Free Radical Polymerization of Diacrylate by Thermal Front

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Thermal autocatalysis can generate propagating fronts, as seen in combustion. The thermal fronts have been used in a process, called self-propagating high temperature synthesis (SHS) discovered in 1967 by Alexandar G. Merzhanov and coworkers.[1] Such processes are used to prepare technologically useful ceramics and intermetallic compounds.[2] Similar effect occurs in exothermic polymerization reactions, such as free-radical polymerization and epoxy curing. Such frontal polymerization is a mode of converting monomer into polymer *via* a localized reaction zone that propagates, most often through the coupling of thermal diffusion and Arrhenius reaction kinetics.

The frontal polymerization reaction was first reported in 1972 by Chechilo and Enikokolopyan.[3] They studied methyl methacrylate polymerization to determine the effect of initiator type and concentration on front velocity as well as the effect of pressure. A great deal of work on the theory of frontal polymerization was performed.[4] The literature up to 1984 has been reviewed by Davtyan *et al.*[5] Pojman and his co-workers demonstrated the feasibility of the propagating front of polymerization in solutions of thermal free-radical initiators in a variety of neat monomers using liquid monomers that form polymers with melting points exceeding the reaction temperature of the front and with a solid monomer.[6] The macrokinetics and dynamics of frontal polymerization have been examined in detail[7] and applications for material synthesis considered.[8]

In this work, we have studied on the frontal polymerization of 1,6-hexanediol diacrylate (HDDA) monomer with persulfate initiator in dimethyl sulfoxide (DMSO). Because of high front temperatures, typically 150-200 ^{o}C, monomers that have low boiling points and thermally unstable initiators that give gaseous byproducts lead to the formation of bubbles. The bubbles not only lead to inhomogeneities in the polymer product but they also interfere with the fundamental studies of the dependence of front velocity on initiator concentration and the conditions for convection-free propagation.[9] The initiators, peroxides and nitriles, produce volatile by-product such as N_2, CO_2, methane, and acetone either from direct decomposition or β-scission. The problems associated with the formation of bubbles can be eliminated by using initiators that produce fewer bubbles. Lupesol(1,1-di(*t*-butylperoxy)-3,3,5-trimethylcyclohexane) is an initiator in the category. It produces less gas per initiating radical than other peroxide initiators. Masere *et al.* have studied the frontal polymerization of multifunctional acrylates using Lupersol and did not have the problem of bubbles in plastic-capped test tube.[10] The other alternative is the use of initiators that do not produce gaseous byproducts. Such initiators include inorganic peroxo compounds like persulfate that yield free radicals upon thermal decomposition and yet produce no gaseous byproducts. Using sodium persulfate as an initiator, Bowden *et al.* have studied frontal polymerization of acrylamide in dimethyl sulfoxide and no bubbles have been observed.[11]

In this study for the frontal polymerization of HDDA using persulfate initiator, we could observe a periodic spin mode in frontal polymerization utilizing HDDA and ammonium persulfate as monomer and initiator, respectively.

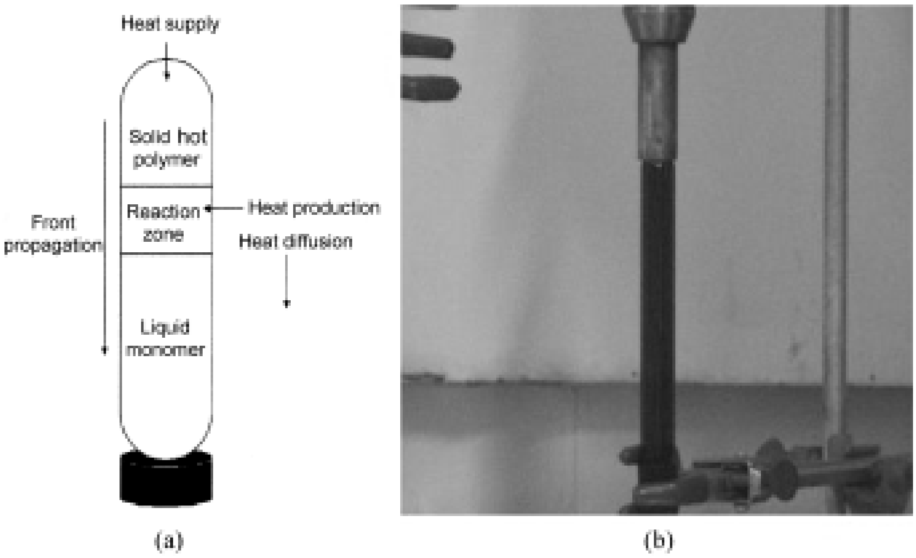
Experimental Section

Reagents. 1,6-Hexanediol diacrylate (HDDA) was used as a monomer and ammonium persulfate were obtained from Aldrich and used as received without further purification. Bromophenol Blue was used as a dye to visualize the propagating front. The dye was dissolved in dimethyl sulfoxide (DMSO). Ammonium persulfate had poor solubility in monomer but the addition of DMSO improved its solubility.

