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Unprecedented Electro-optic Properties in Polymers and Dendrimers Enabled by Click Chemistry Based on the Diels–Alder Reactions

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16.1 Introduction

Organic second-order nonlinear optical (NLO) materials have been intensively studied for several years due to their promising applications in high-speed and broadband information technologies, THz generation/detection systems, optical circuits integrated in silicon chips, and multifunctional nano-devices.[1–4] Recent advances in the use of nano-scale architectural control and Rational molecular design have led to exceptionally large electro-optic (E-O) activities in organic NLO materials and devices. For instance, dendronized NLO chromophores and polymers have shown significant enhancement in poling efficiency by encapsulation of the chromophore with dendritic substituents that can electronically shield the core, π-electrons and form spherical molecular shapes.[5] Another significant improvement of E-O activity was also shown in the supramolecular self-assembly of NLO chromophores surrounded by dendritic moieties that can be poled and crosslinked into a robust extended network.[6]

The ultimate goal for the NLO materials is to simultaneously achieve very large E-O activity, good thermal stability, high optical transparency, and excellent mechanical

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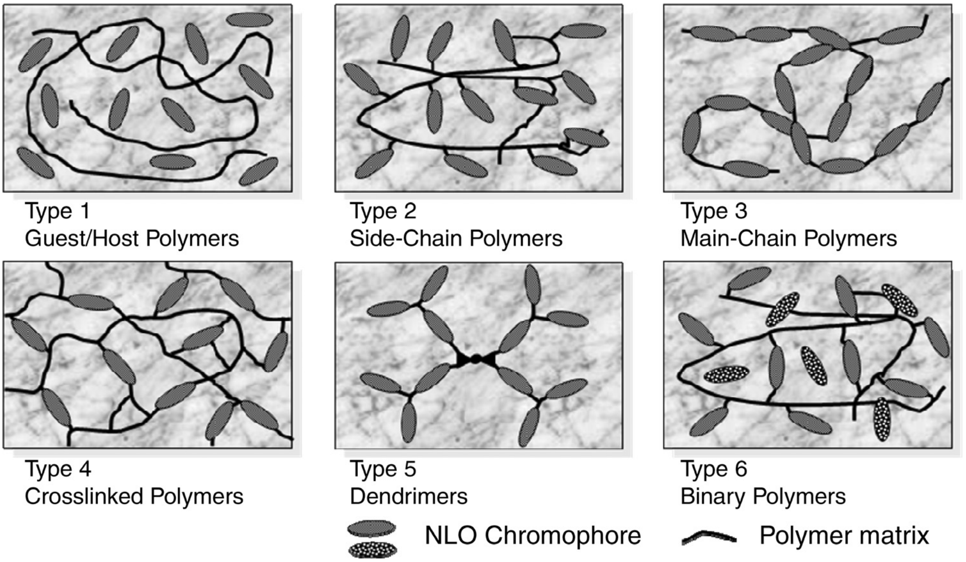

Figure 16.1 *Various types of polymeric NLO materials.*

properties within the same materials. Figure 16.1 represents the various types of polymeric NLO materials developed over two decades. It is highly desirable to covalently incorporate chromophores into polymer networks through postfunctionalization (type 2) and crosslinking reactions (type 4) to improve both their thermal and mechanical properties.[1a,c] The globular shape of dendrimers (type 5) is suitable for obtaining spherical macromolecular structures of encapsulated chromophores and engineering nanoscale macromolecular architectures with pre-organized chromophores.[5] However, low poling efficiency from limited chromophore alignment was found in postfunctionalized and crosslinked NLO polymers and dendrimers due to reduced rotational flexibility of chromophores. Therefore, there is a strong need to establish creative processing/poling protocols using carefully controlled chemistry to overcome the 'nonlinearity–stability trade-off'.

Recently, we have exploited high performance NLO polymers and dendrimers showing unprecedented E-O properties by applying click chemistry based on the Diels–Alder reactions for postfunctionalization and lattice hardening. The reactions meet the stringent requirements of processing/poling protocols with comprehensive material properties. Here we highlight these revolutionary materials achieved by click chemistry, which resulted in ultrahigh E-O coefficients (up to ~380 pm/V), excellent thermal stability and optical transparency, and are suitable for the implementation into novel opto-electronic and photonic devices.

16.2 Diels–Alder Click Chemistry for Highly Efficient Side-chain E-O Polymers[7–10]

Two different synthetic strategies can be used for the preparation of side-chain E-O polymers. One is the polymerization of NLO chromophores attached with reactive groups

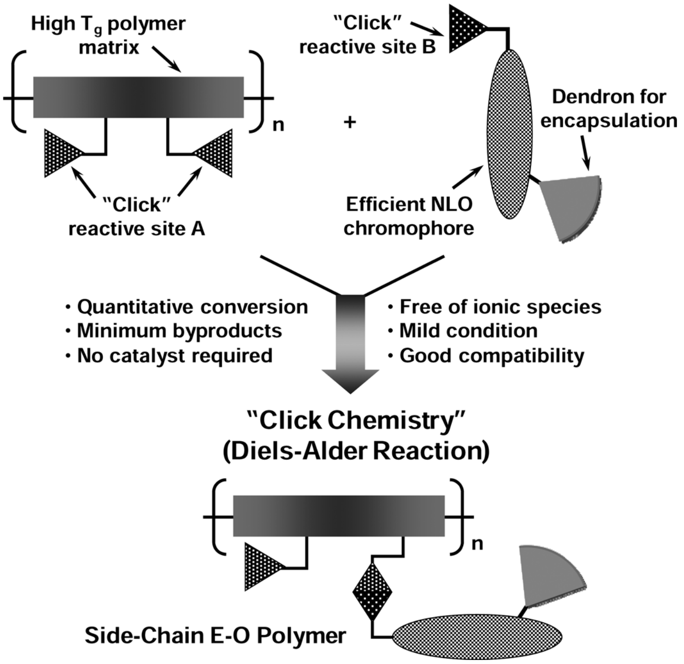

Figure 16.2 *The postfunctionalization method for side-chain E-O polymers by click chemistry based on Diels–Alder reaction.*

by step-growth or chain-growth reactions. The other is the postfunctionalization of the NLO chromophores into conventional linear polymers. The latter approach is a preferred method for systematic molecular engineering of polymers with optimized properties since we can take advantages of well-defined linear polymers as starting materials. Most of the postfunctionalization methods used for making side-chain E-O polymers such as the azo-coupling,[11] tricyanovinylation,[12] Mitsunobu etherification,[13] Knoevenagel condensation[14] and catalyzed esterification,[5c,d] often generate byproducts or trace amount of residual ionic impurities that can significantly attenuate the effective electrical field for poling and cause the DC bias to drift during device operation. To alleviate these problems, the selection criteria for ideal postfunctionalization methods, as illustrated in Figure 16.2, 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.[15]

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. They also inspired a multitude of applications in biology, chemistry and materials science.[16] As a powerful enabling tool, it possesses great potential for meeting the aforementioned stringent criteria for post-functionalization of E-O 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 and can hinder their general applicability for E-O polymers. To solve this problem, the Diels–Alder cycloaddition was selected as an alternative for generating new series of high-performance E-O 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. One of the important features in a Diels–Alder reaction is that the resultant adducts can be thermo-reversibly cleaved to render the starting materials. Wudl and coworkers have reported a thermally amendable polymeric network by the reversible Diels–Alder cycloaddition adapted for fracture self-healing in polymer thermosets.[17] These encouraging results have shown the potential and versatility to create sophisticated properties for polymers.

