

# Frontal Free-Radical Polymerization: Applications to Materials Synthesis

Randy P. Washington and Oliver Steinbock

Department of Chemistry and Biochemistry  
Florida State University, Tallahassee, FL 32306

## Abstract

Frontal polymerization involves the conversion of monomer to polymer in a localized reaction zone that propagates due to the interplay of thermal conduction and temperature-dependent reaction rates. The localization of reactions and the fast increase in temperature are the key features that allow for the rapid synthesis of a wealth of polymer systems with spatially controlled microstructures and morphologies. The conditions for the existence of a stable frontal regime are considered, accompanied by other factors that affect the homogeneity of the product formed. Finally, the application of frontal polymerization in synthesizing uniform composites, hydrogels, simultaneous interpenetrating networks, copolymers, blends, and functional gradient materials is explored.

**Keywords:** frontal polymerization, high temperature synthesis, traveling wave, propagating fronts

## Introduction

During the past two decades, significant advances in the chemistry of polymer synthesis have equipped polymer chemists with unprecedented potential to synthesize polymeric materials with well-defined structures [1–5]. The abundance of novel methods has had a propensity to be guided toward not only synthesizing well-characterized materials, but also expediting the overall synthesis without compromising the intended properties. However, the ability to fabricate advanced materials with specific properties efficiently requires a complete understanding of the polymerization kinetics and the effect of several preparative variables such as temperature, monomer, initiator, etc. In order to achieve this objective, many researchers have devised synthetic methods

that allow the control of the morphology, microstructure, molecular weight, and molecular weight distribution [4,6]. A promising new technique for synthesizing uniform polymers and polymeric networks in a rapid fashion is frontal polymerization (FP). This novel methodology involves the conversion of monomer to polymer in a localized reaction zone that propagates due to the interplay of thermal conduction and temperature-dependent reaction rates.

It is the apparent simplicity of frontal polymerization that has led to this technique being steadily adopted for laboratory scale and possibly industrial polymer syntheses. Indeed, the required technology may be as simple as running the reaction in a test tube or a custom-built reactor at ambient temperature and pressure. There is also the added benefit of minimum energy consumption, since heat is only needed to start the self-sustained propagating reaction. These factors have, in turn, provided the driving force for extensive research efforts directed toward more precisely defining the necessary and sufficient conditions of frontal polymerizations. The aims of these studies have been to define the prerequisite parameters for predictable and reproducible polymer syntheses and to provide a better understanding of the properties of the polymeric materials produced.

The ability to prepare uniform materials in a fast fashion, and perhaps more importantly, to vary the morphology in a controlled manner, is in fact what makes frontal polymerization attractive for many applications. This article addresses frontal polymerization in its broadest sense, focusing on the free-radical mechanism, the underlying chemical processes that can mitigate certain conventional synthetic limitations, and the technologies that are being developed. Thus, this article begins with a discussion of free-radical polymerization. The intention is not to discuss in

---

Address correspondence to Randy P. Washington, Procter and Gamble Co., Miami Valley Laboratory #12, 11810 E. Miami River Road, Cincinnati, OH 45253. E-mail: washington.rp@pg.com

detail the fundamental chemistry involved, but to provide the basic principles that explain the onset of stable traveling fronts and the effect of preparative variables on the corresponding velocities. The general applicability of these principles is illustrated by synthetic examples: composites, hydrogels, simultaneous interpenetrating networks, copolymers, polymer blends, and functional gradient materials. Developments of these fairly new technologies will undoubtedly aid the maturity of frontal polymerization as an accepted and proven route to synthesize materials with superior properties.

### General Behavior

The concept of a traveling wave of polymer formation was first used successfully by Chechilo et al. in 1972 to synthesize polymethyl methacrylate from a homogeneous bulk process under high pressure [7–13]. They termed this process “frontal polymerization” as it operates by a localized reaction zone propagating through a monomer reactant mixture, with consequent polymer formation. High pressure was used to eliminate Taylor and/or double-diffusive instabilities and monomer boiling. It was found that the front velocity increased with increasing initiator concentration and pressure. A numerical analysis of the reaction product showed that not only is the molecular weight distribution very broad compared to isothermal polymerizations, but that a diminution of conversion occurs because of the high temperature [13].

Further development of the field awaited the discovery of other suitable monomers, which did not boil at the front temperature, and in which the stability of the front was maintained. Methyl methacrylate was used in earlier studies, but extensive boiling at high temperature makes this monomer of limited use. Hence, the reaction could only be performed at high pressure. The discovery that methacrylic acid fulfills the requirements, and that, in addition, it facilitates the formation of a stable front, enabled a rapid development of the field [14]. Later, the findings that other monomers, such as acrylamide [15] and n-butyl acrylate [16], would polymerize frontally to a uniform product added extra impetus. Furthermore, researchers reported that the synthesis of polyacrylamide can be carried out in organic solvents [15], without solvents [17–19], or in water [15]. Since then, remarkable advances have been made in the field of frontal polymerization to synthesize well-defined polymers with predetermined microstructure and morphology.