Procedures. A stock solution of the polymerization reactant mixture was prepared by throughly mixing 10 mL of HDDA monomer and 12 mL of initiator solution. The initiator solution was prepared by dissolving ammonium persulfate into DMSO within 1% by weight ratio of the monomer. To monitor the propagation of front by the color change from unreacted monomer solution to reacted polymer solid, 0.04 M Bromophenol Blue solution in DMSO was used. A 20 mL aliquot of the reactant mixture was pipetted into 50 mL beakers followed by the addition of 0.15 mL of the Bromophenol Blue solution to give a green solution. This solution was charged into a 16 mm × 125 mm capped test tube, and frontal polymerization was initiated with a soldering iron. Video images of the polymerization front were obtained using a digital camcorder (Handycam video Hi8, Sony TRV320) and were digitized on personal computer using FireBird DV.

Results and Discussions

Figure 1 shows a process of frontal polymerization. Figure 1a is a scheme of descending frontal polymerization and Figure 1b is an experimental setup in this study. Frontal polymerization was initiated by heating about 1 minutes with commercial soldering iron as shown in Figure 1b. A



(a) (b)

Figure 1. Process of frontal polymerization. (a) A scheme of descending frontal polymerization. (b) An experimental setup in this study.

planar progress of polymerization reaction front with discrete time is shown in Figure 2. The green reactant solution turned pale yellow as the front progressed downwards. The color change in the front propagation is due to the conversion of Bromophenol Blue to its another form *via* free radical coupling.[10] The dye indicator in this study was very useful since the propagating reaction zone could be visualized. In the experiments without addition of the dye solution, we could not monitor the reaction progress clearly although the difference in the optical properties of the monomer and the polymer is quite significant. A plot of the front position versus time produces a straight line whose slope is the front velocity. The velocity was affected by the concentration of initiator and dilution agent of DMSO and was about 1.0 cm/min in this study as shown in Figure 3.

In stirred reactions, a steady state can lose its stability as a bifurcation parameter is varied, leading to periodic oscillations and chaotic behaviors.[12] Propagating thermal fronts can show analogous behavior. The bifurcation parameter for a thermal front is the Zeldovich number;

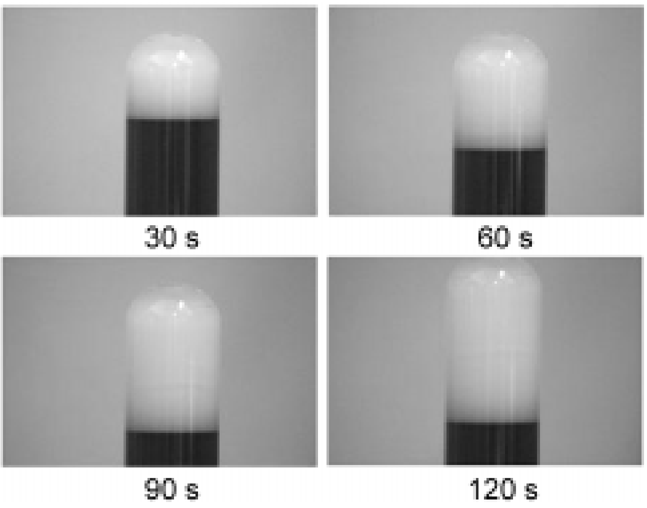

30 s
60 s
90 s
120 s

Figure 2. HDDA frontal polymerization front taken at 30 second intervals after initiation. The dark green zone shows the fresh reactant solution and the pale yellow zone is the polymer synthesized.