We first introduce the Diels–Alder cycloaddition reaction as a general and efficient synthetic method for reversibly crosslinkable E-O polymers.[7] Three different functional moieties, including the derivatives of a CLD-type chromophore **1**, a capped maleimide **2** (dienophile) and furanic ring **3** (diene), were sequentially attached onto the polymer backbone as side chains to afford a crosslinkable E-O polymer PSDACLD (Figure 16.3). The maleimide was protected with furan initially to prevent any crosslinking reaction from occurring prior to the poling and lattice hardening step. The poling temperature is very close to the onset temperature of the retro-Diels–Alder reaction (110 °C) and slightly higher than the typical temperature range used for the Diels–Alder crosslinking reaction (60–80 °C). At this temperature, the material possesses the characteristics of a typical thermoplastic polymer. Concurrently, the chromophores can be effectively reoriented under the poling field. After the poling process, a sequential cooling/curing process (85 °C for 1 h, 75 °C for 1 h, and 65 °C for 1 h) was performed to anneal and crosslink the polymer through the Diels–Alder reaction.

By smartly controlling the poling and crosslinking processes through the reversible Diels–Alder reactions, it allows highly polarizable chromophores to be efficiently poled at the stage of a low viscosity linear thermoplastic polymer. The resulting material exhibits a combination of a very large E-O coefficient (r_{33}) value (76 pm/V at 1.3 μm) and good temporal stability at 70 °C. From this novel crosslinking system, E-O materials with optimal physical properties can be achieved by fine-tuning a processing temperature window of the Diels–Alder and retro-Diels–Alder reactions. Furthermore, modifying the electronic properties of the crosslinking reagents of deactivated furan diester or anthryl groups[8] led to the ability to fine-tune the processing temperature and reversibility of these Diels–Alder reactions to optimize thermal stability and processability. Because of the efficient lattice hardening of the Diels–Alder reaction, these materials also exhibited very good temporal alignment stability, retaining $\sim$80% of their original r_{33} values even after baking at 85 °C for 500 h.

The Diels–Alder reactions can be utilized for click postfunctionalization in order to make side-chain E-O polymers, as shown in Figure 16.4. Maleimide-containing NLO chromophores can trigger click reactions to the polymer backbone (**PMMA-AMA**) with pendant anthracenyl diene moieties to afford **PM-1b**, **PM-2** and **PM-**3, respectively.[9] This synthetic approach is very mild, versatile, quantitative and free of ionic species and catalysts. In the side-chain E-O polymers made by using post-esterification, the typical connection point for side-chain or dendron attachment is limited only through the donor- or the acceptor-end of the chromophores (**A**-type, **PS-FTC**). Although the chromophore

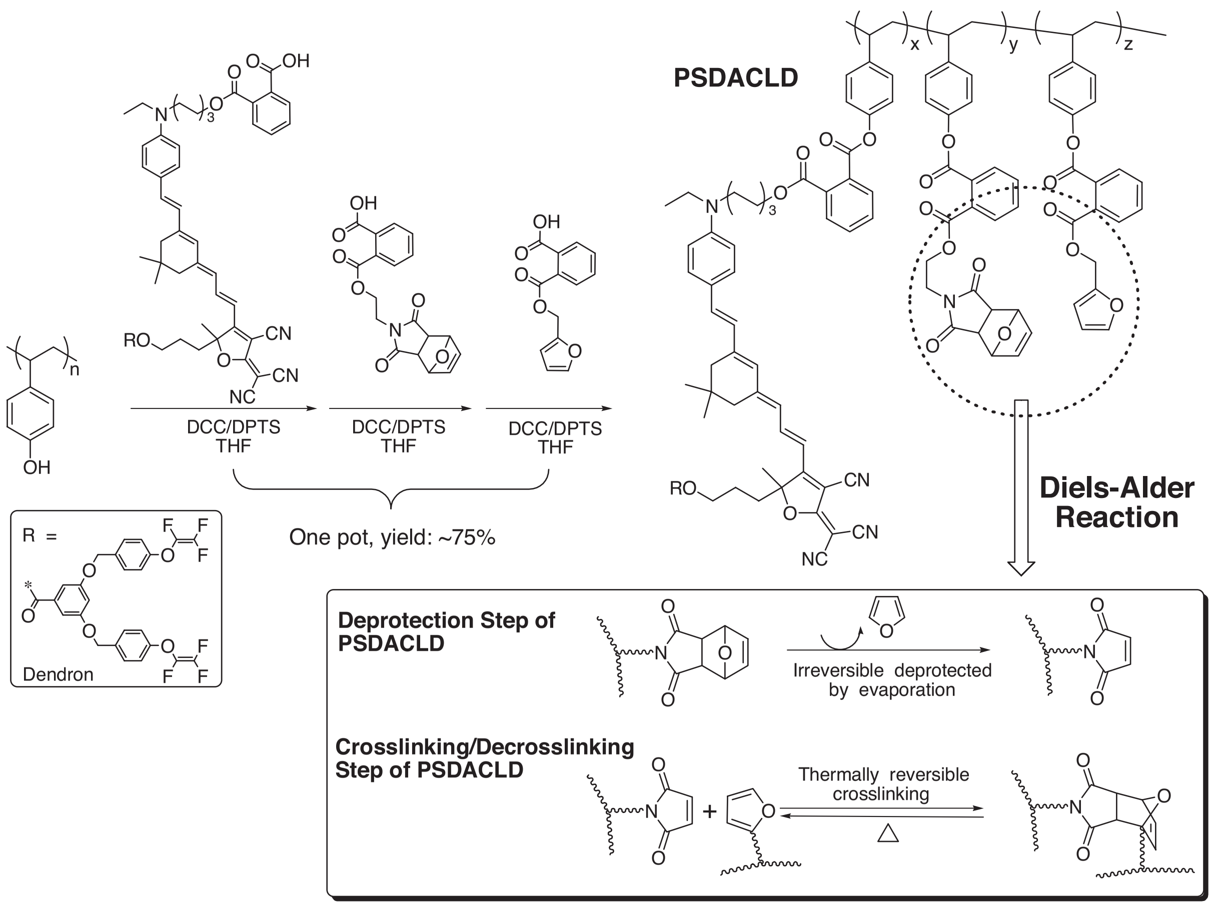

Figure 16.3 *Synthesis of a thermoreversibly crosslinkable side-chain E-O polymer by one-pot postesterification. Reprinted with permission from J. Luo,* et al.*, (2003), Highly efficient and thermally stable electro-optic polymer from a smartly controlled crosslinking process,* Advanced Materials*,* ***15*** *(19), 1635–1638. Copyright 2003 Wiley-VCH.*

