**SHORT COMMUNICATIONS**

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# Segmented polyurethane synthesized by frontal polymerization

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**Abstract** Frontal polymerization (FP) is a mode of converting a monomer into a polymer via a localized reaction zone that propagates through the monomer. In this study, segmented polyurethane was successfully prepared by FP. The reactants, poly (propylene oxide) glycol, 2, 4-toluene diisocyanate and 1,4-butanediol and the catalyst stannous caprylate, were mixed together at an initial temperature in the presence of dimethylbenzene (as the solvent). The reactions were thermally ignited at one end of the tubular reactor, and the resultant hot fronts propagated throughout the reaction reactor. No further energy was required for polymerization to occur. The effect factors of front velocity, stannous caprylate concentration and temperature on the FP, along with comparison of FP with bulk polymerization, were thoroughly investigated. Fourier transform infrared and differential scanning calorimetry were employed to characterize polyurethane (PU). The polymer materials obtained by FP displayed features similar to those obtained by batch polymerization. The reaction time of FP for preparing PU was lower than that of BP.

**Keywords** Frontal polymerization · Polyurethane · Polyether

## Introduction

Nonlinear chemical dynamics has evolved into a mature area of scientific investigation since the discovery of the Belousov–Zhabotinsky reaction in the 1960s. The most promising practical application of nonlinear chemical dynamics to polymer science is frontal polymerization (FP). FP is a mode of converting a monomer into a polymer via a localized reaction zone that propagates, most often, through the coupling of thermal diffusion and Arrhenius reaction kinetics. The first FP reactions were studied in Russia by Chechilo and Enikolopyan in 1972 [1], who applied this technique to methyl methacrylate (MMA) polymerization to determine the effect of initiator type and concentration on front velocity [2] and the effect of pressure [3]. After this preliminary work, a

great deal of work on the theory of FP was carried out [4–9]. Free-radical polymerization is the most widely performed process by FP since it is usually highly exothermic, and the heat of the reaction provides autocatalysis for a polymerization front propagating through a liquid monomer. Pojman and his co-workers have done much work focusing on the feasibility of traveling fronts in solutions of thermal free-radical initiators in a variety of neat monomers at ambient pressure using liquid monomers [10–12] or a solid monomer [13]. However, that is not all. Begishev et al. [14] studied anionic polymerization of ε-caprolactam and frontal ring-opening metathesis polymerization (FROMP) has been successfully achieved with dicyclopentadiene and applied to the forming of interpenetrating networks (IPNs) [15, 16]. Recently, polymerization processes based on FP have

been found to have many applications including the obtainment of temperature-sensitive hydrogels by Washington and Steinbock [17], solvent-free synthesis of polyacrylamide by Fortenberry and Pojman [18], preparation of polymer-dispersed liquid crystal films of improved homogeneity by Mariani et al. [19]; and consolidation of porous materials has a growing interest [19, 20]. Recently, much research in this field has been devoted to the study of FP [21–23]. Mariani et al. [24] prepared polyurethane (PU) frontally by using 1,6-hexamethylene diisocyanate (HDI) and ethylene glycol (EG). In addition to the above features of interest, FP being a self-sustaining reaction should also be considered an energy-saving way of producing polymer materials, with the additional advantage of short reaction times.

In this paper, we report on preparation of segmented PU using 2,4-toluene diisocyanate (TDI), poly (propylene oxide) glycol (PPG) and chain extender 1,4-butanediol (BD) by FP. The influence of catalyst concentration and initial temperature of the reaction mixture on FP is presented, along with a comparison of some samples obtained by FP with those obtained by batch polymerization (BP).

## Experimental

### Materials

Poly (propylene oxide) glycol (hydroxyl number 56 mg KOH/g, average molecular weight 2,000 was supplied by Jinlin Petrochemical Co. The purified TDI, BD, dimethylbenzene and stannous caprylate were supplied by Aldrich and used as received.