Scores of polymerization reactions are highly exothermic and are able to support frontal polymerization. There are three major classes of monomers used in frontal polymerization, which differ basically by their physical properties: propagating fronts that result in (1) thermosets, (2) thermoplastics, and (3) phase-separated polymer (the growing polymer is insoluble in its monomer solution). Much of the work on various monomer systems has been pioneered by the Pojman Group at the University of South-

ern Mississippi, and we will therefore adopt their classification [16,18].

The acrylates are by far the most studied systems because of their reactivity and the availability of kinetic data for numerical studies. Low molecular weight polymers are generally obtained at high initiator concentration, whereas glassy materials are obscured at low levels with crosslinking agents. An increase of the initiator was shown to speed up the reaction, but at the expense of the final conversion, because increased temperature leads to rapid initiator decomposition or “initiator burnout” [10]. Other acrylates that have been produced frontally include benzyl acrylate, hexyl acrylate, and butyl methacrylate [16].

During a descending propagating front of some monoacrylates, the hot polymer “fingers” into the unreacted cold monomer solution, causing a nonuniform product to be formed. Adding an inert filler such as Cabosil to increase the viscosity stabilizes the front, but the homogeneity is greatly compromised [20]. However, researchers have frontally synthesized homogeneous polybutyl acrylate under microgravity conditions [20]. Likewise, monomers like styrene and methyl methacrylate require moderate pressure to prevent monomer boiling. Typically, under these conditions, macroscopically invariant products are produced.

With multifunctional monomers and monomer systems that include crosslinking agents, the polymerization develops in three dimensions to yield strongly crosslinked polymer networks. These dienes are the most valuable group of monomers available for frontal polymerization, since the crosslinking reduces Taylor and double-diffusive instabilities. A sharp frontal interface propagates through the reaction media as polymerization and crosslinking occur simultaneously. The products of these reactions are rigid thermosets, capable of withstanding high temperatures.

Other monomers amenable to frontal polymerization are those having limited miscibility with their polymers. These include carboxylic acid monomers such as acrylic and methacrylic acids [10,14,21]. The homogeneous systems become heterogeneous due to the insolubility of the growing polymer in the reaction media. The insoluble polymer particles coagulate and adhere to the reactor. This provides a discernible polymer-monomer interface whereby the heat of reaction can easily diffuse into the unreacted zone to proliferate further polymer growth. In these systems, instabilities can occur as well. In an attempt to suppress convective instabilities, the technique of rotating the reaction around the axis of propagation was devised. The instabilities yielded to the centrifugal force such that stable fronts were established [22]. Microgravity experiments have also generated convection-free fronts in reactions that under terrestrial conditions are affected by hydrodynamic instabilities [20,23].

Although great strides have been made recently toward a reliable, full experimental analysis of frontal polymerization [7,8,16,18,21,24–29], the determination of necessary and sufficient conditions to obtain a front has remained a source of fre-

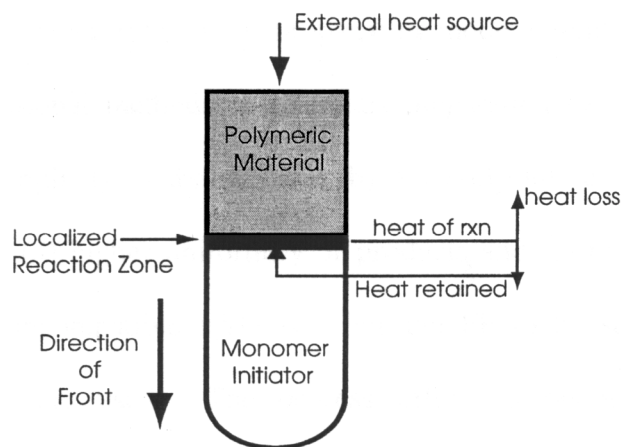
quent experimental and numerical difficulties. A unique combination of initiator, monomer, solvent, and initial temperature must be employed for the FP of each particular monomer. Therefore, understanding the role of each component of FP is crucial for obtaining well-defined polymers and for expanding the scope of FP to other monomers. Several salient aspects of frontal polymerization should be emphasized:

1. The monomer (and solvent) should have high boiling points to avoid boiling. We find that bubbles can interfere with front velocity and lead to a heterogeneous product. The source of bubbles may also be a result of the decomposition of organic initiators. The byproducts of the homolytic cleavage of peroxide and nitriles are carbon dioxide and nitrogen gases, respectively. Persulfate initiators generate free radicals upon thermal induced cleavage of O–O bonds, thus resembling the organic peroxides. However, persulfate does not decompose into any gaseous products. Therefore, persulfate initiators in conjunction with DMSO or DMF have been used to obtain nonporous products. Furthermore, Masere et al. have designed various gas-free initiators for frontal polymerization synthesis [30].
2. The polymerization rate should proceed at imperceptible rates at room temperature and increase drastically at the front temperature. In this way, no bulk polymerization exists and polymerization only starts once perturbed by sufficient thermal energy.
3. The consequent release of thermal energy from the exothermic reaction must be sufficient to sustain a propagating front.

