Polymer Blends by Self-Propagating Frontal Polymerization

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ABSTRACT: The use of self-propagating frontal polymerization to produce polymer blends has been investigated. A homogeneous solution of monomer, polymer (of a second monomer), and initiator is initially heated at a specific location to start a polymerization front that propagates along the system. The obtained polymerization reaction is very fast compared with diffusion, so that the two types of macromolecules remain homogeneously distributed, as in the original monomer/polymer solution. In the case of two incompatible polymers, the system has no time to reach the equilibrium condition where phase separation occurs and a polymer blend is obtained in the form of a metastable solution. Applications to two incompatible pairs (methyl methacrylatestyrene and methyl methacrylate-methacrylic acid) are discussed. Moreover, it has been found that the presence of inert polymer in the initial mixture improves the process performance, leading to more stable propagation fronts, lower front temperatures, and higher monomer conversions. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2695–2702, 1998

Key words: frontal polymerization; polymer blend; polymer compatibility; propagating fronts

INTRODUCTION

Polymer blends are physical mixtures of structurally different polymers that interact by secondary forces, without covalent bonding. The increase of interest in these materials is due to the understanding that new molecules are not always required for the preparation of materials with new macroscopic properties, and that blending can usually be implemented more rapidly and economically than the development of a new chemistry. There is indeed a big incentive toward a better understanding of the fundamentals of the process for preparing polymer blends, as well as toward the improvement of blending technology. The possibility to produce materials with special properties is dependent on the availability of preparation techniques able to control the phase structure of the final polymer blends.^{1,2}

The most common techniques adopted for preparing polymer blends are melting, mixing, casting from common solvents, freeze-drying, and mixing via reaction.¹⁻³ Let us focus on the latter method. The idea is simply first to prepare a homogeneous monomer/polymer solution and then to run a bulk polymerization. The advantage of this method is that it is much easier to obtain miscibility in a monomer/polymer system than in a polymer/polymer system, due to the much larger entropy of mixing involved in the first case. Once a homogeneous solution of the monomer/ polymer pair is obtained, the polymerization reaction is started. If the mobility of the macromolecules is sufficiently low and the polymerization reaction is sufficiently fast, then phase separation does not occur and the macromolecules of the two different polymers remain well mixed. In other

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Figure 1 Schematic diagram of propagating FP.

words, the system is not allowed to reach its thermodynamic equilibrium state, and a metastable homogeneous phase is obtained. This result is actually not easily obtained using bulk polymerization, mainly due to the very large heat of reaction involved. The alternative of a close temperature control would often lead to polymerization rates too slow to freeze the metastable equilibrium state. More promising is to adopt this same concept, but using instead a relatively new polymerization process [i.e., the self-propagating frontal polymerization (FP)].

FP was first introduced by Chechilo and Enikolopvan in 1972.4 In particular, they studied traveling fronts in methyl methacrylate (MMA) polymerization using reactors at high pressure.^{5–7} More recently, Pojman and colleagues investigated the movement of the polymerization front in a variety of systems, including different monomers at ambient pressure, using both liquid⁸⁻¹² and solid¹³ monomers, and solution systems¹⁴ with high-boiling point solvents. The general mechanism of formation and propagation of the polymerization front is based on the interaction between the production of heat by chemical reaction and its dispersion by thermal conduction. In general, the system is constituted by a tube containing a mixture of monomer and a thermal-free radical initiator. When the temperature at one end of the tube is increased above the initiator decomposition temperature, the polymerization reaction starts, and conduction of the heat generated causes ignition of the neighbouring unreacted material. Under suitable conditions, this leads to a reaction front, accompanied by a temperature wave, which travels along the tube with constant velocity, as schematically depicted in Figure 1.

Using a concept similar to the one described for polymer blending, FP has also been used to produce composite materials, where an inorganic powder is dispersed in the polymer matrix to provide special conductivity¹⁶ or thermochromic^{11,17} properties. In the latter case, it has been shown that this material can be prepared better in this way than with traditional homogeneous methods, because the rapid polymerization in the traveling front prevents phase separation.

FP has also been investigated to produce simultaneous interpenetrating polymer networks^{11,15}: two independent and noninterfering monomers can be contemporary crosslinked within a single traveling front, due to the high temperature reached in the front, which makes the rates of the two reactions nearly equal.

