# Synthesis and characterization of a polyester/styrene resin obtained by frontal polymerization

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*Abstract:* The frontal polymerization technique has been successfully applied, for the first time, to obtain an unsaturated polyester/styrene resin. The effect of the ratio of the two aforementioned components, as well as of the type and amount of free-radical initiator on both front velocity and maximum temperature reached by the front, has been thoroughly studied. The resulting products have been characterized in terms of their thermal and dynamic-mechanical behaviour. A comparison of such products with the corresponding materials obtained by the classical batch polymerization technique has evidenced that frontal polymerization allows to reach a higher degree of crosslinking with respect to batch copolymerization and hence a better thermal and mechanical behaviour.

## Introduction

Unsaturated polyester resins (UPER) are among the most widely used thermosets in polymer composites [1]. They are generally obtained by copolymerization of an unsaturated polyester, PE (generally synthesized by the reaction between a derivative of a dicarboxylic acid and a glycol), and an unsaturated monomer (mostly styrene). This latter serves as a solvent and allows the crosslinking of PE to yield a thermoset product.

The crosslinking reaction is highly exothermic, thus making the curing a self-accelerated process [2]. This feature suggested us to explore the possibility of preparing such materials by frontal polymerization (FP).

Indeed, FP is a way of converting a monomer into a polymer by the effect of exothermicity of the polymerization reaction itself. If heat losses are not excessive, a sufficient amount of energy is provided to induce the polymerization of monomer layers close to the hot reaction zone. As a result, a self-sustaining hot front, able to propagate, occurs.

After the first findings of Chechilo et al. [3], who polymerized methyl methacrylate under high pressure, an extensive study was performed by Pojman et al. on acrylic monomers [4-6] and epoxy resins [7]. Lately, Mariani et al. reported on the frontal ring opening metathesis polymerization of dicyclopentadiene (DCPD) [8] and successfully used FP for the obtainment of polyurethanes [9,10] and poly(DCPD)/polyacrylate interpenetrating polymer networks [11].

A number of practical applications of FP have been proposed: White et al. reported on the curing of thick composite materials [12], Pojman et al. prepared a thermo-chromic composite [13], Morbidelli et al. found that unusually homogeneous polymer blends [14] and copolymers [15] with narrow microstructure distribution can be successfully obtained by this technique, and Washington et al. synthesized temperature-sensitive hydrogels [16]. Finally, Mariani et al. prepared polymer-dispersed liquid crystals films having an improved homogeneity [17] and applied FP to the consolidation of porous materials [18].

In this paper, we will present our study on the synthesis and characterization of an UPER and compare its thermal and dynamic-mechanical properties with those of the corresponding material prepared by the classical batch technique.


## Experimental part

### Materials

Maleic anhydride (MA), 1,2-propane diol (PD), styrene, Aliquat$^{®}$ 336 and ammonium peroxodisulfate have been purchased from Aldrich, 2,2'-azoisobutyronitrile (AIBN) and benzoyl peroxide (BPO) from Fluka. All the above materials have been used as received. Aliquat$^{®}$ persulfate (APS) was prepared as described in ref. [19].


### Synthesis of the unsaturated polyester

In a two-neck round bottom flask, 98 g (1.0 mol) of MA and 76 g (1.05 mol) of PD were introduced. The mixture was mechanically stirred for 1 h at 70°C and for 16 h at 120°C at room pressure, and finally for 7 h at 140°C in vacuum (membrane pump). The resultant viscous liquid polyester (Fig. 1), with $[\eta]$ = 0.04 dl/g in $N$-methyl pyrrolidone at 25°C, was used without further purification.
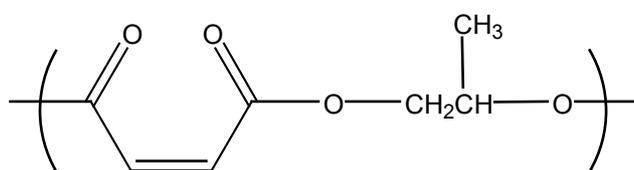


Fig. 1. Chemical structure of the unsaturated polyester (PE) used in the present work


### Copolymerizations

#### Frontal polymerization

In a typical run, a non-adiabatic glass test tube (inner diameter 16 mm) was loaded with the appropriate amounts of PE, styrene 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 variations (instrument accuracy $\pm$ 0.3°C). The junction was immersed about 4 cm from the free surface of the liquid. The front position ($\pm$ 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. Reproducibility of temperature data was within $\pm$ 3°C, and of the front position within $\pm$ 0.5 mm.