### Kinetics and Mechanism

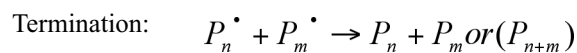
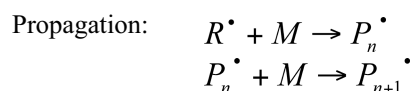
Typical reactive systems utilized in frontal polymerization follow free-radical mechanisms. The method of frontal polymerization adapted from that of self-propagating high temperature synthesis (SHS) used to synthesize technologically advanced ceramics [31,32] is shown in Figure 1. In our case, let us consider a monomer and initiator mixture charged in a standard test tube. The main heat source here is the thermal radiation stemming from the exothermic polymerization reaction. A total conversion of reactants to products by the internal heat source requires that after an initial perturbation (initiation), successive planes of reaction are ignited in the form a self-sustained polymerization wave. If the retained heat (minimal heat loss) is sufficiently high to generate additional initiating radicals, this process progressively leads to the final product without requiring additional energy.

Once frontal polymerization is started by reaction of the initiating species with the monomer functional groups, a chain reaction proceeds very much as in conventional thermal polymerization, except for the control in synthesis temperature and the localized reaction zone. The synthesis of high polymers by free-



**Figure 1. Schematic of frontal polymerization illustrating positive feedback for a sustained traveling wave.**

radical methods proceeds by a path involving the repetitive addition of a monomer to growing radicals, generated from a reactive initiator. Propagation ensues as growing transient radicals are continuously regenerated, through a repetitive cycle of bimolecular reactions. The reactive intermediates of the same type, generated in successive steps, differ in molar mass. The  $\pi$ - to  $\sigma$ -bond conversions result in a characteristic heat release. The mechanism of free-radical polymerizations can expressively be summarized in three primary steps: (1) initiation, (2) propagation, and (3) termination. Where polymerization starts with formation of radicals, termination leads to the final polymer product through polymer radicals interacting.



Typically, the frontal reaction starts in solution and proceeds in a plasticized melt or crystalline state after rapid conversion of monomer into polymer at high temperature. A significant difference in refractive index between the synthesized polymer and the monomer/initiator mixture allows one to optically monitor the progression of the front and to determine its velocity from distance versus time plots. The velocity can be affected by the initiator type and concentration but is on the order of a cm/min.

The influence of temperature on the kinetic quantities considered is determined by the activation energies of the appropriate component reactions. Thus the effective activation energy associated with the rate of polymerization is:

$$E_{\text{eff}} = 1/2E_i + E_p - 1/2E_t$$

where  $E_i$ ,  $E_p$ , and  $E_t$  refer to initiation, propagation, and termination.  $E_p$  and  $E_t$  are normally small, so that for thermally-initiated reactions,  $E_i$  is often the largest. Hence the rate of polymerization would be expected to be more sensitive to variations in the initiator concentration. Indeed, the amount of initiator plays a vital role in determining if a front will exist and, if so, the conversion of monomer to polymer. The front velocity is also tunable by the concentration of the initiator: a power dependence of the velocity on initiator is commonly found.

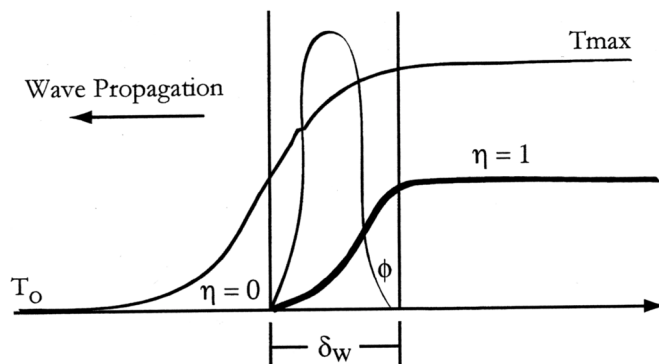
### Temperature Profile

The autocatalytic production of heat undoubtedly triggers the formation of a thermal wave propagating through the reaction vessel. Herein lies one of the major distinctly measurable attributes of the process itself—the S-shaped temperature profile.<sup>21</sup> In order to characterize the temperature profile along the reaction front, a thermocouple is inserted into the solution, which records the temperature evolution at a particular point of the reaction system. After an initial perturbation above the initiation threshold, the reaction begins, followed by a wave propagating at a constant velocity. At this point, a temperature distribution is quickly established as displayed schematically in Figure 2. Additionally, we show the spatial profile of the rate of heat evolution,  $\phi$ , and the degree of completion of the reaction,  $\eta$ , relative to a finite element of the propagating wave,  $\delta_w$ . The region ahead of the wave is the heat-affected zone over which the temperature increases from  $T_0$  to the ignition temperature to the  $T_{\text{max}}$ , corresponding to the point at which  $\phi$  becomes greater than zero and approaches unity with time.

The temperature reaches a very high point, so the wave propagates at a high velocity (as high as 20 cm/min), corresponding to small residence time in the curing zone. Temperature profile measurements show that the temperature can increase locally from  $T_0$  to  $T_{\text{max}}$  in seconds. According to the constant velocity,  $c$ , of the front, the temporal data,  $T(t)$ , can be converted to spatial temperature profiles (i.e.,  $T(x)=T(c t)$ ). Consequently, it is found that the reaction zone is localized to a (traveling) infinitesimal small interval. This localization and the related fast increase in temperature are the key features that allow for the rapid synthesis of a wealth of polymers with spatially defined microstructures and morphologies.

