New Vistas in Frontal Polymerization

Alberto Mariani,[*1] *Simone Bidali,*[1] *Stefano Fiori,*[1] *Giulio Malucelli,*[2] *Laura Ricco*[3]

[1] Dipartimento di Chimica, Università di Sassari, and local INSTM Research Unit, via Vienna 2, 07100 Sassari, Italy
Fax: +39079212069; E-mail: mariani@uniss.it
[2] Dipartimento di Scienza dei Materiali e Ingegneria Chimica, and local INSTM Research Unit, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino, Italy
[3] Dipartimento di Chimica e Chimica Industriale, Università di Genova, and local INSTM Research Unit, via Dodecaneso 31, 16146 Genova, Italy

Summary: Frontal Polymerization is a technique for the synthesis of polymers that, by exploiting the heat liberated by the self-same reaction, generates a hot front that can sustain and propagate itself from one end of the reactor to the other converting monomer into polymer. After the activation and following formation of the front, it is not necessary to provide any other form of energy in order to carry out polymerization. In this article we will summarize some of the recent results we have obtained in the application of Frontal Polymerization to the preparation of polyurethanes, unsaturated polyester resins, and polyacrylates.

Keywords: atom transfer radical polymerization (ATRP); frontal polymerization; polyacrylates; polyurethanes; unsaturated polyester resins

Introduction

Frontal Polymerization (FP) exploits the exothermicity of the self-same reaction and the local dispersion of heat by way of thermal conduction. If the amount of energy dispersed is not too high, this may induce polymerization of monomer molecules close to the source of heat. The result is the formation of a hot front of polymerization that can sustain and propagate itself throughout the reactor.

The first studies on FP were conducted in the ex-USSR on methyl methacrylate (MMA), which was polymerized under extreme pressure conditions (>3000 atm).[1, 2] Subsequently, several vinyl monomers were polymerized at atmospheric pressure.[3-5] In addition, FP has been applied to the curing of epoxy-based materials.[6-8]

For many years the only chemical systems used for FP were those mentioned above and the majority of research in this field was devoted to the study of both the instability of the front[9-16] and modeling.[17, 18]

In 2000 our group started working in this field and paid particular attention to the possibility not only of discovering new chemical systems capable of polymerizing frontally, but also of finding new applications for FP. In particular, we studied polyurethanes,[19, 20] polyester/styrene resins,[21] epoxy resins,[22] polydicyclopentadiene,[23] polyacrylates and Interpenetrating Polymer Networks composed of dicyclopentadiene and polyacrylates[24] synthesized by FP technique. In the present article, we will briefly discuss FP with reference to some of the most recent developments.

Results and Discussion

Generally speaking, experimental work on a new system potentially able to provide *pure* FP is initially devoted to determining the conditions in which it occurs. With the term *pure* we mean FP as the only polymerization process at work in the reactor in a given moment and in particular we mean that spontaneous polymerization does not come about simultaneously.

In order to bring about pure FP, the chemical system being investigated must be inert at relatively low temperatures, but highly reactive at the temperature reached by the front (generally higher than 100° C). This means that sufficiently long pot-lives are necessary. It is obvious that polymerization systems do not always have the above requisites; in order to fulfill these requirements, we have proposed the use of suitable additives [19, 20, 23] which decrease catalyst activity at room temperature without significantly affecting it at the temperatures at which FP occurs.

Pure FP is often (but not always) characterized by a constant velocity of the front (V_f); a typical example is given in Figure 1a, in which the position of the front in relation to elapsed time is shown. Figure 1b displays a typical temperature profile registered using a thermocouple situated at a distance some centimeters from the point in which the front

originated. It may be noted that the temperature does not undergo variations when the front is far away from the thermocouple junction (this is an indication of pure FP), while when the front becomes close to the junction a clear T increase is registered, up to a maximum temperature (T_{max}).
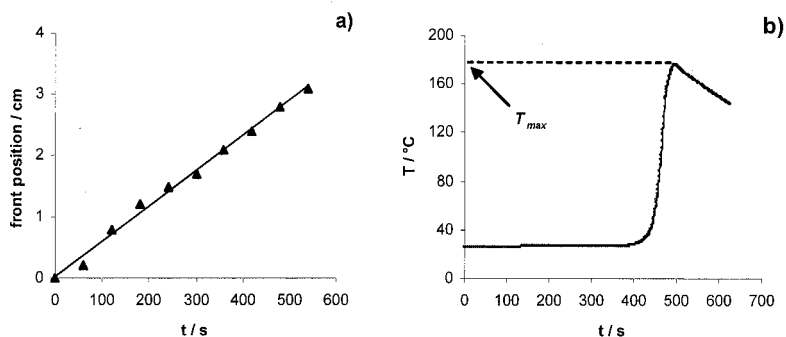

