Interpenetrating polydicyclopentadiene/polyacrylate networks obtained by simultaneous non-interfering frontal polymerization

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Abstract: Interpenetrating polymer networks made of dicyclopentadiene and methyl methacrylate or tri(ethylene glycol) dimethacrylate have been successfully prepared by non-interfering frontal polymerization. The role of catalyst and free radical initiator relative amounts, as well as of monomer ratio, has been thoroughly studied. The conditions under which a pure frontal polymerization occurs, and the related values of both front velocity and maximum temperature reached by the reaction, are presented and discussed.

Introduction

Frontal Polymerization (FP) exploits the heat production due to the exothermal reaction and its dispersion by thermal conduction. If heat losses are not too large, an amount of energy is provided sufficient to induce the polymerization of monomer molecules close to the hot zone. As a result, a self-sustaining hot polymerization front, able to propagate, occurs.

The first studies on FP were performed in the former USSR by Chechilo et al. [1] who polymerized methyl methacrylate (MMA) under high pressure (> 3000 atm). During the last decade, Pojman et al. demonstrated the achievability of FP for a number of vinyl monomers and epoxy resins at ambient pressure [2].

In 1997, Pojman et al. [3] reported on the first synthesis of a Simultaneous Interpenetrating Polymer Network (SIPN) obtained by binary frontal polymerization of tri(ethylene glycol) dimethacrylate (TGDMA, polymerized by free radical polymerization) and diglycidyl ether of bisphenol A (cured by BCl_3/amine to give an epoxy resin). In 1998, Morbidelli et al. showed that polymer blends can be successfully obtained by FP [4]. In particular, PMMA/polystyrene blends with unusually high level of mixibility were prepared by frontally polymerizing MMA in the presence of polystyrene.

More recently, Mariani et al. expanded the field of applications of FP to polydicyclo-pentadiene [5] and polyurethanes [6] by frontally polymerizing the corresponding monomers and reactants in the presence of suitable compounds added to the

reaction mixtures in order to achieve an extended pot-life. In particular, the feasibility of Frontal Ring Opening Metathesis Polymerization (FROMP) of dicyclopentadiene (DCPD) catalyzed by bis(tricyclohexylphosphine)benzylidine ruthenium(IV) dichloride (Grubbs' catalyst, GC) was established. To avoid spontaneous polymerization (SP) and extend pot-life, triphenylphosphine (PPh$_3$) was used as an additive [5].

Indeed, for a pure FP to occur, the polymerization system should be almost inert at relatively low temperature (mostly, room temperature) and highly reactive when heated. If the system shows a tendency to polymerize also at low temperatures, a non-desirable SP takes place, which competes and sometimes prevents FP.

There are at least two easy ways to verify if a pure FP is occurring. Fig. 1 shows the position of a travelling hot front as a function of time. The straight lines well fitting the experimental data indicate that front velocities are constant. Generally, if a simultaneous SP is occurring, deviations from linearity are found.
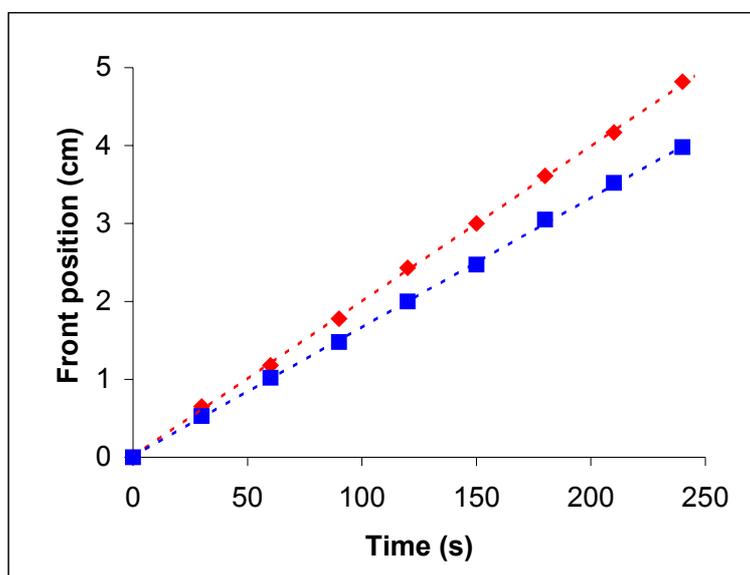

Fig. 1. Front position as a function of time for two typical systems polymerized in the present work (■ DCPD/MMA monomer pair; ◆ TGDMA/DCPD monomer pair)

A second evidence is given by the trend shown in Fig. 2. The horizontal part on the left side of the curve proves that there is no temperature increase, due to SP, before the coming of the front.