### Frontal polymerizations

In a typical run shown in Fig. 1, a glass test tube (inner diameter 15 mm) was filled with TDI, PPG, BD, stannous caprylate catalyst and dimethylbenzene (as the solvent). For example, a typical molar composition (TDI:PPG:BD) was 2.6:1:1. The vessel was shaken in order to obtain a homogeneous mixture, and a K-type thermocouple, connected to a digital thermometer, was used to monitor the temperature change. The junction was immersed at about 1.5 cm from the free surface of the liquid. The upper layer of the mixture was then heated by a soldering iron bar until the formation of a hot propagating front. Front propagation occurred at a constant velocity by conversion of monomer to polymer with almost no formation of bubbles. A video camera was used to record the front position as a function of time, and the maximum temperature of the front was recorded.
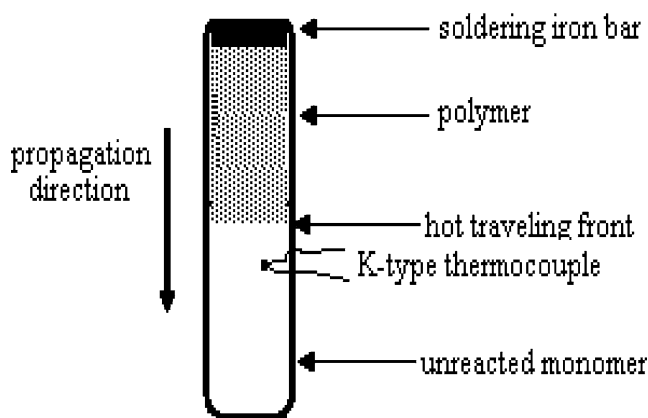


**Fig. 1** Schematic representation of frontal polymerization (*FP*) occurring along a tubular reactor

### Batch polymerizations

Several batch runs had been performed in order to compare the resultant samples with the corresponding ones obtained by FP. In the typical synthesis, the same amounts of each component as quoted above were mixed with vigorous stirring in a reaction vessel, immersed in a thermostatic oil bath set at 85 °C for 3 h. Then, the mixture was cooled back to ambient temperature and stirred for 1 h, along with adding dimethylbenzene to the mixture.

### Characterization

The chemical structure of PU was examined by infrared spectroscopy (FT-IR) in the range 450–4,000 cm$^{-1}$ with 100 scans by an AVATAR-360. The measurement of glass transition temperatures ($T_g$s) of PU was carried out on a Perkin Elmer Pyris instrument. The samples were heated at a rate of 10 °C/min from −100 °C to 100 °C.

## Results and discussion

### Synthesis of segmented PU by FP

Several preliminary experiments were run in order to find a suitable route for obtaining PU by FP. Usually, the pot life is an important factor for FP, since if the pot life is very short, a pure FP will not be achieved, and spontaneous polymerization (SP) could occur. Based on this point, we found that by simple mixing of polyether (average molecular weight 2,000), BD, TDI and stannous caprylate in the presence of dimethylbenzene solvent, an instantaneous SP reaction cannot occur. Also, a longer pot life, which was more than 6 h, could be attained by maintaining the above mixture at the temperature of 10 °C. Some studies [24, 25] reported that an

extended pot life in the synthesis of PUs can be achieved by adding suitable amounts of additive (pyrocatechol) and dimethyl sulfoxide (DMSO) to the reactive components, such as the reactants HDI, EG and a small amount of dibutylin dilaurate (DBTDL) catalyst. However, by pyrocatechol addition (≥0.5 wt%), a pot life could be achieved upto 25 min only. On the other hand, we found that stannous caprylate catalyst is better than DBTDL for preparing PU by FP. It could be explained that the catalyst, stannous caprylate, is not more active than DBTDL [26], which could obtain a longer pot life for FP. This finding allowed us to perform pure FP runs without the simultaneous occurrence of SP.

Figure 2 presents the direct image of propagating fronts of PU. The interface between the polymer and unreacted monomer can be barely seen. The upper layer of the mixture is PU and the bottom layer is unreacted monomers. Front propagation occurred at a constant velocity by conversion of the monomer to PU with almost no formation of bubbles. Also, it can be found that dimethylbenzene is a good solvent in this system, which can disperse the monomers and PU hybrids well.

