

Synthesis and Characterization of High-Impact Polystyrene Using a Multifunctional Cyclic Peroxide as the Initiator

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ABSTRACT: This work deals with the synthesis of high-impact polystyrene (HIPS) using a novel cyclic multifunctional initiator, the diethyl ketone triperoxide (DEKTP), analyzing its effect on the prepolymerization step and its influence over the HIPS final properties. DEKTP showed a low selectivity toward grafting reactions at any of the concentrations of initiator and temperatures evaluated, and

when it was used under a temperature ramp (120–130°C, heating rate = 2°C/min), the synthesis of HIPS was possible with an adequate development of morphology and impact strength (i.e., 67 J/m) depending on DEKTP concentration. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3198–3210, 2009

Key words: initiators; polystyrene; impact strength

INTRODUCTION

The general incompatibility between polymer molecules limited their industrial development in the last century because of the incapability to combine two or more polymers to improve their individual properties. This problem was overcome by the use of interfacial agents that mainly improved the interaction between the phases.¹ An example of materials composed of an interfacial agent that allows combination of both homopolymers components characteristics is that of a thermoplastic modified with a rubber, as it is the case of high-impact polystyrene (HIPS).

HIPS is formed by 6–15 wt % of a rubber dispersed in the form of particles into a polystyrene (PS) matrix where the dispersion is stabilized by the interfacial agent composed of a graft copolymer (rubber-*g*-PS) formed “*in situ*” during the HIPS synthesis.^{2,3} HIPS can be obtained by dissolving an appropriate amount of a rubber, usually polybutadiene (PB) or styrene-butadiene copolymers (SB or SBS), in styrene, followed by the *in situ* polymerization of the styrene monomer. The *in situ* polymerization process is separated in two main stages. The first one, also known as the prepolymerization stage, is mainly carried out by means of the use of chemical initiators that promote the grafting reactions and increase the production of the rubber-*g*-PS graft copolymer.⁴

In this first stage, the volume of the PS phase increases and equals the volume of the PB phase promoting the phase inversion with the subsequent formation of the morphological structure.^{5,6} The temperature reaction is varied between 70 and 100°C depending on the half-life time of the initiator used, although this first stage can also be carried out by thermal polymerization at temperatures in the order of 120°C.

The grafting reaction takes place from very low conversion values (approximately 2%) and it is attributed to the abstraction of the allylic hydrogen atom of the rubber chains by the initiator radicals or to their addition of the 1,4- and 1,2-butadiene units to the double bonds.^{7,8}

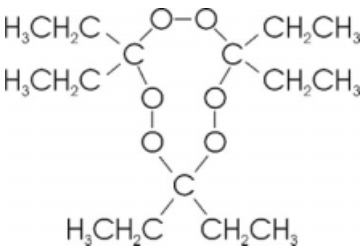
Once the morphology of the disperse rubber phase is established in the first stage and the particles are stabilized by the high viscosity of the matrix, the reaction continues in a second stage, at temperatures in the interval of 140–210°C, where an initiator of higher half-life time is used. Under these new reaction conditions, the monomer is totally consumed and the crosslinking reaction of the rubber phase takes place generally at 95% of styrene conversion, so that the particle has a suitable integrity and is fixed to the matrix to support future processing.⁹

Process innovations to synthesize HIPS have been achieved by different polymerization strategies,^{10–12} the use of new polymerization techniques,¹³ mathematical modeling of the process,^{14,15} and the use of more efficient initiators, especially of the peroxide type.

In this sense, traditional monofunctional initiators have been replaced by linear bifunctional and multifunctional initiators that lead to a rather complex

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TABLE I
Characteristics of the DEKTP Initiator

Molecular structure	T ($^{\circ}\text{C}$)	$k_{d,I} \times 10^6$ (s^{-1})	$t_{1/2}$ (h)
	120	5.6	0.34
	130	15.3	0.13
	mp ($^{\circ}\text{C}$)	$\bar{M}_{w(\text{peroxide})}$ (g/mol)	
	60	306	

$k_{d,I}$, dissociation constant of DEKTP²¹; $t_{1/2}$, half-life time of DEKTP²¹; mp, melting point; $\bar{M}_{w(\text{peroxide})}$, molecular weight of DEKTP.

polymerization kinetics yielding lower prepolymerization times without diminishing the final properties of the product. Thus, 2,5-dimethyl-2,5-di-(2-ethylhexanol peroxy) hexane (Lupersol 256) has been reported to induce the phase inversion at lower conversions, reducing the total polymerization time by 38% in comparison with the polymerization using a monofunctional initiator, without affecting the molecular characteristic of the final product.^{16,17}

On the other hand, with the use of bifunctional initiators it is possible to increase not only the molecular weight of the matrix but also the molecular weight of the graft due to the capability of the species temporarily dead, that is, with peroxide groups which have not been yet decomposed, to reinitiate the polymerization.¹⁸ Other reports have demonstrated that by using bifunctional and multifunctional initiators, it is possible to synthesize HIPS with excellent mechanical properties in less polymerization time (lower than 120 min),¹⁹ in which best results are obtained for most of the cases through the use of a temperature ramp that allows a better control in the peroxide labile groups' dissociation.

This work deals with the synthesis of HIPS using a novel cyclic multifunctional initiator, the diethyl ketone triperoxide (DEKTP), analyzing its effect on the prepolymerization step and its influence over the HIPS final properties.

EXPERIMENTAL PART

Materials

The DEKTP initiator used in the HIPS synthesis was produced in our laboratories according to the procedure described later. The medium *cis*-PB was acquired from Dynasol Elastómeros S.A de C.V, México ($\bar{M}_n = 215$ kg/mol) and was synthesized by solution anionic polymerization. Styrene monomer was purchased from Poliformas Plásticas, Monterrey, México, and was used as received. The initiator

t-butyl perbenzoate (TBPB), polyvinyl alcohol ($\bar{M}_w = 124$ – 186 kg/mol, hydrolysis grade 87–89%), and 3-pentanone (diethyl ketone) were acquired from Aldrich (USA) and used as received. Sodium chloride (Química Dinámica, Monterrey, Mexico) and nonyl phenol (General Electric Specialty Chemicals) were used without further purification. Sulfuric acid, sodium sulfate, hydrogen peroxide, and petroleum ether were obtained from Fermont (Monterrey, Mexico) and were used as received.

DEKTP synthesis

DEKTP initiator was synthesized according to the following procedure²⁰: in a 250-mL Erlenmeyer flask, 4.6 mL of hydrogen peroxide and 7.3 mL of sulfuric acid (70% v/v) were added, and the temperature was kept at -10°C . Then, 5.6 mL of diethyl ketone was added into the reaction solution and the reaction was agitated for 3 h. Thereafter, the organic phase was extracted with petroleum ether and dried with sodium sulfate for 12 h. The petroleum ether was rotoevaporated and the final product was crystallized from methanol yielding a white powder. The main characteristics of DEKTP are summarized in Table I.

Synthesis of HIPS

HIPS were prepared by mass-suspension polymerization as follows: 80 g of PB was dissolved in 920 mL of styrene to carry out the mass polymerization stage (prepolymerization) using different DEKTP concentrations and different temperatures (see Tables II and III) under a heating rate of $2^{\circ}\text{C}/\text{min}$ in the case of using a temperature ramp. In this stage, several samples were taken at different predetermined periods, and hydroquinone was added to deactivate the active chains.

After the phase inversion (15–30% conversion), the suspension medium (2 L of distilled water with

TABLE II
HIPS Synthesis Conditions for the Isothermal Reactions

Material	[DEKTP] ₀ (mol/L)	Temperature in the mass polymerization stage	
		T (°C)	t (min)
HIPS-1	7.79×10^{-4}	120	120
HIPS-2	1.56×10^{-3}	120	120
HIPS-3	3.12×10^{-3}	120	120
HIPS-4	7.79×10^{-4}	130	120
HIPS-5	1.56×10^{-3}	130	120
HIPS-6	3.12×10^{-3}	130	120

1.7 g of poly(vinyl alcohol), 1.6 g of sodium chloride, and 0.55 g of nonyl phenol) were added to proceed with the suspension polymerization (using at this stage TBPB as the initiator), at 125°C for 2 h and 2 h at 150°C in all the cases. The HIPS thus obtained was filtered, washed, and dried. In all the synthesis reactions, the PB concentration was kept constant at 8 wt %.

