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ORIGINAL CONTRIBUTION

# Synthesis of poly(*N*-methylolacrylamide)/polymethylacrylamide hybrids via frontal free-radical polymerization

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**Abstract** In this study, poly(*N*-methylolacrylamide)/polymethylacrylamide (PNMA/PMAA) hybrids were produced successfully by frontal free-radical polymerization at ambient pressure. In a typical run, the appropriate amounts of reactants (*N*-methylolacrylamide, NMA; methylacrylamide, MAA) and initiator (ammonium persulfate) were dissolved in dimethyl sulfoxide at ambient temperature. Frontal polymerization (FP) was initiated by heating the wall of the tube with a soldering iron, and the resultant hot fronts were allowed to self-propagate throughout the reaction vessel. Once initiated, no further energy was required for polymerization to occur. The dependences of the front velocity and front temperature on the initiator concentration, reactant dilution, and NMA/MAA components were thoroughly investigated. The front temperatures were between 69 and 116 °C, depending on the persulfate concentration. We have also investigated the FP of PNMA/PMAA hybrids with *N*-methyl-2-pyrrolidone as solvent. Results show that FP can be exploited as a means for the preparation of PNMA/PMAA hybrids with the potential advantage of higher throughput compared to the traditional mode.

**Keywords** Kinetics · Frontal polymerization · *N*-methylolacrylamide (NMA) · Methylacrylamide (MAA)

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## Introduction

During the past three decades, a significant advance in nonlinear dynamics is frontal polymerization (FP) because it is a promising new technique for synthesizing uniform polymers and polymeric networks in a rapid fashion. FP is a mode of converting a monomer into a polymer via a localized reaction zone that propagates through the coupling of thermal diffusion and temperature-dependent reaction rates (Fig. 1) [1]. Once ignited, the conversion of reactants to polymers by the internal heat source needs no additional energy if the retained heat is sufficiently high to ignite polymerization after an initial initiation. The localized reaction zone and the fast increasing temperature allow the rapid synthesis of many polymers with spatially controlled microstructures and morphologies.

In 1972, the first FP reactions were discovered by Chechilo and Enikolopyan [2, 3] who studied methyl methacrylate (MMA) polymerization in adiabatic conditions under high pressure (>3,000 atm). Subsequently, this method was extended by Pojman and his co-workers [4–11] to include numerous polymers.

Begishev et al. [12, 13] studied the frontal anionic polymerization of ε-caprolactam. Thermochromic composites [14], functionally gradient materials [15, 16], and polymer-dispersed liquid crystal materials have been prepared frontally [17]. The method was also effectively applied to epoxy resins [18] and their interpenetrating polymer networks [7]. Tredici et al. [19] reported on the advantageous application of FP for producing polymer blends. FP was also used by Washington and Steinbock [20] for the preparation of temperature-sensitive hydrogels, by Fortenberry and Pojman for the solvent-free synthesis of polyacrylamide [8], and by Pojman et al. [21] for epoxy-acrylate binary systems.

To extend the number and type of both chemical systems and practical applications, Mariani et al. [22] polymerized dicyclopentadiene by frontal ring opening metathesis polymerization. Fiori et al. [23] produced polyacrylate–poly(dicyclopentadiene) networks frontally. Fiori et al. [24] prepared polyurethanes by FP. Furthermore, polyester–styrene resins prepared by FP were found to achieve higher conversion than those obtained by the usual batch technique [25]. Frontal atom transfer radical polymerization has been achieved [26] as well.

In 2004, Pojman et al. demonstrated FP with thiol-ene systems [27] and with a microencapsulated initiator [28]. In 2005, Chen et al. [29–31] reported on segmented polyurethane and polyurethane–nanosilica hybrid nanocomposites synthesized by FP. Also, in 2005, Lewis et al. [32] reported a detailed study on isothermal FP. Bulut and Crivello [33] reported on photoinitiated cationic FP [34], and Mariani et al. [35] described UV-ignited frontal epoxy curing. In 2006, Binici et al. [36] presented the first spherically propagating polymerization. Chen et al. [37, 38] prepared epoxy resin/polyurethane hybrid networks and urethane–acrylate copolymers.