## Batch polymerization

In the same reactors and by using the same amounts of materials as given above, reactions were carried out for 1 h at 60°C.

### Copolymer characterization

Differential scanning calorimetry was performed with a Mettler DSC 30 instrument in the range from 0 to 200°C, with a heating rate of 10°C/min. For each sample two thermal scans were collected in the aforementioned temperature range.

Dynamic-mechanical thermal analyses (DMTA) were performed on a MKIII Rheometric Scientific instrument at 1 Hz frequency in bending configuration (single cantilever mode). The size of the specimens was c. 10 x 5 x 4 mm. The storage modulus $E'$, the loss modulus $E''$ and the loss factor tan $\delta$ were measured from -30°C to the temperature at which the rubbery state was attained (heating rate: 5°C/min). The glass transition temperature ($T_g$) was assumed as the maximum of the loss factor curve.

The gel content was determined by measuring the weight decrease after extraction with $CHCl_3$ for 24 h.

## Results and discussion

In a first set of experiments, the range of PE and styrene relative compositions has been determined in which their homogeneous mixtures undergo FP. The results reported in Tab. 1 underline that FP takes place if the amount of styrene ($w_s$) is within 20 and 40 wt.-% (referred to the total amount of PE + styrene). Indeed, for a styrene content lower than 20 wt.-% no FP has been observed even when larger amounts of BPO (up to 10 mol-%, referred to the amount of styrene) have been used, probably because of the excessive heat dispersion, which does not allow the hot front to self-sustain. Conversely, for $w_s$ > 40 wt.-% a phase separation occurred. In addition, neat styrene does not sustain an FP front.

The dependence of front velocity, $V_f$, and the maximum temperature reached by the front ($T_{max}$, as indicated in Fig. 2) on the amount of styrene is also reported in Tab. 1. It is noteworthy that the content of the latter monomer has a considerable effect on $T_{max}$, that ranges from 130°C (for $w_s$ = 20%) to 202°C (for $w_s$ = 40%). At variance, the effect on front velocity is less pronounced, viz., $V_f$ = 0.0083 cm/s for $w_s$ = 20 - 30%, and 0.0050 cm/s when $w_s$ = 40%.

In a second set of experiments, the effect of type and amount of radical initiator has been explored. AIBN, BPO and APS have been chosen as typical initiators belonging to three different chemical classes. All these runs have been performed by keeping the weight fraction of styrene constant at $w_s$ = 30%, a choice arising from the consideration that this is the formulation most frequently used in practical applications [1].

Tab. 1. Effect of styrene content on $V_f$ and $T_{max}$ (conc. of BPO, $c_{BPO}$ = 2 mol-%)

| Sample | $w_S$ in wt.-% | Polymerization mode | $V_f$ in cm/s | $T_{max}$ in °C |
|--------|----------------|---------------------|---------------|-----------------|
| FP1 | 20 | FP | 0.0083 | 130 |
| FP2 | 30 | FP | 0.0083 | 172 |
| FP3 | 40 | FP | 0.0050 | 202 |
| FP9-11 | < 20 | none | - | - |
| FP13-15 | > 40 | phase separation | - | - |
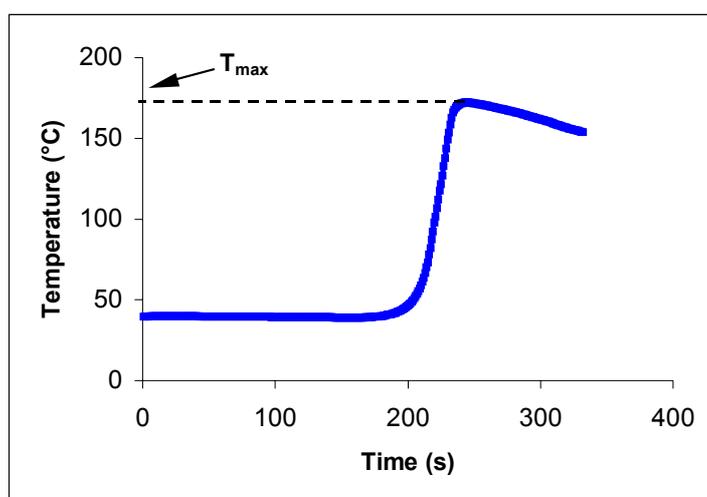


