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Dipolar Chromophore Facilitated Huisgen Cross-Linking Reactions for Highly Efficient and Thermally Stable Electrooptic Polymers

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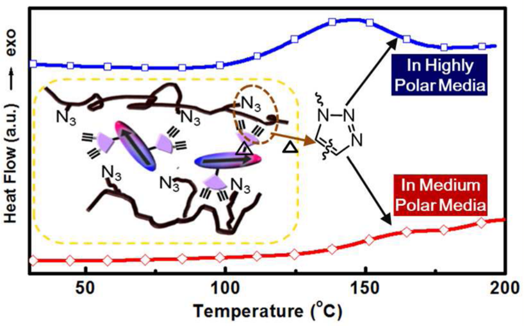
Supporting Information

ABSTRACT: Efficient thermal cross-linking protocol for an azide−alkyne-based Huisgen 1,3-dipolar cycloaddition reaction has been developed for making highly efficient electrooptic (EO) polymers. The material system is based on an azide-containing side-chain copolymer and cross-linkable dendronized chromophores that have two pairs of dendritic bispropargyl ether moiety on the periphery. The dendritic chromophore possesses a tetraene conjugating bridge and strong dialkylaminophenyl donor and CF_3−TCF acceptor. This material system not only provides adequate accessibility for propargyl ether to react azido-containing moieties for efficient cross-linking but also gives the rotational freedom needed for electric field poling. The site isolation offered by the bispropargyl ether dendron effectively suppresses the unwanted side reactions that are usually associated with the decompositions of azides and chromophores. Due to these concerted efforts, it allows the Huisgen 1,3-dipolar cycloaddition reactions to be carried out at moderate temperatures in polar media that have a high concentration of dipolar polyene chromophores. Through sequential electric field poling and in situ cross-linking, the poled films exhibit very large EO activity (up to 147 pm/V at 1.31 μm) with a long-term alignment stability at 85 °C.



Controlling the local environment of an electroactive or a photoactive moiety containing materials has been proven to be an efficient approach for modulating their properties in the bulk.[1] In particular, proper encapsulation with dendritic moieties to provide site isolation of highly dipolar nonlinear optical (NLO) chromophores has been proven as an effective method to alleviate their strong intermolecular electrostatic interactions. This facilitates efficient electric field poling to achieve large electrooptic (EO) coefficients (r_{33} values) of poled polymers.[2] Equally important but less explored is the way to efficiently apply in situ cross-linking chemistry into these dendron-containing NLO materials to preserve their poling-induced polar order.[3]

To serve as an effective cross-linking protocol for large r_{33} EO polymers, the reaction needs to be rapid, efficient, catalyst-free, and inert to highly polarizable but chemically sensitive chromophores.[3c] More importantly, it is highly desirable to be able to tune the rate of cross-linking reaction to avoid precross-linking prior to the poling process.[3] In this context, only very limited numbers of thermal cross-linking reactions are available to be deployed. Recently, Diels−Alder (DA) and Huisgen 1,3-dipolar azide−alkyne cycloadditions have been employed for making high-performance EO polymers.[4,5] In many respects, the Huisgen 1,3-dipolar cycloaddition and the DA cycloaddition reactions share similar features. Both reactions involve a concerted 6π-electron pericyclic mechanism between two reactants,[6] namely, the diene/dienophile pair for DA and 1,3-dipole/dipolarophile pair for Huisgen cycloaddition. The dependences of reactivity and regioselectivity of reaction on the electron densities of these reactants are essentially the same.

However, the major differences between two types of reactions have not been well-elucidated regarding how the in situ reactions affect the electronic and orientational polarization of NLO chromophores or vice versa. By forming cycloadducts and going through structural reorganization, these two types of reactions can impose very different effects on the local dielectric environments of the chromophores. For example, the DA reaction usually forms cycloadducts with reduced polarizability compared to its conjugated reactants (such as the anthracenyl derivatives).[6a] On the contrary, the azide−alkyne-based Huisgen cycloaddition, starting from 1,3-dipole mesomeric structures with low polarity, can produce aromatic (thus more polarizable) triazole moieties with a sizable permanent dipole moment of ~5 D.[6b] In the literature, there is very little information regarding the influence of dipolar chromophores on in situ cycloaddition reactions.[7] As one of the major molecular characteristics, chromophores with large hyperpolarizability (β) tend to possess very large dipole moments (μ, up to 40 D in the condensed state),[3] which can significantly

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influence the dielectric surrounding and the kinetics and energetics of cross-linking reactions.

