Frontal polymerization is a mode of converting monomer into polymer via a localized reaction zone that propagates. Such fronts can exist with free-radical polymerization or epoxy curing. The necessary conditions for the existence of the free-radical frontal polymerization regime are considered. The physicochemical properties of monomers are classified in connection with complications arising in the experiments, including low conversion, convection and bubbles. The density gradient in the reaction zone leading to front decay is the most insidious problem. The analysis of forces that can withstand the Taylor instability allowed us to overcome experimental difficulties and develop approaches to polymerize low-viscosity monomers in the frontal mode. The factors affecting front shape, velocity, conversion, and molecular weight are considered.

Historically, frontal polymerization has been performed in neat monomer but we have been able to obtain fronts of very reactive monomers in high-boiling-point solvents including water, DMSO and DMF. Periodic frontal polymerization modes have been observed, including single and multi-point spin modes in which 'hot spots' (local high-temperature regions) migrate around the front as it propagates. We investigated experimentally the occurrence of the different modes as a function of the initial temperature and the intensity of heat losses and made a qualitative comparison to the results of theoretical analyses based on infinitely narrow reaction zone models.

The future directions of research with frontal polymerization are considered, especially with regard to applications to materials synthesis.

1. Introduction
Thermal reaction fronts in condensed media are very interesting and important phenomena for many reasons. Thermal fronts have been used in a process discovered in 1967 by Merzhanov and Borovinskaya called self-propagating high-temperature synthesis (SHS) to prepare technologically useful ceramics and intermetallic compounds. Such fronts demonstrate a rich variety of dynamical behaviour, including planar fronts, spin modes and chaotic reaction waves. In 1990, one of us (J.A.P.) heard a presentation by Bernard Matkowsky (Northwestern University) on instabilities in SHS, related to the experimental work of Merzhanov and his co-workers. Reasoning that such a thermal front could occur in polymerization reactions, which are also very exothermic, Pojman performed some crude simulations of methyl methacrylate polymerization that showed a front could propagate. Later that year he ordered methacrylic acid instead of methyl methacrylate (by mistake) to test if a front could propagate. The first experiment worked! (We will see later why this was a fortuitous error.) In 1991, Pojman published his preliminary work on polymerization fronts with methacrylic acid as a 'first'. Matkowsky introduced us to the extensive literature on propagating polymerization fronts studied in Russia 20 years earlier via a review by Davtyan et al.

We originally studied polymerization fronts because they are relatively easy dynamical systems to investigate compared with SHS systems that have front velocities about two orders of magnitude greater and temperatures ten times as large. Polymerization systems also offered the possibility of technologically useful materials. In Section 2 we review the original and recent work carried out in the former Soviet Union. We consider the characteristics of frontal polymerization in Section 3, including new results on the effect of pressure on front velocities. The properties of polymer produced frontally are discussed in Section 4.

In Section 5 we describe the experimental methods we employed in our work. We discuss, in Section 6, our new results on the stability of fronts and the sequence of periodic modes we observe. Finally, in Section 7 we consider the future of frontal polymerization, both from the point of view of non-linear dynamics and that of applications to materials synthesis.

Frontal polymerization can be observed with other chemical mechanisms, such as the cationic or amine curing of epoxy resins. We will not discuss these except where they are directly relevant to fronts with free-radical chemistry. We will not consider isothermal frontal polymerization (also called interfacial gel polymerization), which propagates by a different physical mechanism.

2. History of work in the former Soviet Union
A note on terminology: Russian workers have used the term 'frontal polymerization' although we have used both travelling fronts of polymerization or propagating fronts of polymerization. In respect to their priority we will adopt their terminology.

Chechilo et al. were the first to study frontal polymerization. They studied methyl methacrylate polymerization with benzoyl peroxide as the initiator. Fig. 1 is taken from their original data. They performed the reactions in closed metal reactors under pressure so they were unable to observe the front directly.

Chechilo and Enikolopyan studied the effect of pressure on the velocity. Increasing pressure (up to 5000 atm) increased the velocity by effectively increasing the concentration of the monomer and increasing the polymerization rate constant. They reported that drops of polymer descended from the front, which underwent a convective breakdown. This was due to a Taylor instability and/or double-diffusive instability because the product is a molten polymer. By increasing the
leaving a spiral pattern in the product. The entire front propagated around the outside of the 6 cm diameter hot spot propagated behind this system: first, the polymer crystallizes after it forms, which releases heat. Thus, a front of crystallization follows behind the main front. Vitaly and Vladimir Volpert investigated a hot spot propagated 16 times as rapidly as the front propagated.

In bulk polymerizations, as the viscosity increases, the rate of termination decreases causing autoacceleration, which is called the gel effect.\textsuperscript{2,21,22} For a monomer such as methyl methacrylate, the gel effect can play a significant role in the kinetics. Davtyan \textit{et al.} examined the influence of the gel effect on the kinetics of radical polymerization in a front.\textsuperscript{26} In developing a model of front velocity, they found that kinetic constants from isothermal, normal-pressure experiments were adequate for two reasons. Their front velocity data were obtained at high pressure (5000 atm) and the gel effect became important at high conversion. Both factors increased the front velocity.

Begishev \textit{et al.} studied anionic polymerization fronts with $\varepsilon$-caprolactam.\textsuperscript{27,28} The monomer and 2,4-tolulylene-bis carbamoylcaprolactam and sodium caprolactam (activator and catalyst, respectively) were mixed, and the temperature was raised to 353 K, 11 K above the melting point. (The product is a form of nylon.) The front did not propagate with a constant velocity because significant homogeneous reaction occurred at the initial temperature. There were two interesting aspects to this system: first, the polymer crystallizes after it forms, which releases heat. Thus, a front of crystallization follows behind the main front. Vitaly and Vladimir Volpert investigated a model of this two-wave system.\textsuperscript{29} Second, a ‘hot spot’ propagated around the front as it propagated down the tube, leaving a spiral pattern in the product. The entire front propagated with a velocity of the order of 0.5 cm min$^{-1}$, and it was a function of the concentrations of activator and catalyst. The hot spot propagated around the outside of the 6 cm diameter front 16 times as rapidly as the front propagated.