## Effect of catalyst concentration on FP

Three series of experiments with different concentrations of stannous caprylate catalyst by FP have been carried out, each of them keeping constant a specific [NCO]/[OH] molar ratio. In the runs performed at [NCO]/[OH] = 1.3 (mol/mol), dimethylbenzene = 10 wt%, ratio was allowed to vary stannous caprylate concentration between 0.1 wt% to 0.5 wt% (as shown in Fig. 3). The position of the hot front as a function of time is given in parts a, b and c of Fig. 3. As can be seen in Fig. 3, the experimental data for all sets of experiments are well fitted by straight lines, meaning that the propagation of



**Fig. 2** Colorful visual image of the propagating front of polyurethane (*PU*) (inner diameter of the tube is 1.5 cm)

the polymerization front moves at a constant velocity, and presents strong evidence of the existence of pure FP. It was observed that an amount of SP was present and FP was in competition with SP when the stannous caprylate content > 0.7 wt%. For the three sets of experiments, the relationship between the front velocity and the stannous caprylate content was determined. Namely, an increase in catalyst concentration from 0.1 wt% to 0.5 wt% caused an increase in front velocity from 0.20 cm/min to 0.41 cm/min.

Typical temperature profiles of PU by FP are given in Fig. 4. The horizontal part of the curve, ascribing a constant temperature value to zones far from the incoming hot front, points out that SP does not occur; otherwise, a temperature increase should be observed when the exothermicity of reaction begins. Figure 4 displays the maximum temperature ($T_{max}$) of fronts of PU at different concentrations of stannous caprylate by FP. For the three sets of experiments, the relationship between the $T_{max}$ and the stannous caprylate content was determined. Namely, an increase in catalyst concentration from 0.1 wt% to 0.5 wt% caused an increase in $T_{max}$ from 76 °C to 90 °C.

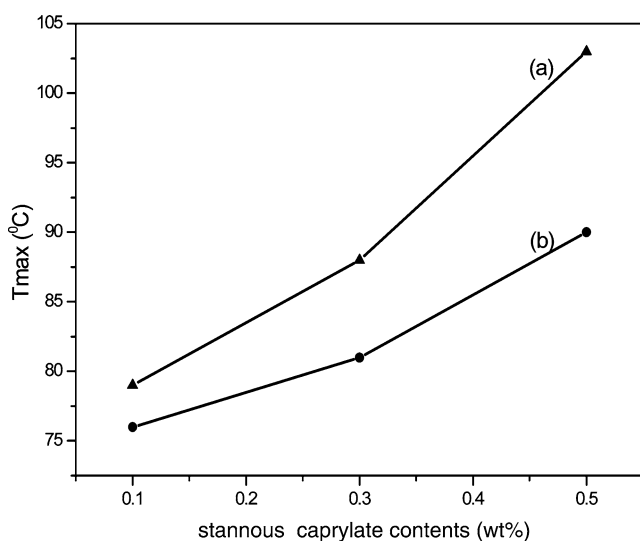Figure 5 presents that $T_{max}$ of PU prepared by FP versus stannous caprlate contents at different initial temperatures of (a) 20 °C and (b) 10 °C. At a lower initial temperature, PU prepared by FP can be obtained at higher stannous caprylate contents along with higher $T_{max}$. However, when the initial temperature was
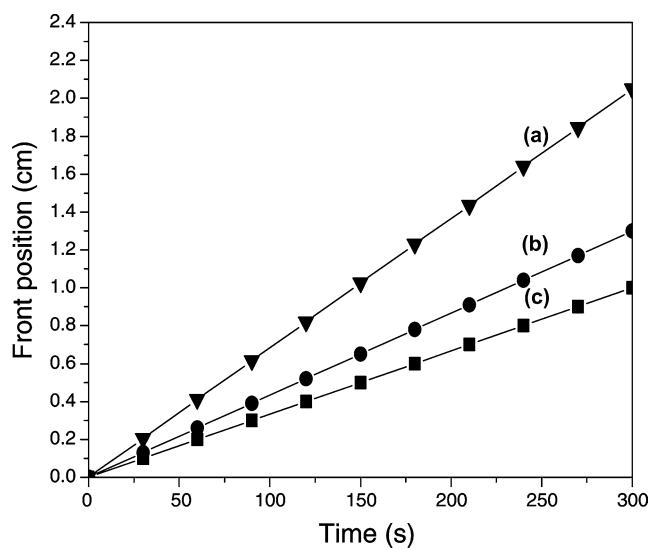