The aim of this work is to show that, by using FP starting from a monomer/polymer solution, it is possible to "freeze-in" the metastable phase where the polymer macromolecules are homogeneously dispersed. The advantage over the bulk polymerization process discussed herein is that, because the front is fast, the local transformation of monomer into polymer is sufficiently rapid to freeze the phase structure also in the case of macromolecules with relatively high mobility. This technique, which is particularly simple and not energetically intensive, is then expected to provide the possibility of producing blends that are difficult to be synthesized in other ways. Of course, there are several drawbacks that need to be considered, particularly in connection with the high temperature values reached at the polymerization front. Herein, we limit ourselves to describe this new technique and to show that it can be used to produce polymer blends.

EXPERIMENTAL

Polystyrene (PSTY)-poly(MMA) [PMMA] blends were prepared from a mixture of MMA (Fluka, Ronkonkoma, NY) and PSTY (Fluka). The solution was placed in a 2.2 cm (i.d.) \times 25 cm test tube and left there for the time required (\sim 12 h) to obtain a uniform mixture. Benzoyl peroxide (97%; Aldrich, Milwaukee, WI) was then added to the solution that was mechanically mixed to achieve a uniform distribution of the initiator. The typical initiator compositions investigated range from 0.5 to 5.0 w/w %. FP of MMA was then started by applying a heat source at the top of the test tube

that was held in a vertical position to avoid convective movements that disturb front stability. Movement of the front through the tube was very clear due to the transformation of the transparent initial solution into the opaque polymer blend. This also made it possible to measure the front velocity and verify that it was constant, except in the vicinity of the tube ends. The same procedure was applied to produce poly(methacrylic acid) [MAA]-PMMA blends. In particular, a homogeneous solution of MAA, PMMA, and benzoyl peroxide was polymerized by FP. Note that as a term of comparison, a PMMA/PSTY blend was also produced by the traditional mixing-reaction method [i.e., the reacting mixture prepared as previously described was polymerized in bulk at constant temperature (T = 323 K for 18 h)].

The temperature profile was measured by using a thermocouple embedded in the reacting mixture. The recorded temperature *versus* time data were then converted into temperature *versus* position values by using the observed constant velocity value. Monomer conversion was determined by gravimetric analysis.

The blend characterization^{1,18} was performed using scanning electron microscopy (SEM) and differential scanning calorimetry (DSC).

The SEM used (Cambridge, Stereoscan 360) was equipped with Energy Dispersion Spectrometry, which enables it to qualitatively analyze the oxygen and carbon content of the sample to identify the presence of PSTY in a matrix of PMMA. The spatial resolution of the apparatus is 3–4 nm; but, in the case of light elements, such as carbon and oxygen, the spatial resolution is smaller (50 nm). The surfaces to be analyzed have been prepared by first sectioning the samples with a lowspeed saw (Buehler, Isomet) at room temperature without any solvent and then fracturing along these sections. Moreover, the fracture surfaces have been coated with gold ions in a sputter coater (Edwards, S150B) to make the polymeric material conductive.

DSC was performed by heating at 20K min⁻¹ from 293K to 523K. Before this, the polymer was flushed with nitrogen at 423K for ~ 5 h to remove the unreacted monomer.

RESULTS AND DISCUSSION

FP in the Presence of Inert Polymer

In the classical FP, the initial mixture is constituted only of monomer and initiator. As described in the Introduction, several works appeared in the literature dealing with different characteristics of the traveling polymerization front and particularly with the dependence of its constant velocity on the various involved operating conditions.^{4,10,19} More recently, a mathematical model of this process has also been developed.²⁰ The main innovation of this model is the inclusion of the depropagation reaction, which becomes important due to the high temperature values reached in the reaction front. For example, in the case of MMA, the front temperature reaches the ceiling temperature where the polymerization reaction is at equilibrium conditions. Thus, in this case, complete conversion cannot be achieved, and the amount of unreacted monomer can be readily computed from the amount of heat of reaction needed to increase the system temperature to the ceiling value, according to the following adiabatic heat balance:

$$T_c = T_0 + \frac{\Delta H(M_0 - \bar{M})}{\rho C_p}$$

where T_C and T_0 are the ceiling and initial temperatures respectively, ΔH is the heat of reaction, M_0 and \bar{M} are the initial and unreacted monomer concentrations, and ρC_P is the heat capacity per unit volume. In the case where significant heat losses are present, the front temperature may decrease below the ceiling temperature, thus leading to larger monomer conversion values. On the other hand, for systems where the adiabatic temperature is lower than the ceiling temperature, monomer conversion is generally complete.²⁰

