# Mechanisms and conditions that affect phase inversion processes. The case of high-impact polystyrene.

Phase inversion in HIPS process

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**Abstract**

The phase inversion during the bulk polymerization of the styrene-polybutadiene system (HIPS manufacturing process) is empirically and theoretically studied in this article. In the experimental work, a series of reactions were performed with benzoyl peroxide as initiator and at temperatures considered of industrial interest (80ºC and 90ºC), varying also the reactor stirring level. Phase inversion was determined by offline viscosity measurements and verified by scanning electron micrography in transmission mode (STEM). The rheological behavior of each reacting system was analyzed and an empirical correlation to predict its apparent viscosity

from fundamental reaction parameters was derived. This was achieved successfully for both before and after the phase inversion point.

Keywords: phase behavior, rheology, impact resistance, polystyrene

**Nomenclature**

| | |
|---|---|
| $\phi_v$ | Vitreous (PS-rich) phase volume fraction |
| $\phi_r$ | Rubber-rich phase volume fraction |
| $\phi_d$ | Dispersed phase volume fraction |
| $\phi_{oc,0}$ | Occluded vitreous phase volume fraction |
| $\overline{\phi_{oc,0}}$ | Average occluded vitreous phase volume fraction at inversion point |
| $\eta_v$ | Apparent viscosity of vitreous phase |
| $\eta_r$ | Apparent viscosity of rubber-rich phase |
| $\eta_{0v}$ | Zero-shear viscosity of vitreous phase |
| $\eta_{vc}$ | Apparent viscosity of St-PS-PB mixture after phase inversion |
| $\eta_{rc}$ | Apparent viscosity of St-PS-PB mixture before phase inversion |
| $\eta_c$ | Apparent viscosity of continuous phase |
| $\eta_d$ | Apparent viscosity of dispersed phase |
| $\zeta$ | Grafting efficiency |
| $\dot{\gamma}$ | Shear rate |
| $w_{PS,v}$ | PS weight fraction in vitreous phase |
| $w_{PB,r}$ | PB weight fraction in rubber-rich phase |
| $w_{PS-g}$ | Grafted PS weight fraction |
| $M_{w,PS}$ | Free PS weight-average molecular weight |
| x | PS conversion |
| $x_{PI}$ | PS conversion at phase inversion point |
| T | Temperature |

## 1. Introduction

High impact polystyrene (HIPS) is a heterogeneous thermoplastic that consists of a polystyrene (PS) matrix with dispersed polybutadiene (PB) particles which often contain occluded PS. Depending on the rubber particle size and the number of occlusions, two typical morphologies are usually identified: a 'salami morphology' (large rubber particle with several occlusions) or a 'core-shell morphology' (relatively small rubber particle with only one large occlusion)[1].

These structures provide the material with improved mechanical properties in comparison with general purpose PS.

The bulk HIPS polymerization process involves three main stages: a pre-polymerization of styrene (St), a finishing polymerization, and a devolatilization. The reacting system is homogeneous only up to 1-5% of monomer conversion[2,3] (although these values were determined using blends, not actually measured during the polymerization), after which PS and PB are no longer miscible, and two phases are separated: a continuous PB-rich phase, and a dispersed PS-St phase[4]. Some authors refer to this system as a *polymeric oil-in-oil emulsion*[5]. Experimental studies – using mixtures of St, PS and PB – have shown that St is almost evenly partitioned between both phases[1] and that each polymer separates almost completely from the other[2], despite the high viscosity of the macromolecular species. This incompatibility between the PS and PB chains, which is predicted in the Flory-Huggins theory, can be improved with the presence of poly(styrene-g-butadiene) copolymers as shown by the measurements of St-PS-PB mixtures prepared by White and Patel[6].

The mechanism and conditions that dictate the phase separation of this system have not been demonstrated yet. This reaction-induced phase separation (RIPS) may either follow a binodal or a spinodal decomposition[7] and, although some authors argue that it can only follow the spinodal line,[8–10] they report no actual measurements to support their views, which are often based on the curing reaction of epoxy resins. These reactions are performed without agitation and thus fail to provide the necessary energy input to favor nuclei formation (which is the accepted mechanism of binodal decomposition[7]), and so proceed following the spinodal. The pre-polymerization of HIPS is performed with intense agitation, which makes it essentially different from curing reactions. As stated by Ludwico and Rosen[4], standard agitators could easily supply the energy needed to cross the phase boundary.

As the polymerization continues to produce free PS and a graft copolymer (PS-g-PB), a critical point is reached where the PS content is such that the mixture undergoes a phase-inversion (PI) process. Thereafter, the PS-rich phase becomes the continuous phase, and the morphology is essentially developed, making the PI point a key moment in the polymerization reaction. The finishing stage is carried out with gentle agitation –to preserve particle size and morphology– and at a higher temperature.

The PI process is affected by many parameters, such as phase viscosity ratio, phase volume fractions, rubber *cis/trans* content, stirring speed, reaction temperature, grafting efficiency (*i.e*, the fraction of grafted St with respect to the total polymerized St), monomer conversion, PS and PB molar weights, etc., all of which have been described empirically by different authors[5,11–17]. For instance, the higher the viscosity of a given phase, the greater its tendency to remain as the dispersed phase[18]. This would imply that, for two St-PS-PB reacting mixtures with identical composition (i.e., same monomer conversion and same grafting efficiency), the one producing a PS with higher molecular weight would invert later, as its phase viscosity would be higher (note that an increase in the molecular weight of PS in the usual industrial range (120-300 kg/mol)[19] would not have any effect on the interfacial tension with PB[20]).