Figure 1: front position as a function of time (a), and temperature profile (b) recorded during a typical FP run (frontal ATRP of tri(ethyleneglycol) dimethacrylate).

Polyurethanes

The first polyurethane obtained by FP step polyaddition was that synthesized by our group starting from 1,6-hexamethylene diisocyanate (HDI) and ethylene glycol (EG) in the presence of dibutyltin dilaurate as catalyst and pyrocatechol (PC) as the additive necessary to ensure a sufficiently long pot-life to the mixture.[19]

After this initial study, we focused our attention on a second system of greater practical interest; in particular, that obtained by the reaction between HDI, 1,6-hexanediol (HD) and poly(ε-caprolactone) diol (PCLD).

As in the previous case, it was again necessary to resort to a catalyst (dibutyltin diacetate, DBTDAc) and to PC as a reaction inhibitor. By this way, it was possible to carry out an extensive and detailed study of the characteristics of polyurethanes obtained by pure FP.

Figures 2a and 2b show the dependence of T_{max} and V_f on the molar concentration of DBTDAc (referred to HDI moles) for different molar ratios between PC and DBTDAc.
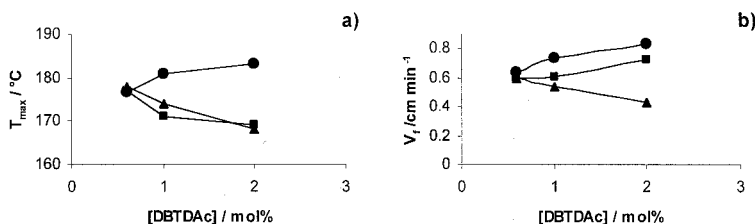
Figure 2: a) T_{max} as a function of catalyst concentration; b): V_f trends as a function of catalyst concentration. ● = [PC] / [DBTDAc] = 6 mol/mol, ■ = [PC] / [DBTDAc] = 8 mol/mol, ▲ = [PC] / [DBTDAc] =11 mol/mol.

From the above plots it can be seen that high amounts of inhibitor induce low values of T_{max} e V_f. This result is in full agreement with those already reported for the FP of PU synthesized from HDI and EG,[19] and also for the Frontal Ring Opening Metathesis Polymerization (FROMP) of dicyclopentadiene.[23]

The DSC analysis (second scan) of two samples from the same mixture composition (HDI : HD : PCLD = 1 : 0.65 : 0.35; 2.5 wt.-% Cab-osil; [DBTDAc]/[HDI] = 1.0 mol-%; [PC]/[DBTDAc] = 6 mol/mol), the first prepared using FP (PF1) and the second by the conventional batch method [25] (PB1), underlines the striking differences between them. Namely, the T_g of PB1 (-50.4 °C) is much lower than that of PF1 (-24 °C). Furthermore, PB1 melts at higher temperatures (139 °C) in comparison to PF1 (121 °C), with a greater enthalpy of fusion (ΔH_m = 59.6 vs. 37.1 J/g). The different thermal behavior of the two samples can be attributed to the different reaction processes used for their preparation. In particular, the conventional batch method allows the product to crystallize in a better way than FP. Indeed, this latter proceeds faster than the batch reaction, thus reducing the ability of macromolecules to rearrange and migrate towards the thermodynamically favorite positions and crystallize. As a consequence, DSC endothermic signals due to the presence of pure PCL blocks disappear.

The shift of T_g value towards lower temperatures might be firstly attributed either to the different reactivity of the two diols (HD and PCLD) in the reaction with HDI at two different temperatures (i.e. the temperature of the conventional batch reaction is lower than that reached during the FP) and/or to a plasticizing effect due to the presence of partially reacted groups in the batch sample, which indeed exhibits lower conversion with respect to PF1. [20]

Moreover, some phase separation phenomena occurring between soft and hard segments might justify the aforementioned differences of T_g, T_m and ΔH_m values of PB1 with respect to PF1. Therefore, the shift of PF1 T_g toward higher temperature values might indicate that PU hard segments are more miscible in FP samples than in their batch counterparts.