Work was also done in Chernogolovka on frontal curing of epoxy resins, both experimentally\textsuperscript{30} and theoretically.\textsuperscript{31,32}

2.1 Frontal polymerization reactors

A tube of methane and oxygen will support a front in the same way that a tube filled with monomer and initiator supports one. If the methane and oxygen are flowed up a tube, then a stationary front can be achieved. A natural goal was to develop a reactor in which the monomer-initiator solution was pumped in such a way that product would continuously flow out, without the input of heat. A large body of work was devoted to developing such a continuous frontal reactor.

Attempts were made with reactors of cylindrical and spherical geometries. Zhizhin and Segal performed a linear stability analysis of a reactor consisting of two concentric cylinders.\textsuperscript{33} A radial, axisymmetric front was supposed because the monomer-initiator would be pumped through the permeable inner cylinder. The viscous reacted polymer was supposed to flow out through the outer permeable cylinder. No buoyancy-driven convection was included. They found that if the resistance of the outer boundary was small, the front would become hydrodynamically unstable. They also considered a reactor with concentric spheres and found similar results. No experimental studies testing these reactor designs were published in non-Russian journals.

Vitaly and Vladimir Volpert and their colleagues in Chernogolovka continued these studies.\textsuperscript{34-39} They found cases where the front would become unstable and develop spin modes and multiple steady-states. More recent numerical studies were performed for the spherical case by Solovyov \textit{et al.}\textsuperscript{40} They found that the front could be unstable and chaotic oscillations with low frequency could result.

All the studies ignored the difference in density between reactants and product, which meant they could not consider buoyancy-driven convective instabilities. From work we will consider shortly, convective instabilities are a major interference when using monomers that form molten polymer. These instabilities seem to be the Achilles’ heel of any continuous frontal polymerization reactor with thermoplastics.

2.2 Recent studies

Some recent work on polymerization fronts without initiator using transition-metal nitrate acrylamide complexes has been performed in Chernogolovka.\textsuperscript{51} Such systems are unique in that the front proceeds at relatively low temperatures (around 100°C) with velocities of the order of 3 cm min$^{-1}$. The fronts were apparently unstable because a spiral pattern was observed in the product. A free-radical mechanism for the polymerization was proposed.

Pojman \textit{et al.} demonstrated the feasibility of travelling fronts in solutions of thermal free-radical initiators in a variety of neat monomers at ambient pressure using liquid monomers that form polymers with melting points exceeding the reaction temperature of the front.\textsuperscript{13,42-44} Balcom \textit{et al.} used magnetic resonance imaging to study fronts of methacrylic acid polymerization.\textsuperscript{45}

3. Characteristics of free-radical frontal polymerization

3.1 Mechanism of polymerization

In spite of the significant differences between the parameters (e.g. energy of activation and front temperature) of SHS and frontal polymerization, the most important dimensionless parameters of these processes are in the same range. It is necessary, however, to consider the distinguishing features of frontal polymerization.

A number of radical polymerization reactions are highly exothermic and able to support the frontal polymerization regime. Let us consider the mechanism of autocatalysis that is a necessary condition for the existence of the frontal mode. A
free-radical polymerization with a thermal initiator can be approximately represented by a three-step mechanism. First, an unstable compound, usually a peroxide or nitrile, decomposes to produce radicals:

\[ I \rightarrow f/2R' \]  

(1)

where \( f \) is the efficiency, which depends on the initiator type and the solvent. A radical can then add to a monomer to initiate a growing polymer chain:

\[ R' + M \rightarrow P_1^* \]  

(2)

\[ P_n^* + M = P_{n+1}^* \]  

(3)

The propagation step (3) continues until a chain terminates by reacting with another chain (or with an initiator radical):

\[ P_n^* + P_m^* \rightarrow P_{n+m}^* \]  

(4)

The major heat release in the polymerization reaction occurs in the propagation step. However, the propagation reaction (3) does not have a sufficiently high activation energy to provide a frontal regime, i.e., a significant reaction rate difference between the reaction and cold zones. Thus, heat cannot be a sufficiently strong and direct activator as it is in SHS reactions. Frontal polymerization autocatalysis takes place through the initiator decomposition step, because the initiator radical concentration is the main control for the total polymerization rate, compared to the gel effect or direct thermal polymerization that may also be present in the frontal polymerization process. The steady-state assumption in the polymerization model gives an approximate relationship between the effective activation energy of the entire polymerization process and activation energy of the initiator decomposition reaction:

\[ E_{\text{eff}} = E_p + (E_i/2) - (E_i/2) \]  

(1)

where \( E_p \) is the activation energy of the propagation step, \( E_i \) is that for the initiator decomposition and \( E_s \) is that for the termination step.

The second term in the right-hand side of eqn. (1) depends on the initiator. Because it has the largest magnitude, this value mostly determines the effective activation energy. Because of this, the initiator plays a significant role in determining if a front will exist and, if so, the temperature profile in the front and how fast the front will propagate. The exception here is hexane-1,6-diol diacrylate, which is so highly reactive that it can be polymerized in the frontal mode without added initiator.

### 3.2 Physical properties of monomers

Some requirements on the physical properties of the polymerization medium itself must also be met. In the early papers on frontal polymerization, the authors\(^\text{19,20,46,47}\) applied very high pressure (up to 5000 atm) to eliminate monomer boiling (methyl methacrylate) and the reaction zone decay due to the density gradient in the reaction zone (Taylor instability). They also managed to observe only downward travelling fronts because natural convection rapidly removed heat from the reaction zone of an ascending front leading to extinction. However, at pressures less than 1500 atm, downward propagating fronts decayed because the polymer was more dense than the monomer. Thus, unless a sufficiently high pressure is applied, it is not possible to obtain a polymerization front with methyl methacrylate.

Summarizing our experimental results\(^\text{13,42,44}\) and reliable experimental data of the other authors\(^\text{19,20,46-48}\) we describe cases when frontal polymerization is expected to be observed. The first case is crosslinking monomers (thermosets), including tri(ethylene glycol)dimethacrylate (TGDMMA), di(ethylene glycol)dimethacrylate (DGDMMA), and divinylbenzene. The free-radical polymerization of these monomers produces rigid crosslinked polymers, which sustain a sharp frontal interface. Some of these monomers are very viscous (e.g. TGDMMA) and allow ascending and horizontally propagating fronts because the natural convection is reduced.

