

Triazolinedione-derived Self-healable Tailor-made Polymethacrylates via Dynamic ‘Click Chemistry’

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Abstract

Synthetic polymers undergo visible impair in countering accidental stimuli that steer them to failure. The self-healing notion has been exploited to mitigate the concerns. The ‘click chemistry’ has been utilized to develop countless polymers with interesting structural and functional features. This overview describes the research works that executed dynamically exchangeable ‘click’ approaches to generate functional self-healing polymethacrylates via tailor-made polymerization.

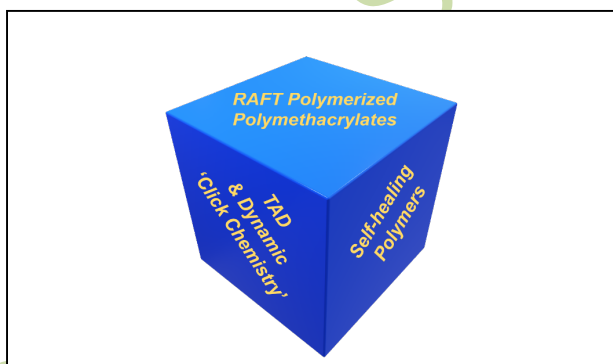
1. Introduction

Common synthetic polymer materials are irresistible to crazes, cracks, or fractures upon countering sudden impact, ultimately driving them to catastrophic failure and reducing their intended service life. Self-healing is one of the commendable strategies effectively exploited (using different reversible ‘click chemistry’) to mitigate the concerns.^{1,2}

Polymeric materials are traditionally healed either extrinsically or intrinsically. However, due to the lack of healing repetitiveness of the former approach, intrinsic systems, e.g., (non)covalent chemistry, host-guest interactions, etc., are widely recognized in macromolecular research.³⁻⁵ Exceptionally, dynamic furan–maleimide Diels–Alder (DA) ‘click chemistry’ has been exploited to generate countless self-healing materials.⁶⁻⁹ However, self-healable polymer materials based on DA chemistry require elevated temperatures ($\approx 50\text{--}70\text{ }^{\circ}\text{C}$) for an extended period ($> 24\text{ h}$) for consolidation.⁹

Because of fast reactivity (within a few seconds to hours) with specific electron-rich substrates under ambient conditions, strongly electrophilic TAD derivatives find an appealing interest in the polymer research community. Noticeably, the azo-derivative can rapidly modify polymers containing specific reactive functionalities via different reversible and irreversible reactions. Moreover, the carmine-red or pink color of the TAD derivatives gradually fades away on completion of the desired response, considered timely feedback.¹⁰⁻¹³ Inspired by the results and to circumvent the drawbacks mentioned above, a TAD-derived dynamic covalent system has been implemented to prepare self-healable polymers.

With a motive to develop polymer materials that can find promising applications in specialty coatings, paints, adhesives, etc., herein, the report describes the execution of

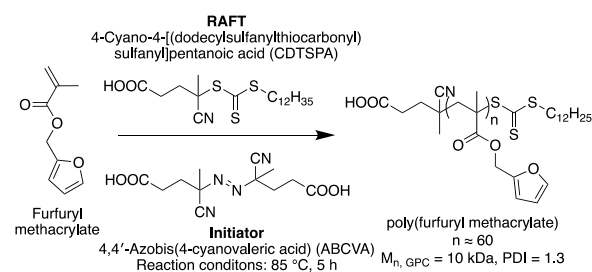


varied reversibly exchangeable ‘click’ approaches for generating functional self-healing polymethacrylates prepared via reversible addition-fragmentation chain transfer (RAFT) polymerization.

