Frontal Ring-Opening Metathesis Polymerization of Dicyclopentadiene

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Introduction. Frontal polymerization entails the conversion of a monomer into a polymer via a localized exothermic reaction zone that propagates through the coupling of thermal diffusion and Arrhenius reaction kinetics. Frontal polymerization was discovered in Russia by Chechilo and Enikolopyan in 1972 using methyl methacrylate under high pressure.[1] The extensive work from Russia was reviewed by Davtyan et al.[2]

Pojman and co-workers studied the macrokinetics and dynamics of frontal polymerization,[3−7] and applications for materials synthesis were also considered.[8,9] Frontal polymerization has been used to prepare a variety of materials, including thermochromic composites,[8] IPNs,[6] thick[10] and film[11] polymer-dispersed liquid crystal materials, and functionally gradient materials.[12,13]

An overwhelming majority of work has been on free-radical systems, but other chemistries can be used. Begishev et al. studied frontal anionic polymerization of ϵ-caprolactam,[14,15] and epoxy chemistry has been used as well.[16−19]

In 1995, Grubbs reported on the synthesis and activities of a new Ru-based catalyst for ring-opening metathesis polymerization (ROMP).[20,21] This complex, known as Grubbs' catalyst (GC), has shown very high activity as a catalyst in the ROMP of several cycloolefins. Because ROMP of dicyclopentadiene (DCPD) is highly exothermic, we sought to test whether such a system could sustain frontal polymerization. For frontal polymerization to occur, the reaction must be highly exothermic and react rapidly at the adiabatic reaction temperature but very slowly at ambient temperature, i.e., have a long pot life. In the present paper, we report our preliminary studies on the frontal ring-opening metathesis polymerization (FROMP) of dicyclopentadiene with commercial reagents in which we were able to reduce the rate of bulk polymerization through the addition of an additive and by lowering the DCPD below its melting point.

Experimental Section. Dicyclopentadiene (DCPD, 95%, Aldrich), bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride (Grubbs' catalyst, 98%, Strem), and triphenylphosphine (PPh_3, 99%, Aldrich) were used as received. Ratios were calculated on a molar basis.

In a typical run, a glass test tube (i.d. 15 mm) already containing suitable amounts of solid GC and PPh_3 was filled with liquid DCPD at 35 °C. After fast dissolution, the reaction mixture was cooled to 27 °C in order to permit solidification of the solution.

Polymerization was initiated by heating the wall of the tube with a thermoelectric heater. Fronts were always performed in the descending mode to avoid buoyancy−convection.[22]

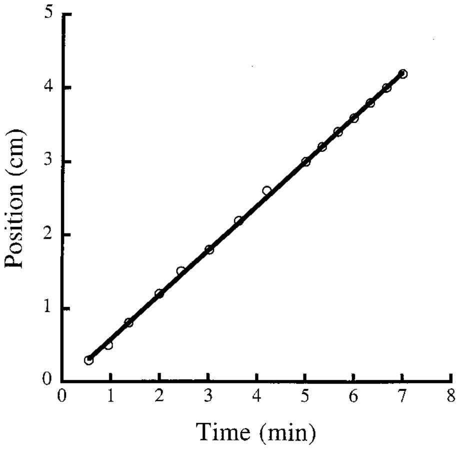

Figure 1. Position of a propagating front as a function of time: [DCPD]/[GC] = 8200 and [PPh_3]/[GC] = 2.7.

Temperature profiles were measured by using copper−constantan thermocouples with a wire diameter of 0.075 mm. The temporal profile was converted to a spatial one using the front velocity.[23]

Results and Discussion. The simultaneous occurrence of bulk polymerization (BP) can be detected in several ways. One of these consists of plotting the position of the front vs time (Figure 1). If a straight line is obtained, then on the time scale of the experiment bulk polymerization does not occur. A second method is the measurement of temperature away from the front. If it remains constant, BP is not occurring significantly.

Our first polymerization attempts were done by mixing GC and DCPD in the liquid state. We always observed BP within a few minutes, a time not sufficient to start and carry out a FP. Grubbs and Woodson reported a suitable and easy method for extending the pot life of an olefin metathesis polymerization by the addition of PPh_3.[24]

We performed a new set of experiments in the presence of various concentrations of both PPh_3 and GC. We have found that, for [DCPD]/[GC] $\geq$ 8000 and [PPh3]/[GC] $\geq$ 2, it is possible to carry out frontal polymerization within 20 min by avoiding BP if the polymer mixture is kept at about 35 °C, i.e., in a liquid state (DCPD mp = 33 °C). This time, although sufficiently long for laboratory purposes, would be inadequate for practical applications.

To overcome this drawback, we dissolved all components at 35 °C and quickly cooled them to 27 °C. This means that FROMP runs were performed on solid mixtures, which melt immediately before being reached by the hot front of propagation. If stored at 7−8 °C, the samples could support a front after 3 weeks.

a. Effect of Catalyst and Additive Concentrations. In Figure 1**,** the front position as a function of time for a typical run is shown. The straight line indicates a constant velocity. In Figure 2 we show a typical temperature profile. We emphasize that before its rapid increase, corresponding to the front passing the thermocouple, no change of temperature has been detected. This is again a confirmation that no BP occurs. The slope of the profile was always very sharp.