Fig. 2. Temperature profile of a typical FP sample obtained in the present work (FP2, see Tab. 1)

The position of the propagating front as a function of time for three typical samples, obtained using the above initiators at the concentration $c_{In}$ = 3 mol-%, referred to the amount of styrene, is given in Fig. 3. All three series of data are well fitted by straight lines, thus indicating that $V_f$'s were constant throughout each run. This finding and the corresponding temperature profiles (an example which has been already reported in Fig. 2) represent a couple of experimental evidences supporting that a *pure* FP occurred. With the term 'pure' we refer to FP as the unique polymerization mode occurring at a given time. In particular, no spontaneous polymerization took place.

By the analysis of Fig. 3 it can be seen that the type of initiator plays an important role on the reaction parameters (see later). Indeed, the different slopes of the straight lines show that the corresponding fronts travelled at different velocities. Namely, at the chosen initiator concentration ($c_{In}$ = 3 mol-%) the samples polymerized by AIBN (sample FP4) and APS (FP5) were characterized by similar $V_f$'s (= 0.0083 and 0.010 cm/s, respectively), while the presence of BPO resulted in a much higher velocity of propagation (= 0.015 cm/s, FP6). The dependence of this latter on the type and amount of initiator is better evidenced in Fig. 4.

A more or less regular $V_f$ rise, due to the increasing amount of initiator, characterizes all three systems. Namely, in the considered concentration range (1 - 10 mol-%) AIBN seems to affect $V_f$ less than the other two initiators, with $V_f$ ranging between 0.0050 and 0.012 cm/s.
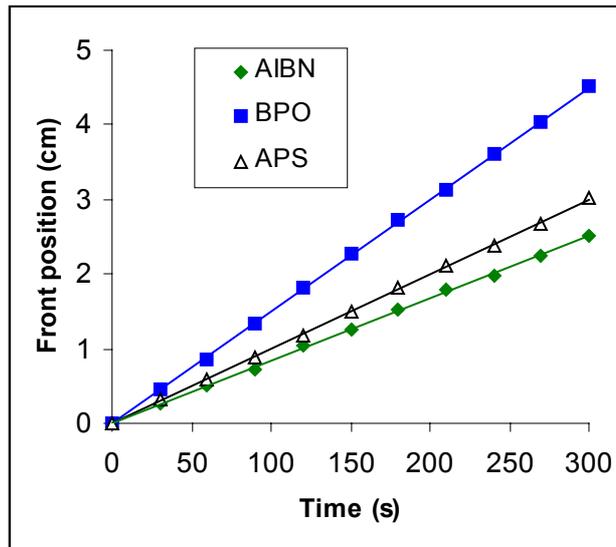
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Fig. 3. Front position as a function of time for three typical samples obtained in this work ($w_s$ = 30 wt.-%, $c_{In}$ = 3 mol-%)
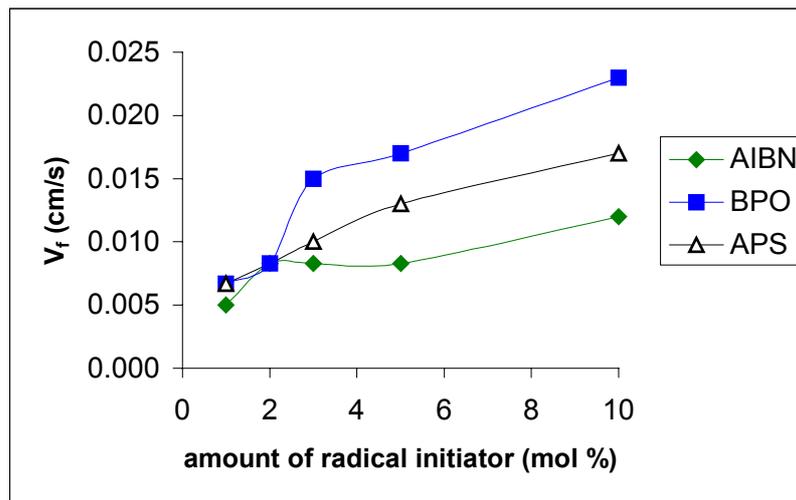