The role of copolymers on PI is not straightforward: on the one hand, an increase in copolymer concentration would stabilize the mixture by reducing the interfacial tension (as observed by Gaillard et al.[21]), thus producing a finer emulsion[22] and reducing its ability to invert. On the other hand, the compatibilizing effect would lower surface energies, reduce interface concavity, help to form a co-continuous mixture and thus *favor* phase inversion. These two opposing effects (increase in compatibility vs decrease in particle size) are not always considered, but have already been observed by Willemse et al.[23].

Regarding particle morphology, several authors have suggested global relationships between particle size and variables such as stirring speed[24,25], initiator concentration[12,26], rubber molecular weight (or rubber-phase viscosity)[25,27], grafting efficiency[12,28], and apparent viscosity[28]. Some efforts have been conducted to model the evolution of particle morphology during the polymerization[8,9], but are quite constrained to several theoretical simplifications. The influence of particle morphology in the final material properties is well-known[29,30] and this highlights the importance of understanding and predicting the PI point. It is of industrial interest to optimize current synthesis recipes, improve production performances, and reduce unnecessary costs while keeping high product standards: a full chemical engineering challenge.

The experimental detection of the PI period remains a challenging and unresolved problem. Direct observation by electron microscopy is not possible because the monomer present in the sample evaporates during its preparation; while adequate samples are impossible to produce with the present cryogenic microtome technology. Thus, only monomer-free (or "unswollen") particle morphologies have been observed by TEM[12,28,31]; and the preferred method for detecting the PI point is based on the apparent viscosity reduction[11]. After phase separation and before the PI point, the continuous rubber-rich phase is usually more viscous than the dispersed PS-rich phase (since normally the rubber molecular weight is higher than that of the free PS). During the inversion transition, while the vitreous (less viscous) phase is becoming the continuous one, the global apparent viscosity first drops, and then increases again after the inversion is completed. In emulsion theory, the viscosity of the mixture depends on several variables such as phase volume fractions, interfacial tension, and particle size, all of which are difficult to measure along the reaction. Published mathematical models (see Section 4) are incapable of accurately estimating the evolution of the apparent viscosity of the HIPS reacting mixture along the prepolymerization.

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Regarding the theoretical prediction of the inversion point, some mathematical models have been developed[32–35] but are almost exclusively for traditional oil/water, non-reacting systems. For polymer mixtures, some equations have been put forward in the works of Jordhamo et al.[14], Ho et al.[36], Chen and Su[37], Kitayama et al.[38], Everaert et al.[39], among others,[40–42] but most of them refer to polymer-polymer blends in molten state (usually during extrusion operations), which is not the case of the HIPS pre-polymerization system. In these models, the PI point is unequivocally determined by the phase viscosity ratio, which is − at least − an oversimplification of this multivariate phenomenon. Few models of the PI process *during* the HIPS polymerization are available. For example, that of Fisher and Hellmann[31] is a coupled kinetic-rheological model with simplified polymerization kinetics that assumes that PI occurs at equal phase volumes and is fitted with experimental data unusual for industrial conditions ($M_{w,PS}$ of 27 000 g/mol). The one developed by Vonka et al.[9] is thermodynamically-based (which neglects the fluid-dynamic effects) and lacks the ability to predict PI under different conditions (retuning of parameters is needed even with small changes in the reaction recipe).

This article aims to provide a new insight on the physics that govern the occurrence and duration of the inversion process during the HIPS pre-polymerization, by studying the effects of the main reaction variables on the evolutions of the apparent viscosity and the particle morphology. Several experiments were carried out involving different reactor conditions, such as temperature, initiator concentration, and stirring speed. The following variables were measured along the reaction: conversion, grafting efficiency, PS molecular weights, morphology, and apparent viscosity. Based on theoretical and empirical aspects regarding the rheology of emulsions, a new empirical model was developed for predicting the evolution of the apparent viscosity of the reacting mixture as a function of phase viscosities, before and after the PI point.

## 2. Experimental work

*Materials*

The styrene monomer was purchased from Plastiformas (Monterrey, México), polybutadiene UBEPOL was provided by Mitsubishi ($\overline{M}_w$ = 610 000 g mol$^{-1}$, $\overline{M}_n$ = 210 000 g mol$^{-1}$, high cis) and both of them were used as received. The chemical initiator, benzoyl peroxide (BPO) with a purity > 98% was purchased from Fluka and recrystallized from a methanol/chloroform mixture. Solvents N,N-dimethylformamide (DMF, anhydrous grade), methylethylketone (MEK, ACS reagent) and tetrahydrofuran (THF, HPLC grade) were purchased from Sigma-Aldrich and used as received.

A 3.8-liter stirred stainless-steel Parr reactor (Series N° 4550, model 4843) contained an external heating jacket, and an anchor-turbine stirrer was used in all the pre-polymerization experiments, while glass ampoules were preferred for the finishing stage.

*Synthesis of HIPS*

Eight polymerizations reactions of St in the presence of PB were carried out varying the pre-polymerization conditions (temperature, agitation rate and initiator concentration) as shown in **Table *1***. All pre-polymerization reactions were carried out at 6%-wt of PB and performed up to a 30% conversion, using BPO for chemical initiation. First, the PB was dissolved in styrene monomer at room temperature for 12 h. Then, the initiator was incorporated into the reactor. The reactor was sealed and pressurized to 100 psi, stirred at 30 rpm (using an anchor-turbine configuration) and heated from room temperature to 80 or 90 °C at 2°C/min. Once the desired temperature was reached, the reaction continued under isothermal conditions (no significant heat generation was observed). The finishing stage was carried out in glass ampoules which were placed into a stainless-steel reactor under 100 lb inert atmosphere, at 150°C and lasted at

least 12 hours to ensure full monomer conversion. All stages, including rubber dissolution; were performed under a nitrogen atmosphere to prevent photo-oxidation.

