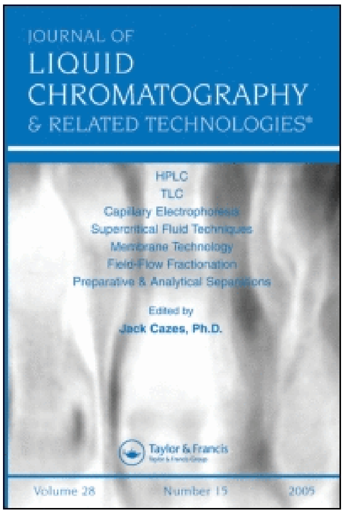

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

GRAFTING EFFICIENCY IN HIGH-IMPACT POLYSTYRENE BY SEC COMBINED WITH THEORETICAL PREDICTIONS FROM A POLYMERIZATION-SEC MODEL

Diana Estenoz[a]; Jorge Vega[a]; Haydée Oliva[b]; Gregorio Meira[a]
[a] INTEC (CONICET) and Univ. Nacional del Litoral, Santa Fe, Argentina [b] Escuela de Ingeniería Química, Univ. del Zulia, Maracaibo, Venezuela

To cite this Article Estenoz, Diana , Vega, Jorge , Oliva, Haydée and Meira, Gregorio(2002) 'GRAFTING EFFICIENCY IN HIGH-IMPACT POLYSTYRENE BY SEC COMBINED WITH THEORETICAL PREDICTIONS FROM A POLYMERIZATION-SEC MODEL', Journal of Liquid Chromatography & Related Technologies, 25: 18, 2781 — 2793

To link to this Article: DOI: 10.1081/JLC-120014949

URL: http://dx.doi.org/10.1081/JLC-120014949

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

JOURNAL OF LIQUID CHROMATOGRAPHY & RELATED TECHNOLOGIES
Vol. 25, No. 18, pp. 2781–2793, 2002

GRAFTING EFFICIENCY IN HIGH-IMPACT POLYSTYRENE BY SEC COMBINED WITH THEORETICAL PREDICTIONS FROM A POLYMERIZATION–SEC MODEL

Diana Estenoz,[1] Jorge Vega,[1] Haydée Oliva,[2] and Gregorio Meira[1,]*

[1]INTEC (CONICET) and Univ. Nacional del Litoral,
Güemes 3450, (3000) Santa Fe, Argentina
[2]Escuela de Ingeniería Química, Univ. del Zulia,
Maracaibo, Venezuela

ABSTRACT

In high-impact polystyrene (HIPS), the grafting efficiency (GE) is the mass of grafted styrene divided by the total mass of polymerized styrene. The GE along a prepolymerization was determined from the UV size exclusion chromatogram of the total polymer. The UV sensor at 254 nm "sees" only the free and grafted polystyrene (PS) chains, but not the polybutadiene (PB) chains. The data processing involves deconvoluting the UV chromatogram into the chromatograms of the free PS and grafted PS by means of polymerization–SEC model. The GE was determined after adjusting (by trial-and-error) the predicted UV chromatogram to the measurement. A single adjustment parameter was used: the ratio between the rate of initiation to the monomer

---

*Corresponding author. E-mail: gmeira@ceride.gov.ar

DOI: 10.1081/JLC-120014949 1082-6076 (Print); 1520-572X (Online)

www.dekker.com

and the rate of initiation to the rubber. The method is quick and accurate, and the estimates were verified by solvent extraction-gravimetry. It is also possible to estimate the GE by deconvolution of the differential refractometer chromatogram. However, in this case a detector calibration is required, and the results are less accurate than when employing the UV sensor.