On the other hand, polymer blends made of polyDCPD and polyacrylates are largely used in a number of applications such as structural composites in automotive and electronic industries (e.g. in printed circuit boards) [7]. Aim of the present work is to contribute to the above applied fields by setting-up suitable experimental conditions for the obtainment of polymer blends by simultaneous non-interfering FP*s*.

In particular, DCPD has been frontally polymerized in the presence of MMA or TGDMA. The latter two monomers have been chosen as representatives of the acrylate family, giving linear and crosslinked polymers, respectively. Since DCPD gives a crosslinked polymer, the resulting polymer blends can be better classified as Simultaneous Semi-Interpenetrating Polymer Networks (SSIPN, for the DCPD/MMA monomer pair), and Simultaneous Interpenetrating Polymer Networks (SIPN, for the DCPD/TGDMA system).
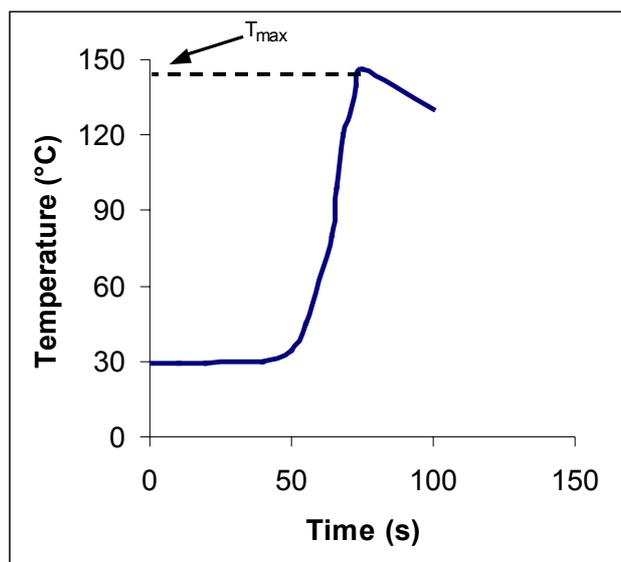
Fig. 2. Temperature as a function of time (data recorded in correspondence to the thermocouple junction for the FP of a typical DCPD/MMA sample)

It has been reported [7] that, in the usual preparation of SSIPN*s* based on DCPD and MMA, a sequential polymerization takes place. This fact is evidenced by the occurring of a double temperature jump due to the heat released by the two independent polymerization reactions. In the present work, we show that, because of the high temperatures reached in the travelling reaction zone, a single hot front exists, i.e., the two polymerizations occur simultaneously.

Experimental part

DCPD, MMA, TGDMA and Aliquat® 336 were purchased from Aldrich. 2,2'-Azoisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were obtained from Fluka. GC was bought from Strem Chem. and PPh_3 obtained from Carlo Erba.
Aliquat® persulfate (APS) was prepared as described in ref. [8].
All materials were used as received.

In a typical run, a non-adiabatic glass test tube (inner diameter 16 mm) was loaded with the appropriate amounts of DCPD, GC, PPh_3, acrylic monomer (MMA or TGDMA) and radical initiator (APS or BPO or AIBN). The mixture was shaken to obtain a homogeneous solution, and a K-type thermocouple connected to a digital thermometer was utilized for monitoring the temperature trend (instrument precision ± 0.3°C). The junction was immersed at about 4 cm from the surface of the liquid. The front position (± 0.5 mm) was recorded as a function of time. The upper layer of the mixture was then heated by a hot soldering iron tip until the formation of a hot propagating front started. As the reaction was complete, samples were allowed to cool to room temperature for an hour, followed by Soxhlet extractions with boiling petroleum ether (as monomer solvent), and chloroform (as solvent of both monomer and PMMA).