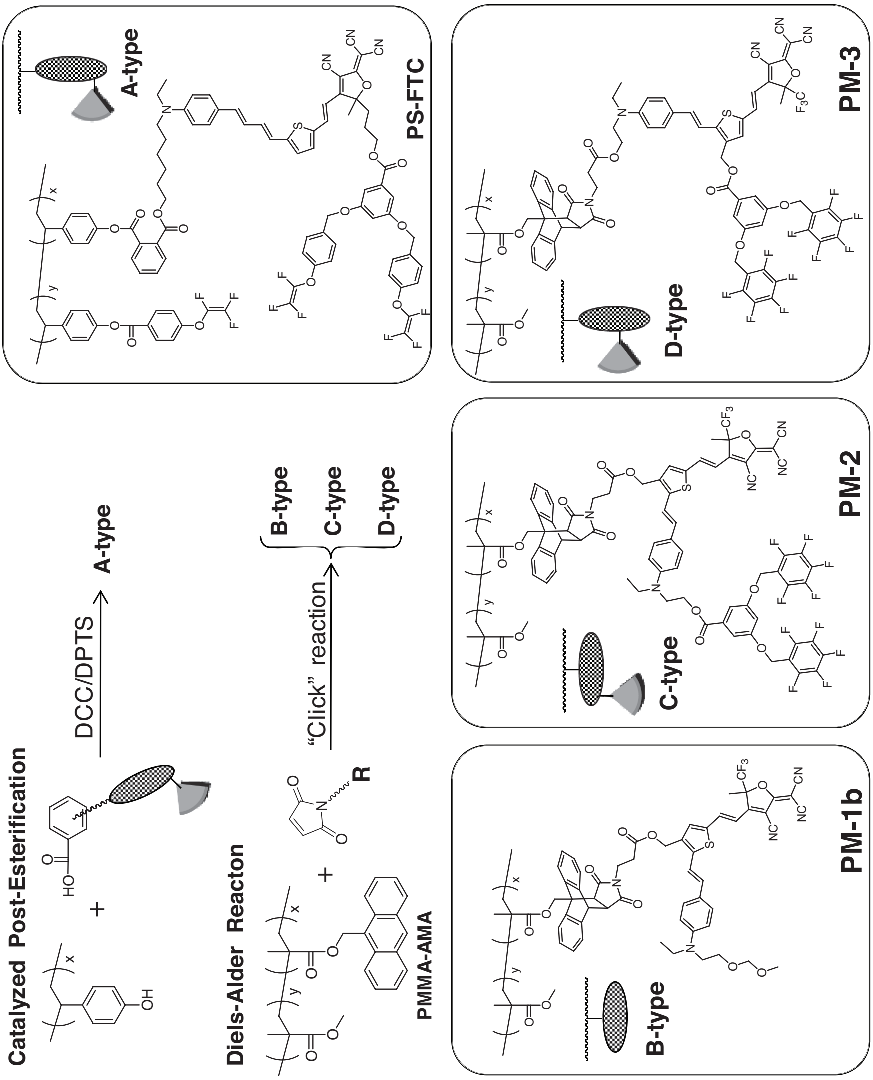

Figure 16.4 *Synthesis of side-chain E-O polymers by using catalyzed post-esterification for* ***PS-FTC*** *and the Diels–Alder click reaction for* ***PM-1b***, ***PM-2*** *and* ***PM-3***. *Inserted illustrations show different anchoring styles of the NLO chromophore into the polymer backbone.*

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 easily created by changing the attaching modes of the chromophore onto the 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. 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 molecularly engineer side-chain dendronized E-O polymers with desirable shape for ease of rotation during poling (**B**-, **C**- and **D**-type). **PM-1b** is the one that bears the center-anchored chromophore as a side-chain (**B**-type or side-on type). **PM-2** also adopts the similar anchoring style, while the donor-end of the chromophore is functionalized with a fluorinated dendron (**C**-type). **PM-3** belongs to the **D**-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**. On the other hand, the T_g of **PS-FTC** only showed ~90 °C. 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-1b**, indicating improved thermal properties by encapsulating the NLO chromophore in fluorinated dendrons.

PM-1b, **PM-2** and **PM-3**, with a 20 wt% chromophore loading level, exhibited excellent poling characteristics. The measured E-O activities were 37 pm/V for **PM-1b**, 60 pm/V for **PM-2** and 57 pm/V for **PM-3** at 1.3 μm. The poled **PM-2** and **PM-3** films showed almost twice r_{33} values compared with the nondendronized counterpart, **PM-1b**. These results demonstrate the effect of using dendritic moieties to improve poling efficiency of polymers. Compared with the **A**-type side-chain dendronized polymer, **PS-FTC**, these polymers exhibited much improved electric-field-dependent poling behavior (Figure 16.5).

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 in 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 3D extended as in the **D**-type **PM-3** to prevent preferential 2D packing of pristine chromophore prolate ellipsoids) or the steric hindrance is reduced for chromophore reorientation (in **C**-type **PM-2**). This clearly demonstrates the advantage of this new center-anchored approach over the previously used head-to-tail connecting side-chain E-O polymers. All of these side-chain dendronized E-O polymers also exhibited

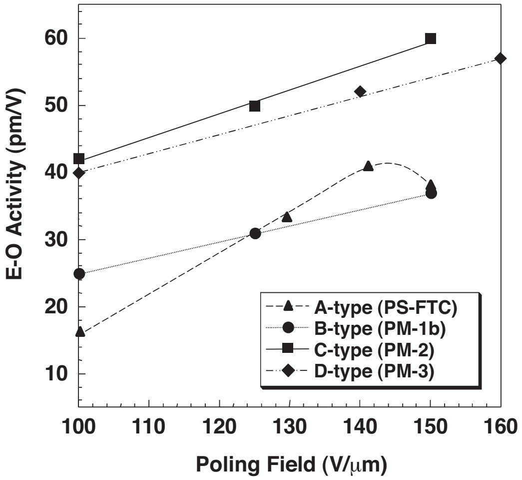

Figure 16.5 *Electric field-dependent poling behavior of different types of side-chain E-O polymers.*

promising alignment stability: more than 80% of their original r_{33} values were retained at 85 °C for more than several hundred hours (Figure 16.6).