The second group of monomers forms polymers that are insoluble in the monomer. Good examples are acrylic and methacrylic acids.\(^\text{13,42,44}\) Insoluble polymer particles adhere to each other during their formation and stick to the reactor or test-tube walls, forming a mechanically durable phase and discernible polymer/monomer interface. (Thus, in this case the adhesive properties of polymer particles withstand the buoyancy force caused by the polymer–monomer density difference.) Nonetheless, Taylor and double-diffusive instabilities partially develop in such systems and manifest themselves as fingering.\(^\text{3,4}\) How well the front sustains itself depends on convection, the polymer glass-transition temperature and molecular weight distribution. Indeed, these properties themselves depend on the initial reactant temperature, initiator type and concentration.\(^\text{44}\)

Nagy and Pojman developed a technique to suppress fingering with methacrylic acid fronts in which the tube was rotated around the axis of front propagation.\(^\text{49}\) The front velocity depended on the fourth power of the rotational frequency, and the amplitude of the front curvature was proportional to the square of the frequency.

The third group of monomers includes all highly reactive monomers that produce thermoplastic polymers, which are molten at the front temperature. Such fronts decay owing to the Taylor instability. Although these polymers are soluble in their monomers (given sufficient time), on the timescale of the front the polymer is effectively immiscible with the monomer. Adding an inert filler such as ultra-fine silica gel (Cabosil) or a soluble polymer increases the viscosity and eliminates the front collapse. Some monomers like styrene and methyl methacrylate require moderate pressure (20–30 atm) to eliminate monomer boiling. Higher-boiling-temperature monomers like butyl methacrylate and butyl acrylate support the frontal regime at ambient pressure in test-tubes. Frontal polymerization of the third group of monomers can be realized in any orientation because the large viscosity of the monomer (Cabosil system) suppresses natural convection. Therefore, no simple continuous frontal polymerization reactions are possible, except with group 3 monomers premixed with a viscosity-enhancing agent. However, adding a filler prevents the production of a homogeneous product unless the product is soluble in the monomer and is used.

A lack of appreciation of these facts led to the appearance of a book\(^\text{50}\) devoted to the dubious experimental observations in a radial frontal polymerization reactor for methyl methacrylate at 40 atm, which contradicts our experimental observations in a transparent pressurized reactor. The front collapses as fingers and drops of polymer fall from the front, as can be seen in Fig. 2. Because Zhizin could not observe the front, we believe he mistook bulk polymerization for a true frontal mode.

All frontal polymerization monomers should be highly reactive in order to maintain the reaction in the presence of heat losses that always occur, and are especially important in narrow tubes. The frequency factor for the propagation rate coefficient should be at least, \( A_p \gg 10^9 \text{ mol}^{-1} \text{s}^{-1} \), based on our experience with reactions in the test-tubes with \(< 3 \text{ cm}^2 \) diameter at ambient temperature. A polymerization front is a thermal wave having existence conditions with respect to the heat loss intensity. In some cases the problem of quenching can be solved by using larger diameter test-tubes or preheating the initial reactants. (Preheating will not work with a fast decomposing initiator, e.g. AIBN, because of the homogeneous reaction in the bulk monomer.)
3.3 Frontal polymerization in solution

We had always assumed that frontal polymerization would only work with neat monomer-initiator solutions. Gusika had considered a model of frontal polymerization through a suspension. However, some recent work has expanded the systems that can be studied. Frontal polymerization of several reactive monomers can be performed in high-boiling-point solvents. Acrylamide polymerization will propagate in water (with some vaporization of water), in dimethyl sulfoxide (DMSO) and in dimethyl formamide (DMF) with several initiators, including sodium persulfate, potassium persulfate, ammonium persulfate and benzoyl peroxide. Interestingly, no gas bubbles are observed with acrylamide-persulfate in DMSO, the only system we have found with this feature at ambient pressure. (The persulfates do not produce volatile side products.) Several other monomers also work in these solvents, including acrylic acid, sodium methacrylate and zinc dimethacrylate. For a monomer to support frontal polymerization in a solvent, the enthalpy of the reaction must be sufficiently high that dilution does not lower the front temperature below a front-sustaining value.

Fronts of acrylamide in DMSO (1:1) are not destroyed by fingering because the polyacrylamide gels. However, a monomer such as acrylic acid, which does not gel in DMSO, exhibits rampant fingering and will not propagate without the addition of a few per cent of bisacrylamide (a difunctional monomer), which produces a crosslinked and solid product. The same is true for acrylamide in DMF.

3.4 Solid monomers

Frontal polymerization of solid monomers has been realized for several systems, and it has additional complicating aspects, such as the effect of density and particle size, that will be considered in another work. (A special type of low-temperature frontal polymerization with γ irradiation was also studied in Russia.) We consider here some results for frontal acrylamide polymerization because they dramatically illustrate an issue that is general to all frontal polymerization.

3.5 Temperature profiles

A polymerization front has a very sharp temperature profile, and profile measurements can provide much useful information. For example, it is important to know how conversion depends on the initial temperature of reactants. The temperature profiles help elucidate the reasons for incomplete conversion and the structure of the front. Several temperature profiles measured during frontal polymerization of methacrylic acid are shown in Fig. 3. The first four profiles are for solutions of benzoyl peroxide in methacrylic acid at different initial temperatures. The fifth profile was obtained for the same monomer with tert-butyl peroxide (tBPO). Despite different initial temperatures the temperature maxima do not change significantly. Conversion is directly proportional to the difference between the maximum and initial temperatures. Profile 5 reflects the use of a more stable initiator, which led to the highest conversion and widest heat conductivity zone. All these facts point to initiator burn out, i.e. when the initiator has been exhausted before the reaction has been completed; more stable initiators give higher conversion. The methacrylic acid front with tBPO was significantly slower, in spite of having the highest reaction temperature. This means that the effective activation energy of a polymerization front is directly correlated to the activation energy of the initiator decomposition, as was expected. The same conclusions with respect to initiator burn out can be drawn for propagating fronts of acrylamide (Fig. 4), which we observed at initial reactant temperatures as low as that of liquid nitrogen. Notice that the conversion is affected by the initial temperature.