Gravimetric analyses indicate that conversions were always >90%. Reproducibility of temperature data was within ± 2°C, and that of the front position was within ± 0.5 mm.

Results and discussion

1. DCPD/MMA monomer pair

1.1 Preliminary experiments

Some preliminary experiments have been performed in order to evaluate the ranges in which the relative amounts of MMA, DCPD, APS (as radical initiator [8]), GC (as FROMP catalyst) and PPh$_3$ (as an additive necessary for extending DCPD pot-life) [5] can vary ensuring a pure FP. It has been found that formulations containing more than 50% of MMA do not polymerize by either FP or SP (at least in the time scale of experiments, i.e. 10 min). In particular, it should be emphasized that neat MMA does not frontally polymerize; in fact, as reported in literature, such monomer is able to sustain a front only under high pressure [1].

Monomer feeds characterized by DCPD/MMA volume ratios equal to 70/30 and 80/20 hardly sustained a front. In addition, a simultaneous SP occurred.

Conversely, DCPD/MMA ratio = 90/10 has been found to give a pure FP by operating in the range 750 mol/mol ≤ [DCPD]/[GC] ≤ 1500 mol/mol. Indeed, for lower amounts of catalyst, FP did not self-sustain, whereas for larger contents of GC a simultaneous SP has been always observed.

The corresponding relative amounts of free-radical initiator have not been found a crucial factor on this respect. This is probably due to the higher stability of the latter at room temperature as compared with GC. Tab. 1 lists some blank runs performed in the absence of APS or GC and compared to the corresponding synthesis carried out in the presence of all components.

Tab. 1. Selected blank runs for the DCPD/MMA = 90/10 (v/v) system, compared with the corresponding synthesis performed in the presence of all components

[APS]/[MMA] in mmol/mol	[DCPD]/[GC] in mol/mol	Polymerization mode	T_{max} in °C	V_f in cm/min
no APS	1000	FP	153	1.7
2.6	1000	FP	161	1.3
2.6	no GC	none	-	-

As can be seen, no FP occurs if no catalyst is present in the reaction medium. On the contrary, FP takes place also in the absence of radical initiator. The extraction of this latter polymer sample by petroleum ether (a solvent of MMA) resulted in the isolation of neat polyDCPD, as confirmed by gravimetry. These findings suggest that FP is mainly due to the exothermicity of DCPD polymerization. The heat released, in turn, causes the decomposition of APS and the subsequent polymerization of MMA. This explanation is in agreement also with the relative values of front velocity (V_f) and maximum temperature (T_{max}, as indicated in Fig. 2), which characterize these runs. Indeed, although the presence of initiator depressed GC activity [9] with the result of decreasing V_f, T_{max} increased because of the contribution derived by the exo-thermicity of MMA polymerization.

On the basis of what is stated above, the following discussion will deal with the effect of the relative amounts of the reaction mixture components in the ranges in which

only a pure FP occurred. In particular, all the following data refer to the DCPD/MMA = 90/10 (v/v) composition.

1.2 Effect of the relative amounts of catalyst and additive

For this set of experiments, APS has been used as a free radical initiator and its content was kept constant ([APS]/[MMA] = 5 mmol/mol). In a previous paper [5], we have shown that pure FP of DCPD can be achieved if a certain amount of PPh$_3$ is added to the reaction mixture containing DCPD and GC, the effect of this additive being that of increasing pot-life. Namely, [PPh$_3$]/[GC] ratios = 2 - 4 mol/mol are particularly effective. In fact, while a simultaneous SP was observed for lower amounts of PPh$_3$, for larger contents of additive no FP occurred. The dependences of front velocity and T_{max} on [PPh$_3$]/[GC] are reported in Tab. 2 for [DCPD]/[GC] = 1000 mol/mol.