Diels–Alder click chemistry can be also utilized in a solid state. As shown in Figure 16.7, the highly reactive anthracenyl **PMMA-AMA** was reacted with maleimide-containing NLO chromophores during the poling process to afford **PA08, PA16**, **PA21**, **PA25**, **PA28**, **PA32**, **PA34** and **PA39** respectively.[10] After adding more than 24 wt% of chromophore contents,

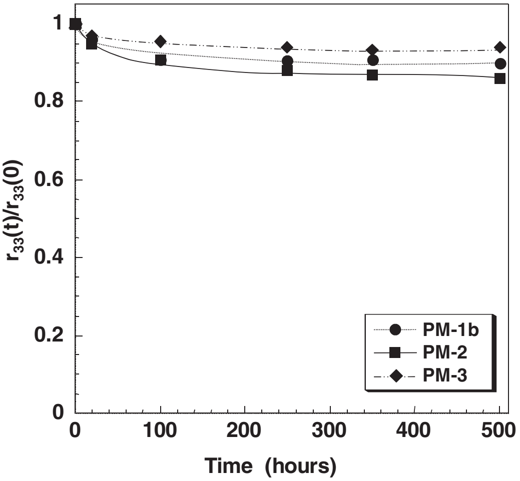

Figure 16.6 *Temporal stability of the side-chain E-O polymers at 85 °C. $r_{33}(0)$: initial r_{33} values; $r_{33}(t)$: r_{33} values at different baking time. Reprinted with permission from T.-D. Kim,* et al.*, (2006), Diels–Alder "Click-Chemistry" for highly efficient electrooptic polymers,* Macromolecules*,* ***39*** *(5), 1676. Copyright 2006 American Chemical Society.*

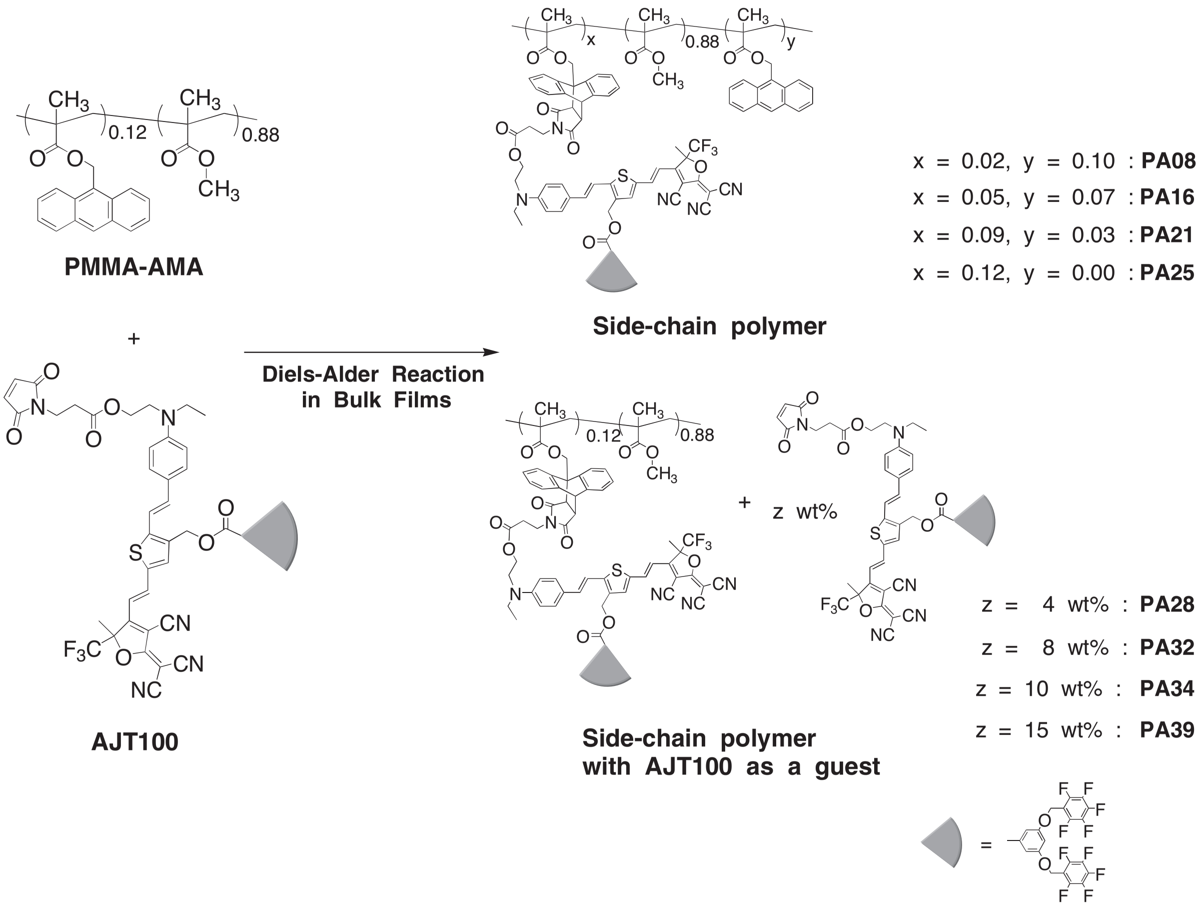

Figure 16.7 In-situ *generated side-chain E-O polymers by solid phase Diels–Alder click reaction. Reprinted with permission from J. W. Kang* et al.*, (2005), Very large electro-optic coefficients from* in situ *generated side-chain nonlinear optic polymers,* Applied Physics Letters, ***87*** *(7), 071109/1. Copyright 2005 American Institute of Physics.*

Table 16.1 *Physical and optical properties of the polymers*

Sample	Composition PMMA-AMA	Composition AJT100	Chromophore contents[a] (wt%)	Poling temperature (°C)	Applied voltage (V/μm)	r_{33}[b] (pm/V)
PA08	0.806	0.194	8	135	100	18
PA16	0.625	0.375	16	120	100	32
PA21	0.510	0.490	21	124	100	43
PA25	0.417	0.583	24	110	100	48
PA28	0.357	0.643	28	107	100	74
PA32	0.278	0.722	30	105	110	99
PA34	0.222	0.778	34	90	120	110
PA39	0.100	0.900	39	80	100	87

[a] The donor–bridge–acceptor core part of chromophoric contents (formula $C_{28}H_{21}F_3N_4OS$, molecular weight 518.6);
[b] E-O coefficient measured by simple reflection at the wavelength of 1.3 μm.

the unreacted chromophore remains as a guest in these systems. Very attractive features of this click reaction, which makes side-chain E-O polymers in the bulk state, are the use of no solvent, quantitative yields and regio-specifically formed adducts without any generation of by-products. As a consequence, it is possible to control the chromophore loading concentration in the polymers by adjusting the chromophore ratio. This system provides a means to afford side-chain E-O polymers with different chromophore concentration to determine its critical loading density at which electrostatic interactions occur in the polymer matrix. Furthermore, the clicked side-chain E-O polymers can act as hosts with unreacted guest chromophores above their certain loading density to form binary NLO polymeric systems.

Measured r_{33} values and poling conditions of these poled polymers are summarized in Table 16.1. Note that **PA21** polymer by the solid-phase reaction corresponds with **PM-3** prepared by the solution reaction. The data of r_{33} values and optimal poling temperatures for **PA21** are very reproducible and are in well agreement with **PM-3**. For an example, the r_{33} values of **PM-3** and **PA21** are 41 and 43 pm/V, respectively, under 100 V/μm of the poling field around 125 °C. The poled films of **PA34** have shown the highest r_{33} value (110 pm/V at 120 V/μm of a poling field). This value is extraordinary in such a high chromophore concentration when compared with other guest–host NLO systems. This behavior can be explained as follows: (1) dendron effects preventing the chromophore-chromophore electrostatic interactions; (2) the difficulty of the chromophore aggregation due to the structural shape; and (3) cooperative effects of binary polymeric systems converted to the side-chain E-O polymers with guest chromophores.

