Associative Polymers as Antimisting Agents and Other Functional Materials via Thiol-Ene Coupling

Thesis by

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Dedicated to:
my mother, for devotion in educating my child’s mind,
my father, for unwavering support,
and my wife, for enduring friendship.

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Abstract

Associating polymers of varying molecular design were studied as potential additives to aviation fuel, aimed to suppress misting and thereby reduce the fuel's fire hazard in crash scenarios. Molecular architectures investigated varied from random placement along polymer chains of associating groups (referred to throughout this work as "stickers") to selective clustering of the stickers at chain ends. Linear chains possessing associating functional groups grafted at random positions along the entire chain were investigated first. Model polymers with matched backbone length were synthesized to examine the effects of degree of functionalization and type of interaction (self-associating or donor-acceptor) on shear and extensional rheology of both dilute and semi-dilute solutions in non-polar hydrocarbon solvents. We found that intramolecular associations dominate the behavior of self-associating chains even in semi-dilute concentrations, leading to chain collapse and reduced shear and extensional viscosities. Mixtures of donor-acceptor chains show much more favorable intermolecular pairing in dilute solutions (as evidenced by the formation of large aggregates), but nevertheless display reduced solution elasticity and extensional viscosity relative to unmodified homologues: sticker pairing interfered with the stretching of the chains in elongational flow. Molecular designs that overcome chain collapse by clustering stickers at the ends of polymer chains were studied next. We showed by theoretical modeling that symmetric linear chains displaying strongly associating endgroups suffer instead from loop formation, which traps the bulk of the polymer into small cyclic aggregates with low mist-control properties. Therefore, we suggest molecular architectures that preclude formation of cyclic supramolecules by employing several different donor-acceptor pairs that do not affect one another ("orthogonal" pairs). This presents a synthetic challenge, i.e., the development of simple and rapid protocols for the preparation of functional polymer materials of controlled architecture and functionality. We developed such convenient protocols (fast, non-wasteful, and scalable procedures) for the functionalization of polybutadiene by thiol-ene addition to yield functional polymers of narrow polydispersity. These powerful, versatile synthetic tools can potentially be applied to add any side-group onto any polymer, copolymer, or block copolymer displaying pendant vinyl groups, with exciting potential applications in fields ranging from organic electronics to drug delivery.

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Foreword

The subject of the present doctoral contribution is at the intersection of two exciting segments of macromolecular science in which the Kornfield lab has been involved for over a decade: the study of polymer self-assembly and the study of functional polymers. Our contribution is twofold. First, we increase the understanding of the behavior of associative functional polymers of various architectures (random, blocky) and type of interactions (self-associating versus specific, directional bonding) in dilute and semi-dilute solutions. In particular, we address the nature of the competition between inter- and intra-chain associations, and the effect of polymer molecular design and molecular parameters on aggregate structure and ultimately on rheological solution properties. Second, we expand the polymer scientist's toolkit for the preparation of well-defined materials with tailored properties by functionalization of polymers bearing pendant vinyl groups via thiol-ene coupling. That is, we present facile, high-yield, and scalable synthetic methods that optimize the combined tasks of (i) synthesizing new functional thiols and (ii) grafting them to polymer chains, in an efficient, rapid, and controlled manner.