Key Words: CCK; HPLC-RP; Validation; ICH; Stability

INTRODUCTION

High-impact polystyrene (HIPS) is an important engineering plastic. The material is heterogeneous, with rubber particles dispersed in a vitreous polystyrene (PS) matrix. It is produced by polymerizing styrene (St) in the presence of a chemical initiator and dissolved polybutadiene (PB). The final product is a mixture of free PS, residual PB, and a styrene–butadiene graft copolymer (GC). In the bulk process, the GC must be produced early in the reaction. The GC also plays an important role in the final product, by increasing the material toughness or impact resistance. The reason of this increase is that it prevents the separation between the continuous (vitreous) phase and the disperse (rubbery) phase.

High-impact polystyrene is normally synthesized through a free-radical mechanism. The reaction can be continuous or batch; and it may be carried out in the bulk, in bulk-suspension, or in solution. The common industrial practice is to carry out a bulk polymerization in a series of continuous reactors. The particle size and the particle morphology are basically determined during the phase inversion period. This period takes place during the prepolymerization stage. The prepolymerization ends at about 30% conversion, and it requires well-stirred conditions.

The St grafting efficiency (GE) is defined as the mass of grafted St divided by the total mass of polymerized St. The GE plays an important role during the phase inversion. For example: a high GE at the beginning of the reaction promotes an early phase inversion and reduces the rubber particle size. During the prepolymerization, the GE is mainly controlled by the chemical initiator. This is because the initiator radical is more effective in attacking the PB than the polystyryl radicals. The initiator half-life is such that the reagent is totally consumed during the prepolymerization.

The GE is normally determined by solvent extraction-gravimetry.[1,2] First, the monomer conversion is measured by precipitation of the total polymer over methanol. Then, the free PS is isolated by solvent extraction from the other two HIPS components (GC + unreacted PB). The grafted PS mass is obtained by subtracting the initial PB mass from the total undissolved mass

(GC + unreacted PB). The technique is slow and tedious. Also, it is subject to error when applied to the early reaction stages, because it is based on a subtraction between similar masses. Finally, the method provides GE values in excess when applied to the bulk process, due to the difficulty of quantitatively extracting the occluded PS that is present in the rubber particles. Other separation techniques, such as a selective polymer precipitation from a dilute solution[3] and thin layer chromatography[4] are also feasible, but they both present limitations for high-molecular weight samples.

Huang and Sundberg[5] have used size exclusion chromatography (SEC) of the total polymer to determine the GE in HIPS. The chromatograph was fitted with a differential refractometer (DR) and a UV absorbance detector at 254 nm. The UV sensor "sees" only the phenyl groups of the free or grafted PS, but not the PB chains. The basis of the method is that the molar masses of the free PS are lower than those of the GC; and therefore, a simple deconvolution can be used to separate the free PS peak from the grafted PS peak (or peaks). Then, the GE is obtained from the ratio between the area under the grafted PS and the total chromatogram area. The method is quick and effective, but it can be only considered as semi-quantitative because arbitrary analytical functions are used to deconvolute the total chromatogram. The method was later tested by Li and Sosa.[6] These authors have fitted the individual chromatograms with exponentially-modified Gaussians. Clearly, the chromatographic technique requires total polymer solubility (i.e., the sample must not contain a rubber gel).

The aim of the present work is to predict the GE along a prepolymerization. To this effect, a similar approach to Refs. 5 and 6 is employed, but without imposing any specific shapes to the deconvoluted chromatograms. Instead, a detailed polymerization–SEC model is used to calculate the chromatograms of the free and grafted PS. Fortunately, detailed polymerization models and SEC are becoming increasingly popular in modern petrochemical plants. The samples that are reanalyzed in this work had been synthesized in a solution polymerization of St in presence of PB at a low conversion.[7] High-impact polystyrene is not industrially produced through solution processes. However, it has been shown that the molecular characteristics of the global polymer mixture obtained from a solution process (and its derived GE) are quite similar to those observed in an equivalent bulk process.[8]

In Estenoz et al.[7] a solvent extraction technique was used to isolate the three polymeric components of HIPS (i.e., free PS, unreacted PB, and GC). Then, the GC was treated by ozonolysis to isolate the grafted PS branches from the copolymer molecules. The molecular weight distributions (MWDs) of the total HIPS, the free PS, the unreacted PB, the GC, and the grafted PS branches were all determined by SEC. Also, a polymerization model was used to predict each of the mentioned MWDs. The molar masses of the free PS and the free PB were obtained from direct calibrations with narrow PS and PB standards.

