# Chapter I Introduction to Associating Polymers for Improved Fuel Fire Safety

# **1.1 Technological Need**

The research presented here has been motivated by the technological need to improve the fire safety of jet fuel, motivated by both aviation safety and antiterrorism. Our efforts have sought to develop a polymer additive capable of suppressing the misting of aviation fuel, thereby delaying and abating the intensity of fires following the crash of a jet aircraft.<sup>1-3</sup>

Over the last 4 decades, on average 2 air carrier accidents have occurred monthly within the US and 15 worldwide. This level persists despite ongoing efforts to eliminate human error and improve security. Of these, an estimated 70% occur on takeoff or landing and are impact survivable. It is further estimated that 40% of the fatalities in such crashes are due to fire caused by combustion of aviation fuel. Thus, some 500–1000 lives per year can be saved by the development of an effective antimisting fuel system.

Perhaps more important is the issue of homeland security: the destructive power of a fully fueled aircraft inspires terrorists to subvert any security measures put in place. This destructive power comes from the fuel—not kinetic energy (in the September 11 attack on the World Trade Center, for instance, both towers absorbed the aircrafts' momentum and survived the initial impact). Threats to high-rise buildings, sports arenas, nuclear power facilities, and other important targets result from the explosion and intense post-crash fire. Thus, the successful incorporation of an antimisting fuel additive would greatly reduce the loss of life and property caused by plane accidents, and render passenger aircraft fuel ineffective as a weapon.

Presently there are no implemented technologies to reduce the fire hazard of fuel in crash scenarios. Our objective has been to develop an antimisting polymer additive to be used at concentrations below 0.1 wt % and at a cost of 1–2 cents per gallon of fuel. At a consumption rate of 19.5 billion gallons of jet fuel for the US airline industry (worldwide consumption is roughly twice that number), the estimated annual global market for such a polymer additive would be on the order of \$0.5–1 billion/year. The requirements of a viable polymer additive for mist control of aviation fuel are given in Table 1.1.

# **1.2** Historical Developments of Polymer Research for Improved Fuel Fire Safety

Attempts in the past to mitigate aircraft crash fires has led to the incorporation of firewalls, flame arresters, fuel-line isolation, fire extinguishing systems, fire-resistant materials, etc., with limited success. As stated in a 1997 NRC report,<sup>4</sup> "the reduction of the fire hazard of [the] fuel [itself] is critical in improving survivability in past crashes." Candidate technologies aimed to provide a post-impact fire-safe fuel were evaluated in the January 2000 report of the Southwest Research Institute, prepared by Bernard Wright under contract to NASA.<sup>5</sup> Based on an extensive review of fuel vulnerability studies and discussions with industry-knowledgeable sources, Mist-Controlled Kerosene (MCK) technology was rated as the most promising and highest priority to date. MCK is conventional Jet-A to which a small concentration (say < 0.3 wt %) of high molecular weight (MW) polymer has been added. When fuel is released from ruptured tanks into the airflow around a crashing aircraft, the polymer interferes mechanically with the formation of mist.

## 1.2.1 Ultra-High Molecular Weight Linear Chains

It has been known since the 1960s that low concentrations of very high molar mass polymers (on the order of  $10^7$  g/mol) have potent effects on both hydrodynamic drag in turbulent flows and on the breakup of liquid jets and drops. Drag reduction refers to the spectacular decrease in the frictional losses under turbulent flow that can result from the addition of part-per-million levels (as low as 0.02 ppm)<sup>6</sup> of long-chain polymer to a fluid. The addition of small quantities of polymer is known to affect the behavior of liquids in jet breakup, spray atomization, and splashing, and has long been used to control drop size in technologies ranging from inkjet printing to agricultural spraying.

## **1.2.1.1 Basis of Effectiveness**

What is the molecular basis for mist suppression and drag reduction by ultra-long polymer chains, and are the phenomena related? Control of drop size using polymer additives is determined by the polymer behavior in elongational flow, which is the dominant mode of deformation in the necking and breakup of fluid elements. Presumably, the stretching of the polymer chains results in large tensile stresses (as observed by large values of extensional viscosity)<sup>7-11</sup> which resist extensional deformation. In capillary breakup

experiments, this behavior serves to greatly extend the lifetime of filaments of Boger fluids, as seen in Figure 1.1. In jet breakup experiments of viscoelastic fluids, polymer molecules damp disturbances, promoting the formation of connecting filaments to produce a beads-onstring morphology<sup>9, 12-14</sup> (Figure 1.2). Mun et al.<sup>10</sup> and Christanti and Walker<sup>15</sup> showed that in jet breakup of dilute and semi-dilute polymer solutions due to natural disturbances, fluids with higher apparent extensional viscosity have larger breakup lengths, larger droplets, and fewer (if any) satellite droplets than Newtonian fluids of equal shear viscosity, density, and surface tension. The most important parameters in characterizing satellite drop suppression of viscoelastic fluids in elongational flow are the fluid's relaxation time and extensional viscosity.<sup>7-9, 11</sup>

