

Advances in the Frontal Ring Opening Metathesis Polymerization of Dicyclopentadiene

Andrea Ruiu, Davide Sanna, Valeria Alzari, Daniele Nuvoli, Alberto Mariani

Dipartimento di Chimica e Farmacia, Università di Sassari, and local INSTM Unit, Via Vienna 2, 07100 Sassari, Italy

Correspondence to: A. Mariani (E-mail: mariani@uniss.it)

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ABSTRACT: The frontal ring opening metathesis polymerization of dicyclopentadiene using first and second generation Grubbs' catalysts is reported. To have sufficiently long pot lives, dimethylaminopyridine is added as an inhibitor. By choosing the proper compositions, it is possible to determine the ranges in which pure frontal polymerization occurs. A thorough study on the effect of the above components on the maximum temperatures reached by the front and on its velocities is performed. Namely, temperatures range from 164 to 205 °C depending on the type of catalyst and the above component ratios. Besides,

front velocities range from 1.0 to 15.0 cm/min, which are one of the lowest and one of the highest values reported so far in any frontal polymerization experiment reported in literature. This finding allows the complete control of the frontal ring opening polymerization of dicyclopentadiene also in practical applications. © 2014 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 2776–2780

KEYWORDS: dicyclopentadiene; frontal polymerization; cross-linking; metal-organic catalysts; ROMP

INTRODUCTION Polydicyclopentadiene (PDCPD) is usually obtained by ring opening metathesis polymerization (ROMP) of its monomer in a highly exothermic reaction due to the release of ring strain energy (Fig. 1).^{1,2}

Generally speaking, ring opening metathesis reactions are usually catalyzed by transition-metal alkylidene complexes.^{3–8} Among all, the best known are those developed by Grubbs et al. (GC), which are ruthenium-based and characterized by very high activity.^{4,9}

The so-called Grubbs' catalysts of first and second generation (GC1 and GC2, respectively) are depicted in Figure 2. GC2, which is much more reactive than GC1, has been developed in the latest years.^{10,11}

This results in very fast reactions that are difficult to be handled; on this respect, latent systems that react fast, but only upon ignition, are mostly preferred.¹² In a recent paper, P'Pool and Schanz reported an inhibiting method to increase the pot life of the ROMP polymerization system, by adding an organic base, such as pyridine, 1-methylimidazole, or *N,N*-dimethylaminopyridine (DMAP), which forms a deactivated complex with the Grubbs' catalysts.¹³ By this method, pot life is reported to increase from few seconds to several hours.

Frontal polymerization (FP) is an alternative synthetic method that allows obtaining polymer materials by a simple reaction route, short time and low energy consumption.^{14–16} FP allows the fast conversion of monomer into polymer by

exploiting the heat produced by the exothermicity of the self-same polymerization reaction. An igniting event causes the formation of a hot polymerization front that allows the propagation of the reaction: the front is able to self-sustain and propagate throughout the monomeric mixture.^{17–34}

Frontal ROMP (FROMP) of DCPD was performed for the first time by Mariani et al.³⁵ using the first generation Grubbs' catalyst, obtaining high front temperatures and velocities, which were dependent on the monomer/catalyst ratio. However, the pot life was so short (just a few seconds) that the polymerization mixture had to be immediately cooled under the DCPD melting temperature to avoid spontaneous polymerization,³⁵ thus limiting the number of possible practical applications of the technique. It should be also emphasized that the above study was limited to the first generation catalyst, which was the only commercially available at the time.

In this work, we present our latest studies on FROMP of DCPD with GC1 and GC2 first. The effect of their inhibition by DMAP addition, and the influence of the monomer/GC/DMAP ratios are also reported.

EXPERIMENTAL

Materials

DCPD, toluene, GC1 GC2, and DMAP were purchased from Sigma Aldrich and used as received, without further purification.



FIGURE 3 Sample synthesized by FROMP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It should be evidenced that, despite the high temperatures reached, all FP experiments give rise to clear, bubble-free samples (Fig. 3).

All successful FP experiments are characterized by constant V_f 's, as evidenced also by the straight lines displayed in Figure 4, in which the position of the front as a function of time is reported for all samples.