Due to the large thermal and concentration gradients, polymer fronts are highly susceptible to buoyancy-induced convection [6, 29, 39, 40]. Descending fronts of thermoset formation are normally immune to convection unless the reactor is tilted with respect to the gravitational vector [41]. To overcome the instabilities, especially with monofunctional monomers, Masere et al. [42] added fillers or performed the reactions in weightlessness [43].

Most of the typical reactive systems utilized in FP follow free-radical mechanisms since free-radical polymerizations are usually highly exothermic, and autocatalysis is provided by the Arrhenius dependence of the initiator decomposition. The thermal initiators provide the most important feature; that is, the system should not have a significant reaction rate at room temperature but must react rapidly at the adiabatic reaction temperature. Typically, frontal free-radical polymerization starts in solution with the formation of radicals and terminates with final products after the rapid conversion of monomer into polymer at high temperature. Because of the difference in refractive index between the monomer/initiator mixture and the polymer, we can optically monitor the propagation of the front as a function of time.

For frontal free-radical polymerization, there are some important factors to consider for the frontal mode to exist. First, any reaction of the monomer(s) at ambient temperature is prohibited. Then, an initial energy input (heat or light) should produce radicals enough to ignite polymerization. The conversion of monomer(s) to polymer is highly exothermic, which induces a self-propagating thermal wave or reaction inducing a boundary separating polymer and liquid monomer(s), as shown in Fig. 1. The last one is that the monomer(s) should have a high boiling point to prevent bubble formation induced by the high temperature at the epicenter of the traveling front, or the reaction must be performed under pressure [6, 44]. FP based on free-radical polymerization carried out under a condition satisfied with such regulations and with a stable front presents an attractive practical way to prepare many materials, such as thermochromic composites [14] and functionally gradient materials [15, 16].

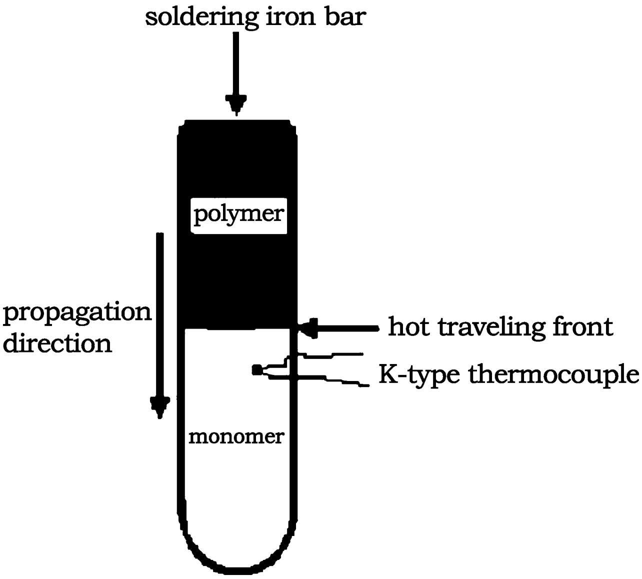


**Fig. 1** Schematic of propagating front of the PNMA/PMAA hybrid by FP (inner diameter of the tube is 15 mm)

Polymers with improved physical and processing properties can be obtained by reacting a conventional monomer with small amounts of acrylamide [45]. One of the most important acrylamide family members is *N*-methylolacrylamide (NMA), which is a water-soluble functional monomer keeping its methylol group upon polymerization. This group can later undergo crosslinking reactions and self-condensation, and even reactions with groups of other polymers [45]. As a crosslinker, the application of NMA either with the dye or as a post-treatment may solve the problems of incomplete fixation in deep shades and a lack of migrating ability that suffered from reactive dyes on wool [46]. They can also be used for dentin pretreatment. Dentin pretreatment with dentin primers containing hydrophilic monomers has become an important means to improve the bond strength of resin composites to etched dentin. It is generally considered that these dentin primers could restore the collapsed collagen to almost its original state, and alters the collagen-fiber wettability. Fukushima et al. [47] has prepared water solutions containing water-soluble *N*-methylolacrylamide or *N*-methylolmethacrylamide for experimental dentin primers. Results show that such dentin primers improved the bond strength. Meanwhile, they are applied for tunnel construction works in both Hallandsasen, Sweden, and in Romeriksporten, Norway, during the period 1995–1997 [48] and for the gelcasting system [49]. The other acrylamide is MAA; it can also be applied to set ceramic suspensions in the gelcasting system [49]. The copolymer of MAA and other acrylamides may be prepared for temperature-sensitive hydrogels [50, 51], conductive polymer [52], and nonporous materials [53]. Polymers containing *N*-methylol acrylamide (NMA) and prepared by emulsion copolymerization with other vinyl monomers, such as MAA, are widely used in applications such as binders for nonwoven fabrics, protective coatings, latex paints, and adhesives [54].