Mist suppression and drag reduction seem to share the same origin in viscous and elastic effects arising from the distortion and relaxation of long polymer chains.<sup>16, 17</sup> Experimental and computational studies have confirmed that polymer chains in turbulent flow become highly extended compared to their equilibrium conformations, especially near the wall, and that the ability of the polymers to stretch is essential to drag reduction. Lumley<sup>18, 19</sup> and others<sup>20, 21</sup> proposed that drag reduction originates from the large increase in elongational viscosity associated with chain stretching, resulting in the damping of small eddies and thickening of the viscous sublayer. de Gennes<sup>22</sup> and others<sup>23</sup> suggested that drag reduction is caused instead by the elastic properties of the polymers, i.e., that the polymer molecules prevent production of turbulent velocity fluctuations on small scales by absorbing the small-scale turbulence energy as elastic energy. This energy can then be dissipated by polymer relaxation.<sup>17, 24-26</sup>

# 1.2.1.2 The Longer the Better

Ultra-high molecular weight linear chains have been shown to be extremely effective mist-control agents.<sup>8, 27</sup> Chao et al. reported that linear polyisobutylene (PIB) chains of molecular weight  $5-10 \times 10^6$  g/mol were effective at reducing flammability of sprays of Jet-A fuel at concentrations as low as 50 ppm, and that mist-control ability increased with both increasing molecular weight and concentration.<sup>8</sup> With increasing concentration of  $6 \times 10^6$  g/mol PIB, the effect progressed from suppression of smaller droplets to formation of continuous large filaments with no liquid breakup (Figure 1.3). Chao and coworkers reported that the single most important parameter in determining antimisting effectiveness was the

elongational viscosity of the solution (determined by tubeless siphon height measurements). This result was confirmed by Smolinski et al. for dilute PIB/mineral oil solutions by a combination of experiments and computations using an FENE-P dumbbell model.<sup>11</sup>

#### **1.2.1.3** Shear Degradation

As a rough criterion, Chao and coworkers<sup>8</sup> proposed that polymer additives for antimisting in jet fuels must be of MW ~  $10^7$  g/mol to be truly effective. Unfortunately, linear chains of such size undergo scission in high strain regions of turbulent flow, rendering their use impractical (the additive must be reintroduced after each pumping station or added at the point of delivery). One manifestation of this flow-induced degradation is the decrease in drag reduction activity with distance along a pipe segment.<sup>24</sup>

# 1.2.2 Associating Polymers

It has been suggested that shear degradation of polymer drag-reduction/mist-control additives may be overcome by turning to associative polymers, i.e., polymer chains capable of interacting through non-covalent bonds (e.g., hydrogen bonds). The objective then is to design shear-stable chains of molecular weight on the order of  $1 \times 10^6$  g/mol that can aggregate at polymer concentration on the order of 1000 ppm into large clusters that themselves are effective mist-control/drag-reducing agents.

Two important examples of associating materials that have been investigated as potential mist-control/drag-reduction additives are ABA triblock copolymers designed so that the solvent is selectively good for one block and poor for the other (such as Kratons), and linear chains possessing hydrogen-bonding functional groups grafted at random positions along the entire chains (Figures 1.4 and 1.5). Kratons are polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) rubbers that can form flower-like micelle structures by association of the poorly soluble polystyrene endblocks in solvents such as heptane and kerosene, resulting in significantly enhanced shear viscosity. Experiments showed that although Kratons are able to increase droplet size in atomization due to higher values of shear viscosity, they do not lead to any enhancement in elongational viscosity relative to shear viscosity (i.e.,  $Tr \equiv \eta_E / \eta_s \cong 3$ , as expected for Newtonian fluids), and are therefore poor mist-control additives.<sup>28</sup>

Linear polymer chains possessing hydrogen-bonding functional groups grafted at random positions along the entire chains received the most attention. An important class of such polymers involves functional side-groups capable of pair-wise self-associations, such as ICI's FM-9 polymer (Figure 1.4a), and Exxon's alpha-olefin derivatives (Figure 1.4b). These were shown to be effective mist-control agents in the semi-dilute regime, but suffered from unacceptably high shear viscosity enhancements at these concentrations, as well as from poor solubility in non-polar hydrocarbon solvents such as jet fuel. More sophisticated attempts involved the development of systems with "directional bonding"<sup>29-31</sup> from a hydrogen-bond donor to a hydrogen-bond acceptor (Figure 1.5), expected to achieve control of extensional rheological properties at lower concentrations than self-associating systems. Malik and Mashelkar<sup>30</sup> (Figure 1.5b) demonstrated that mixing two polymers bearing complementary proton-accepting and proton-donating groups leads to the formation of interpolymer complexes even at concentrations below the overlap concentration of the individual polymers. These interpolymer complexes (IPC) were reported to enhance dragreduction activity, both in terms of greater initial drag-reduction activity (by up to a factor of 6 when comparing IPCs with their non-associating precursors),<sup>30</sup> and in terms of increased resistance to shear degradation.<sup>29-31</sup> That is, molecules involved in IPCs were found to have increased shear-stability compared to non-associating polymer of the same molecular weight—a more stringent criterion than merely improving on the stability of ultra-long polymers.