*Characterization*

Samples were taken along each reaction to determine monomer conversion, St grafting efficiency, molecular weight distributions, apparent viscosity and, in some cases, to analyze their morphology. A small amount of hydroquinone was added to every sample immediately after being taken to deactivate the propagating chains while they were introduced in a dry ice to lower the temperature.

Samples taken for calculating monomer conversions were dissolved in toluene and stirred during 12 h. Then, St was isolated from the polymeric sample by precipitation in methanol. Solids were filtered and vacuum-dried at 50°C until constant weight.

Free PS was isolated from the rest of the polymeric species by solvent extraction, using a MEK/DMF 50:50 (volume ratio) mixture. After 12 h agitation, the mixture was centrifuged at -20°C for 4 h at 10000 rpm. The insoluble precipitate obtained (namely PB and PB-g-PS) was vacuum-dried at 50°C until constant weight. The soluble free PS was precipitated in methanol, filtered and vacuum-dried at 50°C until constant weight. The grafted PS mass was obtained from the difference between the insoluble mass and initial PB mass and the St grafting efficiency was obtained from the ratio between the grafted and total bound St masses.

The molecular weight distributions and average molecular weights of each polymeric components were determined by size-exclusion chromatography (SEC) at room temperature using a Waters 1515 chromatograph fit with a set of μ-Styragel$^{TM}$ columns and a differential refractometer detector Waters 2487 employing THF as carrier solvent. A "universal" calibration was obtained from a set of PS standards.

Apparent viscosity was measured with a Brookfield LVTDV-II viscometer, using a LV#4 spindle at four different shear rates: 0.063, 0.126, 0.316 and 0.632 s$^{-1}$ at 25°C. Viscosity of PB-St solutions of varying concentrations were also measured with this device at the same shear rates, but using the LV#1 spindle, suited for lower viscosities.

Finally, the morphology of selected samples was examined by a scanning transmission electron microscopy (STEM) on a JEOL JSM-7401F at 30 kV. Samples were prepared by an ultramicrotomy technique and stained with osmium tetra-oxide (OsO$_4$) vapors.

## 3. Experimental results

**Figure 1** shows the effects of BPO concentration, reaction temperature, and stirring speed on: (a) the monomer conversion, (b) the weight-average molecular weight of the free PS (Mw$_{PS}$), and (c) the grafting efficiency (ζ). The evolution of all three variables resulted as expected from this type of polymerization[26,43] (ignoring the isolated outliers of subfigure (b)): regardless of stirring speed, the reactions with the lower initiator concentration produced polymers of higher molecular weights and lower grafting efficiencies. It appears that temperature has a greater effect on grafting efficiency than on molecular weight, while the opposite is observed with the initiator concentration. This is due to the fact that the reactions involving an attack on the rubber are more thermally activated than the initiator decomposition[43]. Stirring speed showed no appreciable effect on either variable. Grafting efficiency measurements are somewhat scattered around a mean, which is usual given the empirical uncertainties that arise from the extraction technique (before PI, the amount of graft copolymer is not substantial and after PI, it is difficult to extract the occluded PS from the PB-rich droplets, thus producing an error by excess[44]).

**Figure 2** compares the evolution of the apparent viscosity of the polymerizing mixture for the investigated stirring speeds. For all other conditions held constant, the increase in agitation produced mixtures with lower viscosity, except for reactions 3 and 7 (90 °C, 0.05%wt BPO),

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which showed almost no change. Moreover, all reactions at 30 rpm followed an almost identical evolution before PI, and separated in two groups after PI: a high-viscosity one (associated with the higher $Mw_{PS}$ of reactions 1 and 3, both with 0.05%wt BPO) and a low-viscosity one (in line with the low molecular weights of reactions 2 and 4, which were run with 0.1%wt BPO). At 60 rpm, all curves seem to differ, both before and after PI. Sorted in descending order, the viscosity curves would correspond to the following reacting conditions: low temperature, low [BPO] > low temperature, high [BPO] ~ high temperature, low [BPO] > high temperature, high [BPO].

This behavior should be explained by a change in the average droplet diameter: an increase in agitation may favor both coalescence and particle break-up, depending on the dispersed-phase fraction, stabilizer/emulsifier concentration and global physical properties[45,46]. In this case, it is likely that, given the low values of stirring speeds and the high volume fraction of dispersed particles (both before and after the PI), the increase in stirring speed has favored coalescence over break-up, producing larger particles and, in consequence, a lower apparent viscosity[47]. The only reaction that showed little variation in viscosity with stirring speed is the one carried out at 90ºC and 0.1%wt BPO; in this case, the increase in the coalescence rate may have been counteracted by a reduction in the interfacial tension caused by an increased grafting efficiency and molecular weight. The role of copolymers on interfacial properties and mean particle diameter has been previously reported[48], and the present results seem to indirectly support the following: an increase in either the concentration or the molecular weight of the grafted PS reduces interfacial tension (up to a limit) and produces smaller particles.