In this work, we describe how we produced poly(*N*-methylolacrylamide)/polymethylacrylamide (PNMA/PMAA) hybrids using NMA and MAA via frontal free-radical polymerization at ambient pressure. To avoid bubbles from peroxide or nitrile initiators, we used persulfate [39]. Because the front velocity is a function of particle size and the initial density, we chose to perform a study in solvent. To make the persulfate soluble with the monomers, all components were dissolved in dimethyl sulfoxide (DMSO). The effect factors of front velocity, ammonium persulfate concentration, temperature, and solvent on the FP were thoroughly investigated.

## Experimental section

### Materials

DMSO, *N*-methyl-2-pyrrolidone (NMP), NMA, MAA, and ammonium persulfate were supplied by Aldrich and used as received.

### FP of PNMA/PMAA hybrids

For the synthesis of PNMA/PMAA hybrids by FP, the appropriate amounts of NMA, MAA, and ammonium persulfate (used as initiator) were mixed together at ambient temperature in the presence of DMSO (acted as the solvent) in a flask. A typical composition was [NMA]/[MAA]=1.68 mol/mol, [monomer]/[DMSO]=0.82 mol/mol, and ammonium persulfate=0.74wt%. The flask was shaken vigorously for several times to obtain a homogeneous mixture. Then, the mixture was poured into a 10-ml (*D*=15 mm) test tube. The filled vessel was clamped into a holder approximately 1 cm.

The upper side of the mixture was then heated by a soldering iron until the hot propagating front commenced (as shown in Fig. 1). The reaction mixture was kept at about 20–25 °C to slow bulk polymerization. Figure 2 presents the direct images of propagating the front of the PNMA/PMAA hybrid. The interface between the polymer and unreacted monomer can be barely seen. The upper layer of mixture is the PNMA/PMAA hybrid and the under layer is unreacted monomer–initiator mixture. Front propagation occurred at constant velocity by the conversion of monomers to PNMA/PMAA hybrids with almost no formation of bubbles.

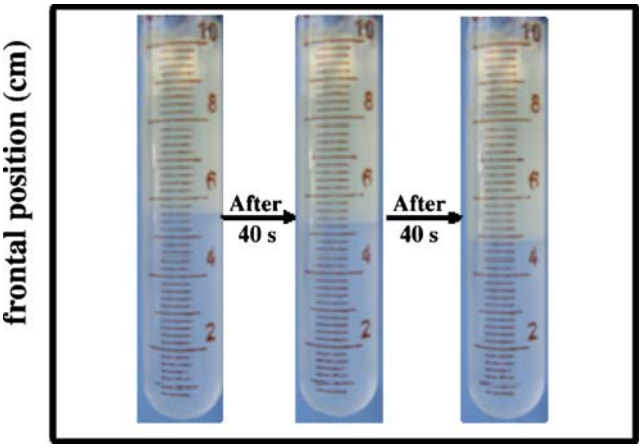


**Fig. 2** Visual images of the propagating front of the PNMA/PMAA hybrid. The initial conditions are [NMA]/[MAA]=1.68 mol/mol, [monomer]/[DMSO]=0.82 mol/mol, and ammonium persulfate=0.74wt% (inner diameter of the tube is 15 mm)

The frontal velocities ($V_{\text{front}}$) were inspected by measuring the distance that the front traveled in a given time in terms of centimeter per minute. A constant velocity with almost no bubbles was obtained when pure FP occurred.