#### **1.2.3** Termination of Research

To date, the most extensive and most successful attempt to develop a polymer-modified fuel that improves fire-safety was the FAA-funded Anti-Misting Kerosene (AMK) program centered on ICI's proprietary FM-9 polymer. AMK was an engineering-focused program with emphasis on practical testing. By trial and error a fuel formulation was produced that reduced the post-crash fire; however, the program eventually failed because it lacked the scientific effort necessary to obtain fundamental understanding of how to make necessary adjustments.

The termination of research on polymer additives for mist control of jet fuels was precipitated by negative publicity arising from a controlled impact demonstration (CID) conducted by the FAA and NASA on December 1, 1984. The intent of the CID was to test the effectiveness of Mist-Controlled Kerosene under realistic conditions of a survivable crash, using a 3000 ppm FM-9 formulation. Unfortunately, the test was not performed as planned and the remotely piloted Boeing 720 commercial aircraft was landed at a high yaw angle of  $13^{\circ}$ , resulting in a huge fireball. Despite appearances, careful review of the CID photographic evidence revealed that the large initial plume of burning fuel self-quenched, did not penetrate the interior of the aircraft, and left the fuselage with only minor fire damage,<sup>3</sup> so that a large number of passengers could have safely escaped during the ~ 1 ½ minute time interval over which the fire subsided. Similar controlled crashes with untreated Jet-A produced such an intense fireball that the fuselage melted and its contents were engulfed in flames. Thus, MCK *did* perform as intended. Nevertheless, by 1986 the Department of Transportation had cancelled the entire program. Without the prospect of a market, industry followed suit.

# **1.3** Overview of the Present Work

As mentioned earlier, prior efforts failed because they did not aim to obtain a molecular understanding of material properties. Our interest has been to develop such a fundamental understanding, i.e., to provide the scientific foundation for utilizing non-covalent interactions in the preparation of functional polymers which are both resistant to shear degradation and effective mist-control/drag-reducing agents. The specific materials and selection of properties to investigate reflect the specific engineering objective that motivated our research: improving the fire-safety of fuels, especially aviation fuel. Technologically, the results can be expected to have broad relevance to suppression of splashing and misting in applications as diverse as agricultural spraying and ink-jet printing.

#### 1.3.1 Objectives

We address the knowledge gap in the existing literature. In particular, the few reports of promising effects of randomly functionalized associating polymers have not examined the role of molecular variables, such as chain length or sticker density. Our first objective was therefore to establish the relationship between molecular properties and solution behavior, i.e., the connections between molecular design, aggregate structure, rheological properties, and performance in drag reduction and mist suppression (Figure 1.6) for randomly functionalized associative polymers. Our next objective was to use that understanding to molecularly design, synthesize, and test new generations of associative polymers. Our

technological objective was to eventually develop a polymer formulation that enables control of the extensional rheological properties of dilute solutions, while satisfying the requirements set out in Table 1.1.

#### **1.3.2 Materials Studied**

We investigated four generations of polymer additives (Figure 1.7), starting where the literature stopped, i.e., with the study of randomly functionalized chains with self-associating side-groups, and the study of randomly functionalized chains with complementary side-groups. A critical aspect of our work is that we prepared model molecules that allowed us to isolate the effect of associations from that of other parameters, such as chain size. More precisely, the synthetic methods we used allowed us to prepare homologous series of polymer chains identical in every respect (in length, architecture, chemical makeup, etc.) except for the nature and number of the functional groups. Our solution to that synthetic challenge enabled us to achieve the molecular control necessary to generate the fundamental understanding which was lacking in prior studies.

#### 1.3.3 Organization

Chapter 2 deals with the solution properties of linear chains possessing self-associating functional groups grafted at random positions along the entire chains (Figure 1.7.1). Their shear and extensional rheological properties are presented in conjunction with new theoretical insight into structural changes arising from interactions. Chapter 3 tests the literature assertion that randomly functionalized linear chains featuring complementary groups (Figure 1.7.2) can provide satisfactory mist control at dilute or semi-dilute concentrations. New understanding generated in the above studies led to molecular designs that cluster interacting groups at chain ends. Computational modeling of the association behavior of linear chains displaying strongly associating endgroups (Figure 1.7.3) is reported in Chapter 4. We conclude our discussion of associating polymers for improved fuel fire safety with promising directions indicated by model predictions.