Tab. 2. Dependence of front velocity and T_{max} on [PPh$_3$]/[GC]

[PPh$_3$]/[GC] in mol/mol	V_f in cm/min	T_{max} in °C
2	1.3	154
3	1.2	156
4	0.8	144

As shown, the larger the amount of additive, the slower the front velocity, ranging between 1.3 cm/min for [PPh$_3$]/[GC] = 2 mol/mol to 0.8 cm/min for [PPh$_3$]/[GC] = 4 mol/mol. In particular, for [PPh$_3$]/[GC] ≤ 3 mol/mol the system seems to be characterized by very similar features, which are better evidenced by analyzing the T_{max} values. Indeed, after a relatively sharp increase from 144°C (for [PPh$_3$]/[GC] = 4 mol/mol) to 156°C (for [PPh$_3$]/[GC] = 3 mol/mol) no significant further increment has been found for [PPh$_3$]/[GC] = 2 mol/mol, for which T_{max} = 154°C.

The effect of the relative amount of catalyst has been investigated by keeping the [PPh$_3$]/[GC] mole ratio constant and equal to 3. It has been found that pure FP takes place for 750 mol/mol ≤ [DCPD]/[GC] ≤ 1500 mol/mol. Actually, for [DCPD]/[GC] > 1500 mol/mol the propagating front was not able to self-sustain or did not exist at all; for [DCPD]/[GC] < 750 mol/mol the simultaneous occurrence of SP was found.

Tab. 3 and Fig. 3 show how front velocity and T_{max}, respectively, depend on the amount of catalyst (expressed as [DCPD]/[GC] mole ratio). As could be expected, a decrease of GC concentration resulted in a corresponding decrease of both those parameters (from 1.6 cm/min and 171°C, at [DCPD]/[GC] = 750 mol/mol, to 1.1 cm/min and 133°C, at [DCPD]/[GC] = 1500 mol/mol).

A further observation can be done by fitting the experimental points in Fig. 3 with a straight line. The extrapolated value of $T_{max} \cong 208$°C (corresponding to an infinite concentration of GC) can be taken as a useful approximation of the adiabatic temperature of this monomer system. It should be pointed out that a similar extrapolation cannot be done by increasing the corresponding amount of initiator. In fact, as already stated, frontal polymerization of neat MMA cannot be achieved at ambient pressure, and consequently it can be assumed that its FP is possible mainly because

of the heat released by DCPD polymerization. In other words, FP is ruled by DCPD reaction features.

Tab. 3. Dependence of front velocity on the amount of catalyst

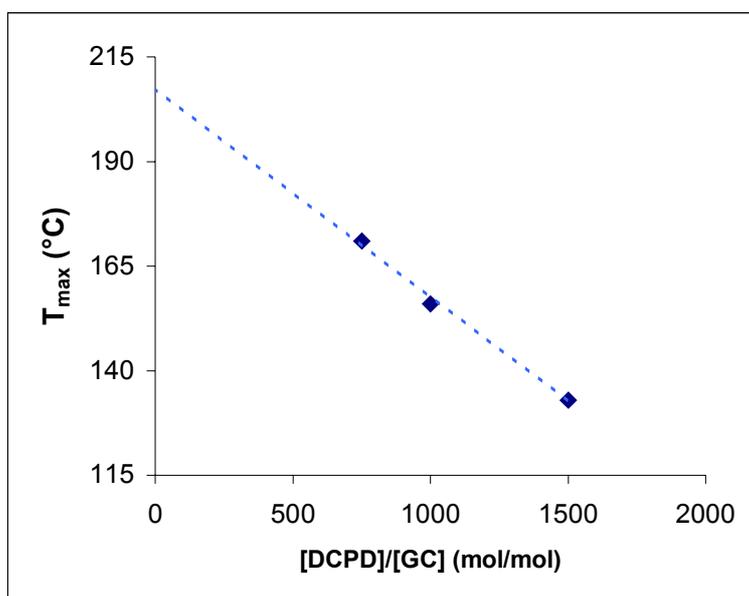| [DCPD]/[GC] in mol/mol	V_f in cm/min
1500	1.1
1000	1.2
750	1.6

Fig. 3. Dependence of T_{max} on the amount of catalyst

Since the adiabatic polymerization temperature of neat MMA is $T_{adb,MMA}$ = 256°C [4] and that of DCPD is $T_{adb,DCPD}$ = 206°C [5], a rough estimation of the adiabatic polymerization temperature of the present system can be calculated as follows:

$$T_{adb}^{est} = T_{adb,MMA} \cdot f_{MMA} + T_{adb,DCPD} \cdot f_{DCPD} = 256°C \cdot 0.1 + 206°C \cdot 0.9 = 211°C \qquad (1)$$

(where f_{MMA} and f_{DCPD} are the corresponding volume fractions)

in good agreement with the aforementioned extrapolated value of 208°C.