Processing of HIPS

After the synthesis, following the procedure described in a previous paper,²¹ all the different HIPS samples were injection molded under the following experimental conditions: injection temperature = 240°C, injection pressure = 130 bar, and injection rate = 50 s to obtain the specimens for several analysis.

Characterizations

Physicochemical property (at the prepolymerization stage)

The polymer mass ($P = PB + PB\text{-}g\text{-}PS + PS_{\text{free}}$) was isolated from the monomer as follows: (i) 5 g of the samples were taken at different predetermined periods of time and dissolved in 30 mL of toluene; (ii) after 12 h of agitation at room temperature, the polymer was precipitated from methanol, filtered and dried under vacuum at 50°C until constant weight. The free polystyrene (PS_{free}) was isolated from the rest of the copolymers ($PB + PB\text{-}g\text{-}PS$) through the

solvent extraction technique as follows: (a) 0.5 g of each sample was dissolved in 25 mL of methyl ethyl ketone/dimethylformamide (MEK/DMF; 50% in volume) mixture; (b) after 12 h of agitation at room temperature, the mixture was centrifuged at 20,000 rpm at -20°C for 4 h, and then an insoluble precipitate and a soluble supernatant were obtained; (c) the insoluble precipitate ($PB + PB\text{-}g\text{-}PS$) was isolated from the soluble fraction and dried under vacuum at 50°C until constant weight, and (d) the soluble fraction which corresponds to the PS_{free} was precipitated from methanol, filtered and dried under vacuum at 50°C until constant weight.

Conversion and PS produced in the HIPS synthesis

The conversion (X) and the main characteristics of the PS produced in the HIPS synthesis (i.e., PS_{total} , PS_{graft} , and PS_{free}) were calculated as follows:

$$X = \frac{P - PB}{ms} \times 100 \quad (1)$$

where ms represents the initial monomer mass charged to the reactor.

$$PS_{\text{total}} = PS_{\text{graft}} + PS_{\text{free}} \quad (2)$$

The PS_{total} is obtained by subtracting P from the amount of PB in the recipe, and from PS_{free} value, PS_{graft} can be obtained.

Grafting degree, grafting efficiency, and grafting density (N_t^*)

The grafting degree (GD) is defined as the ratio between the mass of grafted PS branches and the original mass of PB in the recipe; the grafting efficiency (GE) is defined as the ratio between the graft PS branches and the total PS; and the grafting density (N_t^*) that denotes the average number of branches per backbone of PB molecule was calculated as follows²²:

$$GD = \left[\frac{PS_{\text{graft}}}{PB} \right] \times 100 \quad (3)$$

TABLE III
HIPS Synthesis Conditions for the Nonisothermal Reactions

Material	[DEKTP] ₀ (mol/L)	Temperature profile in the mass polymerization stage			
		T ₁ (°C)	t ₁ * (min)	T ₂ (°C)	t ₂ * (min)
HIPS-7	7.79×10^{-4}	120	80	130	60
HIPS-8	1.56×10^{-3}	120	60	130	50
HIPS-9	3.12×10^{-3}	120	40	130	40

t_1^* and t_2^* , time required in each case to reach the necessary conversion for the phase inversion to take place. Heat rate: 2°C/min.

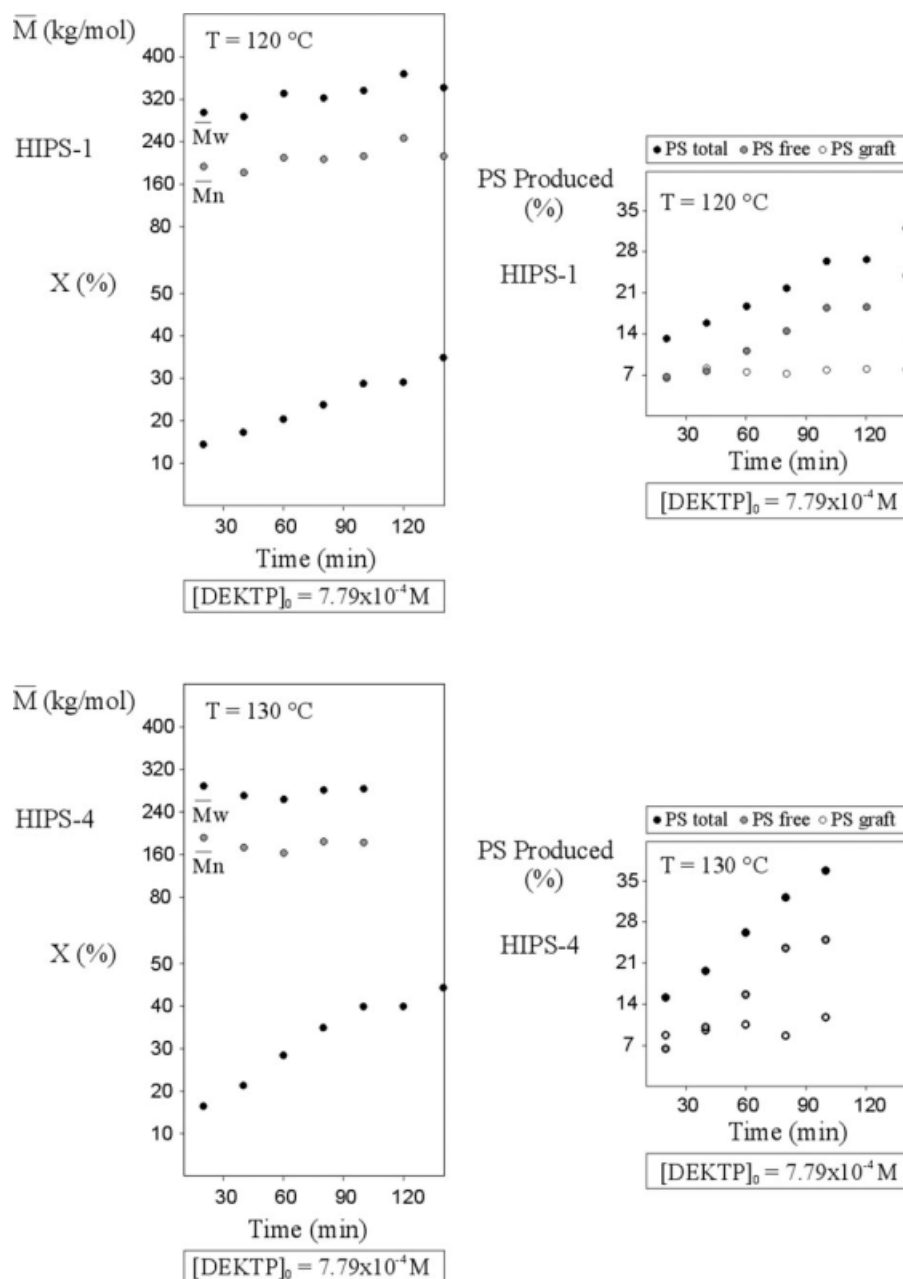


Figure 1 Evolution of molecular weights, conversion, and produced PS as a function of time for the HIPS synthesized under isothermal conditions at 120 and 130°C for a $[\text{DEKTP}]_0 = 7.79 \times 10^{-4} \text{ M}$.

$$\text{GE} = \left[\frac{\text{PS}_{\text{graft}}}{\text{PS}_{\text{total}}} \right] \times 100 \quad (4)$$

$$N_t^* = \left[\frac{\text{PS}_{\text{graft}}}{\text{PB}} \right] \times \left[\frac{\overline{M}_n \text{ PB}}{\overline{M}_n \text{ PS}_{\text{free}}} \right] \quad (5)$$

Gel content

The gel content (insoluble fraction), determined from the HIPS samples at total monomer conversion, was considered as the volume fraction (Φ_d). The gel fraction (insoluble fraction) ($\text{PS}_{\text{graft}} + \text{PS}_{\text{occluded}} + \text{PB}$)

was isolated from the soluble fraction (free PS) by dissolving 1 g of final HIPS sample in 25 mL of toluene and using the centrifugation technique under the following conditions: 45 min at 20,000 rev/min at -20°C . The insoluble fraction was separated from the soluble one, both fractions were dried under vacuum at 50°C to constant weight, and the gel content was gravimetrically calculated.