The molar masses of the GC and the total HIPS were obtained by interpolation (with the instantaneous St composition) between the homopolymer calibrations. The polymerization model assumed a kinetic mechanism that included chemical initiation, thermal initiation, chain transfer (to the rubber, the solvent, and the monomer), propagation, termination (by combination and disproportionation), and pure crosslinking between primary rubber radicals. The model considers a homogeneous process, the gel effect, and a reaction volume contraction. The kinetic parameters were all taken from the literature.[9,10] The least-known kinetic parameter was the initiation ratio $k_{i,m}/k_{i,r}$, where $k_{i,m}$ is the reaction rate between the initiator primary radical and the monomer, and $k_{i,r}$ is the reaction rate between the same primary radical and a butadiene repeating unit contained either in the unreacted PB or in the GC. As expected, $k_{i,m}/k_{i,r}$ exhibits a large effect on the GE and, for example, a 30% decrease in this ratio increases the GE by around 25%.

The GC isolated from the reaction samples in Estenoz et al.[7] was later reanalyzed.[11,12] In Estenoz et al.[11]a novel polymerization–ideal SEC model was developed to evaluate the errors (due to the chromatographically-complex nature of the copolymer) on the obtained MWD and branching distribution. The polymerization model was an extension of that in Estenoz et al.[7] The total GC was classified into several branched topologies, with each topology being characterized by the number of trifunctional grafting points per molecule. The polymerization model first calculated the MWD of each branched copolymer topology. Then, the corresponding mass chromatogram was predicted assuming a perfect fractionation and using the Zimm–Stockmayer expression to calculate hydrodynamic volumes.[13] The chromatogram of the total GC was obtained by adding the chromatograms of all individual copolymer topologies. In Vega et al.[12] the GC of Estenoz et al.[11] was further investigated. More specifically, SEC-viscometry was combined with predictions from the polymerization model of Estenoz et al.[11] to estimate the ε exponent of $g^{\varepsilon} = g'$, where g is the branching parameter based on the radii of gyration, and g' is the branching parameter based on the intrinsic viscosities. For the three investigated GC samples in tetrahydrofurane (THF) at 25°C, the following value was determined for the sought empirical exponent: $\varepsilon \cong 2$.[12]

PROPOSED METHOD

This work is aimed at determining the GE in HIPS along the prepolymerization stage. To this end, the polymerization–SEC model presented in Estenoz et al.[11] was used to fit the theoretical UV chromatogram of the total polymer to the corresponding SEC measurement. A single model parameter was adjusted, i.e., the initiation ratio $k_{i,m}/k_{i,r}$.

The required raw data consists of:

a) The UV chromatogram of the total HIPS;
b) The reaction recipe (including the MWD of the initial PB), and the reaction conditions;
c) The monomer conversion;
d) The PS calibration; and
e) The ε exponent of $g^{\varepsilon} = g'$, and the Mark-Houwink parameters of PS, PB, and of a linear St–Bd block copolymer exhibiting similar values of the average composition and the molar mass.

