

Dynamic furan/maleimide bond-incorporated cyclic polymer for topology transformation



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ABSTRACT

The transformation of polymer topological structures by using an external stimulus has gained increasing attention because it is a versatile method to modify the properties of polymeric materials. Herein, cyclic poly(methyl methacrylate) linked by a dynamic covalent furan/maleimide bond was rationally designed and prepared. SEC, FTIR, NMR, and MALDI-TOF characterizations all confirmed the successful preparation of the polymer. By using the (retro)Diels-Alder reaction at a high temperature (110 °C), the cyclic polymer was transformed to a linear monopolymer or linear multiblock polymer. In addition, the cyclic topology can also be fixed by eliminating the vinyl double group of furan/maleimide adduct by the photoinduced radical thiol-ene reaction. This work provides a novel and facile approach for cyclic-to-linear topological transformation, and many potentials based on this thermal-responsive polymer are envisioned.

1. Introduction

It is well known that the topology of a given polymer has significant effects on the properties and performance of the polymer [1]. During the past decades, the cyclic topology has attracted more and more attention because of its some specific properties and functions. For example, compared with its linear counterpart, the cyclic polymer usually has higher glass transition temperature, lower melt viscosities, smaller hydrodynamic volume, and higher refractive index because of the lack of polymer chain ends [2–10]. However, stimuli-responsive polymeric materials, which can respond to external stimuli such as light, heat, pH, and redox environment, have received great attentions because their various applications including sensors, self-healing materials, and drug delivery systems [11–20]. Among them, the cyclic-to-linear topological transformation has gained great importance because the topological changes in polymers usually induce some changes in their properties. Some elegant works have been reported on this issue. Recently, Yamamoto et al. synthesized several kinds of telechelic polymers that contain anthryl or coumarin end groups and triggered the reversible linear–cyclic topological transformation by using light or heat [21]. The photoinduced cyclic-to-linear topological conversion of polylactide, which contains *o*-nitrobenzyl groups as photocleavable linkers, was well illustrated by Tezuka et al. They found that T_m of the resulting linear stereocomplex polymer was 40 °C higher than that of

the cyclic precursor and that the properties of polylactide homocrystals were affected by the topological transformation as well [22]. Deffieux and coworkers demonstrated the reversible conversion between linear and cyclic poly(ethylene oxide)s with iron tetraphenylporphyrin ends stimulated by redox, solvent, and pH. This rapid conversion could be indicated by the color change of polymer solution [23,24]. Monteiro et al. achieved monocyclic and linear multiblock polystyrene chains, which are linked by cleavable disulfide bonds. The monocyclic and linear multiblock polystyrene chains can be recovered to their linear precursors easily by using reversible redox-responsive thiol/disulfide groups [25]. Reversible hydrogen bonding was used by Barner-Kowollik to realize the folding/defolding of single polymer chains by tuning the temperature [26]. Our group reported the photoinduced reversible transformations between single diselenide bond-incorporated monocyclic polystyrene chain and multidiselenide bond-incorporated multiblock cyclic chain by manipulating the polymer concentration. Both of them could be transformed to the linear precursor, and the transformation can be triggered by redox stimuli [27]. Tang and coworkers illustrated applications based on the cyclic-to-linear topological transformations. The photoinduced transformation from cyclic morpholino oligomers to linear counterparts could be applied to control gene expression [28,29].

It is well known that furan/maleimide-based Diels-Alder reaction has gained great attentions for its characteristic of thermal reversibility.