Size exclusion chromatography

Molecular weights of the free PS were determined by SEC, using a Hewlett Packard chromatograph fit

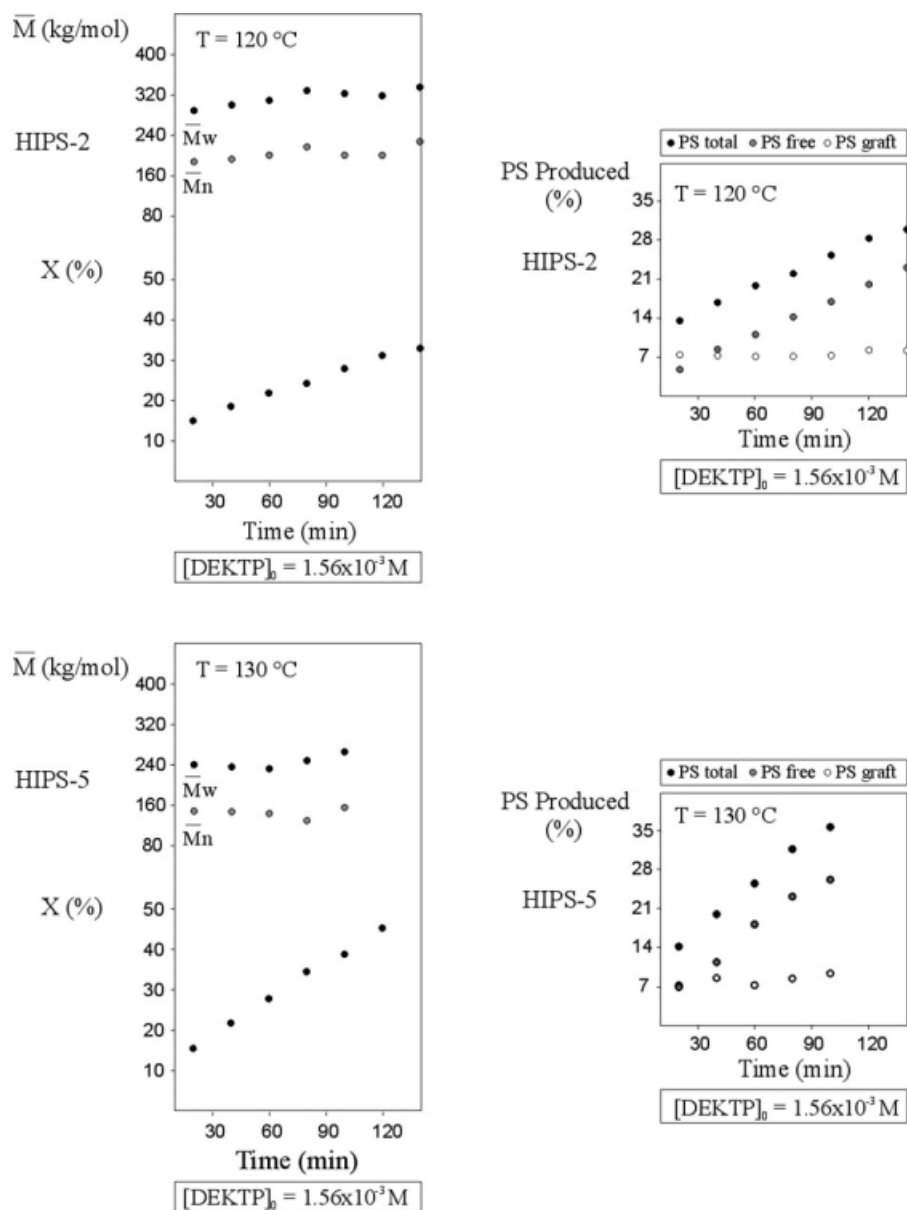


Figure 2 Evolution of molecular weights, conversion, and produced PS as a function of time for the HIPS synthesized under isothermal conditions at 120 and 130°C for a $[\text{DEKTP}]_0 = 1.56 \times 10^{-3} \text{ M}$.

with a set of ultrastrogel columns (of nominal pore 10^5 , 10^4 , and 10^3 Å). In all the cases, a linear molecular weight calibration was obtained with PS standards. Tetrahydrofuran (THF, HPLC grade) was used as the solvent, and the samples were analyzed at room temperature.

Morphology

Internal morphology and particle size distribution were analyzed from injection-molded specimens by TEM as described later.

Number-average particle diameter

The apparent number-average particle diameter (\bar{D}_n) was estimated with the aid of an image analyzer software, Image Pro 3.0. For each HIPS obtained, several TEM micrographs were analyzed and more than 100 particles were measured.

Transmission electronic microscopy

Transmission electron microscopy (TEM) examination was performed in a JEOL TEM at 10 kV on samples cut with a LEICA ULTRACUT ultramicrotome and stained with osmium tetroxide. The