3.6 Velocity dependence on initiator concentration

Chechillo et al. studied methyl methacrylate polymerization with benzoyl peroxide as the initiator. By placing several thermocouples, they could infer the front velocity and found a 0.36 power dependence of the velocity on the benzoyl peroxide.
The power functional dependence for velocity versus initiator concentration. More detailed studies for several initiators showed 0.223 for tBPO, 0.324 for benzoyl peroxide (BPO) and 0.339 for cyclohexylperoxide carbonate. Pajman et al. reported a detailed study of tri(ethylene glycol) dimethacrylate (TGDMA) frontal polymerization. The power functional dependence for velocity versus initiator concentration was different for all three: AIBN (0.20), BPO (0.23), LPO (0.31).

3.7 Effect of pressure

Experiments were performed in a custom-built reactor of our design that allowed isobaric and isothermal conditions (Fig. 5). We found that the front velocity was a function of the applied pressure, even at low values of less than 30 atm. As the pressure is increased, the velocities decrease, exactly opposite to the behaviour observed by Chechilio and Enikolopyan at high pressures! At the low pressures we employ, we are not affecting the rate constants of polymerization but suppressing bubbles.

There are three sources of bubbles. All the thermal initiators we have investigated (except sodium persulfate, which is insoluble in most monomers) produce volatile by-products, such as CO₂, methane and acetone. It is an inherent problem with all commercially available peroxide or nitrile initiators.

Another source of bubbles is dissolved gas and water in the monomer. Gases can be removed under vacuum but water is extremely difficult to remove from methacrylic acid and TGDMA. Less than 1 mg of water will result in 2 cm³ of water vapour at the front temperature of 200°C and 1 atm of pressure. The only certain solution to all three sources is to perform reactions under pressure.

Bubbles can increase the velocity of fronts in standard closed test tubes initially at ambient pressure by as much as 30% compared to fronts free of bubbles under high pressure. The expansion of bubbles is part of the velocity by forcing unreacted monomer up and around the cooling polymer plug that is contracting; poly(methacrylic acid) is ca. 25% more dense than its monomer. This means that the pressure increases during the reaction because the tube is sealed, except for leakage around the initial polymer plug.

Fig. 6 shows the front velocity as a function of the inverse of the applied pressure. As the pressure is increased the velocity decreases because the volume of the bubbles is decreased, following Boyle's law. Pressure is not affecting the rate of polymerization but the rate of front propagation because of the expansion of the medium. A similar phenomenon was observed by Merzhanov with SHS materials that created a porous product.

We can write the velocity as:

\[ v(\rho) = v_0 + \frac{\text{const}}{\rho} \]  

where the constant will be a function of the number of moles of gas produced in the front. Therefore, the higher the initiator concentration, the higher is the applied pressure necessary to obtain the true front velocity.

To determine the true front velocity dependence on initiator concentration requires that the effect of bubbles be eliminated. We did not do this in earlier publications, which are necessarily limited in their application to developing a numerical model of frontal polymerization. Different initiators can yield different amounts of gas. Thus, the velocity depends not only on the kinetics of the initiator decomposition, but also on the amount of gas produced and on the applied pressure.

Poly(methacrylic acid) formed in a front in a test-tube initially at ambient pressure is opaque but translucent when produced under at least 34 atm pressure. Very small bubbles scatter light and make the material opaque when, in fact, the polymer itself is clear. This is also true with butyl acrylate fronts. Cabosil has a refractive index close enough to poly(butyl acrylate) that the initial solution and product are translucent, as can be seen in Fig. 7.

If TGDMA is partially reacted to produce a gel before front initiation, no bubbles appear as the front propagates. Gelling can be accomplished by allowing TGDMA-initiator to sit at room temperature for several days or by heating to 40°C until gelation occurs.) In ungelled TGDMA, copious bubble production occurs. It seems that the gel prevents nucleation of bubbles before complete crosslinking makes it impossible to form bubbles.

Pajman et al. found an unusual mode of propagation when there are large amounts of bubbles. In studying fronts of methacrylic acid polymerization with AIBN initiator, they observed convection that periodically occurred under the front at the same time as the front deformed and undulated. The period of convection was ca. 20 s and remained constant during the entire front propagation. Such behaviour was seen with other initiators at concentrations of at least 1%, unless
that natural convection evened out the front. Pojman 3.8 Front curvature changes periodically in time. This periodicity is probably though a radial temperature gradient exists. We had supposed Fronts of methacrylic acid polymerization are often flat, even liquid motion caused by the hydrodynamical instability instability can (and does) appear in this case. The instability is not independent of the pressure. This is a usual assumption for pressure is maintained near ambient (see below). Three factors seem to favour the appearance of the instability: high initiator concentration, low pressure and high initial solution temperature. All these factors increase the number and size of gas bubbles.

Volfert et al. have analysed the effect of the thermal expansion of the monomer on the thermal stability and concluded that the reaction front becomes less stable than without thermal expansion. The effective thermal expansion can be increased because of the bubbles, and it can affect the stability conditions considerably.

The next step in this analysis was connected with the hydrodynamical instability. As is known beginning with the work of Landau, a gaseous flame can be unstable because of the thermal expansion of the gas near the reaction zone. Polymerization fronts are similar to flames. Hence, we can expect that under some conditions hydrodynamical instability can appear. This was found experimentally for frontal polymerization of methacrylic acid, where the monomer is liquid and the polymer solid.

To explain the experimental results, a stability analysis was fulfilled under the assumption that the isobaric approximation could be used. This approximation means that the density of the medium depends on the temperature, but is independent of the pressure. This is a usual assumption for slow combustion. Paradoxically, the analysis shows that there is no hydrodynamical instability in this model. It shows that the model cannot be applied for all experimental conditions because of the gas bubbles.

For large external pressures, there are no gas bubbles, and the isobaric approximation can be used. The instability is not observed experimentally, which is in agreement with the analytical results. If the external pressure is low (ca. 4 atm), the gas bubbles appear, the effective density depends on pressure, and the isobaric approximation cannot be used. The instability can (and does) appear in this case.

