is 25 and 20 wt %, respectively. **PM-2** also adopts the similar anchoring style, while the donor end of the chromophore is functionalized with a fluorinated dendron (**D**-type). **PM-3** belongs to the **C**-type construction, in which the chromophore is attached to polymer backbone via its donor end and also incorporated with a fluorinated dendron on its bridge center.

Thermal analysis using differential scanning calorimetry (DSC) showed relatively high glass transition temperatures (T_gs) in these PMMA-type polymers: 152 °C for **PM-1a**, 154 °C for **PM-1b**, 140 °C for **PM-2**, and 135 °C for **PM-3**. This can be attributed to the rigidity introduced by the bulky anthryl-maleimido Diels−Alder adducts. From thermogravimetric analysis (TGA), the onset decomposition temperatures for the dendronized polymers **PM-2** and **PM-3** are roughly 50 °C higher than those of the nondendronized **PM-1a** or **PM-1b**, indicating improved thermal properties by encapsulating the NLO chromophore in fluorinated dendrons.[5a]

For poling and E−O property measurements, the corresponding polymer solutions in cyclopentanone (11−14 wt %, filtered through a 0.2 μm syringe filter) were spin-coated onto indium

Chart 1. Illustration of Different Types of Side-Chain Nonlinear Optical (NLO) Polymers; (Right) an Example of an A-Type Side-Chain Dendronized Polymer PS-FTC



tin oxide (ITO) glass substrates. The films were baked in a vacuum oven at 85 °C overnight to ensure the removal of the residual solvent. Then, a thin layer of gold was sputtered onto the films as the top electrode for high electric field poling. The r_{33} values were measured using the simple reflection technique at the wavelength of 1.31 μm.[19] The poling conditions and measured r_{33} values of these polymers are summarized in Table 1. **PM-1b**, **PM-2**, and **PM-3**, with a 20 wt % chromophore loading level, exhibited excellent poling characteristics. Among them, the poled **PM-2** films showed the highest r_{33} value (60 pm/V), which is almost twice that of the nondendronized counterpart, **PM-1b**. The **PM-3** film also showed a high r_{33} value of 57 pm/V. These results demonstrate the effect of using dendritic moieties to improve poling efficiency of polymers. They are also in good agreement with the previously reported side-chain dendronized **PS-FTC** polymers.[5b] It should be noted that **PM-1a**, an analogue of **PM-1b**, has the lowest r_{33} value (33 pm/V) despite its higher chromophore loading level (25 wt %). During the poling process, films made of this polymer also are prone to dielectric breakdown when the poling field exceeds 125 V/μm. We believe that the strong electrostatic interactions between highly dipolar chromophores significantly hinder the poling efficiency of NLO polymers in high loading density.

Compared to the **A**-type side-chain dendronized polymer, **PS-FTC**, these polymers exhibited much improved electric-field-dependent poling behavior (Figure 1). Within the poling field range between 100 and 160 V/μm, the E−O activities of **PM-2** and **PM-3** increase linearly with the increase of the applied field. For example, under a poling field of 100−125 V/μm, the poled films of **PM-2** and **PM-3** show large r_{33} values of 48 and 40 pm/V, respectively which are ∼70−80% of their optimal E−O activity calculated by using a two-level model. For comparison, we can only obtain 36% of the optimal E−O activity for the **A**-type **PS-FTC**. Moreover, these new side-chain dendronized polymers, **PM-2** and **PM-3**, can achieve high poling efficiency over a much broader range of poling fields (100−160 V/μm). This is because the center site of chromophoric bridge has been activated for polymer or dendron attachment, through which either the chromophore shape is modified (more 3-D extended as in the **C**-type **PM-3** to prevent preferential 2-D packing of pristine chromophore prolate ellipsoids) or the steric hindrance is reduced for chromophore reorientation (in **D**-type **PM-2**). This clearly demonstrates the advantage of this new center-anchored approach than the previously used head-to-tail connecting approach in our first-generation side-chain dendronized polymers.

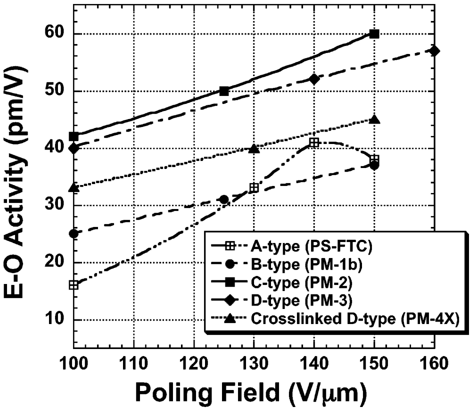


Figure 1. Electric field-dependent poling behavior of different types of side-chain dendronized polymers.

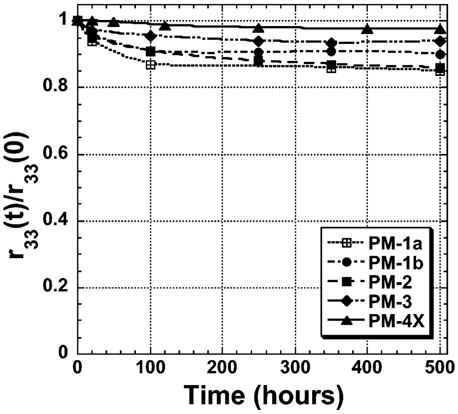


Figure 2. Temporal stability of the side-chain NLO polymers at 85 °C. $r_{33}(0)$: initial r_{33} values; $r_{33}(t)$: r_{33} values at different baking time.