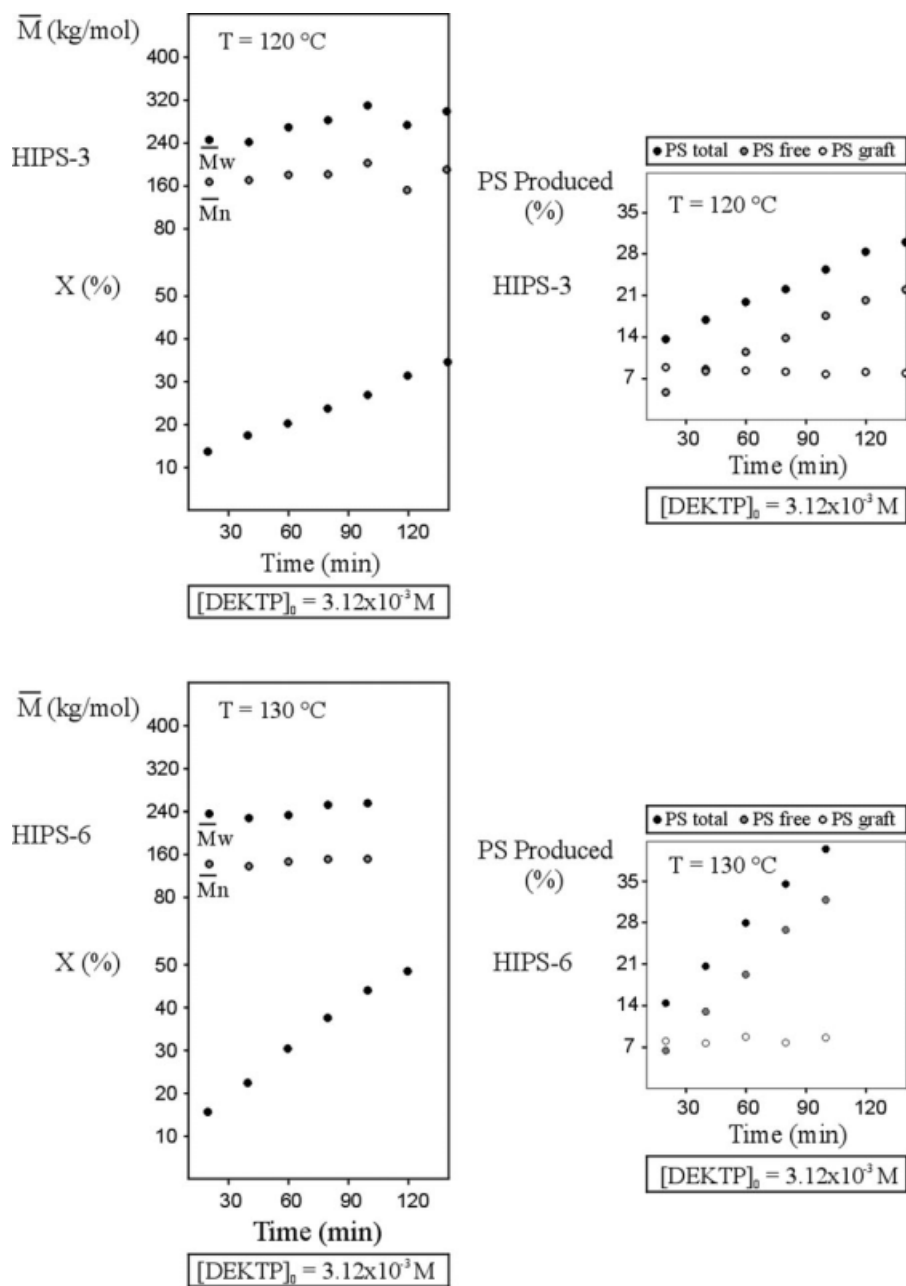


Figure 3 Evolution of molecular weights, conversion, and produced PS as a function of time for the HIPS synthesized under isothermal conditions at 120 and 130°C for a $[DEKTP]_0 = 3.12 \times 10^{-3} M$.

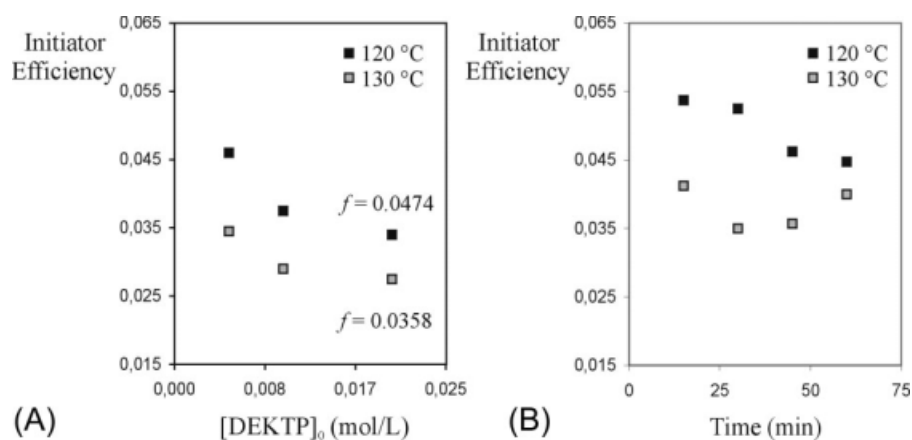


Figure 4 Initiator efficiency as a function of (A) initiator concentration and (B) polymerization time.

TABLE IV
Main Features of the Rubber and the Vitreous Phases at the Phase Inversion

Material	X_{IF}	GD (%)	N_t^*	$\overline{M}_{nPS_{free}}$
HIPS-1	28.78	99.24	1.01	213,000
HIPS-2	31.21	103.28	1.12	200,000
HIPS-4	34.93	107.76	1.27	184,000

X_{IF} , conversion at the phase inversion point; GD, grafting degree; N_t^* , grafting density; $\overline{M}_{nPS_{free}}$, number-average molecular weight of the PS_{free} .

sample cuts were performed at a temperature of -120°C in the ultramicrotome chamber and -40°C at the knife yielding cuts of 70–120 nm width.

Differential scanning calorimetry

For each sample of HIPS-1, HIPS-2, and HIPS-4, about 10 mg of material were sealed in an alumi-

num pan, and differential scanning calorimetry (DSC) measurements were performed with a TA instrument, DSC 2920, at a temperature range from 20 to 120°C , applying a heating rate of $5^\circ\text{C}/\text{min}$ and using the heating-cooling-heating cycle. The jump of the heat capacity at constant pressure (ΔC_p) registered at the T_g interval of the vitreous phase was obtained.

Impact strength test

Notched Izod impact strength tests were carried out according to ASTM-256 at 25°C on injection-molded specimens $60.5\text{ mm} \times 12.2\text{ mm} \times 3.2\text{ mm}$, on a CSI 137 impact testing machine.

RESULTS AND DISCUSSION

Figures 1–3 show the evolution of the molecular weights (\overline{M}_w and \overline{M}_n) and the conversion as a function of polymerization time, using different DEKTP

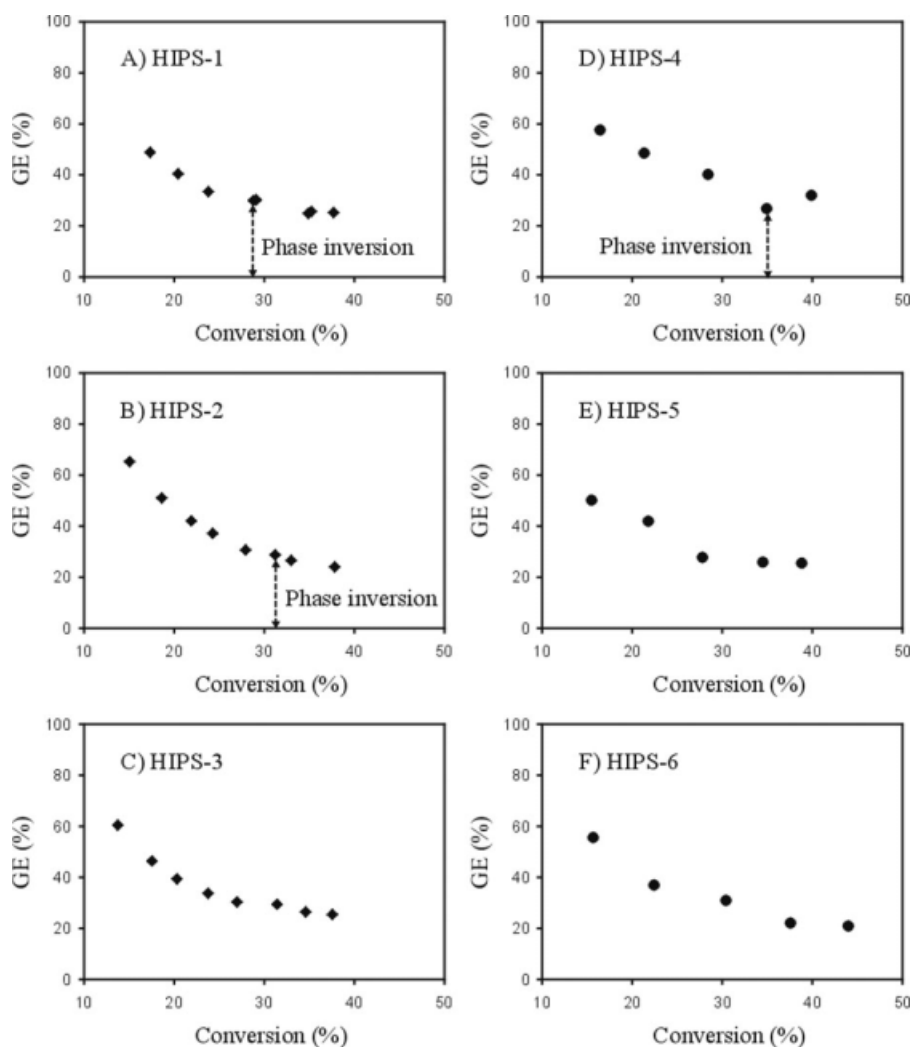


Figure 5 Behavior of the grafting efficiency as a function of conversion for the HIPS synthesized at 120 and 130°C at different initiator concentrations.

concentrations, and in each case, the results obtained at different temperatures (isothermal reactions, at 120 and 130°C) are compared. From the figures it can be observed that regardless of the concentration of DEKTP, the molecular weights increase as the polymerization reaction progresses and they are lower at higher temperatures.

Polymers with uniquely high molecular weights (ca. 350,000 g/mol for DEKTP concentration of $7.79 \times 10^{-4}M$) can be produced after 2.5 h of polymerization, at 120°C, in the presence of the trifunctional initiator.

