



A new reactive polymethacrylate bearing pendant furfuryl groups: Synthesis, thermoreversible reactions, and self-healing



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ARTICLE INFO

Article history:

Received 4 November 2016

Received in revised form

9 December 2016

Accepted 10 December 2016

Available online 12 December 2016

Keywords:

Post-modification

Furan-containing polymethacrylates

Crosslinked networks

Diels-Alder reaction

Retro-Diels-Alder reaction

Self-healing

ABSTRACT

We report a new methacrylate copolymer having pendant furfuryl groups (PFu) reactive to maleimide-bearing compounds to form thermally-induced crosslinked networks exhibiting self-healability through thermoreversible Diels-Alder (DA)/Retro-DA reactions. The PFu is synthesized by a combination of a facile radical polymerization with post-modification methods through a base-catalyzed coupling reaction and a thermally-induced thiol-ene radical addition reaction. The resulting PFu is effective toward DA reaction with a maleimide-bearing crosslinker at moderate or elevated temperatures, yielding highly crosslinked films through DA linkages. Thermal analysis and spectroscopic studies along with NMR model study with small molecular weight precursors suggest the formation of DA-crosslinked networks at 50–100 °C and the occurrence of retro-DA reaction at >125 °C. The resulting DA-crosslinked network is dynamic, exhibiting self-healing through the occurrence of thermoreversible DA/retro-DA reactions, confirmed with sol-gel transition and optical microscopy.

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1. Introduction

Three-dimensionally crosslinked networks with covalent linkages providing high mechanical properties as well as great thermal and solvent resistance have been utilized as effective building blocks for the development of a variety of multifunctional polymeric materials useful in nanoscience and industrial fields [1–3]. Numerous methods have been explored to synthesize covalently crosslinked networks. Conventional methods utilize either a chain-growth polymerization of vinyl monomers in the presence of multifunctional crosslinkers or a step-growth polymerization through polycondensation or polyaddition of polyfunctional monomers. These methods consequently yield polymeric materials crosslinked with permanent linkages, typically carbon-carbon bonds [4–6]. Recent advance is the development of new methods to synthesize reversible networks crosslinked with dynamic (labile) covalent linkages; the formed networks enable to self-heal or self-repair damaged cracks. Such self-healability is a highly desired property of crosslinked materials because their built-in ability to

repair physical damages effectively prevents catastrophic failure to extending their lifetime [7–13]. A variety of dynamic linkages have been explored, including disulfide [14–18], hindered urea [19,20], alkoxyamine [21,22], diarylbibenzofuranone (a dimer of arylbenzofuranone) [23], boronic ester [24–26], and etc. [27].

Of particular interest is the covalent linkage formed through thermally-induced Diels-Alder (DA) reaction, a [4 + 2] cycloaddition of a diene and a dienophile (hereafter DA linkage). Promisingly, the formed DA linkage can be cleaved through retro-DA reaction at elevated temperatures to the corresponding diene and dienophile. Typically employing furan and maleimide moieties, this unique thermoreversible DA/retro-DA chemistry enables DA-crosslinked materials to attain self-healability. Several approaches have been explored for the synthesis of thermally-induced DA-crosslinked materials, which can be characteristic of furan-functionalized compounds or polymers [28–30]. Polycondensation or polyaddition of furan and maleimide-functionalized compounds were explored to synthesize various step-growth polymers [31–33] including polyurethanes [34–37] and epoxy resins [38] crosslinked with DA crosslinkages. Chain growth polymerization of monomers labeled with a pendant furfuryl group allows for the synthesis of relatively high molecular weight linear (co)polymers bearing pendant furan groups (PFu). These polymers include

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mainly polymethacrylates [39–42] as well as polycarbonate [43], and epoxy oligomer [44]. DA-crosslinked networks can be formed from a reactive blend of the resulting PFu with maleimide-functionalized crosslinkers. The fabrication of DA-crosslinked networks based on polymethacrylates bearing both pendant furan and furan-protected maleimide groups is also reported [45–47].

Another approach involves post-modification of functional polymers with small furan-containing molecules. This approach could also allow for the synthesis of a variety of furan-bearing polymers with different chemical structures. Examples include polybutadiene [48,49], polyamides [50], polyketones [51,52], and epoxy resins [38,53]. Despite these advances, the exploration of post-modification to develop new furan-containing polymers, particularly polymethacrylates, is highly beneficial. This approach could circumvent the occurrence of premature crosslinking reactions because of undesirable side reactions such as self-condensation of furfuryl groups or DA reactions between furfuryl and maleimide groups during radical polymerization.

Herein, we report the synthesis of a new methacrylate copolymer having pendant furfuryl groups (PFu) by a combination of a facile free-radical solution polymerization with post-modification methods through a base-catalyzed coupling reaction and a thermally-induced thiol-ene radical addition reaction. As illustrated in Scheme 2, a free radical polymerization of 2-hydroxyethyl methacrylate and 2-ethylhexyl methacrylate yielded a POH copolymer. The pendant hydroxyl groups were converted to methacrylate esters by a facile esterification, thus forming PMA. Then, a click-type thiol-ene addition reaction of furfuryl mercaptan to the methacrylate groups allowed for the synthesis of PFu having pendant furfuryl groups. The ability of the resulting PFu toward DA crosslinking with different amounts of a bismaleimide (BM) as a model crosslinker was characterized with gel content measurements, thermal analysis, and spectroscopic studies of the formed DA-crosslinked networks. In addition, model NMR study for a reactive blend of small molecular weight furan and maleimide precursors were conducted to get an insight into the effect of temperature on the occurrence of DA/retro DA reactions. Further, the self-healability of the DA-crosslinked networks through thermoreversible DA/retro-DA reaction was examined with sol-gel transition in anisole and optical microscopy (Scheme 1).

