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One-Pot Synthesis of Graft Copolymer by Combination of Free Radical Polymerization and Polyaddition

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Graft copolymers have characters of both stem and graft chains. Owing to the characteristic structures, graft copolymers have wide applications such as biomaterials, absorbents, compatibilizing agents, detergents, and separation materials.[1]

Polymers bearing thiol moieties have been used as excellent polymeric chain transfer agents for radical graft copolymerization.[2,3] However, the reactivity of thiol moieties typically requires cumbersome protection−deprotection processes.[2] Contrary to this, polyaddition of bifunctional cyclic dithiocarbonates and diamines can directly afford polymers bearing two thiol moieties in their repeating units.[4] The cyclic dithiocarbonate monomers can be easily prepared from epoxides and CS_2.[5] We have already reported that a partially cross-linked polymer bearing thiol moieties serves as a polymeric chain transfer agent, which is a precursor for core-cross-linked graft copolymers.[3] We extended the graft copolymer synthesis to a linear precursor and herein report that graft copolymers with controllable molecular weight can be obtained by a combination of free radical polymerization and polyaddition.

The polymeric chain transfer agent was prepared by polyaddition of trimethylene dipiperidine and a bifunctional five-membered cyclic dithiocarbonate prepared from bisphenol A diglycidyl ether and CS_2.[5] The polyaddition proceeded quantitatively at room temperature and afforded a polymer bearing thiol moieties (poly(mercaptothiourethane)) (M_n = 8800, M_w/M_n = 3.34). Without any isolation process, subsequent free radical graft polymerization was conducted in a degassed sealed tube after addition of methyl methacrylate (MMA). A radical initiator, 2,2′-azobisisobutyronitrile (AIBN), was added at the polyaddition process to simplify the polymerization procedure. The reason why MMA was employed is avoidance of recombination of propagating radicals leading to formation of cross-linked polymers. The amount of MMA toward the thiol moieties was varied from 15 to 400. MMA was consumed quantitatively regardless of the feed ratio, and soluble polymers were obtained in high yields (see Supporting Information). However, the polymerizations using styrene or acrylamide derivatives afforded insoluble polymers under the same conditions, probably due to the recombination. The size exclusion chromatography (SEC) profiles of the polymers detected by refractive index (RI) and UV (254 nm) detectors synchronized, indicating that the stem polymer (RI and UV active) and the polyMMA segment (RI active and UV inactive) distribute averagely (Figure 1). Namely, the precursor polymer and polyMMA not grafted are negligibly included. This fact and the shifts of the SEC profiles to high molecular weight region confirm that graft copolymers, polythiourethane-*g*-polyMMA, were produced. The molecular weights estimated by SEC also manifested the structure of the graft copolymer by the underestimated molecular weights estimated by SEC with RI and viscometer (see Supporting Information).[6]

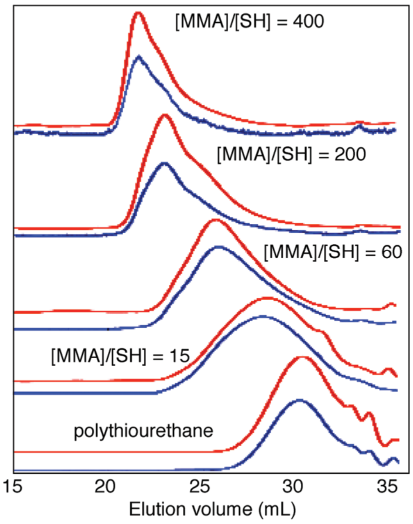
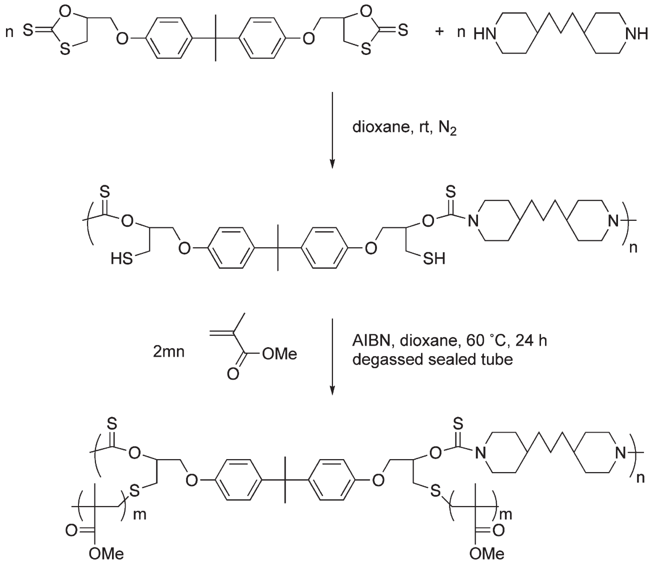


Figure 1. SEC profiles of polythiourethane-*g*-polyMMA (RI: red; UV: blue).