The behaviors presented by the molecular weights, along with the rates of polymerization reached on the PS formation (estimated from the slope of the curves of conversion vs. polymerization time in a previous work²³), presuppose that at these reaction temperatures, the initiator decomposes through a mechanism of sequential scission of the peroxide sites in a similar way to what was observed by Cerna et al.²⁴

Once the unimolecular scission of the initiator has taken place, a primary diradical with two peroxide sites, that have not yet been decomposed is formed. Diradicals thus produced can in turn initiate, propagate, and effectively end the polymerization. The polymeric chains formed from these diradicals are susceptible of further breakage on the remaining peroxide sites, leading to an increase in molecular weight, typical behavior described for multifunctional initiators.^{25–27}

With respect to the behavior of the produced PS (PS_{total} , PS_{free} , and PS_{graft}) it can be observed that regardless of the concentration of initiator used, an increase in temperature from 120 to 130°C causes an increase in the production of PS, given by the greater concentration of radicals in the reaction medium. However, the kind of PS that increases its production belongs to the total PS and, particularly, to the free PS ($PS_{total} = PS_{free} + PS_{graft}$) because in all the cases the values of PS_{graft} remain without presenting significant changes, approximately to 7%. This fact is indicative of the low selectivity of the initiator to grafting reactions at any of the concentrations of initiator and temperatures evaluated.

On the other hand, it is noted that while the concentration of initiator is increased to an order of magnitude (from 7.79×10^{-4} to $3.12 \times 10^{-3}M$), changes on conversion does not undergo significant variations and the amount of PS_{graft} is decreased. These facts may be indicative of a poor performance or low efficiency of the initiator.

Previous studies reveal,²³ in a similar way to what was reported by Kim et al.,²⁸ a decrease in the initiator efficiency as its concentration is increased. However, contrary to what was reported by Kim et al.,

the DEKTP efficiency also decreases with an increase in polymerization temperature (Fig. 4). This anomalous behavior may suggest that the efficiency of the different peroxide sites is not identical or that side reactions such as termination by primary radical and/or induced decomposition are occurring, which are most important as the viscosity increases with an increase in the initiator concentration.

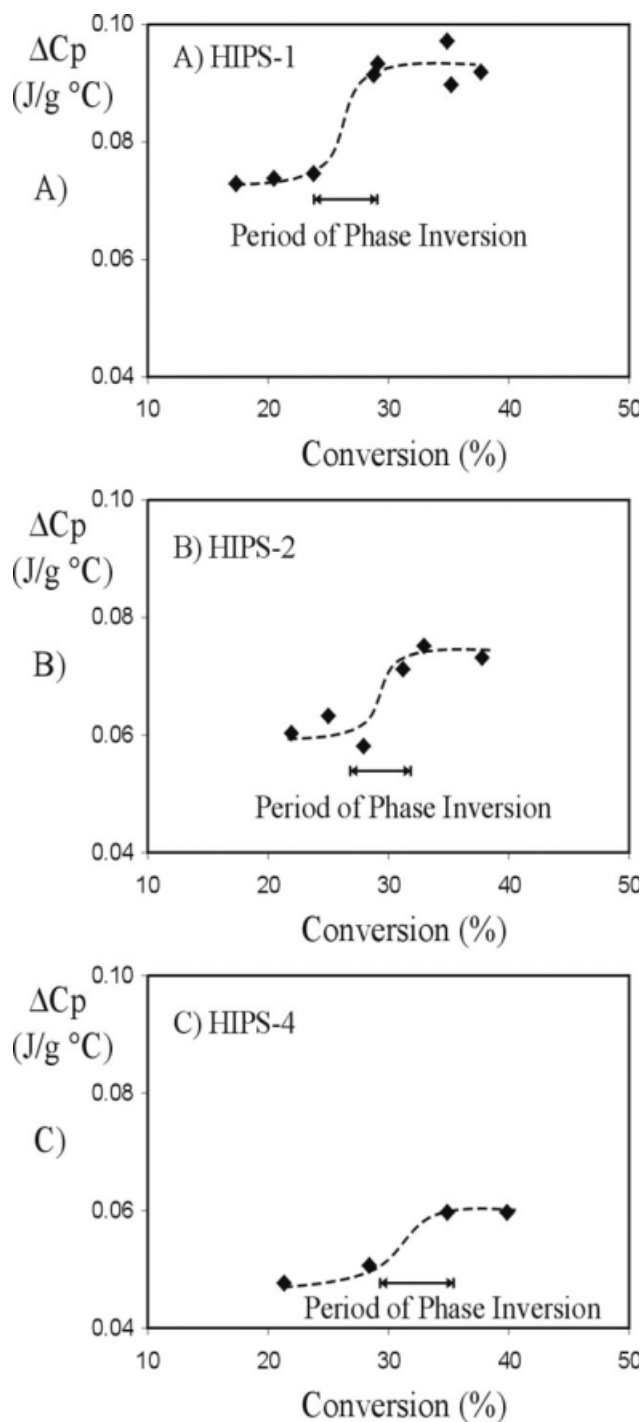


Figure 6 Behavior of ΔC_p as a function of conversion for the different synthesized HIPS.

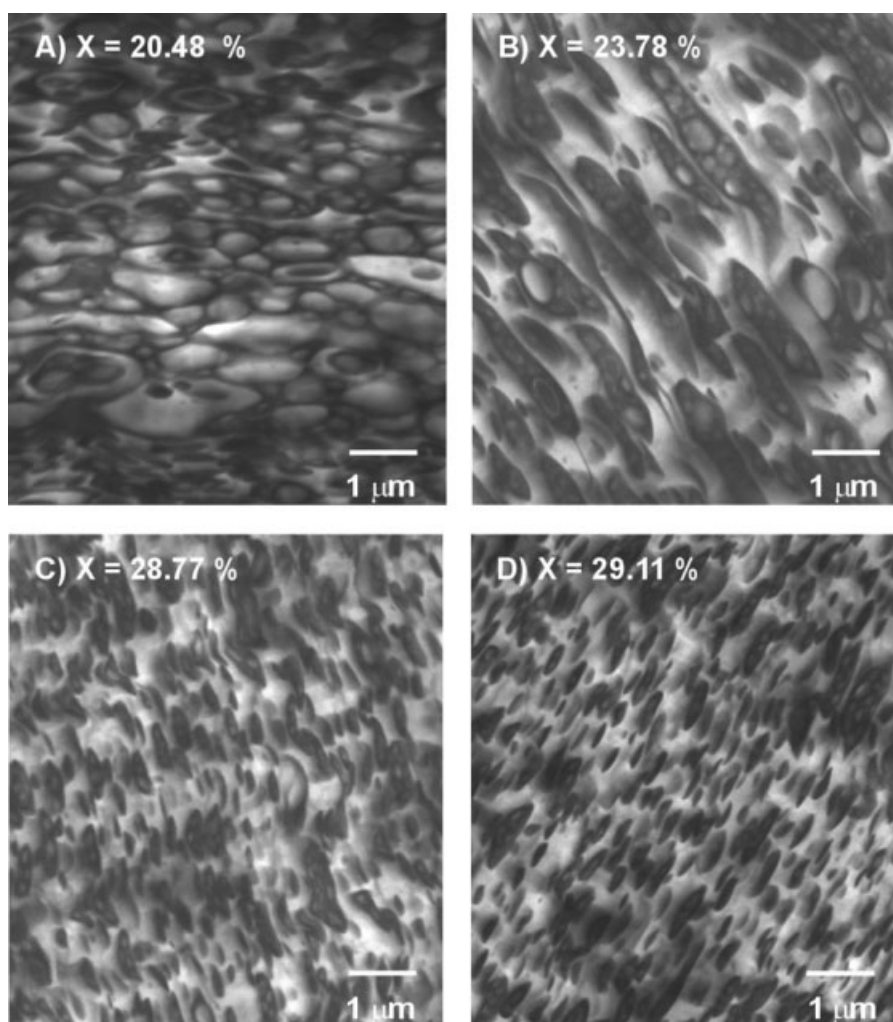


Figure 7 Morphological development for HIPS-1 as a function of conversion (samples evaluated after monomer extraction by evaporation).