### Applications of Frontal Polymerization

Polymerization reactions in a self-propagating mode present an attractive practical alternative to conventional methods of materials preparation for a variety of reasons. These include (a) simplicity of the process, (b) relatively low energy requirement, (c) rapid synthesis time, (d) higher uniformity of products, and (e) the possibility to arrest phase separation in incompatible sys-



**Figure 2. Spatial profiles of the frontal polymerization process.**

tems. For the FP to be self-sustaining, highly exothermic reactions are used. The process offers an opportunity to synthesize polymerization reactions at extreme thermal gradients, under conditions such that adiabatic considerations are commonly invoked for theoretical analysis and conversion calculations.

The small conversions and broad molecular weight distributions are predominately influenced by the number of initiating radicals produced during the high temperature synthesis. Such a temperature effect is common to most monomers and is one of the caveats of frontal polymerization in solution or solid state. Pojman et al. [21] have strategically used a dual initiator system where the velocity is controlled by the least stable one, but the more stable one determines the conversion. Fortenberry et al.<sup>19</sup> [19] added an inert filler, barium carbonate, to reduce the front temperature of solid polyacrylamide fronts. Lower front temperature led to higher conversions and higher weight average molecular weight polymer.

The advent of intermittent convective instabilities, convective flows and front stability has threatened the growth of this technique. There is compelling numerical and experimental evidence that the stability of the front can be summarized by the Zeldovich number [33],

$$Z = \frac{T_{\text{max}} - T_0}{T_{\text{max}}} \frac{E_{\text{eff}}}{RT_{\text{max}}}$$

The reaction is assumed to occur in an infinitely narrow region with activation energy,  $E_{\text{eff}}$ , initial temperature  $T_0$ , and maximum temperature  $T_{\text{max}}$ . This bifurcation parameter can be judiciously adjusted to obtain a stable front, such that the products are void of instability defects. Low initial temperature and reduced heat losses are conditions conducive for stable fronts.

Given stable fronts, these types of reactions may provide an attractive energy-efficient approach to the synthesis of simple and complex materials including solids, composite materials, and

crosslinked networks. Because of the rapid conversion in the localized reaction zone, novel thermochromic composites [34,35] have already been realized. Unique polymer blends [36] as well as uniform copolymers [37] have been synthesized within minutes. Chekanov and Pojman [38] developed a novel frontal polymerization method to produce functionally gradient materials [38] in which the composition was externally controlled by an adaptable feed system. Pojman et al. [39] extended this investigation by considering binary fronts in which two noninterfering mechanisms are occurring in the same system. Washington and Steinbock [40] synthesized thermosensitive hydrogels without phase separation or microaggregation. We review each of these systems as exemplars, as the unique features of frontal polymerization are greatly exploited to produce a wealth of uniform polymeric materials.

Other polymerization mechanisms, such as cationic or amine curing of epoxy resins, are able to support frontal polymerization as well. Amine curing has been used alone to fabricate polymer dispersed liquid crystals [41], and in conjunction with radical polymerization to develop novel interpenetrating networks [39]. Gradient refractive index materials have been synthesized by isothermal frontal polymerization (also known as interfacial gel polymerization) 42–47, but the system propagates by a dynamic interplay between the reaction kinetics and the Trommsdorf–Norris gel effect [48,49].

#### *Filled Materials*

Interest in inorganic/organic composite materials is due to their possession of vastly diverse of properties associated with either of the separate components [50–53]. The manufacture of thick filled materials is difficult because multicomponent systems often undergo phase separation or sedimentation. However, if mixing takes place on a lower molecular level and polymerization is swiftly achieved with concomitant crosslinking, phase separation may be kinetically controlled. Nagy et al. [34] reasoned that the rapid rise in temperature followed by crosslinking could freeze in the metastable state of components to generate a uniform composite. That goal was achieved by fabricating a temperature sensor based on the bulk immobilization of the thermochromic  $\text{CoCl}_2$ -glycerol solution in a rigid three-dimensional polymer network.

Robust reversible thermosensitive composites were prepared as follows: a cobalt-glycerol solution was uniformly dispersed in an acrylamide-triethylene glycol dimethacrylate comonomer solution, supplemented with benzoyl peroxide. The metastable mixture is subjected to frontal polymerization in the form of a viscous pellet at ambient temperature and pressure. In comparison to batch studies, frontal polymerization afforded a superior composite material: batch materials were subjected to phase separation and sedimentation. The rapid rise in the temperature and the consequent accelerated crosslinking freezes in the nonequilibrium phase distribution during synthesis. Thus, with

this synthetic route, engineered multicomponent composite materials of great homogeneity are easily achievable in a shorter time period.