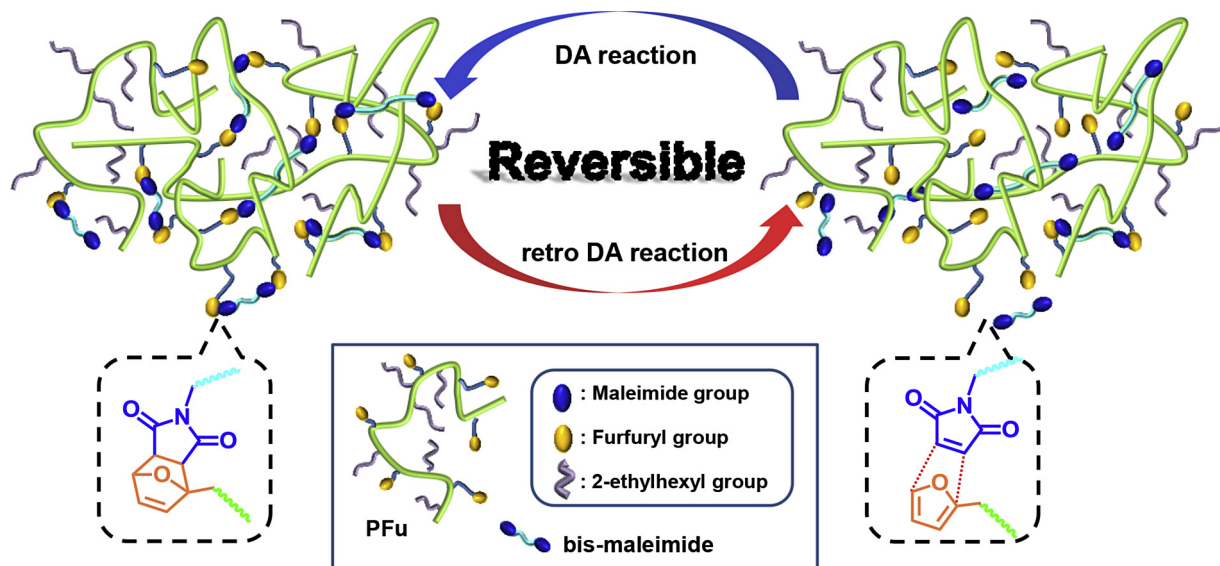
2. Experimental

Materials. 2,2'-Azobis(2-methylbutyronitrile) (AMBN, >98%), *n*-butyl mercaptan (Bu-SH, 95%), triethylamine (Et₃N, >99.9%), methacryloyl chloride (MA-Cl, >97%), furfuryl mercaptan (Fu-SH, 99%), and 1,1-(methylene di-4,1-phenylene)bismaleimide (BM) were purchased from Aldrich and used as received. 2-Ethylhexyl methacrylate (EHMA) and 2-hydroxyethyl methacrylate (HEMA) from Aldrich were purified by passing them through a column filled with basic alumina to remove inhibitors.

Synthesis of POH. EHMA (15.3 g, 77 mmol), HEMA (10.0 g, 77 mmol), Bu-SH (0.5 wt% based on monomer mixtures, 150 μ L), and anisole (34 mL) were mixed in a 50 mL Schlenk flask. The mixture was deoxygenated by purging under nitrogen for 40 min and placed in an oil bath preheated at 70 °C. The nitrogen-prepurged AMBN solution (0.15 g, 0.8 mmol) in anisole (0.5 mL) was injected into the Schlenk flask to initiate polymerization. Polymerization was stopped after 3 h by cooling the reaction vessel in an ice bath. For purification, as-synthesized polymer solutions were precipitated from cold diethyl ether and dried in vacuum oven at room temperature for 18 h.

Synthesis of PMA. A mixture containing Et₃N (3.5 mL, 25 mmol) and POH (1.0 g, 5 mmol of OH groups) dissolved in anhydrous tetrahydrofuran (THF, 150 mL) was purged with a nitrogen gas for 10 min in an ice-bath. After the dropwise addition of a clear solution of MA-Cl (2.4 mL, 25 mmol) in THF (10 mL), the resulting mixture was stirred at room temperature overnight. The formed solids as by-products (Et₃N-HCl adducts) were removed by vacuum filtration. Solvents were removed by a rotary evaporation, and residues were dissolved in dichloromethane (200 mL). The formed solution was washed with water (100 mL) and brine solution (50 mL) three times, and then dried over MgSO₄. After being concentrated using a rotary evaporation, the solution was precipitated from hexane. The precipitates were isolated and dried in a vacuum oven at room temperature for 18 h.

Synthesis of PFu. PMA (0.6 g, 1.7 mmol of methacrylate group), AMBN (0.24 g, 1.3 mmol), and Fu-SH (1.34 mL, 13.3 mmol) were dissolved in a solvent mixture (10 mL) of anhydrous THF and DMF (1/3 v/v) in Schlenk flask. The resulting mixture was degassed by three freeze-pump-thaw cycles and stirred at 75 °C for 24 h. The



Scheme 1. Thermoreversible DA/retro-DA reactions for self-healing of dynamically-crosslinked networks prepared from a reactive mixture containing PFu having pendant furfuryl groups and a bismaleimide model crosslinker.

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