Thus, the radicals produced by decomposition of DEKTP are inefficient to produce the abstraction of the allylic hydrogen from the PB, resulting in a very low response to grafting reactions (see values of N_t^* , Table IV).

Figure 5 shows the behavior of GE for the different HIPS isothermally synthesized (at 120 and 130°C). An exponentially decreasing behavior with a more pronounced drop at 30% conversion can be seen in all the cases. This suggests that until $X = 30\%$, the grafting reaction takes place, minimizing the occurrence of this reaction at the point of phase inversion. After the phase inversion, the grafting reaction practically does not occur so that the PS_{total} formed substantially corresponds to PS_{free} .

To corroborate the fact that the most pronounced drop in the curve of GE versus reaction time (t) indicates the occurrence of the phase inversion, the evaluation of ΔC_p for different samples taken from the reactor for the reactions HIPS-1, HIPS-2, and HIPS-4

was carried out. The results of these evaluations are shown in Figure 6. At conversion values approximately to 30%, a considerable leap in the ΔC_p values can be observed, which is associated with the point of phase inversion. This behavior is attributed to the fact that the vitreous state for fragile systems presents a wide variety of structural arrangements, which indicates that a greater ΔC_p at the T_g of the system has taken place, in our case, when the fragile PS phase becomes the continuous phase after phase inversion.

In a forceful way, the morphologies for the HIPS-1 (Fig. 7) confirm the fact that the phase inversion has occurred at conversion close to 30%, previously identified by the curve of GE and even observed with the evaluation of ΔC_p .

However, when comparing the point of phase inversion for HIPS-1, HIPS-2, and HIPS-4 (Fig. 6), an increase in initiator concentration (compare HIPS-1 vs. HIPS-2) and/or an increase in temperature

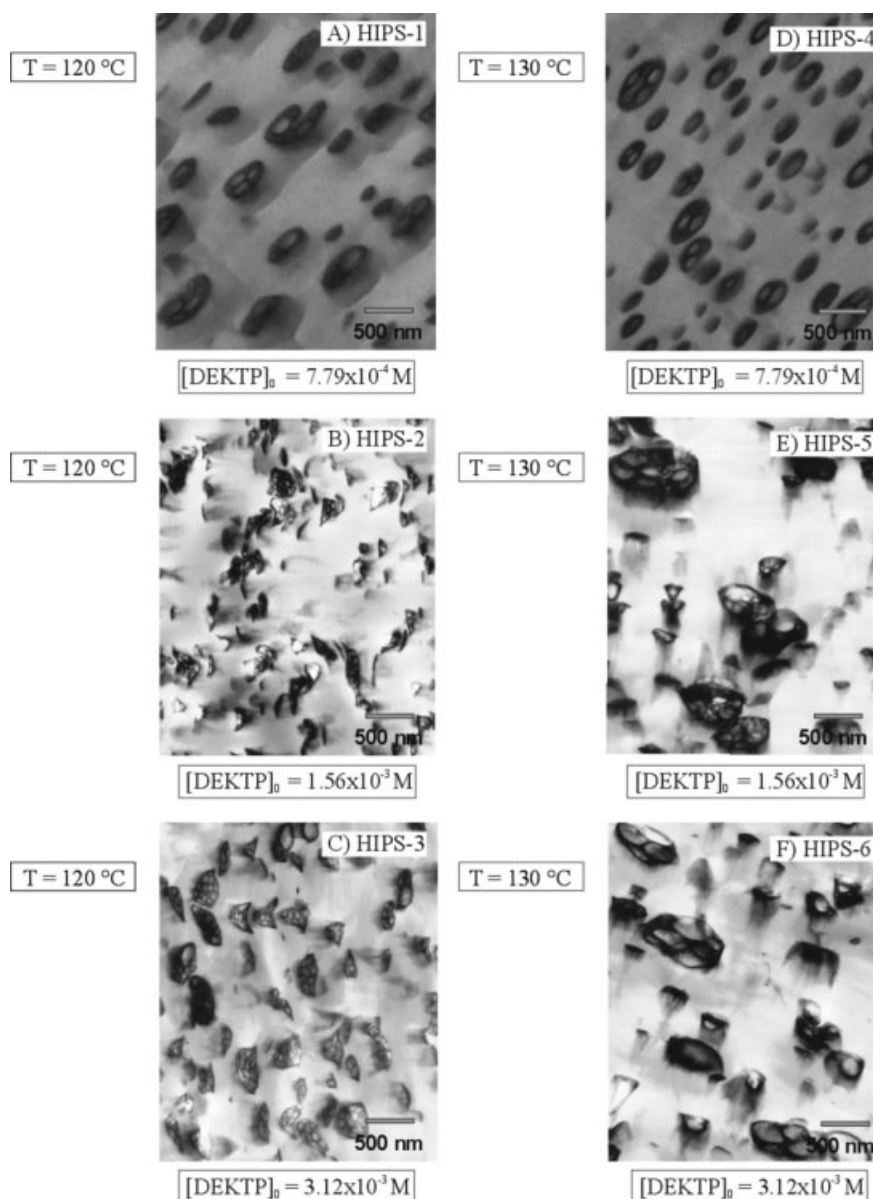


Figure 8 Morphological behavior for the synthesized HIPS, as a function of temperature, at different initiator concentrations.

(compare HIPS-1 vs. HIPS-4) can be observed, that is, the point of phase inversion shifts slightly to higher conversion values. This behavior is explained by the fact that the greater the amount of PS grafted, due to higher initiator concentration and higher temperatures (see values of N_i^* and GD in Table IV), the more stabilized is the system. If the morphology presented before the phase inversion is co-continuous and that it ensures its presence by the action of interfacial grafting are taken into account, with higher values of grafts, a greater amount of PS is required to overcome the co-continuity leading to the phenomenon of phase inversion.

With regard to the morphological characteristics developed in the different synthesized HIPS, Figure 8

TABLE V
Main features of the Rubber Phase and Impact Strength of the Synthesized HIPS

Material	\bar{D}_n^a (nm)	Φ^b (gel)	IS ^c (J/m)
HIPS-1	260	20.8	20.34
HIPS-2	219	25.5	25.62
HIPS-3	247	33.9	32.56
HIPS-4	228	23.3	20.82
HIPS-5	306	30.1	32.03
HIPS-6	320	33.7	43.24
HIPS-7	212	24.7	32.02
HIPS-8	308	30.0	53.39
HIPS-9	429	32.2	66.73

^a \bar{D}_n : Number average particle diameter determined by TEM.

^b Φ_d : volume fraction determined from the gel.

^c IS: impact strength.

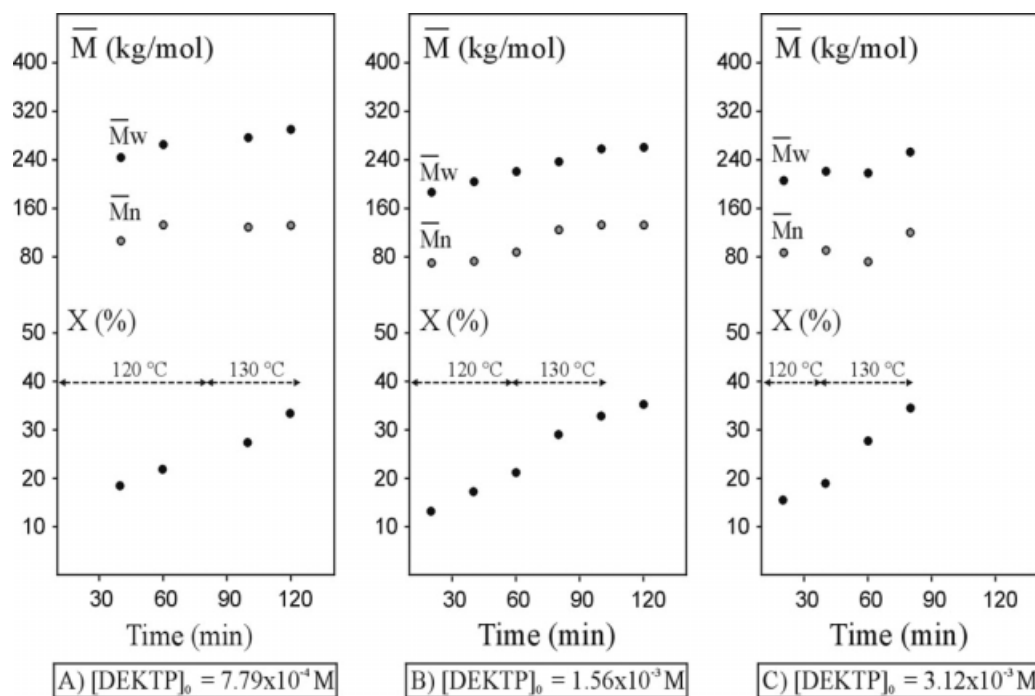


Figure 9 Evolution of molecular weights and conversion as a function of time at different initiator concentrations using temperature ramp.