For azide−alkyne-based Huisgen cycloaddition to be used for cross-linking EO polymers, the stability of azides and their possible side reactions with chromophores are of primary concern. Results from the kinetics study of Huisgen reactions have shown that this type of reaction usually requires relatively high temperatures (up to 150−190 °C) to overcome the activation energy barrier ($\Delta G^{\neq}$ up to 26 kcal/mol) when there is no catalyst used.[8,9] However, the possible decomposition of azide at such high temperatures to generate reactive nitrenes tends to create many side reactions.[8c,10] The required high reaction temperatures also pose some complications in implementing Huisgen reactions as the cross-linking protocols for EO polymers that possess highly nonlinear chromophores. Due to large β values (over $6000\cdot10^{-30}$ esu at 1.9 μm), these chromophores are essential as the active component for high-performance EO materials and devices; however, they only have a rather limited thermal stability.[2b] Furthermore, strong charge transfer of these molecules renders them very susceptible to reactions with diene/dienophile and dipole/dipolarophile moieties.

In this work, we report examples of highly efficient cross-linkable EO polymers (AJP12/EOD1 and AJP12/EOD2) to tackle these challenges. As shown in Figure 1, the material system is based on blending two cross-linkable dendronized chromophores EOD1 and EOD2, having two pairs of dendritic bispropargyl ether moieties on the periphery together with an azide-containing side-chain copolymer AJP12. The dendritic central core is based on a large β push−pull chromophore with a tetraene conjugating bridge and strong dialkylaminophenyl donor and CF_3−TCF acceptor. This material system provides not only adequate accessibility between reactive propargyl ether and azido moieties for efficient solid-state reactions, but also rotational freedom needed for electric field poling of dipolar chromophores. The nanoscale site isolation offered by the bispropargyl ether dendron effectively suppresses the unwanted side reactions, such as the reactive azides caused chromophore decomposition. These concerted efforts facilitate the Huisgen 1,3-dipolar cycloaddition reactions to be carried out at modest temperatures in the presence of dipolar chromophores. Through sequential electric field poling and in situ cross-linking, the poled films of these polymers exhibit very large EO activity (up to 147 pm/V at 1.31 μm) with remarkable long-term alignment stability (>90% of the initial r_{33} value could be retained after 500 h at 85 °C).

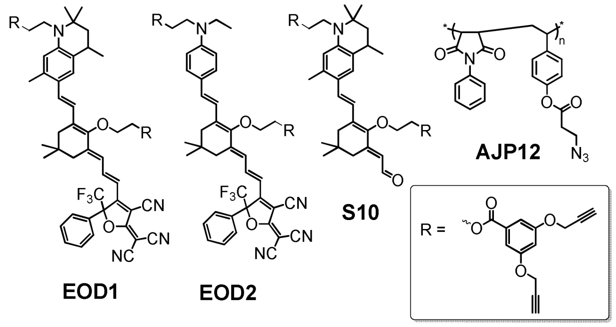

Figure 1. Chemical structures of cross-linkable dendronized NLO chromophores EOD1 and EOD2, the bridge precursor S10, and the copolymer AJP12.

Two dendronized chromophores, EOD1 and EOD2, were synthesized in good yield by reacting the precursor bridge aldehydes with a CF_3−Ph−TCF acceptor, respectively. Both of the resulting chromophores are amorphous with clear glass transition temperatures (T_g) at 71 °C and 60 °C, respectively. The alternating copolymer AJP12 was obtained with 87% yield through the radical polymerization of the azido-functionalized styrene and *N*-phenyl maleimide using 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator. The number-average molecular weight (M_n) of AJP12 is 47 700 Da with a polydispersity of 2.88 measured by gel permeation chromatography (GPC). The presence of the azide group was confirmed by its Fourier transform infrared (FTIR) spectrum with the asymmetric stretching band of azide around 2102 cm^{-1} and by the ^{1}H NMR spectrum with the chemical shift of CH_2N_3 peak at 3.75−3.43 ppm. The information can also be used to verify the corresponding molar ratio of the copolymer. The study of differential scanning calorimetry (DSC) indicates that no obvious T_g can be observed up to 150 °C for AJP12. However, a decent exothermic peak can be found between 160 and 210 °C, which is ascribed to the thermal decomposition of the azide moiety.