It should be noted that the incidental undesirable simultaneous occurrence of spontaneous polymerization should result in front velocities that are not constant and, consequently,

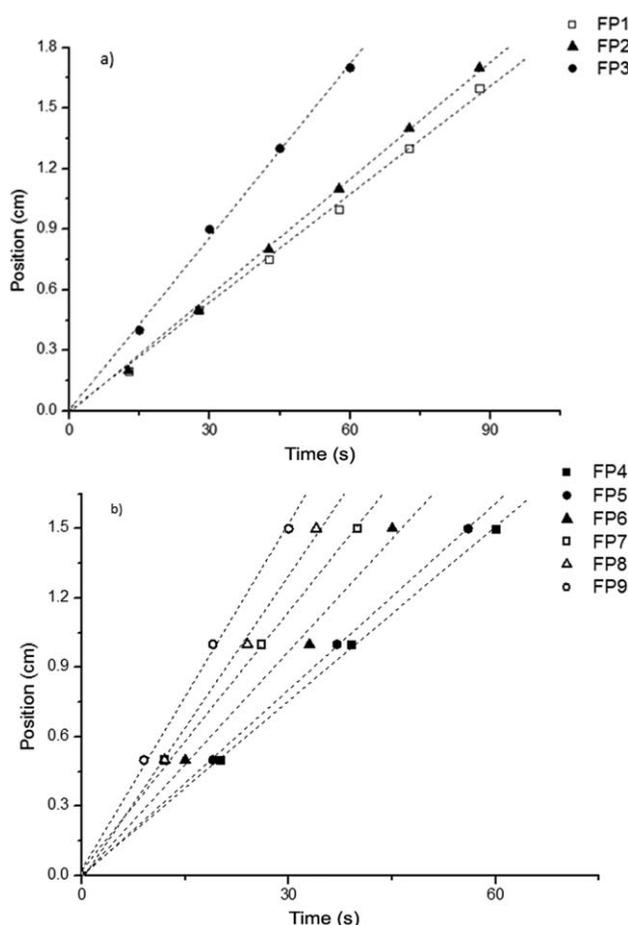


FIGURE 4 Front position as a function of time for the samples prepared using: a) GC1; b) GC2.

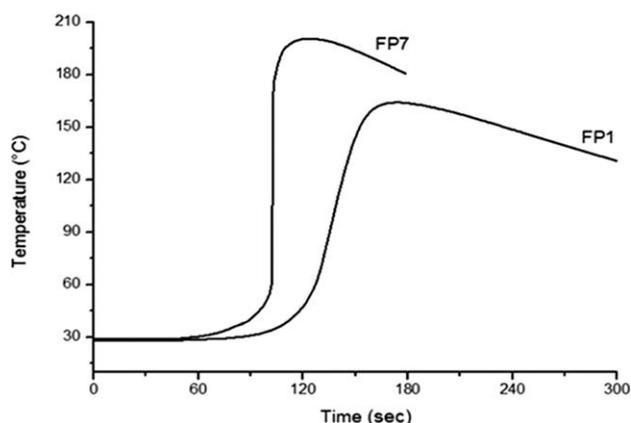


FIGURE 5 Thermal profiles of samples FP1 and FP7.

the positions of the fronts as a function of time should be represented by curvilinear trends.

Moreover, a confirmation that no spontaneous polymerization occurs before FP ignition is given also by the horizontal part of the curves reported in Figure 5. This indicates that the temperature of the reaction mixtures is constant until the front approached the thermocouple junction. Indeed, if a spontaneous polymerization would occur, a temperature increase due to the exothermicity of the reaction should be recorded.

After some preliminary experiments, in which it was found that at least an equimolar amount of DMAP referred to the catalyst is necessary in order to have sufficiently long pot lives, the effect of the ratio between DCPD and GC1 or GC2 is initially studied by keeping the DMAP/GC molar ratio constant and equal to 1.0 mol/mol.