As previously discussed, in this work we consider a different initial reacting mixture, because the monomer is diluted in the polymer that does not participate in the reaction, but increases the ratio (heat capacity/heat produced) in the system, thus leading to lower temperature values of the reaction front. When these are lower than the ceiling temperature, the effect of the depropagation reaction is expected to vanish and the monomer conversion complete. This is the case of both the systems considered in this work (i.e., PMMA/ PSTY), where MMA is polymerized in the presence of PSTY and PMAA/PMMA where MAA is polymerized in the presence of PMMA. For example, in a PSTY/PMMA (30/70) blend, we measured a frontal temperature of 395K, whereas the MMA ceiling and adiabatic temperatures are 494K and 529K, respectively. It is worth noting that lower front temperatures lead to lower values of the front propagating velocity. In particular, for the PMMA/PMAA system, the observed propagation velocity (~ 0.2 cm min⁻¹) is lower than that measured under similar conditions, but with the monomer MAA alone (~ 0.8 cm min⁻¹)^{8,10} (i.e., without diluting it with PMMA).

Thus, in conclusion, the presence of the inert polymer in the initial reacting system has the effect of decreasing both the temperature and the velocity of the polymerization propagating front. The first one has a beneficial effect on the process. because too high temperatures are expected to lead to exceedingly low molecular weights of the produced polymer or to hydrogen abstraction reactions along the polymer chains leading to branched chains. Although accurate information about the structure of macromolecules produced by FP is not yet available,^{10,21} this is certainly one of the open problems of these processes. On the other hand, a decrease in the front temperature is also beneficial for those systems where the adiabatic temperature is larger than the ceiling temperature. In this case, a reduction of the front temperature makes the depropagation reaction negligible, thus increasing the final monomer conversion. Finally, it should be noted that exceeding amount of inert polymer would lead to front temperatures that could not sustain its advancement. This provides an upper bound to the amount of polymer that can be introduced in the system.

Another positive aspect in the introduction of the inert polymer deals with the front stability. This has in fact the effect of increasing the viscosity of the system that stabilizes the front, thus making FP possible in cases where it would not be possible with the monomer alone, at ambient pressure. This is the case of MMA, which was produced earlier by FP only at high pressure.⁵⁻⁷ In this work, this was produced at ambient pressure by adding PMMA to the monomer to avoid sinking of the hot polymer just formed and evaporation of the monomer.

In Figure 2, the heat of polymer mixing as a function of composition for the two systems considered is shown.²² In the same figure, the horizontal line indicates the Schneier value that provides the limit above which polymers are immiscible. It is clear that both systems are thermodynamically incompatible. In the next two sections, we will see that the proposed technique is able to produce rather homogeneous blends in both cases, by substantially freezing the homogeneous solution structure present in the initial monomer/polymer system.



Figure 2 Heat of mixing as a function of weight percentage of the first component in PSTY-PMMA and PMMA-PMAA blends.

PMMA/PSTY

Two typical micrographs obtained with SEM, representing the microstructure of the polymer blend obtained with FP for two different polymer compositions are shown in Figure 3(a, b). It appears that the blend structure is constituted by a polymer matrix of PMMA, where PSTY spherical units of ~ 1 μ m diameter are dispersed. The uniform distribution of these domains is the first indication of the capability of the FP process to "freeze-in" the homogeneous structure of the initial monomer/polymer mixture. This can be confirmed by comparison with the phase structure of a PMMA/PSTY blend prepared with an extruder²³ shown in Figure 4. In this case, the homogeneity of the structure is obtained by a different mechanism, based on the shear stress and pressure obtained inside the extruder. It can be seen that the final morphology is quite similar in the two cases (note the scale difference in the two figures). It is worth noting that, in the blend produced by FP, the spherical units appear to be swollen, compared with those obtained with the extruder. This is because, in the case of FP, despite addition of the inert polymer, the front temperature slightly exceeds the boiling temperature of the monomer MMA, which undergoes evaporation. This is confirmed by the fact that, if the electron beam is left for a few seconds on the swollen spherical units, they release the included vapors, thus decreasing