16.3 Diels–Alder Click Chemistry for Crosslinkable E-O Polymers Containing Binary NLO Chromophores[18,19]

Many studies of polymeric E-O materials have shown that lattice hardening approaches can significantly improve long-term alignment stability. However, a reduction of 20–40% in E-O activity is usually accompanied by such approaches, since typical poling of conventional thermoset E-O polymers is achieved through sequential lattice hardening and poling process, resulting in severely limited chromophore reorientation. The Diels–Alder cycloaddition reaction for the lattice hardening method can tune temperature windows for crosslinking and poling. This Diels–Alder reaction has been applied successfully in lattice hardening processes of E-O polymers with both high nonlinearity and thermal stability. We have extended the concept of binary systems into crosslinkable E-O polymers through Diels–Alder click reactions to further incorporate highly polarizable NLO chromophores. This combined effort demonstrates that binary mixtures of chromophores can be loaded into side-chain E-O polymers and efficiently poled to give E-O activities higher than the summed value of two added chromophores. These systems can also be mildly cured to ensure a thermally stable E-O response.

The crosslinkable E-O polymers containing binary chromophores exist as a three-component guest–host system (Figure 16.8): **PMMA-AMA** as a host polymer, guest chromophore **AJC146**, and secondary chromophore **1a**, **1b**, or **1c**.[18] The chromophores are functionalized with maleimido moieties, which can act as an active crosslinker to react with the anthracenyl side-chains on **PMMA-AMA**. After solid-state Diels–Alder click reactions, they form chromophore-embedded networks. **BMI**, 1,6-bismaleimidohexane, was also included as a passive crosslinker for a parallel comparison. After curing **PMMA-AMA/BMI/AJC146**, the main absorption bands (two major absorption sub-peaks, centered at the wavelengths of 799 nm and 951 nm) of **AJC146** remained unchanged when the same amounts of anthracenyl and maleimide groups were equivalent. However, it underwent a significant decrease in intensity (25–40%) if an excess amount of maleimide was used. This suggests that the anthracenyl group has a higher reactivity toward maleimide and can serve as a scavenger to prevent the polyenic chromophore from reacting with maleimide. In all cases, the chromophore absorption bands remained almost unchanged throughout the thermal curing and poling, indicating that good chromophore stability was achieved under a mild curing condition and carefully adjusted diene–dienophile ratios.

All poling processes were performed at temperatures of around 110 °C with a poling field ranging from 75 to 125 V/μm. Both poling fields and currents were monitored *in-situ* to optimize the entire process. All of the binary systems exhibited very large r_{33} values (up to 237–263 pm/V). However, it is hard to achieve more than 200 pm/V in a singular chromophore system even at higher chromophore loading levels. These results suggest the structural features for the chromophores and processing control desirable for binary systems. The shape of a guest chromophore, **AJC146**, is a roughly prolate ellipsoid while chromophoric crosslinkers (**1a**, **1b**, or **1c**) are Λ-shaped. During poling and annealing processing, such a combination of chromophores can minimize the formation of antiparallel or close head-to-tail centrosymmetric stacking between chromophores. Furthermore, chromophoric crosslinkers can provide further modification of the polymer hosts, through the *in-situ* Diels–Alder crosslinking, leading to better homogeneity and stability to additional polyenic chromophore dopants. In this process-induced morphological confinement, both guest chromophores and *in-situ* generated active polymer networks could respond cooperatively to the poling field. Side-chain E-O polymers can also crosslink with Diels–Alder reactions in the form of binary chromophoric systems.[19] Figure 16.9 shows a schematic illustration for chromophore aligning/lattice hardening processes from a side-chain E-O polymer **PM-AJL**. Side-chain chromophore contents were adjusted to 8 wt% with an anthracenyl group in PMMA-AMA to further crosslink the binary systems. A guest chromophore **AJL28** and passive crosslinker **TMI** were added with different concentrations to maximize poling efficiency and alignment stability. Direct spin-coating of the dissolved mixture in 1,1,2-trichloroethane (~8 wt%) gave high optical quality thin films,