The following procedure is proposed:

1. Adopt an initial value for $k_{i,m}/k_{i,r}$;
2. For the free PS, and from the data in b), c) and d), calculate the MWD and the corresponding UV chromatogram;
3. For each rth copolymer topology, and from the data in b) and c): i) calculate the weight-molar mass distribution $G_r(M)$, and the variation of the mass fraction of St with the molar mass $w_{St,r}(M)$, and ii) obtain the variation of the grafted PS mass with the molar mass from the product of the two previous functions;
4. For each copolymer topology and from the results of 3., and the data in d) and e), calculate the theoretical UV chromatograms assuming an ideal fractionation and the Zimm–Stockmayer model;[11]
5. Calculate the UV chromatogram of the total GC by adding the UV chromatograms of all copolymer topologies;
6. Calculate the predicted UV chromatogram of the total HIPS, by adding the UV chromatograms obtained in 2. and 5. (the PB chains are not seen by the UV sensor);
7. Compare the predicted chromatogram in 6. with the measured UV chromatogram, modify the initiation ratio, and iterate until an acceptable fit;
8. By simulating the polymerization model, obtain the predicted masses of the free PS ($m_{PS,f}$) and of the grafted PS ($m_{PS,g}$) (these values represent the areas under the predicted chromatograms of the free and grafted PS); and
9. Calculate the GE from $[m_{PS,g}/(m_{PS,g} + m_{PS,f})]$.

It is interesting to note, that the area under total UV chromatogram provides a direct measurement of the monomer conversion. Thus, the monomer conversion requirement in c) above could be substituted by an appropriate UV detector calibration obtained by injecting known masses of free PS. In this case, the mass of the injected sample is also required.

Additionally, step 4. of the procedure could be substituted by an interpolation (with the copolymer composition) between the individual PS and PB calibrations. Clearly, in this case the PB calibration must be also included in item d) above.

Apart from the UV signal, the DR signal of the total HIPS can be also used to determine the GE. In this case, however, the DR chromatogram must be deconvoluted into all three polymeric components of HIPS. This estimation is expected to be less precise than that of the UV signal because: i) (as is it explained below) the grafted PS mass is calculated from a difference between two similar masses; and ii) the specific refractive index increment of PS differs from that of PB, and, therefore, a DR calibration is required. Alternatively, the DR calibration could be replaced by the ratio of the specific refractive index increments of PS and PB, at the given analytical conditions.

EXPERIMENTAL

Samples were taken at 8, 12, and 16 hrs, from a solution polymerization of St in the presence of PB and tert-butyl peroctoate. The reaction was carried out in a 1 L glass reactor at 70°C.[7] The polymer was isolated from the unreacted monomer by precipitation in methanol. The monomer conversion and the solid contents were gravimetrically determined. The GE was measured by solvent extraction-gravimetry. The grafted PS mass was calculated by subtracting the initial PB mass from the added masses of unreacted PB and GC. Since the samples were taken from a solution process, the GE determinations by solvent extraction were not biased by contamination of the rubber phase with occluded PS. All measurements were carried out in triplicate, and the results are reproduced in the first three rows of Table 1.[7] No clear tendency is observed for GE from the given measurements.

The original PB, and the three reaction samples, were reanalyzed by SEC. After precipitation of the total polymer from the reaction mixture, the samples were dried, redissolved, and injected into a Waters ALC244 chromatograph fitted with a full set of (six) μ-Styragel columns, a DR, and a UV sensor at 254 nm. The carrier solvent was THF at 1 mL/min and 25°C. The injection volume was 0.25 mL, and the nominal polymer concentration was 1.0 mg/mL. From a set of narrow PS and PB standards, the following homopolymer calibrations were obtained: $\log(M_{\mathrm{PS}}) = 12.23 - 0.1650\,V$; and $\log(M_{\mathrm{PB}}) = 12.0406 - 0.1669\,V$. The DR sensor was calibrated by injecting known masses of PS and PB, and measuring the areas under the corresponding chromatograms. The DR calibrations for PS and PB resulted in: $v_{\mathrm{PS}} = 289{,}000$ dL/g, and $v_{\mathrm{PB}} = 203{,}000$ dL/g.