Accordingly, it can be added that, although MMA cannot sustain a polymerization front at ambient pressure when used alone, the presence of a second monomer induces its FP to high conversion (as confirmed by the polymer yields calculated by gravimetry). To our knowledge, this is the first time that heat released by the FP of a monomer is exploited to sustain the front of a second polymerizing system not able to frontally polymerize under the same conditions, if alone. We think that this finding could significantly extend the field of monomers to be used in FP formulations, and allows for a larger use of this technique to practical applications.

1.3 Effect of type and concentration of free-radical initiator

This set of experiments was carried out by keeping constant the following reaction conditions: DCPD/MMA = 90/10 (v/v), [DCPD]/[GC] = 1000 mol/mol, [PPh$_3$]/[GC] = 3 mol/mol. Three initiators, belonging to different chemical classes, were tested: AIBN, BPO and APS. Experimental front velocity data are presented in Fig. 4, in which the different behavior of the three systems is evident. In particular, BPO gives the highest front velocity and the increase of this parameter is almost proportional to initiator concentration (from 1.7 cm/min, in the absence of BPO, to 2.2 cm/min at [BPO]/[MMA] = 10 mmol/mol).
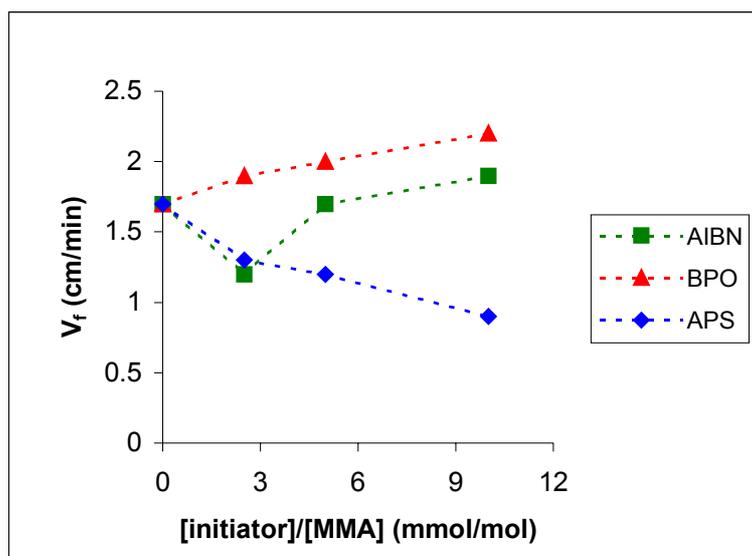

Fig. 4. Dependence of V_f on type and concentration of free radical initiator

APS showed an opposite behavior, namely, the larger the amount of initiator, the slower the front velocity (only 0.9 cm/min at [APS]/[MMA] = 10 mmol/mol). This fact could be explained by the aforementioned finding that GC activity is depressed by the presence of even small amounts of APS. An intermediate behavior characterizes AIBN, which depressed GC activity more than BPO but, for [BPO]/[MMA] > 2.5 mmol/mol, positively contributed to raise the front velocity as its amount increased.

The corresponding T_{max} data are reported in Fig. 5. While AIBN and BPO are characterized by similar behaviors, APS differs for [initiator]/[MMA] ratios > 5 mmol/mol. Indeed, due to the contribution of MMA polymerization to the total amount of heat released, an increase of T_{max} from 153°C (when no radical initiator was present) to ≈158°C (at [initiator]/[MMA] = 5 mmol/mol) was observed.