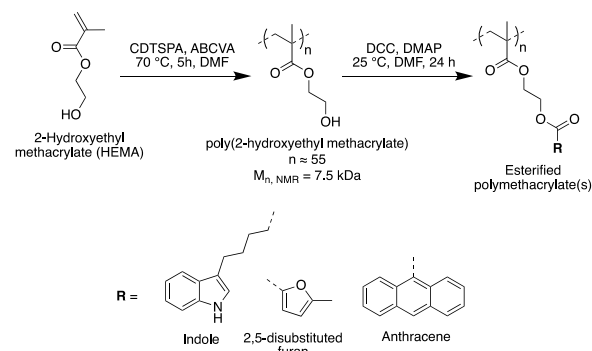
2. Experimental

The generalized procedure to obtain tailor-made functional polymethacrylates has been depicted in Schemes 1 and 2. Initially, a tri-arm star-block copolymer (BCP) comprising of polycaprolactone (PCL) core and poly(furfuryl methacrylate) (PFMA) shell was synthesized by ring-opening polymerization (ROP) and RAFT polymerization techniques to generate a shape-memory and self-healable polymethacrylate. The furfuryl pendants of the BCP were modified with a bis-maleimide (BM) derivative via DA chemistry to generate a covalent adaptable network (Scheme 3). Notably, the DA polymer network exhibited good self-healing efficacy ($\sim 75\%$) due to the thermally-stimulated dynamism of DA covalent bonds. In addition, the crystalline-melting characteristic of PCL induced the shape memory feature in the BCP network. However, the consolidation mechanism of the self-healing polymer network based on maleimide-based DA chemistry was slow (24 h) and necessitated high-temperature conditions ($> 60\text{ }^{\circ}\text{C}$). Therefore, a multifunctional heteronuclear dienophile, e.g., 1,2,4-triazoline-3,5-dione (TAD) derivative, was exploited, which reversibly reacted with several reactive functionalities, e.g., indole anthracene, furfuryl, and 2,5-disubstituted furan, at a relatively faster rate (1-2 min) and ambient conditions

(Scheme 4-7). Accordingly, tailor-made polymethacrylates with suitable functional pendants, viz., indole, anthracenyl, furfuryl, and 5-methyl-2-furoate, were synthesized via RAFT polymerization and subsequently reacted with a bifunctional TAD derivative to generate the self-healable polymer network. The conjugation mechanism of the 'click' reaction was rationalized via density functional theory (DFT) analysis. The dynamic covalent bonds endowed the self-healing characteristics (with efficacy > 80 %) within the TAD 'clicked' polymer network.



Scheme 1. Generalized procedure to synthesize poly(furfuryl methacrylate) via thermally initiated RAFT polymerization. The number-average molecular weight (M_n) and polydispersity index (PDI) of the polymer was determined via gel-permeation chromatography (GPC) analysis.

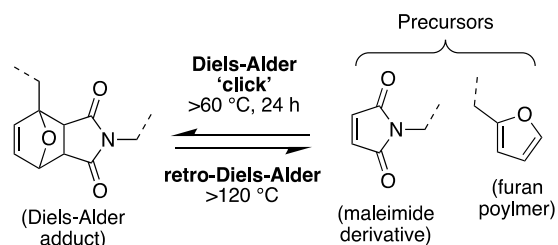


Scheme 2. Generalized procedure to synthesize poly(2-hydroxyethyl methacrylate) via RAFT polymerization and its post-polymerization modification via esterification to graft different reactive functionalities.

3. Result and discussion:

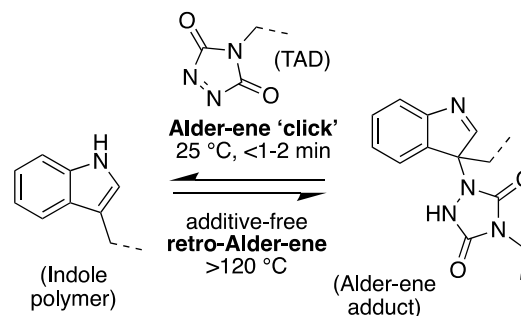
Initially, a shape memory polymer network was developed with self-healing (and recycling) behavior by thermo-reversible DA crosslinking of star-block copolymer (containing furfuryl pendants) with a bifunctional maleimide derivative (Scheme 3). For this, a tri-arm macro-RAFT agent based on PCL was synthesized and exploited to generate the star BCP via thermally-initiated polymerization of furfuryl methacrylate (FMA). The DA polymer network was insoluble at ambient temperatures. However, after heating at 120 °C, the film was entirely solubilized (within 30 min) due to the retro-DA chemistry. Evaporation of the solvent and

subsequent heating at 60 °C (for 24 h) restored the original cross-linked state of the material (with solution recycling efficiency of >90%, as evidenced by the tensile test). Using a scratch test, it was shown that the retro-DA reaction facilitated the healing of surface cracks. Additionally to the self-healing and recycling, the films showed pronounced shape memory effects with good shape recovery and fixity ratios, which was attributed to the melting and crystallization of the PCL phase.