To investigate the influence of dipolar chromophores on the reactivity of Huisgen cycloaddition reaction, EOD1 and its precursor S10 were mixed with AJP12 in a 1:1 molar ratio between azide and alkyne moieties to obtain binary embodiments of AJP12/EOD1 and AJP12/S10, respectively. Figure 2 shows the DSC study of the reaction kinetic behavior of AJP12/EOD1 and AJP12/S10 in the solid state. The DSC trace of AJP12/EOD1 shows a distinct unimodal exothermic peak from ~90 to 175 °C with a peak temperature (T_{max}) at 145 °C, which corresponds to the Huisgen cycloaddition reaction between the azide and alkyne moieties. It is worthy to note that this range of reaction temperatures is similar to or even lower than the typical temperatures observed for such reactions without metal catalysts.[5b,11]

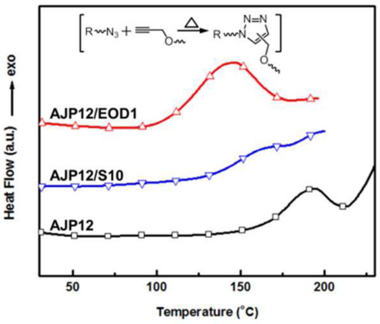

Figure 2. Thermal analysis of AJP12/EOD1 and AJP12/S10 using DSC at a ramping rate of 10 °C/min under nitrogen.

This implies that the reaction's activation energy barrier has been decreased considerably in the presence of large β chromophores. This temperature range is also lower than the individual thermal decomposition temperature of AJP12 and EOD1/2, which can minimize potential side reactions during the cross-linking of these polymers. In stark contrast, no obvious exothermic peak was found for AJP12/S10 until the temperature was ramped to around 135 °C, which is considerably higher (~45 °C) than the onset reaction temperature of AJP12/EOD1. The shifted bimodal DSC peaks in the spectrum of AJP12/S10 are probably due to the

Huisgen cycloaddition reaction superimposed with the decomposition of the azide moiety. The direct comparison of DSC spectra for AJP12/EOD1 and AJP12/S10 showed that in the presence of large β chromophoric (more polar) moiety, the azide–alkyne-based Huisgen 1,3-dipolar cycloaddition could be activated at these modest temperatures and proceeded in a much more expeditious manner without the complication of other side reactions.

To verify the above analysis, the thin films cast from AJP12/EOD1 and AJP12/S10 were isothermally cured at 120 °C for 5 min. The temperature and time scale of this curing condition are similar to those used for poling, since the chromophore dipoles need to be aligned with the applied electric field prior to the cross-linking reaction. The progression of reactions was monitored by the change of the characteristic peaks in their FTIR spectra upon curing. The relative intensity of the asymmetric stretching vibration (ν_{as}) of the azide group at around 2102 cm^{-1} and the distinguished strong terminal alkyne stretching band at 3300 cm^{-1} were carefully followed. For AJP12/EOD1, both characteristic bands of azide and terminal alkyne moieties in the spectra of the cured sample decreased significantly by 60–70% (Figure 3).

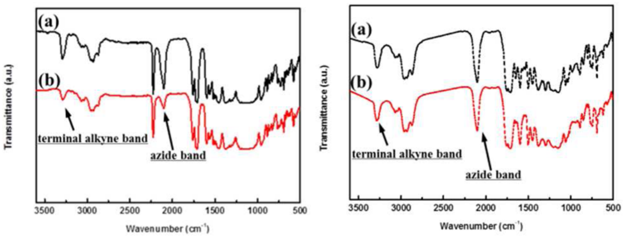

Figure 3. FTIR spectra of AJP12/EOD1 (left) and AJP12/S10 (right): (a) before the curing, and (b) after the curing at 120 °C for 5 min.

This curing process also converted the highly soluble AJP12/EOD1 composite into robust films with excellent solvent resistance that can withstand polar solvents like tetrahydrofuran (THF), trichloroethane (TCE), and acetone. These results indicate that a very efficient cross-linking reaction occurred between azide and alkyne moieties in the solid state. On the contrary, the distinct stretching bands of azide and alkyne groups in the spectra of AJP12/S10 films only underwent minor changes after curing, implying the ineffectiveness of the Huisgen 1,3-dipolar cycloaddition reaction under the same curing condition. This analysis supports the hypothesis that the high concentration of dipolar polyene chromophores provides a polar media to facilitate the cross-linking via 1,3-dipolar cycloaddition. It is also consistent with previous studies of the solvent effect on 1,3-dipolar cycloaddition, which showed rate enhancement from nonpolar solvents to dipolar aprotic solvents as a result of increased dipole moment of the transition structure relative to the reactants.[6b,8]