#### *Hydrogels*

The study of hydrogels and their response to external environment is of special interest because of their potential as drug delivery systems [54,55], actuators [56,57], and separation devices [58,59]. Temperature-sensitive hydrogels undergo a reversible swelling-deswelling transition with a small change of temperature near the phase transition point [60,61]. A frequently studied thermosensitive hydrogel is based on solution free-radical crosslinking copolymerization of the monomer N-isopropylacrylamide and the crosslinker N-N-methylenebisacrylamide. The availability of preparation techniques allowing the synthesis of hydrogels with structural uniformity is limited by the exothermicity of the polymerization reaction which induces phase separation of linear poly(N-isopropylacrylamide) chains, PNIPAM, at 32°C [62]. Therefore, to generate uniform hydrogels, small samples are usually produced at low monomer and initiator concentration and at low synthesis temperature that circumvent spatial inhomogeneities and microaggregation. Under these reaction conditions, the rates of polymerization and gelation are low, requiring longer time to synthesize hydrogels.

Charged with the knowledge that the rapid polymerization in a localized reaction zone could negate phase separation and lead to a homogeneous product, Washington and Steinbock [40] reported the frontal synthesis of isopropylacrylamide hydrogels at high monomer and initiator concentration. It is found that in addition to a more rapid synthesis of hydrogels, a substantial increase in the homogeneity of the microstructure of the hydrogel with respect to the solution polymerization is obtained. Moreover, large hydrogel samples with similar equilibrium swelling ratio can be readily produced without the effect of microaggregation and phase separation.

#### *Interpenetrating Networks*

Interpenetrating polymerization is a mode of preparing two or more crosslinked polymers to produce a mixture in which phase separation is not as extensive as in normal blending or mixing. Preparations of simultaneous interpenetrating networks (SINs) are carried out by two independent and noninterfering crosslinking mechanisms in bulk, solution, or dispersion. In the simplest case, monomer I is combined with crosslinking and initiator to form network I. Network I is then swollen with monomer II, which is then itself polymerized and/or crosslinked. With highly incompatible polymers, thermodynamics of phase separation occurs before crosslinking takes place. Therefore, there has been a great challenge to synthesize IPN with resolvable domain structures.

Based on the above concepts of frontal polymerization, Pojman

et al. [39] proposed that the high temperature observed in a localized reaction zone could be exploited in such a way that two mechanistically independent polymerizations could operate at the same rate. A series of SINS have been developed employing both epoxy (step) and acrylic (chain) polymerizations. The dual curing system of alkylamine (Epicure 3271) and boron trichloride-amine complex is dissolved in an epoxy monomer diglycidyl ether of Bisphenol A. The mixture of tri(ethylene glycol) dimethacrylate and benzoyl peroxide initiator, is then added to the solution. Similarly, interpenetrating polydicyclopentadiene/polyacrylate networks were recently reported by Fiori et al. [63].

The rapid polymerization in a localized reaction zone allows for controlled in situ frontal polymerization of acrylic/epoxy resins. The compatibility of IPN is enhanced because the polymers are interlocked in a three-dimensional structure during polymerization before phase separation occurs. A single thermal wave, instead of two sequential ones, propagated through the reaction mixture, rapidly convert the viscous liquid into an interlocked polymer network. This fast and efficient way of synthesizing "homogeneous" SINS by matching the reaction rates of the individual reaction is difficult to achieve in conventional techniques. These hybrid composites can be designed for potential use in a wide range of applications. Structural diversity is achieved through control of the relative ratio of acrylic and epoxy monomers.

### *Copolymers*

The detailed microstructure and compositional heterogeneity of copolymers can have a determining influence on copolymer properties. Through copolymerization, the polymer properties are widely varied from soft, flexible elastomers to hard, stiff thermoplastics and thermosets. One of the major drawbacks to batch copolymerization is related to the copolymer composition control. These compositional drifts are incompatible and cause phase separation. To control the compositional drifts, copolymers are often synthesized at the azeotropic point, where monomer feed and copolymer have the same composition [64]. Operationally, the degree of heterogeneity can be controlled by charging the reactor with a monomer mixture identical in composition to the resultant copolymer.

To overcome any corrective actions to prevent composition drift, researchers reported the high temperature synthesis of a host of copolymers such that the azeotropic conditions are invoked [37]. This case can be called an "ideal copolymerization," since the monomer enter the copolymer in the amount determined by their relative concentrations in the monomer feed. The small finite reaction zone and the accompanied rapid temperature rise reduce compositional drifts, thereby limiting phase separation and producing narrow chain composition distribution.

Another remarkable application of frontal polymerization stems from improvements in the synthesis of alternating styrene-

maleic anhydride copolymers [65]. This system is one of the most thoroughly investigated and industrial relevant copolymers. It is usually made by conventional free-radical polymerization below 80°C [66]. At higher temperatures, random ST-MA copolymers are formed. The monomer feed can also influence the microstructure of the copolymer. However, the high temperature copolymerization of styrene and maleic anhydride in propagating fronts afforded alternating arrangements at all monomer feed ratios. Thus, a facile way of exclusively obtaining an ordered sequence of repeating units is readily developed.