**Fig. 3** Front position versus time at an initial temperature of 10 °C. **a** PU prepared by FP at [NCO]/[OH] = 1.3 mol/mol; stannous caprylate = 0.5 wt%; dimethylbenzene = 10 wt%, **b** PU prepared by FP at [NCO]/[OH] = 1.3 mol/mol; stannous caprylate = 0.3 wt%; dimethylbenzene = 10 wt%, **c** PU prepared by FP at [NCO]/[OH] = 1.3 mol/mol; stannous caprylate = 0.1 wt%; dimethylbenzene = 10 wt%
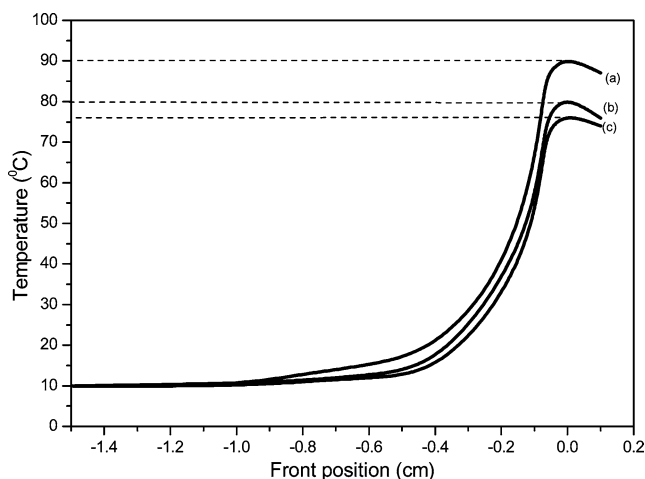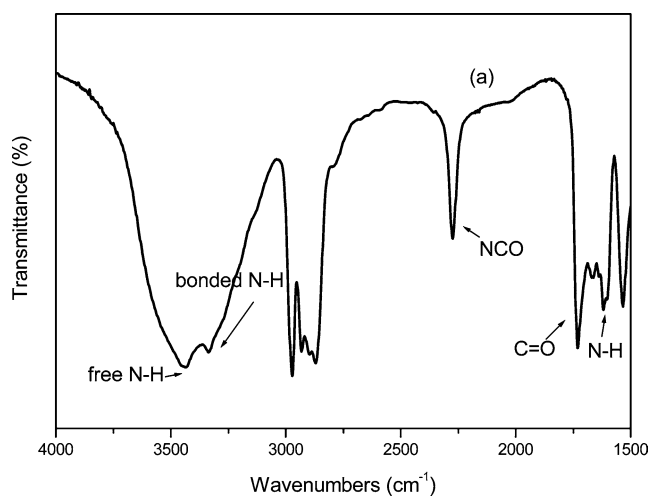
Fig. 4 Typical temperature profiles of PU by FP at an initial temperature of 10 °C. **a** PU prepared by FP at [NCO]/[OH] = 1.3 mol/mol; stannous caprylate = 0.5 wt%; dimethylbenzene = 10 wt%, **b** PU prepared by FP at [NCO]/[OH] = 1.3 mol/mol; stannous caprylate = 0.3 wt%; dimethylbenzene = 10 wt%, **c** PU prepared by FP at [NCO]/[OH] = 1.3 mol/mol; stannous caprylate = 0.1 wt%; dimethylbenzene = 10 wt%
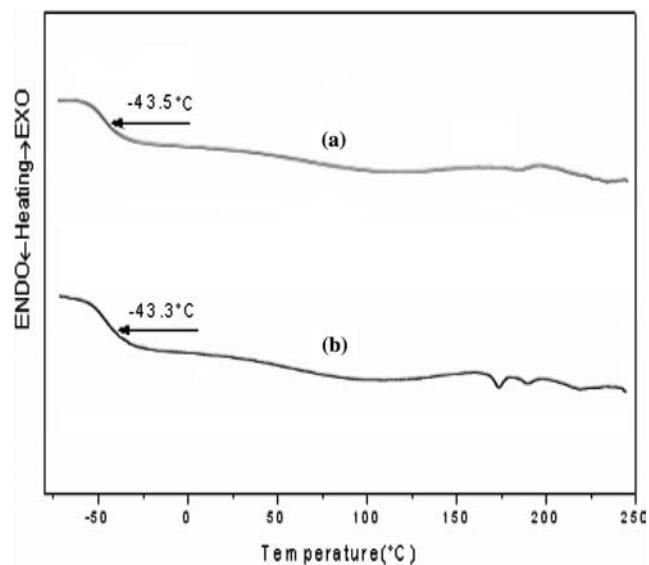


