ABSTRACT

Since its inception, the ‘click chemistry’ concept is widely exploited to design numerous advanced materials having interesting structural and functional properties (e.g., self-healing, self-cleaning materials) alike the nature-mimetic materials. This study reports the execution of different dynamic ‘click chemistry’ in developing new classes of self-healable tailormade functional polymethacrylates. The functional polymers were characterized using FT-IR, ^{1}H-NMR, UV-Vis, GPC, TGA, DSC, SAXS, and AFM analyses. Furthermore, the DFT calculation was carried out using small organic compounds to rationalize the polymer ‘click’ reaction. The self-healing property of functional polymers was evaluated by scratch-and-heal analysis, which was monitored using optical microscopy (OM), FESEM as well as via tensile tests. Firstly, 3-arm star-block copolymers (BCP) consisting of polycaprolactone (PCL) core and a poly (furfuryl methacrylate) (PFMA) shell were synthesized by RAFT polymerization. The furfuryl moities of these BCP were modified via Diels-Alder (DA) reaction using bis-maleimide (BM). In addition to good self-healing efficacy (~75 %) due to dynamic DA covalent bonds, the incorporation of PCL, as soft segments, into the hard PFMA-BMI DA crosslinked adduct induced the shape-memory feature in the 3-arm star BCP. Nevertheless, the crosslinking and self-healing processes using BMI were relatively slow and demanded high temperature for accomplishments. Therefore, the heteronuclear dienophiles like 1,2,4-triazoline-3,5-dione (TAD) derivatives were used that led to faster dynamic ‘click’ conjugation with several reactive functionalities, e.g., indole, anthracene, furfuryl, and 2,5-disubstituted furan. For this purpose, functional tailormade polymethacrylates having suitable reactive pendants viz., indole, anthracyl, furfuryl, and 5-methyl-2-furoate, were synthesized and reacted with TAD derivative. The dynamic covalent bonds in the TAD-polymer adduct induced the self-healing characteristics (with efficacy > 80 %) within the TAD ‘clicked’ polymethacrylates. The indole containing polymers did undergo very fast thermoreversible Alder-ene (AE) ‘click’ reaction with bisTAD which resulted in self-healable polymethacrylates. The anthracyl group containing polymers did undergo dynamic DA ‘click’ reaction with the TAD derivatives. The anthracyl polymethacrylates exhibited strong fluorescence characteristics, which was tuned by incorporating varied molar content of TAD functionalities. Interestingly, in the furfuryl containing polymers, the furfuryl group did undergo dynamic conjugation with TAD derivatives via an electrophilic substitution (ES) ‘click’ route. But when the furan group has the substitution of alkyl or ester or acid functionalities at its 2 and 3 position it did undergo dynamic DA ‘click’ conjugation. Both the TAD ‘clicked’ furan systems induced self-healing characteristics in the functional polymethacrylate.

Keywords: ‘click chemistry,’ TAD, functional polymethacrylate, RAFT, DFT, self-healing, Alder-ene, Diels-Alder, Electrophilic Substitution (ES). Fluorescence.