As can be seen in Figures 6 and 7, the minimum amount of GC1 that allows obtaining a pure FP (i.e., without the simultaneous occurrence of spontaneous polymerization) corresponds

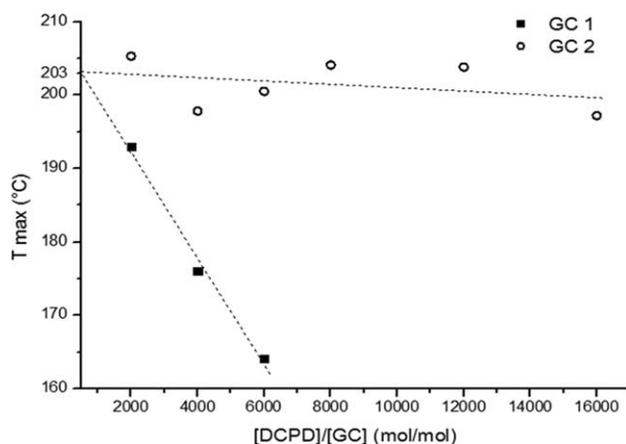


FIGURE 6 T_{\max} as a function of the DCPD/GC molar ratio (DMAP/GC = 1 mol/mol). The two interpolation lines cross the T_{\max} axis almost at the same value ($T = 203$ °C), very close to the adiabatic temperature of 206 °C.³⁵

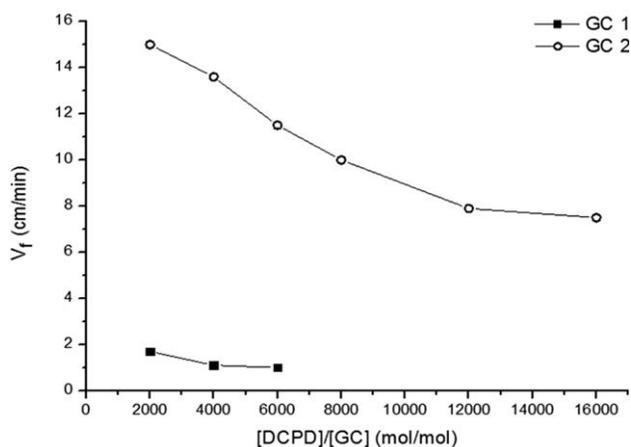


FIGURE 7 V_f as a function of the DCPD/GC molar ratio (DMAP/GC = 1 mol/mol).

to DCPD/GC1 = 6000 mol/mol. It is worthy to note that, when GC2 is used instead of GC1, such a ratio is much larger, that is 16,000 mol/mol, thus confirming the increased efficiency of this second catalyst.

The maximum temperatures reached by all fronts are reported in Figure 6. As can be seen, the effect of the type of catalyst is very marked. Indeed, while in the presence of GC1 relatively large temperature differences are found by varying its concentration (from 193 to 164 °C as the DCPD/GC molar ratio ranges from 2000 to 6000 mol/mol, respectively), when GC2 is used no significant temperature differences are found, although the effective DCPD/GC molar ratio is much larger. Namely, in this second case T_{max} is always close to 206 °C. This is the adiabatic temperature of the system,³⁵ as also confirmed by both the two straight interpolation lines, which cross the T_{max} axis very close to that value, at ca. 203 °C.

This different behavior is also reflected by the V_f trends reported in Figure 7. Indeed, while in the presence of GC1 V_f range from 1.0 to 1.7 cm/min as the DCPD/GC1 molar ratio is varied from 6000 to 2000 mol/mol, respectively, when GC2 is utilized front velocities raise from 7.5 to 15.0 cm/min. It should be highlighted that this latter value is one of the highest reported so far in any FP experiments reported in literature.³⁶

Besides, the much higher activity of GC2 as compared with GC1 is further confirmed together with the effectiveness of DMAP as inhibiting compound at low temperature. On the other hand, the high V_f values found in the presence of GC2 are in agreement with the corresponding temperatures reached by the fronts. Actually, it is well known that, generally, the higher T_{max} , the higher V_f . This can be explained as follows: when a front moves fast there is less time for the polymerization heat to dissipate and T_{max} values remain relatively high. In the present case, fronts resulting from DCPD polymerization in the presence of GC1 are relatively slow, which results in the big variation of T_{max} ; at variance, the use of GC2 result in fronts that are so fast that heat dissipa-