Fig. 4. Dependence of $V_f$ on the type and amount of initiator ($w_s$ = 30 wt.-%)

Conversely, the effect of BPO is quite remarkable, especially when its concentration is increased from 2 to 3 mol-%. In fact, the corresponding front velocites sharply increased from 0.0083 to 0.015 cm/s. Furthermore, $V_f$ as high as 0.023 cm/s has been reached for a BPO content of 10 mol-%. An intermediate behaviour is shown by APS, in the presence of which the front velocity increased from 0.0067 cm/min for APS = 1 mol-% to 0.012 cm/s for 10 mol-% of APS.

Fig. 5 shows the effect of the content of the above radical initiators on $T_{max}$. As can be seen for all systems, the higher the initiator content the higher $T_{max}$, but some differences among the three formulations are evident. In particular, AIBN and BPO influenced $T_{max}$ more than APS. In fact, when their content was equal to 1 mol-% the corresponding $T_{max}$ were relatively low (86 and 95°C for BPO and AIBN, respectively), but for $c_{In}$ = 10 mol-%, $T_{max}$ as high as 200 (AIBN) and 222°C (BPO) have been reached. The effect of BPO is particularly strong when doubling its amount from 1 to 2 mol-%, which results in a $T_{max}$ jump from 86 to 172°C.
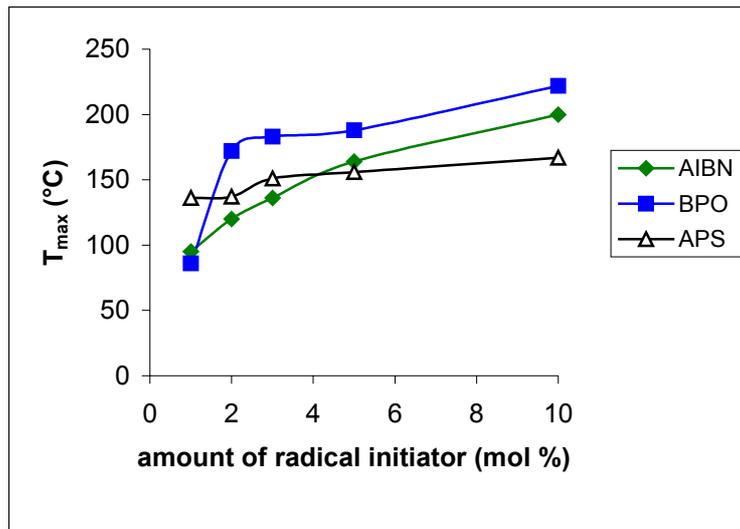
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Fig. 5. Dependence of $T_{max}$ on the type and amount of initiator ($w_s$ = 30 wt.-%)

The dependence of $T_{max}$ on APS content is much less pronounced; namely, in the considered range (1 - 10 mol-%) $T_{max}$ varied only from 136 to 167°C. However, in the case of APS, 10 mol-% corresponds to 24 wt.-% (referred to the total sample weight). Because of this large amount, the above initiator behaves also as an effective diluent of the reaction mixture, thus dispersing heat and not allowing for sharp temperature increments.