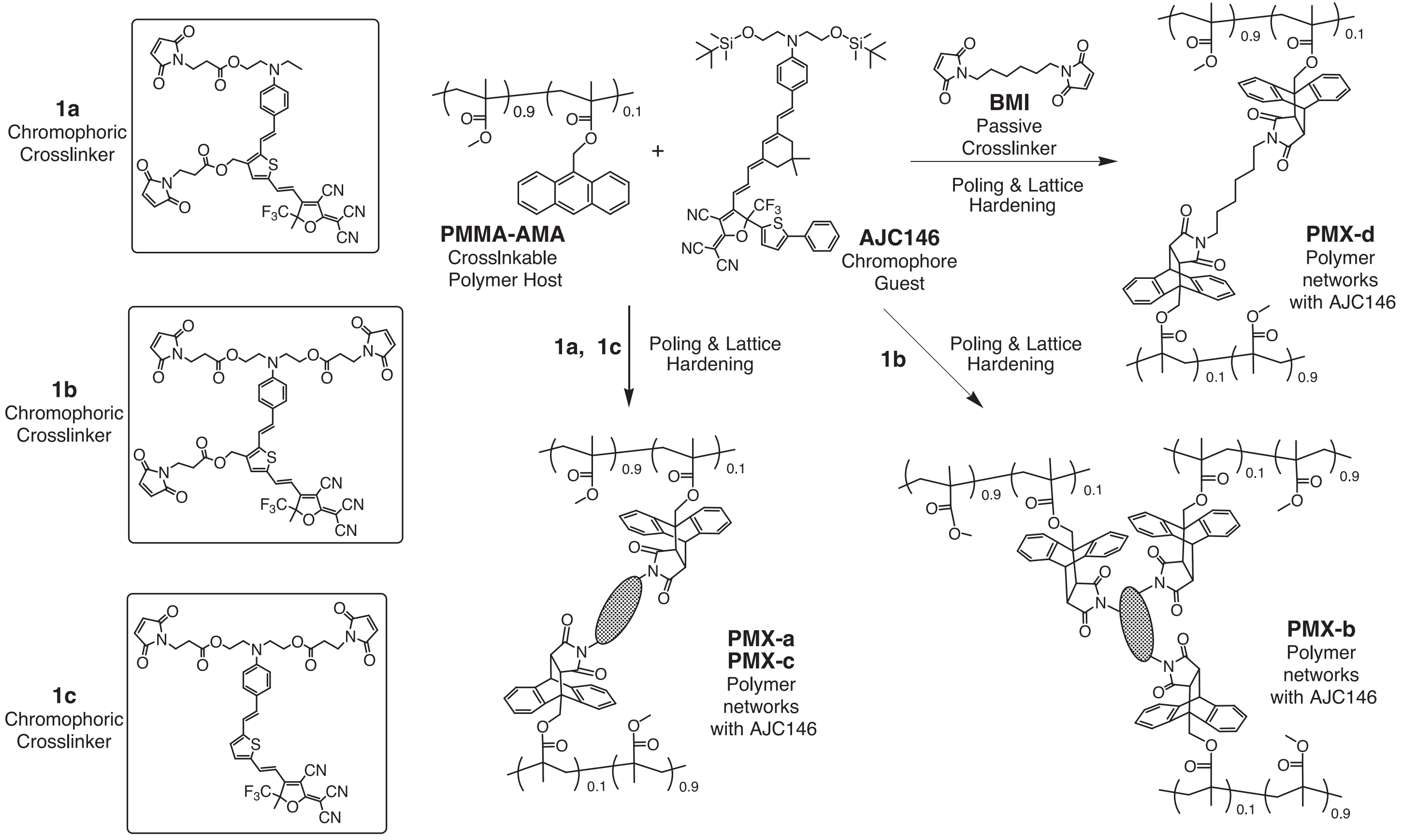

Figure 16.8 *In-situ poling and Diels–Alder click crosslinking of guest–host crosslinkable E-O polymers containing binary chromophores. Reprinted with permission from A. K.-Y. Jen, T.-D. Kim and J. Luo, (2006), Ultralarge and Thermally Stable Electro-optic Activities from Diels–Alder Crosslinkable Polymers Containing Binary Chromophore Systems,* Advanced Materials, ***18*** *(22), 3038–3042. Copyright 2006 Wiley-VCH.*

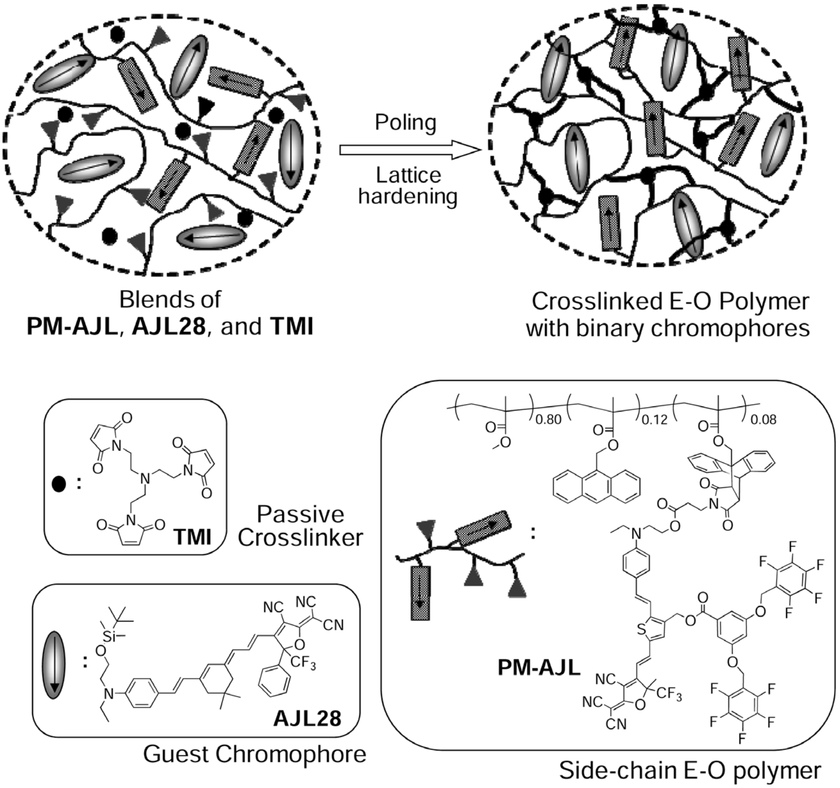

Figure 16.9 *A crosslinked E-O polymer in-situ generated by Diels–Alder click reaction in a side-chain E-O polymer with binary chromophores. Reprinted with permission from T.-D. Kim,* et al.*, (2008), Binary chromophore systems in nonlinear optical dendrimers and polymers for large electrooptic activities,* Journal of Physical Chemistry*,* ***112*** *(21), 8091. Copyright 2008 American Chemical Society.*

which were then subjected to the electric field to form a poled crosslinked polymer. We observed lowered poling efficiency at an excess amount of **TMI** due to polyenic chromophore decomposition by maleimide groups. The concentration of the side-chain chromophore can also affect poling efficiency in the binary crosslinked polymers. Careful control of **TMI** content (1–2 wt%) and side-chain chromophore concentration (8%) was taken into account to maximize EO activity and lattice hardening. A continuous increase in r_{33} values can be seen with the increase of guest chromophore **AJL28** in **PM-AJL**.

The highest r_{33} value of 387 pm/V was obtained for the film containing 30% of **AJL28**, which is significantly larger than that (198 pm/V) of singular guest chromophore **AJL28** in **PMMA-AMA**. This result suggests that binary chromophores in different morphological confinement can cooperatively respond to the poling field. The binary systems may also provide a unique nanoenvironment for enhancing local field factors. However, further increase in the chromophore contents led to saturation or decrease in E-O coefficients due to severe aggregation of chromophores. In addition, a poling voltage higher than 75 V/μm across the films resulted in catastrophic electrical breakdown. All crosslinked E-O polymers showed good thermal alignment stability. After an initial fast decay, *ca* 75% of these E-O activities could be maintained at 85 °C for over 500 h. This demonstrates that the binary systems can be efficiently poled and cured to form thermally stable E-O lattices. These results are again a great demonstration of the advantages offered by binary chromophoric systems combining with well-controlled lattice hardening and poling methodology via Diels–Alder click reactions.

16.4 Diels–Alder Click Chemistry for NLO Dendrimers[19,20]

E-O activities of NLO materials can be significantly improved by encapsulating the chromophore with substituents that can electronically shield the core and form spherical molecular shapes. In order to create a structurally more well-defined and stable NLO material, we have explored dendrimers with multiple dendritic chromophores branched out from a passive core unit. The most important advantage of NLO dendrimers is that the active volume fraction of chromophore can be maximized without phase separation and aggregation. It occurs easily in the guest–host polymeric systems when the chromophore is highly loaded. The dendrimers are also expected to have reproducible physical and optical properties with well-defined molecular structures.

Three-arm NLO dendrimers (**D3-PS** and **D3-DA**) were synthesized by post-esterification and Diels–Alder click reactions between the three branches of desirable core molecules and the chromophore precursors that are surrounded by perfluorinated-phenyl dendrons as the exterior moieties (Figure 16.10).[19] In case of **D3-PS**, the resulting *N*-acrylurea and anhydride by-products should be removed by repetitive precipitation after the condensation reaction. As described in Chapter 2, a trace amount of residual ionic impurities or by-products can significantly attenuate the effective poling electrical field and possibly cause the DC bias drift during device operation. To alleviate this problem, the Diels–Alder click chemistry was selected as an alternative for generating a new high-performance NLO dendrimers. In order to conduct Diels–Alder click reactions for the NLO dendrimer, a maleimide-containing NLO chromophore and an anthryl-containing diene core were prepared. The poled NLO dendrimer **PS-DA** was constructed by the Diels–Alder reaction during the poling in solid films.