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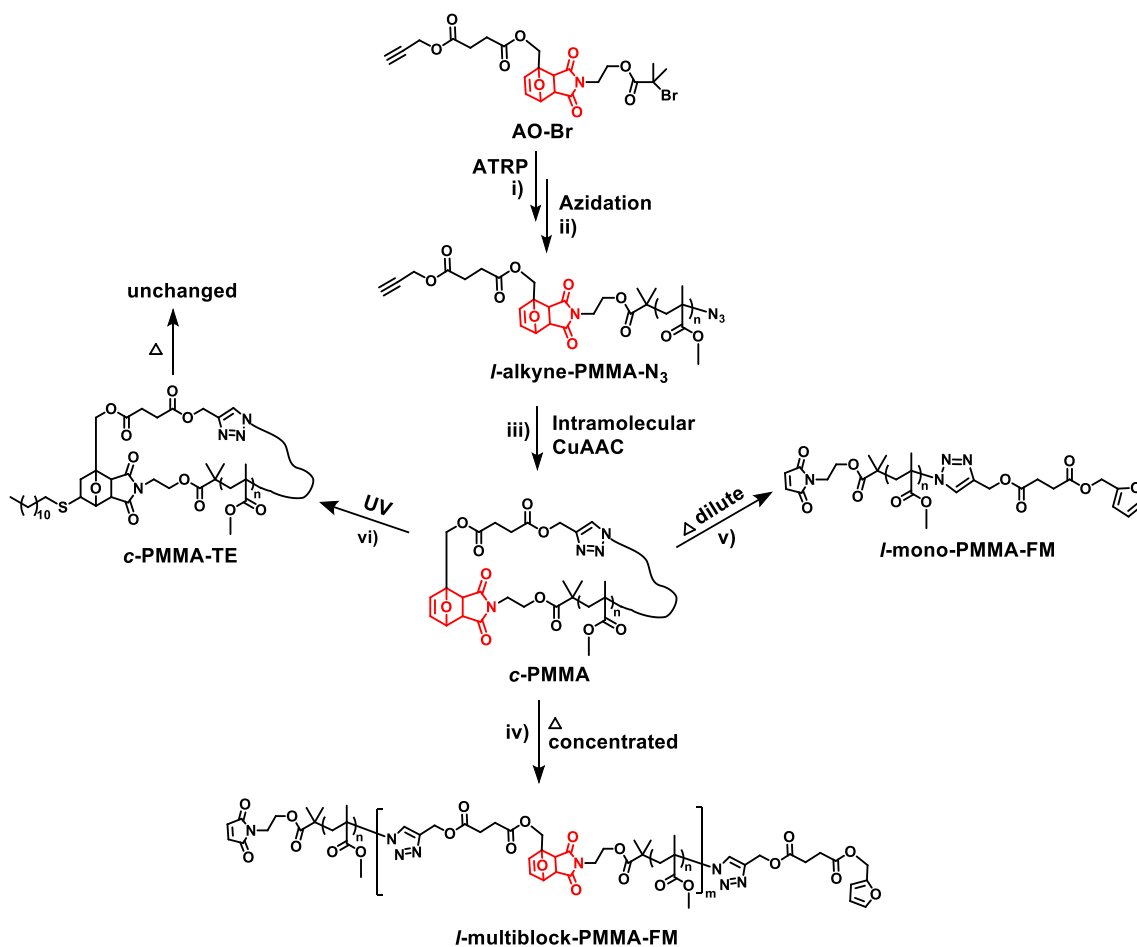
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At a low temperature (60 °C), furan can react with maleimide to form the furan/maleimide adduct (dynamic furan/maleimide bond), which regenerates the reactants by heating (110 °C), i.e., (retro)Diels-Alder reaction [30–32]. Thus far, the thermally reversible Diels-Alder reaction has been used for various applications such as thermal sensors, recyclable materials, and self-healing materials [33–38]. For example, based on the reversible Diels-Alder reaction, a kind of biodegradable shape-memory elastomer was achieved by Chujo et al. [39] Bowman et al. illustrated the 3D photofixation lithography by using reversibly cross-linking Diels-Alder networks [40]. In the present study, we introduced dynamic Diels-Alder motifs into the polymer chain to induce the cyclic-to-linear transformation. First, we synthesized a cyclic poly (methyl methacrylate) (PMMA) chain, wherein the furan/maleimide dynamic covalent bond was embedded. The transformations from cyclic PMMA to linear multiblock polymer and linear monopolymer were then realized by manipulating the reaction temperature and concentration of the polymer. Furthermore, the cyclic PMMA was postmodified successfully by photoinduced radical thiol-ene “click” reaction on the vinyl bond of furan/maleimide adduct; therefore, the (retro)Diels-Alder reaction was stopped, and the thermally stable PMMA ring was obtained. The synthetic routes of the cyclic polymer and the topological transformation of the polymer are illustrated in Scheme 1. The present study offers a novel cyclic–linear topological transformation and can enrich the research on cyclic polymers and its related area.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA, $\geq 98\%$) was inhibited during storage, and the inhibitor was removed from it by neutral alumina column chromatography. Cuprous bromide (CuBr, Aldrich, 98%) was freshly purified by stirring it in acetic acid overnight, washed with acetone, and dried in vacuum. 2-Bromoisobutyryl bromide (Macklin, 98%), propargyl alcohol (AR, $\geq 97\%$), cuprisorb (Seachem), furfuryl alcohol (Energy Chemical, 98%), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, Energy Chemical, 99%), cupric bromide (CuBr₂, Aldrich, 99%), sodium azide (NaN₃, Aldrich, $\geq 99.5\%$), 1-dodecanethiol (SCR, $\geq 98\%$), and 2,4,6-trimethylbenzoyldiphenyl phosphine oxide (TPO) were used as received. Anhydrous dichloromethane was freshly collected from an Innovative Technology PS-MD-5 solvent purification system. 2-Aminoethanol ($\geq 99\%$), sodium bicarbonate (NaHCO₃, $\geq 99.5\%$), anhydrous sodium sulfate (Na₂SO₄, $\geq 99\%$), sodium hydrogen sulfate (NaHSO₄, $\geq 99\%$), anhydrous methanol ($\geq 99.5\%$), neutral alumina, and petroleum ether were purchased from Chinasun Specialty Products Co., Ltd. without any further purification. Maleic anhydride ($\geq 98.5\%$), succinic anhydride ($\geq 99\%$), *N,N'*-dicyclo-hexylcarbodi-imide (DCC, 99%), 4-dimethylaminopyridine (DMAP, $> 99\%$), triethylamine (TEA), tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), furan, anhydrous diethyl ether, ethyl acetate, chloroform, toluene, acetone, hexane, 1,4-dioxane, and all other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without any



Scheme 1. Schematic illustration of preparation of *c*-PMMA and the topological transformations. (i) AO-Br/MMA/CuBr/CuBr₂/PMDETA = 1/100/0.1/0.01/0.25, acetone as solvent, 50 °C, 2.5 h; (ii) *l*-alkyne-PMMA-Br/NaN₃ = 1/30, DMF as solvent, 30 °C, 24 h; (iii) CuBr/PMDETA = 1/2, toluene as solvent, dilute condition, 50 °C; (iv) toluene as solvent, concentrated condition, 110 °C for 24 h and then 60 °C for 5 days; (v) toluene as solvent, dilute condition, 110 °C, 24 h; (vi) *c*-PMMA/1-dodecanethiol/TPO = 1/5/0.4, 1, 4-dioxane as solvent, 365-nm UV irradiation, 5 h.

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