Regarding the PI point, no major effect is observed between the two stirring speeds, except perhaps in the 80ºC and 0.05%wt BPO reactions. Molau and Keskkula[5] reported that agitation speed is vital to ensure phase inversion, but does not necessarily affect its dynamics (a higher stirring speed will not automatically promote an earlier inversion and *vice versa*). The PI

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periods for each run were estimated from the apparent viscosity local maximum and minimum for each case, and summarized in *Table 2*.

**Figure 3** shows a closer view of the phase inversion paths for each reaction. For the investigated temperature range, the BPO concentration considerably affects the molecular weights of the synthesized PS and, consequently, the mixture viscosity. The beginning of the PI process seems to depend strongly on the coupled effects of initiator concentration and reaction temperature: a simultaneous increase of both delayed the PI the furthest. The PI point (viscosity local minimum) is greatly shifted towards higher conversions when increasing initiator concentration.

The observed effect on PI is possibly due to the presence of graft copolymer in the mixture, which is somewhat higher in the reactions at 90 ºC, as expected. Given that the copolymer chains are preferably located at the interface of the rubber/PS particles[31,43], their effect on the polymer mixture is comparable to that of a surfactant: they are expected to increase phase "compatibility"[21,28,48,49] by reducing the surface tension of the mixture. Under such conditions, One would expect two opposing effects. On the one hand, by accumulating at the interfaces, the graft copolymer stabilizes the PS droplets before the inversion, so that coalescence is thermodynamically and sterically hindered, as previously reported with copolymers and surfactants[50–54]. This effect causes a delayed inversion point due to the coagulating difficulty of the PS nuclei. On the other hand, by providing a certain compatibility between the PS-rich and the PB-rich phases[55], the graft copolymer favors the beginning of the inversion period: even though phase immiscibility still holds, the influence of the dispersed phase on the mixture properties becomes increasingly important, as surface energies are reduced and particle deformability is enhanced.

Moreover, since surface-active components tend to increase interfacial viscosity[56], grafted PS may contribute to increase the viscosity of the PB-rich phase. In addition, if enhanced grafting is coupled with a decrease in $Mw_{PS}$ (e.g. by increasing initiator concentration), then a lower PS-rich phase viscosity is to be expected. These effects may favor the inversion process, since as previously reported[14,39,53,57], the lower the phase viscosity ratio $\left( \eta_d / \eta_c \right)$, the easier for the low viscosity phase (i.e., the PS-rich phase) to become the continuous phase. Besides, a decrease in the PS molecular weight, also implies shorter graft copolymer chains. This lowers its effect on surface tension, and thus favoring PI.

These effects are probably present and competing in the reacting system, and the prevailing effect will eventually have an impact on the phase inversion period in one way or the other. On a general scale, the effect of an emulsifier on the PI of a two-phase system is not straightforward. Experimental work has been reported[51,53,58–60] and shows different results according to the emulsion type and the emulsifier characteristics, including average molecular weight of copolymers. There is no general trend as to whether the increase of an emulsifier concentration promotes or delays the PI point. This is because concentration is not the only variable related to surface-active components that should be considered: its affinity towards a given phase and how it changes with operating conditions also play substantial roles[61,62].

*Morphology*

For each reaction, samples before and after the apparent viscosity minima were observed by TEM, to verify the occurrence of the inversion phenomenon. As an example, **Figure 4** presents the micrographs taken for run 3 (90ºC, 0.05%wt, 30 rpm) at 8.2% conversion (a) and 13% conversion (b). The light-gray areas represent the PS-rich phase and the dark gray, the PB-rich phase. As observed, after PI (subfigure (b)) the particle 'salami' morphology is developed.

Particle size distributions for this reaction, estimated with an image-analysis technique, can be found in the Supplementary Material.

All the images corresponding to post-PI systems were also processed with an image-analysis technique, to estimate the fraction of occluded vitreous phase in each reaction immediately after the inversion point. Since the monomer evaporates during the sample preparation, a correction is needed for determining the occluded phase volume. However, if the occluded *fraction* (portion of the particle that is occupied by the continuous phase) is of interest, no correction is required since, being a proportion, such corrections cancel out. With this technique, the internal phase ratio, $\phi_{oc}$, may be approximated to such occluded fraction and computed for each particle. The Supplementary Material contains additional results regarding the analysis performed to each TEM image: both an increase in BPO concentration and in temperature yield particles with a higher internal phase ratio. Since both these conditions favor the generation of graft copolymer, which acts as a surfactant, this behavior is interestingly similar to what has been observed for O/W/O systems[61]. This means that the mechanisms frequently studied for simple systems may also apply for this complex monomer-polymer-polymer-copolymer mixture, especially the role of interfacial tension (which is seen here through the concentration of graft copolymer).

Moreover, the approximate internal phase ratio of each particle varies according to its size. The dependence also seems in agreement with previously published results in O/W/O emulsions[61], which show that the increase in the occluded fraction with particle size is much steeper for small particles than for large ones. This means that bigger particles may accommodate a larger number of occlusions, but as particle size increases, this ability is less efficient. Interestingly, this behavior is observed regardless of the reaction recipe.

All reactions show a mean internal phase fraction *at the inversion point*, $\overline{\phi_{oc,0}}$, of around 0.35-0.5, with the experiments at 60 rpm being slightly lower than those at 30 rpm. The average occluded fraction was computed from the area of the vitreous occlusions and the area of each particle, assuming spherical geometry.

*Rheological behavior*

The apparent viscosity of each sample was studied at four different stirring speeds of the Brookfield viscometer: 0.3, 0.6, 1.5, and 3 RPM, which, according to the equipment geometry, result in shear rates of 0.063, 0.126, 0.316 and 0.632 s$^{-1}$ respectively. These rates seem low, but have proven enough to observe the strong pseudoplastic behavior of the reacting mixture.