The following Mark–Houwink constants were used in the data processing:[12] (i) for PS: $K_{\mathrm{PS}} = 1.279 \times 10^{-4}$ and $\alpha_{\mathrm{PS}} = 0.712$; ii) for PB: $K_{\mathrm{PB}} = 4.570 \times 10^{-4}$

Table 1. Grafting Efficiency Along a Solution Polymerization; The Independent Measurements of the First Three Rows[7] Are Compared with Estimates via the Proposed SEC-Model Technique when Using the UV or the DR Chromatograms

	Sample Taken at[7]		
	8 hrs	12 hrs	16 hrs
Monomer conversion by gravimetry (%)[7]	8.82	13.39	17.60
Solid content by gravimetry (%)[7]	10.8	15.29	19.41
Grafting eff. by solvent extr.-gravimetry (%)[7]	**6.25**	**5.85**	**7.8**
Grafting eff. by UV chrom.-model (%)	**6.9**	**7.2**	**7.4**
Grafting eff. by DR chrom.-model (%)	**5.5**	**5.7**	**5.9**
Predicted sampling times (for both adjustments)	7.2 hrs	11.9 hrs	16.9 hrs

and $\alpha_{PB} = 0.693$; and iii) for a linear St–Bd block copolymer homologue of an average composition and average molar masses similar to those of the global GC: $K_{lin} = 3.20 \times 10^{-4}$ and $\alpha_{lin} = 0.693$. The adopted branching exponent was: $\varepsilon = 2$.[12]

Figure 1(a) shows the DR chromatogram of the initial PB. The corresponding MWD is not presented here, but it was used as an input to the polymerization model. Fig. 1(b–d) and Fig. 2, respectively, show the DR and UV chromatograms of the total polymer contained in the three reaction samples. The areas under the DR chromatograms are shown proportional to the solid content measurements, while the areas under the UV chromatograms are shown proportional to the monomer conversion measurements. The high-molecular weight shoulders correspond to the GC. These shoulders are more evident in the DR chromatograms than in the UV chromatograms.

RESULTS AND DISCUSSION

Grafting Efficiency by Deconvolution of the UV Chromatogram

Figure 2 presents the result of applying the proposed method to the UV chromatograms. The polymerization–SEC model was adjusted after three

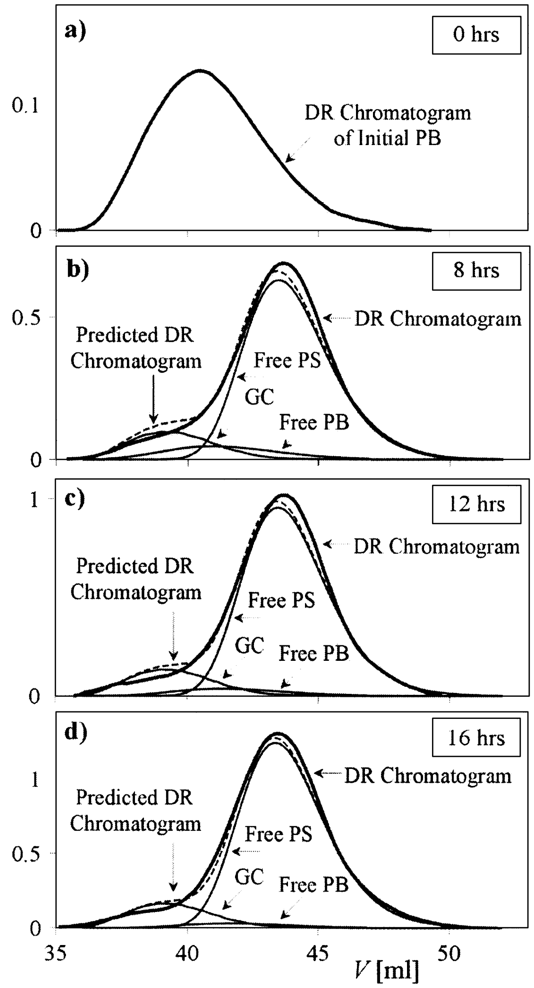

Figure 1. Differential refractometer chromatograms of: (a) the initial PB; and (b–d) the total polymer contained in samples taken at 8, 12, and 16 hrs (in bold trace). (b–c) The total predicted chromatograms (in dashed trace) are compared with the measurements. The thin continuous lines represent the predicted chromatograms of the individual HIPS components.