TABLE 3 V_f and T_{max} of samples synthesized in the presence of GC2: effect of the amount of DMAP

| Sample | DMAP/GC2 (mol/mol) | DCPD/GC2 (mol/mol) | V_f (cm/min) | T_{max} (°C) |
|--------|--------------------|--------------------|----------------|----------------|
| FP12 | 1 | 2,000 | 15.0 | 205 |
| FP16 | 2 | 2,000 | 11.8 | 205 |
| FP17 | 4 | 2,000 | 6.8 | 201 |
| FP18 | 8 | 2,000 | 4.0 | 199 |
| FP7 | 1 | 16,000 | 7.5 | 197 |
| FP13 | 2 | 16,000 | 5.6 | 199 |
| FP14 | 4 | 16,000 | 3.4 | 196 |
| FP15 | 8 | 16,000 | 2.2 | 197 |

tion is almost completely avoided, thus accounting for the higher front temperatures, always close to the adiabatic value.

A second series of experiments is devoted to the study of the amount of inhibitor. As mentioned above, when the DMAP/GC molar ratio is <1 pot lives are always shorter than 10 min as evidenced by the temperature increase in their reaction mixtures that is recorded before ignition. On the other hand, when DMAP/GC1 ≥ 2 mol/mol the fronts are too inhibited to self-sustain. On this basis, the following study is carried out on the GC2 system only and, more specifically, for DMAP/GC2 ranging from 1 to 8 mol/mol.

Namely, the systems characterized by the highest and the lowest DCPD/GC2 molar ratios are considered (TABLE 3).

First of all, it is found that all systems exhibit a much increased pot life, which becomes as long as 20–30 min. The effect on the temperature reached by the front is not particularly relevant; actually, only a slight decrease of the T_{max} is observed as the content of inhibitor increases for the system in which the DCPD/GC2 is kept equal to 2. However, in all cases the temperature is close to the aforementioned adiabatic one. At variance, front velocities are largely affected by the amount of DMAP. Particularly, when DCPD/GC2 = 2000 mol/mol, V_f ranges from 15.0 down to 4.0 cm/min while, when DCPD/GC2 = 16,000 mol/mol, V_f decreases from 7.5 to 2.2 cm/min, thus allowing for a good control of the whole system, which may be of interest in practical applications.

CONCLUSIONS

The recent developments in ROMP research field were exploited in the present work in order to achieve a complete control of the FROMP of dicyclopentadiene also for practical applications in which easy protocols are requested. Actually, this latter was already reported several years ago by Mariani et al.³⁵ but its protocol was not easily applicable mostly due to the immediate reaction of DCPD when put in contact with the catalyst (GC1), even if in the presence of an inhibitor (triphenyl phosphine). The evolution of the first generation

Grubb's catalyst to the commercially available GC2 and the finding of new, more effective inhibiting systems such as DMAP, allowed us to successfully perform the FROMP of DCPD in very short times and quantitative yields on systems characterized by sufficiently long pot lives. Moreover, it has been possible to delimitate the mutual molar ratios between monomer, catalyst and inhibitor that make the FP able to occur. Finally, it has been possible to determine the conditions for having polymerization fronts varying along a large velocity range, namely from 1.0 to 15.0 cm/min, which respectively are one of the lowest and one of the highest values reported so far in any published frontal polymerization experiment.