For the investigated ranges of weight fraction, molecular weight, and shear rate, the PS present in the mixture behaves as a Newtonian fluid[63], while the PB solution is strongly pseudoplastic. This was also observed by Menezes and Graessley[64]; and seem to indicate that the rheological behavior of the mixture is mainly determined by the rubber-rich phase. Regarding the inversion point, since the range of shear rates is quite narrow, no major shifts were observed between each curve. As previously reported[11], the inversion point was little affected by the shear rate at which viscosity was measured.

## 4. Empirical model for the evolution of apparent viscosity

For given reaction conditions (*i.e.*, polymerization temperature, initiator concentration, stirring speed, etc.), phase inversion will occur at a defined conversion range and, if the vitreous phase is less viscous than the rubber-rich one, then the apparent viscosity of the mixture will go through the minimax points as described in **Figure 2** and **Figure 3**. The evolution of such curves (before and after the PI) was predicted by the following methodology, which is divided in two modules: one concerning the prepolymerization kinetics and another involving the viscosity correlation.

*Polymerization module*

The batch and bulk polymerization of HIPS was mathematically modelled following Estenoz *et al*[43]. The model is based on a kinetic mechanism that assumes homogeneous polymerization and involves chemical and thermal initiation, monomer propagation, transfer to monomer and to the rubber, and combination termination. This mechanism is described in **Table 3**. The autoacceleration or "gel" effect is taken into account by making the rate constant of combination termination to depend on conversion (following Friis and Hamielec[65]). The set of equations are presented in Appendix A (in Supplementary Material), and were solved with solver for stiff and nonlinear ordinary differential equations. To integrate the expressions for the $Mw_{PS}$, an Euler method was employed.

The model was adjusted to fit the measurements of St conversion, $Mw_{PS}$, and grafting efficiency); and was used to provide the viscosity equations with smooth evolutions of $Mw_{PS}$ and $\zeta$, thus obtaining continuous theoretical curves.

*Viscosity correlation module*

In emulsion theory, the emulsion viscosity is higher than the continuous phase viscosity, due to the contribution of the dispersed phase viscosity, the average dispersed particle size, and the dispersed phase volume fraction[66]. On these grounds, it was suggested that the viscosity curves should follow the evolution of the viscosity of a PB-rich continuous/PS-rich dispersed emulsion before PI, and then that of a PS-rich continuous/PB-rich dispersed emulsion after PI. More precisely, by considering the PS droplets occluded in the PB-rich particles after the PI point, this mixture actually consists of a PS-rich/PB-rich/PS-rich *double-emulsion*. For this system, and as shown in Appendix B (in Supplementary Material), the dispersed phase fraction, $\phi_d$, was calculated from both the rubber-rich phase fraction $\phi_r$ and the initial internal phase fraction $\phi_{oc,0}$. Before PI, $\phi_d = \phi_v$.

The viscosity prediction was assumed independent of the shear rate, since the local minimum was seen to be little affected by it (further details available in Supplementary Material). Therefore, based on the quality and availability of the experimental points, the set of curves at 3 RPM ($0.632$ s$^{-1}$) was chosen for this fitting procedure.

Several equations have been developed over the past 60 years to model the viscosity of emulsions. The most relevant for the system under study are summarized in *Table 4*, and were tested against the experimental data at $0.632$ s$^{-1}$. When possible, the adjustable parameters were modified to fit the measured values. However, none of the equations showed good fitting results, mainly for the following two reasons: i) all these models were fitted with systems whose continuous phase viscosity, $\eta_c$, is constant (*i.e.*, the continuous phase is always the same liquid), which is not the case in this reacting system ($\eta_c = \eta_{c_{(x,Mw_{PB})}}$) as styrene is transferred from the continuous to the dispersed phase as the reaction proceeds; ii) none of the equations include a particle size effect, which is key to understand the differences between the observed viscosities at the studied stirring speeds. In this work, this effect is contemplated through the concentration of graft copolymer, which is the responsible for altering the particle diameter during the reaction (at a given stirring speed) as, behaving like a surfactant, it modifies the interfacial energy of the polymerizing system.

Analyzing the equations in **Table 4**, the relative viscosity ($\eta/\eta_c$) is seen to be an increasing function of the dispersed phase volume fraction. In the reacting system analyzed in this work, this is not necessarily the case, since the viscosity of the mixture increases during the polymerization both because the continuous phase becomes increasingly viscous and because new dispersed phase is formed. Since the continuous phase changes at the PI point, the fitting of the experimental data is done separately before and after PI.

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a)  Before PI

**Figure 5** shows the evolution of the relative viscosity for each reaction before the PI point, as measured by the Brookfield viscometer at 0.632 s$^{-1}$. As observed, none of them is strictly increasing. Based on the non-monotonic evolution of this curve, the following empirical correlation for the apparent viscosity of the system before PI ($\eta_{rc}$) was derived and adjusted to fit the experimental data:

$$\eta_{rc} = \eta_r \left(1 + c_1 Mw_{PS}{}^{c_2} w_{PS-g}{}^{c_3} \phi_v e^{-\{c_4 \phi_v{}^{c_5}\}}\right) \tag{1}$$

where $\phi_v$ is the vitreous phase volume fraction, $w_{PS-g}$ the weight fraction of grafted PS, $Mw_{PS}$ the PS molecular weight in kg/mol, and $\eta_r$ the rubber-rich phase viscosity in cP. The latter has been found to fit the following expression at 0.632 s$^{-1}$ (in good agreement with the results reported by Sardelis et al.[25]), where $w_{PB,r}$ is the weight percentage (%wt) of dissolved rubber and $\eta_r$ is the viscosity in cP:

$$\eta_r = 237.7\left(1 + 4.587 \cdot 10^{-6} \cdot w_{PB,r}{}^{5.731}\right) \tag{2}$$