iterations, and a good agreement is observed between the experimental chromatogram and the total predicted chromatogram. The adjusted model parameter finally resulted in: $k_{i,m}/k_{i,r} = 1.3$, and this value is close to reported literature values.[14,15] The deconvoluted chromatograms are also presented in Fig. 2, and the corresponding GE predictions are shown in Table 1. The predicted

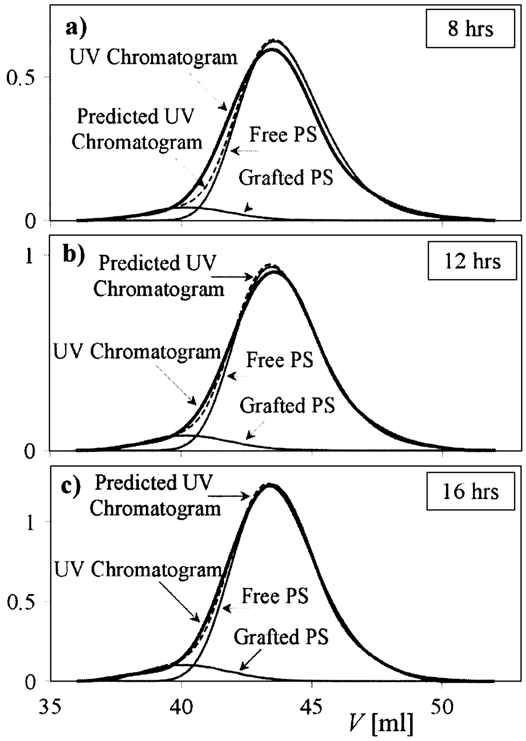

Figure 2. UV chromatograms of the total polymer contained in samples taken at 8, 12, and 16 hrs (in bold trace). (a–c) The total predicted chromatograms (in dashed trace) are compared with the measurements. The thin continuous lines represent the predicted chromatograms of the grafted and free PS.

values show a slight increase in GE with conversion, and these values are close to the measurements by solvent extraction-gravimetry. Table 1 also presents the estimated polymerization times at the measured monomer conversions, according to the adjusted polymerization model. These estimates are lower than the real values for the 8 and 12 hr samples, while the opposite occurs for the 16 hr sample.

Grafting Efficiency by Deconvolution of the Differential Refractometer Chromatogram

To further illustrate the chromatographic technique, consider estimating the GE by deconvolution of the DR chromatogram. In this case, and apart from the raw data listed under b)–e) above, the DR calibrations v_{PS} and v_{PB} are required (or more specifically, the ratio v_{PS}/v_{PB}). The following procedure was applied:

1. Adopt an initial $k_{i,m}/k_{i,r}$;
2. From the data in b) and c), predict the MWDs of the free PS, the residual PB, and each of the branched copolymer topologies;
3. From the data in d) and the results in 2, calculate the DR chromatogram of the free PS as follows: i) the ordinates are given by $[v_{PS} \times G_{PS}(M)]$, where $G_{PS}(M)$ is the theoretical mass–molar mass distribution, and ii) the abscissas are obtained from the PS molecular weight calibration;
4. From the data in d) and the results in 2, calculate the DR chromatogram of the residual PB as follows: i) the ordinates are given by $[v_{PB} \times G_{PB}(M)]$, where $G_{PB}(M)$ is the theoretical mass–molar mass distribution, and ii) the abscissas are obtained from the PB molecular weight calibration;
5. For each copolymer topology, and from the data in d) and the results in 2, calculate the DR chromatogram as follows: i) the ordinates are given by $\{v_{PS}\, w_{St,r}(M) + v_{PB}[1 - w_{St,r}(M)]\}\, G_r(M)$, where $G_r(M)$ is the mass–molar mass distribution for the rth topology, and $w_{St,r}(M)$ is the variation of the St mass fraction with the molar mass for the rth topology; and ii) the elution axis is obtained assuming an ideal SEC fractionation and the Zimm–Stockmayer model;[11]
6. Calculate the DR chromatogram of the total GC by adding the chromatograms of all the branched copolymer topologies;
7. Obtain the total predicted DR chromatogram by adding the chromatograms obtained in 3, 4, and 6;
8. Compare the measured DR chromatogram with its prediction, modify the initiation ratio, and iterate until an acceptable fit;
9. At the measured monomer conversion, the polymerization model provides the total masses of the free PS ($m_{PS,f}$), residual PB (m_{PB}), and GC (m_{GC}); with these values being proportional to the areas under the corresponding chromatograms.
10. Calculate the GE from $[m_{PS,g}/(m_{PS,g} + m_{PS,f})]$ with $m_{PS,g} = m_G + m_{PB} - m_{PB}{}^0$, where $m_{PB}{}^0$ is the initial PB mass.

The model parameter was adjusted after three iterations, yielding: $k_{i,m}/k_{i,r} = 1.7$. This value is somewhat higher than the UV estimate. The initiation ratio $k_{i,m}/k_{i,r}$, and its associated GE, exhibit a negligible effect on the polymerization rate. For this reason, and for the number of digits presented in the last row of Table 1, the new predicted reaction times coincide with those of the UV predictions.

The final total DR chromatograms, as predicted by the SEC-model, are shown in Figs. 1(b–d), together with their corresponding deconvolutions. Note, that the total mass and average molar masses of the free PB decrease along the polymerization. Compared to the UV solution, the following can be observed: (i) the chromatogram fit is not as good; and ii) the GE estimates are not as close to the solvent extraction-gravimetry measurements. The lower accuracy of the DR method is a consequence of including the masses of the grafted and free PB chains in the data treatment.

CONCLUSIONS

The developed technique was tested on samples taken from a batch solution polymerization. However, similar results are to be expected if applied to a continuous bulk process.[16] The reasons for this are: (a) any batch reactor is dynamically similar to a series of continuous reactors operating in the steady-state; and b) the global polymer mixture obtained from a solution process is similar to the global polymer mixture obtained from a bulk process.[8]

When applied to the bulk process, the proposed technique is expected to provide better GE estimates than the standard solvent extraction-gravimetry method. This is because the chromatographic technique analyzes the total dissolved polymer, thus reducing the contamination errors associated to solvent extraction method.

The proposed technique is theoretically more accurate than previous methods that employ arbitrary functions for deconvoluting the UV chromatogram.[5,6] The main limitation of the present data treatment is that it requires a detailed polymerization–SEC model. However, the procedure could be considerably simplified if the theoretical UV chromatograms of the free and grafted PS, obtained from the polymerization-SEC model, were fit to simple analytical functions. In this case, one would simply adjust the sought functions to the measurements. This approach would again be semi-quantitative, but considerably more precise than when using arbitrary distributions.

ACKNOWLEDGMENTS

We greatly appreciate the financial support received from the following institutions: CONICET and Universidad Nacional del Litoral (Argentina); Universidad del Zulia and CONDES-LUZ (Venezuela); and our FONACIT-CONICET international agreement.