An interaction of thermal and hydrodynamical instabilities was observed experimentally. In this case, the intensity of the liquid motion caused by the hydrodynamical instability changes periodically in time. This periodicity is probably caused by the thermal instability.

3.8 Front curvature
Fronts of methacrylic acid polymerization are often flat, even though a radial temperature gradient exists. We had supposed that natural convection evened out the front. Pojman et al. have found that it is not buoyancy-driven convection that keeps the front flat, but rather the presence of large amounts of bubbles. If the initiator concentration is low with methacrylic acid, the front is actually concave. With low initiator concentration (or in a pressure reactor), a few small bubbles are observed to migrate slowly toward the centre of the front and then disappear into the polymer.

Because the tubes are diabatic, the temperature is higher in the centre. TGDMA fronts are convex because the higher temperatures in the centre cause faster reaction and a faster front velocity. The change in volume during reaction, \( \Delta V_{\text{eq}} \), is another factor that must be considered. For mono-acrylates, the volume change during reaction is ca. 20%. The higher temperature in the centre causes faster reaction and therefore a greater rate of conversion. Because the isothermal contraction for the isothermal polymerization of methacrylic acid is much greater than the thermal expansion, the more converted centre region contracts. However, TGDMA is a dimethacrylate and has a small reaction volume, so the front cannot contract upward.

4. Properties of polymer produced via frontal polymerization
4.1 Conversion
A problem with propagating fronts is that the rapid increase in temperature causes rapid initiator decomposition or 'burnout', which can lead to low conversion. If frontal polymerization is to have practical utility, then high conversion must be achieved. A possible method to achieve this goal is to use two initiators with sufficiently different energies of activation that one initiator will only start decomposing after the first initiator has been consumed. Pojman et al. measured the conversion of double bonds as a function of initiator concentration and investigated a dual initiator system consisting of BPO and the more stable tBPO. These experiments showed that using a stable initiator provides better conversion, because the tBPO alone was almost as good as the dual system. The advantage of the dual system is that the front velocity is determined by the least stable initiator (providing a fast front) but the conversion is determined by the more stable one.

Conversion can also be limited by thermodynamics. Because the polymerization reactions are exothermic, the equilibrium conversion decreases with increasing temperature. A relationship between temperature and the equilibrium monomer concentration (assuming unit activity coefficients) can be derived, in which \( [\text{M}]_0 \) is the standard monomer concentration used to calculate the \( \Delta S^\circ \) and \( \Delta H^\circ \).

\[
T = \frac{\Delta H^\circ}{\Delta S^\circ + R \ln ([\text{M}]_0/[\text{M}]^\circ)}
\]

For an adiabatic polymerization, the maximum conversion is uniquely determined by the \( \Delta H^\circ \) and \( \Delta S^\circ \) of polymerization. As the temperature increases, the equilibrium conversion is reduced and can be related by:

\[
z = 1 - \frac{1}{[\text{M}]_\text{initial}} \exp \left( \frac{\Delta H^\circ - T \Delta S^\circ}{RT} \right)
\]

The relationship for the temperature and conversion for adiabatic self-heating is:

\[
T = T_i + z \Delta H^\circ/C_P
\]

The solution of eqn. (IV) and (V) provides the conversion achieved in adiabatic polymerization. Fig. 8 shows the results for methyl methacrylate with an initial temperature of 25 °C, using thermodynamic data from Odian. The conversion is 0.93, which means that, independent of initiator burnout,
may exhibit very different conversions at the same temperature. For example, zero conversion will be obtained at degrees of polymerization less than 150, with a maximum nonetheless, thermodynamics must be considered when selecting candidates for frontal polymerization. Similar monomers may exhibit very different conversions at the same temperature. For example, zero conversion will be obtained at 310°C with styrene but a-methylstyrene will not react above 330°C with methyl methacrylate.

4.2 Molecular weight distributions

For all the work done in Russia, no molecular weight distribution (MWD) of any polymer produced in a front was published. However, Enikolopyan et al. analytically calculated the MWD assuming the reaction takes place at the front temperature and that the initiator is consumed. They predicted unimodal molecular weight distributions with average molecular weight decreased with increasing initiator concentrations.

Gel permeation chromatography (GPC) showed that poly(methacrylic acid) from fronts had multimodal, broad MWDs with surprisingly high molecular weights. Given that the front temperatures exceed 200°C and the initiator concentrations are large (ca. 1%), it was unexpected that high-molecular-weight polymer was produced (>10^5). Poly(methacrylic acid) does precipitate from the neat monomer-initiator solution, and so the gel effect was invoked. Pojman et al. found in a recent study that these high molecular weights were the result of crosslinking via intermolecular anhydride formation.

To determine the true MWD for an acrylate under frontal polymerization conditions, they studied butyl acrylate fronts and anhydride formation is not possible. The MWDs followed the trend that one would expect from the classical steady-state theory of free-radical polymerization. Poly(butyl acrylate) produced in fronts had broad (M_w/M_n = 1.7–2.0) but unimodal molecular weight distributions with M_w < 10^5). The average molecular weight decreased with increasing initiator concentrations.

5. Experimental

5.1 Experiments at ambient pressure

A solution of de-gassed neat monomer and initiator was placed into a test tube. If benzoyl peroxide (BPO) was used as the initiator, fronts were initiated by the addition of ca. 0.5 ml of N,N-dimethylaniline (DMA) to the top of the solution. For other initiators, ca. 0.5 ml of a BPO–methacrylic acid solution was added together with 0.5 ml of DMA to the top of the solution. The heat liberated by the polymerization initiated by the DMA-BPO redox reaction started the front. Reactions were video-taped, and the position as a function of time was determined.

Analysis of captured images was performed with Image 1.41 (from NIH). IR imaging was carried out using an InfraBrimics Model 760 IR camera with a mercury-cadmium telluride detector with closed circle cooling and equipped with a germanium 3 x zoom lens.

5.2 Experiments performed under pressure

For pressure (up to 50 atm) experiments the reaction vessel was placed in an all-glass pressurized chamber and oriented in such a manner that the sealed end was at the top and the open end in the downward direction (Fig. 5). A movable airtight piston at the open end contained the reactants. An increase in pressure in the pressure chamber caused the piston to move inwards in the reaction tube and vice versa to compensate for any resulting pressure difference between the chamber and the reaction tube. A subminiature thermocouple probe [Omega TMQS5-0.020(G)-12°] passed through the piston and was formed into a spiral parallel to the front surface for temperature profile measurements.