The weight-percent of active chromophore content is 40% for **D3-PS** and 38% for **D3-DA**. The NLO dendrimers can be directly spin-coated to form a monolithic molecular glass without any prepolymerization process. Through an *in-situ* post-functionalization process during the electric field poling, a very large E-O coefficient ($r_{33} = 109$ pm/V) was achieved for **D3-DA**. This is significantly higher than the r_{33} value from **D3-PS** ($r_{33} = 79$ pm/V), which was prepared by catalyzed post-esterification condensation. This is due to easier alignment of dendronized chromophores before forming Diels–Alder adducts covalently bonded with anthracenyl core units. Electric fields were as high as 110 V/μm applied to the NLO dendrimer film. Furthermore the screening effect, provided by the peripheral groups of dendrimer allows the chromophores to be spatially isolated, and the large void-containing structure of dendrimers provides the needed space for efficient reorientation of the chromophores. The globular geometry of dendrimers is ideally suited for the spherical shape modification of chromophores. In terms of chromophore alignment stability, the

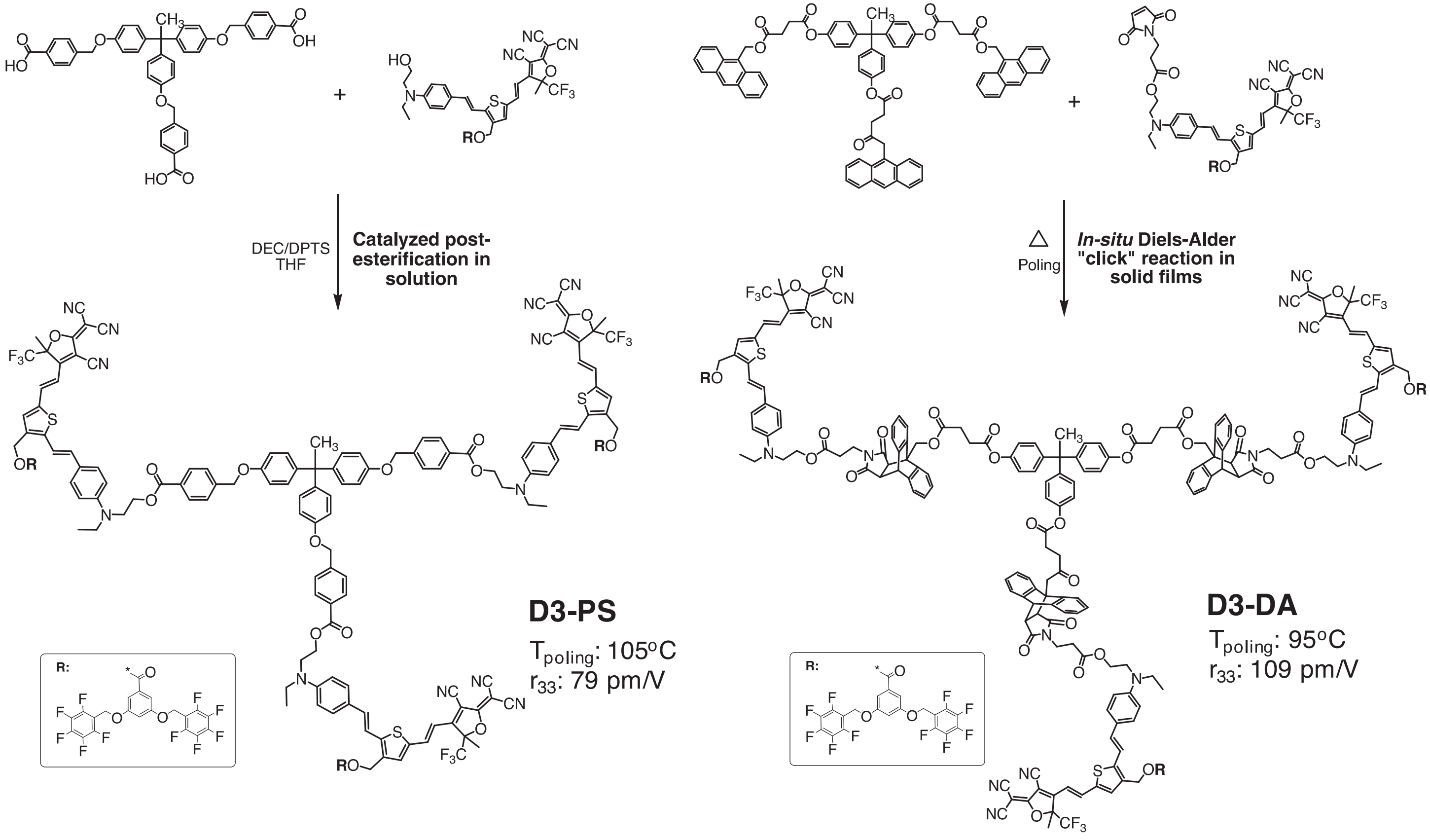

Figure 16.10 Synthesis and E-O activity of ***D3-PS*** and ***D3-DA*** for multiarm NLO dendrimers.

dendrimers showed very promising results, retaining more than 90% of their original r_{33} values after several hundred hours at 85 °C. Unfortunately we could not achieve any appreciable r_{33} values from **D3-DA** with additional guest polyenic-type chromophores due to chemical sensitivity of the polyenic chromophore towards the Diels–Alder reactions. However, since a polar substitution such as a methoxy group in the middle of the polyenic chromophore has provided significantly reduced dienic reactivity, we expect that improved poling efficiency and chemical stability are highly achievable in the NLO dendrimer systems afforded by Diels–Alder click reaction in the future.

Multidiene functionalized chromophores (**EOD1**, **EOD2**, **EOD3**, and **EOD4**), shown in Figure 16.11, were prepared to utilize Diels–Alder click reactions as a means of *in-situ* crosslinking for NLO dendrimers.[20] **EOD1–4** were obtained using the carbodiimide-mediated esterification between each dendronic acid and the dihydroxylated chromophore. These materials possess clear glass transition temperatures measured by DSC, which indicate amorphous solids. The processing temperature window for crosslinked NLO dendrimers can be controlled by tuning the electronic properties of the diene branches. In addition, the lattice-hardening of **EOD1–4** also converts the electron-rich dendrons into rigidified cyclic structures with far fewer electrons. This leads to a less polarizable environment. As a result, a considerable blue shift could be observed in their absorption spectra. Compared with the absorption maxima (λ_{max}) for **EOD4** (776 nm), the λ_{max} of the blend system (**EOD4** and **TMI**) blue-shifted 40 nm (to 736 nm) even before the thermal curing. This is attributed to the partial reaction between the reactive anthryl and maleimido groups.

The films were baked in a vacuum at 50 °C overnight to ensure the removal of any residual solvent. Although the baking temperature is well below the T_g of the dendrimers, all of the films prereacted to a certain extent during this step because of the highly reactive nature of the dienes and **TMI**. This reaction increases molecular weight and dielectric strength of the materials and leads to films with moderate solubility in organic solvents such as acetone. Moreover, the interchain Diels–Alder adducts can be thermally dissociated through the retro-Diels–Alder reaction. This can be tapped to further enhance the alignment of chromophores during poling. With all these dynamics encountered, the optimal poling temperature is strongly dependent on proper balance between their T_gs (after pre-crosslinking), T_{dis}s (dissociation) and T_xs (crosslinking) to accomplish high poling efficiency (Table 16.2). High-temperature and high-voltage poling could also be applied concurrently to increase lattice hardening. Upon removal of the electric field and cooling to room temperature, the poled films of **EOD1–3** showed large E-O coefficients (r_{33} = 63–99 pm/V), which are much higher than those from the guest–host EO polymer (**AJL8/APC**) or the uncrosslinked **EOD5**, which contains a similar chromophore. Over 90% of the original E-O activities could be retained at 100 °C for more than 500 h.