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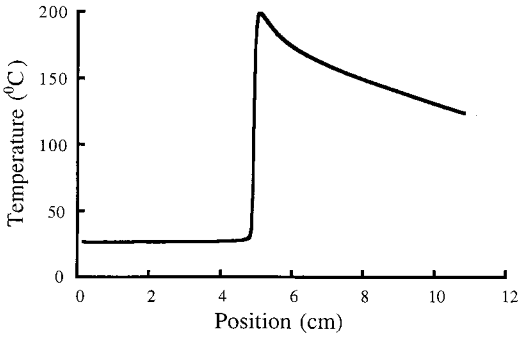

Figure 2. Temperature profile of a front with [DCPD]/[GC] = 3300 and $[PPh_3]/[GC] = 2.6$.

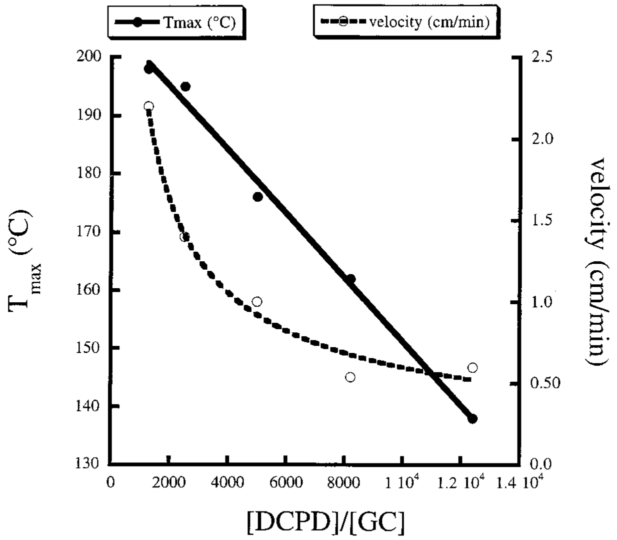

Figure 3. Dependence of T_{max} and front velocity on catalyst concentration: $[PPh_3]/[GC] = 2.6$.

We studied the maximum front temperature (T_{max}) as a function of GC concentration. To have comparable data, these experiments were accomplished by keeping the $[PPh_3]/[GC]$ ratio constant and equal to 2.6. T_{max} has been found to be dependent on the [DCPD]/[GC] ratio. This is due to the fact that we have chosen to carry out these experiments in nonadiabatic conditions, which are those preferentially met in practical applications. The dependence of T_{max} on the concentration of GC is reported in Figure 3. The experimental points are well fitted by a straight line.

The intercept on the T_{max} axis, at ca. 205 °C, is in excellent agreement with the adiabatic temperature of 206 °C, which we determined by performing a ROMP of DCPD in a large “adiabatic” reactor. The variation in the front temperature can be partially explained by the effect of the [DCPD]/[GC] ratio on the front velocity (Figure 3). As expected, the velocity increases with higher concentrations of GC. The latter always ranged between 0.4 and 2.6 cm min^{-1}. Attempts at performing FROMP experiments at GC concentration higher than those indicated in Figure 3 did not produce reproducible results because of simultaneous bulk polymerization. Experiments run at lower GC concentrations resulted in fronts that extinguished because of heat loss.

b. Effect of $[PPh_3]/[GC]$ Ratio. The [DCPD]/[GC] ratio was kept equal to 8200, and we varied the $[PPh_3]/[GC]$ ratio between 1.0 and 3.8, but reproducible results, in terms of both front velocity and T_{max}, were obtained only for $[PPh_3]/[GC] \geq 2$. In fact, for lower ratios, bulk polymerization always occurred to some extent; as a consequence, i.e., for $[PPh_3]/[GC] = 1$, front velocity ranged between 0.5 and 0.9 cm min^{-1}. The effect of $[PPh_3]$ is probably due to the competition between PPh_3 and the incoming monomer. The T_{max} reached by samples polymerized at various PPh_3 concentrations, $[PPh_3]/[GC]$ from 2 to 3.5, was 160 ± 1 °C, indicating that the amount of additive is not an important parameter on this respect. The front velocity is only weakly dependent on this parameter. For [DCPD]/[GC] = 8200 the velocity ranged from 0.5 ($[PPh_3]/[GC]$ of 3.8) to 0.6 cm min^{-1} ($[PPh_3]/[GC]$ of 2).

The T_{max} for the frontal samples suggests that the mechanism for polymerization is the same as in bulk adiabatic polymerization. DSC analysis indicated that the frontal samples were completely converted.

Conclusions. We have determined the experimental conditions for the frontal polymerization of DCPD, which is the first example of a monomer polymerized by FROMP. Polymerization occurs very easily, especially if started from a solid mixture containing DCPD, catalyst, and an additive. The amounts of both additive and catalyst necessary for high conversion are quite low. Furthermore, by addition of PPh_3 and storing at 7−8 °C for 3 weeks, all samples have kept their frontal polymerization capability. These results demonstrate that FROMP may be useful for applications in which sufficiently long pot life and fast reaction times are required.

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