Measurements of PU intrinsic viscosity underline that the samples synthesized by FP have greater molecular weights than those produced with the batch method (PF1: $[\eta]$ = 0.43 dl/g; PB1: $[\eta]$ = 0.35 dl/g, in m-cresol at 25 °C).

Furthermore, extraction runs with a solvent (dichloromethane) displayed higher conversion values for FP samples (PF1: 75%) in comparison to the batch ones (PB1: 50%). This might be attributable to the much higher temperature reached during FP runs as compared to the conventional route. However, in FP experiments such a high temperature is kept only for a few seconds and degradation phenomena (occurring in batch runs for prolonged heating) are not present, at least in relevant extent.

A full description of the above results is reported in ref. 20.

Unsaturated Polyester Resins

Unsaturated polyester resins are widely used as components in composite materials.[26] They are generally obtained by the reaction between an unsaturated polyester (UPE) and a vinyl monomer. In our study, we frontally cured the UPE synthesized from maleic anhydride and 1,2-propanediol. As the curing agent, we used styrene (St), which is the most widely used monomer for these purposes in practical applications. The literature suggests other valid alternatives: hydroxyethyl acrylate (HEA) and/or a diurethane diacrylate (acrylic acid 2-[6-(2-acryloyloxy-ethoxycarbonylamino)-hexylcarbamoyloxy]-ethyl ester, UA).[27] The reactions between the UPE and the curing agents cited above are highly exothermic, by this way permitting rapid FP.

Also in this study, the relative amounts of all the components were varied so as to find the conditions in which pure FP occurred. When St was used, it was found that its concentration could vary between 20 and 40 wt.-%. At lower concentrations, FP was not observed even with relatively high amounts of radical initiator (benzoyl peroxide, BPO). On the other hand, when the St content was > 40 wt.-%, a phase separation was observed. Figure 3 shows the dependence of T_{max} on both type and concentration of radical initiator for an amount of styrene equal to 30 wt.-% (which is typically found in commercial products). Three initiators belonging to three different chemical classes have been used:

BPO, azobisisobutyronitrile (AIBN) and Aliquat[®] persulfate (APS).

An increase of T_{max} due to an increase of the initiator concentration has been found in all the experiments, an effect which is particularly evident in the case of BPO and AIBN. On the contrary, in the same range of relative initiator concentrations (1-10 mol%), the APS curve showed only a limited increase.

This result is probably due to the diluting effect exerted by such initiator characterized by a high molecular weight ($MW = 930$) which, having to be used in relatively high weight percentages, probably contributes to heat dispersion by dilution and does not permit a large temperature increase. The materials obtained by FP have been compared with the corresponding samples prepared by the classical batch methods. DSC analyses have shown that FP allows quantitative conversions in small lapses of time, while using batch methods far lower conversions can be obtained even for relatively long reaction times (1 h vs. few minutes). Furthermore, FP copolymers are characterized by higher T_g values in comparison to those of the batch reaction (136 vs. 92 °C in first scan; 153 vs. 106 °C, in second scan).
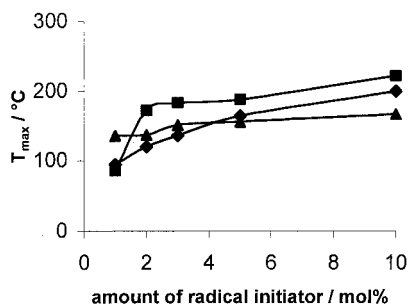

Figure 3: Dependence of T_{max} on the type and amount of initiator ($w_{St} = 30$ wt.-%). ■ = BPO, ♦ = AIBN, ▲ = APS.

On the basis of what has been reported in ref. 27, later on St has been substituted by HEA and UA as curing agents. These latter, with respect to St, have the advantage of being less volatile as well as of conferring better mechanical properties to the copolymer.