In addition to reaction efficacy, the structural integrity of dipolar polyene chromophores against highly reactive azide species during reaction is equally important. The FTIR spectra clearly showed that the characteristic stretching band of the cyano group at 2226 cm^{-1} in AJP12/EOD1 films remained almost unchanged after thermal curing at 120 °C for 5 min (Figure 3). As a more quantitative tool, the UV–vis–NIR spectroscopy study was conducted to evaluate the stability of chromophore in the presence of numerous azide groups in these cross-linked polymers. The cured films of both AJP12/EOD1 and AJP12/EOD2 showed nearly unchanged π–π^* intramolecular charge transfer (ICT) band in terms of its position, band shape, and peak absorbance (Figure S1, Supporting Information (SI)). Furthermore, the neat mixture of EOD1 and methyl azidoacetate (MAA) at a 1:1 molar ratio was cured at 120 °C for 5 min, and its ^{1}H NMR spectrum was taken (Figure S2, SI). This measurement showed the sustainance of peaks that are associated with the chromophore backbone and the appearance of new peaks in the 5.1 to 5.3 ppm region. The latter corresponds to methylene substitution on the triazole rings that are derived from the methylene azido group of MAA with an upfield NMR peak at 3.8 ppm. These new methylene proton peaks reveal the formation of mixed 1,4- and 1,5-regioisomers of triazoles. All of these analyses clearly show that the potential chemical attacks of very reactive azide to dipolar polyene chromophores are effectively suppressed in these EO materials.

To study the influence of in situ thermal Huisgen reaction on poling efficiency and EO properties of polymers, the formulated TCE solutions of AJP12/EOD1 and AJP12/EOD2 (with 9 wt % solid content) were filtered through a 0.2 μm PTFE syringe filter and spin-coated onto indium–tin–oxide substrates to afford micrometer-thick films. The films are in high optical quality, and the morphology study by atomic force microscopy (AFM) showed the films are homogeneous with low surface roughness (Figure S3, SI). After being baked overnight at 50 °C under vacuum to remove the residual solvent, a thin layer of gold was sputtered onto the films to function as a top electrode for contact poling.

With an externally applied voltage of 100 V/μm, the films were heated from 70 to 120 °C with a ramping rate of 10 °C/

Table 1. Summary of Physical Properties of AJP12/EOD1 and AJP12/EOD2, along with Related Parameters

material entries	N of dye[a] ($\times 10^{20}$ cm^{-3})	λ_{max} (nm)[b]	T_g[c] (°C) host	T_g[c] (°C) guest	T_{dec}[c] (°C)	poling field (V/μm)	poling temp.[d] (°C)	r_{33}[e] (pm/V) at 1.31 μm	alignment stability at 85 °C[f] (%)
AJP12/EOD1	2.20	860	>150	71	204	100	120	147	93
AJP12/EOD2	2.26	792		60	201	100	120	123	93

[a] N is the number density of loaded chromophores. $N = N'w\rho/M_w$, where N' is Avogadro's number, w is the weight percentage of dendritic chromophores in material entries, M_w is the molecular weight of the chromophore, and ρ is the density of material (with the assumption of ρ = 1.0 g/cm^3). [b] Wavelengths of the absorption maxima on thin film after curing. [c] Analytic results of DSC at a heating rate of 10 °C/min on thermo-equilibrated samples under nitrogen: T_g, glass transition temperature; T_{dec}, onset decomposition temperature. [d] Optimum poling temperature for the poling field. [e] Initial EO coefficients, r_{33}, measured by a simple reflection technique at 1.31 μm. [f] The percentage of r_{33} values remaining after isothermal heating at 85 °C for 500 h under nitrogen.

min under nitrogen. Once the temperature reached 120 °C, the films were cooled to room temperature, and the poling field was removed. The r_{33} values of the poled and cured films were measured by using the modified Teng–Man simple reflection technique at the wavelength of 1.31 μm.[12] These poled films showed excellent poling characteristics and very large r_{33} values with 147 pm/V and 123 pm/V obtained for AJP12/EOD1 and AJP12/EOD2, respectively, as tabulated in Table 1.

The temporal alignment stability of these cross-linked EO polymers was tested by isothermal heating at 85 °C. After the initial minor decay (~7%), the r_{33} values stayed almost unchanged for more than 500 h. To test thermal stability of these films at even higher temperatures, the poled samples were sequentially exposed to temperatures of 100, 110, 120, and 130 °C for 30 min at each temperature. Both of the cross-linked films of AJP12/EOD1 and AJP12/EOD2 retained >78% of their original r_{33} values after these thermal excursions, which testifies the efficient cross-linking between azide and alkyne.

In summary, our study clearly showed that nanoscale architectural control and polar media effect could be exploited to facilitate thermal Huisgen cycloaddition for efficient poling and cross-linking of new high performance EO polymers. These poled polymers exhibit very large EO activity (up to 147 pm/V at 1.31 μm) with remarkable long-term alignment stability at elevated temperatures. We expect that such polar media facilitated in situ Huisgen reactions be generally applicable to the design and synthesis of new cross-linkable organic π-functional materials for photonic and electronic applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and additional characterization not included in the manuscript (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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