A very good fit is observed between the predicted evolution of equation (1) and the experimental data in **Figure 5**. The derived correlation accounts for the changes in interfacial properties (and consequently, particle size) through the weight average molecular weight of the grafted PS branches and the copolymer concentration (here behaving as a surfactant). Accounting for the stirring speed effect is more troublesome and the adjustable parameters ($c_1$, $c_2$, $c_3$ and $c_4$) are here reported for each agitation rate studied. With a sufficiently high number of stirring speed values, this correlation could be certainly improved.

b)  After PI

For the already inverted systems, the volume fraction of the discrete phase, $\phi_d$, must contemplate the occluded continuous phase, which can only be computed from the originally

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trapped occlusions ($\overline{\phi_{oc,0}}$) and the mixture composition at the PI point (essentially, $x_{PI}$). In the derivation of the correlation for the viscosity after inversion, the following hypotheses were assumed[1,3,43]: i) no occlusions migrate to the continuous phase, ii) the St partition coefficient is constant and assumed equal to 1, iii) the phase volumes are additive, and iv) the propagation rate constants are identical in both phases. Under these assumptions, the dispersed phase volume fraction may be computed algebraically as shown in Appendix B (in Supplementary Material) and is related to the rubber-phase fraction through $\phi_d = \frac{\phi_r}{1-\phi_{oc}}$. These hypotheses also yield a constant $\phi_d$ even as the polymerization reaction proceeds, since the volume contraction of the St-PS mixtures is the same in both the continuous and the occluded phases.

The empirical correlation for the mixtures after PI resulted in:

$$\eta_{vc} = \eta_v\left(1 + c_6 Mw_{PS}{}^{c_7} w_{PS-g}{}^{c_8} \phi_d\right) \tag{3}$$

where $Mw_{PS}$ is the weight-average free PS molecular weight (in kg/mol), $w_{PS-g}$ is the grafted PS weight fraction and $\phi_d$ the dispersed phase volume fraction. $\eta_v$ (in cP) is the viscosity of the vitreous phase and was computed using the correlation by Kim and Nauman[63]:

$$\eta_v = \frac{\eta_{0v}}{\left(1 + \frac{\eta_{0v}\dot{\gamma}^{1.2}}{35000}\right)^{0.6}} \tag{4}$$

where $\eta_{0v}$ (in cP) is the viscosity at very low shear rates and is calculated with the following equation, by the same authors (T in ºK):

$$\eta_{0v} = 1000exp\left\{-11.091 + \frac{1109}{T} \right. \tag{5}$$
$$+ M_{w,PS}{}^{0.1413}\left[12.032 w_{PS,v} - 19.501 w_{PS,v}{}^2 + 2.923 w_{PS,v}{}^3 \right.$$
$$\left.\left. + \frac{1}{T}\left(-1327 w_{PS,v} + 1359 w_{PS,v}{}^2 + 3597 w_{PS,v}{}^3\right)\right]\right\}$$

*Model adjustment*

The kinetic constants were adjusted to fit the experimental measurements of conversion, $Mw_{PS}$ and $\zeta$ as shown in **Figure 1**. In the viscosity correlations, the parameters were adjusted to fit the viscosity curves for each reaction. The model predictions are represented in **Figure 6**, where a general good agreement with the measurements is observed.

The adjusted parameters are listed in *Table 5* (parameters for the polymerization module were taken from literature[43,65,67]). A sensitivity analysis was performed in order to check for physical consistency of the model. A $\pm$ 10% variation of each parameter resulted in a viscosity variation of no greater than $\pm$ 15%.

## 5. Theoretical results during the PI process

Combining the results of the polymerization module and the viscosity correlations developed in the previous section, some interesting properties may be compared between each reaction at the onset of the inversion process. Some of the physical parameters associated with this phenomenon are the dispersed phase volume fraction, $\phi_v$, the phase viscosity ratio, $r_R$, and the grafting efficiency, $\zeta$. **Figure 7** shows the predicted values of such parameters during the polymerization. The experimental apparent viscosities and the PI region have been added as a visual aid.

As observed, none of the inversion periods begin at equivolume conditions, a criterion that is commonly adopted on theoretical grounds[3,31] but is evidently far from being correct. Furthermore, the system that inverts the latest (reactions 4 and 8) show the lowest phase viscosity ratios and the highest grafting efficiencies.

## 6. Conclusions

The polymerization of styrene in the presence of PB has been studied under different reaction conditions, focusing on the phase inversion phenomenon through the evolution of the apparent viscosity of the reacting mixture along the prepolymerization. The results show that it is possible to predict the evolution of such viscosity before and after the PI process. The description of the co-continuous transition remains a challenge, but it is likely that, if enough experimental evidence were gathered, a comprehensive model could be developed to accurately predict the inversion point for each reaction recipe.

An empirical correlation was developed for predicting the viscosity evolution of the St-PS-PB mixture during the polymerization of St under the investigated conditions. The proposed equations accurately describe the apparent viscosity before and after the PI period, as the system behaves like a polymeric oil-in-oil emulsion. Naturally, the adjusted parameters are valid under the reaction conditions investigated; should these change considerably, the fitting procedure would have to be performed again to obtain a different set of values. This correlation itself is not the prime goal of this work, but rather the methodology followed to obtain phase behavior predictions.