Conversely, while for larger amounts of initiator, polymerization media containing AIBN and BPO were characterized by higher T_{max} (= 169°C at [initiator]/[MMA] = 10 mmol/mol), in the case of APS T_{max} decreased down to 133°C for [APS]/[MMA] = 10 mmol/mol. It is, therefore, confirmed what was already stated by the analysis of front velocity data (Fig. 4) on the negative effect of this compound on the GC reactivity. In fact, being the yields quantitative in any of the above experiments, differences in T_{max} cannot be attributed to different amounts of heat released in the three systems but, more probably, to the velocity at which that release happened.
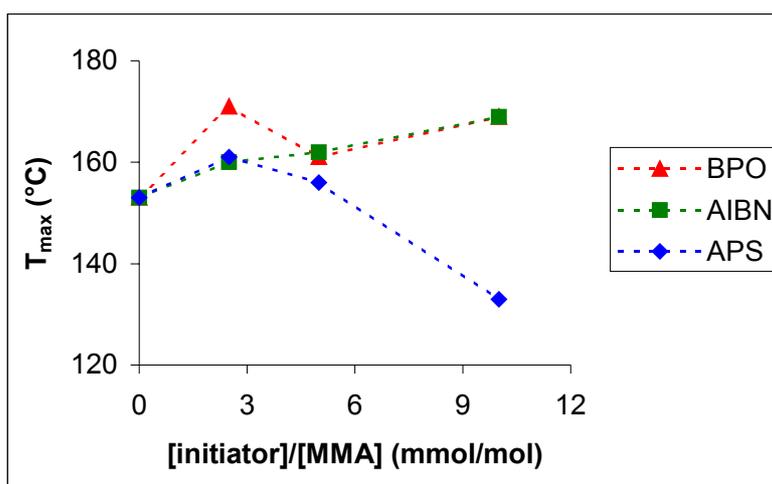
Fig. 5. Dependence of T_{max} on type and concentration of free radical initiator

2. TGDMA/DCPD monomer pair

2.1 Preliminary experiments

On the basis of what has been done for the DCPD/MMA monomer pair, [DCPD]/[GC] = 1000 mol/mol and [PPh$_3$]/[GC] = 3 mol/mol have been taken as reference values also for this system; analogously, [APS]/[TGDMA] has been fixed to 5 mmol/mol (Tab. 4). Also for this monomer pair, the undesirable occurrence of SP was checked by monitoring front velocity and temperature data as functions of time (Fig. 1 and Fig. 6, respectively).

Tab. 4. Selected preliminary runs for the TGDMA/DCPD system

TGDMA/DCPD volume ratio	[APS]/[TGDMA] in mmol/mol	[DCPD]/[GC] in mol/mol	Polymerization mode	T_{max} in °C	V_f in cm/min
100/0	5	0	FP	163	1.2
90/10	5	1000	FP	161	1.2
75/25	5	1000	FP	140	1.0
50/50	5	1000	SP	-	-
10/90	5	1000	does not sustain front	-	-
0/100	0	1000	FP	202	2.4

Under these conditions, it has been found that, for TGDMA/DCPD < 75/25 (v/v), FP is accomplished together with SP or does not self-sustain. On the contrary, TGDMA volume fractions ≥ 0.75 allow for a self-sustaining pure FP. Accordingly, all the following data are referred to the ratio TGDMA/DCPD = 75/25 (v/v).
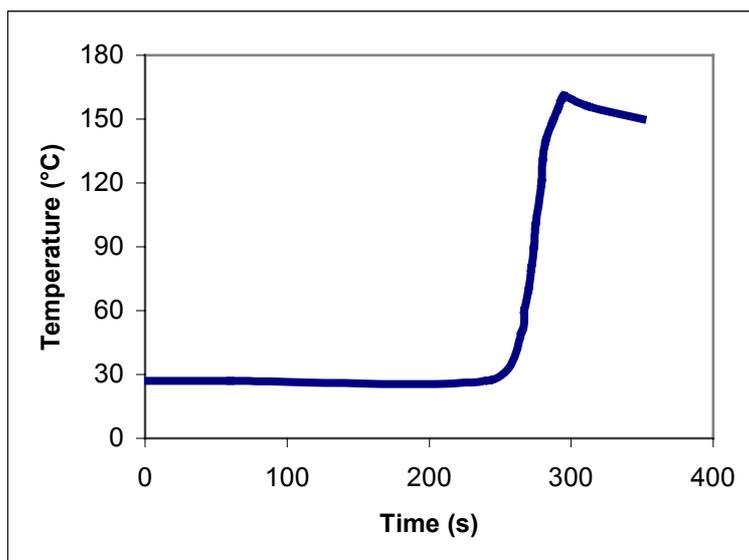
Fig. 6. Dependence of temperature on time for a typical TGDMA/DCPD sample (data recorded in correspondence of the thermocouple junction)