All of these side-chain dendronized polymers also exhibited promising alignment stability: more than 80% of their original r_{33} values were retained at 85 °C for more than several hundred hours (Figure 2).

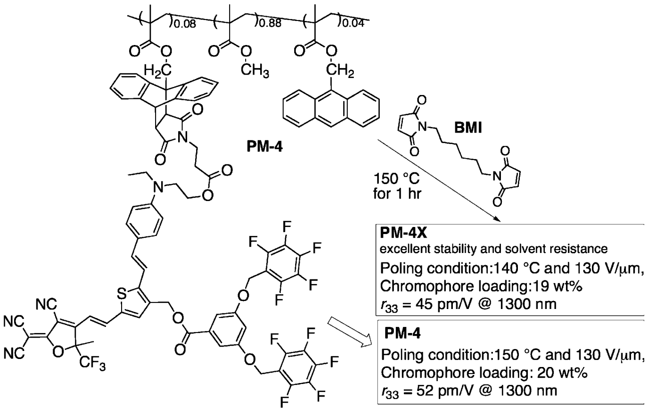
All these polymers have good solubility in common organic solvents, such as tetrahydrofuran, dichloromethane, and cyclopentanone, and have excellent film-forming ability. Good solubility of these polymers, however, limits the selection of suitable top cladding polymers that can be used for the fabrication channel waveguide devices.[20] In the past, many guest−host NLO polymers or side-chain polymers were excluded as core materials because of their poor solvent resistance.[21] Thus, it is highly desirable to be able to cross-link NLO polymers prior to their poling. However, this cross-linking process often results in lower poling efficiency due to increased rigidity in these polymers.[5f,22] To address this issue, a feasibility study was performed on the poling of a **C**-type polymer hardened by the Diels−Alder "click" chemistry. **PM-4**, a polymer that possesses the similar structure of **PM-3** but has some unreacted anthryl groups, was synthesized (Chart 2) by carefully controlling the stoichiometry of reagents. By adding 3.6 wt % of bismaleimide into the solution of **PM-4** and following the similar processing steps described above, the prepared films were further annealed at 150 °C for 1 h to form cross-linked **PM-4X**.[23] The resulting thin films possess excellent solvent resistance toward polar organic solvents, such as THF, chloroform, and cyclopentanone. But most amazingly, this pre-cross-linked polymer **PM-4X** showed ∼90% of the E−O activity compared to that can be obtained from **PM-4** under the similar poling condition. This indicates that the poling efficiency is only slightly affected by this pre-cross-linking

Table 1. Physical and Optical Properties of Side-Chain E−O Polymers PM1−3[a]

polymer	T_g (°C)	T_d (°C)	M_n (PDI)	density of chromophore (wt %)	λ_{max} (nm)	poling temp (°C)	applied voltage (MV/cm)	r_{33} (pm/V) at 1.3 μm
PM-1a	152	210	47 100 (3.79)	25	710	150	125	33
PM-1b	154	210	44 300 (3.67)	20	710	150	150	37
PM-2	140	258	48 300 (3.91)	20	690	135	150	60
PM-3	135	261	47 800 (3.88)	20	690	130	160	57

[a] T_g = glass transition temperature measured by DSC under nitrogen at the heating rate of 10 °C/min; T_d = onset decomposition temperature measured by TGA under nitrogen at the heating rate of 10 °C/min; M_n = number-averaged molecular weights of polymers estimated by GPC calibrated by narrow-distributed polystyrene standards; PDI = polydispersity reported as M_w/M_n; density of chromophores = the donor−bridge−acceptor core part of chromophoric moiety (formula $C_{28}H_{21}F_3N_4OS$, molecular weight 518.6) is counted for chromophore loading density; λ_{max} = maximum absorption wavelength of thin solid films by UV/vis spectroscopy; r_{33} = E−O coefficient measured by simple reflection at the wavelength of 1300 nm.[19]

Chart 2. E−O Property Comparison between a C-Type Side-Chain Dendronized Polymer PM-4 and Its Cross-Linked Analogy, PM-4X



treatment. The cross-linked polymer **PM-4X** also demonstrated great temporal stability with its r_{33} value maintained at 95% of its initial value. Since good poling efficiency, temporal stability, and solvent resistance can be simultaneously achieved in this cross-linked **C**-type polymer, it provides a great prospect of using this type of material for multilayer device integration.

In conclusion, several new side-chain E−O polymers have been synthesized by using the Diels−Alder postfunctionalization method. This synthetic approach is very mild, versatile, quantitative, and free of ionic species and catalysts. Three different macromolecular architectures have been created by covalently attaching the center site of the chromophore bridge to a polymer backbone or a dendritic moiety. The resulting polymers exhibited high dielectric strength, excellent optical quality, good processability, and reliable poling behaviors. The combination of large E−O coefficient (∼60 pm/V at 1.3 μm), high thermal stability, and good solvent resistance warrants these NLO polymers as good candidates for multilayer integrated E−O devices.

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Supporting Information Available: Detailed synthetic procedures and characterization data for the monomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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