## *Characterization of the copolymers*

In order to compare the copolymers obtained through FP with those prepared by means of traditional batch polymerization, we have investigated some of their thermal and dynamic-mechanical properties. Initially, we made some DSC measurements in order to check whether the copolymerization process was complete or not; as an example, two DSC thermograms related to an FP and a batch copolymer are reported in Fig. 6 (traces A and B, respectively).
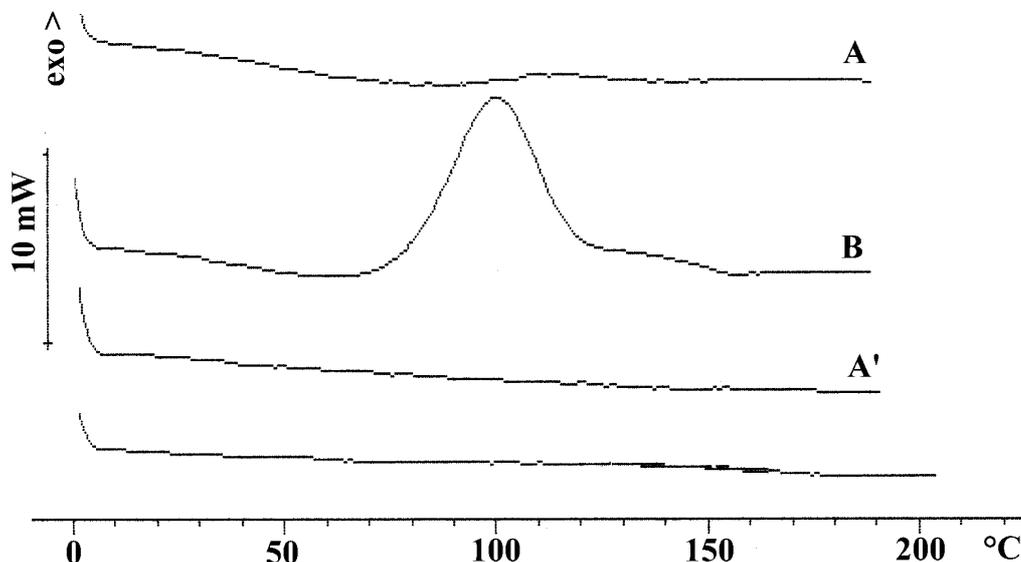


Fig. 6. DSC thermograms related to FP5 (traces A and A') and B1 (traces B and B')

6

First of all, referring to the FP copolymer (FP5), only a very weak exothermal signal related to the occurrence of a residual thermal polymerization is evident (trace A). The signal completely disappears when a second thermal scan is performed on the same sample (trace A').

To the contrary, as far as the batch copolymer B1 is concerned, its thermogram (trace B) shows a big exothermal peak whose maximum is located at about 100°C and is attributed to the large amount of residual polymerization heat. Also this peak disappears when a second thermal scan is carried out on the same sample, as reported in the same figure (trace B'). Therefore, a different thermal behaviour for the two copolymers has to be pointed out: unlike the batch polymerization, FP allows to synthesize in a very fast way copolymers having a higher degree of conversion and hence a higher thermal stability with respect to those obtained by batch polymerization.

For all systems investigated it was not possible to determine $T_g$ values by DSC, because of the small variation of the specific heat in the temperature range investigated, even by increasing the heating scan rate [20]. To the contrary, DMTA represents a very sensitive technique in order to evaluate their glass transition temperatures [21]. The $T_g$ values of the two copolymers, referred to two consecutive DMTA scans performed on the same sample, are collected in Tab. 2.

Tab. 2. $T_g$ values for the two copolymers determined through DMTA measurements

|  | $T_g$ in °C | |
| --- | --- | --- |
|  | 1$^{st}$ scan | 2$^{nd}$ scan |
| FP copolymer (FP5) | 136 | 153 |
| Batch copolymer (B1) | 92 | 106 |

As an example, a typical DMTA trace related to the FP5 copolymer is reported in Fig. 7: the presence of a broad peak in the tan $\delta$ curve is evident, together with a small shoulder located at lower temperatures: the maximum of tan $\delta$ can be assumed as the $T_g$ of the sample; the shoulder, which does not disappear when a second scan on the same sample is performed (Fig. 8), can be attributed to small motions of pendant groups ($\beta$ transition) [22]. The DMTA traces related to a batch copolymer (Fig. 9, 1$^{st}$ scan) show a similar behaviour with respect to the FP curve, but at much lower temperatures the presence of a broad peak and of a small shoulder in the tan $\delta$ curve is evident. Moreover, the storage modulus of the batch copolymer is characterized by lower values with respect to the FP copolymer.

From the data of Tab. 2 it can be noted that FP copolymers exhibit higher $T_g$ values with respect to those obtained through batch copolymerisation, i.e., the frontal polymerization allows to reach a higher degree of crosslinking with respect to batch copolymerization. Moreover, if the thermal scan is repeated on the same sample already subjected to DMTA evaluation, a shift of the $T_g$ value towards higher temperatures is observed. This behaviour can be explained by an increasing degree of crosslinking due to residual thermal polymerization that takes place during the first heating of the sample.