Temperature profiles were measured by using a K-type thermocouple by measuring the temperature at fixed point as a function of time. Subsequently, they were converted to a spatial one using the front velocity [27].

## Characterization

The weight-loss of the PNMA/PMAA hybrids on heating was studied by thermogravimetric analysis (TGA) using a thermogravimetric apparatus Shimadzu–TGA 50 under a nitrogen atmosphere. The measurements were taken with a heating rate of 10 °C/min from 30 to 700 °C. The sample was prepared by drying in a vacuum oven at 90 °C for 2 days at a pressure of 70 kPa for solvent removal.

## Results and discussion

Our preliminary work focuses on how to prepare PNMA/PMAA hybrids by FP with a stable front but without the occurrence of spontaneous polymerization (SP). The pot life is the amount of time the reagents can remain at ambient temperature before spontaneously polymerizing.

We assessed the pot life by preparing tubes with the reactants, leaving them at ambient temperature and visually determining at what time they spontaneously polymerized. We found solutions of NMA, MAA, ammonium persulfate ([NMA]/[MAA]=1.68 mol/mol, [monomer]/[DMSO]= 0.82 mol/mol, ammonium persulfate=0.74wt%) were inert at room temperature for more than 10 h but very reactive after being heated for several seconds with a soldering iron. The formation of self-propagating and stable fronts, as shown in Fig. 2, indicates that the FP could be achieved in this system.

One of the key features in pure FP without SP is a constant front velocity. To verify if a constant-velocity front could be achieved, the position of the hot front as a function of time at [NMA]/[MAA]=1.68 mol/mol, [monomer]/[DMSO]=0.82 mol/mol, and ammonium persulfate= 1.0wt% is given in Fig. 3; the experimental data are well fitted by straight line, meaning that a constant-velocity, self-sustaining front was obtained.

However, a constant front velocity can be found although SP is occurring if FP is fast compared with SP on the time scale needed to complete the polymerization. A convenient way to verify the occurrence of pure FP is given by the analysis of temperature profiles (the K-type thermocouple located the position of 3.0 cm from the free surface). The typical temperature profile obtained is shown in Fig. 4. This experiment was performed with a molar ratio of [NMA]/[MAA]=1.68 mol/mol, [monomer]/[DMSO]= 0.82 mol/mol, and initiator concentration (ammonium persulfate=1.0wt%). As shown in Fig. 4, in less than 3.5 cm, the temperature increases 80 °C, and the $T_{\max}$ is 102 °C. Due to the constant temperature value in the region far from the incoming hot front, there is a horizontal part of the curve that means that SP is not occurring simultaneously.

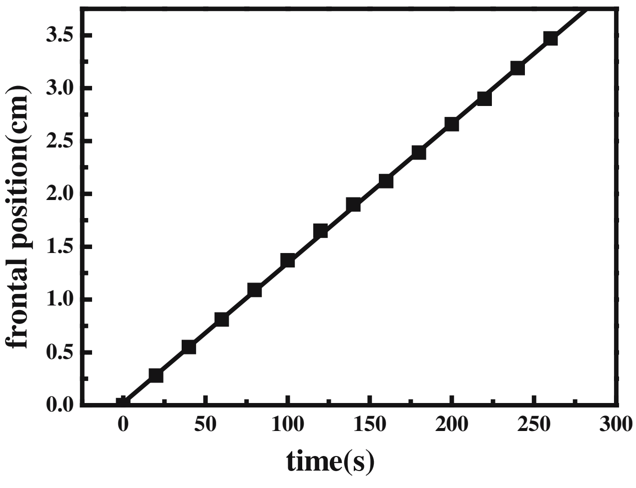


**Fig. 3** Front position vs time for a typical run of the PNMA/PMAA hybrid prepared by FP at [NMA]/[MAA]=1.68 mol/mol, [monomer]/[DMSO]=0.82 mol/mol, and ammonium persulfate=1.0wt%