Scheme 3. Development of shape-memory self-healing tailor-made polymethacrylate block copolymer based on dynamic furan-maleimide Diels-Alder (DA) 'click chemistry'.⁹

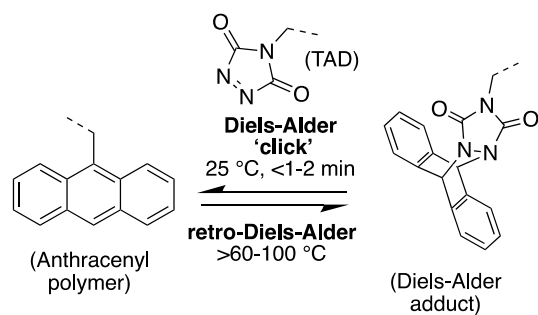
Nevertheless, the crosslinking and self-healing processes using BM were relatively slow (> 24-36 h) and demanded higher temperatures (\approx 60-120°C) for accomplishments. Hence, the research attention turned towards the newly bloomed 1,2,4-triazoline-3,5-dione (TAD) 'click chemistry' in macromolecular science, which is exceedingly fast and undergo completion within a few seconds to minutes (without any catalysts) with specific reactive partners under ambient conditions.



Scheme 4. Development of self-healing tailor-made (co)polymethacrylate based on dynamic indole-TAD Alder-ene (AE) 'click chemistry'.^{14, 15}

Accordingly, self-healing (co)polymethacrylates were generated using dynamic indole-TAD AE 'click chemistry' (Scheme 2 and 4). Briefly, the work includes the RAFT (co)polymerization of a hydrophilic monomer, such as 2-hydroxyethyl methacrylate (HEMA) (and methyl methacrylate and *n*-butyl methacrylate as comonomers) using a RAFT agent and thermal initiator. The hydroxyl end groups of the resultant (co)polymer were esterified to incorporate indole

functionalities. Later these indole-modified (co)polymers were reacted with 4,4'-(4,4'-diphenylmethylene)-bis-(1,2,4-triazoline-3,5-dione) (bisTAD), respectively, at an ambient condition to produce AE 'click' networks within <1-2 min, which was further characterized via FTIR analysis. The dynamic behavior of the 'click' linkages was evidenced by the differential scanning calorimetry (DSC) analysis. The crosslinked polymers were insoluble at room temperature but found soluble in DMF solvent within 45 min at 130 °C. The self-healing test of the polymer samples was carried out via the scratching-healing method. A notch was made upon the individual polymer surfaces and heated at retro-Alder-ene temperature up to different timings. As analyzed via optical microscopy, the scratch was entirely healed within 1 h. Interestingly, the increase in molar content of bisTAD eventually improved the crosslink density with a higher content of AE (exchangeable) conjugates within TAD 'clicked' (co)polymethacrylates that led to fast healing.

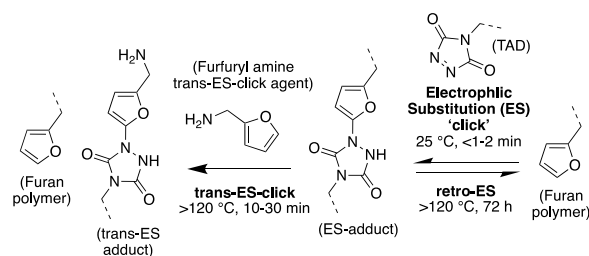


Scheme 5. Development of self-healing tailor-made polymethacrylate based on reversible anthracene-TAD DA 'click chemistry'.¹⁶