Finally, the measurement of the gel content evidenced the following values:

100% for the FP copolymer, and 83% for the batch copolymer.

These data confirm that the degree of crosslinking reached through the FP reaction is larger than that achieved by means of batch copolymerization.
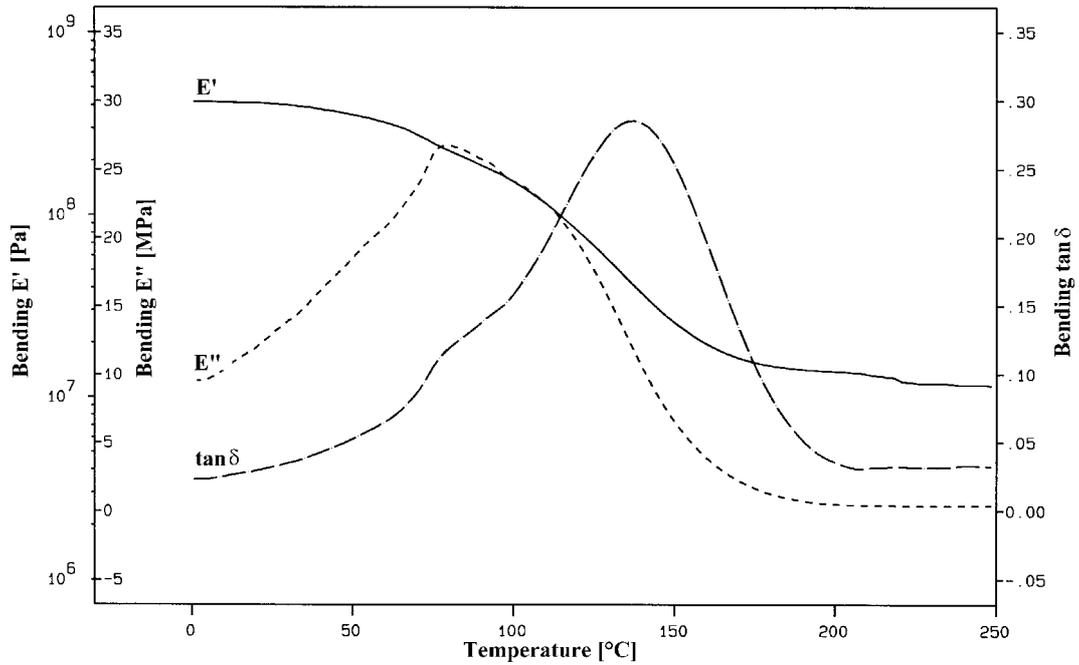


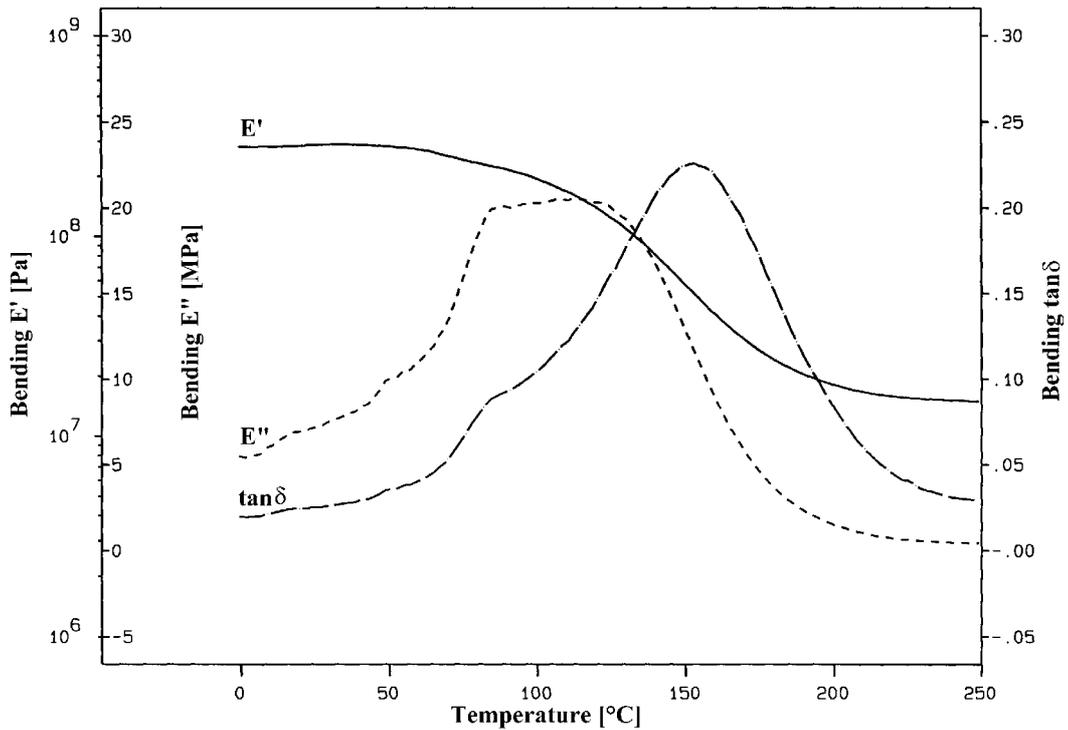Fig. 7. DMTA spectrum related to a FP copolymer, 1st scan