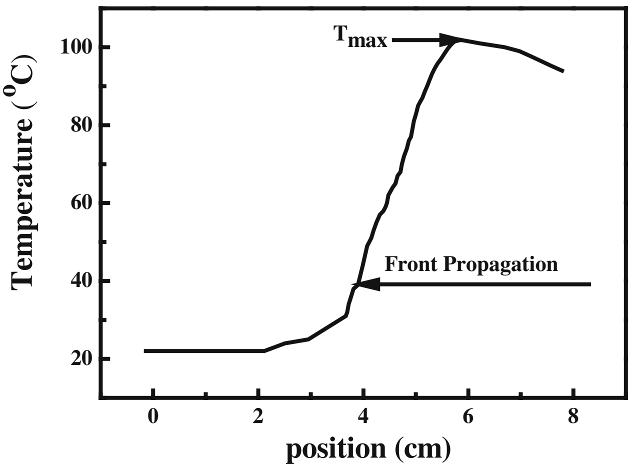


**Fig. 4** Typical temperature profile of the PNMA/PMAA hybrid by FP at [NMA]/[MAA]=1.68 mol/mol, [monomer]/[DMSO]=0.82 mol/mol, and ammonium persulfate=1.0wt%

### Effect of initiator concentration

Initiator concentration is an important factor in FP. If the initiator concentration is too low, the front will be extinguished because of heat loss. Conversely, the pot life will be too short if the initiator concentration is too large. To find the optimal ammonium persulfate concentrations for obtaining PNMA/PMAA hybrids by FP with stable front, several runs were performed at different ammonium persulfate concentrations, varying from 0 (no initiator added) to 1.72 wt%, whereas [NMA]/[MAA] ratio was held at 1.68 mol/mol and [monomer]/[DMSO]=0.82 mol/mol. For ammonium persulfate less than 0.5wt%, no front propagated. Conversely, for ammonium persulfate >1.72wt%,

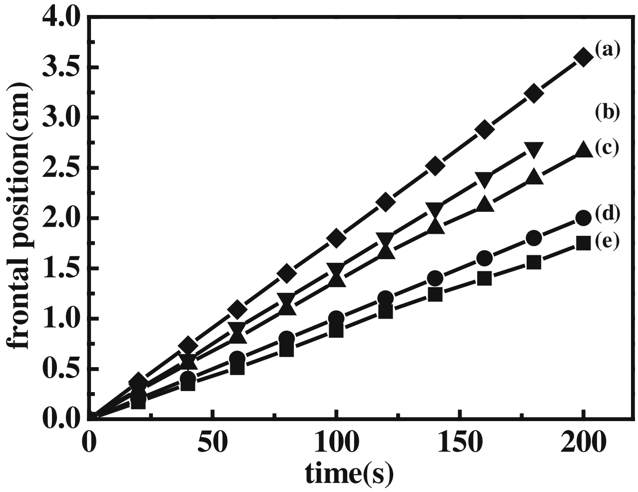


**Fig. 5** Front position vs time of PNMA/PMAA hybrids prepared by FP at [NMA]/[MAA]=1.68 mol/mol; [monomer]/[DMSO]=0.82 mol/mol and **a** ammonium persulfate=1.72wt%, **b** ammonium persulfate= 1.23wt%, **c** ammonium persulfate=1.0wt%, **d** ammonium persulfate= 0.74wt%, and **e** ammonium persulfate=0.5wt%

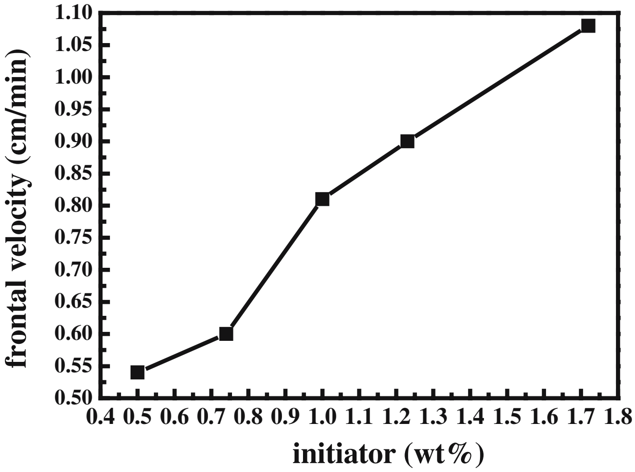


**Fig. 6** Frontal velocity of PNMA/PMAA hybrids prepared by FP vs concentrations of the initiator at [NMA]/[MAA]=1.68 mol/mol and [monomer]/[DMSO]=0.82 mol/mol

notable SP existed. Therefore, the data were obtained for ammonium persulfate between 0.5 and 1.72wt%.