< 5.00 μm >

Figure 3 Scanning electron micrograph of PSTY-PMMA blend synthesized by FP. (a) PSTY-PMMA blend containing 65% by weight of PMMA. (b) PSTY-PMMA blend containing 70% by weight of PMMA.

their dimension as illustrated in the right part of Figure 3(b). Herein, the spherical units are quite similar to those obtained through extrusion (Fig. 4). This problem could be avoided by operating the FP process under sufficient pressure.

The microstructure of the samples produced by FP is independent of radial position; in fact, due to the presence of the inert polymer in the reacting mixture, the reaction front temperature is lower than in the case where the monomer alone is polymerized, thus making the radial temperature gradients negligible. Moreover, to avoid heat losses, the test tubes have been insulated during the reaction.

As a term of comparison, let us now analyze the microstructure obtained with the traditional mixing via the bulk reaction process described in the Experimental section. In Figure 5(a, b) is shown two typical micrographs corresponding to two different

locations inside the polymer sample. It seems that this is characterized by two different blends: one corresponding to Figure 5(a), where a rather homogeneous distribution has been achieved similar to that obtained with FP [Fig. 3(a, b)]. In the other one, corresponding to Figure 5(b), significant phase separation has clearly occurred. Even if the magnification is the same as in Figure 5(a), no spherical segregated phase is present, and only the PMMA matrix can be seen. The simultaneous presence of these two different microstructures in the same sample can be explained, considering that, in a bulk polymerization, the reaction takes place slowly; thus, at the beginning, the viscosity of the reacting medium is low and the first produced polymer remains at high temperature for a time long enough for phase separation to occur [Fig. 5(b)]. On the other side, the product formed later is synthesized in a highly viscous medium, where the mobility of the macromolecules is largely reduced to lead to the well-dispersed microstructure shown in Figure 5(a).

As further confirmation that a metastable structure has been obtained through the FP process, the corresponding samples have been kept for ~ 4 h at 438K, which is above the glass transition temperature of both PMMA and PSTY. From the micrographs of two samples with different compositions reported in Figure 6(a, b), it seems that, during the thermal treatment phase, separation has occurred. The phase structure obtained in this case is characterized by wide do-



Figure 4 Scanning electron micrograph of PSTY-PMMA blend containing 70% by weight of PMMA obtained with an extruder.





🗲 5.00 μm 🏲

Figure 5 Scanning electron micrograph of PSTY-PMMA blend containing 70% by weight of PMMA; synthesized in bulk.

mains of the two polymers, which indeed resemble those shown in Figure 5(b). This is a straightforward confirmation that the FP process is able to lock a metastable structure of the polymer blend.

To confirm the composition of the matrix and the spherical units described herein, an elemental analysis has been performed. Because the aim is really only to distinguish between MMA and STY, a qualitative analysis that can indicate which phase contains oxygen and which does not is sufficient. This can be performed also on fracture surfaces that are not perfectly smooth, but slightly corrugated. Because the diameter of the electron beam used is 50-100 Å, the analysis could not be performed on the surface of the samples of Figure 3(a, b), which are characterized by an homogeneous distribution of too small spherical domains in the matrix. Therefore, we have first analyzed the sample produced *via* bulk polymerization, which has larger phases due to the occurred phase separation. It was found that the matrix, shown in Figure 5(b), is rich in oxygen (i.e., it is constituted largely by PMMA). As further confirmation, the elemental analysis has also been performed on the sample treated thermally [shown in Fig. 6(a)]. In this case, two sufficiently large phases are formed: one constituted by the continuous matrix and the other by the closed domains, which resulted from the aggregation of the spherical units due to phase separation. The results obtained are shown in Figure 7(a, b). The matrix, which is similar to that shown in Figure 5(b) corresponding to the material produced in the bulk process, is much richer in oxygen [Fig.





Figure 6 Scanning electron micrograph of PSTY-PMMA blend synthesized by FP and kept for 4 h at 438K. (a) PSTY-PMMA blend containing 70% by weight of PMMA (the right-hand side is a magnification of the region within the rectangle). (b) PSTY-PMMA blend containing 70% by weight of PMMA.