As an example, the following system has been studied: HEA + UA (whole concentration of 30 wt.-%) + UPE (70 wt.-%). The ratio between the above components has been varied

keeping constant the amount of APS, used as radical initiator (3 mol% referred to the number of the vinyl groups). By increasing the amount of UA, a slight increase of T_{max} was found: from 124 °C for UA/HEA = 0, up to 147 °C for UA/HEA = 0.5 wt.-%, this latter being the maximum quantity of UA that allows the creation of a homogenous solution of all the reaction components. In the same interval, V_f remains constant at 0.6 cm/min.

This latter parameter has been found to be of scarce dependence on the quantity of APS. In fact, in the case of the mixture having the following composition in weight: UPE : HEA : UA = 70 : 21 : 9, V_f varied between 0.4 (APS = 1 mol%) and 0.5 cm/min (APS = 10 mol%). A detailed presentation of this latter study is reported in ref. 28.

Frontal Atom Transfer Radical Polymerization

We have also verified the possibility of combining FP and Atom Transfer Radical Polymerization, ATRP,[29] towards which we directed our interest not so much with the aim of obtaining 'living' polymers and/or those characterized by a low degree of polydispersity, but rather as an alternative way of arriving at the FP of acrylic monomers instead of the classical radical polymerization. In fact, the latter requires large amounts of radical initiators which cause several problems linked to the type of initiator, such as, for example, the presence of bubbles in the final product due to the development of gas from the initiator decomposition.

In particular, we polymerized tri(ethyleneglycol) dimethacrylate (TGDMA), using CBr_4 as the initiator and a compound formed of equimolar quantities of CuBr and tris(2-aminoethyl)amine (TREN) as the catalyst.

The comparison among samples obtained by frontal ATRP, batch polymerization and frontal classical radical polymerization was deemed of interest.

For constant initiator concentrations ([CBr_4] = 0.2 mol% with respect to TGDMA), the evaluation of V_f and T_{max} has underlined how the variation of [catalyst] leads to V_f values ranging from 0.24 (for [CuBr] = 0.2 mol%) to 0.60 cm/min (for [CuBr] = 1.0 mol%) and to T_{max} values between 149 and 173 °C (for [CuBr] = 0.2 and 0.5 mol%, respectively).

With the catalyst concentration kept constant ([CuBr] = 0.2 mol%), V_f values were found almost the same (ca. 0.26 cm/min), with T_{max} varying between 145 and 153 °C by a variation of [CBr_4] between 0.2 and 0.5 mol%.

The study carried out confirmed indeed that FP does allow faster synthesis with respect to

conventional methods (just a few minutes, depending on V_f and reactor length, instead of hours). Moreover, by comparing DSC thermograms (not shown) of frontally and conventionally-obtained materials it has been found that the former are characterized by higher (full) conversion degree, the latter always showing an exothermal peak due to residual polymerization (DSC, first scan).[30]

Finally, with respect to the samples obtained by frontal classical radical polymerization, those synthesized using frontal ATRP displayed better thermal resistance, as well as absence of bubbles. In fact, the former samples show a degradation temperature onset at *ca.* 235 °C, against $T_{onset} = 280$ °C of samples obtained by frontal ATRP.

We retain that our approach permits the extension of FP towards an even wider number of practical applications. All details on this work have been published in ref. 30.

Experimental Part

In a typical FP run, a glass test tube is loaded with suitable quantities of the reaction components as listed above. FP is triggered by heating the upper end of the tube with a hot soldering iron tip. A thermocouple probe linked to a digital temperature reader is used for recording the temperature profile (sampling rate: 1 Hz; accuracy: 0.1 °C). Front velocity is monitored with an accuracy of 0.05 cm/min.

Conclusions

In this article we have briefly illustrated some of the synthetic potentials of FP by presenting several recent developments investigated by our research group.

On the basis of the whole set of evidences presented above it can be concluded that FP is turning out to be a technique of potential great use for the production of a growing number of polymers. The materials produced are characterized by properties that are on a par with, and often better than, those prepared by conventional synthetic techniques. Furthermore, the reaction times are much shorter than those of the classical techniques (a few minutes instead of hours).

However, it is necessary to recognize that the results obtained so far refer to laboratory syntheses carried out on a few grams of reactants. At present, there are no studies yet that have focused on possible effects of scale up as far as typical T_{max} and V_f values of the

various systems in question are concerned. Obviously, studies of this kind are absolutely necessary before the technique could be extensively used in any practical application.