### *Polymer Blends*

Intimately blended polymer systems as engineering materials have extensively been studied for their microphase behavior and synergistic properties [44,67,68]. Blending can be implemented into new technology more rapidly and economically to meet strict performance needs than the development of a new chemistry. Several different approaches have been used to prepare polymer blends such as melting, mixing, casting from common solvents, and template polymerization, with the latter mode noted as the simplest one [69]. In this case, a polymer is synthesized in the presence of an inert preformed polymer. Unfortunately, many multicomponent polymer systems are incompatible, which induces phase separation and self-aggregation. These kinetic and thermodynamic phenomena thwart the hope of achieving uniform and synergistic behavior.

Tredici et al. [36] devised a method of improving the miscibility of the polymers by freezing in the metastable state of the monomer/polymer mixture before phase separation of the two polymers could occur. The researchers reported the frontal preparation of a series of polystyrene (PSTY)-polymethyl methacrylate (MMA) blends from a mixture of MMA and PSTY. SEM micrographs of the PSTY-MMA blends showed spherical PSTY composition dispersed in the PMMA matrix with an average particle size of 1  $\mu\text{m}$  and uniform distribution. This was attributed to the rapid reaction in the localized reaction zone of the self-propagating front. The shifts in properties also accompany the changes in molecular arrangements produced by the rise in temperature. With rapid heating, low molecular weight polymers may compatibilize on a molecular length scale. This metastable state is subsequently fossilized by crosslinking. In contrast, conventional preparation is too slow to arrest phase separation, and thereby leads to samples that separate into two distinct phases consisting primarily of the individual components.

### *Functional Gradient Polymers*

A recent subject in polymer/materials synthesis is the preparation of functionally gradient materials (FGMs). The introduction of a compositional gradient in a polymer matrix or a composite can dramatically alter its properties, with different attributes being specifically engineered for an intended purpose. Several

different approaches [70–72] have been used to prepare FGMs dependent on the intended purpose, but all share the common theme of using a feed system to generate the gradient.

Organic materials can exhibit nonlinear absorption in such a way that intense optical pulses are strongly attenuated and low-intensity light is highly transmitted. When these materials are embedded in a polymer matrix, optical limiters are developed that can be useful for protecting human eyes from high power lasers [73]. Two patents have been granted for the frontal production of functionally gradient polymeric materials [74,75]. Chekanov and Pojman [38] reported a “novel programmable frontal polymerization” technique for synthesizing functionally gradient material where a hyperbolic dye gradient is observed along the front axis. Researchers had found earlier that this distribution achieved the maximum attenuation [76]. A nonlinear optical rod is produced in semibatch reactors into which the optical dye is continuously flowed along with components of the free-radical polymerization into an ascending front. As layers of mixture are added atop the ascending propagating front, the dye enters the copolymer composition in the amounts determined by its relative concentration in the semibatch feed. A gradient of morphology was observed when a comonomer was added in similar fashion.

## Conclusions

Significant advances in polymer synthesis techniques have opened the way to the development of polymers with tailored molecular architectures and physical properties. By carefully controlling polymerization reactions, synthetically well-known polymers and crosslinked networks can be produced with novel microstructures and morphologies. Our synthetic schemes are partly aimed at the development of new approaches and methods for the preparation of large molecules with defined architecture and shape. Frontal polymerization provides a versatile and facile methodology for the preparation of polymers with control of the major variables that affect polymer properties. For diverse monomer and initiator systems, well-defined polymers can be prepared with low degrees of compositional or morphological heterogeneity. Selective technologically advanced examples of various polymers are presented to authorize the adaptability and the scope of frontal polymerization. In general, we find the following to hold true:

1. Polymerization fronts generate large samples rapidly with minimum energy input.
2. Novel uniform materials can be produced. Multicomponent systems often undergo phase separation because upon polymerization the transient components become immiscible.
3. Outstanding mechanical properties can be achieved in polymer blends, copolymers, and SINs since compatibility is achieved on a molecular level.

4. From an industrial standpoint, a major virtue of frontal polymerizations is that they can typically be carried out under relatively undemanding conditions.

## Acknowledgments

This work was supported by the Florida State University. RPW expresses gratitude to UNCF and Merck for financial assistance. We thank Professor John Pojman for careful reading of the manuscript.