The pressurized chamber was submerged in a large temperature-controlled water bath equipped with an oblong window. A motorized video camera monitored the downward propagating front in the reaction chamber. A mass flow controller (Omega FMG 7201) maintained a 100 ± 1 cm³ min⁻¹ nitrogen flow upwards along the sides of the reaction vessel to prevent an increase in temperature in the pressure chamber. The nitrogen was equilibrated to the water-bath temperature via a copper coil before entering the chamber.

The epoxy monomer diglycidyl ether of bisphenol A (DGEBA) was cured with a boron trichloride-amine complex (BCl₃–NR₂) from Ciba-Geigy.

Monomers were of reagent grade (Aldrich) and used without further purification. AIBN from Pfaltz & Bauer was recrystallized from methanol before use. All reactions were performed in 2.2 x 25 cm culture tubes (Kimax) unless otherwise indicated.

5.3 Experiments to study spin modes

The experimental arrangement is shown in Fig. 9. A solution of methacrylic acid and BPO was equilibrated in an ethylene glycol–water bath. The front was initiated and, as it propagated, the tube was withdrawn from the bath to maintain a fixed distance between the front and the coolant. The position of the front could be determined by the narrow melt zone.
immediately beneath it. Control of heat losses was also realized under free-convective heat exchange conditions by using different cooling liquids and their temperature variation (Fig. 10).

Temperature measurements were made with unsheathed fine-gauge thermocouples (OMEGA T 0.000 COCO-005) and a Strawberry Tree A/D board on a Macintosh IIcx. Profiles were determined by measuring the temperature at a fixed point as the front propagated down onto a thermal couple that was formed into a spiral parallel to the front. (The spiral decreased the heat flux in the thermocouple.) Using the front velocity, the temporal profile was converted to a spatial profile.

6. Modes of frontal polymerization

Planar front propagation was the first frontal polymerization regime studied in detail. The existence of periodic regimes and nonplanar modes was expected in frontal polymerization because of the close similarity between the propagation mechanism of frontal polymerization and SHS processes where periodic (unstable) modes have been known. Spin modes have been discovered for two different polymerization systems. Oscillatory modes are referred to as 'unstable' because they are found beyond the thermal stability boundary of the steady-plan propagating thermal wave. However, those modes are observed experimentally; they are reproducible and stable in time. To avoid misunderstanding we will call them periodic modes.

Experimental study of frontal polymerization of methacrylic acid has shown the existence of a rich variety of periodic regimes. At ambient initial temperature and heat exchange to room temperature air only a stable planar front mode exists. Decreasing the initial temperature of reactants, as well as increasing the intensity of heat losses in frontal polymerization of methacrylic acid, leads to the occurrence of periodic modes. Thus the magnitude of heat losses is an important factor for studying periodic regimes and a convenient control parameter. Control of heat losses was realized under free and forced convective heat-exchange conditions by using various cooling liquids at different temperatures.

We now describe the sequence of modes observed during frontal polymerization for a 2% w/v BPO solution in methacrylic acid as a function of the initial temperature and heat loss intensity.

6.1 Pseudo-pulsation regime

This is the first new regime appearing after planar front propagation as the intensity of heat loss is increased. Pseudo-pulsations were observed in 16 mm diameter test-tubes in an ambient temperature air flow and in 25 mm test-tubes immersed in an unstirred 25°C water bath (Fig. 11). In both cases, radial temperature gradients due to heat losses cause front curvature. The front convexity grows gradually (Fig. 11), and at some critical front curvature (profile 2 in Fig. 11), rapid radial propagation occurred eliminating the front curvature and making the front flat again (profile 4 in Fig. 11). This phenomenon quickly repeats itself many times and, for an observer of the external sample surface, (e.g. frontal polymerization of solid monomers and SHS) it can appear as a pulsating front. In 16 mm test-tubes the pseudo-pulsation regime manifested itself as rapid 2 mm front advances ('jumps', observed on the polymer surface) with a frequency of 3 pseudo-pulsations min⁻¹. The 'jump' length was 1.5 mm for 25 mm test-tubes with a frequency of 4 pseudo-pulsations min⁻¹.

A periodic mode of propagation in SHS has been attributed to a one-dimensional front oscillation. The product has a 'pancake' structure with layers of incompletely reacted materials between completely converted product, which is consistent with a true one-dimensional instability and not a pseudo-pulsation.

6.2 Multi-point spin modes

Lowering the water bath temperature to 21°C allowed us to observe a multi-point spin mode (Fig. 12). This regime manifests itself as many spinning heads adjacent to the tube wall. Multiple heads appear and disappear on the sample surface moving along spiral trajectories (2-5 mm long) crossing each other and leaving a characteristic reticulated pattern on the surface. A similar phenomenon has been observed in SHS.

6.3 Several-head spin mode

The initial monomer temperature cannot be lowered below 21°C by immersion in a water bath because heat loss
quenches the front. The further decrease of the initial solution temperature is only possible by using the experimental setup shown in Fig. 9. The clearance, $\Delta$, between the front and the coolant interface, together with the coolant temperature, determines the radial and longitudinal temperature gradients. At an initial solution temperature of 0°C and with a 1.5 mm clearance, it is possible to observe a few-head spin mode, which has the specific pattern shown in Fig. 13. It is difficult, however, to separate heat losses and initial temperature effects in this case; probably they act together. The several-head spin mode also take place in $\varepsilon$-caprolactam frontal polymerization$^{27,28}$ and in SHS.$^{67}$

### 6.4 Single-head spin mode

The most impressive pattern (a large translucent spiral in Fig. 14) has a single-head spin mode that can be realized by decreasing the clearance down to 0.5 cm at 0°C initial temperature. The single 'hot spot' propagated around the front (itself moving with a velocity of 0.66 cm min$^{-1}$) with a period of 1.3 min. The direction of the single head spinning is arbitrary and can change during front propagation. The spin mode is most impressive when observed with an infrared camera. Fig. 15 shows montages of a single head spiralling around the tube, in visible light and IR. In the visible range, spin modes can be inferred from a perturbation in the front shape.