Figure 7 Traces of elemental analysis of the PSTY-PMMA blend containing 70% by weight of PMMA: synthesized by FP and thermically treated. (a) Matrix. (b) Closed domains. C = carbon, O = oxygen, Au = gold.

7(a)] than the closed domains [Fig. 7(b)], thus indicating that the first one is constituted of PMMA and the second of PSTY.

Note that the small amount of oxygen in the closed domains should be attributed to the depth of penetration of the electron beam. In fact, because this spreads below the surface for $\sim 1 \div 2$ μ m and it excites the electrons of the sample included in a volume of $\sim 2 \mu$ m,³ the analysis also reveals the underlying domains of PMMA.

PMMA/PMAA

For this system, due to the large difference in the glass transition temperatures of the two polymers (i.e., $T_{g \text{ PMMA}} = 378 \text{K}$ and $T_{g \text{ PMAA}} = 501 \text{K}$),²⁴ it was possible to use DSC to investigate the morphology of the obtained blends. In Figure 8(a) is shown the DSC diagram for a PMMA/PMAA blend prepared through FP as described in the Experimental section. The heat flow curve decreases without exhibiting any inflection point, which would indicate a glass transition. At higher

temperature ($\sim 170^{\circ}$ C), the polymer softening begins and at $\sim 250^{\circ}$ C fusion occurs. The sample is left melted for few minutes, cooled back at room temperature, and then DSC analysis is repeated. In the obtained trace [shown in Fig. 8(b)], two glass transitions, which did not occur in the original sample, are clearly apparent. These results indicate the presence in the second sample, and not in the first one, of two polymer phases. Thus, again, we can conclude that the FP process is able to lock the homogeneous morphology of the initial monomer/polymer mixture, whereas after fusion the thermodynamic phase separation conditions are achieved as a consequence of the increased mobility of the polymer chains. This is confirmed by the values of the two glass transition temperatures measured in Figure 8(b). The first one $(\sim 378 \text{K})$ is equal to that of PMMA, whereas the second one, although larger (~ 413 K), is lower than the one reported above for PMAA. This is so probably because the molecular weights produced in a FP, at least with the operating conditions adopted



Figure 8 DSC scans of PMMA-PMAA blend containing 80% by weight of PMAA prepared by FP. (a) Original sample. (b) Sample after fusion.

in this experiment, are rather $low.^{21}$ It is worth mentioning that by repeating the DSC analysis over and over again, after the first fusion of the polymer, the same trace as in Figure 8(b) is obtained.

CONCLUSIONS

A method for producing blends of incompatible polymers has been devised by polymerizing one monomer, in the presence of the preformed polymer of the other monomer, fast enough to prevent phase separation of the two polymers. This is based on the use of self-propagating FP that allows us to freeze the initial morphology of the system (i.e., the one corresponding to the monomer/polymer mixture). The procedure has been demonstrated in the case of two different monomer pairs by characterizing the obtained polymer blends by DSC and SEM. This is probably an easier and less energy intensive method to achieve this result than other classical techniques (e.g., extrusion).

Furthermore, the analysis of FP systems characterized by the presence of an inert compound (the polymer mixed in the monomer/initiator solution) has disclosed two important features that are both derived from the decrease of the frontal temperature. First, in the cases where conversion is limited by the attainment of ceiling temperature,²⁰ this leads to an increase in monomer conversion. Moreover, it becomes possible to polymerize systems that cannot sustain a propagating front at ambient pressure. For example, FP of PMMA is performed at high pressure⁴⁻⁷ to prevent evaporation of MMA, which also disturbs front stability. If an inert compound is present, lower temperature values are obtained and evaporation does not occur.

It is important to stress that, even though the results of this work are rather promising, further investigations are needed to assess the actual potential of this technique with respect to practical applications. In particular, it is important to investigate the molecular weight of the polymer synthesized by FP in the presence of an inert compound. There is some evidence^{10,21} that, in general, FP processes lead to low molecular weight polymers, due to the high temperature values involved. This problem should have been at least partly overcome by the technique described above, because front temperature is decreased by the presence of the inert, thus leading to larger molecular weights.

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