16.5 Conclusions

Our recent results from organic second-order NLO materials development have shown dramatically enhanced E-O activity compared with that of the past two decades. High-performance E-O polymers and dendrimers were demonstrated by a facile and reliable Diels–Alder click reaction for postfunctionalization and lattice hardening to improve EO

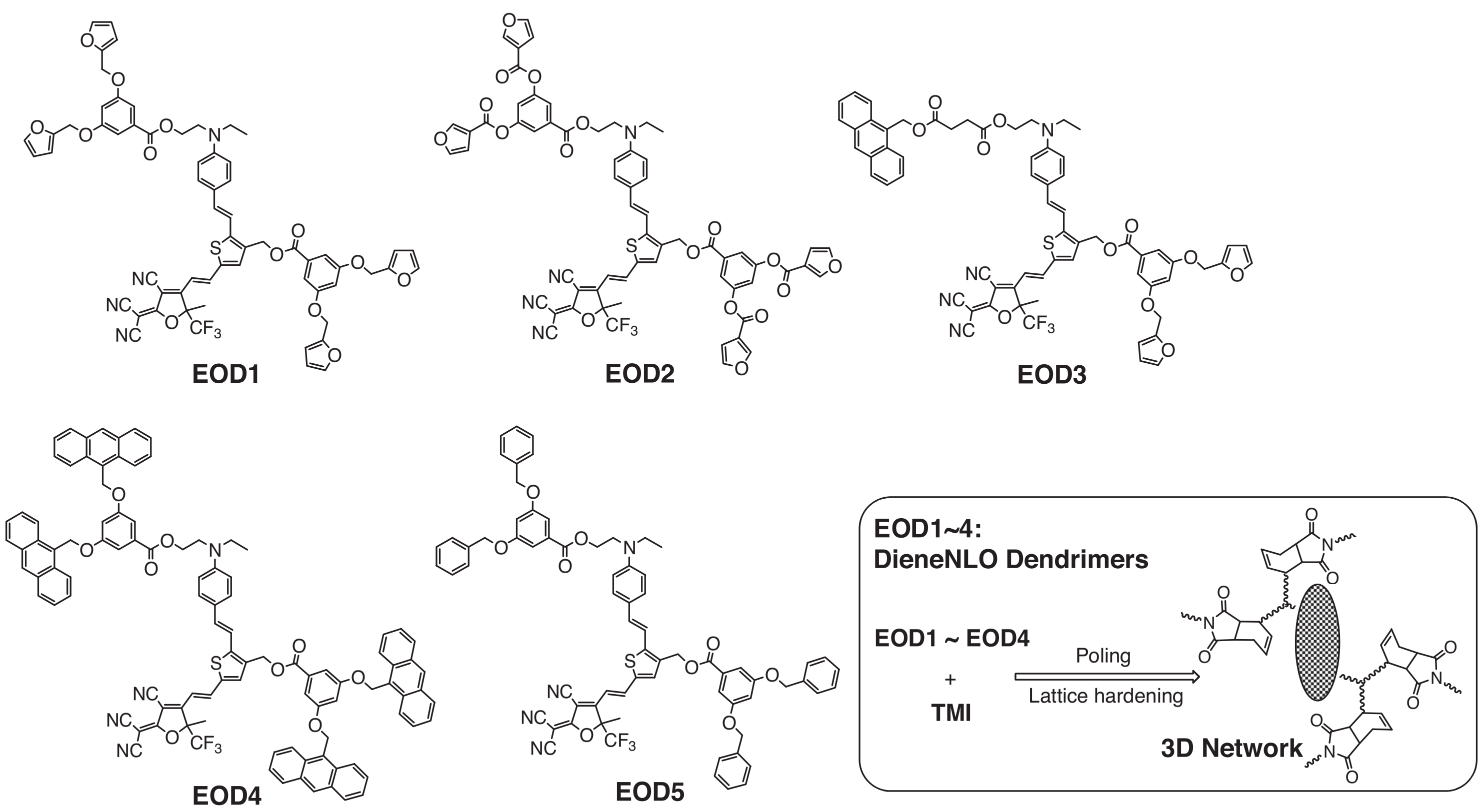

Figure 16.11 *Diene NLO dendrimers (**EOD1**, **EOD2**, **EOD3**, and **EOD4**) and a Fréchet–dendron chromophore (**EOD5**) for Diels–Alder reactions to form a 3D network. Reprinted with permission from A. K.-Y. Jen,* et al.*, (2007), Highly efficient Diels–Alder cross-linkable electro-optic dendrimers for electric-field sensors,* Advanced Functional Materials, ***17*** *(14), 2557–2563. Copyright 2007 Wiley-VCH.*

Table 16.2 *Summary of the physical properties of NLO dendrimers EOD1–5*

	Dye content[a] (wt%)	λ_{max}[b] (nm)	λ_{max}[c] (nm)	T_g[d] (°C)	T_x[d] (°C)	T_{dis}[d] (°C)	T_{dec}[d] (°C)	Poling voltage (V/μm)	Poling temperature (°C)	r_{33} (pm/V)	Temporal stability[e] (%)
EOD1	31.9	721	714	62	93	124	181	110	130	99	99
EOD2	30.9	708	706	102	136	167	169	75	115	63	90
EOD3	34.7	742	716	73	93,134	120	155	120	120	87	94
EOD4	25.3	776	724	154	RT to 65	>200	245	—	—	—	—
EOD5	40.1	719	—	57	—	—	200	60	60	52	—
AJL8/APC	15.8	711	—	140	—	—	—	100	140	40	80

[a] Net weight percentage of chromophore within dendrimers.

[b] The wavelengths of the absorption maxima for the sample without **TMI**.

[c] The wavelengths of the absorption maxima for the sample with **TMI**.

[d] Analytic results of DSC at the heating rate of 10°C/min on thermo-equilibrate samples: T_g, glass transition temperatures; T_x, onset crosslinking temperatures; T_{dis}, onset dissociation temperatures of retro-Diels–Alder reactions; T_{dec}, onset decomposition temperatures.

[e] Temporal stability after isothermal heating at 100°C for 500 h.

activity and thermal stability. The systematic exploitation of a nanoscale architecture control approach and supramolecular self-assembly has created a series of amorphous molecular NLO materials, combining well-defined properties of small molecules with facile processability. With these novel approaches, the E-O coefficients of a series of nanoengineered materials have reached ∼380 pm/V, which is more than one order of magnitude higher than that of the state-of-the-art inorganic material, lithium niobate. These materials also possess excellent thermal stability and optical transparency, which are suitable for the implementation into novel opto-electronic and photonic devices. This significant breakthrough will lead to a new paradigm of developing high-bandwidth, low-energy-consumption and light-weight devices for telecommunications, computation and sensing applications.

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