Scheme 1. Synthesis of Polythiourethane-*g*-PMMA by Sequential Polyaddition and Free Radical Polymerization



It is of notice that the molecular weight of the polymer increased as the feed ratio of MMA (Figures 1 and 2 and Supporting Information) and that the molecular weights determined by NMR and SEC with a RALLS (right angle laser light scattering) agreed with the theoretical values (Figure 2).[7] On the other hand, the molecular weights increased with the conversion and almost agreed with the theoretical values (see Supporting Information). Although the polydispersity indexes are not narrow (M_w/M_n = 2.12−7.74), these results resemble to those of

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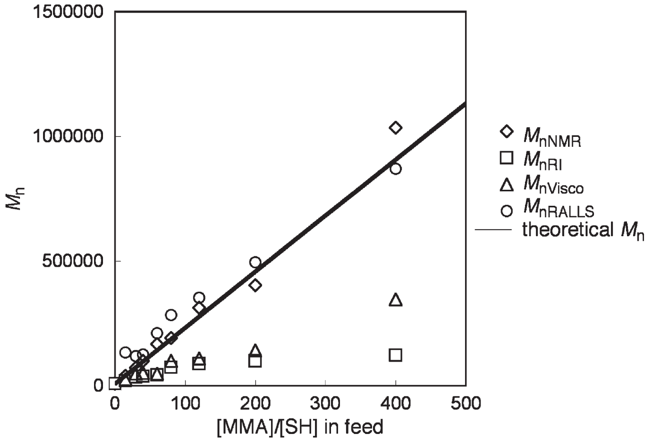
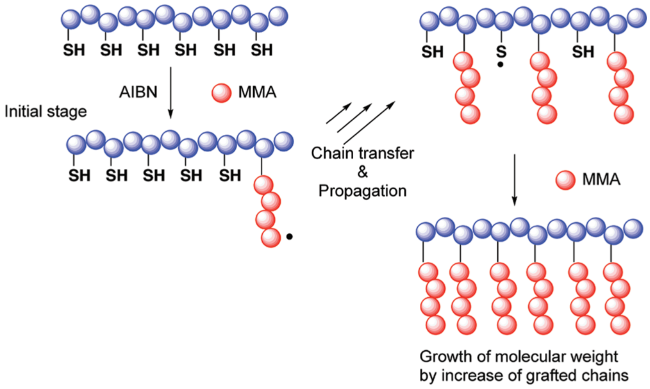


Figure 2. Relationships between MMA feed ratio and molecular weights of polythiourethane-*g*-polyMMA.

Scheme 2. Plausible Mechanism of the Graft Polymerization from Poly(mercaptothiourethane)



controlled polymerizations. However, a plausible mechanism of this polymerization differs with that of controlled radical polymerizations, as indicated in Scheme 2. First, polymeric thiyl radical forms by hydrogen abstraction with the primary radical from AIBN. Then, polymerization of MMA occurs. The propagating end chain-transfers to thiol or AIBN. The very low frequency of the disproportionation between the grafted chain ends was supported by the fact that ^{1}H NMR signals assignable to the alkene end groups[8] were not observable (see Supporting Information). Continuous increase of grafted chains takes place by repeated chain transfer of many thiol moieties in one chain, which led to growth of molecular weight by increase of a number of grafted chains. The long-lived propagating radicals in the very viscous mixture, which was supported by a pseudo-first-order kinetics (see Supporting Information), would also have contributed the growth of the molecular weight, in a similar manner with the radical polymerizations in viscous systems such as in ionic liquids.[9]

In conclusion, graft copolymers with controllable molecular weights could be prepared by a one-pot reaction consisting of polyaddition and subsequent free radical polymerization. The majorities of this system are the facile process in one-pot, the easily accessible precursors for the polymeric chain transfer agent, and no need of polymeric atom transfer radical polymerization initiators or reversible chain transfer agents. We are now exploring the application of the graft copolymers originating from the unique characters of sulfur-containing polymers (e.g., metal absorption ability)[10] and variable grafted chains.

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Supporting Information Available: Experimental procedures and polymerization results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) The high molecular weight fraction in Figure 1 might exceed the exclusion limit of this SEC analysis. Other SEC profiles obtained using a SEC system with a higher exclusion limit are indicated in the Supporting Information.

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