$$Z = (T_m - T_o)/T_m \times E_{eff}/RT_m. \tag{1}$$

The frontal polymerization reaction is assumed to occur in an infinitely narrow region in a single step with activation energy E_{eff}, initial temperature T_o and maximum temperature T_m. A great deal of theoretical work has been devoted to determining the modes of propagation that occur.[13,14] In a one-dimensional tube system, the constant velocity front becomes unstable as Z is increased. Experimental study of frontal polymerization of methacrylic acid has shown the existence of a rich variety of periodic regimes.[15] At ambient initial temperature with heat exchange to room temperature air, only a stable planar front mode exists. Decreasing the initial temperature of the reactants as well as increasing the rate of heat loss leads to the occurrence of periodic modes in the system. Recently, Pojman *et al.* have found a single head spin mode with diacrylate system using triethylene glycol

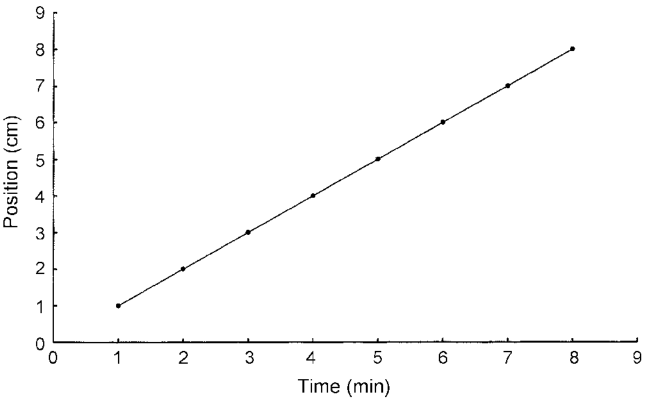


Figure 3. Plot of the front position versus time. It produces a straight line whose slope is the front velocity.

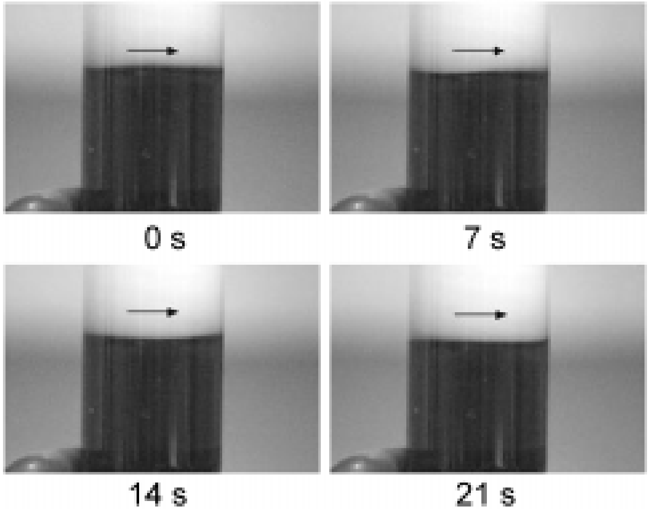


Figure 4. Image which shows a front propagating with a non-planar mode in HDDA frontal polymerization by increasing the ratio of DMSO in the reactant mixture. In this case, the reactant mixture was prepared by mixing 10 mL of HDDA and 14 mL of initiator solution. The arrow indicates the head of spin mode. The image is obtained from 7 minutes after the initiation.

dimethacrylate monomer at room temperature.[10] The reason for an easy formation of spin mode at room temperature in the diacrylate systems is that the effective energy of activation of diacrylate is much higher than a monoacrylate because it forms a crosslinked network. Spin modes are characterized by a non-planar front with one or more hot spots that move in a helical path along the axis of the reaction vessel. The spinning heads alter the polymer morphology, producing a nonuniform material. It is a major interference in frontal polymerization that limits its commercial viability.

The frontal polymerization using HDDA and gas free initiator of ammonium persulfate in this study have also showed a periodic spin mode by increasing the volume ratio of the initiator solution to the used monomer. In a single-head spin mode, a hot spot was observed to travel down the test tube in a spiral fashion. Figure 4 shows a visual image of a single-head spin mode in the presence of an indicator. The track of the spin mode can be clearly seen in the polymer rod. Increasing the ratio of the initiator solution in this study has an effect lowering the front temperature and increasing heat loss by dilution.

Conclusion

This study shows that the frontal polymerization of 1,6-hexanediol diacrylate is possible by using gas free initiator of ammonium persulfate. We have also observed a spin mode in the frontal polymerization by varying reaction condition. Frontal polymerization is a self-sustaining process in which a localized reaction zone or front propagates through a monomer being converting into the polymer. High exothermicity of the polymerization reaction and Arrhenius dependence for the polymerization rate are the most important requirements for a monomer to support a front. The frontal polymerizations are usually carried out without solvent, which means that the final product does not need to be separated from the solvent and no contaminated solvent requiring disposal.

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