In general, the behaviour of the polymerizing system is determined by the initial temperature of reactants and the magnitude of heat losses. The experimental propagation mode depends on the coolant temperature and clearance $\Delta$, for a given initiator concentration and tube diameter. The phase diagram of the experimental stability boundaries is shown in Fig. 16.

The use of different initiators does not significantly affect the qualitative picture of the periodic regimes. Spin modes were observed with the initiators BPO, tBPO, lauroyl peroxide and AIBN, which have significantly different activation energies of disintegration. An essential feature of non-linear dynamical behaviour is its universality. Although the chemical mechanism of front propagation is specific to each system, the fact that the front is the result of Arrhenius dependence of reaction rate coupled to thermal diffusion means that the qualitative features of the modes of propagation are system independent, as we will see in the next section. This universality of front behaviour is demonstrated with frontal curing of epoxies. Using 40% BC1$_3$-amine complex with DGEBA resin, a front can propagate in a tube immered in ambient-temperature water. Under these conditions, methacrylic acid fronts show multi-point spin modes. As Fig. 17 shows, the epoxy front exhibits a single head spin mode.

### 6.5 Stability analysis

The numerical and theoretical analysis of the non-stationary equations describing the thermal reaction wave propagation in condensed media showed a rich variety of dynamical behaviour.$^{16,63,64-72}$ In general, the linear stability analysis of the longitudinally propagating fronts in the cylindrical adiabatic reactors with one overall reaction and no physical complications predicted that the expected frontal mode for the given reactive medium and diameter of reactor is governed by the Zeldovich number, where $T_m$ is the maximum temperature...
Decreasing the initial temperature of the reactants increases the Zeldovich number (if the conversion does not change) and drives the system away from the planar front propagation mode into non-stationary regimes. Moreover, the stability analysis of the reaction-diffusion equations describing the propagation of reaction waves along the cylindrical sample predicts the existence of the spin modes with different numbers of heads. Some of the non-planar frontal polymerization regimes described above, such as single and multi-point spin modes, have very similar topologies to those predicted theoretically; namely, the perturbed solutions show the front structure with temperature maxima rotating as a whole around the cylinder axis with constant angular velocity. Depending on the Zeldovich number and the tube diameter (provided kinetic parameters are kept constant) the number of spinning heads can vary from one to infinity as the tube diameter increases.

This analysis provides some qualitative insight into the factors that can affect the stability of a front but does not directly apply to our experiments. The model ignores heat loss and is based on a one-step reaction model.

7. Future of frontal polymerization

7.1 Dynamics

In the area of dynamics, several questions remain.

1. What is the exact relationship between heat loss and the modes of propagation?
(2) We have not discussed frontal polymerization of solid monomers because the systems are complicated by the additional variables of particle size, density and the effects of filtration of molten monomer through the porous medium. Even though the front temperatures are very high, we do not observe nonplanar modes of propagation when the initial temperature is as low as 77 K. We do not know why.

(3) What is the experimental relationship between tube size and number of spinning heads?

(4) Can multiplicity of spin modes be observed experimentally? In other words, can more than one propagation mode exist under the same experimental conditions?

(5) What is the effect of complex reaction kinetics on the front stability?

Determining the answer to these and other questions regarding the dynamical behaviour of polymerization fronts will not only expand our understanding of thermal fronts but will also assist the development of frontal polymerization as a technique for producing current materials in a new way and the synthesis of unique products.

7.2 Applications to materials synthesis

We have seen that frontal polymerization is an excellent tool for studying dynamics in thermal fronts and is an interesting approach for polymer synthesis. But is it useful?

We expect that this approach will ultimately have three benefits over traditional methods of polymer synthesis: (1) reduced energy costs, (2) reduced waste production and (3) unique morphologies. One unique feature of frontal polymerization is the rapid and uniform conversion of monomer to polymer. Performing an adiabatic polymerization of a neat monomer is difficult at best and dangerous at worst, but it can be advantageous because the heat of the reaction is used to increase the rate of reaction, making for very rapid conversion. Also, the lack of solvent eliminates the need to separate the polymer from the solvent and residual monomer, which requires energy and can have environmental ramifications.

For large quantities of commodity polymers, such as polymethyl methacrylate and polystyrene, frontal polymerization does not seem to offer enough advantages to justify its implementation. Current technologies are well developed and have a huge capital investment associated with them. However, some polymers, such as poly(butyl acrylate) and poly(acrylic acid) are prepared in batch bulk reactors because the cost of removing solvent from product prepared in a continuous reactor is so great. A CSTR can be difficult to operate for some systems due to the difficulty of stirring viscous polymer–monomer solutions.

Unfortunately, there are two problems with the frontal polymerization reactors previously proposed: the low molecular weight of the polymer and convective instabilities. The low molecular weight is inherent with the high front temperatures and relatively high initiator concentrations necessary with less reactive monomers such as styrene and methyl methacrylate. Even if low-molecular-weight polymer is desired, a continuous frontal reactor would be plagued by instabilities caused by changes in viscosity during reaction and buoyancy-driven convection. A possible solution could be a frontal reactor consisting of a porous medium that would eliminate buoyancy-driven convection. Hydrodynamic instabilities caused by the difference in viscosity could be a problem, but we have observed with butyl acrylate that the hot polymer is less viscous than the unreacted monomer. If the temperature of the product were adjusted to match the viscosity of the monomer, then the problem could be avoided. Further work on porous frontal reactors needs to be undertaken.

7.2(a) Interpenetrating polymer networks. The macroscopic properties of a polymer are not only determined by the molecular weight but also the morphology of the material, especially for thermosets (materials that harden irreversibly when heated). Crosslinked polymers must be prepared in situ because the polymer has an infinite viscosity and does not flow. Interpenetrating polymer networks (IPNs) consist of two polymers, of which at least one must be crosslinked, that are intertwined at or near the molecular level.

Preparation of IPNs is normally accomplished by swelling a crosslinked polymer with another monomer, which is then itself polymerized, usually with crosslinking. Another method involves the simultaneous crosslinking of two independent and non-interfering monomers. Matching the rates of polymerization can be difficult but without such rate matching significant phase separation can occur.