Fig. 6 The Fourier transform infrared (*FT-IR*) spectra (1,500–4,000 cm$^{-1}$) of PU by FP at initial temperature of 10 °C. [NCO]/[OH] = 1.3 mol/mol; dimethylbenzene = 10 wt%; stannous caprylate = 0.5 wt%



Fig. 5 $T_{max}$ of PU by FP versus stannous caprylate contents at different initial temperatures of **a** 20 °C and **b** 10 °C



Fig. 7 DSC curves of PU. **a** PU obtained by FP at an initial temperature of 10 °C; [NCO]/[OH] = 1.3 mol/mol; stannous caprylate = 0.5 wt%, **b** PU obtained by BP at [NCO]/[OH] = 1.3 mol/mol; stannous caprylate = 0.5 wt%

lowered to 0 °C, flat stationary fronts became unstable, and spin modes developed. Figure 5 demonstrats the effect of the initial temperature on the $T_{max}$ of PU prepared by FP. It was observed that $T_{max}$ of PU at an initial temperature of 20 °C was relatively higher than that obtained at an initial temperature of 10 °C. On the basis of this result, it can be inferred that by 10 °C initial temperature, FP for PU suitably occurred in our reacting system.

## Materials characterization

Fourier transform infrared characterization

Figure 6 presents the Fourier transform infrared characterization (FT-IR) spectra of PU prepared by FP at an initial temperature of 10 °C, [NCO]/[OH] = 1.3 mol/mol, dimethylbenzene = 10 wt%, and stannous capry-

late $=0.5$ wt%. As is shown in Fig. 6, the bending vibration absorption peaks of N–H group at 1,535 cm$^{-1}$, the stretching vibration absorption peaks of C=O group at 1,730 cm$^{-1}$, the stretching vibration absorption peaks of free N–H group at 3,425 cm$^{-1}$ and bonded N–H group at 3,334 cm$^{-1}$ can also be observed, which strongly indicated that the product by FP had a chemical structure similar to that obtained by BP [27].

### Differential scanning calorimetry characterization

Typical differential scanning calorimetry (DSC) scans for samples of pure PU prepared by FP and BP are presented in Fig. 7. Figure 7 displays the $T_g$s of PU by different approaches. It is observed that both front and batch samples show similar $T_g$, partly because the products prepared by FP had chain structure and morphology similar to those prepared by BP.

## Conclusions

In this study, the synthesis of PU by FP has been successfully carried out. The experimental data for both FP experiments are well fitted by straight lines, meaning that the fronts propagate with constant velocities. The polymer materials obtained by FP displayed features similar to those obtained by BP. FT-IR spectra of PU by FP displayed the characteristic absorption peaks, which were almost the same as those of PU by BP. In addition, there was little difference of $T_g$s of PU by FP compared to those by BP. The above results allow us to conclude that FP can be exploited as an alternative means for preparation of PU with the additional advantages of high velocity. It should be possible to use FP to commercially synthesize both PUs with less energy than traditional batch methods.

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