Scope and limitation of the copper free thermal Huisgen cross-linking reaction to stabilize the chromophores orientation in electro-optic polymers

Submitted by Clément Cabanetos on Mon, 06/01/2015 - 14:28

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Type de publication
Article de revue

Auteur
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Pays
Royaume-Uni

Editeur
Royal Society of Chemistry

Ville
Cambridge

Type
Article scientifique dans une revue à comité de lecture

Année
2011

Langue
Anglais

Date
Janv. 2011

Numéro
1

Pagination
157-167

Volume
2

Titre de la revue
Polymer Chemistry

ISSN
1759-9954
New methacrylate copolymers incorporating two complementary thermally cross-linkable groups (azide or ethynyl) for implementation in electro-optic devices were synthesized and their nonlinear optical properties were investigated. These copolymers were prepared from a monomer containing Disperse Red 1 (DR1) as active NLO chromophore which is end substituted either by an azide or ethynyl group connected via a rigid (phenyl) or flexible spacer (alkyl chain). The second monomer is either a trimethylsilyl-propargyl methacrylate, or an azidopropyl methacrylate or a trimethylsilyl-phenyl methacrylate. The determination of the reactivity ratios showed that the monomer containing the DR1 chromophore is more reactive than trimethylsilyl-propargyl methacrylate. The cross-linking temperatures of these polymers range from 150 °C to 187 °C depending on the rigidity of the spacers connecting the cross-linkable units. These polymers displayed relatively high macroscopic electro-optic stability, enhanced upon cross-linking by more than 40 °C relative to non-cross-linked polymers. The results underscore the importance of the flexibility of the spacers to achieve the stable bulk electro-optic response. While rigidity is favorable to maintain the orientation of the chromophores, the optimal polymer is the one containing a flexible and a rigid spacer, since the mobility of the reactive groups is a key parameter which guarantees a high cross-linking conversion within the polymer. This study demonstrates the versatility of this new cross-linking process because we showed that the reactive groups (azide or trimethylsilylacetylated groups) can be interconverted (on the chromophore or as polymer side chain) with no change on the overall electro-optic activity and its thermal stability. Furthermore, preliminary kinetic study indicates that the Huisgen reaction rate can be controlled by the substituent on the ethynyl group opening the possibility to tune the cross-linking temperature by the careful choice of this substituent.

DOI 10.1039/C0PY00203H [10]
Titre abrégé Polym. Chem.

Liens

Publié sur Okina (http://okina.univ-angers.fr)