The position of the front as a function of time is given in Fig. 5 for [NMA]/[MAA]=1.68 mol/mol, [monomer]/[DMSO]=0.82 mol/mol, and (a) ammonium persulfate=1.72wt%, (b) ammonium persulfate=1.23wt%, (c) ammonium persulfate=1.0wt%, (d) ammonium persulfate=0.74wt%, and (e) ammonium persulfate=0.5wt%. As seen in Fig. 5, the experimental data for all sets of experiments are well fitted by straight lines, meaning that the fronts propagate with constant velocities. This is strong evidence that pure FP is occurring. Meanwhile, the slope becomes sharper with higher concentration of initiator, pointing out that the velocity of the PNMA/PMAA hybrid fronts increases with an increase of ammonium persulfate concentration.

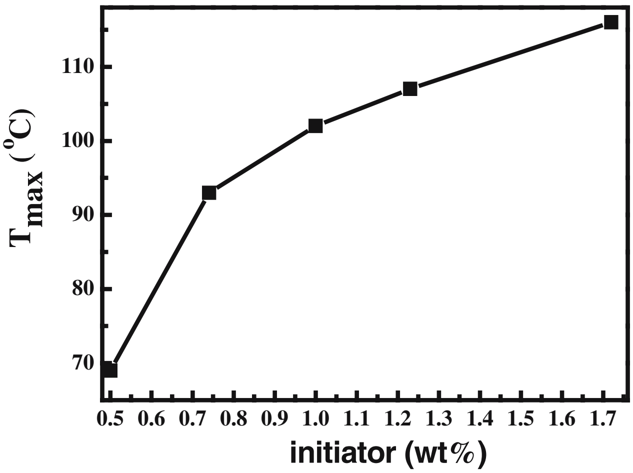


**Fig. 7** $T_{max}$ of the PNMA/PMAA hybrids prepared by FP vs concentrations of the initiator at [NMA]/[MAA]=1.68 mol/mol and [monomer]/[DMSO]=0.82 mol/mol

**Table 1** Effect of DMSO concentration in the reaction mixture on $T_{max}$ and front velocity of PNMA/PMAA hybrids[a]

| Amount of monomer (wt%) | $T_{max}$ (°C) | Front velocity (cm/min) |
|---|---|---|
| 33 | No front propagated | |
| 50 | 102 | 0.81 |
| 66 | 139 | 2.04 |

[a] [NMA]/[MAA]=1.68 mol/mol and [ammonium persulfate]/[monomer]=0.0083 mol/mol

Figure 6 shows the velocity dependence as a function of the persulfate concentration at a constant concentration of [NMA]/[MAA]=1.68 mol/mol and [monomer]/[DMSO]=0.82 mol/mol. As has always been seen in free-radical chain growth FP [27, 38], the velocity monotonically increases with the initiator concentration from 0.54 to 1.08 cm/min.

The front temperature is plotted in Fig. 7 as a function of the concentration of ammonium persulfate, whereas [NMA]/[MAA]=1.68 mol/mol and [monomer]/[DMSO]=0.82 mol/mol. It is observed that an increase of initiator concentration from 0.5 to 1.72wt% caused an increase of $T_{max}$ from 69 to 116 °C. The $T_{max}$ dependence on the initiator concentration is similar to the corresponding velocity trend; the $T_{max}$ monotonically increases with the initiator concentration. We emphasize that our experiments were performed under nonadiabatic conditions, and for this reason, the increased velocity reduced the time for heat lost.