2.2 Effect of the initiator concentration (APS)

Tab. 5 lists T_{max} and V_f values of three samples in which the relative amount of the radical initiator APS has been varied. As shown above, both these parameters raise by increasing the amount of initiator (from 132°C and 0.7 cm/min, at [APS]/[TGDMA] = 2.5 mmol/mol, to 147°C and 1.0 cm/min, at [APS]/[TGDMA] = 10 mmol/mol), which is a behavior opposite to that characterizing the DCPD/MMA system (Fig. 4 and Fig. 5). An explanation of this finding could be that, contrary to what was found for the DCPD/MMA system, in the present formulation the vinyl monomer is in excess and able to self-sustain a front. Consequently, FP is probably ruled by the features of TGDMA reaction. In other words, although APS depresses GC activity, the contribution to the feasibility of FP in the TGDMA/DCPD system is mostly due to TGDMA.

Tab. 5. Effect of APS concentration on T_{max} and V_f.

[APS]/[TGDMA] in mmol/mol	T_{max} in °C	V_f in cm/min
2.5	132	0.7
5.0	140	1.0
10	147	1.0

2.3 Effect of the concentration of catalyst

In this set of experiments, the concentration of APS and the [PPh$_3$]/[GC] ratio ([APS]/[TGDMA] = 5 mmol/mol; [PPh$_3$]/[GC] = 3 mol/mol) have been kept constant, and GC has been varied in the range 750 mol/mol ≤ [DCPD]/[GC] ≤ 8200 mol/mol. However, for [DCPD]/[GC] = 750 mol/mol, FP always occurred simultaneously with SP. Conversely, for [DCPD]/[GC] = 8200 mol/mol, FP started but was not able to self-sustain.

T_{max} and front velocity values of the two runs in which pure FP was observed are reported in Tab. 6.

Tab. 6. Effect of the concentration of catalyst on T_{max} and V_f

[DCPD]/[GC] in mol/mol	T_{max} in °C	V_f in cm/min
1000	140	1.0
1500	142	0.8

As can be seen, for the amounts of GC listed here only a slight difference in front velocity was found (T_{max} remained practically constant). Also in this case, the higher the amount of GC, the higher V_f, although no dramatic differences have been found in the considered range.

Conclusions

The application of FP to the obtainment of interpenetrating polymer networks by simultaneous non-interfering polymerization reactions has been demonstrated. Polymerizations were fast and characterized by high conversions.

In contrast to what was previously reported in the literature for these monomer systems [1,7], due to the heat released by DCPD polymerization, it has been possible to frontally polymerize MMA at ambient pressure. Furthermore, DCPD and the acrylic monomer (MMA or TGDMA) polymerized simultaneously, as demonstrated by a single jump of the temperature.

These findings open wide possibilities to obtain several other polymer blends by FP, also including those in which a non-frontally polymerizable monomer is present.

[1] Chechilo, N. M.; Khvilivitskii, R. J.; Enikolopyan, N. S.; *Dokl. Akad. Nauk SSSR* **1972**, *204*, 1180.

[2] Khan, A. M.; Pojman, J. A.; *TRIP* **1996**, *4*, 8.

[3] Pojman, A. J.; Elcan, W.; Khan, A. M.; Mathias, L.; *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 227.

[4] Tredici, A.; Pecchini, R.; Sliepcevich, A.; Morbidelli, M.; *J. Appl. Polym. Sci.* **1998**, *70*, 2695.

[5] Mariani, A.; Fiori, S.; Chekanov, Y.; Pojman, J. A.; *Macromolecules* **2001**, *34*, 6539.

[6] Fiori, S.; Mariani, A.; Ricco, L.; Russo, S.; submitted to *Macromolecules*.

[7] Sjardijn, W.; Snel, J. J. M.; *US Patent* 5109073, **1992**.

[8] Masere, J.; Chekanov, Y.; Warren, J. R.; Stewart, F. D.; Al-Kaisi, R.; Rasmussen, J. K.; Pojman, J. A.; *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3984.

[9] This finding was also confirmed by adding APS to a reaction medium consisting only of DCPD and GC.