REFERENCES AND NOTES

- 1 H. S. Eleuferio, US Patent 3, 074, 918, **1963**.
- 2 C. Slugovc, *Macromol. Rapid Commun.* **2004**, *25*, 1283–1297.
- 3 R. R. Schrock, *J. Organomet. Chem.* **1986**, *300*, 249–262.
- 4 P. Schwab, M. B. France, J. W. Ziller, R. H. Grubbs, *Angew. Chem. Int. Edit. Engl.* **1995**, *34*, 2039–2041.
- 5 M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956.
- 6 J. A. Love, J. P. Morgan, T. M. Trnka, R. H. Grubbs, *Angew. Chem. Int. Edit.* **2002**, *41*, 4035–4037.
- 7 J. S. Kingsbury, J. P. Harrity, P. J. Bonitatebus, A. H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 791–799.
- 8 T. S. Halbach, S. Mix, D. Fischer, S. Maechling, J. O. Krause, C. Sievers, S. Blechert, O. Nuyken, M. R. Buchmeiser, *J. Org. Chem.* **2005**, *70*, 4687–4694.
- 9 P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100–110.
- 10 J. P. Morgan, R. H. Grubbs, *Org. Lett.* **2000**, *2*, 3153–3155.
- 11 T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann, *Angew. Chem. Int. Edit.* **1999**, *38*, 2416–2419.
- 12 S. Naumann, M. R. Buchmeiser, *Macromol. Rapid Commun.* **2014**, *35*, 682–701.
- 13 S. P'Pool, H.-J. Schanz, *J. Am. Chem. Soc.* **2007**, *129*, 14200–14212.
- 14 J. A. Pojman, *J. Am. Chem. Soc.* **1991**, *113*, 6284–6286.
- 15 A. Morales, J. A. Pojman, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 3850–3855.
- 16 J. D. Mota-Morales, M. C. Gutiérrez, M. L. Ferrer, I. C. Sanchez, E. A. Elizalde-Peña, J. A. Pojman, F. D. Monte, G. Luna-Bárceñas, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 1767–1773.
- 17 S. Scognamillo, V. Alzari, D. Nuvoli, A. Mariani, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 2486–2490.
- 18 R. Sanna, D. Sanna, V. Alzari, D. Nuvoli, S. Scognamillo, M. Piccinini, M. Lazzari, E. Gioffredi, G. Malucelli, A. Mariani, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 4110–4118.
- 19 E. Gavini, A. Mariani, G. Rasso, S. Bidali, G. Spada, M. C. Bonferoni, P. Giunchedi, *Eur. Polym. J.* **2009**, *45*, 690–699.
- 20 V. Alzari, A. Mariani, O. Monticelli, L. Valentini, D. Nuvoli, M. Piccinini, S. Scognamillo, S. B. Bon, J. Illescas, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 5375–5381.
- 21 A. Mariani, S. Bidali, S. Fiori, G. Malucelli, E. Sanna, *E-Polym.* **2003**, *44*, 1–9.
- 22 S. Scognamillo, V. Alzari, D. Nuvoli, A. Mariani, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 4721–4725.
- 23 A. Brunetti, E. Princi, S. Vicini, S. Pincin, S. Bidali, A. Mariani, *Nucl. Instrum. Meth. B.* **2004**, *222*, 235–241.
- 24 V. Alzari, D. Nuvoli, S. Scognamillo, M. Piccinini, E. Gioffredi, G. Malucelli, S. Marceddu, M. Sechi, V. Sanna, A. Mariani, *J. Mater. Chem.* **2011**, *21*, 8727–8733.
- 25 S. Scognamillo, V. Alzari, D. Nuvoli, J. Illescas, S. Marceddu, A. Mariani, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 1228–1234.
- 26 A. Mariani, S. Fiori, S. Bidali, V. Alzari, G. Malucelli, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 3344–3352.
- 27 S. Scognamillo, C. Bounds, M. Luger, A. Mariani, J. A. Pojman, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 2000–2005.
- 28 J. Illescas, R. Sanna, V. Alzari, D. Nuvoli, M. Casu, E. Rivera, A. Mariani, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 4618.
- 29 D. I. Fortenberry, J. A. Pojman, *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 1129–1135.
- 30 Y. A. Chekanov, J. A. Pojman, *J. Appl. Polym. Sci.* **2000**, *78*, 2398.
- 31 L. Chen, T. Hu, H. Yu, S. Chen, J. A. Pojman, *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 4322–4330.
- 32 Y. Fang, L. Chen, S. Chen, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 1136–1147.
- 33 S. Chen, T. Hu, Y. Tian, L. Chen, J. A. Pojman, *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 873–881.
- 34 S. Russo, A. Mariani, V. N. Ignatov, I. I. Ponomarev, *Macromol.* **1993**, *26*, 4984–4985.
- 35 A. Mariani, S. Fiori, Y. Chekanov, J. A. Pojman, *Macromol.* **2001**, *34*, 6539–6541.
- 36 C. Nason, T. Roper, C. Hoyle, J. A. Pojman, *Macromol.* **2005**, *38*, 5506–5512.