According to the available measurements, the most important parameters that affect viscosity curves were phase composition (a function of conversion), the occluded phase fraction (after PI) and overall particle size, whose effect was deemed to be the result of stirring speed, $Mw_{PS}$, and the copolymer weight fraction. Since the mixture presents non-Newtonian behavior, the analysis was performed at a (chosen) constant shear rate. For different shear rate values, the adjustable parameters and continuous phase viscosities should be recalculated.

The challenge of predicting mixture viscosity after the PI point lies on the fact that the dispersed phase fraction depends both on the initially occluded continuous phase and on the amount of

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rubber-rich phase present at that moment, which is itself a function of the St conversion at the inversion point, $x_{PI}$. Thus, estimating the PI period for a given polymerization only using viscosity models was proven unviable. However, validating such models with real quantifiable data could set the basis for a better understanding the complex physicalchemistry that govern the PI process. A theoretical model to predict both phase separation and phase inversion is currently under work.

According to the presented experimental results, the produced graft copolymer plays a major role on the dynamics of phase inversion, with the reduction of interfacial tension being the key factor. A reduction in interfacial tension causes dispersed particles to be prone to interfacial deformation, which may lead both to larger or smaller particles depending on the relative effect on coalescence and break-up frequencies. It is then conceivable that there is an optimum recipe where phase inversion occurs readily at low conversions, produces a desired particle size distribution, and maximizes the use of rubber by increasing the amount of PS occlusions. Further experimental results are required to validate this conjecture.

**Authorship**

Dr. Casis and Dr. Acuña have conducted the experimental part of this work, from its design to the data acquisition. Dr. Morales has supervised the experimental reactions and has critically revised the drafting of the paper. Mr. Maffi performed the extensive analysis on the experimental evidence, implemented the mathematical model, developed the empirical correlations and drafted the article. Dr. Estenoz has critically analyzed the contents of the manuscript, helped to develop the interpretation of the empirical data and is the responsible for approving the submission of this article.

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## 8. Tables

**Table 1**

| Run # | [BPO] (%wt) | $T_{prepol}$ (°C) | Agitation speed (rpm) |
|---|---|---|---|
| 1 | 0.05 | 80 | 30 |
| 2 | 0.1 | 80 | 30 |
| 3 | 0.05 | 90 | 30 |
| 4 | 0.1 | 90 | 30 |
| 5 | 0.05 | 80 | 60 |
| 6 | 0.1 | 80 | 60 |
| 7 | 0.05 | 90 | 60 |
| 8 | 0.1 | 90 | 60 |

**Table 1**. Recipes of the performed polymerizations.

**Table 2**

| T | [BPO] | RPM | |
| °C | %wt | 30 | 60 |
|---|---|---|---|
| 80 | 0.05 | 12 – 15 % | 10 – 14 % |
| | 0.1 | 13 – 17 % | 15 – 18 % |
| 90 | 0.05 | 10 – 12 % | 10 – 12 % |
| | 0.1 | 15 – 18 % | 15 – 18 % |

**Table 2**. Inversion periods for each run.

**Table 3**

| Proposed kinetic mechanism | Nomenclature | |
|---|---|---|
| *Initiation* | St | Monomer |
| $$3St \xrightarrow{k_{i0}} 2S_1^\bullet$$ | $S_1^\bullet$ | Monomer radical |
| $$I_2 \xrightarrow{f\,k_d} 2I^\bullet$$ | $I_2$ | Initiator |
| $$I^\bullet + St \xrightarrow{k_{i1}} S_1^\bullet$$ | $I^\bullet$ | Initiator radical |
| $$I^\bullet + B \xrightarrow{k_{i2}} P_0^\bullet$$ | $B$ | Unreacted butadiene unit |
| $$P_0^\bullet + St \xrightarrow{k_{i3}} P_1^\bullet$$ | $P_0^\bullet$ | Primary radical produced by attack to a butadiene unit |
| *Propagation* | $P_1^\bullet$ | Copolymer radical with one styrene unit |
| $$S_n^\bullet + St \xrightarrow{k_p} S_{n+1}^\bullet$$ | $P_n^\bullet$ | Copolymer radical with n repetitive units of St in active branch. |
| $$P_n^\bullet + St \xrightarrow{k_p} P_{n+1}^\bullet$$ | $S_n^\bullet$ | Free PS radical with n repetitive units. |
| *Transfer* | $S_n$ | PS with n repetitive units. |
| $$S_n^\bullet + St \xrightarrow{k_{fM}} S_n + S_1^\bullet$$ | $P_n$ | Copolymer with n repetitive St units. |
| $$P_n^\bullet + St \xrightarrow{k_{fM}} P_n + S_1^\bullet$$ | | |
| $$P_0^\bullet + St \xrightarrow{k_{fM}} B + S_1^\bullet$$ | | |
| $$S_n^\bullet + B \xrightarrow{k_{fG}} S_n + P_0^\bullet$$ | | |
| $$S_n^\bullet + P_n \xrightarrow{k_{fG}} S_n + P_n^\bullet$$ | | |
| *Termination* | | |
| $$S_n^\bullet + S_m^\bullet \xrightarrow{k_{tc}} S_{n+m}$$ | | |
| $$S_n^\bullet + P_m^\bullet \xrightarrow{k_{tc}} P_{n+m}$$ | | |
| $$P_n^\bullet + P_m^\bullet \xrightarrow{k_{tc}} P_{n+m}$$ | | |
| $$P_n^\bullet + P_0^\bullet \xrightarrow{k_{tc}} P_n$$ | | |
| $$S_n^\bullet + P_0^\bullet \xrightarrow{k_{tc}} P_n$$ | | |
| $$P_0^\bullet + P_0^\bullet \xrightarrow{k_{tc}} P_0$$ | | |