## References

1. Colombani, D. 1997. *Prog. Polym. Sci.* 22, 1649–1720.
2. Gaynor, S., Greszta, D., Shigemoto, T., Mardare, D., Matyjaszewski, K. 1994. *Abstr. Pap. Am. Chem. Soc.* 208, 473–Poly.
3. Matyjaszewski, K. 1995. *Abstr. Pap. Am. Chem. Soc.* 209, 182–Poly.
4. Matyjaszewski, K., Gaynor, S., Greszta, D., Mardare, D., Shigemoto, T. 1995. *Macromol. Symp.* 98, 73–89.
5. Sawamoto, M., Kanaoka, S., Omura, T., Higashimura, T. 1992. *Abstr. Pap. Am. Chem. Soc.* 203, 4–Poly.
6. Yang, Y. L., He, J. P., Hua, F. J. 2001. *Acta Chim. Sin.* 59, 301–310.
7. Khanukaev, B. B., Khanukaev, B. B., Enikolopyan, N. S. Comb. 1974. *Explos. Shock Waves* 10, 562–568.
8. Khanukaev, B. B., Kozhushner, M. A., Enikolopyan, N. S. 1974. *Dokl. Phys. Chem.* 214, 84–87.
9. Chechilo, N. M., Enikolopyan, N. S. 1976. *Dokl. Phys. Chem.* 230, 840–843.
10. Chechilo, N. M., Khvilivitskii, R. J., Enikolopyan, N. S. 1972. *Dokl. Akad. Nauk SSSR* 204, 1180–1181.
11. Chechilo, N. M., Enikolopyan, N. S. 1974. *Dokl. Phys. Chem.* 214, 174–176.
12. Davtyan, S. P., Surkov, N. F., Rozenberg, B. A., Enikolopyan, N. S. 1977. *Dokl. Phys. Chem.* 232, 64–67.
13. Enikolopyan, N. S., Kozhushner, M. A., Khanukaev, B. B. 1974. *Dokl. Phys. Chem.* 217, 676–678.
14. Pojman, J. A. J. 1991. *Am. Chem. Soc.* 113, 6284–6286.
15. Pojman, J. A., Curtis, G., Ilyashenko, V. J. 1996. *Am. Chem. Soc.* 115, 3783–3784.
16. Pojman, J. A., Ilyashenko, V., Khan, A. M. 1996. *J. Chem. Soc. Faraday Trans.* 92, 2824–2836.
17. Pojman, J. A., Nagy, I. P., Salter, C. 1993. *J. Am. Chem. Soc.* 115, 11044–11045.
18. Pojman, J. A., Fortenberry, D., Khan, A., Ilyashenko, V. 1998. In *Synthesis Characterization of Advanced Materials*, Serio, M. A., Gruen, D. M., Malhotra, R., Eds., American Chemical Society: Washington, DC, Vol. 681, pp. 220–235.
19. Fortenberry, D., Pojman, J. A. 2000. *J. Polym. Sci., Pt. A: Polym. Chem.* 10, 224–230.
20. Pojman, J. A., Khan, A. M., Mathias, L. 1997. *Microgr. Sci. Tech.* X, 36–40.
21. Pojman, J. A., Willis, J., Fortenberry, D., Ilyashenko, V., Khan, A. 1995. *J. Polym. Sci., Pt. A: Polym. Chem.* 33, 643–652.
22. Nagy, I. P., Pojman, J. A. J. *Phys. Chem.* 1996. 100, 3299–3304.
23. Ainsworth, W., Pojman, J. A., Chekanov, Y. A., Masere, J. 2001. In *Polymer Research Microgravity: Polymerization and Processing*, ACS Symposium Series No. 793, Downey, J. P., Pojman, J. A., Eds., American Chemical Society: Washington, D. C., pp 112–125.
24. Goldfeder, P. M., Volpert, V. A., Ilyashenko, V., Khan, A. M., Pojman, J. A., Solovoyov, S. E. 1997. *J. Phys. Chem. B* 101, 3474–3482.
25. Golubev, V. B., Gromov, D. G., Korolev, B. A. 1992. *J. Appl. Polym. Sci.* 46, 1501–1502.