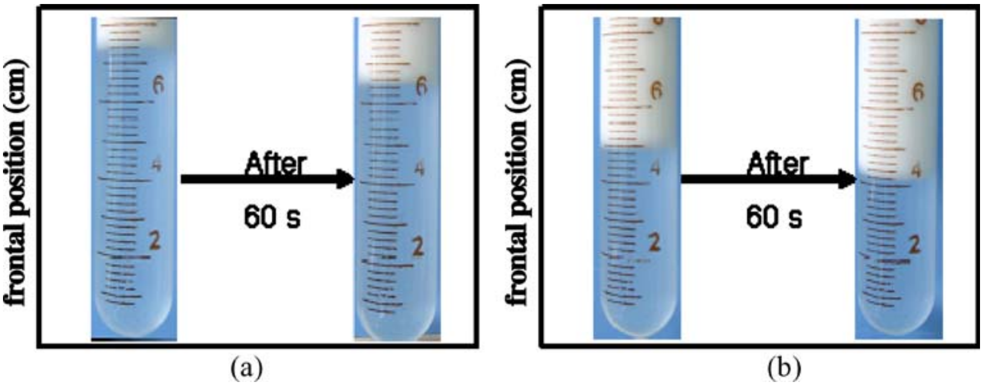
## Effect of reactant dilution

We investigated the effect of the DMSO concentration on both $T_{max}$ and front velocity. The resultant data are listed in Table 1. For monomer concentration=33wt%, no front propagated; whereas for monomer concentration >33wt%, a dilution of the reactants resulted in an obvious decrease of $T_{max}$ from 139 to 102 °C for monomer concentration ranging from 66 to 50wt%. The effect of dilution on front velocity is more evident, going from 2.04 cm/min down to

**Table 2** Effect of NMA/MAA components in the reaction mixture on $T_{max}$ and front velocity[a]

| Amount of NMA (wt%) | Amount of MA (wt%) | $T_{max}$ (°C) | Front velocity (cm/min) |
|---|---|---|---|
| 22.0 | 27.5 | Front stopped propagating until propagated about 2.2 cm | |
| 24.8 | 24.8 | 48 | 0.57 |
| 33.0 | 16.5 | 102 | 0.81 |
| 37.1 | 12.4 | 112 | 1.14 |

[a] Initiator=0.99wt% and solvent=49.5wt%



(a) (b)

**Fig. 8** Visual images of the propagating fronts of the PNMA/PMAA hybrids. The initial conditions are **a** [NMA]/[MAA]=1.68 mol/mol, [monomer]/[NMP]=1.042 mol/mol, and ammonium persulfate=1.0wt%; and **b** [NMA]/[MAA]=1.68 mol/mol, [monomer]/[NMP]=1.042 mol/mol, and ammonium persulfate=0.5wt% (inner diameter of the tube is 15 mm)

0.81 cm/min. The decrease of $T_{max}$ is related to the reduction in the heat-producing species and to the decreased velocity that increases the time for heat lost under nonadiabatic conditions.

### Effect of NMA/MAA components

Table 2 shows the observed $T_{max}$ and front velocity of different components of NMA and MAA. It is observed that an increase of NMA concentration from 24.8 to 37.1wt % caused an increase of $T_{max}$ from 48 to 112 °C. Meanwhile, front velocity goes from 0.57 up to 1.14 cm/min. With "selfcross-linkable" property [54], NMA shows higher reactivity than that of MAA. As more NMA was added, the higher reactivity of NMA dominated, and the front velocity increased. Due to the increased velocity that reduces the time for heat lost under nonadiabatic conditions, the $T_{max}$ increased.

### Effect of ammonium persulfate concentrations with NMP as the solvent

We have also investigated the synthesis of PNMA/PMAA hybrids with NMP as the solvent at different ammonium persulfate concentrations. Figure 8 presents the direct images of propagating the fronts of PNMA/PMAA hybrids at (a) [NMA]/[MAA]=1.68 mol/mol, [monomer]/[NMP]=1.042 mol/mol, and ammonium persulfate=1.0wt%; and (b) [NMA]/[MAA]=1.68 mol/mol, [monomer]/[NMP]=1.042 mol/mol, and ammonium persulfate=0.5wt%. The stable and self-sustaining fronts propagated at constant velocity. The data of $T_{max}$ and front velocity at different ammonium persulfate concentrations are listed in Table 3. The velocity monotonically increases with the initiator concentration, and due to the increased velocity that decreases the time for heat lost under nonadiabatic conditions, the $T_{max}$ monotonically increases with the initiator concentrations as well.