Acknowledgments

[1]   N. M. Chechilo, N. S. Enikolopyan, *Dokl. Phys.Chem.* **1975**, *221*, 392.
[2]   N. M. Chechilo, N. S. Enikolopyan, *Dokl. Phys.Chem.* **1976**, *230*, 840.
[3]   J. A. Pojman, *J. Am. Chem. Soc.* **1991**, *113*, 6284.
[4]   A. M. Khan, J. A. Pojman, *Trends Polym. Sci.* **1996**, *4*, 253.
[5]   D. I. Fortenberry, J. A. Pojman, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1129.
[6]   Y. Chekanov, D. Arrington, G. Brust, J. A. Pojman, *J. Appl. Polym. Sci.* **1997**, *66*, 1209.
[7]   C. Kim, H. Teng, C. L. III Tucker, S. R. White, *J. Comp. Mater.* **1995**, *29*(9), 1222.
[8]   J. A. Pojman, W. Elcan, A. M. Khan, L. Mathias, *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 227.
[9]   J. A. Pojman, V. M. Ilyashenko, A. K. Khan, *J. Chem. Soc., Faraday Trans.* **1996**, *92*(16), 2825.
[10]   B. McCaughey, J. A. Pojman, C. Simmons, V. A. Volpert, *CHAOS* **1998**, *8*(2), 520.
[11]   G. Bowden, M. Garbev, V. M. Ilyashenko, J. A. Pojman, S. E. Solovyov, A. Taik, V. A. Volpert, *J. Phys. Chem. B* **1997**, *101*(4), 678.
[12]   V. M. Ilyashenko, J. A. Pojman, *CHAOS* **1998**, *8*(1), 285.
[13]   J. A. Pojman, R. Craven, A. Khan, W. West, *J. Phys. Chem.* **1992**, *96*, 7466.
[14]   I. P. Nagy, J. A. Pojman, *J. Phys. Chem.* **1996**, *100*, 3299.
[15]   J. Masere, F.T. Stewart , J. A. Pojman, *CHAOS* **1999**, *9*(2), 315.
[16]   I. R. Epstein, J. A. Pojman, *CHAOS* **1999**, *9*(2), 255.
[17]   S. E. Solovyov, V. M. Ilyashenko, J. A. Pojman, *CHAOS* **1997**, *7*(2), 331.
[18]   P. M. Goldfeder, V. A. Volpert, V. M. Ilyashenko, A. M. Khan, J. A. Pojman, S. E. Solovyov, *J. Phys. Chem. B* **1997**, 101, 3474.
[19]   S. Fiori, A. Mariani, L. Ricco, S. Russo, *Macromolecules* **2003**, *36*, 2674.
[20]   A. Mariani, S. Bidali, S. Fiori, G. Malucelli, E. Sanna, *e-Polymers* **2003**, *044*, 1.
[21]   S. Fiori, G. Malucelli, A. Mariani, L. Ricco, S. Russo, E. Casazza, *e-Polymers* **2002**, *057*, 1.
[22]   A. Mariani, S. Bidali, M. Sangermano, G. Malucelli, R. Bongiovanni, A. Priola, *J. Polym. Sci. Part A: Polym. Chem.* **2004**, in press.
[23]   A. Mariani, S. Fiori, Y. Chekanov, J. A. Pojman, *Macromolecules* **2001**, *34*, 6539.
[24]   S. Fiori, A. Mariani, L. Ricco, S. Russo, *e-Polymers* **2002**, *029*, 1.
[25]   L. G. Dammann, G. M. Carlson, U.S. Patent 4,788,083, **1988**.
[26]   A. Fradet, P. Arlaud, in *Comprehensive Polymer Science* (Eastmond, G.C., Ledwith, A.; Russo, S.; Sigwalt, P. *eds.*), Vol. 5, pp. 331-344, Pergamon Press, Oxford, **1989**.
[27]   S. B. Smith, U.S. Patent 6,277,939, **2001**.
[28]   S. Fiori, A. Mariani, S. Bidali, G. Malucelli, *e-Polymers* **2004**, *001*, 1.
[29]   K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921.
[30]   S. Bidali, S. Fiori, A. Mariani, G. Malucelli, *e-Polymers* **2003**, *60*, 1.