26. Gromov, D. G., Frisch, H. L. 1992. *J. Appl. Polym. Sci.* 46, 1499–1500.
27. Khan, A. M., Pojman, J. A. 1996. *Trends Polym. Sci.* (Cambridge, U.K.) 4, 253–257.
28. Pojman, J. A., Fortenberry, D., Ilyashenko, V. 1997. *Inter. J. Self-Prop. High-Temp. Synth.* 6, 355–376.
29. Pojman, J. A., Volpert, V. A., Volpert, V. A. 2002. In *Self-Propagating High-Temperature Synthesis of Materials*, Borisov, A. A., De Luca, L. T., Merzhanov, A. G., Eds., Taylor and Francis: New York, pp 99–118.
30. Masere, J., Chekanov, Y. A., Warren, J. R., Stewart, F., Al-Kaysi, R., Rasmussen, J. K., Pojman, J. A. 2000. *J. Polym. Sci., Pt. A: Polym. Chem.* 38, 3984–3990.
31. Merzhanov, A. G., Rogachev, A. S. 1992. *Pure Appl. Chem.* 64, 941–953.
32. Merzhanov, A. G. 1990. *Adv. Mater.* 2, 570–572.
33. Zeldovich, Y. B., Barenblatt, G. I., Librovich, V. B., Makhviladze, G. M. 1985. *The Mathematical Theory of Combustion and Explosions*, Consultants Bureau: New York.
34. Nagy, I. P., Sike, L., Pojman, J. A. 1995. *J. Am. Chem. Soc.* 117, 3611–3612.
35. Nagy, I. P., Sike, L., Pojman, J. A. 1995. *Adv. Mat.* 7, 1038–1040.
36. Tredici, A., Pechhini, R., Shepcevich, A., Morbidelli, M. 1998. *J. Appl. Polym. Sci.* 70, 2695–2702.
37. Tredici, A., Pechhini, R., Morbidelli, M. 1998. *J. Polym. Sci., Pt. A: Polym. Chem.* 36, 1117–1126.
38. Chekanov, Y. A., Pojman, J. A. 2000. *J. Appl. Polym. Sci.* 78, 2398–2404.
39. Pojman, J. A., Elcan, W., Khan, A. M., Mathias, L. 1997. *J. Polym. Sci., Pt. A: Polym. Chem.* 35, 227–230.
40. Washington, R. P., Steinbock, O. 2001. *J. Am. Chem. Soc.* 123, 7933–7934.
41. Gill, N., Pojman, J. A., Willis, J., Whitehead, J. B. 2003. *J. Polym. Sci. Polym. Chem.* 41, 204–212.
42. Masere, J., Lewis, L. L., Pojman, J. A. 2001. *J. Appl. Polym. Sci.* 80, 686–691.
43. Ishigure, T., Nihei, E., Koike, Y. 1994. *Appl. Opt.* 33, 4261–4266.
44. Jeon, H. G., Hudson, S. D., Ishida, H., Smith, S. D. 1999. *Macromolecules* 32, 1803–1808.
45. Park, C. W., Lee, B. S., Walker, J. K., Choi, W. Y. 2000. *Ind. Eng. Chem. Res.* 39, 79–83.
46. Wang, H. M., Tao, X. M., Newton, E., Chung, T. S. 2002. *Polym. J.* 34, 575–583.
47. Zhang, F., Zhang, Q. J. 2000. *Acta Polym. Sin.* 538–544.
48. Spade, C. A., Volpert, V. A. 1999. *Math. Comp. Modeling* 30, 67–73.
49. Texier-Picard, R., Pojman, J. A., Volpert, V. A. 2000. *Chaos* 10, 224–230.
50. Bae, J. M., Honma, I., Hirakawa, S. 1999. *J. Korean Phys. Soc.* 35, S315–S319.
51. Novak, B. M., Ellsworth, M. W. 1993. *Mat. Sci. Eng. A-Struct.* 162, 257–264.
52. Schmidt, H., Krug, H. 1994. *ACS Sym Ser* 572, 183–194.
53. Schmidt, H. K. 1996. *Macromol. Symp.* 101, 333–342.
54. Kim, S. W., Bae, Y. H., Okano, T. 1992. *Pharmaceut. Res.* 9, 283–290.
55. Peppas, N. A., Bures, P., Leobandung, W., Ichikawa, H. 2000. *Eur. J. Pharm. Biopharm.* 50, 27–46.
56. van der Linden, H., Herber, S., Olthuis, W., Bergveld, P. 2002. *Sensor Mater.* 14, 129–139.
57. Kato, N., Yamanobe, S., Takahashi, F. 1997. *Mat. Sci. Eng. C-Biomim.* 5, 141–147.
58. Umeno, D., Kano, T., Maeda, M. 1998. *Anal. Chim. Acta.* 365, 101–108.
59. Kondo, A., Fukuda, H. 1997. *J. Ferment. Bioeng.* 84, 337–341.
60. Galaev, I. Y. 1995. *Usp. Khim.* 64, 505–524.
61. Schild, H. G. 1992. *Prog. Polym. Sci.* 17, 163–249.
62. Gehrke, S. H., Palasis, M., Akhtar, M. K. 1992. *Polym. Int.* 29, 29–36.
63. Fiori, S., Mariani, A., Ricco, L., Russo, S. 2002. *e-Polymers* 29, 1–10.
64. Odian, G. 1991. *Principles of Polymerization*, 3rd ed., John Wiley & Sons, Inc.: New York.
65. Szalay, J., Nagy, I., Banyai, I., Deak, G., Bazsa, G., Zsuga, M. 1999. *Macromol. Rapid Comm.* 20, 315–318.
66. Seymour, R. B., Garner, D. P. 1978. *Polym. News* 4, 209–214.
67. Vatalis, A. S., Kanapitsas, A., Delides, C. G., Viras, K., Pissis, P. J. 2001. *Appl. Polym. Sci.* 80, 1071–1084.
68. Lay, S., Sommer, J. U., Blumen, A. 2000. *Macromol. Symp.* 149, 31–36.
69. Poul, D. R., Newman, S. 1978. *Polymer Blends*, Academic Press: New York.
70. Manjubala, I., Sivakumar, M., Kumar, T. S. S., Rao, K. P. 2000. *J. Mater. Sci.-Mater. M.* 11, 705–709.
71. Novikov, V. V., Poznanskii, O. P. 1999. *Powder Metall. Met. C+* 38, 217–219.
72. Cherradi, N., Kawasaki, A., Gasik, M. 1994. *Compos. Eng.* 4, 883–894.
73. Crane, R., Lewis, K., Stryland, E. V., Koshnevisan, M., Eds. 1995. *Materials for Optical Limiting*. Materials Research Society: Pittsburgh.
74. Pojman, J. A., McCardle, T. W. 2000. US. 6,057,406.
75. Pojman, J. A., McCardle, T. W. 2001. US. 6,313,237.
76. Miles, P. 1994. *Appl. Opt.* 33, 6965–6969.