shows the change in the morphology as a function of the initiator concentration and the reaction temperature (isothermal reactions at 120 and 130 °C, respectively). It can be observed that an increase in the temperature yields bigger rubber particles with bigger occlusions (except for the lower DEKTP concentration), which can be explained by taking into account the parameters that govern the morphological development in HIPS, such as (i) the interfacial tension, (ii) the viscosity ratio of the two phases, and (iii) the shear rate.

As in our case, the shear rate was maintained constant for all the polymerization reactions, the interfacial tension and the viscosity ratio ($[\eta_{PB/St}]/[\eta_{PS/St}]$) are responsible for the morphological changes. Moreover, these two parameters are influenced by the PS_{graft} produced and by the M_n PS, respectively. In this sense, as the amount of graft PS (lower interfacial tension) and M_n PS (lower viscosity ratio) are increased, the particles tend to be smaller. Taking into account the inability of the initiator to produce graft reactions, independently from the temperature

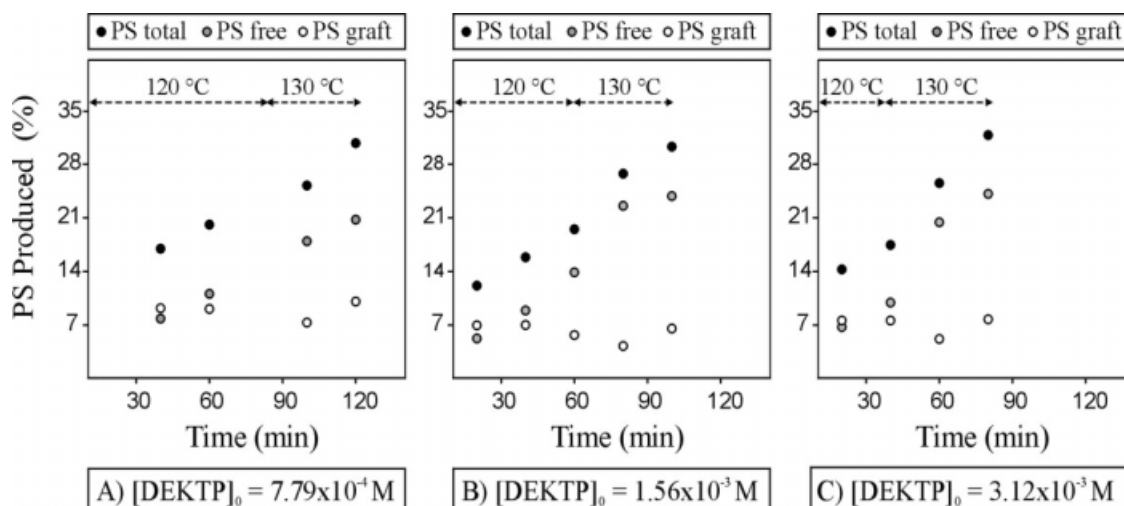


Figure 10 Behavior of the produced PS as a function of polymerization time at the different concentrations of initiator evaluated using temperature ramp.

used, and the polymer lower molecular weight at 130°C, the size of the rubber particles is increased due to an increase in the relationship of viscosities $[\eta_{\text{PB/St}}]/[\eta_{\text{PS/St}}]$. The decrease in the number of occlusions and the increase in the rubber particle size (see Table V), as temperature is increased from 120 to 130°C at the different DEKTP concentrations evaluated, indicate that the occlusions coagulate among them, which in turn decrease as the morphology tends to be more stable (at 120°C) in accord with Leal Wilhelm.²⁹ This author states that the morphological development is a balance between kinetic and thermodynamic processes, where the driving force is the minimization of the interfacial energy because of the systems with higher interfacial tension, yielding simple morphologies with smaller occlusions per particle.

On the other hand, the reaction temperature was manipulated to control the decomposition rate of the peroxide sites, which are responsible for the styrene homopolymerization reaction as well as the grafting reaction of PS onto the rubber, and the effect of these variations on the morphological and molecular parameters was evaluated in different synthesized materials. Table III shows the reactions of HIPS-7, HIPS-8, and HIPS-9, which were obtained using a temperature ramp. Figure 9 shows the evolution of molecular weight and conversion as a function of polymerization time at the different DEKTP concentrations studied.

Regardless of the concentrations of DEKTP used, it is noted that the maximum values of X are similar to those obtained under isothermal conditions at 120°C. However, the molecular weights are, in all cases, lower than those obtained at 120 and 130°C, generating a decrease in the viscosity ratio ($[\eta_{\text{PB/St}}]/[\eta_{\text{PS/St}}]$). On the other hand, for $[\text{DEKTP}] = 1.32 \times 10^{-3}$ and $2.64 \times 10^{-3} \text{ M}$, once again, the multifunctional character of the initiator (sequential decomposition of its peroxide sites) in the evolution of the molecular weight is evident.

With regard to the PS production under these new experimental conditions, it is shown in Figure 10 that the amount of free PS is increased while the amount of graft PS substantially is reduced as the DEKTP concentration is increased, the latter being 6.5% at the higher DEKTP concentration when compared with 7% obtained under isothermal conditions.

It can also be seen in Figure 11 that the values of GE obtained in the case of using a temperature ramp, regardless of the DEKTP concentration used, are similar to those obtained under isothermal conditions (see Fig. 5). These results confirm, on one hand, the low efficiency of the initiator, and on the other hand, a substantial increase in the interfacial