**Table 3**. Proposed kinetic mechanism of styrene polymerization in presence of rubber.

**Table 4**

| Model | Author | Parameters |
|---|---|---|
| $\eta = \eta_c\left(1 + 2.5\phi_d + b{\phi_d}^2 + c{\phi_d}^3\right)$ | Several authors[68–71] | b, c |
| $\eta = \dfrac{\eta_c}{1 - c\phi_d}$ | Oliver and Ward[72] | c |
| $\eta = \eta_c\left(1 - \dfrac{\phi_d}{\phi_p}\right)^{-a\phi_p}$ | Krieger and Dougherty[73] | a |
| $\eta = \eta_c\left(1 - \dfrac{\phi_d}{b}\right)^{-ab}$ | Modified Krieger and Dougherty | a, b |
| $\eta = \eta_c(1 - k\phi_d)^{-2.5}$ | Roscoe[74] | k |
| $\eta = \eta_c A e^{C\phi_d}$ | Broughton and Squires[75] | A, C |
| $\eta = \eta_c e^{\frac{b\phi_d}{1 - z\phi_d}},\ \text{with } b = \dfrac{ar + 1}{r + 1}$ | Mooney[76] | a, z |
| $\eta = \eta_c\left(\dfrac{1}{1 - (h\phi_d)^{1/3}}\right)$ | Sibree[77] | h |
| $\eta = \eta_c\left(1 + \dfrac{2.5\phi_d}{2(1 - c\phi_d)}\right)^2$ | Eilers[78] | c |
| $\eta = \eta_c 10^{\frac{C_1 C_2 \phi_d}{1 - C_2 \phi_d}}$ | Maron and Madow[79] | $C_1$, $C_2$ |
| $\eta = \eta_c A e^{B[C]\phi_d}$ | Sherman[56] | A, B. [C] is taken equal to $w_{cop}$ |
| $\eta = \eta_c(1 + 2.5\phi_d)$ | Einstein[80] | -- |
| $\eta = \eta_c\left(\dfrac{1}{1 - {\phi_d}^{1/3}}\right)$ | Hatschek[81] | -- |
| $\eta = \eta_c\left(1 + \dfrac{2.5\phi_d}{6(1 - \phi_d)}\right)^6$ | Bredée and de Booys[82] | -- |
| $\eta = \eta_c\left[1 + \phi_d\left(\dfrac{2.5r + 1}{r + 1}\right)\right]$ | Taylor[83] | -- |
| $\eta = \eta_c\left[1 + \phi_d\left(\dfrac{2.5r + 1}{r + 1}\right) + 2.5\left(\phi_d\left(\dfrac{2.5r + 1}{r + 1}\right)\right)^2\right]$ | Choi and Schowalter[84] | -- |
| $\ln\left(\dfrac{\eta}{\eta_c}\right) = \left(\dfrac{2.5r + 1}{r + 1}\right)\left(\phi_d + {\phi_d}^{5/3} + {\phi_d}^{11/3}\right)$ | Leviton and Leighton[85] | -- |

**Table 4**. Models for emulsion viscosity that were tested to fit the experimental data.

**Table 5**

| Parameter | 30 rpm | 60 rpm |
|-----------|--------|--------|
| $C_1$ | 2733.4 | 1193.6 |
| $C_2$ | -0.1912 | 3.0425 |
| $C_3$ | 0.6514 | 3.1961 |
| $C_4$ | 12.3988 | 19.5266 |
| $C_5$ | 2.9554 | 1.4520 |
| $C_6$ | 0.0764 | 0.0016 |
| $C_7$ | 1.3954 | 2.5234 |
| $C_8$ | 0.0128 | 0.7786 |

**Table 5**. Model parameters implemented in the viscosity correlations.

## 9. Figure legends

**Figure 1**. Effect of the BPO concentration on the time evolution of conversion (a), PS Mw (b) and grafting efficiency (c) in prepolymerizations carried at 80 °C and 90 ºC, at 30 rpm. Markers refer to each reaction as follows: circles, 0.05%wt and 80ºC; squares, 0.1%wt and 80ºC; diamonds, 0.05%wt and 90ºC; triangles, 0.1%wt and 90ºC. Black markers: 30 rpm; white markers: 60 rpm. Lines correspond to the predicted evolution according to the polymerization model.

**Figure 2**. Apparent viscosity of the pre-polymerizing mixture as a function of monomer conversion. Markers refer to reaction number as defined in **Table 1**.

**Figure 3**. Apparent viscosity of pre-polymerizing mixture for each pair of reactions at different stirring speeds. Markers refer to reaction number as defined in **Table 1**.

**Figure 4**. TEM images for run 3 at 8.2% conversion (a) and 13% conversion (b).

**Figure 5.** Relative viscosity of the polymerizing system before phase inversion, at the investigated stirring speeds. Markers refer to reaction number as defined in **Table 1**.

**Figure 6**. Predicted evolution of the apparent viscosity of each reaction mixture.

**Figure 7**. Predicted system properties during the phase inversion process. White markers correspond to viscosity measurements at 60 rpm, while black markers at 30 rpm. They are included in the figure as a visual aid.