REFERENCES

1. Sundberg, D.C.; Tang, M.Y.; Arndt, J. Grafting of Styrene onto Polybutadiene Lattices in Batch and Semicontinuous Reactors. J. Dispers. Sci. Technol. **1984**, *5*, 433–445.
2. Aerdts, A.M.; de Krey, J.E.; Kurja, J.; German, A.L. Emulsifier Free Grafting of Styrene and Methyl Metacrilate Concurrently onto Polybutadiene and Determination of the Copolymer Microstructure. Polymer **1994**, *35* (8), 1636–1647.
3. Van Ballegooie, P.; Rudin, A. Grafting Behaviour of Copolymers of Styrene and Ortho-Vinylbenzaldehide. J. Polym. Sci., Polym. Chem. Edn. **1988**, *26*, 2449–2464.
4. Min, T.I.; Klein, A.; El-Aasser, M.S.; Vanderhoff, J.W. Morphology and Grafting in Polybutylacrilate-Polystyrene Core-Shell Emulsion Polymerization. J. Polym. Sci., Polym. Chem. Edn. **1983**, *21*, 2845–2861.
5. Huang, N.J.; Sundberg, D.C. A Gel Permeation Chromotography Method to Determine Grafting Efficiency During Graft Copolymerization. J. Polym. Sci. Polym. Chem. Ed. **1994**, *35*, 5693–5698.
6. Li, J.; Sosa, J. Grafting Studies of HIPS Before and After Phase Inversion. In *Polymer Preprints*, 2nd Ed.; Div. of Polymer Chem. Inc., Am. Chem. Soc., 1999; Vol. 40, 69–70.
7. Estenoz, D.A.; González, I.M.; Oliva, H.M.; Meira, G.R. Polymerization of Styrene in the Presence of Polybutadiene: Determination of the Molecular Structure. J. Appl. Polym. Sci. **1999**, *74*, 1950–1961.
8. Fischer, M.; Hellmann, G.P. On the Evolution of Phase Patterns During the High-Impact-Modified Polystyrene Process. Macromolecules **1996**, *29*, 2498–2509.
9. Estenoz, D.A.; Valdéz, E.; Oliva, H.M.; Meira, G.R. Bulk Polymerization of Styrene in Presence of Polybutadiene: Calculation of Molecular Macrostructure. J. Appl. Polym. Sci. **1996**, *59*, 861–885.
10. Brandrup, J.; Immergut, E.H. *Polymer Handbook*, 3rd Ed.; Wiley: New York, 1989.
11. Estenoz, D.A.; Vega, J.R.; Oliva, H.M.; Meira, G.R. Analysis of a Styrene-Butadiene Graft Copolymer by Size Exclusion Chromotography. I. Computer Simulation Study for Estimating the Biases Induced by Branching Under Ideal Fractionation and Detection. Int. J. Polym. Anal. Charact. **2001**, *6*, 315–338.
12. Vega, J.R.; Estenoz, D.A.; Oliva, H.M.; Meira, G.R. Analysis of a Styrene-Butadiene Graft Copolymer by Size Exclusion Chromotography. II. Determination of the Branching Exponent with the Help of Polymerization Model. Int. J. Polym. Anal. Charact. **2001**, *6*, 339–349.

13. Zimm, B.H.; Stockmayer, W.H. The Dimension of Chain Molecules Containing Branches and Rings. J. Chem. Phys. **1949**, *17* (12), 1301–1314.
14. Brydon, A.; Burnett, G.M.; Cameron, G.G. Free-Radical Grafting Monomers to Polydienes. II. Kinetics and Mechanism of Styrene Grafting to Polybutadiene. J. Appl. Polym. Sci. Polym. Chem. Ed. **1974**, *12*, 1011–1021.
15. Estenoz, D.A.; Meira, G.R. Grafting of Stryrene onto Polybutadiene: Calculation of the Molecular Macrostructure. J. Appl. Polym. Sci. **1993**, *50*, 1081–1097.
16. Estenoz, D.A.; Meira, G.R.; Gómez, N.; Oliva, H.M. Mathematical Model of a Continuous Industrial High-Impact Polystyrene Process. AIChE J. **1998**, *44*, 427–441.

Received May 15, 2002
Accepted June 7, 2002
Manuscript 5879