**Table 3** Effect of initiator concentration in the reaction mixture on $T_{max}$ and front velocity of PNMA/PMAA hybrids[a]

| Amount of ammonium persulfate (wt%) | $T_{max}$ (°C) | Front velocity (cm/min) |
|---|---|---|
| 0.125 | Front stopped propagating until propagated about 0.86 cm | |
| 0.25 | 54 | 0.53 |
| 0.5 | 102 | 0.76 |
| 1.0 | 110 | 0.84 |

[a] [NMA]/[MAA]=1.68 mol/mol and [monomer]/[NMP]=1.042 mol/mol

### Materials characterization

#### TGA characterization

Figure 9 is the TGA thermograms comparing the PNMA by BP with the PNMA/PMAA hybrid by FP. The TGA spectra result allows us to conclude that the PNMA/PMAA hybrid shows higher thermal resistance than that of pure PNMA,

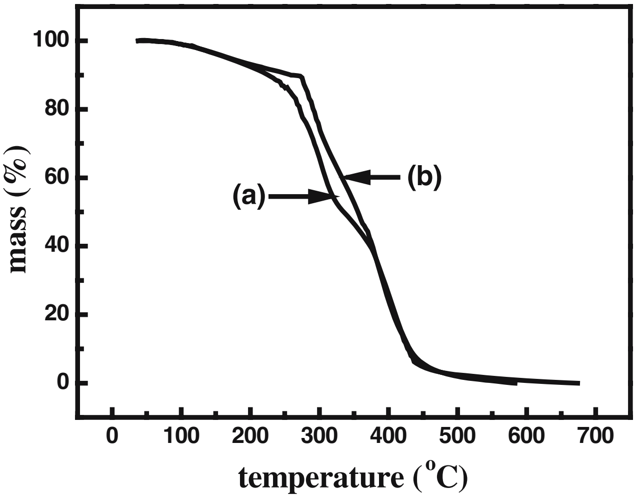


**Fig. 9** TGA curves of **a** PNMA prepared by FP at [NMA]/[DMSO]=0.773 mol/mol, and ammonium persulfate=1.5wt%; and **b** the PNMA/PMAA hybrid by FP at [NMA]/[MAA]=1.68 mol/mol, [monomer]/[DMSO]=0.82 mol/mol, ammonium persulfate=1.5wt%

which might be attributed to the presence of covalent bonds between NMA chains and MAA chains. As shown in Fig. 9, the conversion of PNMA/PMAA hybrid is about 90%.

## Conclusions

The first synthesis of PNMA/PMAA hybrids by frontal free-radical polymerization has been successfully carried out. We have found that, in NMA, MA, and ammonium persulfate ([NMA]/[MAA]=1.68 mol/mol, ammonium persulfate=0.5wt%) dissolved in DMSO ([monomer]/[DMSO]=0.82 mol/mol) or NMP ([monomer]/[NMP]=1.042 mol/mol), SP did not occur, and a pot life of more than 4 h can be obtained at ambient temperatures even without the addition of an inhibitor. The longer the pot life, the longer the reagents can be stored before igniting the front.

In agreement with the data of other published FP systems, our experimental data for all FP experiments are well fitted by straight lines, meaning that the fronts propagate with constant velocities. Meanwhile, the temperature profile provides direct evidence that only pure FP occurs without any SP for a horizontal part, and $T_{\max}$ are obtained in the profile. A dilution of the reactants resulted in an obvious decrease of $T_{\max}$ and front velocity.

TGA characterization indicates that PNMA/PMAA hybrids are produced, and frontally prepared samples of PNMA/PMAA hybrids show higher thermal stability than those of frontally prepared PNMA. The above results allow us to conclude that FP might be exploited as an alternative means for the preparation of PNMA/PMAA hybrids.

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