In Chapter 5, we carefully investigate the general usefulness of our chosen synthetic method for the preparation of homologous series of well-defined, functional polymers. We present fast, efficient, and scalable protocols for the synthesis and addition by thiol-ene coupling of various functional side-groups to polymers bearing pendant vinyl groups. The

procedure preserves the structure of the prepolymer material and allows powerful tuning of molecular properties by control of the nature and extent of functionalization.

# 1.4 Figures and Tables



**Figure 1.1** Sequence of video images showing capillary thinning and breakup for Newtonian and viscoelastic filaments. The plate diameter in both sequences is 3 mm. Note that the Newtonian filament (top row) is axially non-uniform due to gravitational sagging, while the Boger fluid (bottom row) forms a nearly cylindrical filament that persists much longer than a Newtonian filament of the same viscosity.<sup>7</sup> (Reproduced with permission.)



**Figure 1.2** Effect of viscoelasticity on jet breakup due to a forced disturbance for PEO/glycerol/water solutions of nearly constant shear viscosity, surface tension, and density.<sup>9</sup> (a) 50% glycerol/water, (b)  $0.3\% \ 1 \times 10^5$  g/mol PEO, (c)  $0.1\% \ 3 \times 10^5$  g/mol PEO, (d)  $0.05\% \ 1 \times 10^6$  g/mol PEO, and (e)  $0.043\% \ 5 \times 10^6$  g/mol PEO. Flow direction is from left to right; image size is 20,000 µm × 2,000 µm. Note the nonlinear decrease in concentration required to achieve a given breakup morphology as polymer MW increases; e.g.,  $1/20^{\text{th}}$  the concentration of  $1 \times 10^6$  g/mol PEO is sufficient to produce the effect of  $3 \times 10^5$  g/mol PEO. (Reproduced with permission.)



**Figure 1.3** Effect of mist control additive concentration on spray morphology, as seen for polyisobutylene of  $M_w = 6 \times 10^6$  g/mol and  $M_w/M_n = 4.3$  in Jet-A at air velocity of 67 m/s and fuel flow of 0.33 cm<sup>3</sup>/s.<sup>8</sup> (Reproduced with permission.)



**Figure 1.4** Examples of self-associating polymers. Interactions are pair-wise via dimerization of carboxylic acid side groups. (a) FM-9 random copolymer developed by ICI having undisclosed composition and molar mass,<sup>32</sup> (b) copolymer of 1-octene (99 mol %), methyl undecenoate (< 1 mol %), and undecenoic acid (0.02–0.5 mol %) of molecular weight  $2-5 \times 10^6$  g/mol developed by Schulz and coworkers at Exxon.<sup>29, 31</sup>



**Figure 1.5** Examples of hydrogen-bond donor/acceptor random copolymer pairs. (a) Carboxylic acid groups as proton donors (polymer structure was given in Figure 1.4b) and pyridine moieties as proton acceptors (~ 8 mol %) on chains of  $M_w \sim 2 \times 10^6$  g/mol, developed at Exxon.<sup>29, 31</sup> (b) Carboxylic acid groups as proton donors (~ 3 wt % methacrylic acid) on chains of  $M_w \sim 4.7 \times 10^5$  g/mol, and pyridine groups as proton acceptors (~ 4 wt %) on chains of  $M_w \sim 2.1 \times 10^6$  g/mol, developed by Malik and Mashelkar.<sup>30</sup>



**Figure 1.6** Our objectives are to establish the connections between polymer molecular structure, polymer self-assembly, solution rheological properties, and polymer performance in drag reduction and mist suppression.



**Figure 1.7** Alternative strategies using self-assembly of associating polymers in dilute solutions to control drop breakup in elongational flow.

Criteria	Fluid Physical and Chemical Requirements
Improved fire safety	Fuel must not produce fine drops when accidentally
	released during a crash
Compatibility with aircraft	Addition of antimisting agent must not cause significant
fuel system	changes to other fuel physical and chemical properties, such as shear viscosity, acidity, etc.
	Fuel must remain single-phase over a wide range of use conditions
Ease of transport, storage, and use	Polymer design must confer sufficient stability that additives introduced at the point of production survive to the point of delivery
Low cost	Selection of polymer backbone and functional groups must take into account feasibility and cost of large scale production
Environmentally friendly	Polymer must burn cleanly
Marginal water uptake	Polymer must have low affinity for water

**Table 1.1**Fundamental Requirements of an Ideal Polymer Additive for Mist Control ofAviation Fuel

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