Traveling Fronts of Methacrylic Acid Polymerization

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Traveling Fronts of Addition-Polymerization with a Solid Monomer

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An autocatalytic reaction in an unstirred vessel can support a constant velocity wavefront resulting from the coupling of diffusion to the chemical reaction. Propagating fronts of polymerization have been studied in the former Soviet Union.[1-10] We have been investigating polymerization fronts with high boiling point monomers that can be studied visually[11-13] and by NMR.[14]

Propagating fronts of solid-state combustion reactions have been studied as a means to make new materials[15-17] and to observe nonlinear propagation phenomena such as pulsating and spinning fronts.[18-28]

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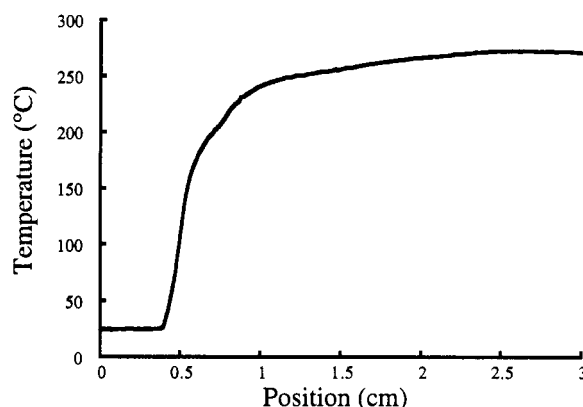(28) Anselm-Tamburini, U.; Munir, Z. A. *J. Appl. Phys.* **1989,** *66,* 5039–5045.

Figure 1. The temperature profile of a polymerization front propagating through solid acrylamide with 0.5 w/w % AIBN.

We wished to study fronts of polymerization with solid monomers for three reasons: to search for nonlinear propagation behavior, to explore the possibility of a new mode of materials synthesis with reduced energy costs, and to study front propagation without interference from buoyancy-induced convection observed with liquid monomers.[13] Anionic polymerization fronts of a solid monomer have been studied in Russia with ε-caprolactam,[8,9] but the fronts did not exhibit constant velocities. We report here the first investigation of traveling fronts of polymerization with solid acrylamide and a free-radical initiator.

Acrylamide was ground in a rock tumbler with glass beads until a uniform powdered mixture was obtained (about 8 h), and then the initiator was mixed in with a mortar and pestle. The powder was packed into glass tubes, and fronts were initiated with a soldering iron. A region of solid polymer could be observed to propagate through the powdered monomer. No noticeable melt zone was observed. Reactions were videotaped, and the position determined as a function of time. All reactions produced constant velocity fronts. Some experiments were performed with triethylene glycol dimethacrylate (TGDMA) mixed into the acrylamide. All chemicals were reagent grade and obtained from Aldrich.

The temperature profile was measured using a miniature thermocouple (Omega). The temperature versus time data were converted to a temperature versus position plot using the measured front velocity. Because reactions had the potential to explode, all were performed behind a safety shield in a hood. Most polymer materials were porous because of the gas produced by initiator decomposition.

A variety of initiators were found to support fronts, including benzoyl peroxide, azobisisobutyronitrile (AIBN), potassium persulfate, ceric ammonium nitrate, ceric ammonium sulfate, bromate/malonic acid, lead dioxide, and lithium nitrate.

The temperature profile is smooth, as indicated in the plot of temperature versus position in Figure 1 and sharper than with a liquid monomer.[11-13] The lack of convection is the reason for the difference. Notice that around 160 °C, the gradient decreases. This is most likely due to endothermic side reactions that produce ammonia. Either intra- or intermolecular imidization can occur.[29] Intermolecular imidization would produce a cross-linked, insoluble polymer; our samples were water soluble.

The velocity is weakly dependent on the tube size. The velocity was 15% greater in a 2.5-cm (i.d.) tube than in a 0.6-cm tube. This is presumably because the autocatalyst is heat, and the system is open to heat loss.

The degree of monomer conversion with AIBN is strongly dependent on the initiator concentration, with 0.8% AIBN, 95% of the monomer reacted but only 50% reacted with 2% AIBN.

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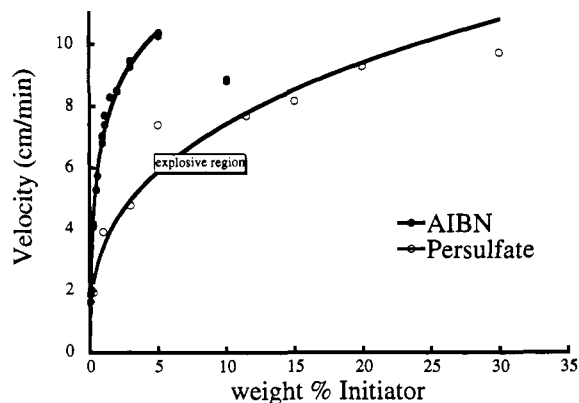
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Figure 2. The velocity dependence of the AIBN concentration in a 0.13 cm (i.d.) tube. The curve for the AIBN data is velocity = 7 + 4.8 log(% AIBN); for the persulfate data, velocity = 3.4 × (% persulfate)$^{0.34}$.

The conversion was determined by adding bromine[30] and titrating the excess iodimetrically.[31] The number of growing chains that are terminated by an initiator radical (primary termination) increases with higher concentrations of initiator, decreasing conversion.

The velocity dependence on initiator concentration for AIBN and potassium persulfate is shown in Figure 2. The velocities are about an order of magnitude greater than with methacrylic acid.[11] The higher velocities result from higher front temperatures (272 °C compared to 195 °C) and the greater reactivity of acrylamide compared to methacrylic acid.[32]

The velocities do not show a consistent dependence on the amount of initiator. The persulfate system follows a power function dependence but AIBN follows a logarithmic dependence up to 5%. The velocity decreases at 10% AIBN, but fronts propagate with up to 30% persulfate; between 5% and 12% persulfate the system is unstable and an explosion often results. We are unable to explain the difference in concentration dependence.

We are currently investigating the differences between polymer formed homogeneously and in a propagating front.

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