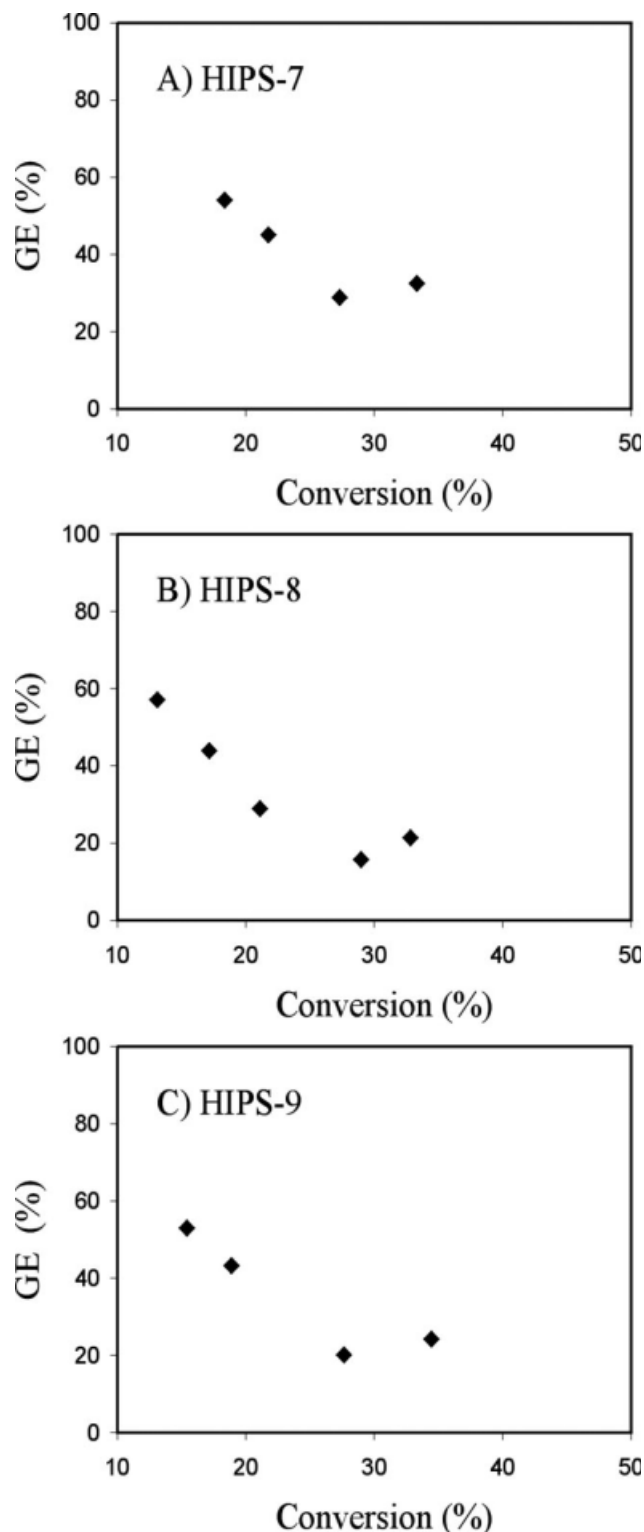


Figure 11 Grafting efficiency as a function of conversion for the HIPS synthesized using temperature ramp.

tension that give rises to an increase in the particle size (Fig. 12). The morphological changes obtained as the result of using a temperature ramp provoke substantial improvements in the mechanical

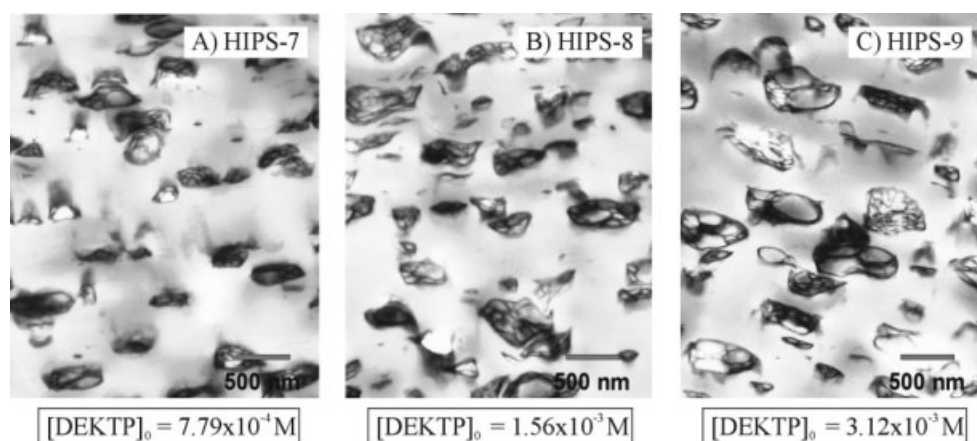


Figure 12 Morphologies developed as a function of initiator concentration using temperature ramp during the HIPS synthesis.

properties of the synthesized HIPS, mainly on the impact strength (see Table V).

CONCLUSIONS

A new multifunctional cyclic initiator, the DEKTP was satisfactorily used as the initiator in the HIPS synthesis. The results obtained from different reactions under isothermal and temperature ramp conditions revealed that the DEKTP presented a low selectivity to grafting reactions at any of the concentrations of initiator and temperatures evaluated. An increase in temperature from 120 to 130°C yielded bigger rubber particles with bigger occlusions, in which the morphological changes were attributed to higher values of interfacial tension and viscosity ratio ($[\eta_{PB}/St]/[\eta_{PS}/St]$).

When the DEKTP was used under a temperature ramp (120–130°C, heating rate = 2°C/min), it was possible to synthesize HIPS with an adequate development of the morphology and impact strength values, in the order of 67 J/m, depending on DEKTP concentration.

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References

- Paul, D. R. *Polymer Blends*; Academic Press: New York, 1978; Vol 2.
- Fisher, M.; Hellmann, G. P. *Macromolecules* 1996, 29, 2498.
- Haaf, F.; Breuer, H.; Echte, A.; Schmitt, B. J.; Stabenow, J. *J Sci Ind Res* 1981, 40, 659.
- Park, J. Y.; Park, O. O. *Adv Polym Technol* 1996, 15, 145.
- Sardelis, K.; Michels, H. J.; Allen, G. *Polymer* 1987, 28, 244.
- Schmitt, B. J. *Angew Chem Int Ed Engl* 1979, 18, 273.
- Gupta, V. K.; Bhargava, G. S.; Bhattacharyya, K. K. *J Macromol Sci Chem* 1981, 16, 1107.
- Manaresi, P.; Passalacqua, V.; Pilati, F. *Polymer* 1975, 16, 520.
- Stein, D. J.; Fahrback, G.; Adler, H. *Adv Chem Ser* 1975, 142, 148.
- Díaz De León, R. PhD. Dissertation, Centro de Investigación en Química Aplicada; Saltillo, Coahuila, Mexico, 2003.
- Demirors, M. *Polym Prepr* 1999, 40, 71.
- Riess, G.; Gaillard, P. *Polymer Reaction Engineering*; Hanser Publishers: Munich, Germany 1983; p 221.
- Desbois, P.; Walzelhan, V.; Niessner, N.; Deffieux, A.; Carlotti, S. *Macromol Symp* 2006, 240, 194.
- Meira, G. R.; Luciani, C. V.; Estenoz, D. A. *Macromol React Eng* 2007, 1, 25.
- Estenoz, D. A.; Meira, G. R.; Gómez, N.; Oliva, H. M. *AIChE J* 1998, 44, 427.
- Estenoz, D. A.; Leal, G. P.; Lopez, Y. R.; Oliva, H. M.; Meira, G. R. *J Appl Polym Sci* 1996, 62, 917.
- Ivanchev, S. S.; Ballova, G. D.; Egorova, E. I.; Maladzyanova, L. F.; Vyleghanina, K. A.; Gol'dsthein, I. L.; Potiforova, M. P. *Int Polym Sci Technol* 1974, 4, 1.
- Chen, C. C. *Polym Eng Sci* 2000, 40, 441.
- Acuña, P. Master's Dissertation, Centro de Investigación en Química Aplicada; Saltillo, Coahuila, Mexico, 2003.
- Eyler, N.; Cañizo, A. I.; Alvarez, E. E.; Cafferata, L. F. R. *Tetrahedron Lett* 1003, 34, 1745.
- Morales, G.; Díaz de León, R.; Acuña, P.; Flores Flores, R.; Montalvo Robles, A. *Polym Eng Sci* 2006, 46, 1333.
- Gasperowics, A.; Laskawski, W. *J Polym Sci Part A: Polym Chem* 1976, 14, 2875.
- Cerna, J. PhD. Dissertation, Centro de Investigación en Química Aplicada, 2002.
- Cerna, J.; Morales, G.; Eyler, G. N.; Cañizo, A. I. *J Appl Polym Sci* 2002, 83, 1.
- Sheng, W.-C.; Wu, J.-Y.; Shan, G.-R.; Huang, Z.-M.; Weng, Z.-X. *J Appl Polym Sci* 2004, 94, 1035.
- Paul, B. K.; Lu, K. A. U.S. Pat. 6,703,460-B1 (2004).
- Mejía Martínez, E. Bachelor's Dissertation, Centro de Investigación en Química Aplicada; Saltillo, Coahuila, Mexico, 2006.
- Kim, K.-J.; Liang, W.; Choi, K. Y. *Ind Eng Chem Res* 1989, 28, 131.
- Leal Wilhelm, G. P. Ph.D. Dissertation, Universidad del País Vasco, Spain, 2003.