Elean et al. reasoned that high temperature in the front could make the rates of the two reactions nearly equal. Therefore, they studied binary polymerization fronts to develop a new method of producing novel polymeric alloys and composites. The free-radical polymerization of (triethylene glycol) dimethacrylate (TGDMA) was carried out together with the polymerization of the epoxy monomer diglycidyl ether of bisphenol A (DGEBA), using the dual curing system of an alkyl amine (Epicure 3271) and a boron trichloride–amine complex (BCl3–NR3).

They determined that a single front and not two sequential fronts propagated. The front velocity was shown to decrease with an increase in the relative amount of the free-radical monomer up to 50% after which the velocity increased. The convex nature of the velocity versus percentage monomer curve was due to a competition between dilution of one polymerization system and concentration of the other polymerization system.

The preparation of simultaneous interpenetrating polymer networks (SINS) is difficult and often uses a photo-polymerization process, which inherently limits the size of the material that can be produced. Using propagating fronts eliminates the size restriction. We believe that using frontal methods for producing IPNs is a promising area of research.

7.2(b) Curing large composites. The manufacture of thick composites is difficult because the internal temperature lags behind the surface temperature. If the surface cures faster than the interior regions, resin can be trapped in the interior, which leads to non-uniform composition and voids. Another problem is thermal spiking during which the heat produced in the interior cannot escape and builds up. The autocatalytic nature of the curing process can lead to a thermal runaway and non-uniform composition. Very slow heating rates can solve this problem, but at the expense of increased processing time.

The continuous production of composites is a promising technological application of frontal polymerization. The approach reduces imperfections and production costs for a high value added product. White, at the University of Illinois, developed two continuous curing processes for producing graphite fibre composites (Fig. 18). The first is used for...
large rectangular-shaped objects. Layers of prepreg (graphite fibre material impregnated with the epoxy thermost resin) are placed into a mould that is heated from below. Pressure (25 psi) is applied until the front reaches near the top of the mould, the pressure is released and another layer of prepreg is inserted; the process is repeated until the desired thickness. White has shown that the process produces a superior product in less time.

The second approach is for the production of cylindrical objects, such as helicopter rotors or energy-storing fly wheels. A filament winding procedure has been developed in which resin-impregnated fibres are wound onto a heated mandrel at a rate that matches that of the expanding cure front. Korotkov et al. independently developed a model for such a process.\(^3\)

Currently, such parts must be cured in a large autoclave or at room temperature using resins that can cure under ambient conditions. Room-temperature curing means the resin must be impregnated into the fibre matrix while the resin is still liquid. Cleveland has shown that the most efficient way to do this is to use a low viscosity matrix that allows the filler to sediment. Sedimentation results in non-machinable; the temperature-induced colour changes and the difference in density between filler and monomer allow the filler to sediment. Sedimentation results in non-machinable materials. Composite produced with a filler is added to a viscous melt. The necessary and sufficient conditions for frontal curing must be established and the stable regimes of propagation determined, especially as a function of heat losses.

7.2(c) Filled materials. Sedimentation is a serious problem for filled materials, which contain small fibres or particles. At normal processing temperatures, resin viscosity is low and fillers settle causing gradients in composition and properties. This is less of a problem for thermoplastic materials because the filler is added to a viscous melt. However, thermosets formed from crosslinking monomers, require filler to be polymerized in situ. There are several ways to do this:

Photopolymerization: The filler scatters light making it impossible to polymerize thick materials. Also, if the reaction occurs at low temperature, then the conversion is low because the high viscosity that develops during curing limits molecular mobility needed for reaction of residual monomer and pendant groups.

Thermal curing: The high temperature maintains a low viscosity until a larger extent of reaction than with photopolymerization, which encourages high conversion. However, at elevated temperatures, the monomers have a low viscosity and the difference in density between filler and monomer allows the filler to sediment. Sedimentation results in non-uniform compositions.

Nagy and Pojman demonstrated that frontal polymerization could be used to overcome these problems. They prepared a novel material — a thermochromic composite with colour transition from 80 to 140 \(^\circ\)C.\(^7,8\) The cobalt-glycerine merisation could be used to overcome these problems. They composed of prepolymers that could be used for the process.\(^3\)

Currently, such parts must be cured in a large autoclave or at room temperature using resins that can cure under ambient conditions. Room-temperature curing means the resin must be impregnated into the fibre matrix while the resin is still liquid. Cleveland has shown that the most efficient way to do this is to use a low viscosity matrix that allows the filler to sediment. Sedimentation results in non-machinable; the temperature-induced colour changes and the difference in density between filler and monomer allow the filler to sediment. Sedimentation results in non-machinable materials. Composite produced with a filler is added to a viscous melt. The necessary and sufficient conditions for frontal curing must be established and the stable regimes of propagation determined, especially as a function of heat losses.

8. Conclusions

(1) In general, downward frontal polymerization can be realized only after elimination of Taylor instability. Some systems do not require such efforts due to the interactions in the polymer phase, such as crosslinking or polymer particles' adhesion withstanding the buoyancy force caused by the polymer–monomer density difference.

(2) Upward and horizontal propagating fronts become possible after decreasing the natural heat convection in the liquid monomer. Some systems allow such front directions without additional efforts because of high natural monomer viscosity and high front velocity.

(3) Some monomers can support fronts in solvents if they are highly reactive and highly exothermic, such as acrylamide. Until the polymer produced inherently gels, a crosslinking agent or filler must be added to prevent fingering.

(4) Bubbles can significantly affect the appearance of the polymer and the front velocity.

(5) Conversion and the molecular weight distributions can vary significantly with different initiators and different initiator concentrations.

(6) Propagating polymerization fronts demonstrate a rich variety of periodic modes, which are very close to those observed in SHS processes in spite of significant reaction mechanism differences. We conclude that the qualitative stability features are only determined by the mechanism of front propagation. However, the specific reaction kinetics influence the stability boundaries and some unique instabilities occur through the coupling of convection and thermal instabilities.

(7) The initial temperature of reactants and the magnitude of heat losses are the control parameters for periodic modes.

(8) Frontal polymerization is most likely to be useful in the production of large composites, IPNs and filled materials. However, significant chemical and dynamical issues need to be solved.

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