The following research work reports the exploitation of anthracene-TAD dynamic DA 'click chemistry' in developing self-healing fluorescent polymethacrylate. Herein, a self-healable polymethacrylate network was prepared based on the reversible anthracene-TAD ultrafast DA reaction. A random copolymer of HEMA and methyl methacrylate (MMA) was generated via RAFT polymerization. The methacrylate copolymers comprising repetitive hydroxyl pendants were esterified with 9-anthracenecarboxylic acid. The anthracene group acted as the 'click' partner to the TAD moiety (Scheme 5). Adding TAD derivatives to the anthracenyl-modified copolymers generated a crosslinked network within 1-2 min under ambient conditions. The reaction was noticeably faster than anthracene-maleimide DA cycloaddition, demanding >120 °C and 48-96 h for completion. The rapid DA reaction of the TAD-anthracene system was rationalized via DFT calculations and spectroscopic analysis by taking different anthracene and TAD model organic derivatives. The healing characteristics of the TAD 'clicked' polymethacrylate was analyzed by microscopic analyses. Noticeably, the TAD 'clicked' anthracenyl polymer network was thermoreversible just beyond >60-70°C (evidenced by UV-Vis spectroscopy) and exhibited excellent healing characteristics (with retaining the material integrity) within 4-5 h (at 130 °C), which is

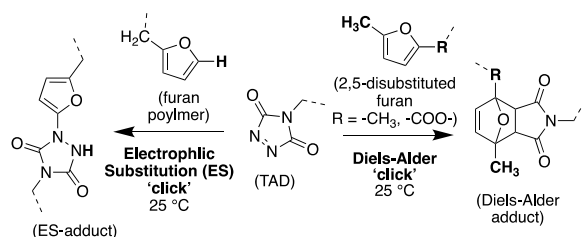
significantly better than the anthracene-maleimide system that demands >200 °C-250 °C (or 100 °C for >7 days) to exhibit dynamism or remendable features.

Next, this brief reports the inception and exploitation of a new dynamic 'click chemistry' based on furfuryl-TAD conjugation in a self-healing polymer toolbox (Scheme 6). The chemical skeleton of TAD is analogous to maleimide, which has been widely utilized as a dienophile in dynamic DA 'click' conjugation with furan at a relatively slower rate and elevated temperature (as explained above). However, unlike the conventional furfuryl-maleimide DA cycloaddition, the (furfuryl groups of) poly (furfuryl methacrylate) (PFMA) undergone modification with multifunctional TAD derivatives via electrophilic substitution (ES) 'click' conjugation under ambient conditions at a relatively faster rate (<1-2 min). The reaction was further elucidated via the DFT study, which showed the derivation of the ES-click adduct ($\Delta G = -25.5$ kcal/mol) via the formation of a single urazolyl zwitterionic intermediate and two transition states.



Scheme 6. Development of self-healing tailor-made polymethacrylate based on fast and reversible furfuryl-TAD ES 'click chemistry'.¹⁷

Interestingly, the reversibility of the TAD 'clicked' ES σ -covalent bonds can be activated at elevated temperatures ($\approx 130^\circ\text{C}$) that endowed the healing features within the TAD-derived polymethacrylate. The viscoelastic properties of the TAD 'clicked' ES polymethacrylates (with different molar content of TAD) were further analyzed via a rheology experiment. Also, inspired by the work of Du Prez and coworkers,^{10, 12} a trans-ES-click approach (like the transesterification reaction) was executed to elucidate the dynamism of furfuryl-TAD conjugation. The reaction between the furfuryl group and TAD functionality via the 'ES-click' reaction is highly exothermic and thermodynamically favorable, impeding the facile release of TAD functionalities from the ES network at the retro-ES temperature regime ($\approx 130^\circ\text{C}$). Consequently, the network demanded >24-72 h for complete reversibility (as evidenced by the solubility study and self-healing analysis). Interestingly, the addition of excess 'trans-ES-click' furfuryl amine functionalities (with higher reacting efficiency w.r.t TAD than FMA) stimulated the faster release of TAD molecules from ES (crosslink) conjugates (within 10-30 min) and so the reversible exchange at 130 °C.