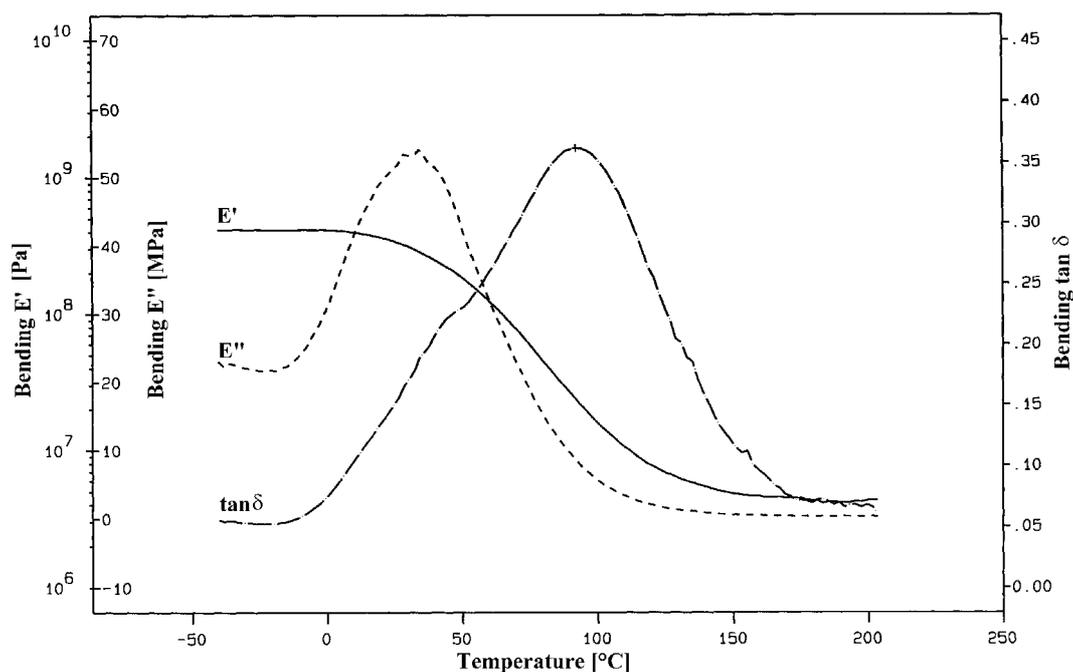Fig. 8. DMTA spectrum related to a FP copolymer, 2nd scan

Fig. 9. DMTA spectrum related to a batch copolymer, 1st scan

## Conclusions

A polyester/styrene resin has been successfully prepared by FP for the first time. The samples have better thermal and mechanical properties than those obtained by the classical batch technique.

Furthermore, FP samples can be obtained in very short times and in quantitative yields. In addition, no special apparatuses are needed.

These findings point out that FP is a convenient alternative way for preparing such materials also in practical applications in which these resins are widely used. It is also noteworthy that under our conditions styrene has been found for the first time to undergo frontal polymerization.

Further studies on different monomers are in progress and will be reported in a subsequent paper [23].

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