Scheme 7. Development of self-healing tailor-made polymethacrylate based on dynamic 2,5-disubstituted furan-TAD DA 'click chemistry'.¹⁸

As described in the last work, the furfuryl group underwent dynamic conjugation with TAD derivatives via an ES 'click' reaction pathway. Interestingly, when the 2 and 3 carbon centers of a furan group have the substitution of alkyl or ester or acid functionalities, it conjugated with the TAD derivative via a reversible DA 'click' route (Scheme 7). Accordingly, the reversibility of DA-click reaction based on 2,5-disubstituted furan (diene) and TAD (dienophile) functionalities was implemented in developing self-repairable functional tailor-made polymethacrylates. Polymethacrylate bearing 5-methyl-2-furoate pendants (act as the 'click' partner of TAD derivative) was prepared via RAFT polymerization and esterification, and DA 'clicked' with TAD derivatives. After adding the TAD derivatives, the 'click' post-polymerization modification was accomplished within 2 h under ambient conditions. As evidenced by the DSC analysis, the DA-click generated new σ -bonds were dynamic at an elevated temperature (130 °C) that endowed the self-healing characteristics (with an efficiency of > 90%) in the TAD 'clicked' polymers (within 2-5 h).

4. Conclusions

This study reports the exploitation of TAD-derived dynamic 'click' conjugations in developing a new class of functional polymethacrylates that can overcome certain drawbacks related to the delayed post-polymerization modification, e.g., furfuryl-maleimide DA 'click chemistry.' Dynamic chemistry has been successfully utilized to develop polymers associated with dual self-healing and shape-memory characteristics. Without employing any external additives or 'transclick' concept, a few self-healable functional polymethacrylates were synthesized based on dynamic indole-TAD AE 'click chemistry.' The fluorescence properties of the self-healing polymethacrylate based on dynamic anthracene-TAD DA 'click' conjugation can be tailored by varying the molar content of TAD derivatives. The dynamic ES-click chemistry (elucidated via a 'trans-ES-click' approach) has been successfully exploited to develop self-healing polymethacrylate with furfuryl pendants. Interestingly, unlike the furfuryl groups, the 2,5-disubstituted furan functionalities exclusively preferred the dynamic DA cycloaddition pathway, which was elucidated via preparing self-healing polymethacrylates.

Meanwhile, polymer science has fairly implemented the significance of employing TAD-derived 'click' conjugation in the gigantic field of macromolecules. Although the initial mechanism (Scheme 3) describes the

execution of the furan-maleimide dynamic system in developing tailor-made polymethacrylates with shape-memory and self-healing features, multifunctional (aliphatic or aromatic) TAD can be used similarly to establish the same.

Due to their wide range of physical properties, functional polyurethanes (PUs) are enormously exploited in different fields of application. However, the utilization of TADs in the realm of PUs is yet to be explored. Recently, the development of the shape-memory assisted self-healing (SMASH) concept has gained wide popularity in healing visible cracks (especially using PUs). The inclusion of 'exotic' TAD-based dynamic 'click' conjugations can be used in developing the same.

Furthermore, from recyclability and reusability perspectives, biobased or biodegradable polymers or elastomers are widely used for several applications. Indeed, the inclusion of TAD 'clicked' dynamic conjugation in such biobased polymers can improve material integrity by endowing self-healing and recycling characteristics.

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6. Notes and References

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7. About the author

After completing his higher school studies, P.M. moved to Vidyasagar University (India) to achieve the Bachelor of Science and Master of Science degrees in Chemistry. He has qualified CSIR-UGC-NET and GATE exams and was awarded (JRF/ SRF by CSIR) fellowship to pursue Ph.D. He has conducted his doctoral research activities under the guidance of Prof. Nikhil K. Singha and obtained a Ph.D. in Polymer Chemistry from Rubber Technology Centre, Indian Institute of Technology (IIT) Kharagpur. During his doctoral tenure, under the co-supervision of Prof. Dr. Brigitte Voit and Dr. Frank Böhme, he has been a guest researcher for three months in the Leibniz Institute of Polymer Research (IPF) Dresden e. V. He is the holder of the Prof. Sabu Thomas best Ph.D. thesis award. After completing his Ph.D. at IIT Kharagpur, he has moved to California, USA, to perform postdoctoral research in the laboratory of Prof. Seth M. Cohen at the University of California, San Diego.

